

**EGE UNIVERSITY
GRADUATE SCHOOL OF APPLIED AND NATURAL SCIENCES**

(MSc THESIS)

**SYNTHESIS OF METAL ORGANIC FRAMEWORKS
(MOF) BY USING DIFFERENT SOLVENTS AND
USAGE IN LIQUID PHASE ADSORPTION AND AS
CATALYST**

Esra YILMAZ

Supervisor: Prof. Dr. Ferhan Sami ATALAY

Department of Chemical Engineering

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ESRA YILMAZ tarafından **Yüksek Lisans** tezi olarak sunulan “**Synthesis of metal organic frameworks (MOF) by using different solvents and usage in liquid phase adsorption and as catalyst**” başlıklı bu çalışma E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliği ile E.Ü. Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi’nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 14.08.2015 tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

Jüri Üyeleri:

İmza

Jüri Başkanı : Prof.Dr. Ferhan Sami ATALAY

Raportör Üye : Prof.Dr. Süheyda ATALAY

Üye :Prof. Dr. Sacide ALTINKAYA

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E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliğinin ilgili hükümleri uyarınca Yüksek Lisans Tezi olarak sunduğum “Synthesis of metal organic frameworks (MOF) by using different solvents and usage in liquid phase adsorption and as catalyst” başlıklı bu tezin kendi çalışmam olduğunu, sunduğum tüm sonuç, doküman, bilgi ve belgeleri bizzat ve bu tez çalışması kapsamında elde ettiğimi, bu tez çalışmasıyla elde edilmeyen bütün bilgi ve yorumlara atıf yaptığımı ve bunları kaynaklar listesinde usulüne uygun olarak verdiğimi, tez çalışması ve yazımı sırasında patent ve telif haklarını ihlal edici bir davranışımın olmadığını, bu tezin herhangi bir bölümünü bu üniversite veya diğer bir üniversitede başka bir tez çalışması içinde sunmadığımı, bu tezin planlanmasından yazımına kadar bütün safhalarda bilimsel etik kurallarına uygun olarak davrandığımı ve aksinin ortaya çıkması durumunda her türlü yasal sonucu kabul edeceğimi beyan ederim.

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ÖZET

FARKLI ÇÖZÜCÜLERDEN METAL ORGANİK KÜMELERİN (MOF) SENTEZLENMESİ VE BU SENTEZİN SIVI FAZLI ADSORPSİYON İŞLEMİNDE VE KATALİZÖR OLARAK KULLANILMASI

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Bu çalışmada metal organik kümeler hidrotermal/solvotermal yöntem ve ultrasonik yöntemle desteklenen iyonotermal yöntem ile sentezlenmiştir. Sonrasında sentezlenen bu malzemelerin adsorbent ve katalizör olarak kullanımı araştırılmıştır.

Adsorbsiyon deneylerinde, toluen ve nitrobenzen gibi aromatik organik birleşikler ve metil oranj ve metil kırmızı gibi boyaların atık sulardan uzaklaştırılması çalışılmıştır. Başlangıç konsantrasyonu, temas etme süresi, adsorbent miktarı ve sıcaklık gibi parametrelerin etkisi en uygun adsorbsiyon isoterminin, adsorbsiyon kinetiğinin, adsorbsiyon termodinamiğın ve dengeye gelme zamanının belirlenmesi için araştırılmıştır.

Çalışmanın esterleşme kısmında, kimyasal olarak kararlı bu yapıların asitliği sülfonasyon işlemi ile artırılmıştır ve asetik asitin esterleşme reaksiyonlarında kullanılmıştır. Esterleşme reaksiyonunda, asit - alkol molar oranı, sıcaklık, sülfonasyon, tekrar kullanılabilirlik, katalizör yüklenmesi gibi farklı parametrelerin etkisi incelenmiştir. Katalizör performansını ortaya çıkarmak için katalizörün hiç kullanılmadığı deneyler de yapılmıştır.

Anahtar sözcükler: Metal organik kümeler, adsorpsiyon, esterleşme, aromatik organikler, boyalar, asetik asit, kesikli reaktör.

ABSTRACT

SYNTHESIS OF METAL ORGANIC FRAMEWORKS (MOF) BY USING DIFFERENT SOLVENTS AND USAGE IN LIQUID PHASE ADSORPTION AND AS CATALYST

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In this study, metal organic frameworks were synthesized with hydrothermal/ solvothermal method and ionothermal assisted by ultrasonic method. Then their usage as adsorbent and catalyst were studied.

In adsorption experiments, aromatic organic compounds including toluene and nitrobenzene and dyes such as methyl orange and methyl red adsorption experiments were investigated. The effects of the parameters such as initial concentration, contact time, adsorbent dosage, and temperature on the adsorption capacity were investigated for the determination of the best fit adsorption isotherm, adsorption kinetics, adsorption thermodynamics, and equilibrium time.

In esterification part of the study, chemically stable MOF structures were sulfonated and used as catalyst in esterification reactions of acetic acid. With using metal organic frameworks as catalysts, high conversions were obtained in the production of esters which are among the most important chemical products. In esterification reaction, the effects of different parameters such as alcohol, temperature, sulfonation, reusability, catalyst loading, alcohol to acid molar ratio were investigated. And experiments without catalyst were also carried out to elaborate the performance of the catalyst.

Keywords: Metal organic Frameworks, adsorption, esterification, aromatic organics, dyes, acetic acid, batch reactor.

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NOMENCLATURE

<u>Symbol</u>	<u>Explanation</u>
q_e	amount of adsorbate adsorbed on the volume adsorbent
C_e (mg/L)	solute concentration remaining in the solution
Q_o (mg/g)	the maximum adsorption capacity
b (L/mg)	a constant related to the free energy of the adsorption
b (L/mg)	refers to the Langmuir constant
C_0 (mg/L)	the adsorbate initial concentration
RL	the adsorption nature
K_F experimentally	the Freundlich adsorption capacity calculated
n	the Freundlich constant.
C_t (mg/l) contact time	Adsorbate concentration remaining in solution in each
C_0 (mg/l)	Initial adsorbate concentration in solution
k (time ⁻¹)	The boundary layer diffusion constant
q_t (mg/g)	amount adsorbed at time t
k_p (mol/gmin ^{0.5})	the rate constant of intraparticul diffusion
t (min)	adsorption time
k_1 (min ⁻¹)	the rate constant of pseudo-first-order kinetic
q_e (mg/g)	amount adsorbed at equilibrium
k_2 (g/mg/min)	the rate constant of the pseudo-second-order kinetic
R (8.314 J/mol/K)	the gas constant
T (K)	the temperature
ΔH	the enthalpy change
ΔS	entropy change
ΔG°	Gibbs free energy change

Abbreviations

BDC	1,4- benzene dicarboxylate;
ST	Supertetrahedron

VNP	Very Narrow Pore
BTC	1,3,5-benzenetricarboxylic acid
SBU	secondary building units
bpy	4,4-bipyridine
TMBDC	tetra metil benze 1,4 dikarboksilat
DES	Deep Eutectic Solvents
HBA	hydrogen bond acceptor
HBD	hydrogen bond donor
ChCl	Choline chloride
IL	ionic liquids
NB	nitrobenzene
MB	methylene blue
AC	activated carbon
MO	methyl orange
MWCNT	multi walled carbon nanotube
PAAC	Phragmites australis
OMA	Ordered Mesoporous Alumina
Fe-CMK-3	Ordered mesoporous carbon
MG	Malachite green
LAM	lipoid adsorption material
RB19	Reactive Blue 19
MIAA	Modified immobilized activated alumina
CTAB	cetyltrimethylammonium bromide
LHHW	Langmuir-Hinshelwood-Hougen-Watson
PH	pseudohomogeneous
ER	Eley Rideal
LH	Langmuir Hinshelwood
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
AAS	Atomic Absorption Spectrophotometry
BzMN	Benzylidenemalononitrile

EtCC	Thyl α -cyanocinnamate
H ₂ BDC	Terephthalic Acid
H ₃ BTC	Trimesic Acid
DMF	N,N-dimethylformamide
HF	Hydrofluoric Acid
DMU	Dimethyl Urea
BET	Brunauer–Emmett–Teller
FT-IR	Fourier Transform Infrared
TGA	Thermal Gravimetric Analysis

1. INTRODUCTION

The metal organic frameworks (MOFs), a new class of hybrid materials, consist of metal ions connected by organic linkers and have a high porosity. They have all of the advantages of both organic and inorganic porous materials. Metal organic frameworks are composed of organic connectors which are bridged between the metal ions. They draw attention because of their low densities, high surface areas, tunable pore size, and high porosities. These materials, known as the new member of the porous materials, have been widely investigated in various application areas such as separation (Yang and Yan, 2011), gas adsorption and storage (Couck et al., 2009), catalyst (Vu et al., 2013; Wu et al., 2013; Lin et al., 2012), adsorption of organic molecules (Yanga et al., 2011; Lenga et al., 2014), and drug delivery (Taylor-Pashow et al., 2009). Although one of the most important usage areas of MOFs is the adsorptive removal of hazardous and noxious substances, their adsorption abilities have been relatively unexplored compared to the other adsorbents such as activated carbon or zeolites (Achmann et al., 2010; Jia et al., 2013). Due to peculiar features, such as high surface area, its usage as catalyst and in adsorption of various liquids and gases are promising. In the adsorption processes, the regeneration of these substances, compared to zeolite and activated carbon which necessitate high temperatures and cost, tends to require less processing. All of these advantages make it superior to the other porous materials.

Especially in developed countries, although the rapidly developing industrialization simplifies the human life, it causes many environmental problems. So the large amounts of waste water are generated by industries or domestic usage of water. This fact creates a requirement for developing efficient and better methods or technologies of wastewater treatment process. There are several contaminants in wastewater such as volatile organic compounds, organic dyes, phenolic compounds, aromatic organic compounds, heavy metals and so on. These compounds are very harmful for all creatures and environment. So, the many of wastewater treatment processes are applied. Pollution in water creates a serious threat to ecosystems often contain organic and inorganic origin chemicals.

Among them, the aromatic compounds and dyes which are investigated in this thesis are in the group of the organic contaminates.

Aromatic organic compounds such as nitrobenzene and toluene, studied in this thesis, are important materials in the chemical industries and are used as starting materials or solvents in various chemical reactions. These two substances are classified as carcinogenic, flammable and toxic substances (Choi et al., 2009; Wibowo et al., 2007). Their presence in water, even a small amount, is a major environmental concern. Hence the removal of these compounds from wastewater is necessitated before release into the environment (Wibowo et al., 2007).

For removal of different aromatic compounds from wastewater, several studies have been conducted by using numerous technologies such as adsorption, thermal or catalytic oxidation, membrane separation processes, and biological treatment methods. Adsorption technology that does not require high operating temperatures with a high cost is considered as one of the most competitive methods. This method, in particular, for the removal of low concentrations of aromatic organic contaminants from water has become one of the widely used methods (Yanga et al., 2011). The adsorptive technique is based on the ability to be selective of the porous adsorbent for certain compounds. Compounds having suitable size and shape can easily access the pores of the solid adsorbent and so these compounds can be removed using the adsorptive technique.

Dyes in wastewater are also serious problem. They discharge into the receiving waters because they are used several industries such as textile, paper, leather, plastic and so on. The discharge of this effluent to water bodies is one of the major environmental problems. The presence of dye materials greatly affects the quality of water. Even at a low concentration of dye in water is visible and can cause negative effect all living creatures or environment. Depending on the exposed time and dye concentration they have chronic or acute effects on the exposed living creatures. In addition to that, many dyes are considered to be toxic and carcinogenic (Robinson et al., 2002). Hence, the elimination of dye stuffs from wastewater is necessitated. They may enter into the environment or water bodies during production or application. Especially in textile industry, large amounts of highly colored effluents are manufactured. In the world, the exact

amount of dyes produced and discharged is unknown. But they are predicted roughly as 7×10^5 – 1×10^6 tons per year dyes are produced and 10-15% of them are discharged into the environment (Forgacs et al., 2004; Gupta and Suhas, 2009). Colored dye effluent increases with the production and application of dye in the textile and other industries (MOF paper dye). Large scale production and application of them cause the rising of environmental pollution and serious health effect (Forgacs et al., 2004).

The nonbiodegradable nature of most dyes in the environment makes their removal from effluents necessary. There are several physical, chemical and biological de-colorization methods for wastewater treatment such as precipitation and coagulation/flocculation, biodegradation, ion exchange, chemical oxidation, filtration and adsorption that have been reported for the removal of dyes from industrial effluents (Faisal et al., 2007; Qin et al., 2009). Adsorption technology that does not require high operating temperatures with a high cost is considered as one of the most competitive methods. And also by using this technique many of dye stuffs can be removed simultaneously.

The adsorption of dyes on various materials such as activated carbon (Gomez et al., 2007], molecular sieve (Qin et al., 2009; zhao et al., 1996), clay (Tahir and Rauf, 2006), zeolite (Wang and Zhu, 2006) and agricultural wastes such as lemon (Kumar, 2007) and coir pith based activated carbon (Namasivayam and Kavitha, 2002) and orange peel (Arami et al., 2005) have also been widely studied.

In the adsorption processes, the regeneration of these substances, compared to Zeolite and activated carbon which necessitate high temperatures and cost, tends to require less processing. All of these advantages make it superior to the other porous materials.

Esters are usually derived from an inorganic acid or organic acid with an alcohol. A lot of chemicals which have industrial importance such as methyl, ethyl, butyl and hexyl esters are produced by esterification reaction. Esters have broad applications in medicine, biology, chemistry and industry. Some of these application areas are; plasticizers, plastics, textiles, adhesives, coatings, leather

(film coating and leather finishes). They are widely used in the production of pesticides and paint formulations. Also they can be used as chemical intermediate and used as monomers in the production of copolymers.

Since the esterification reaction of acrylic acid and hexanol is reversible and slow reaction it requires acidic catalyst because of the proton requirement to start the reaction. The esterification reactions performed by using homogeneous catalysts such as sulfuric acid, hydrofluoric acid and para-toluene sulfonic acid; but these are toxic, corrosive and often hard to remove from the products. Thus it is keenly desirable to develop new types of solid acid catalysts to replace them, because the solid acid is less toxic and facilitates the recovery and recycling of catalysts (Altiokka and Ödeş, 2009).

The aim of this thesis is to synthesize metal organic frameworks and use these materials as catalyst and adsorbent.

In the first part of this study metal organic frameworks were synthesized by hydrothermal/ solvothermal methods and ionothermal method assisted by ultrasound.

In the second part of this study, aromatic organic compounds and dyes adsorption experiments were conducted on. The effects of the parameters such as initial concentration, contact time, adsorbent dosage, and temperature on the adsorption capacity were investigated for the determination of the best fit adsorption isotherm, adsorption kinetics, adsorption thermodynamics, and equilibrium time.

In the third part of this study, production of acetic acid esters was investigated in a batch reactor. The other aim of this thesis is to study esterification reaction between acetic acid and different alcohols and the effects of different parameters such as alcohol, temperature, sulfonation, reusability, catalyst loading, alcohol to acid molar ratio on the reaction yield were investigated.

2. THEORETICAL BACKGROUND

2.1. Metal Organic Frameworks (MOFs)

2.1.1. Definition

Metal organic frameworks, a new member of porous materials, are composed by the organic connectors which are bridged between the metal ions and have a high porosity. Metal–Organic frameworks (MOFs) are also known as porous coordination polymers, have been introduced to chemistry field in 1990s. They have all of the advantages of both organic and inorganic porous materials.

They offer ease of control over the pore size and shape by changing the metal nodes and/or linkers. They have also many excellent properties such as low density, high surface area, tunable pore size and high porosity. Therefore, they draw great attention of researchers. These materials have a large application areas including, separation (Yang and Yan, 2011), gas adsorption and storage (Couck et al., 2009), catalyst (Vu et al., 2013; Wu et al., 2013; Lin et al., 2012), adsorption of organic molecules (Yanga et al., 2011; Lenga et al., 2014), and drug delivery (Taylor-Pashow et al., 2009).

While one of the most important usage areas of MOFs is the adsorptive removal of hazardous and noxious substances, their adsorption abilities have been relatively unexplored when compared with the other adsorbents such as activated carbon or zeolites (Achmann et al., 2010; Jia et al., 2013). In the adsorption processes, the regeneration of these substances, compared to zeolite and activated carbon which necessitate high temperatures and cost, tends to require less processing. High surface area, easy tunability with changing ligands and/or metal nodes types and high porosity of these materials make them excellent porous material among traditional porous materials. Besides the all these advantages, the only disadvantages of these hybrid materials is that having low thermal stability (generally limited to 300-400°C), this situation does not make it possible for application at high temperatures.

Figure 2.1 shows various MOFs structure.

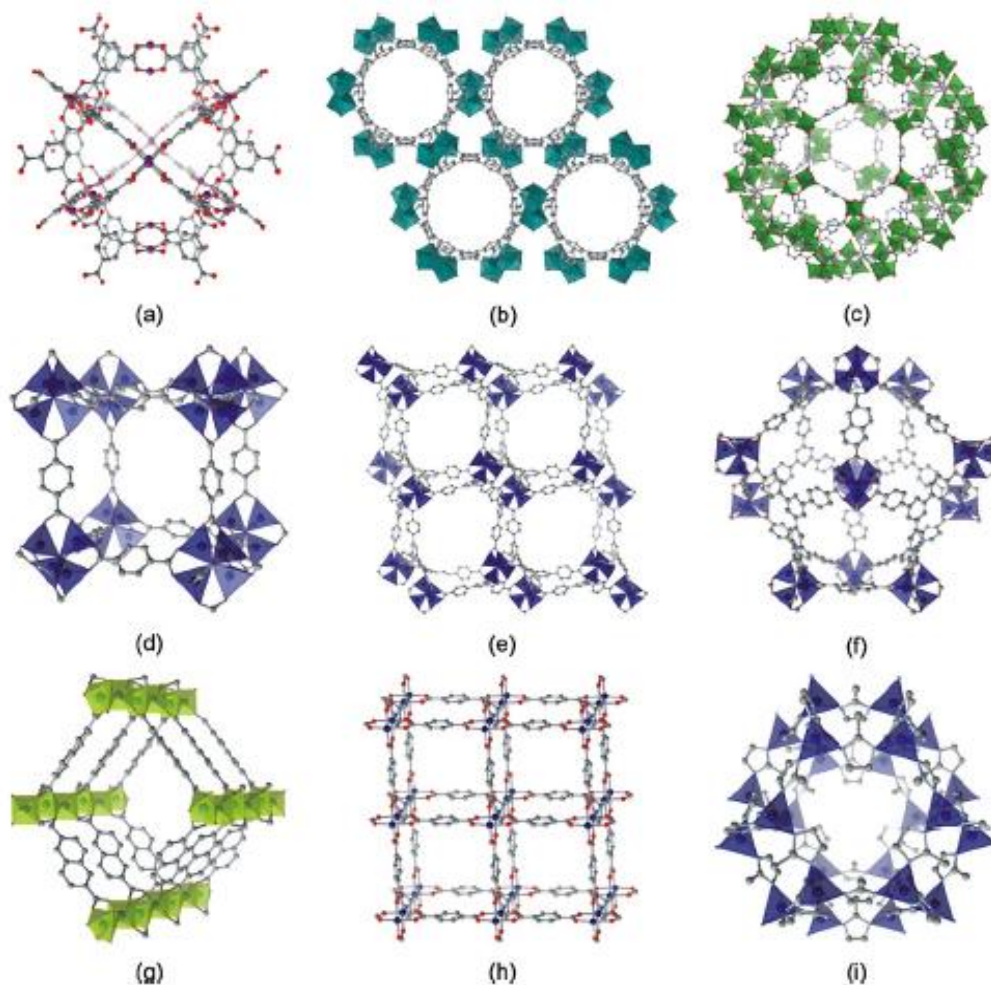


Figure 2.1 Structures of various MOFs (Henschel A., et al., 2011)

There have been many MOFs reported. Among the large number of metal organic frameworks, MIL-101, MIL-53 (Fe), CuBTC and MIL-125 (Ti) are selected for this study because of their easy preparation, cost effective and easy regeneration.

2.1.2. Types of MOFs

MIL-101

MIL-101 (MIL for materials of institut Lavoisier) is one of the metal organic frameworks. It was first synthesized by Férey et al. from Cr^{3+} ion and terephthalic acid (Férey et al., 2005). Its supertetrahedral structure is formed by rigid terephthalate linkers and trimeric chromium (III) octahedral clusters. The chemical formula for MIL-101 is $\text{Cr}_3\text{O}(\text{F}/\text{OH})(\text{H}_2\text{O})_2[\text{C}_6\text{H}_4(\text{CO}_2)_2]$ and has a

high pore diameter, pore volume ($\approx 1.9 \text{ cm}^3/\text{g}$), and surface area ($\approx 5900 \pm 300 \text{ m}^2/\text{g}$). So these advantages make it the material of choice for the removal of many harmful contaminants.

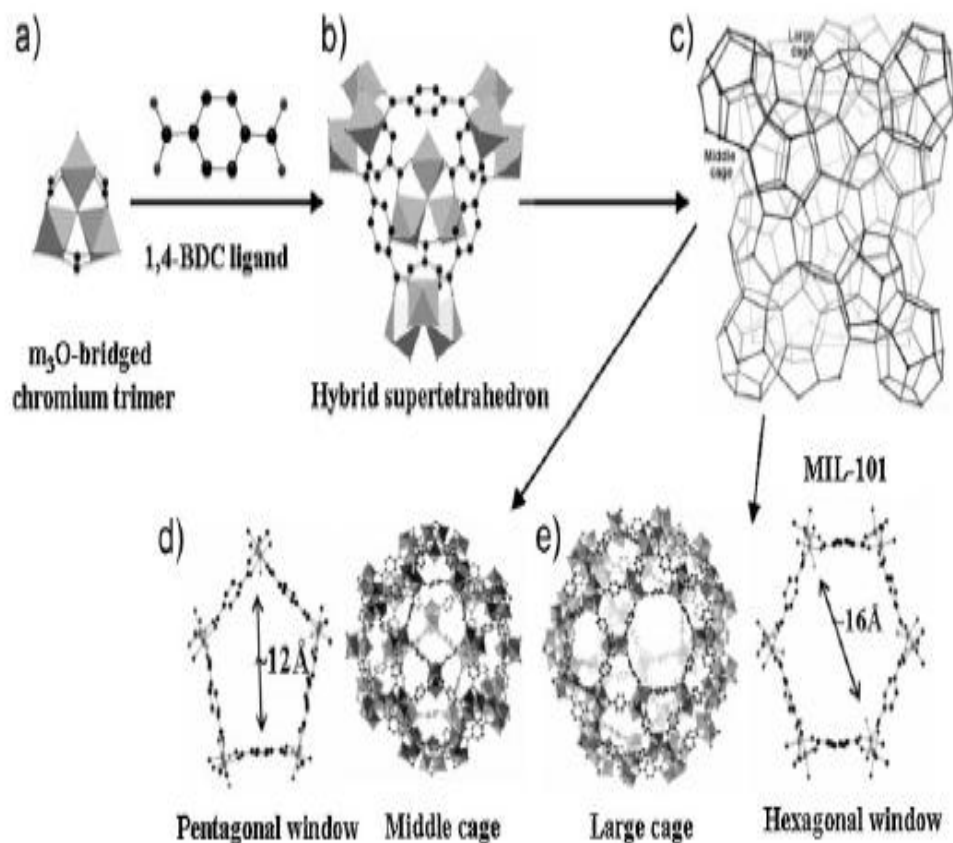


Figure 2.2 MIL -101 Crystal structure a) trimer of chromium octahedral and linker (1,4-BDC), b) supertetrahedron, c) polyhedral MIL-101 consists of two types of cages, e) hexagonal structure large cage, f) pentagonal structure, middle cage (Hong et al. 2009).

MIL-101 is formed by the organic terephthalic acid linker (1,4- benzene dicarboxylate; BDC) and inorganic chromium trimers (Figure 2.2a). A Supertetrahedron (ST) building unit is formed by linkage of rigid terephthalate ligands and four trimeric chromium (III) octahedral clusters. Six of terephthalate ligands are linked to six edges of these four octahedral clusters (Figure 2.2b). Then MOF is formed with a combination of these STs. This structure includes two types of cages. One of them is fully of pentagonal faces (consist of 12 pentagonal faces) which has 29 Å internal diameter. And the other one includes 16 faces, 12 of them pentagonal and 4 of them is hexagonal. And this cage is relatively larger than the first cage. And the internal diameter of this large cage is 34 Å (Figure 2.2c,d,e) (Hong et al. 2009)

MIL-101 can be synthesized in high yields and at a lower cost when compared to other MOFs. And it has been widely studied for adsorption (Hasan et al., 2013; Kim et al., 2013), catalysis (Riberio et al., 2013) and gas storage applications (Lin et al., 2012; Llewellyn et al., 2008). For example, adsorption of sulfur containing materials (Wu et al., 2014), dyes (Haquea et al., 2010; Lenga et al., 2014; Chen et al., 2012), and aromatics (Yanga et al., 2011; Qin et al., 2014) using MIL 101 has been extensively investigated.

MIL-53 (Fe)

MIL-53 series has the molecular formula of $M_{III} (OH) \cdot (O_2C-C_6H_4-CO_2) \cdot H_2O$ ($M = Al^{3+}, Cr^{3+}$ or Fe^{3+}) (Gordon et al., 2012). The chemical formula of MIL-53 (Fe) is $Fe_{III} (OH)_{0.8} F_{0.2} [O_2C-C_6H_4-CO_2]$ (for fluorinated material, HF acid is used in synthesis) or $Fe (OH) (O_2C-C_6H_4-CO_2) \cdot x$ (solvent), (No HF acid). HF acid is used for higher crystallization.

MIL-53 (Fe) is formed by infinite chains of trans-corner-shared $[FeO_4(OH/F)_2]$ or (FeO_6) octahedral units crosslinked by 1,4 benzenedicarboxylate (BDC) ligands to give a 3D net in which one-dimensional channels run parallel to the inorganic backbone of the structure. Thus, as presented in Figure 2.3 and 2.4, rhomb-shaped one dimensional channels are formed that run along the axis of the structure (Osta et al., 2012).

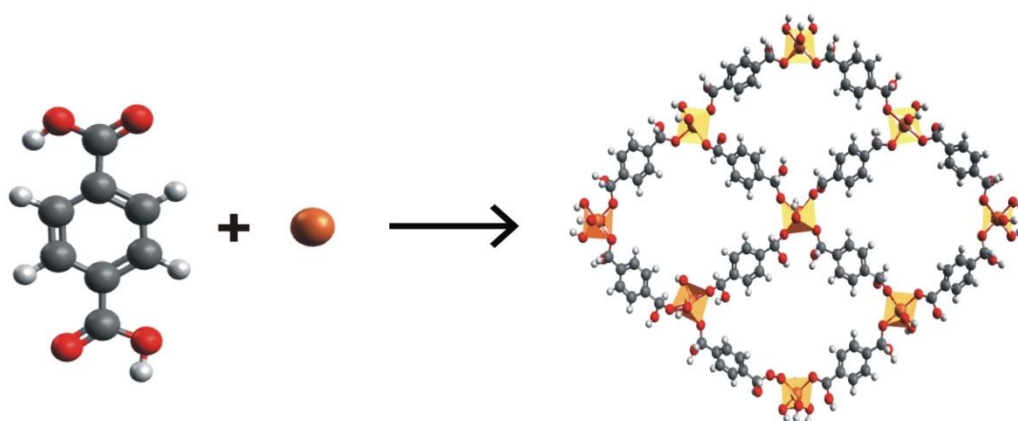


Figure 2.3 Crystal structure of MIL-53 (Fe) with view along chains of FeO_6 octahedra

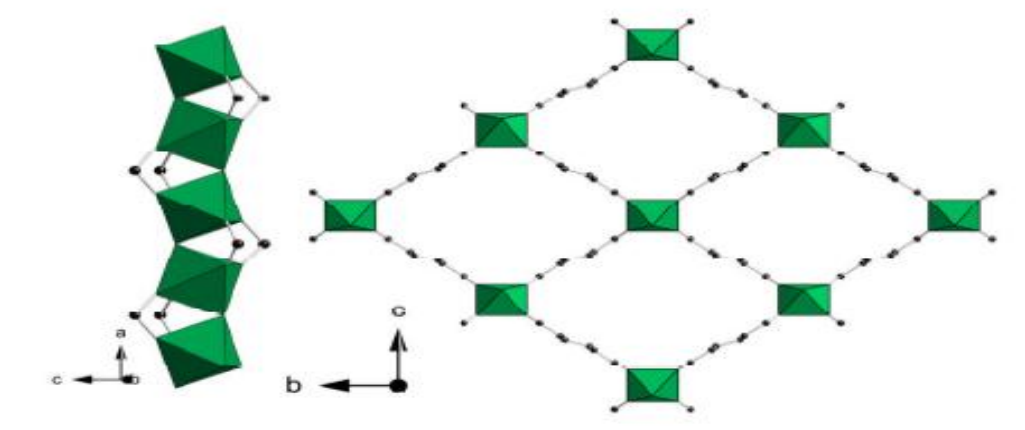


Figure 2.4 Trans-corner-shared (FeO_6) octahedral units (left) crosslinked by 1,4 benzenedicarboxylate (BDC) ligands to give a 3D net and large pore framework of MIL-53 (Fe) (right). Ferrous octahedral is shown in green, black spheres represent the carbon atoms of the organic linker.

Unlike other MOFs, MIL-53 (Fe) does not have high surface area. Because of its flexible structure, it opens its pores only in the presence of guest molecules.

This material can be used in various applications such as adsorption of waste and gases thanks to the breathing feature of it. Figure 2.5 shows open and closed pores of MIL-53.

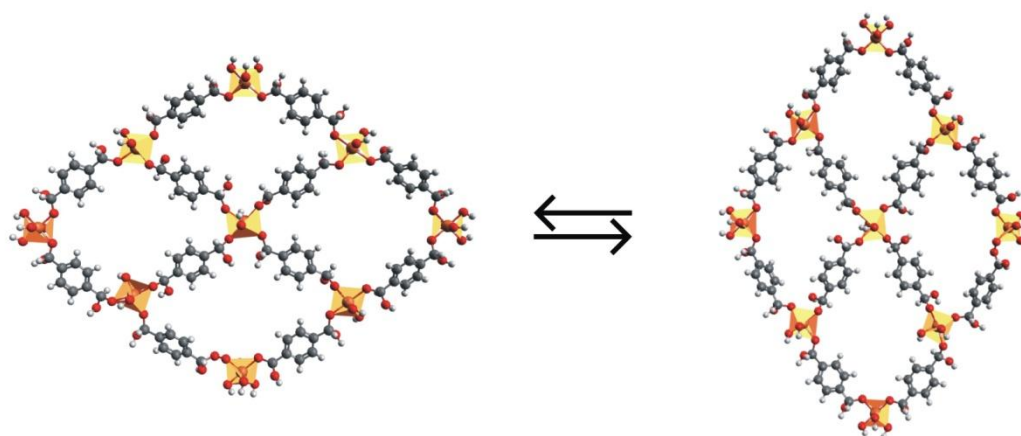


Figure 2.5 Structure of MIL-53 with open and closed pores

Its anhydrous form, pores are closed and this form is named as very narrow pore (vnp) form. The transition between the anhydrous (MIL-53(Fe)vnp) and the hydrated forms (MIL-53(Fe)np) occurs through the presence of an

intermediate (MIL-53(Fe)int) triclinic phase where half of the pores are filled with water molecules while the others are closed and empty (Llewellyn et al. 2009). Pore volume changes in response to external stimuli such as temperature, pressure or guest molecules. Figure 2.6 shows the changing of MIL-53 pore structure

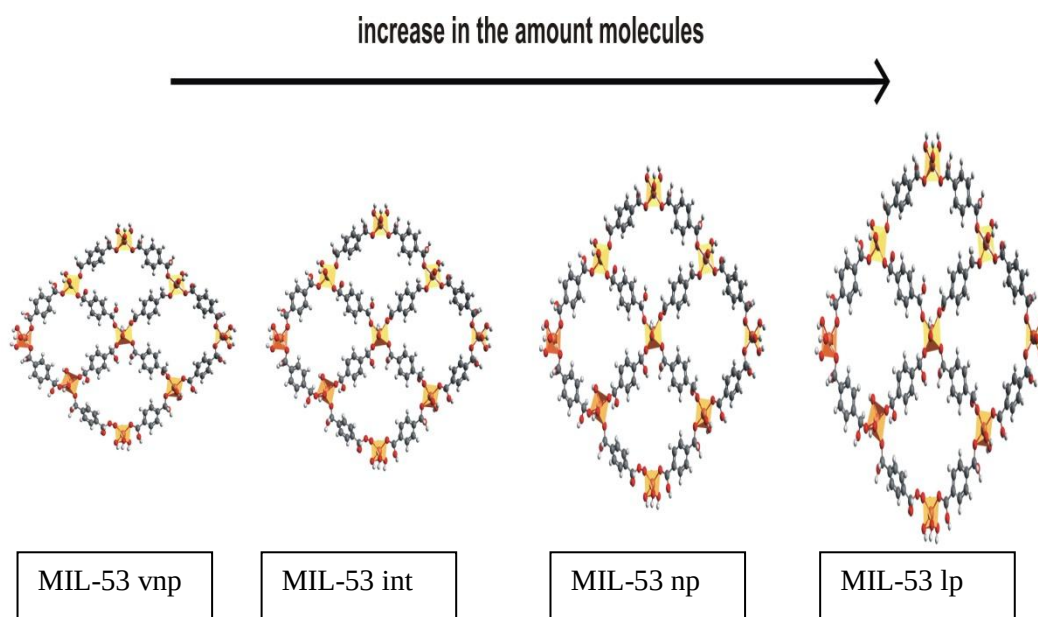


Figure 2.6 Changing of MIL-53 pore volume with increasing in the amount of guest molecules

Flexibility is one of the remarkable features of MOF materials, that is a reversible structural transformation property of the most of the MOFs that includes stretching, “breathing”, rotational functions of the framework structure (Fletcher et al. 2005; Serra-Crespo et al. 2012). MIL-53 series are examples of flexible material. And MIL-53 (Fe) studied in this thesis is one of them. The inorganic part of MOF is often associated with a rigid behavior, whereas the organic moieties correspond to flexibility (Férey and Serre, 2009) Therefore pore volume changes because of flexibility. This behavior arise from the presence of external stimuli (e.g., temperature, hydrostatic pressure, presence of a sorbate or guest molecule) which is granted by the weak interactions within the framework structure, including coordination bonds, H-bonds, p-electron stacking interactions.

Cu-BTC (HKUST-1 or MOF-199)

CuBTC [$\text{Cu}_3(\text{BTC})_2$] or HKUST-1 was first reported in 1999 by Chui et al (Chui et al., 1999). The paddle wheel complex is constructed from the axial copper (Cu^{2+}) ion and 1,3,5-benzenetricarboxylic acid ligands forming a sequence of square cages (Khan and Jhung, 2012). As shown in Figure 2.7, paddle wheel SBU's of this material consists of two Cu^{2+} ions and four 1,3,5-benzenetricarboxylic acid ligands. The figure shows the paddle wheel coordination of copper ions. Water molecules directly bonded to copper ions are represented by an oxygen atom only. The removal of coordinated water molecules by thermal activation procedures reveals the open-metal sites (unsaturated copper sites), which are known to enhance the ability of the materials to adsorb particular molecules. This structure has two types of pores (9 and 6 Å). Figure 2.8 also shows the paddle wheel and CuBTC structure in detail. In this figure, two copper ions form a dimeric unit with four bridging carboxylates creating a square planar geometry around two adjacent copper sites. The two copper ions in the paddlewheel coordinate to the oxygen of two water molecules to create a double square pyramidal geometry for the two metal sites in the hydrated form of the structure. Activation of the material prior to adsorption studies results in the removal of the terminal water molecules resulting in a coordinatively unsaturated metal site. The rigid, porous structure of the CuBTC framework combined with the accessibility of the activated metal sites upon dehydration has led to a lot of interest in adsorption, separation and catalysis applications.

This material is very interesting because of easy preparation, flexibility and open metal site. The positive effect of unsaturated metal sites is that these sites can decrease the energy barrier for adsorption and particularly, improve adsorption performance. And also high surface area and large pore volume of this material benefit the total adsorption capacity.

The chemistry of highly porous Cu-BTC has been intensively studied, due to its potential applications such as in gas sorption and storage (Bordiga et al., 2007; Chowdhury et al., 2009; Raganati et al., 2014), adsorption (Khan and Jhung, 2012; Feng et al., 2013), catalysis (Wee et al., 2010), etc.

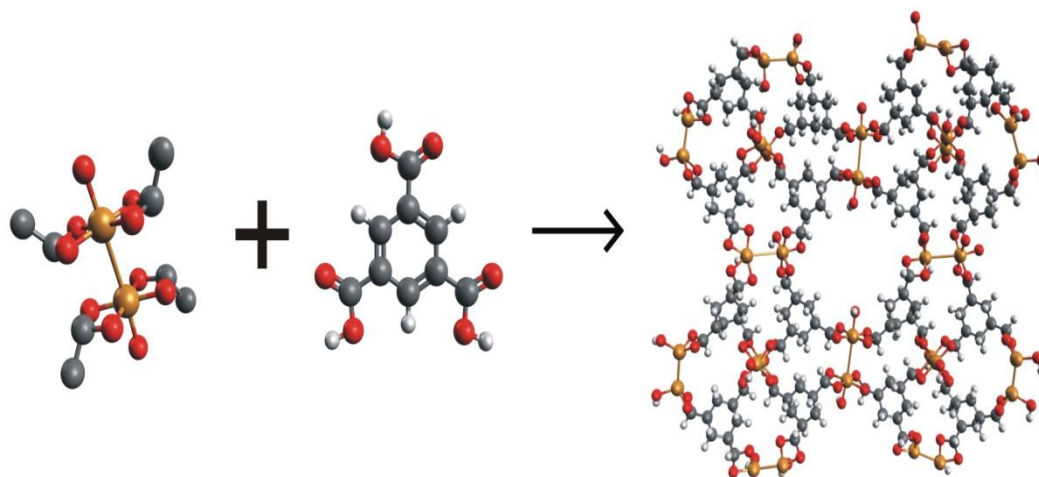


Figure 2.7 Paddle-wheel units, composed from two copper ions (blue spheres) and five oxygen atoms of water (for each copper atom), organic ligand, trimesic acid, and crystal structure of CuBTC. Two copper ions and four tricarboxylate ligands combine to form 3D structure. Cu^{2+} is yellow; O is red; C is light grey.

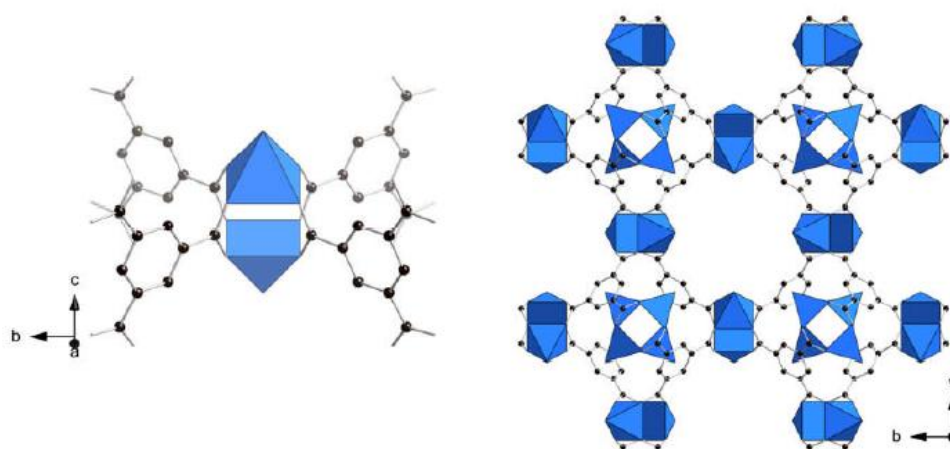


Figure 2.8 Paddle-wheel units and crystal structure of CuBTC. Two copper ions and four tricarboxylate ligands combine to form 3D structure. Blue polyhedral represent the square pyramidal CuO_5 . Black spheres represent the carbon atoms.

MIL-125 (Ti)

MIL-125 (Ti) is formed from cyclic octamers constructed from corner or edge sharing octahedral titanium units. These octamers are connected to 12 other cyclic octamers through BDC linkers, leading to a porous three dimensional quasi-cubic tetragonal structure having two types of cages, an octahedral (12.5

$\text{\AA}$) and a tetrahedral ($6\text{\AA}$) cage. The chemical formula for MIL-125(Ti) is $\text{Ti}_8\text{O}_8(\text{OH})_4-(\text{O}_2\text{C}-\text{C}_6\text{H}_5-\text{CO}_2)_6$.

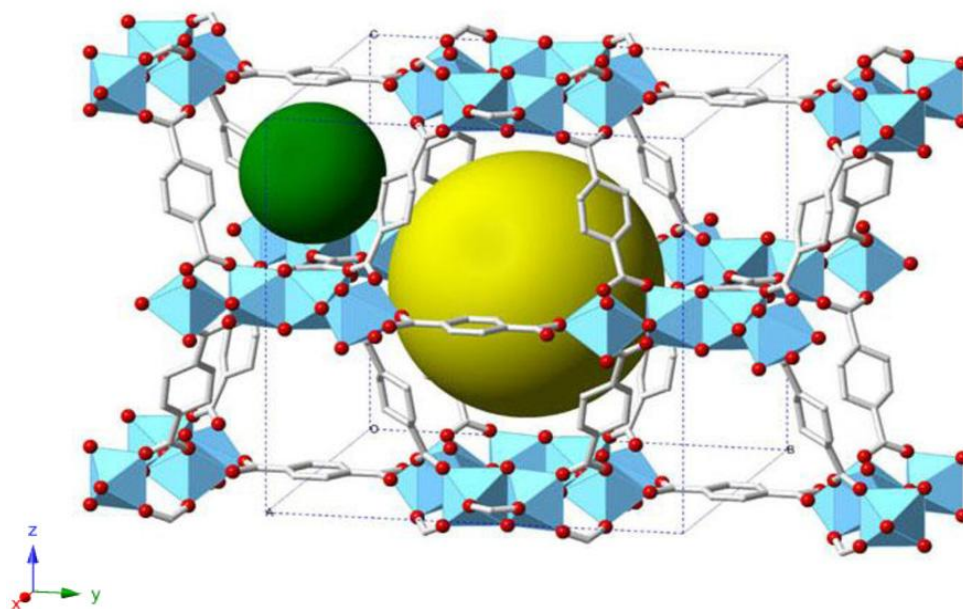


Figure 2.9 Structure of MIL-125

2.1.3. Design and Synthesis of Metal Organic Frameworks

Metal organic frameworks are composed by the organic ligands as linkers who are bridged between the metal ions or metal clusters (as nodes). Generally metal ions are used with appropriate linkers in the synthesizing of MOFs. Figure 2.10 shows the assembly of metal ions and ligands to form MOF (Kuzak, 2013).

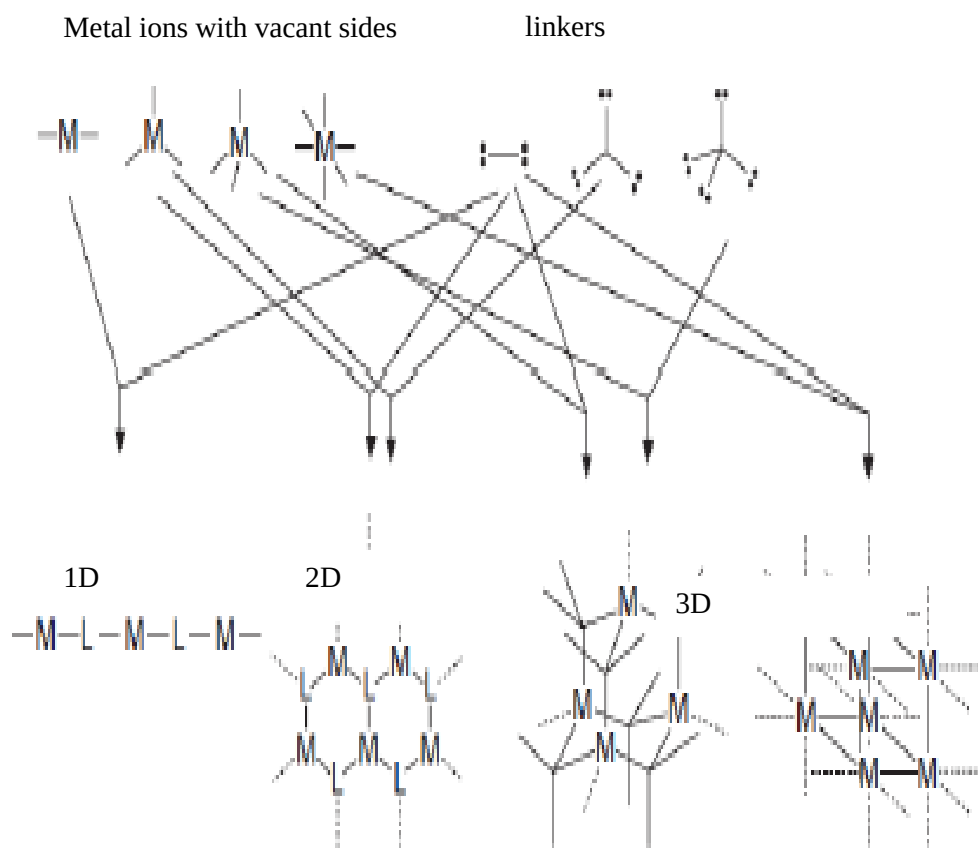


Figure 2.10 Assembly of nodes and linkers to form structures: nodes on the left top, and linkers on the top right, forming metal organic structures in the middle (Kuzak, 2013).

It is known that mostly transition elements are used with appropriate linkers for the construction of MOFs. The number of sites (coordination numbers) available for binding ligands at the metal center range from 2 to 12 depending upon the choice of d- or f block metal and its oxidation state. Since, the electrons added to the transition metals go into the d-orbitals, however, because the energy of the 4s orbital is lower than the 3d orbital, the 4s orbital fills first. So, the outermost d orbitals are incompletely filled with electrons, then, transition metals can easily give and take electrons. It is common that metal ions can aggregate around a small anion, such as O_2^- , OH^- or Cl^- , or with the donors of the bridging linker such as a carboxylate group. Therefore, using transition elements allow generating framework structures that they can have varied directionality of linkers bringing ability to control pore size and shape.

The ligands can be electrically neutral, anionic, or cationic. The most frequently used neutral organic linkers are pyrazine and 4,4-bipyridine (bpy). These linkers are especially useful as pillars in the construction of pillared-layer in 3D networks. The most widely used anionic linkers are carboxylates because they have the ability to aggregate metal ions into clusters and thereby form more stable frameworks. Cationic organic ligands are relatively little used, owing to their low affinities for cationic metal ions. Some organic ligands are shown in Figure 2.11.

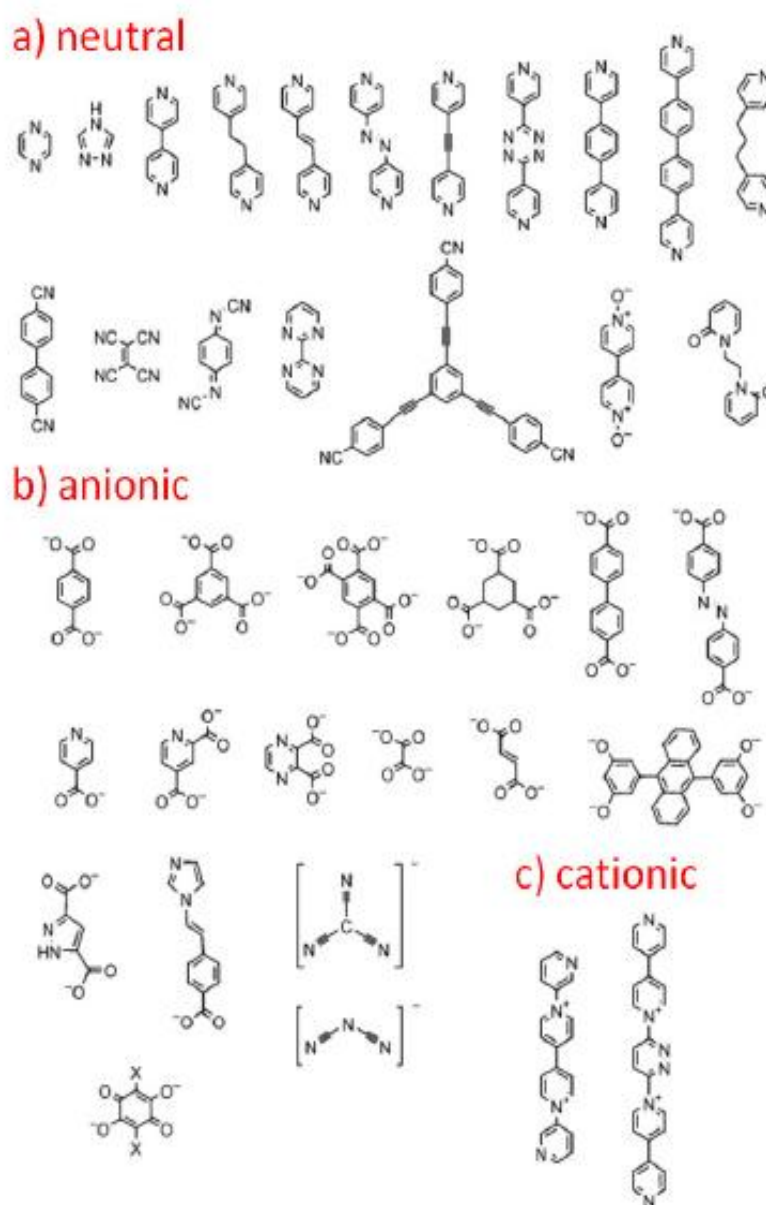


Figure 2.11 Structure of some organic ligands (BDC: benzen 1,4 di carboxilate, TMBCD: tetra metil benze 1,4 dikarboksilat) (Kira Khaletskaya, 2014)

MOFs can be regarded as materials assembled by inorganic building units, (secondary building units (SBUs)), containing metal ions or their clusters which are connected by organic linkers to result rigid multidimensional frameworks. The SBU concept helps the prediction of MOF structure. Examples of some SBUs that are commonly used in synthesis of MOFs are illustrated in Figure 2.12. The paddle-wheel motif represents a square-planar SBU, the basic zinc-carboxylate displays an octahedral SBU and oxygen-centered metalcarboxylate trimer represents the trigonal prismatic geometry. The best known carboxylate based MOFs are e.g. HKUST-1 ($[\text{Cu}_3(\text{btc})_2(\text{H}_2\text{O})_3]_n$) with paddle-wheel motif $[\text{Cu}_2(\text{O}_2\text{C})_4(\text{H}_2\text{O})_2]$ and MOF-5 with an octahedral $[\text{Zn}_4\text{O}(\text{O}_2\text{C})_6]$ SBU.

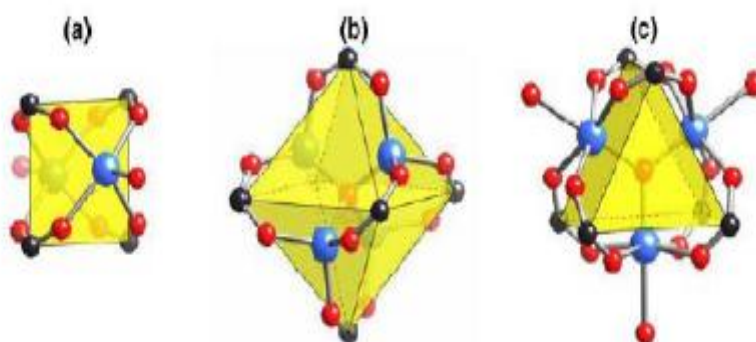


Figure 2.12 Inorganic SBUs commonly used in synthesis of MOFs a) square paddle – wheel; b) octahedral structure and c) trigonal oxo-centered trimer. Blue is metals; black is carbon. (Kira Khaletskaya, 2014)

The assemblies of inorganic SBUs and organic linkers are mainly realized through coordination bonds. Besides, other weak attractive interactions such as hydrogen bonds, π - π , CH- π and Van-der-Waals interactions play a role in construction of the extended structures. In MOF synthesis, the formation process proceeds usually automatically and therefore, is called *self-assembly*. The big diversity of inorganic SBUs and organic linkers is the main reason for the huge number of MOFs reported today.

MOF structure can be changed with respect to different organic linkers, inorganic metal cation and synthesis condition. Figure 2.13 shows two types of MOFs obtained from Cu^{2+} ion connected by 1,3,5 benzenetricarboxylic acid and 4,4'4''-benzene -1,3,5-triyl tri benzoic acid.

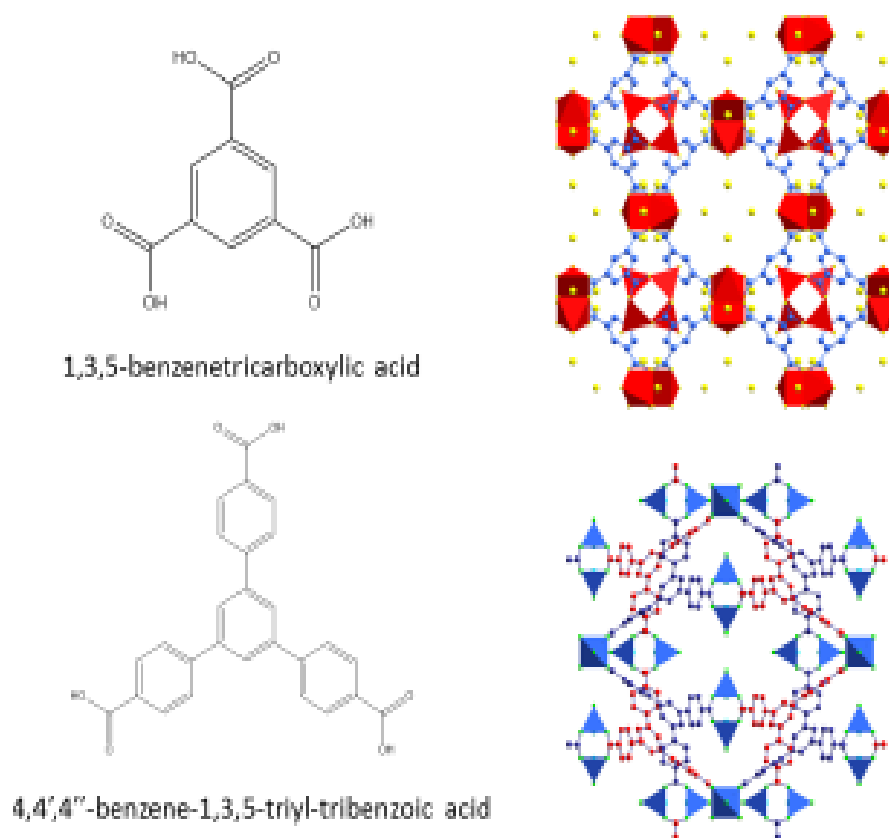


Figure 2.13 Changing of copper based MOF structure by using two different ligands, the former is HKUST-1 and the latter is MOF-14. (Munn, 2013)

As seen in Figure 2.13; MOF structure can be changed by using different organic ligands while keeping the metal cation the same. In addition to that, MOF structure can be also varied with changing of metal cations when the same ligand is used. Figure 2.14 shows three MOFs that have been synthesised with the 1,4 benzenedicarboxylic acid ligand and various metal cations in varying oxidation states. This figure highlights the effect of the metal cation in framework design.

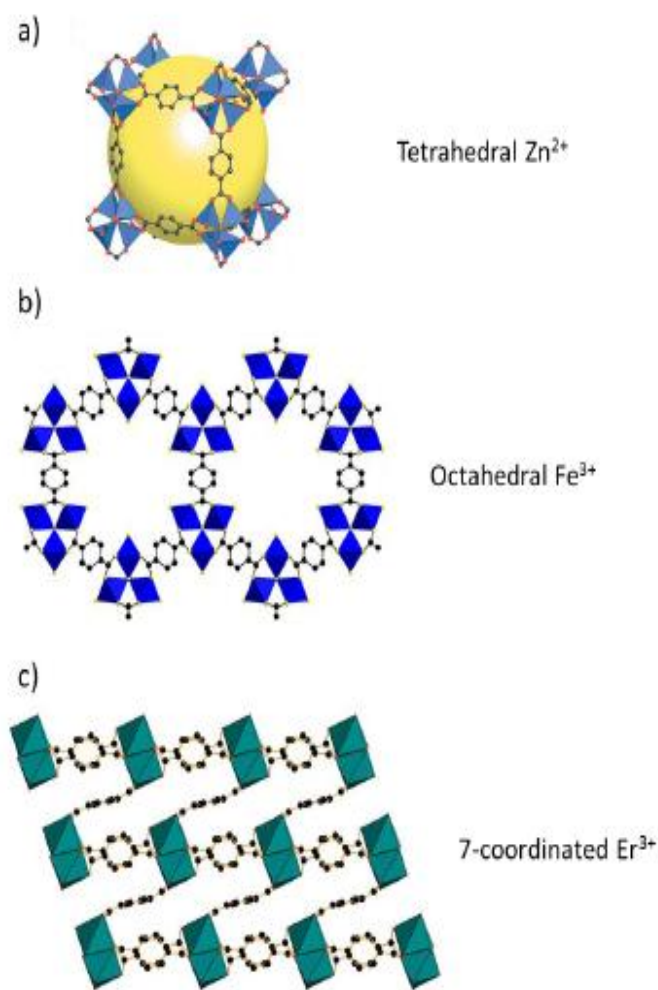


Figure 2.14 Changing the metal source while keeping the organic ligand the same a) MOF-5; b) MIL-88 (Fe); c) $\text{Er}_2(\text{BDC})_3$ (Munn, 2013).

As well as the metal cations and organic ligands chosen for MOF synthesis define the resultant framework structure. However, the synthetic conditions have been shown to play a major role in defining the outcome of a given reaction. The metal salt used as the source for a particular metal cation can affect how a reaction proceeds.

Millange et al. studied the how synthesis duration (as a synthesis condition) effects on MOF structure. They obtained two different MOFs, MOF-235 and MIL-53 (Fe) having different properties. Figure 2.15 shows schematic representation of this study.

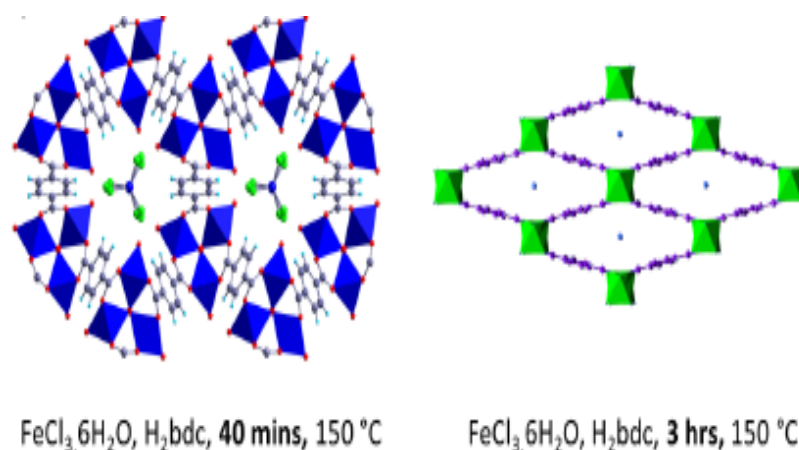


Figure 2.15 Effect of synthesis conditions on MOF structure (Munn, 2013).

MOFs can be synthesized by self assembly of organic ligands and metal ions. MOFs can be synthesized by means of several ways such as solvothermal, hydrothermal, ultrasonic, microwave irradiation, electrochemical and mechanochemical synthesis. In this study, selected MOFs were synthesized with solvothermal/hydrothermal and ionothermal assisted by ultrasonic methods.

Hydrothermal or Solvothermal Synthesis Methods

Solvothermal synthesis method can be considered as more comprehensive method. This method is similar to hydrothermal synthesis method. Only difference between these two methods are that; while in hydrothermal synthesis method water is used as solvent, in this method all solvents can be used. Organic ligands, metal complexes and solvents are placed in Teflon lined stainless steel autoclave. And reaction is performed at specified temperature, pressures and time. After that, obtained MOFs are purified and dried for usage. Disadvantage of this method is reaction takes place a long times from several hours up to several months, depending upon the MOF of interest and the reaction solvent, reaction temperature, reagent concentrations, and other factors. Figure 2.16 shows the schematic of a typical Teflon lined autoclave reactor.

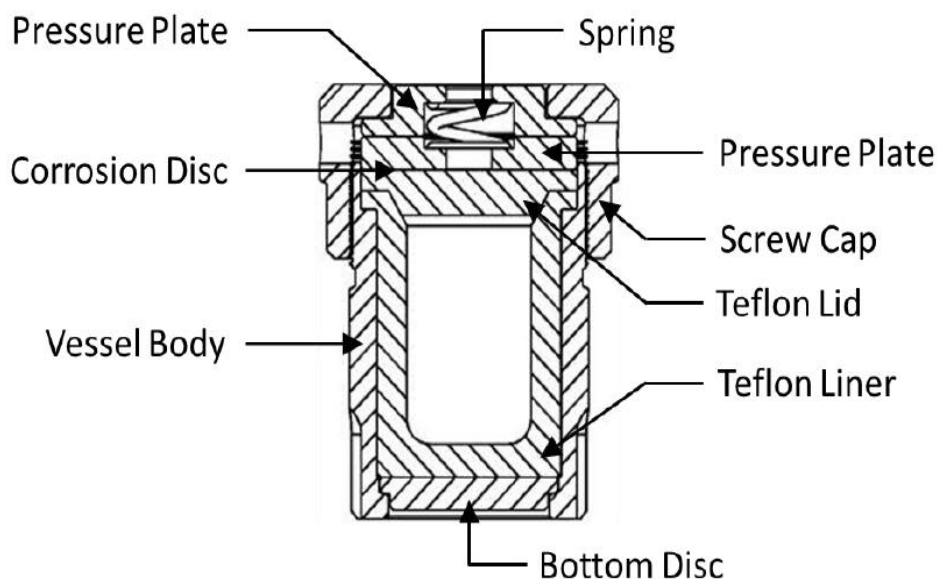


Figure 2.16 Schematic of Teflon lined autoclave reactor (Munn 2013)

Ultrasonic synthesis method

In case of ultrasonic-assisted synthesis, the cavitation collapse of the vacuum bubbles produced in the sonochemical reaction leads to very fast and intense local heating and high pressure, which allow both a rapid synthesis and a tuning of the kinetics of the reaction. The approaches are facile, rapid and environmentally friendly, but it is not easy to control the morphology and the size of the resulted nanocrystals.

Ionothermal synthesis method

A common method for synthesizing materials is hydrothermal or solvothermal synthesis. In this method water or organic solvent is used then heating the resulting solution in a sealed autoclave under autogenous pressure.

Recently, the chemistry inside the autoclaves has been altered by replacing the molecular solvent (water/organic solvent) with an ionic solvent (ionic liquid), this has been termed ionothermal synthesis. The ionothermal method is the use of an ionic liquid or eutectic mixture as the reaction solvent and, in many cases, also as structure directing agent in the preparation of crystalline solids.

Taking advantage of the physico-chemical, economical and ecological advantages of deep eutectic solvents (DESs) in the ionothermal synthesis of materials, eutectic mixtures are now regarded as promising and particularly attractive media for large-scale synthesis of new MOF structures. Different from ILs (two-component systems with anions and cations), which were also used for the MOF synthesis, DESs also contain neutral ligands such as urea that can induce structure-directing effects making DES a solvent of choice for the preparation of MOFs. To date, efforts have been made toward the ionothermal synthesis of new porous MOFs in DESs, due to the multiple roles that they can play in such synthesis.

Ionothermal synthesis has some advantage such as the synthesis takes place at nearly ambient pressure, eliminating safety concerns associated with high hydrothermal pressures. Many reactions can take place using simple containers such as round bottomed flasks or glass vials. However, it has been shown that even the addition of a very small amount of water to the system can generate significant pressures.

Ionic liquids have many drawbacks including their high cost of manufacturing, the complex synthesis, purification and toxicity in nature. This was the starting point of the deep eutectic solvents. The concept was forced to avoid the disadvantages of the ionic liquids to get a more rational concept of new biocompatible, low cost solvents for industrial application. To overcome these disadvantages of ionic liquids, Deep Eutectic Solvents (DES), a new type of ionic liquids, has emerged. DES can be prepared combining with two components, one of them is hydrogen bond donor (HBD) and the other is hydrogen bond acceptor (HBA). The main features of these components are cheap, biodegradable and renewable. By simple mixing of these two components in certain ratio, eutectic mixture is formed. DES has a lower melting point of either of the individual components. The eutectic mixtures are generally characterized by a very large depression of freezing point, generally higher than 150 °C.

Urea, renewable carboxylic acids (oxalic acid, paratoluene sulfonic acid, etc.) and renewable polyols such as glycerol and carbohydrates are examples of a hydrogen bond donor group. Choline chloride (ChCl), one of the quaternary

ammonium salt, is the most widespread component used for formation of DES due to its low cost, biodegradable and non toxic structure. They are obtained easily from biomass by extraction or synthesized from fossil reserves. DESs derived from ChCl gather many advantages such as (1) low price, (2) chemical inertness with water (i.e. easy storage), (3) easy to prepare since DESs are obtained by simply mixing two components, thus by-passing all problems of purification and waste disposal generally encountered with ILs and (4) most of them are biodegradable, biocompatible and non-toxic, reinforcing the greenness of these media.

As compared to traditional organic solvents, DESs are not considered as volatile organic solvents and not flammable, making their storage convenient. Their physico-chemical properties (viscosity, density, conductivity, among others) are very similar to the one of the ionic liquids. Additionally, like ILs, the physico-chemicals properties of DESs can be tuned almost infinitely by changing the nature of the quaternary ammonium salt and the hydrogen-bond donor, making possible the preparation of task-specific DESs. As compared to ILs, DESs have however notable advantages stemming from (1) their convenient synthesis (100% atom economy), (2) their very low price since most of DESs can be prepared from readily accessible chemicals and (3) their low toxicity, especially DESs derived from ChCl and renewable chemicals. Clearly, these notable ecological and economical advantages of DESs now open alternative routes for the emergence of ionic fluids at a larger scale. It should also be noted that although components of DESs are potentially reactive chemicals, their auto-association by a hydrogen bond drastically limits their reactivity, allowing their use in many fields of research (Zhang et al., 2012).

Deep Eutectic Solvents (DES)

Due to recent issues about the environmental pollution, ever growing industrial production and more stringent environmental regulations, environmentally friendly solvents for industrial processes have gained ever greater importance. In past few decades there have been many studies regarding ionic liquids (IL) and their employment as solvents.

Deep eutectic solvents (DES) are type of ionic solvents composed of two or three cheap and safe materials which are capable of associating with each other, through hydrogen bond interactions, to form a eutectic mixture and have a lower melting point of either of the individual components. DES's can be prepared combining with a hydrogen bond donor (HBD) (amides, carboxylic acids) and hydrogen bond acceptor (HBA) (quaternary ammonium salts). Figure 2.17 shows typical structures of hydrogen bond acceptor and hydrogen bond donors used for DESs synthesis.

Deep eutectic solvents are in the group of green solvents which are low toxicity, low miscibility, easily biodegradability under environmental conditions, high boiling point, and easily to recycle after use. Another advantage of these solvents is their easy and cheap fabrication by simply mixing two or three compounds, avoiding additional volatile organic solvents as synthesis medium. Even more, these precursors are normally cheap, easily available, biodegradable and non-toxic compounds as quaternary ammonium salts (usually choline chloride) combined with different hydrogen bond acceptors as natural amino acids (i.e. alanine or glycine) or carboxylic acids present in fruits and vegetables.

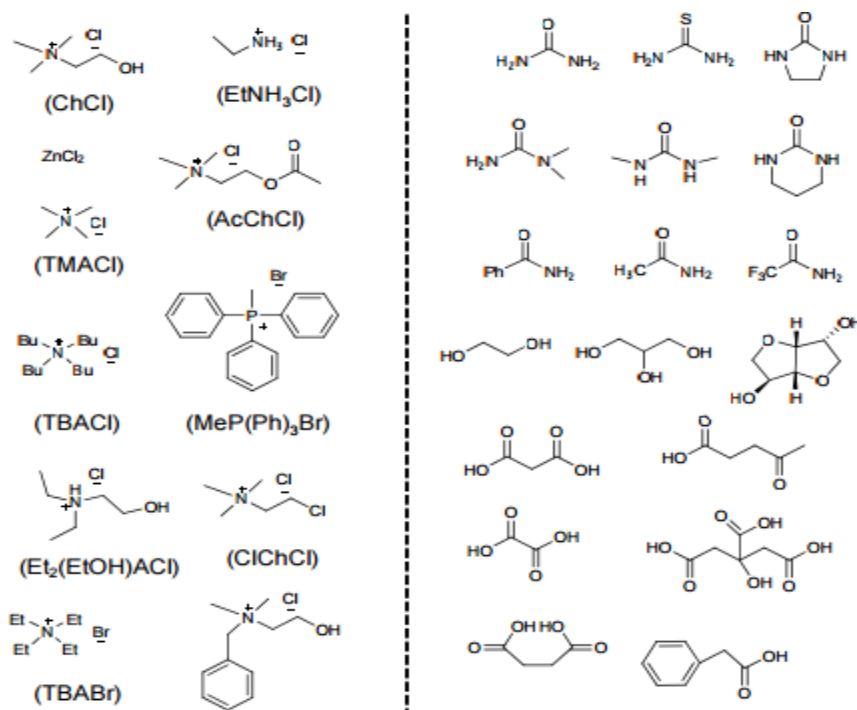


Figure 2.17 Hydrogen bond donor and acceptor used for preparation of DES (Zhang et al., 2012).

The melting point of the deep eutectic solvent is lower than the melting points of its starting components. For example the freezing points of choline chloride and urea are 302 °C and 133°C, respectively. The ratio of HBA and HBD for eutectic point is given as 1:2 in the literature (Zhang et al. 2012). The freezing point of obtained DES is given as 12°C. The depression in the freezing point is obtained from 302°C and 133°C to 12 °C. Figure 2.18 shows the individual melting points of A and B components (point T_A and T_B) and deep eutectic solvent formed by these components (point T_E) having concentration C_E which is eutectic composition.

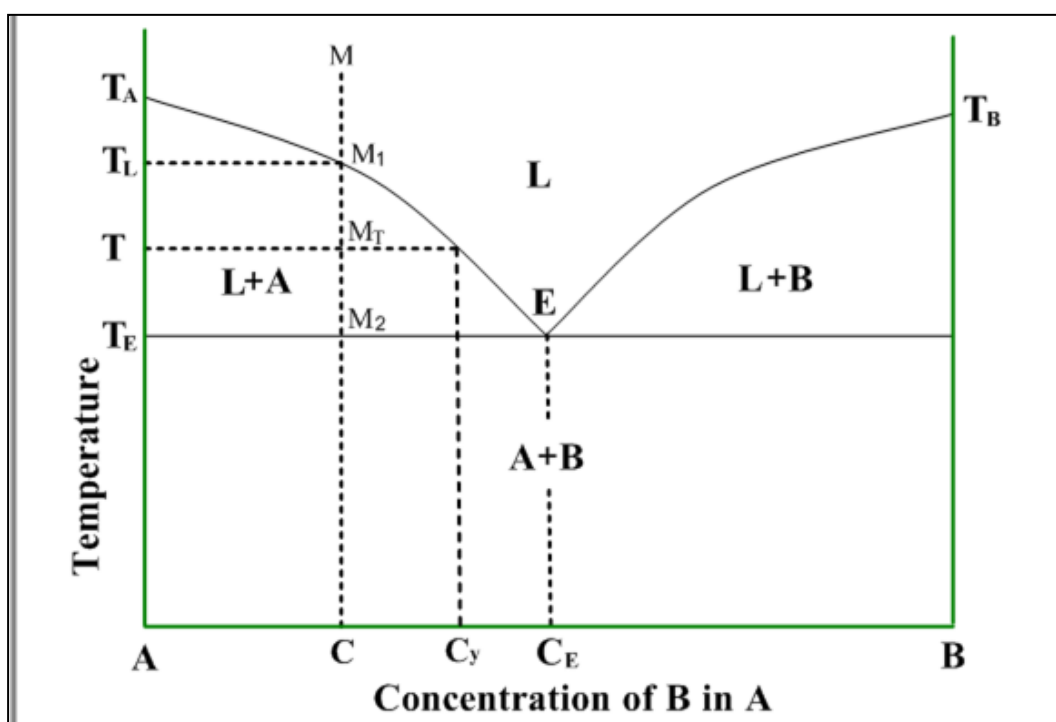


Figure 2.18 Temperature vs Composition Diagram of An Eutectic Solvent. T_A = melting point of A; T_B = melting point of B; T_E = melting point of deep eutectic solvent (A+B); L+A = Liquid + Solid A; L+B = Liquid + Solid B.

The components are linked through hydrogen bonds and Deep eutectics could be formed due to delocalization of charge. The delocalization of charge mostly appears because of hydrogen bonding. The depression of the melting/freezing point is possible by reason of charge delocalization. The complexing agent (typically a H-bond donor) mostly forms a complex with the anion to delocalize the charge of the anion. Furthermore, the interaction with the cation is reduced and the greater the ability of the complexing agent to form hydrogen bonding the stronger the decrease of the melting/freezing point. Further,

as already known for ionic liquids, the lower the symmetry of the cation of the organic salt is, the more diminished is the melting/freezing point.

Synthesis of inorganic materials is usually conducted in a solvent medium at high pressures. Due to low volatility of DES, the process for the formation of crystals is simplified and risks of working at high pressures (due to the volatility of common organic solvents) are avoided. Table 2.1 shows DES obtained from choline chloride and different HBD and eutectic points.

Table 2.1 Melting points of DES prepared by choline chloride and different HBD (Zhang et al., 2012).

HBA	HBD	HBA : HBD	Melting point of HBA (°C)	Melting point of HBD (°C)	Melting point of DES, T _f (°C)
ChCl	Urea	1:2	302	133	12
ChCl	Thiourea	1:2	302	182	69
ChCl	1-methyl urea	1:2	302	101	29
ChCl	1,3 dimethyl urea	1:2	302	104	70
ChCl	Adipic acid	1:1	302	152	85
ChCl	Benzoic acid	1:1	302	122	95
ChCl	Citric acid	1:1	302	156	69
ChCl	Malonic acid	1:1	302	135	10

Figure 2.19 shows the formation of DES from HBA and HBD with a molar ratio (1:2).



Figure 2.19 Formation of DES

2.2. Adsorption

2.2.1. Definition and Types of Adsorption

Adsorption is defined as a separation process based on transfer of atoms, molecules or ions in the liquid/gas phase to a solid surface. The special solids which gas or liquid particles attached are called adsorbent. The substances adsorbed are called adsorbate. Adsorption is a phenomenon occurs at the surface; the molecules are taken up by the surface.

Adsorption is first used for gases in 1773 by C.W. Scheele and in 1785 for liquids by Lowitz. It is also defined as a process for removal of certain substances from a solution by using substances that can hold these substances (Gupta and Suhas 2009).

Attractive forces between ions, atoms and molecules in any solid lattice are balanced by other forces which are around them. However attractive forces of molecules on a solid surface are unbalanced. Due to the presence of unsaturated surface strength on solid surfaces, gases or liquid molecules are held to the solid surface. The molecules or atoms being accumulated on the surface of the adsorbent and creates an adsorbate film. So the surface tension of the solid is reduced by adsorption of gas or liquid molecules. This phenomenon decreases the surface energy of the system. Reducing of the surface energy is a spontaneous event. With the adsorption phenomenon, free energy of system is in a decrease. So, adsorption is also spontaneous event (Özer, 2004; Savcı, 2005).

Adsorption has a great environmental importance because it eliminates the pollutants in both liquid and gas media. There are mainly two types of adsorption, including physical and chemical adsorption.

Physical Adsorption

It is a type of adsorption which involves intermolecular forces such as van der Waals (weak intermolecular) attractive forces, hydrogen bonds between the adsorbate and adsorbent. These forces are weak and reversible. Adsorbed substances hold to the surface single or multilayered. Adsorption can be

multilayer and adsorbent can be recovered easily. Activation energy of adsorption is low and low temperature range is sufficient for physical adsorption.

Chemical Adsorption

It is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond. This type of adsorption involves valency forces that are sharing of electrons between adsorbent and adsorbate. It is much stronger than the physical adsorption and the resulting temperature is greater than the reaction temperature. It is often very difficult to separate chemically adsorbed molecule (solid, liquid, gas) from surface. Chemical adsorption is irreversible. Hence the increasing of temperature leads to further adsorption.

The difference between physisorption and chemisorption of liquid or gaseous adsorbate on solid adsorbent does not usually present great difficulties. Both kinds of adsorption are distinguished by:

1. Heat of adsorption: in physisorption, heat of adsorption is low, and it is great in chemisorption.
2. Physical adsorption can be monolayer or multilayer adsorption whereas chemisorptions can be only monolayer.
3. Physisorption is rapid and reversible process while chemisorptions may be slow and irreversible.
4. In physisorption, electron transfer does not occur between adsorbent and adsorbate but in chemisorptions, electron transfer occurs.

Factors effecting adsorption process

- **pH**

One of the most important parameters effecting adsorption is pH value. Due to hydrogen (H^+) or hydroxyl (OH^-) ions are strongly adsorbed, adsorption of other ions are affected by the pH of the solution.

- **Temperature**

Adsorption process is generally exothermic process by which adsorption increases with temperature decreases.

- **Adsorbate and solvent properties**

The solubility of the solute is a factor for controlling of adsorption equilibrium. In general, there is an inverse relationship between the solubility of solute in the liquid phase and the adsorption rate of the solute. With increasing of the resolution, the solvent-soluble bond is strengthened and the amount of adsorption decreases.

- **Polarity**

General rules describing the effect of a polarity on adsorption, polar solute would prefer more polar adsorbent. That is, polar substances will be more adsorbed from non polar solvent.

- **Adsorbent properties**

The most important parameter effecting adsorption process in the surface characteristics of adsorbent is surface area and with increasing of the surface area value, adsorption capacity increased. Therefore porous materials provide a high adsorption capacity. Activated carbon, cytosine, zeolites, clays, some industrial waste and agricultural waste are located as frequently used adsorbent. Recently, metal organic frameworks (MOFs), a new class of hybrid materials, have also been used in many adsorption applications.

Adsorbents should be non-poisonous and non toxic, harmless for environment, insoluble in water, easily available, cheap and reusable and have a large surface area, functional groups for interacting with adsorbates, availability must be proven scientifically

2.2.2. Adsorption Isotherms

Adsorption is an equilibrium reaction, which describes the information of the nature of solute-surface interaction and specific information about

concentration of the adsorbate and the degree of the accumulation on to the surface of the adsorbent at specific temperature (Thirumal and Kaliappan, 2011).

After reaching adsorption equilibrium, the amount of substances dissolved in the solution does not change. The amount of adsorbed material depends on the adsorbate concentrations and ambient temperature. At a constant temperature, adsorbed amount of substance depends on the solution concentration. At a constant temperature, when equilibrium is reached, adsorption isotherm is obtained by plotting the amount of adsorbate adsorbed on the volume adsorbent (q_e) against solute concentration remaining in the solution (C_e). The amount of adsorbate adsorbed on the volume adsorbent is calculated by using following equation.

$$q_t = (C_0 - C_t) \frac{V}{W}$$

where C_0 and C_e (mg/L) are the liquid phase concentrations of the solute at time = 0 and equilibrium time respectively. V (L) is the volume of the solution and W (g) is the weight of the adsorbents used.

To define the adsorption isotherm, several mathematical expressions such as Langmuir, Freundlich, Redlich-Peterson, Temkin have been developed. Among them, the most well known and widely used models are Freundlich and Langmuir isotherm models.

To determine which adsorption isotherms are fitted well with experimental data, all isotherm equations are applied. With linearization of adsorption isotherms, most appropriate isotherm can be selected. However, experimental data can be fitted well with one or more isotherms.

Langmuir Isotherm

Langmuir isotherm equation is first developed a theoretical adsorption isotherms by I.Langmuir (Langmuir, 1918). Langmuir isotherm model is the simplest and most applicable model and includes some assumptions. These assumptions are;

- Whole surface the adsorbent has the same adsorption activity for adsorption.
- There is no interaction between the adsorbed molecules. Therefore amount of adsorbed substances on volume surface does not affect adsorption rate.
- The adsorbed layer is made up of a single layer of molecules. The maximum adsorption is achieved when the molecules are bonded to adsorbent to form a saturated layer.
- Adsorption is a reversible process. The adsorbed molecules do not move on the surface of the adsorbent. However, they can be lost back to the solution.
- The enthalpy of adsorption is the same for all molecules independently of how many have been adsorbed.

Expression for the Langmuir isotherm:

$$q_e = \frac{Q_0 \times b \times C_e}{1 + b \times C_e}$$

Linearized forms of this model equation:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b}$$

where;

Q_0 is the maximum adsorption capacity (mg/g)

b is a constant related to the free energy of the adsorption (L/mg)

The slope and intercept of plots of C_e/q_e versus C_e , at different temperatures, were used to calculate Q_0 and b .

For further understanding of the adsorptions, a dimensionless constant called the separation factor or equilibrium parameter, RL should be also determined (Hasan et al., 2013).

$$RL = \frac{1}{1 + bC_0}$$

where;

b refers to the Langmuir constant (L/mg)

C_0 is the adsorbate initial concentration (mg/L).

RL value indicates the adsorption nature to be either unfavourable ($RL > 1$), linear ($RL = 1$), favourable ($0 < RL < 1$) or irreversible ($RL = 0$).

Freundlich Isotherm

According to Freundlich model, Adsorbate is located on an adsorbent surface area heterogeneously. Freundlich derived the following equation to describe the adsorption of the solutions (Freundlich, 1906).

$$Q_e = K_F \times C_e^{1/n}$$

K_F is the Freundlich adsorption capacity calculated experimentally.

n is the Freundlich constant.

In this equation constants K_F and n values are depended on the temperature, adsorbent type and adsorbate.

Linearized forms of this model equation:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

The Freundlich isotherm constants K_F and n are determined from the intercept and slope of the plot of $\log q_e$ versus $\log C_e$.

Classification of Isotherms

The adsorption isotherms were classified into 4 groups by Giles et al. This classification is based on the shape of isotherms (Giles et al., 1960).

C isotherm: C isotherm curve is a line passing from the origin (Figure 2.20.a). This means that the ratio of adsorbed amount on solid and adsorbate remaining in the solution are always same for all concentration. This ratio is

usually called as "distribution coefficient" or "partition coefficient". C isotherm is valid for a narrow range of concentrations of contaminants. Generally, this isotherm is not suitable for example, if the solid (adsorbent) has a limited number of adsorption sites, the isotherm becomes nonlinear due to a possible plateau.

L isotherm: The ratio of the adsorbate concentration remaining in solution and adsorbed amount on the solid decreases with increasing of the adsorbate concentration, and consequently provides a concave curve (Figure 2.20.b). This situation indicates that the solid reaches the saturation. The curve has plateau is generally classified in two subgroups:

- Curve reaches a plateau which means the adsorbate has a limited adsorption site or capacity.
- Curve has not any plateau. Because the adsorbent has not a limited adsorption capacity.

H isotherm: H isotherm is a type of L isotherm has a high initial slope (Figure 2.20.c). This isotherm shows that strong adsorbate adsorbent interaction.

S isotherm: S isotherm is the sigmoid shape curve has a turning point (Figure 2.20.d). Such isotherm is always a result of at least two opposing mechanisms. The non-polar organic compounds adsorption is a typical example of this isotherm. This phenomenon is called as 'cooperative adsorption' and is also observed for surfactants (G. Limousin et al.,2007).

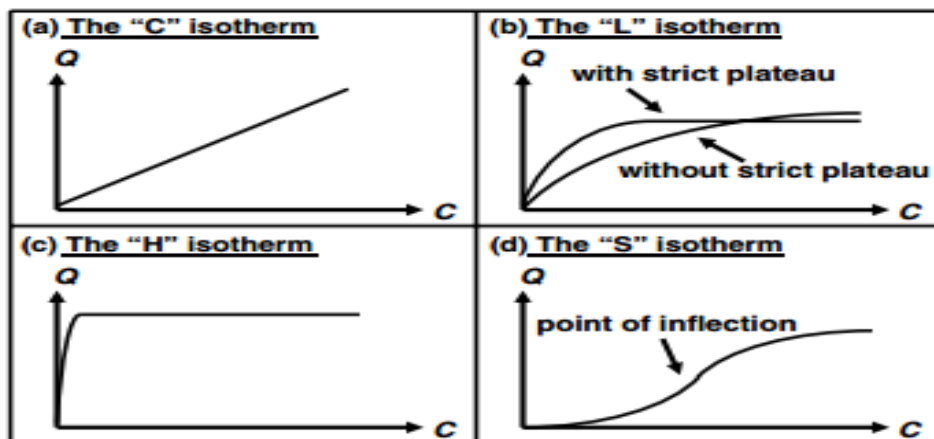


Figure 2.20 Four main types of adsorption isotherms. (G. Limousin et al.,2007)

2.2.3. Adsorption Kinetics

To elucidate what kind of adsorption mechanism occurs during the adsorption, there are various kinetic models. With investigation of adsorption kinetic models, adsorbate-adsorbent contact time or retention time can be found.

There are 4 main steps in the process of adsorption.

- 1) Adsorbate is in gas or liquid phase, diffuses towards to the film boundary layer of adsorbent. (Bulk solution transport). This step is often neglected due to the increasing of rate with mixing of solution.
- 2) Adsorbate came to the film layer moves towards the adsorbent pores. (Boundary layer diffusion).
- 3) Then adsorbate moves through the pore spaces of adsorbent and reaches to the surface where adsorption is occurred. (Intraparticle diffusion).
- 4) Finally, the adsorbate is hold to the adsorbent pores. (Sorption).

If the solution does not mixed, the first step is the slowest and this step can determine the adsorption rate. Therefore, if the fluid is stirred, adsorption rate will increase. The last step is too fast to be measured and the first step is accelerated by mixing the solution, so the second and third steps determine the rates of adsorption.

Boundary layer diffusion

While the boundary layer diffusion is occurred in the first few minutes of the adsorption process, intraparticle diffusion time is the larger part of adsorption process. Hence, it can be said that intra-particle diffusion step can be generally adsorption rate determining step. To understand whether the boundary layer step effects the first minutes of the adsorption process, the following equation is used.

$$-kt = \ln \frac{C_t}{C_0}$$

$-\ln C_t / C_0$ against the first adsorption times (for the first 5 -15 minutes) is plotted. If R^2 value (correlation coefficient value) is close to unity, it can be said that boundary layer effect controls the adsorption.

C_t : Adsorbate concentration remaining in solution in each contact time (mg/l).

C_0 : Initial adsorbate concentration in solution (mg/l).

k : The boundary layer diffusion constant (time^{-1})

Intraparticle Diffusion Model

Generally, intraparticle diffusion model is used for identify the adsorption mechanism. For determining the effect of intraparticle diffusion in the adsorption process, q_t against the square root of time value is plotted. The graph of q_t versus square root of time consists of two phases; the initial part is a boundary layer effect while the second linear part is intraparticle diffusion effect. Slope of second part will give rate constant of intraparticle diffusion and if R^2 value (correlation coefficient value) is close to unity, this model can be said to control the adsorption. If the intercept of second linear part is zero, it can be said intraparticle diffusion is only rate limiting step. The positive intercept value indicates rapid adsorption process (Leng, F., et al, 2014).

$$q_t = k_p t^{0.5} + I$$

where;

q_t is amount adsorbed at time t (mg/g),

k_p is the rate constant of intraparticle diffusion ($\text{mol/gmin}^{0.5}$)

t is adsorption time (min),

Pseudo-First-Order Kinetic Model (Lagergren Equation)

Pseudo first order kinetic model equation is;

$$\frac{dq}{dt} = k_1(q_e - q_t)$$

And linearized form of this model equation is;

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

where;

q_e is amount adsorbed at equilibrium (mg/g),

q_t is amount adsorbed at time t (mg/g),

t is adsorption time (min),

k_1 is the rate constant of pseudo-first-order kinetic (min^{-1}).

The rate constant k_1 is determined from the slope of the plot of $\ln(q_e - q_t)$ versus contact time (t) (Lagergren, 1898).

Pseudo- Second- Order Kinetic Model

Pseudo second order kinetic model equation is;

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

And linearized form of this model equation is;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where;

q_e is amount adsorbed at equilibrium (mg/g),

q_t is amount adsorbed at time t (mg/g),

t is adsorption time (min), and

k_2 is the rate constant of the pseudo-second-order kinetic (g/mg/min).

The rate constant k_2 is determined from the intercept of the plot of t/q_t versus contact time (t).

2.2.4. Adsorption Thermodynamic

Thermodynamic parameters like Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) should be calculated to fully understand how the adsorption mechanism. These parameters are calculated by using adsorption results which conducted at different temperature.

The Gibbs free energy change ΔG can be calculated by the following equation:

$$\Delta G^0 = -RT \ln b$$

The enthalpy change ΔH can be obtained by using the van't Hoff equation:

$$\ln b = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

where;

R is the gas constant (8.314 J/mol/K),

T is the temperature (K)

b is adsorption coefficient (equilibrium constant of Langmuir) obtained from Langmuir equation. It is equal to the ratio of the amount adsorbed (x/m in mg/g) to the adsorptive concentration (y/a in mg/l) (Mohammed, 2011).

$$b = \left(\frac{x}{m}\right) \cdot \left(\frac{y}{a}\right)$$

According to the van't Hoff equation, the van't Hoff plot of $\ln b$ against $1/T$ was plotted, then the enthalpy change (ΔH) and entropy change (ΔS) were obtained from the ($-\text{slope} \times R$) and ($\text{intercept} \times R$) of the van't Hoff plot respectively.

The negative ΔH° indicates that the adsorption process between adsorbate and adsorbent is exothermic and positive value indicates adsorption process is endothermic. The negative ΔG° suggests that the adsorption process is spontaneous. The positive entropy change, ΔS , indicates the increased

randomness at the solid/solution interface during the adsorption process (Chen C., et al. 2012; Haquea, E., et al., 2010).

2.2.5. Use of Adsorption in the removal of aromatic compounds

Nitroaromatic Compounds and Nitrobenzene

Nitroaromatic compounds are formed by direct nitration of benzene (or derivatives) with nitric acid in the presence of a sulfuric acid catalyst at 50 to 65°C (Çakır, 2010).

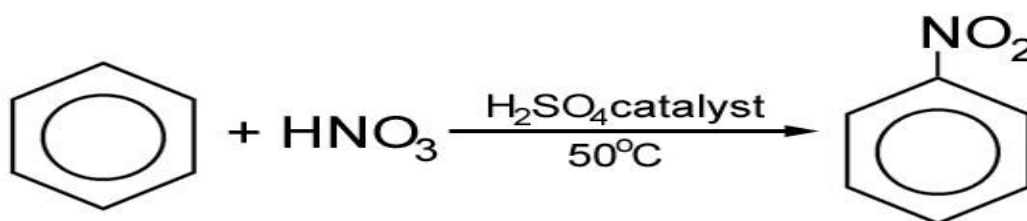


Figure 2.21 Nitration of benzene

Nitroaromatic compounds include the nitro group that is directly attached to the aromatic ring. They are important in industry and are often obtained by the direct nitration by using different ratio of nitric acid / sulfuric acid.

The nitration reaction and mechanism of benzene is shown in Figure 2.21 and 2.22, respectively.

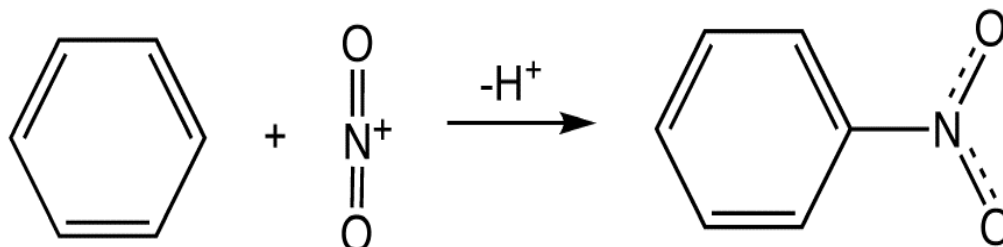


Figure 2.22 Nitration mechanism of benzene

Nitrobenzene

Structurally, nitrobenzene consists of a benzene ring with a single substituted nitro group (Figure 2.23) (EPA, 2009). Nitrobenzene compounds are formed by the substitution of one nitro group with one of the hydrogen atoms of benzene ring. This compound is light or dark yellow and an oily liquid with a bitter almond odor.

Schematic illustration of nitrobenzene is shown in Figure 2.23.

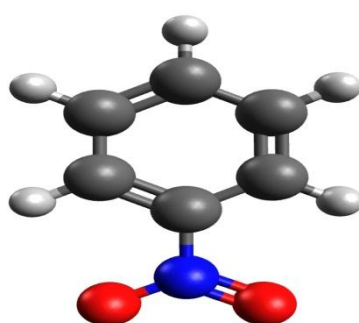


Figure 2.23 Chemical structure of nitrobenzene

Table 2.2 Physical and Chemical Properties of Nitrobenzene (EPA, 2009)

Molecular formula	C ₆ H ₅ NO ₂
Molar mass	123.06 g/mol
Appearance	Yellow colored liquid
Boiling Point	210.9 °C
Melting Point	5.7 °C
Density	1.199 g/cm ³ (20°C)
Solubility in water	0.19 g/100 mL (20°C)
Vapor pressure	0.15 mm Hg 25°C de (20 Pa, 20°C)

Nitrobenzene Production and Usage Areas

The first synthesis of nitrobenzene in 1834 was carried out by reaction of benzene with nitric acid gas by E. Mitscherlich. The first commercial production was performed in England in 1856. (IARC Monograph, 1996).

Nitrobenzene is a synthetic aromatic compound. An important part of this compound (95 to 98%) is used in the synthesis of aniline, and the other part is

used in rubber, soaps, pesticides, dye and pharmaceutical industry (Dai et al., 2010). Nitrobenzene is also used as solvent in oil refining, and in the synthesizing of some organic compounds such as cellulose acetate, dinitrobenzene, dichloroanilin and acetaminophen (EPA 2009).

According to the researches made in of 1994, nitrobenzene production is estimated to be approximately 2,133,800 tons in world (EHC 230, 2003). About one-third of which was produced in the U.S. U.S. production of nitrobenzene has been increasing in recent years, from 435,000 tons in 1986 to 533,000 tons in 1990 to 740,000 tons in 1994 (IPCS, 2003) (EPA 2009; EHC 230, 2003). It is seen that depending on the production capacity in US, the amount of aniline production increases year by year.

Toluene

Toluene is a clear, colorless and flammable volatile organic compound with pungent odor. While its solubility in many of the organic solvent is very high, in water is relatively poor (Taş, 2008).

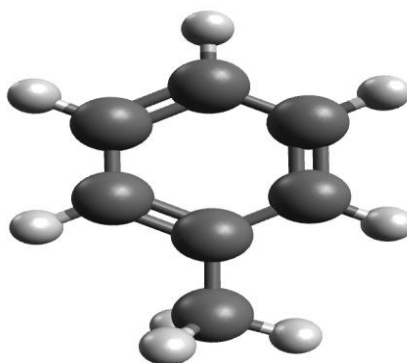


Figure 2.24 Chemical structure of toluene

Table 2.3 Physical and Chemical Properties of Toluene (Taş, 2008)

Cas number	108-88-3
Molecular formula	C ₆ H ₅ CH ₃
Molar mass	92.13 g/mol
Appearance	Colorless liquid
Boiling Point	111 °C
Melting Point	-139 °C
Density	0.861 g/cm ³ (20°C)
Solubility in water	1g / 100 mL (20°C)
Vapor pressure	28.1 mm Hg

Toluene Production and Usage Areas

Toluene is produced in two ways. One of them is the petroleum catalytic conversion; the other is the conversion of aliphatic hydrocarbons to aromatics. And also it is produced as byproduct in coke production from coal.

Usage areas of toluene are so wide such as, as solvent, thinner in the paint, rubber, printing, cosmetic, cleaning agents, inks, adhesives and resin industries. And also it is used in synthesis of several chemicals like benzene, phenol, xylene and as a raw material in the production of explosives. Toluene is also blended to petrol in order to increase the octane ratings (Deshpande and Shah, 2011).

Toluene dissipates into the environment and water during usage and transport of it. Toluene is toxic substance and it causes skin disease, irritation of eyes, respiratory system disorders, kidney, heart and liver damage (Meunprasertdee and Chotisuwan, 1995, 2010). Its presence in water, even at low concentrations, is a major environmental concern. Breathing in toluene vapours can cause drowsiness, dizziness, headache, sickness and memory problems. Overdose inhalation of toluene can cause coma, heart disease and even death. Therefore, it is one of the pollutants restricted by EPA. EPA allows the maximum amount of toluene in water as 1 g / L (ATSDR, 2000).

2.2.6. Use of Adsorption in the removal of organic dyes

Today, technology development and population growth leads to excessive pollution of water resources. Effluents of many industries such as textiles, paper and printing constitute environmental pollution due to the inclusion of synthetic dyes. Dyes in the effluent of many industrial wastewaters have the most difficult removal among the other contaminants. Their complex and synthetic origin aromatic structure makes them resistant to biodegradation (Ayar et al., 2007; Qin et al., 2009). Dye effluents pose a major threat to the environment and living creature. Some dyes possess toxicity, mutagenic and / or carcinogenic effects (Robinson et al., 2002). In addition, dyes lead to changing of the color of the water. So that photosynthesis occurs in water affected adversely. The lack of photosynthesis leads to a reduction in the amount of the dissolved oxygen in the

water, and accordingly leads to the reduction in the amount of aerobic microorganism. In addition, lack of oxygen can create a significant danger to the life of other creatures in need of oxygen. Therefore, disposal of dye-containing wastewater into the environment without treatment is very dangerous in terms of both human health and ecosystem.

Currently, there are more than 100000 dyes which are used in textile or other industries. Every year, 7×10^5 tons of dyestuffs are produced and up to 10-15% of them are discharged to the water (Robinson et al., 2001). In a relatively high amount of water consumed during textile production processes. This situation causes the increasing of wastewater during process.

Dyes show high resistance to oxidation, temperature, light and biological initiative. Colors, nonbiodegradable properties and toxicity on living creatures create a requirement for removal from wastewater. (Kumari and Abraham, 2007; Cauto, 2009; Kocaer and Alkan, 2002).

There are several physical, chemical and biological de-colorization methods for wastewater treatment. In general, biological de-colorization methods of dyes are ineffective, due to their resistance to aerobic degradation. Moreover, execution of anaerobic biological treatment methods for removal of dyes can cause generation of carcinogenic aromatic amines in the process. Physical methods like flocculation and reverse osmosis are insufficient non destructive methods. These methods are based on principle of transferring of contaminate to another medium. Therefore they lead to the formation of secondary pollution.

In chemical treatment of dyes, in generally, chlorine or ozone can be used. With these techniques, color and organic contaminants can be eliminated but, required amount of chemicals are very high. Therefore these techniques are not economically.

Adsorption technology that does not require high operating temperatures with a high cost is considered as one of the most competitive methods. The method is recognized for its high efficiency, low cost, simplicity, reusability of the adsorbent and easy recovery. And also by using this technique many of dye stuffs can be removed simultaneously.

Classification of Dyes

Dyes are generally composed of two main groups; chromophores and auxochromes. The former consists of a group of atoms, and is also responsible for producing color. Normally all hydrocarbons are colorless but chromophores which are non saturated groups are bond to them and leads to the formation of colored substances. This combined structure is named as chromogen. And the other part of dyes, auxochromes, support the chromophores in terms of fiber coloring and provide to the chromophores a large number of property such as water-soluble, enhanced affinity toward the fibers and also they alters the ability of the chromophore in terms of absorbing of the light (Gupta and Suhas, 2009). Some auxochrome groups amino group (-NH₂), carboxyl (-COOH), sulfonate (-SO₃H) and hydroxyl (-OH) (Savcı, 2005). The most commonly used chromophore groups in dyes is the azo group (-N=N-), carbonyl (-C=O), methyl group (-C-H₃) nitro and nitroso (-NO₂ and -N=C respectively) and quinoid groups. (Christie, 2001; Kaykıoğlu and Debik, 2006).

Dyes show structural diversity and they are classified according to solubility, chemical structure (nature of chromophores) and also according to their application to the fiber (dyeing properties) (Hunger 2003). This classification is shown in Table 2.4.

Table 2.4 Classification of Dyestuffs

Based on Solubility	Based on Types of Chromophores	Based on Dyeing Properties
• Water - soluble Dyes • Zwitter ion Dyes • Water - insoluble Dyes • Cationic Dyes • Anionic Dyes	• Azo Chromophore • Anthraquinone • Indigoid • Polymethine and Related Chromophores • Di and Triarylcarbenium and Relate Chromophores • Phthalocyanine Chromophore • Fluorescent Dyes • Quinophthalone Dyes • Nitro and Nitroso Dyes • Stilbene Dyes • Formazan Dyes • Triphenodioxazine Dyes	• Acid Dyes • Basic Dyes • Disperse Dyes • Direct Dyes • Reactive Dyes • Solvent Dyes • Sulfur Dyes • Vat Dyes

Dyes and dye stuffs are generally used in the textile industry and 60 % of them are examples of azo dyes.

Dyes classified according to how they are used in the dyeing process are;

Acid Dyes:

They are sodium salts of a sulfonic ($-\text{SO}_3\text{H}$), carboxylic ($-\text{COOH}$) or phenol organic acid. And their general formula is expressed as $\text{Bm-SO}_3\text{Na}^+$ (Bm is chromophore group of dyes). These water soluble and bright colored substances are used in several industries like; food, textile (nylon, wool, silk, modified acrylics, leather and so on), cosmetics and paper. If this types of dyes are classified as chemical structure (chromophore structure), they are listed as azo, nitro or nitroso, anthraquinone, triphenylmethane, azine, xanthenes.

Basic (Cationic) Dyes:

Basic dyes are cationic dyes consist of a colorless anion and colored cation (Gupta and Suhas, 2009). The reason for calling these dyes as cationic dyes is that they give colored cations in the solution. They include N and S atoms as positive charge carriers. They are used for paper, polyacrylonitrile, nylons, polyesters and in medicine too. (Başer ve İnancı, 1990). The principal chemical classes are diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine and acridine (Hunger 2003).

Disperse Dyes:

They are generally insoluble in water. The dyeing process is carried out by dissolving the these dyes in the hydrophobic fiber. They are used mainly on polyester and to some extent on nylon, cellulose, cellulose acetate, and acrylic fibers. They generally contain azo, anthraquinone, styryl, nitro, and benzodifuranone groups.

Direct Dyes:

They are used for dyeing of cotton, paper, rayon, leather, wool, silk and nylon. They are water soluble anionic dyes. These are sodium salts of sulfonic and

carboxylic acids like acid dyes. But dyeing process of acid and direct dyes are different from each other. Direct dyes are drawn directly from dye solution into the fiber without any chemical bonds are formed between fibers and dyes. Generally the dyes in this class are polyazo compounds, along with some stilbenes, phthalocyanines and oxazines (Hunter 2003).

Reactive dyes

Reactive dyes have a simple chemical structure. Molecular weights of them generally between 69-221 g/mol. Covalent bond, a type of chemical bond, occurs between fiber and dye molecules. They are the only dye type forming chemical bonds. They strongly attached to the fibers because of this chemical bond. In addition to the chromophore group, all reactive dyes have a reactive group that is capable of directly reacting with the fiber and have also a group providing solubility of the dye molecule. (Mercimek, 2007). They find their uses for cotton and other cellulosics, wool and nylon. And they contain azo, anthraquinone, triarylmethane, phthalocyanine, formazan, oxazine, etc as chromophoric groups.

Solvent Dyes:

They are used for plastics, gasoline, lubricants, oils, and waxes. These dyes are solvent soluble (water insoluble). They have apolar structure due to the lack of polar groups, such as sulfonic group, carboxylic group or quaternary ammonium. The principal chemical classes are predominantly azo and anthraquinone, but phthalocyanine and triarylmethane are also used.

Sulfur Dyes:

They are used in dyeing of cotton, rayon, silk, leather, paper, and wood. They have intermediate structures. Even they have relatively small groups of dyes, good washing properties and low costs make them economically important.

Vat Dyes:

These types of dyes are water insoluble. Such water-insoluble dyes can not affect to the fibers without any additional processing. These are used mainly for

cotton, wool and nylon. These water-insoluble dyes are with principal chemical class containing anthraquinone (including polycyclic quinones) and indigoids (Hunger 2003).

AZO DYES

The number of azo dyes constitutes the most important class of organic dyes. Azo dyes constitute a significant portion within the different types of dye. All dyes used in dyeing method have the azo group ($-N=N-$) in their structure as chromophore except for vat and sulfur dyes. A large number of these dyes produced in the world and used in a variety of applications. Resulting colored wastewater is particularly associated with their presence (Khodadoust, S. and Ghaedi, M., 2014). Methyl orange, methyl red are examples of azo dyes.

Methyl Orange

Methyl Orange is a water-soluble monoazo dye (Figure 2.25) and widely used in textile, printing, paper, medicine, food industry and research laboratories. Its structure is also characterized by sulphonic groups, which are responsible for the high solubility of these dyes in water. Because aqueous solution of it acts as a weak acid, it is used as acid-base indicator in analytical chemistry laboratory by exhibiting orange color in basic medium and red in color in acidic medium.

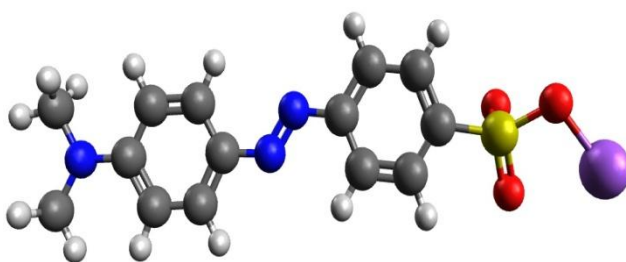


Figure 2.25 Methyl Orange Structure, purple is sodium, blue is nitrogen, yellow is sulphur, red is oxygen, dark grey is carbon and light grey is hydrogen

Table 2.5 Physical and Chemical Properties of Methyl Orange

Cas number	547-58-0
Molecular formula	C ₁₄ H ₁₄ N ₃ NaO ₃ S
Molar mass	327.33 g/mol
Density	1.28 g/cm ³
Melting point	>300°C
Solubility	0.5g / 100 mL water
UV-vis (λ_{max})	463 nm

Methyl Red

Methyl red is an indicator dye that turns red in acidic solutions. It is an azo dye and is a dark red crystalline powder. Methyl Red was chosen for the purpose of removing from wastewater because of its intense color (λ_{max} 410 nm) in aqueous systems and low biodegradability due to the presence of benzene rings.

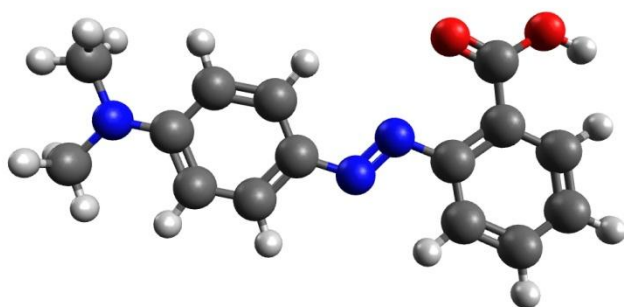


Figure 2.26 Methyl Red Structure, blue is nitrogen, red is oxygen, dark grey is carbon and light grey is hydrogen

Table 2.6 Physical and Chemical Properties of Methyl Red

Cas number	493-52-7
Molecular formula	C ₁₅ H ₁₅ N ₃ O ₂
Molar mass	269.30 g/mol
Density	0.791 g/cm ³
Melting point	179-182°C
Solubility	Soluble in ethanol
UV-vis (λ_{max})	410

2.3. Esterification

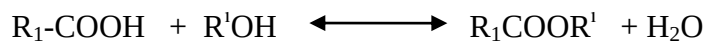
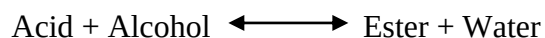
2.3.1. Mechanism of Esterification Reaction

Esters can be formed by the reaction of a carboxylic acid with an alcohol forming the ester and water molecules. These reactions are very important and a common type of reaction in the chemical industry. Esters are common in organic chemistry and biological materials, and often have a characteristic pleasant, fruity odor. This leads to their extensive use in the fragrance and flavor industry. Esters are used as raw materials for emulsifiers or as oiling agents for foods, spin finishes and textiles; lubricants for plastics; paint and ink additives and for mechanical processing; personal care emollients; surfactants and base materials for perfumes. Ester bonds are also found in many polymers.

Esterification reaction occurs by the reaction of carboxylic acid and alcohols forming the ester and water in the presence of acidic catalyst. The parameters which mostly influence the esterification reaction are catalyst amount, reaction temperature, reaction time and molar ratio of alcohol to acid. These reactions are very important and a common type of reaction in the chemical industry. Esterification reactions are slow and reversible. Esterification reactions are also limited by thermodynamic equilibrium. Hence, the equilibrium should be shifted towards the products according to Le Chatelier's principle by using excess reactant or removal of the one or both of the products.

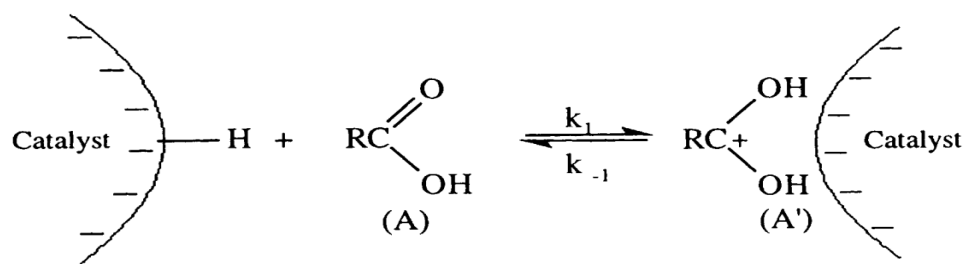
Esterification reaction without catalyst is slower because carboxylic acid gives proton by protolysis. Therefore, esterification should be occurred with help of an acid catalyst that acts protogenic. Even though homogeneous acid catalysts like HCl, H₂SO₄ very effective in esterification reactions, they aren't preferred due to cause corrosion and byproducts. Also these catalysts have a big disadvantage of separating problems (Altıokka and Ödeş, 2009; Sert and Atalay, 2010). The advantage of a heterogeneous catalyst is well known, and the use of solid ion exchange resin as the catalyst has the following advantages; (a) the catalyst can be easily separated from the reaction products by decantation or filtration (b) continuous operation in column and reusability are possible (c) the

side reaction can be eliminated and the product purity is high (Xu, 2009). The equation for the reaction between an acid and an alcohol is:

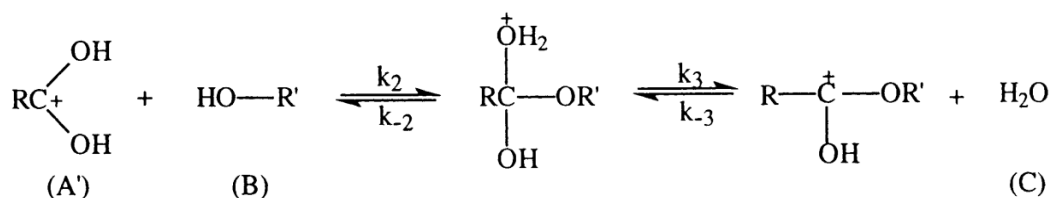


The reaction initiates with taking of a proton by carboxylic acid from catalyst. The proton is attached to one of the oxygen which is double bonded to carbon.

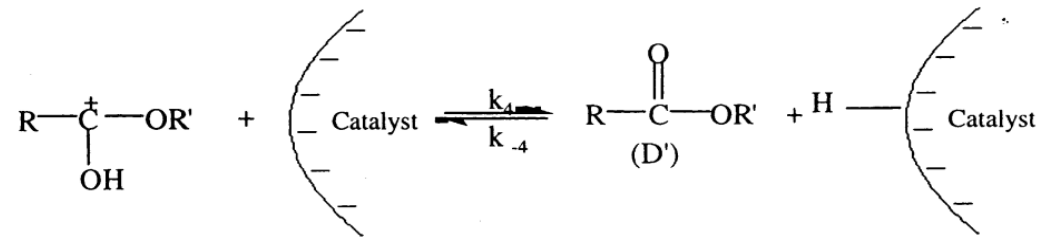
The transfer of the proton to the oxygen gives it a positive charge. This results in a fair amount of positive charge on the carbon atom.



The positive charge on the carbon atom is attacked by the hydroxyl group of the alcohol molecule. After that, a molecule of water is lost from the ion.



Finally, the catalyst is recovered by the transfer of proton from the ion to the catalyst surface:



Heterogeneous catalytic reaction steps over a catalyst are;

1. Mass transfer of the reactants from the bulk fluid to the external surface of the catalyst particle
2. Diffusion of reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface
3. Adsorption of reactant A onto the catalyst surface
4. Reaction on the surface of the catalyst
5. Desorption of products
6. Diffusion of the products from the interior of the catalyst particle to the pore mouth at the external surface
7. Mass transfer of the products from the external catalyst surface to the bulk fluid.

Steps of heterogeneous catalytic reaction over a catalyst are shown in Figure 2.27.

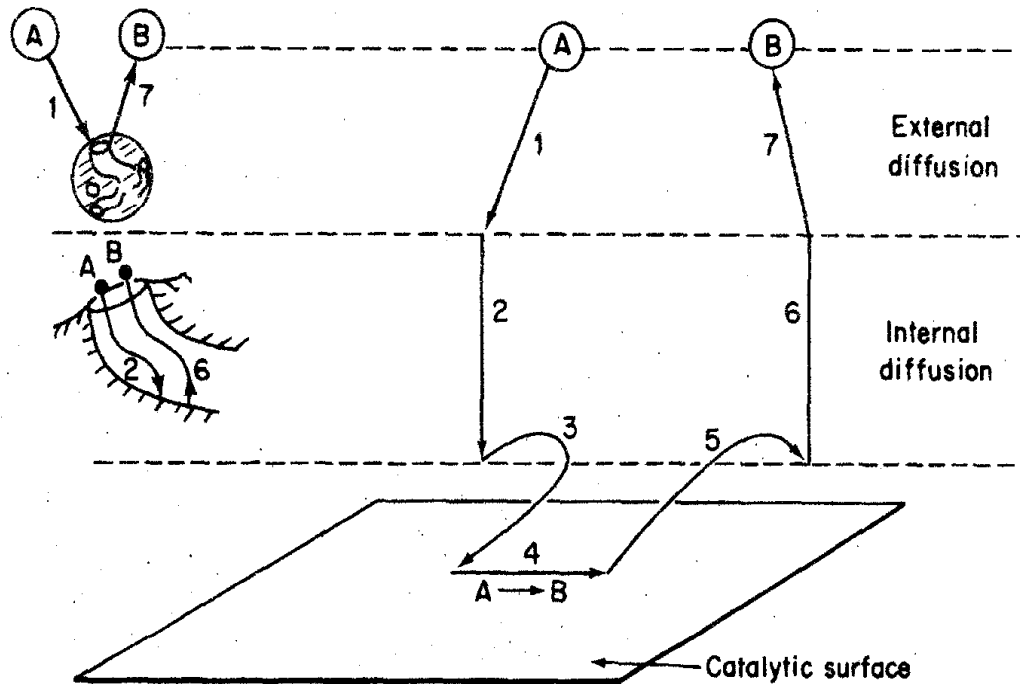


Figure 2.27 Steps in a heterogeneous catalytic reaction (Fogler, 1999)

Rate controlling step of a heterogeneous reaction must be predicted to determine the reaction rate. The kinetics and rate-controlling steps are deduced by noting how the progressive conversion of particles is influenced by particle size and operating temperature. Temperature, time, particle size etc. are a guide to experimentation and interpretation of experimental data.

In heterogeneous systems, the effects of inter-particle and intra-particle mass and heat transfer limitations are to be considered. In these cases when the rate is very high then the limitations are controlling, but when the rate is too low, the chemical reaction rate itself is the controlling step (Levenspiel, 1999).

The possible rate controlling steps and their application in ion exchange catalysts are grouped into three sections, namely;

- The surface reaction
- Internal mass transfer
- External mass transfer

Most of researchers working on esterification kinetics, found the controlling rate step as surface reaction (Ali et al., 2007; Akbay and Altıokka, 2011, Altıokka and Ödeş, 2009).

2.3.2. Catalysts

Esterification reactions proceed with or without a catalyst. However, Esterification reaction without catalyst is slower because rate depends on the autoprotolysis of the carboxylic acid. Therefore, esterification should be occurred with help of an acid catalyst that acts as a proton donor to the carboxylic acid.

Different catalysts used for esterification reactions are listed in Table 2.7.

Table 2.7 Catalysts used for esterification reactions

Homogeneous

Sulfuric acid, Toluenesulfonic acid, Phosphonic acid, Hydrochloric acid, Ferric sulfate hydrate, Methyl thiosulphate, Hydroiodic acid, Aluminium trichloride, Niobic acid, Alkyl benzene sulfonic acid

Heterogenous

Ion exchange resins, H-Z type solid acids, Enzymes, Solid super acids, Ion exchange membranes

Heterogenized Homogeneous

Polyolefin supported sulfonic acid, Heteropolyacid supported on activated carbon. Solid acids of metal oxide promoted with SO_4^{2-} H_3PO_4 supported on silica gel, Solid super acid of $\text{Zr}(\text{OH})_4$ exposing with H_2SO_4 by calcinations, Solid acid having salts of $\text{H}_3\text{PW}_{12}\text{O}_{40}\text{Cs}_2 \cdot 5\text{PW}_{12}\text{O}_{40}$

Even though homogeneous acid catalysts like HCl , H_2SO_4 very effective in esterification reactions, they aren't preferred due to cause corrosion and byproducts. Also these catalysts have a big disadvantage of separating problems (Altıokka and Ödeş, 2009; Sert and Atalay, 2010).

The advantages for heterogeneous catalysis over those performed in the presence of mineral acids may be pointed in:

- Unlike the homogeneous catalysis, it does not include toxicity, corrosiveness,
- They can also be used repeatedly over a prolonged period without any difficulty in handling and storing them

- The catalyst can be easily separated from the reaction products by decantation or filtration and the product will be highly pure where the actual exclusion of the side reactions is expected (Xu, 2009).

In the last decades, homogeneous catalysts which used because of the need of acidic catalyst are replaced, due to corrosion, waste generation and separation problems, by the heterogeneous catalysts. However studies on the heterogeneous catalysts with high conversions without the need of any additional processes are still carried on. The usage of ion exchange resins, which are the most often used heterogeneous catalysts, is limited by their low thermal stability to lower temperatures and low conversions are obtained in long reaction durations. Same situation is valid for heteropolyacids, moreover the hardness of preparation, costs and low surface area constituted the disadvantages for esterification reactions.

Using metal organic frameworks as catalysts, high conversions can be obtained in the production of esters which are among the most important chemical products and this study aims to study the synthesis of the appropriate MOF's and their application on the esterification reactions of the acetic acid.

This study plans to use MOF's which do not have the said disadvantages and have advantages such as ability to be designed for usage area, ease of preparation, their environmentally friendly nature, high surface area and high pore volume. All of this advantages increases usability of MOF's.

2.3.3. Acetic Acid Esters

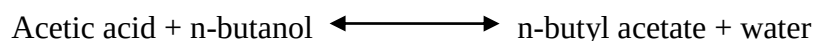
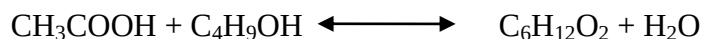
In today's world esters are among the most important chemical products. They have a wide application area as solvents, plasticizers, surfactants and also as a raw material in the production of the polymers and the pesticides.

Acetic acid esters have the most important place among the other esters. Esterification reaction of acetic acid with different alcohols is reversible and limited by chemical equilibrium. Forward reaction is esterification reaction of the acetic acid with alcohol; the reverse reaction is the hydrolysis reaction of the resulting ester. Because of the esterification reaction is reversible, conversions are very low and reaction is slow. And due to reactants in reaction medium,

possibility of encountering with byproducts is very high. It is observed that using a reactant in excess amount, to promote higher conversion, is only aggravated the problem.

Butyl Acetate

Butyl acetates are commonly manufactured by esterification of butanol and acetic acid with the presence of catalytic sulphuric acid under reflux conditions with the following reaction:



n-Butyl acetate (Figure 2.28) is an important solvent in the chemical industry. Primarily used in coating and painting processes, it has also been applied in pharmaceutical industries and cosmetic formulations as an artificial flavor in recent years. In addition, due to its pleasant fruity (rather like pears) odor, it is also used as a component in synthetic flavors of fruits. Because of its low toxicity and environmental impact, n-butyl acetate has become an important replacement to such toxic and teratogenic solvents as ethoxy ethyl acetate. It is conventionally synthesized from direct esterification of n-butanol with acetic acid.

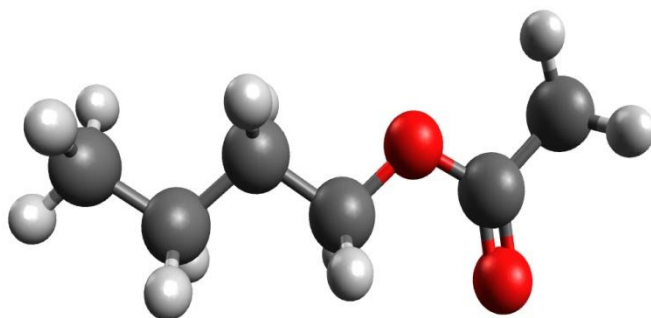


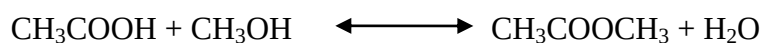
Figure 2.28 Butyl acetate structure, red is oxygen, dark grey is carbon and light grey is hydrogen

Table 2.8 Physical and Chemical Properties of Butyl Acetate

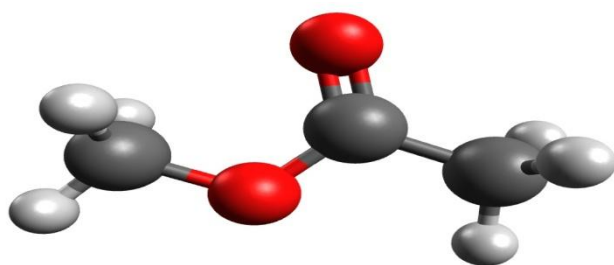
Chemical Formula	C₆H₁₂O₂
Molecular Weight, g/mol	116.16
Density, g/cm³ (20 °C)	0.8825
Appearance	Colorless liquid
Melting Point, °C	-78
Boiling Point, °C	126.1
Solubility in Water (20 °C)	0.68 g / 100 mL

Methyl acetate

Methyl acetate (MeOAc) is produced by the liquid-phase reaction of acetic acid (HOAc) and methanol (MeOH) catalyzed by sulphuric acid or a sulphonic acid ion-exchange resin in the temperature range of 310–325 K and at atmospheric pressure. The reaction is;



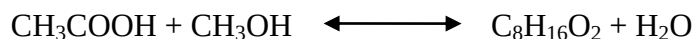
Methyl acetate (Figure 2.29) is used as solvent for the production of coating materials, nitro-cellulose, cellulose acetate, cellulose ethers, and celluloid. It is also used with a wide variety of resins, plasticizers, lacquers and certain fats.

**Figure 2.29** Methyl acetate structure, red is oxygen, dark grey is carbon and light grey is hydrogen**Table 2.9** Physical and Chemical Properties of Methyl Acetate

Chemical Formula	C₃H₆O₂
Molecular Weight, g/mol	74.08
Density, g/cm³ (20 °C)	0.932
Appearance	Colorless liquid
Melting Point, °C	-98
Boiling Point, °C	56.9
Solubility in Water (20 °C)	25 %

Hexyl Acetate

Hexyl acetate is an ester has the molecular formula of $C_8H_{16}O_2$. It is mainly used as a solvent for resins and polymers. It is also used as paint additive to improve its dispersion on a surface.



Hexyl acetate (Figure 2.30) is also used as a flavoring because of its fruity odor, and it is naturally present in many fruits (such as apples and plums) as well as alcoholic beverages.

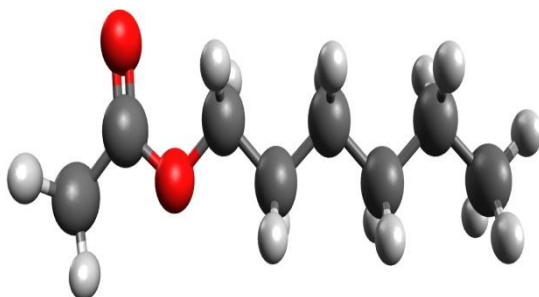


Figure 2.30 Hexyl acetate structure, red is oxygen, dark grey is carbon and light grey is hydrogen

Table 2.10 Physical and Chemical Properties of Hexyl Acetate

Chemical Formula	$C_8H_{16}O_2$
Molecular Weight, g/mol	144.21
Density, g/cm³ (20 °C)	0.8673
Appearance	Colorless liquid
Melting Point, °C	-80
Boiling Point, °C	171.5
Solubility in Water (20 °C)	0.4 g / 1000 mL

2.3.4. Usage of MOF in Esterification Reaction as Catalyst

MOFs are organic coordination structures, consist of metal ions connected by organic linkers and have high porosity. Metal organic frameworks are composed by the organic connectors which bridged between the metal ions. They draw attention because of their low densities, high surface areas and high porosities. In literature, it has been reported that while surface area of zeolite is 500 m² /g, mesoporous material is 1000 m² /g, porous carbon is 1500 m² /g, the

surface area of MOF-5 is $3800 \text{ m}^2 / \text{g}$ and MOF-177 is $5500 \text{ m}^2 / \text{g}$. Due to the high surface area, MOFs are generally used in gas adsorption, and also these materials are suitable as catalyst usage.

MOFs have been used as catalysts in the Knoevenagel reaction (Hasegawa et al., 2007) Friedel-Crafts reaction (Horcajada, 2007) oxidation (Xamena et al., 2008), transesterification (Zhou et al., 2009). Zhou et al. (Zhou et al., 2009) have used MOFs as catalyst in the production of ethyl methyl carbonate and 50% of conversion, have been achieved. Goesten et al. (Goesten et al., 2011) have synthesized MOFs by using Cr metal salts and increased the acidity of the MOF by exposing sulfation then they have used the MOF in the liquid phase esterification reaction.

Characterization of prepared MOF's will provide data on the surface area, crystal structure and thermal stabilities and effect of preparation technique on the structure will be determined. Using different metal salts prepared MOF's will be sulfated to gain acidic properties. With this, a catalyst with high conversion, ease of separation from the reaction mixture and high reusability will be synthesized.

The preparation and characterization of highly acidic MOF's are included in the literature in limited numbers. In addition to that there is no any study on their usage on the production of acetic acid esters are present in the literature.

Moreover in the case of achieving high conversions using prepared MOF's and reactants on their stoichiometric ratios, the separation costs will be lowered to the point that they can be neglected and with eliminating the need of hybrid processes economical and efficient production of esters will be provided. Besides the esterification of acetic acid with methanol, butanol and hexanol will be carried out on the batch reactors and the effects of MOF loading, MOF types, acid/alcohol ratio on the acetic acid conversion will be studied. With the characterization of MOF's which are prepared with different techniques, the effect of preparation techniques on the structure and catalytic activity and in addition to that using alcohols with different carbon content steric effect on the acetic acid conversion will be studied.

3. LITERATURE REVIEW

3.1. Removal of aromatic compounds by liquid phase adsorption

Aromatic organic compounds such as nitrobenzene and toluene, studied in this study, are important materials in the chemical industries and are used as starting materials or solvents in various chemical reactions. Although having these advantages, they are classified as carcinogenic, flammable and toxic substances (Choi et al., 2009; Wibowo et al., 2007). Their presence in water, even a small amount, is a major environmental concern. Hence the removal of these compounds from wastewater is necessitated before release into the environment (Wibowo et al., 2007).

For removal of different aromatic compounds from wastewater, several studies have been conducted by using numerous technologies such as adsorption, thermal or catalytic oxidation, membrane separation processes, and biological treatment methods. Adsorption technology that does not require high operating temperatures with a high cost is considered as one of the most competitive methods. This method, in particular, for the removal of low concentrations of aromatic organic contaminants from water has become one of the widely used methods (Yang et al., 2011). The adsorptive technique is based on the ability to be selective of the porous adsorbent for certain compounds. Compounds having suitable size and shape can easily access the pores of the solid adsorbent and so these compounds can be removed using the adsorptive technique.

Oliveira et al., (2002) researched adsorptive removal of thiophene and toluene on AgY, NiY ZnY and NaY zeolites. Characterizations of synthesized materials were conducted and BET surface area of NaY was obtained as 519 m²/g. The other synthesized adsorbents had smaller surface area when compared to NaY. Experimental results showed the ion exchanged technique of Y zeolite increased the adsorption capacity for aromatics and compounds which includes sulphur in organic liquid mixtures. They found out the adsorption of thiophene was higher than toluene on all of adsorbents.

Wibowo et al., (2007) investigated removal of benzene and toluene from solutions with adsorption technique. They used activated carbons such as F-400, F-400 Cox, and F-400 Tox as adsorbents. BET surface area of these adsorbents were in a range of 850-950 m²/g and in the order of F-400Tox < F-400 < F-400Cox. However, the maximum adsorption capacity of benzene and toluene was found on F-400Tox. The minimum one was found on F-400Cox. This showed, when carbon basicity was enhanced, the dispersive interactions were increased too. The adsorption mechanism of benzene and toluene by F-400 Tox (acidic structure) was explained with the π - π interaction between the carbon basal plane and the aromatic rings of benzene and toluene.

Wei et al. (2010) investigated synthetic nanocrystalline HAP for nitrobenzene adsorption. Isotherm models, Langmuir and Freundlich, were studied and they found out Freundlich model was matched well with experimental datas. Results of thermodynamic studies indicated that the adsorption process between nitrobenzene and nanocrystalline HAP was exothermic, spontaneous and physisorption. When the adsorbent dosage was 5 g/L, percentage amount of NB adsorption was achieved as 52.4 %. When the amount of adsorbent was increased to 20 g/L, removal of nitrobenzene adsorption was obtained as 95 %. They also compared synthetic nanocrystalline HAP with several adsorbent types. And they found the NB adsorption capacity of nanocrystalline HAP as 5.754 mg/g at 282 K. This result indicated nitrobenzene adsorption capacity on activated carbon (100 mg/g) was higher than synthetic nanocrystalline HAP. This situation was explained with the higher surface area of activated carbons (around 1000 m²/g) with comparing nanocrystalline HAP (42.32 m²/g).

Adsorptive removal of nitrobenzene (NB) on carbon materials (C1 and C2) which released from the combustion of ligneous biomass was studied by Dai et al. (2010). The BET surface area of C1, C2 and activated carbon was found as 851, 30 and 1432, respectively. The percentage removal of NB (NB: 50 mg/L) after 3 h was achieved as 92%, 27% and 81% by using C1, C2 and AC, respectively. In this paper, methylene blue (MB) adsorption was also investigated. The percentage removal of MB (MB: 50 mg/L) after 3 h was 87%, 23 % and 74 % using C1, C2 and AC, respectively. The maximum NB and MB adsorption amounts on C1 were found as 294 and 238 mg/g, respectively. These values were compared with AC

(344 mg/g). And it was found that NB and MB adsorption on C1 was lower than AC. Hence, the obtained results showed that the materials which include carbon obtained from the ligneous biomass combustion was cheap and harmless to the environment adsorbent for NB.

Rauthula and Srivastava (2011) studied with activated carbon as adsorbent for the removal of nitrobenzene and humic acid. They also investigated desorption experiments. According the results of characterization, ACC had meso porous nature. Existence of various types of functional groups on ACC surface was observed by Fourier transform infra-red (FTIR) spectra. Thermo gravimetric analysis profile showed that the ACC was stable up to 300°C. The BET surface area of ACC was 171.05m²/g. They found that the adsorption kinetics obeyed the pseudo second order kinetic model and intraparticle diffusion model was also used to estimate the adsorption mechanism. Thermal regeneration of adsorbents were also studied and it was found that ACC showed excellent regeneration ability in the adsorption of NB and HA.

A summary on the removal of aromatic compounds by liquid phase adsorption is given in Table 3.1.

Table 3.1 Asummary on the removal of aromatic compounds by liquid phase adsorption

Reference	Adsorbent	Adsorbate	Study	Results
Zhu et al. (2014)	Organoclays	Nitrobenzene	Enhancing adsorption capacity of organoclays, characterization and usage in adsorptive removal of Nitrobenzene	capacity for adsorbing hydrophobic organic contaminants has been enhanced
Wei et al. (2014)	Hydroxyapatite–gelatin (HAP–GEL) nanocomposite	Nitrobenzene	adsorbent was developed and characterized and used in nitrobenzene adsorption The effects of various parameters on nitrobenzene adsorption were investigated.	The maximum adsorption capacity was estimated to be 42.373 mg/g. Adsorption was found as physisorption, spontaneous and exothermic process.
Wen et al. (2012)	a novel lipid adsorption material (LAM)	Nitrobenzene	A lipid adsorption material (LAM) was synthesized and adsorption studies were conducted. The effect of adsorbent dosage, contact time, temperature and the initial concentration of nitrobenzene on adsorption was also studied.	Adsorption kinetics obeyed pseudo-first-order model Adsorption process was spontaneous and exothermic reaction. The adsorption capacity and removal efficiency of LAM (94.3 %) was higher than that of GAC (91.9 %).
Jadhav et al. (2013)	Granulated Activated Carbon	Nitrobenzene , aniline and phenol	The single solute equilibrium adsorption experiments and also binary experiments were carried out.	Adsorption of individual adsorbates, the adsorption capacity of the GAC was in the order NI > AN > PH.
Lin et al. (2015)	HKUST-1 (MOF)	p-nitrophenol	Removal of <i>p</i> -nitrophenol from water The adsorption kinetics, isotherms and thermodynamics were investigated.	HKUST 1 was found to possess an adsorption capacity of~400mg/g.

Table 3.1 A summary on the removal of aromatic compounds by liquid phase adsorption (continued)

Reference	Adsorbent	Adsorbate	Study	Results
Lovino et al. (2013)	Activated carbon	Toluene and Naphthalene	In this work, Toluene and Naphthalene adsorption tests both in mono and binary systems were carried out.	Toluene is adsorbed to a greater extent than Naphthalene, both in single and binary systems because of a different steric hindrance of the molecules.
Stofela et al. (2015)	Organoclay (Spectrogel-C)	Toluene	Liquid phase adsorption of toluene on organoclay and effect of different parameters on adsorption capacity was investigated.	Adsorptive removal percentage is 90 %. Toluene adsorption was endothermic process. Regeneration of used adsorbents was achieved by washing with ethanol.
Jing et al. (2015)	Poplar leaves reclamation for porous granules	Nitrobenzene	Poplar leaves reclamation for porous granules and their application in nitrobenzene removal from aqueous solution	The adsorption was spontaneous. The experimental results fitted well with the pseudo second-order model and Langmuir isotherm model. About 60 % adsorption removal was achieved

3.2. Removal of Organic Dyes by Adsorption

Dyes in wastewater are also serious problem. They discharge into the receiving waters because they are used several industries such as textile, paper, leather, plastic and so on. The nonbiodegradable nature of most dyes in the environment makes their removal from effluents necessary. There are several physical, chemical and biological de-colorization methods for wastewater treatment such as precipitation and coagulation/flocculation, biodegradation, ion exchange, chemical oxidation, filtration and adsorption that have been reported for the removal of dyes from industrial effluents (Faisal et al., 2007; Qin et al., 2009). Adsorption technology that does not require high operating temperatures with a high cost is considered as one of the most competitive methods. And also by using this technique many of dye stuffs can be removed simultaneously.

Li et al., (2005) prepared an activated carbon which coated with TiO_2 (TiO_2/AC) by solgel method. And they used the synthesized AC for removal of methyl orange by photocatalytic degradation. The factors affecting the efficiency of MO oxidation such as the methyl orange initial concentration, the pH, and the electric power of UV lamp were studied. According to experimental results, they concluded that degradation efficiency of MO was higher by using TiO_2/AC than only TiO_2 particles or a mixture of TiO_2 and AC. By using this technique, 98% of MO was degraded.

Santhi et al., (2010) performed adsorption of methyl red onto the activated carbon obtained from the annona squamosa seed. The maximum removal of MR was achieved as 82.81 %when pH 5, adsorbent dosage was 0.2g/ 50mL and initial concentration was 25 ppm. However, they did not conducted the regeneration of used adsorbent.

Asuha et al., (2010) synthesized mesoporous TiO_2 by hydrothermal method and they used it for removal of methyl orange. They found the surface area of synthesized material as $161.2\text{m}^2/\text{g}$. the adsorption data fitted with Langmuir and Freundlich isotherm methods and maximum adsorption capacity, Langmuir constant, was found as 454.5 mg/g. They achieved 87% removal of MO. In this study regeneration of adsorbent was studied with 1 M NaOH solution and 0.05 M

acetic acid solution. However, in the second usage of adsorbent, the percentage removal of MO was found as 20%.

Zhu et al., (2010) synthesized a bioadsorbent including two structure; chitosan-coated magnetic nano-sized materials γ -Fe₂O₃ and multi walled carbon nanotubes (m-CS/ γ -Fe₂O₃/MWCNTs), to understand the effect of MWCNTs on adsorption capacity for methyl orange, and they used these bioadsorbents in MO adsorption. It was found out that pseudo second order kinetic model explained the adsorption mechanism and Langmuir isotherm was found as the better matched model with experimental values. And the Langmuir constant of m-CS/ γ -Fe₂O₃/MWCNTs was found as 66.6 mg/g for MO removal. The adsorption capacity was increased from 9.99 mg/g to 31.52 mg/g with the addition of the carbon nanotubes.

Adsorptive removal of methyl orange and methyl violet on activated carbon obtained from *Phragmites australis* (PAAC) was studied by Chen et al., (2010). BET characterization results indicated that surface area and pore volume of synthesized PAAC was 1362 m²/g and 1.27 cm³/g, respectively. Langmuir, Freundlich and Temkin isotherm models were conducted and the maximum adsorption capacity was found as 238.1 mg/g. It was also found that Temkin isotherm was fitted well the experimental results.

Yao et al., (2011) studied about adsorptive removal of methyl orange on MWCNTs. The equilibrium adsorption data were analyzed by Langmuir, Freundlich and Temkin models and the results showed that the correlation coefficient values obtained from Langmuir isotherm closed to unity that's meaning this isotherm model matched better with experimental data. To understand the adsorption mechanism pseudo first order, second order and the intraparticle diffusion models were studied. The MO adsorption experimental data can be best described by pseudo-second order kinetic model. Maximum adsorption capacity of the adsorbent was calculated from Langmuir equation as 52.86 mg/g, they also conducted thermodynamic studies and they found the process was endothermic and spontaneous.

A summary on the removal of organic dyes by adsorption is given in Table 3.2.

Table 3.2 A study on the removal of organic dyes by adsorption

Reference	Adsorbent	Adsorbate	Study	Results
Yahyaei et al. (2014)	Ordered Mesoporous Alumina (OMA)	methyl orange, bromothymol blue, reactive yellow, methyl violet	Removal of dye pollutants from binary systems was investigated.	OMA was a good adsorbent for rapid removal of dyes (especially anionic ones) from aqueous solution. The adsorption kinetic data of binary dyemixtures follows the competitive statistical rate theory (SRT) model well.
Peng et al. (2014)	Ordered mesoporous carbon (Fe-CMK-3) with iron magnetic nanoparticles	Orange II (O II) and cationic dye methylene blue (MB)	The effect of various process parameters were performed.	The maximum monolayer adsorption capacity for O II and MB dyes were 269 and 316 mg g ⁻¹ , respectively. pseudo second-order model and Langmuir adsorption isotherm model were fitted the experimental data.
Aboua et al. (2015)	activated carbon from the shells of Macor_e fruit	Methylene blue (MB) and methyl orange (MO)	Removal of dyes by activated carbon from the shells of Macore fruit.	the percentage adsorption removal was found more than 98% for the two dyes. The adsorption process was a favourable, endothermic and spontaneous phenomenon.
Ghamgosar et al. (2014)	TiO ₂ electrodes	Organic dyes, and ruthenium complexes	Organic dyes and ruthenium complexes were investigated.	A simple and relatively rapid method was described to determine the equilibrium binding constant for sensitizer dye adsorption on TiO ₂ .
Leng et al. (2015)	Bio-char derived from sewage sludge by liquefaction	Malachite green (MG) and Methylene blue (MB)	Malachite green (MG) and Methylene blue(MB) adsorption on bio charged derived from sewage sludge by liquefaction.	The bio-chars were effective on Malachite green (MG) and Methylene blue(MB) removal from aqueous solution. Additionally, liquefaction of SS with acetone as the solvent at low temperature (280°C) would favor the production of bio-char adsorbent in terms of bio-char yield and MG and MB adsorption capacity.

Table 3.2 A study on the removal of organic dyes by adsorption (continued)

Reference	Adsorbent	Adsorbate	Study	Results
Singla et al. (2015)	Boron nitride nanomaterials	Brilliant green (BG) and methyl orange(MO)	Adsorption removal of dyes by using boron nitride nanomaterials	The surface areas of BN nanoparticles and nanosheets were 120.68 m ² /g and 50.02 m ² /g. Percentage removal of BG and MO on BN nanoparticles was found as 90 and 70 %, respectively when adsorbent amount was 0.02 gram
Heibati et al. (2015)	Activated carbons prepared from walnut and poplar woods	AR 18	Adsorption of the dye AR 18 was studied.	Maximum adsorption capacity was found as 30.3 and 3.91 for activated carbons prepared from walnut and poplar woods (ACW and ACP), respectively.
Mahamad et al. (2015)	Activated carbon from pineapple waste biomass	Methylene blue (MB)	Dye removal with activated carbon from pineapple waste biomass	Surface area of prepared adsorbent was 914.67 m ² /g and adsorption capacity at 288.34 mg/g.
Isah et al. (2015)	Coconut shell based activated carbon	Reactive Blue 19 (RB19)	Reactive Blue 19 dye adsorption	About 80 % dye removal was achieved at 28 °C (adsorbent dosage = 1.0 g/L, dye solution pH = 12.0, contact time = 20 min)
Wasti and Awan, (2014)	Modified immobilized activated alumina (MIAA)	Cibacron reactive yellow	Adsorption of textile dye onto modified immobilized activated alumina	The removal efficiency of Cibacron reactive yellow dye with an initial concentration of 400 mg/L was greater than 90% for 90 min contact time. MIAA can be regenerated thermally and chemically with the dye removal efficiency remained above 85% during the first 4 regeneration cycles.

3.3. Usage of MOFs in Liquid Phase Adsorption

The metal organic frameworks (MOFs), a new class of hybrid materials, consist of metal ions connected by organic linkers and have a high porosity. They have all of the advantages of both organic and inorganic porous materials. Metal organic frameworks are composed by the organic connectors which are bridged between the metal ions. They draw attention because of their low densities, high surface areas, tunable pore size, and high porosities. These materials, known as the new member of the porous materials, have been widely investigated in various application areas such as separation (Yang and Yan, 2011), gas adsorption and storage (Couck et al., 2009), catalyst (Vu et al., 2013; Wu et al., 2013; Lin et al., 2012), adsorption of organic molecules (Yanga et al., 2011; Lenga et al., 2014), and drug delivery (Taylor-Pashow et al., 2009). While one of the most important usage areas of MOFs is the adsorptive removal of hazardous and noxious substances, their adsorption abilities have been relatively unexplored compared to the other adsorbents such as activated carbon or zeolites (Achmann et al., 2010; Jia et al., 2013). Due to peculiar features, such as high surface area, adsorption of various liquids and gases are promising. In the adsorption processes, the regeneration of these substances, compared to zeolite and activated carbon which necessitate high temperatures and cost, tends to require less processing. All of these advantages make it superior to the other porous materials.

Haque et al., (2010) reported adsorption of methyl orange (MO) on chromium MIL-101 and MIL-53. The adsorption capacity and adsorption kinetic constants of MIL-101 were found higher than MIL-53 (Cr), due to larger pore size and surface area of MIL-101. Adsorptive removal studies of MO at different temperatures revealed that the adsorption was an endothermic and spontaneous process.

Patil et al., (2011) synthesized MIL-53 (Al) hydrothermally then they investigated nitrobenzene (NB) adsorption on this material. Adsorption amount of NB decreased with an increasing of temperature. Effect of pH on NB adsorption was also investigated and any significant difference was not observed in acidic pH. The obtained results revealed that adsorption experimental data were followed Sips and Redlich Peterson isotherms. The maximum NB adsorption

capacity on obtained MIL-53(Al) was 610 mg/g, greater than organoclays (100 mg/g) and zeolites (267.2 mg/g). However, it was found lower than that of modified commercial activated carbons (1443.53 mg/g). The BET surface area of MIL-53(Al) and modified activated carbon were 1235 and 926 m²/g and maximum nitrobenzene uptake onto this material and AC were 610 and 1443.53 mg/g, respectively. The NB adsorption capacity of MIL-53(Al) was found out as lower than that of AC while surface area of MOF was higher because of nonavailability of mesopores in MIL-53(Al).

Haque et al., (2011) studied adsorption interaction between methyl orange (MO), methylene blue (MB) and MOF-235. The adsorptive performance of MOF-235 was much greater than activated carbon. Thermodynamic calculations showed MO and MB adsorption was a spontaneous and endothermic.

Chen et al., (2012) studied kinetic and thermodynamic of xylenol orange adsorption on MIL-101. Adsorption kinetics and isotherms results revealed that pseudo second order kinetic model and Langmuir adsorption isotherm fitted well for the adsorptive removal of XO on MIL-101. The thermodynamic parameters, including free energy, enthalpy, and entropy of adsorption, were calculated from the result of Langmuir isotherms, and the results showed the adsorption of XO on MIL-101 was exothermic. They studied the regeneration of MIL-101 with NaOH solution. But they claimed the MOF structure could be destroyed while using the NaOH solution, and the surface area decreased with the increasing of regeneration cycles. They investigated pH effect on adsorption capacity of XO on MIL-101 and they explained that the adsorbed amounts of XO decreased with increasing pH. This situation indicated the adsorption mechanism of XO on MOF was electrostatic interaction between the XO and the adsorbents. They also compared the adsorption capacity of MIL-101 with MCM-41 and active carbon, the amount of adsorption of MCM-41 was lower than the others. Active carbon was only suitable for dye adsorption at low concentration, while MIL-101 had a high dye adsorption capacity at low and high concentrations. Hence, they concluded MIL-101 was a good candidate for removal of dyes, and can be reused for many times.

Huo and Yan, (2012) studied with malachite green as dye and MIL-100 (Fe) as adsorbent. They investigated the adsorption interaction between them. For

comparing of different adsorbent, they studied with MIL-101, MIL-53(Al) and activated carbon. However, MIL-100 (Fe) was found as the only material which had a much higher MG adsorption capacity. The high adsorption capacity, good solvent stability, and excellent reusability make MIL-100(Fe) promising as a novel adsorbent for MG adsorptive removal from liquid solution.

Moreira et al., (2012) studied xylene isomers and ethylbenzene (EB) adsorption onto MIL-125(Ti) for separation in liquid phase. It was found that MIL-125 (Ti) was suitable for separation of p-xylene from the other xylene isomers, especially at a low feed concentration of xylene.

Kim et al., (2013) studied liquid phase adsorption of selected chloroaromatics (chlorobenzene, 2-chlorotoluene, 1,3- dichlorobenzene, and 2-chloroanisole) onto various metal organic frameworks were investigated including MIL-125, NH₂-MIL- 125, UiO-66, MIL-101, and Cu₃(BTC)₂. It was found out that their adsorption capacity was much higher than that of activated carbon under the same conditions. The chloroaromatic adsorption experimental data can be best described by pseudo-second order kinetic model, and the adsorption equilibrium experiments showed dye adsorption was fitted by Langmuir model. The thermodynamic study revealed adsorption of 2-chloroanisole on NH₂-MIL-125, MIL-101, and activated carbon was spontaneous and exothermic. The adsorption rate constants increased with temperature and showed a dependence on the size of pore and surface functionality of the MOFs.

Qin et al., (2014) synthesized MIL-101 doped with palladium and used in vapour phase adsorption of toluene and hydrogen storage. Compared with MIL-101, usage of PdCl₂-functionalized MIL-101 enhanced toluene adsorption capacity. While toluene uptake by MIL-101 was 1110 mg/g, toluene uptake by 3wt % PdCl₂/MIL-101 was 1285 mg/g. H₂ uptake also increased with the addition of palladium.

Trens et al., (2014) investigated the adsorption of a xylene mixture onto MIL-101(Cr) experimentally and theoretically. The adsorbed amount of p-xylene is higher than the adsorption of o- or m-xylene onto MIL-101. This was discussed in terms of stacking in the cavities of MIL-101. The filling of the small cavities of

MIL-101 was found more difficult in the case of m-xylene which was interpreted by a weaker interaction with the cavities walls.

Leng et al., (2014) studied with MIL-101, a metal-organic framework, and uranine adsorption studies from aqueous solution were also conducted. The effects of several factors on adsorption were investigated including contact time, pH value, and initial concentration of adsorbate. They also studied the adsorption kinetics and isotherms. The uranine adsorption experimental data can be best described by pseudo-second order kinetic model, and the adsorption equilibrium experiments showed uranine adsorption was fitted by Langmuir model. It was also found that the adsorption capacity of MIL-101 was greater than the zeolitic imidazolate framework, ZIF-8 indicating the significance of the electrostatic interactions between MIL-101 and uranine and the significance of having large pore size of MIL-101 could not be ruled out for the adsorption interaction. Adsorption thermodynamic results showed that interaction between uranine and MIL-101 was endothermic and spontaneous.

Lin et al., (2014) studied adsorption behaviour of Cu-BTC for methylene blue. Synthesizing and characterization of Cu-BTC were investigated. Adsorption equilibrium was fitted well with Langmuir. Thermodynamic parameters confirmed that the adsorption process was spontaneous and exothermic. The maximum adsorptive removal has been achieved at the pH 7. The possible mechanism and the adsorption behavior of the adsorption of MB onto Cu-BTC were investigated. The adsorbent Cu-BTC could be easily regenerated after washing with ethanol. The experimental results suggested that Cu-BTC materials have potential application for the wastewater treatment containing MB.

Shen et al., (2014) synthesized hierarchically mesostructured MIL-101 with different mineralizing agents such as anhydrous sodium acetate or hydrofluoric acid as a mineralizing agent and cetyltrimethylammonium bromide (CTAB) as a structure-directing agent. Then they used these MOFs in adsorption of MO and MB from wastewater. The obtained results revealed that in adsorption of MB, MIL-101 that was synthesized by sodium acetate showed higher performance than others. The MB and MO adsorption experimental data can be

best described by pseudo-second order kinetic model, and the adsorption equilibrium experiments showed dye adsorption was fitted by Langmuir model.

Adsorption of Orange II on iron-benzenetricarboxylate (Fe(BTC)) was conducted by Garcia et al., (2014). Experimental results revealed that the adsorption capacities of Fe(BTC) were much greater than activated carbon. The adsorption equilibrium experiments showed Orange II adsorption was fitted by Langmuir model. The kinetic study showed that pseudo second order kinetic model was fitted with experimental results, indicating the coexistence of chemical and physical adsorption. In this study intra-particle diffusion was found as the rate controlling step of adsorption process. And the results indicated the adsorption of dye on Fe(BTC) was exothermic, feasible and spontaneous process. The high recovery of the dye showed that Fe(BTC) can be employed as an effective and reusable adsorbent for the removal of Orange II from aqueous solutions.

3.4. Synthesis and Characterization of MOF

MOFs can be synthesized by self-assembly of organic ligands and metal ions. MOFs can be synthesized by means of several ways such as solvothermal, hydrothermal, ionothermal, ultrasonic, microwave irradiation, electrochemical and mechanochemical synthesis. In this study, selected MOFs were synthesized with solvothermal/hydrothermal and ionothermal assisted ultrasonic methods.

Solvothermal synthesis method can be considered as more comprehensive method. This method is similar to hydrothermal synthesis method. Only difference between these two methods are that; while in hydrothermal synthesis method water is used as solvent, in this method all solvents can be used. Organic ligands, metal complexes and solvents are placed in Teflon lined stainless steel autoclave. And reaction is performed at specified temperature, pressures and time. After that, obtained MOFs are purified and dried for usage. Disadvantage of this method is reaction takes place a long times from several hours up to several months, depending upon the MOF of interest and the reaction solvent, reaction temperature, reagent concentrations, and other factors. Table 3.3 shows some studies involving synthesized of MOFs by solvothermal method.

Ionothermal method is a method which ionic liquids are used in synthesis of MOFs. Ionic liquids are acting as reaction medium. They have many advantages; high thermal stability, ionic conductivity and negligible vapor pressure. Thus, ionothermal method eliminates the necessity of high pressure which is required for solvothermal method. Expensiveness and environmentally unfriendly production method led to the replacement of the ionic liquid with deep eutectic solvents. Ionothermal synthesis of MOFs are summarized in Table 3.4.

Sonochemical synthesis method can also be used for synthesis of MOFs. In case of ultrasonic-assisted synthesis, the cavitation collapse of the vacuum bubbles produced in the sonochemical reaction leads to very fast and intense local heating and high pressure, which allow both a rapid synthesis and a tuning of the kinetics of the reaction. Table 3.5 shows studies involving synthesis of MOFs by ultrasonic method.

Table 3.3 Synthesis of MOFs by Solvothermal method

MOF	Metal	Organic Linker	Solvent	Temperature (°C)	Time (h)	Usage Area	Reference
MIL 125	Ti{OCH(CH ₃) ₂ } ₄ , Titanium isopropoxide	H ₂ BDC	DMF/metanol	150	16	Adsorptive removal of chloroaromatic compounds onto metal organic frameworks	Kim, et al. (2013)
UiO 66	ZrCl ₄	H ₂ BDC	DMF	220	16		
MIL 101	Cr(NO ₃) ₃ ·9H ₂ O	H ₂ BDC	Water	220	8		
Cu ₃ (BTC) ₂	Cu(CO ₂ CH ₃) ₂ · H ₂ O	H ₃ BTC	Ethanol	150	48		
MOF 235	FeCl ₃ ·6H ₂ O	H ₂ BDC	DMF/ethanol	80	24	Adsorption of methyl orange (MO) and methylene blue (MB) on MOF 235	Haque et al. (2011)
MIL 101	Cr(NO ₃) ₃ ·9H ₂ O	H ₂ BDC	Water	220	8	Naproxen and clofibric acid adsorption from water on two different metal organic frameworks	Hasan et al. (2012)
MIL 100 Fe	Fe ⁰	H ₃ BTC	Water	180	2		
MIL 53 Al	Al(NO ₃) ₃ · 9H ₂ O	H ₂ BDC	Water	150	24	Bisphenol A adsorption	Zhou et al. (2013)
MIL 53 Fe	FeCl ₃ ·6H ₂ O	H ₂ BDC	DMF	150	15	The photocatalytic decolorization of methylene blue dye in aqueous solution	Du et al. (2011)
MOF 5	Zn(NO ₃) ₂ · 6H ₂ O	H ₂ BDC	DMF	120	21	Synthesis and supporting of MOF 5 with palladium and catalyst usage	Opelt et al. (2008)

MOF-74	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	H_4DHTP	DMF	rt	18	Synthesis and Characterization	Krishna murthy and Agarwa l (2014)
MIL-47	VCl_3	H_2BDC	Water	200	96	Synthesis and Characterization	Barthel et et al. (2002)
						Vapor phase separation of xylene isomers	Finsy et al. (2008)

H_2BDC = 1,4-benzene-dicarboxylic acid; H_3BTC = 1,3,5-benzene-tricarboxylic acid; H_4DHTP = 2,5-dihydroxyterephthalic acid; rt: room temperature; DMF = dimethylformamide

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[illegible]

Table 3.5 Synthesis of MOFs by Sonochemical method

MOF	Metal	Organic Linker	Solvent	Temperature (°C)	Time (h)	Usage Area	Reference
$\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3$	$\text{Cu}_2(\text{OAc})_4(\text{H}_2\text{O})_2$	H_3BTC	Etanol/DMF	25	5	Synthesis and characterization	Khan and Jhung (2009)
MOF 177	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	H_3BTB	NMP	20-60	nc	CO_2 adsorption, comparison of sonochemical method with microwave synthesis method	Jung et al. (2010)
MIL 53 Fe	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$,	H_2BDC	DMF	50	35	Synthesis and characterization	Gordon et al. (2012)
				60	16		
				70	6		
				7, 11, 15	nc	Synthesis and characterization and comparison of synthesis methods	Haque et al. (2010)
MIL 88	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	Fumaric acid	DMF	0, 20, 50	0.5, 1, 1.5, 2	Synthesis and characterization	Chalati et al. (2011)

H_3BTB = 1,3,5-Tris(4-carboxyphenyl)benzene; NMP = N-Methyl-2-pyrrolidone

3.5. Esterification of acetic acid catalyzed by different catalysts

There are a number of studies related to the esterification reactions which are catalyzed by different resins reported in the literature.

Chen et al. (1999) investigated esterification of acrylic acid with 1-butanol in a heterogeneous solid-liquid reaction system. The catalysts used in this study, solid acids such as an acidic salt of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$. Liquid acid catalysts including heteropolyacids and H_2SO_4 and also organic resins like Nafion and Amberlyst 15 were also used in this study. At the end of the experiments, they found out that the catalytic activity of liquid acids increased as the acid strength increased. According to experiments made by solid catalyst acids and ionic resins; it was demonstrated that the activity of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ was almost retained after the addition of water, while the activities of the organic resins greatly decreased.

Lilja et al. (2002) studied esterification of acetic, propionic and pentanoic acid with different alcohols including methanol, ethanol, butanol, 2-butanol 1-propanol, 2-propanol, in the existence of a fibrous polymer-supported sulphonic acid catalyst, called Smopex-101 by at 60 °C. Amberlyst 15 and a homogeneous catalyst, liquid HCl were also investigated to compare with Smopex- 101. The experimental results were matched with a second order model and a more advanced adsorption based model.

Gangadwala et al. (2003), carried out esterification of acetic acid with n-butanol in the existence of different ion exchange resins. The used resins were Amberlyst-15, Amberlite IR-120, TX-66 and Inidon-130. The effect of various parameters such as molar ratio of alcohol to acid, temperature, catalyst loading, and particle size was investigated to examine the kinetic model. Pseudo homogeneous, Eley-Rideal, Langmuir-Hinshelwood-Hougen-Watson (LHHW), and modified LHHW models were studied.

In the study of Altıokka and Çıtak (2003), the kinetics of esterification of acetic acid with iso-butanol in a stirred batch reactor with the solution of dioxane, studied with and without catalyst. The reaction rates for the temperature range 318 to 348 K and the equilibrium constants were found. The uncatalyzed reaction was

found to be second-order reversible. On the other hand, the reaction was found to occur between an adsorbed alcohol molecule and a molecule of acid in the bulk fluid with catalyst (Eley-Rideal model). Also, it is observed that the initial reaction rate decreased with alcohol and water concentrations and linearly increased with that of acid.

Teo and Saha (2004) studied esterification of acetic acid with isoamyl alcohol using Purolite CT-175 as catalyst. Temperature and alcohol acid molar ratio were also investigated. The experiments were carried out in a stirred batch reactor. It was seen that the equilibrium conversion of acetic acid was enhanced as temperature and alcohol acid ratio were increased. They explained the catalyst could be reused. LHHW and ER kinetic models were used and LHHW model was well fitted with the experimental data. The nonideality of each species in the reacting mixture was accounted for by using the activity coefficient by the use of the UNIFAC group contribution method. The surface reaction is the rate-limiting step.

Ali and Merchant (2006) investigated kinetic study of the esterification of acetic acid with 2-propanol with different ionic exchange resins Dowex 50Wx8-400, Amberlite IR-120, and Amberlyst 15. The experiments were conducted at different conditions; a range of temperature of 303 to 343 K; the molar ratios acid to alcohol of 0.5, 1, and 2; and catalyst loadings of 20, 40, and 60 g/L. With increasing of temperature, acid to alcohol ratio and catalyst loading, the reaction kinetics for the three catalysts increased. The pseudohomogeneous (PH), Eley Rideal (ER), Langmuir Hinshelwood (LH), modified Langmuir Hinshelwood (ML), and Pöpkén (PP) models were found to predict reaction kinetics. Although the ML model was found out the best for predicting reaction kinetics, the PP model was better for system catalyzed by Amberlyst-15.

Delgado et. al. (2007) studied on esterification of lactic acid and ethanol catalyzed by Amberlyst 15. The adsorption constants for the four components on Amberlyst 15 were determined by performing adsorption experiments between two non-reacting species. The values found for the adsorption constants follow the order: water > ethanol > lactic acid > ethyl lactate. Experimental kinetic data of the esterification and the hydrolysis reactions were correlated simultaneously with

the Langmuir–Hinshelwood (LH) and pseudo-homogeneous (PH) models. The LH model gave the best agreement with the kinetic experimental data. The activity coefficients were calculated according to the UNIQUAC model.

Izci and Bodur (2007) conducted on the esterification of acetic acid with iso-butanol in 1,4-dioxan as a solvent with and without catalyst. Reactions were carried out in batch reactor. Various parameters effect on esterification including catalyst type (Dowex 50 Wx2, Amberlite IR-120), temperature, stirrer speed and catalyst loading were investigated and then reaction rates were found. The kinetics of the heterogeneous catalyzed esterification reaction was correlated by a kinetic model based on pseudo-homogeneous catalysis. As a result, it was found that the activity of the Dowex50Wx2 was more than the activity of Amberlite IR- 120.

Kolah et al. (2008) investigated esterification of succinic acid with ethanol to form monoethyl and diethyl succinate. The reaction was carried out in batch reactor in isothermal conditions and macroporous Amberlyst-15 ion -exchange resin was used as catalyst. Different parameters including temperature, initial molar ratios of ethanol to succinic acid and catalyst loading were studied for kinetic modelling. A pseudohomogeneous mole fraction model matched well with the experimental data.

Esterification of acrylic acid with propylene glycol was studied by Altiokka et. al.(2009). Amberlyst-15 was used as a heterogeneous catalyst. The reaction was conducted in a batch reactor. Effect of temperature, alcohol to acid molar ratio, inhibitor, phenothizine, catalyst loading was studied. The simultaneous dimerization/polymerization of acrylic acid and products, in addition to the reversible esterification reaction, was proposed as the reaction mechanism. Kinetic equations corresponding to the reaction mechanism have also been developed.

A summary on the esterification reactions catalyzed by heterogeneous catalysts is given in Table 3.6.

Table 3.1 A summary on the esterification reactions catalyzed by heterogeneous catalysts

Referance	Substrate	Catalysts	Remark	Conditions	Results
Shimizu et.al. (1987)	Octanoic acid Butanol	Amberlyst 15	Kinetic and reactor modeling	80 °C, 250 rpm	Pseudo homogeneous
Dakshinamuty et.al. (1992)	Acetic acid n-propanol	Indian CX-125	Kinetic and reactor modeling	323-363 K	Pseudo homogeneous
Chaktabarti et.al. (1993)	Acetic acid Methanol	Amberlyst 15	Kinetic and reactor modeling	323-353 K <760 rpm	Pseudo homogeneous
Bhatnagar et.al. (1994)	Butyric acid Butanol	Amberlyst 15	Kinetic and reactor modeling	338-358 K CL:2-15wt% 2:1 - 8:1	Pseudo homogeneous E: 52 kJ/mol
Venimadhavan et.al. (1994)	Acetic acid Methanol	Amberlyst 15	Kinetic study and Adsorption	313-323 K	LHHW mechanism
Xu and Chuang (1996)	Dilute acetic acid Methanol	Amberlyst 15 Amberlyst 35 Amberlite IRA-	Batch reactor performance	313-373 K CL:1.5-4.5 wt%	80% conversion

Table 3.6 A summary on the esterification reactions catalyzed by heterogeneous catalysts (continued)

Reference	Substrate	Catalysts	Remark	Conditions	Results
Xu and Chuang (1997)	Acetic acid Methanol	Amberlyst 15	Intraparticle diffusion effect	353 K	h=0.77 dp >1 mm h=0.94 dp <0.6 mm
Yadav and Kulkarni (2000)	Lactic acid iso-propanol	Indion 130 Amberlyst 15, 36 Amberlite IR-120	Catalyst selection	333-363 K	Amberlyst 36
Pöpken et.al. (2000)	Acetic acid Methanol	Amberlyst 15	Homogeneous and heterogeneous kinetics	303-343 K	Power Law model
Liu and Tan (2001)	Propionic acid 1-butanol	Amberlyst 15 Amberlyst 35, 39	Kinetic study	353 – 383 K	Eley Rideal (acid) E:14.1 kcal/mol
Lilja et.al. (2002)	Propionic and pentanoic acid Methanol, Ethanol	Amberlyst 15 Smopex 101 HCl	Homogeneous and heterogeneous	60°C MR:4:1-1:4	Second order model
Sanz et.al. (2002)	Lactic acid Methanol	Dowex 50-W Amberlyst 15 Amberlyst 36	Homogeneous and heterogeneous kinetics	313-353 K MR:0.5-5 CL:1-6wt%	LH model 48.67 kJ/mol

Table 3.6 A summary on the esterification reactions catalyzed by heterogeneous catalysts (continued)

Reference	Substrate	Catalysts	Remark	Conditions	Results
Teo and Saha (2004)	Acetic acid iso-amyl alcohol	Purolite CT-175	Kinetic study	333-363 K 2.5-10wt% MR: 2:1-10:1	LHHW 47 kJ/mol
Ali and Merchant (2006)	Acetic acid 2-propanol	Dowex 50Wx8-400 Amberlite IR-120 Amberlyst 15	Kinetic study	303-343 K 0.5-2 CL:20-60 g/L	MLH 57, 59, 64 kJ/mol
Çitak (2006)	Acetic acid iso-butanol	Amberlite IR-120	Deactivation time	318-368 K	25 days (use)
Winkler et.al. (2006)	Metil asetat Butanol	Amberlyst 15	Transesterification kinetic	313-333 K	LHHW model
Ali et.al. (2007)	Propionic acid propanol	Dowex 50Wx8-400	Kinetic study	303-343 K MR:1-4 CL: 10-60 g/L	MER (alcohol) 67.3 kJ/mol
Kolah et.al. (2007)	Citric acid Ethanol	Amberlyst 15	Kinetic study	78-120°C CL:1-5wt% MR:15-5	For MEC,DEC, TEC, DEE; 76, 83, 73, 102 kJ/mol

Table 3.6 A summary on the esterification reactions catalyzed by heterogeneous catalysts (continued)

Reference	Substrate	Catalysts	Remark	Conditions	Results
Izci et.al. (2007)	Acetic acid iso-butanol	Dowex 50Wx Amberlite IR- 120	Kinetic study	333-348 K CL: 5-10-25%	Pseudo homogeneous 59.3 kJ/mol
Ragaini et.al. (2007)	Dilute acetic acid 2-etil 1-ol	Amberlyst 15	Performance	372 K	67% conversion
Delgado et.al. (2007)	Lactic acid ethanol	Amberlyst 15	Homogeneous and heterogeneous kinetics	325-358 K R:0.5-6 CL: 1-6 wt%	LH 52.29 kJ/mol
Kolah et.al. (2008)	Succinic acid Ethanol	Amberlyst 15	Homogeneous and heterogeneous kinetics	78-120°C CL:1-5wt% MR:10-20	Pseudo homogeneous E for MES and DES; 66,70 kJ/mol
Ali and Merchant (2009)	Acetic acid Benzyl alcohol	Dowex 50Wx8- 400	Kinetic study	303-353 K MR:1-3, 10-60 g/L	LHHW 55.4 kJ/mol
Altıokka and Ödeş (2009)	Acrylic acid Propylene glycol	Amberlyst 15 Amberlyst 36	Kinetic study	323-353 K CL: 3-5-8wt%	Pseudo homogeneous 15.5 kJ/mol

Table 3.6 A summary on the esterification reactions catalyzed by heterogeneous catalysts (continued)

Reference	Substrate	Catalysts	Remark	Conditions	Results
Sert and Atalay (2010)	Acetic acid Butanol	Sulfated zirconia	Kinetic study	328-343 K, MR:1 CL: 3 g/L	ER (alcohol) 59.2% conversion
Sert and Atalay (2012)	Acrylic acid 1-Butanol iso-Butanol Hexanol	Zirconia supported TPA	Batch reactor performance	338-358 K R:1	For higher conversion, shorter and less branched chain
Komon et.al. (2013)	Acrylic acid 2-ethyl 1- hexanol	Amberlyst 39 Amberlyst46 Amberlyst70 Amberlyst131	Batch reactor performance	353-393 K CL: 1-10 wt% MR:7:1- 1-7	Amberlyst70 E: 50.1 kJ/mol
Karakuş et al. (2014)	Acrylic Acid Isobutyl Alcohol	Amberlyst 15 Amberlyst131 Dowex 50wX-400	Kinetic study	338-358 K CL:10-20 g/L MR: 1-3	Amberlyst131 E:53.8 kJ/mol
Buluklu et al. (2013)	Acrylic Acid Hexanol	Amberlyst 15 Amberlyst131 Dowex 50wX-400	Batch reactor performance	338-358 K CL:10-20 g/L MR: 1-3	Amberlyst131 E:53.8 kJ/mol

3.6. Usage of MOFs as catalyst

Wee et al., (2010) studied with nanomaterial of $\text{Cu}_3(\text{BTC})_2$ incorporating Keggin heteropolyacid conveniently prepared at room temperature and recovered by freeze drying outperforms ultrastable Y zeolite in acid catalysed esterification reaction. Esterification reaction of acetic acid with 1-propanol was carried out. Conversion of acetic acid with and without catalyst was performed and at the end of 7 hours, 15 and 5 % conversion was obtained with and without catalyst, respectively. Esterification reaction was conducted at 60°C and 1:40 molar ratio of acetic acid and 1-propanol, and 2.23 wt% of catalyst was used. These catalysts were hydrothermally synthesised micron-sized HPW/ $\text{Cu}_3(\text{BTC})_2$ and ultrastable Y zeolite (CBV 720). HPW/ $\text{Cu}_3(\text{BTC})_2$ with 65 nm sized and 50 nm-sized HPW/ $\text{Cu}_3(\text{BTC})_2$ catalysts were also synthesized and used in esterification reaction. By using these catalysts in esterification reaction, 30% conversion of acetic acid was achieved.

Zalomaeva et al., (2010) studied with iron tetrasulfophthalocyanine (FePcS). They added MIL-101 to FePcS to give a hybrid material FePcS/MIL-101. Synthesis, characterization and catalytic performance of these materials were carried out in this study. They concluded the hybrid material showed an excellent catalytic performance in oxidation of aromatic substrates with tBuOOH when compared with homogeneous FePcS. without leaching of iron or chromium.

Xamena et al. (2008) studied with metal organic frameworks as catalyst. Tetralin oxidation reaction was performed using a composition of two MOFs as an efficient catalyst. Two metal organic frameworks, $[\text{Cu}(2\text{-pymo})_2]$ and $[\text{Co}(\text{PhIM})_2]$ used for the aerobic oxidation of tetralin, yielding α -tetralone ($\text{T}=\text{O}$) as the main product. Both materials were found as stable and recyclable under the reaction conditions. Kinetic studies showed important differences between the two MOFs, as a consequence of the different catalytic behavior of their central metal ions. $[\text{Cu}(2\text{-pymo})_2]$ is highly active for the activation of tetralin to produce tetralinhydroperoxide ($\text{T}-\text{OOH}$), and less efficient in reacting the peroxide. Meanwhile, the use of the cobalt catalyst involves a long induction period for the reaction. However, once $\text{T}-\text{OOH}$ is formed, Co^{2+} rapidly and efficiently transforms this into $\text{T}=\text{O}$, with high tetralone-to-tetralol ratio ($\text{T}=\text{O}/\text{T}-\text{OH}$ of *ca.*

7). The combination of both materials has revealed as a convenient strategy for preparing a highly efficient, selective and reusable catalyst for the liquid phase aerobic oxidation of tetralin.

Xamena et al., (2007) synthesized palladium based MOF (Pd-MOF) and used it as catalyst for alcohol oxidation, Suzuki C–C coupling, and olefin hydrogenation. It was said the synthesized material could be reused. The Pd-MOF showed shape-selectivity for olefin conversion. The presence of palladium atoms in well-defined microporous channels opens the possibility of performing shape selective catalysis with these materials.

Goesten et al., (2011) studied sulfation and characterization of MOFs and their usage in esterification reaction of acetic acid and n-butanol without solvent. Sulfation was performed with triflic anhydride and sulfuric acid in nitromethane as a solvent. Acetic acid butanol molar ratio was taken as 1:1. Catalyst loading was set as 3 g/mol of acetic acid. After recovering the catalyst, it was filtered, stored at 423 K, and reused. The sulfonated MOFs demonstrated superior catalytic activity in esterification reaction and thermal stability of these materials were said excellent when compared with acidic resins.

Phan et al., (2010) synthesized MOF-5 and investigated its usage as heterogeneous catalyst for friedel–crafts alkylation reactions of toluene with benzyl bromide. The synthesized solid acid catalyst was characterized using a variety of different techniques, such as XRD, SEM, TEM, TGA, FT-IR, AAS, and nitrogen physisorption measurements. It was concluded the used MOF-5 catalyst could be facilely separated from the reaction mixture, and could be reused several times without significant degradation in catalytic activity. The initial reaction was carried out using 5mol% MOF-5 catalyst relative to benzyl bromide at 80 °C for 6 h. Complete conversion was achieved within 6 h with no trace amount of benzyl bromide being detected by GC. Effects of temperature on reaction conversion and selectivity were studied in the range of 60–80 °C, using 5mol% MOF-5 catalyst and toluene:benzyl bromide molar ratio of 5:1.

Phan et al., (2013) was studied Ullmann-type coupling reaction using metal-organic framework MOF-199 as an efficient recyclable solid catalyst MOF-199) was synthesized, and characterized by several methods including XRD, SEM, TEM, TGA, FT-IR, AAS, and nitrogen physisorption measurements. The MOF-199 was used as an efficient recyclable solid catalyst for the Ullmann-type reaction between aryl iodides and phenols to form diaryl ethers. High conversions were achieved for the transformation at the catalyst concentration of 5 mol%, in the presence of MeONa as a base. Due to the rare availability and the high cost, Cs₂CO₃ should only be used for the case of deactivated aryl iodides or deactivated phenols. The MOF-199 catalyst could be facilely separated from the reaction mixture by simple filtration, and could be reused several times without a significant degradation in catalytic activity. The Ullmann-type reaction could only proceed in the presence of the solid MOF-199 catalyst, and the contribution from leached active species in the liquid phase, if any, was negligible.

Leus et al., (2013) investigated Ti-functionalized NH₂-MIL-47: An effective and stable epoxidation catalyst The catalytic performance of this V/Ti-MOF was examined for the oxidation of cyclohexene using molecular oxygen as oxidant in combination with cyclohexanecarboxaldehyde as co-oxidant. A significantly higher cyclohexene conversion was observed for the bimetallic catalyst compared to the non-functionalized material. Moreover, the catalyst could be recycled at least 3 times without loss of activity and stability. No detectable leaching of V or Ti was noted.

Hartmann and Fischer (2012) synthesized amino-functionalized MIL-101. Fe-MIL-101-NH₂ ($S_{\text{BET}} = 3438 \text{ m}^2/\text{g}$), Al-MIL-101-NH₂ ($S_{\text{BET}} = 3099 \text{ m}^2/\text{g}$) and CAU-1 ($S_{\text{BET}} = 1492 \text{ m}^2/\text{g}$), and tested catalytic performance of synthesized materials. They used the materials in the Knoevenagel condensation of benzaldehyde with malononitrile and with ethyl cyanoacetate, respectively. It is shown that the expected products benzylidenemalononitrile (BzMN) and ethyl α -cyanocinnamate (EtCC) are formed with selectivities exceeding 99% and yields of 90 to 95% after 3 h (for BzMN). Due to the very small pore windows of CAU-1 (0.3 to 0.4 nm) the reaction proceeds much slower over this catalyst in comparison to the amino-MIL-101 derivatives, which possess open pore windows

of up to 1.6 nm. Moreover, the catalyst Al-MIL-101-NH₂ is recyclable without significant loss of activity.

Calleja et al., (2014) tested copper-based MOF-74 as acid catalyst in Friedel–Crafts acylation of anisole. The influence of reaction variables such as the type of acylating agent and solvent, and the reaction temperature has been studied. Cu-MOF-74 achieved a remarkable catalytic performance in terms of anisole conversion and p-MAP yield. Additionally, the structural MOF-74 phase was preserved when using diluted concentrations of acetyl chloride as acylating agent. The catalytic activity of Cu-MOF-74, in terms of anisole conversion and selectivity to p-MAP product, was also found as superior to other Cu-containing MOF materials (HKUST-1) and conventional inorganic acid catalysts, such as aluminum-containing microporous zeolites (H-ZSM-5 and BETA) and mesoporous ordered materials (Al-MCM-41). Cu-MOF-74 also showed high stability and remarkable catalytic performance for seven consecutive reaction cycles when this MOF material was used in the best reaction conditions.

Nguyen et al., (2011) synthesized a highly porous metal–organic framework (IRMOF-8) by a solvothermal method, and used as an efficient heterogeneous catalyst for the Friedel–Crafts acylation reaction of toluene with benzoyl chloride in a magnetically stirred round bottom flask fitted with a reflux condenser. The solid catalyst was characterized by XRD, SEM, TEM, TGA, FT-IR, AAS and nitrogen physisorption measurements. High conversions were achieved in the presence of a catalytic amount of the IRMOF-8 (1–5 mol%) without the need for an inert atmosphere. The solid catalyst could be facilely separated from the reaction mixture by simple centrifugation, and could be reused without a significant degradation in catalytic activity. No contribution from homogeneous catalysis of active acid species leaching into the reaction solution was detected.

Phan et al., (2012) studied Paal–Knorr reaction catalyzed by metal–organic framework IRMOF-3 as reusable heterogeneous catalyst (IRMOF-3) was synthesized from the reaction of zinc nitrate hexahydrate and 2-amino-1,4-benzenedicarboxylic acid by solvothermal method. Physical characterizations of the material were achieved with different techniques including XRD, SEM, TEM,

TGA, FT-IR, AAS and nitrogen physisorption measurements. The IRMOF-3 was used as an efficient heterogeneous catalyst for the Paal–Knorr reaction of benzyl amine with 2,5-hexanedione. Excellent conversions were obtained under mild conditions in the presence of 3 mol% catalyst. The IRMOF-3 catalyst could be reused several times without a significant degradation in catalytic activity.

Liu et al., (2014) synthesized MOF-supported chromium catalyst (IRMOF-3-SI-Cr) for ethylene polymerization, which has been characterized by a variety of physical methods. The results demonstrated that the MOF structure in this heterogeneous system may play an important role in ethylene polymerization. Combined with traditional homogeneous catalysts, these emerging MOFs materials could be used for olefin polymerization with some unique advantages.

Zhao et al., (2012), synthesized Ni@MOF-5 (7.4 wt.% Ni) by wet impregnation strategy to deposit nickel on MOF-5 framework. They used the material for hydrogenation of C=C bond using crotonaldehyde as a probe molecule under mild reaction conditions (conversion>90.0%, selectivity>98.0%, 2.0 MPa, 100 °C, 40 min). They found Ni@MOF-5 displayed much higher catalytic activity in comparison with that of the industrial catalyst Ni/SiO₂. Furthermore, the catalyst could be reused for several times with the preservation of MOF-5 structure. They concluded MOF-5 was a novel candidate of support for hydrogenation catalyst.

Novelty Statement

As shown from the studies listed above, metal organic frameworks have received an increased attention as new generation porous materials. In this study;

- MIL-101 (Cr), CuBTC, MIL-53 (Fe) and MIL-125 (Ti) were synthesized with solvothermal method.
- MIL-101 (Cr) and MIL-53 (Fe) were used to adsorb toluene and nitrobenzene in liquid phase.
- MIL-101 (Cr), CuBTC and MIL-53 (Fe) were used to adsorb methyl red and methyl orange in liquid phase.
- The produced MOF's (MIL-101 (Cr), CuBTC, MIL-53 (Fe) and MIL-125 (Ti)) were characterized by TGA, XRD and BET methods.

- ❖ To increase the acidity of produced MOF's, sulfonation was performed for MIL-101 (Cr), MIL-53 (Fe) and MIL-125 (Ti) which were produced by solvothermal method. These MOF's were coded as MIL-101s, MIL-53s and MIL-125s.
- ❖ MIL-101 (Cr) and MIL-53 (Fe) were synthesized by ultrasound assisted ionothermal method using two different eutectic solvents (ChCl-urea and ChCl-DMU), designated as D1-MIL-101, D2-MIL-101, D1-MIL-53, D2-MIL-53.
- ❖ D1-MIL-101, D2-MIL-101, D1-MIL-53, D2-MIL-53 were sulfonation to increase the acidity of MOF's and coded as D1-MIL-101s, D2-MIL-101s, D1-MIL-53s, D2-MIL-53s.
- ❖ These sulfated MOF's were characterized by TGA, XRD and BET methods.
- ❖ The catalytic activities of MOF's were tested in the esterification of acetic acid with methanol, butanol and hexanol.

In literature, there are many studies about the adsorption behavior of MOF's in vapor phase. However, the adsorption of aromatic pollutants by using MIL-101 (Cr) and MIL-53 (Fe) had not been characterized. Our study demonstrates that MIL-101, CuBTC and MIL-53 are very efficient to adsorb nitrobenzene, toluene, methyl red and methyl orange.

Also, the differences in the structural and textural properties of MOF's which are synthesized by different method, solvothermal or ionothermal, were studied. The effect of ultrasound in ionothermal synthesis and also effect of sulfation on the acidity of MOF's were investigated.

The effect of sulfonation on the structure and stability of MOF's are not clear in the literature. This study provides both the effect of sulfation and comparison of different synthesis methods on the catalytic activity of MOF's.

4. EXPERIMENTAL STUDY

4.1. Chemicals

MOF chemicals

In this study, MOFs were synthesized by solvothermal and ultrasound assisted ionothermal methods. Table 4.1 shows the used chemicals in synthesis of MOFs.

Table 4.1 Chemicals used in synthesis of MOFs with different methods

	MOF	Metal Salt	Organic Ligand	Solvent
Solvothermal Synthesis	MIL-101	$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	H_2BDC^*	Water, HF^*
	MIL-53 (Fe)	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	H_2BDC	DMF^*
	CuBTC	$\text{Cu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	H_3BTC^*	Ethanol/water
	MIL-125	Titanium isopropoxide	H_2BDC	DMF
Ultrasound assisted Ionothermal Synthesis	MIL-101 (D1-MIL-101)	$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	H_2BDC	DES 1 $\text{ChCl}^* \text{-Urea}$
	MIL-101 (D2-MIL-101)	$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	H_2BDC	DES 2 ChCl-DMU^*
	MIL-53 (Fe) (D1-MIL-53)	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	H_2BDC	DES 1 ChCl-Urea
	MIL-53 (Fe) (D2-MIL-53)	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	H_2BDC	DES 2 ChCl-DMU

* H_2BDC = TPA, terephthalic acid; H_3BTC = Trimesic acid; DMF = N,N-dimethylformamide; HF = hydrofluoric acid; ChCl = choline chloride; DMU = dimethyl urea

DES chemicals

In ultrasound assisted ionothermal synthesis, two different eutectic solvents were used. DES 1 is composed of choline chloride (ChCl) and urea as hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD), respectively. The freezing points of choline chloride and urea are 302°C and 133°C , respectively (Zhang et al. 2012).

The ratio of HBA and HBD for eutectic point is given as 1:2 in the literature (Zhang et al. 2012). To prepare DES 1, a predetermined amount of ChCl and urea were mixed and heated to 80°C with stirring bar till a clear liquid was formed (about 30-60 min). The freezing point of DES 1 is given as 12°C. In the preparation of DES 2, the ratio of ChCl to dimethyl urea for eutectic point is given as 1:2 in literature (Zhang et al., 2012). The depression in the freezing point is obtained from 302°C and 133°C to 70 °C (Zhang et al., 2012).

Table 4.2 DES chemicals used in ionothermal synthesis method and freezing points

DES	HBA	HBD	HBA:HBD	T _f (°C)	Reference
DES 1	ChCl	Urea	1:2	12	(Zhang et al. 2012)
DES 2	ChCl	Dimethyl urea	1:2	70	(Zhang et al. 2012)

4.2. Synthesis of MOFs by solvothermal method

MIL-101 was synthesized according to the method described in the literature (Férey et al. 2005). Cr(NO₃)₃ .9H₂O, terephthalic acid, HF were mixed with de ionized water with a molar ratio of 1:1:0.25:267. The prepared solution of 30mL was transferred into a teflon-lined stainless steel autoclave reactor (Figure 4.1a) and then kept in an electrical oven at 220°C for 8 h. At the end of 8 hours, the autoclave reactor was cooled down to room temperature and then obtained green solid was doubly filtered off using two glass filters to remove the surplus terephthalic acid. To ensure further purification, the solid product was washed with hot ethanol and then dried at 150°C for four hour and washed with NH₄F solution. Finally, the obtained MIL-101 solids were activated overnight at 150°C and kept in a desiccator before using as adsorbent or catalyst.

MIL-53(Fe) was prepared according to the report by Férey and co-workers (Millange et al. 2010). Iron chloride (FeCl₃.6H₂O). and terephthalic acid (TPA) and HF were mixed in a solvent of N,N-dimethylformamide (DMF) with a molar ratio of 1:1:1:280. The precursor solution was transferred to a teflon lined stainless steel autoclave and heated at 150°C for 3 days. The synthesized yellow MIL-53(Fe) solid was washed with methanol to remove the DMF solvent from the pores of material. And then methanol is substituted with water (1 g of MIL-53 in 0.5 L of water) and this yellow powder was dried naturally in air.

The synthesis of CuBTC was performed on the basis of the earlier reported method (Carson et al. 2009). 0.33 grams of benzene 1, 3, 5 tri-carboxylic acid (BTC) was dissolved in 10 ml solution of ethanol and N, N Dimethyl Formamide (DMF), each with an equal proportion of 5 ml. After this, 0.692 grams of copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) was dissolved in 5 ml water. Both the solutions were mixed and stirred for 10 minutes. Then, the final solution was put in the autoclave. After this, the autoclave was put in the oven at 100°C for 10 hours. After the given time, the autoclave was taken out from the oven and allowed to cool. Then, the filtration was carried out to separate the crystals. Then, it was dried in the oven for 2 hours at 100°C . After taking it out from the oven, it was washed with methanol. Then, again, it was dried for 2 hours at 100°C . In the end, it was taken out from the oven and stored in desiccator.

MIL-125 was synthesized with the same procedure reported by (Kim et al. 2013) titanium isopropoxide of 9 mmol of and 15 mmol of terephthalic acid were dissolved in a 50 mL solution of N,N-dimethylformamide and methanol (9:1, v/v). The mixture was transferred to Teflon lined stainless steel autoclave and heated 16 h at 423 K. After cooling to room temperature, the white powder obtained was recovered by filtration and washed several times with DMF and methanol. Finally, the white solid powder was activated at 423 K for 12 h. All stages of MOF synthesis are schemed in Figure 4.1.

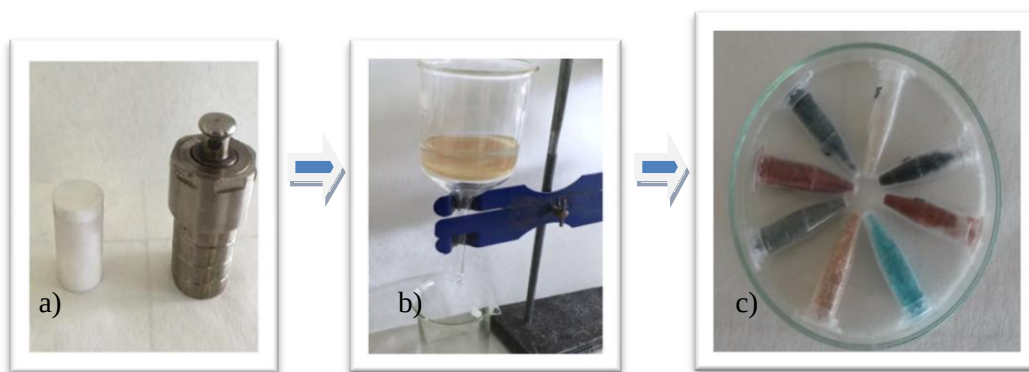


Figure 4.1 a) Teflon lined autoclave for synthesising of MOFs b) glass filter for purification of synthesized MOFs c) obtained MOFs

4.3. Synthesis of MOFs by ultrasound assisted ionothermal method

In ionothermal MOF synthesis, two different DESs were used. Table 4.2 shows, hydrogen bond donor and acceptor parts of used DESs.

In ionothermal synthesis MOFs, metal salts, organic linker and HBD and HBA of DES were mixed in the given molar ratios (Table 4.3). Then the mixture is heated above the eutectic temperature and then ultrasonic generator (VCX 500, SONICS, 175 W) (Figure 4.2) is used for 30 min. After that the mixture was heated 110 °C for 3 days. After cooling to room temperature, the solid was recovered by filtration and washed several times with hot ethanol for purification. Finally, the solid powder was activated at 423 K for 12 h.

Table 4.3 MOF synthesizing by using DES

Metal Salt	Organic Ligand	DES	MOF	Molar ratio (metal salt: organic ligand: HBA of DES: HBD of DES)
Cr(NO₃)₃. 9H₂O	H ₂ BDC	DES 1	D1-MIL-101	1:1:5:10
		DES 2	D2-MIL-101	1:1:5:10
FeCl₃. 6H₂O	H ₂ BDC	DES 1	D1-MIL-53	1:0.5:7:14
		DES 2	D2-MIL-53	1:0.5:7:14



Figure 4.2 Ultrasonic generator (VCX 500, SONICS, 175 W)

4.4. Sulfonation of synthesized MOFs

Sulfonation was performed to give acidic property to the prepared MOFs. Sulfonation of synthesized MOFs were carried out according to the method described in the literature (Goesten et al. 2011). Sulfuric acid in the presence of trifluoromethanesulfonic anhydride (triflic anhydride, $\text{ Tf}_2\text{O}$) was used and nitromethane (CH_3NO_2) was also used as solvent. The molar ratio was MOF-incorporated terephthalate/ H_2SO_4 / $\text{ Tf}_2\text{O}$ = 1:1:1.5. The mixture was continuously stirred in an orbital shaker at room temperature. After 60 min, the solid product was filtered off, rinsed with ultrapure water and acetone, soaked in ethanol for 24 h at 343 K, and stored at 433 K. Sulfated samples were designated with subscript s, such as MIL-101_s, MIL-53 (Fe)_s, MIL-125_s, D1-MIL-101_s, D2-MIL-101_s, D1-MIL-53_s, D2-MIL-53_s. Schematic representation for sulfation of MOFs is shown in Figure 4.3.

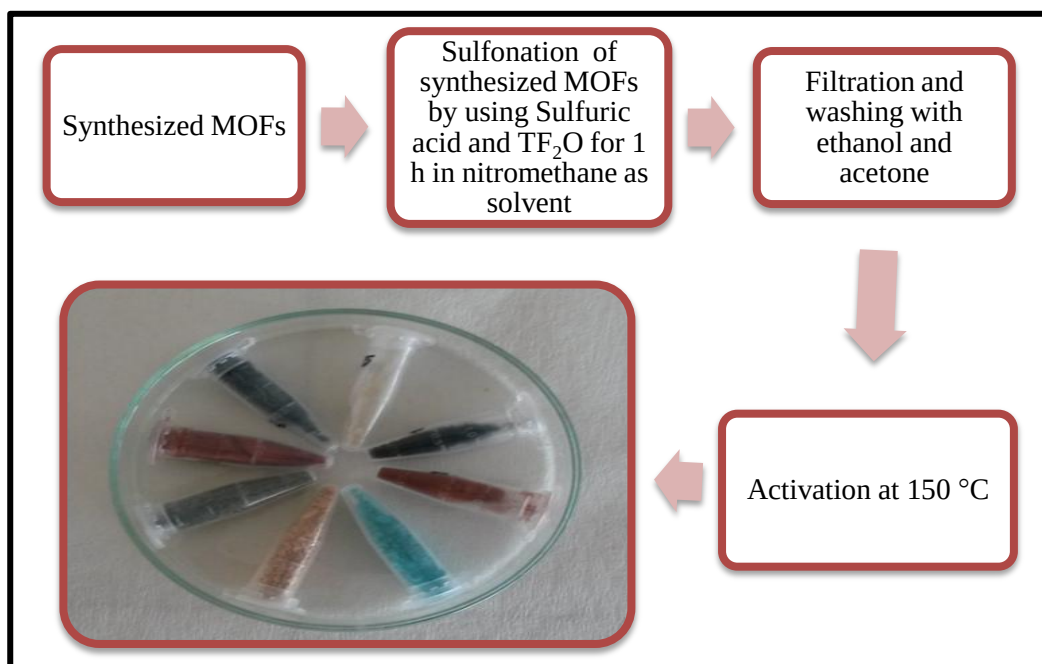


Figure 4.3 Schematic representation of sulfation of synthesized MOFs

4.5. Characterization of synthesized MOFs

X-ray powder diffraction is an efficient analytical technique used to identify and characterize unknown crystalline materials. X-ray powder diffraction patterns were obtained with a Philips X'Pert Pro diffractometer (Bruker, with CuK α radiation).

Adsorption measurements are widely used for the investigation of the texture of porous materials. Measurement of the surface area and adsorption isotherm of nitrogen on the MOFs were obtained at 77 K using a Micromeritics Gemini - 2380 apparatus. Before the nitrogen adsorption was accomplished, the humidity content in the MOFs (MIL-101, CuBTC, MIL-53 (Fe), MIL-125, D1-MIL-101, D2-MIL-101, D1-MIL-53 and D2-MIL-53) pores was evacuated for 4h at 150° C to remove the water molecules from the pores of the MOFs. The specific surface area values of the MOFs were calculated with the Brunauer–Emmett–Teller (BET) method and the Langmuir method using the adsorption data of the nitrogen adsorption isotherm.

TGA is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change. The thermal stability of these MOFs were investigated by thermal gravimetric analysis (TGA), using a TGA/DSC 111-Model simultaneous thermal analyzer with a range between 30° C and 500° C with a heating rate of 5° C/min. The sample weight of the MOFs was between 10 and 15 mg.

4.6. Adsorption Studies

The adsorption behaviour of toluene, nitrobenzene, methyl red and methyl orange onto synthesized MOF's was studied.

4.6.1. Adsorption of Toluene and Nitrobenzene

Aqueous stock solutions of toluene and nitrobenzene (500 ppm) were prepared by dissolving them in deionized water. To determine the adsorbate concentrations, the absorbance values of solutions were measured with a UV-vis Spectrophotometer (Carry-50) at 204.9 nm for toluene and 265 nm for nitrobenzene. The calibration curves were obtained from the spectra of the standard solutions (20–100 ppm). Before adsorption, the MOFs (MIL-101 and MIL-53 (Fe)) were dried overnight at 150 °C for MIL-101 and 70 °C for MIL-53 (Fe) and was kept in a desiccator. Then 50 mL of the aqueous toluene and NB solutions with different initial concentrations were prepared in volumetric flasks and then an exact amount of MOFs (50 mg) was placed into the solutions. The

adsorbate solutions with the adsorbents were placed in orbital shaker and agitated for a fixed time (up to 2h) with a speed of 200 rpm at 298 K. The pH was adjusted to ~5 by either 0.1 mol/L NaOH or HCl solution for dye adsorption. Samples taken at certain intervals were filtered with with syringe filter (PTFE, hydrophilic, 0.45 μ m) in order to remove the adsorbents from the solution, and the adsorbate concentration was determined, after dilution (if necessary), with absorbance value obtained from UV spectra. Operating conditions of toluene and NB adsorption studies are given in Table 4.4 and 4.5

4.6.2. Adsorption of Methyl Red and Methyl Orange

An aqueous stock solutions of dyes (methyl orange and methyl red) (400 ppm) were prepared by dissolving these adsorbates in deionized water. To determine the adsorbate concentrations, the absorbance values of solutions were measured with a UV-vis Spectrophotometer (Carry-50) 440 nm for methyl red, 460 nm and for methyl orange. The calibration curve was obtained from the spectra of the standard solutions (20–100 ppm).

Before adsorption, the adsorbents were dried overnight at 150 °C for MIL-101, 110 °C for CuBTC and 70 °C for MIL-53 (Fe) and were kept in a desiccator. 50 mL of aqueous adsorbate include solutions with different initial concentration (from 25 to 400 ppm) were prepared in volumetric flasks and then an exact amount of MOFs (50 mg) were put in them. The adsorbate solutions with the adsorbents were placed in orbital shaker and agitated for a fixed time (up to 3h) with a speed of 200 rpm at 298 K. The pH was adjusted to ~5 by either 0.1 mol/L NaOH or HCl solution for dye adsorption. Samples taken at certain intervals were filtered with with syringe filter (PTFE, hydrophilic, 0.45 μ m) in order to remove the adsorbents from the solution, and the adsorbate concentration was determined, after dilution (if necessary), with absorbance value obtained from UV spectra

A mass-balance relationship, Eq. (1) was used to calculate the amount of adsorbate adsorbed onto the MOFs in various conditions:

$$q_t = (C_0 - C_t) \frac{V}{W} \quad (1)$$

where C_0 and C_t (mg/L) are the liquid phase concentrations of the adsorbate at time = 0 and t , respectively. V (L) is the volume of the adsorbate solution and W (g) is the weight of the adsorbents used. To obtain the thermodynamic parameters of adsorption such as ΔG (free energy change), ΔH (enthalpy change) and ΔS (entropy change), the adsorption was repeated at 308 and 318 K.

Parameters investigated in adsorption study are shown in Table 4.4, 4.5, 4.6, 4.7. The experimental schedule for adsorption experiments is given in Figure 4.4, 4.5, 4.6, 4.7.

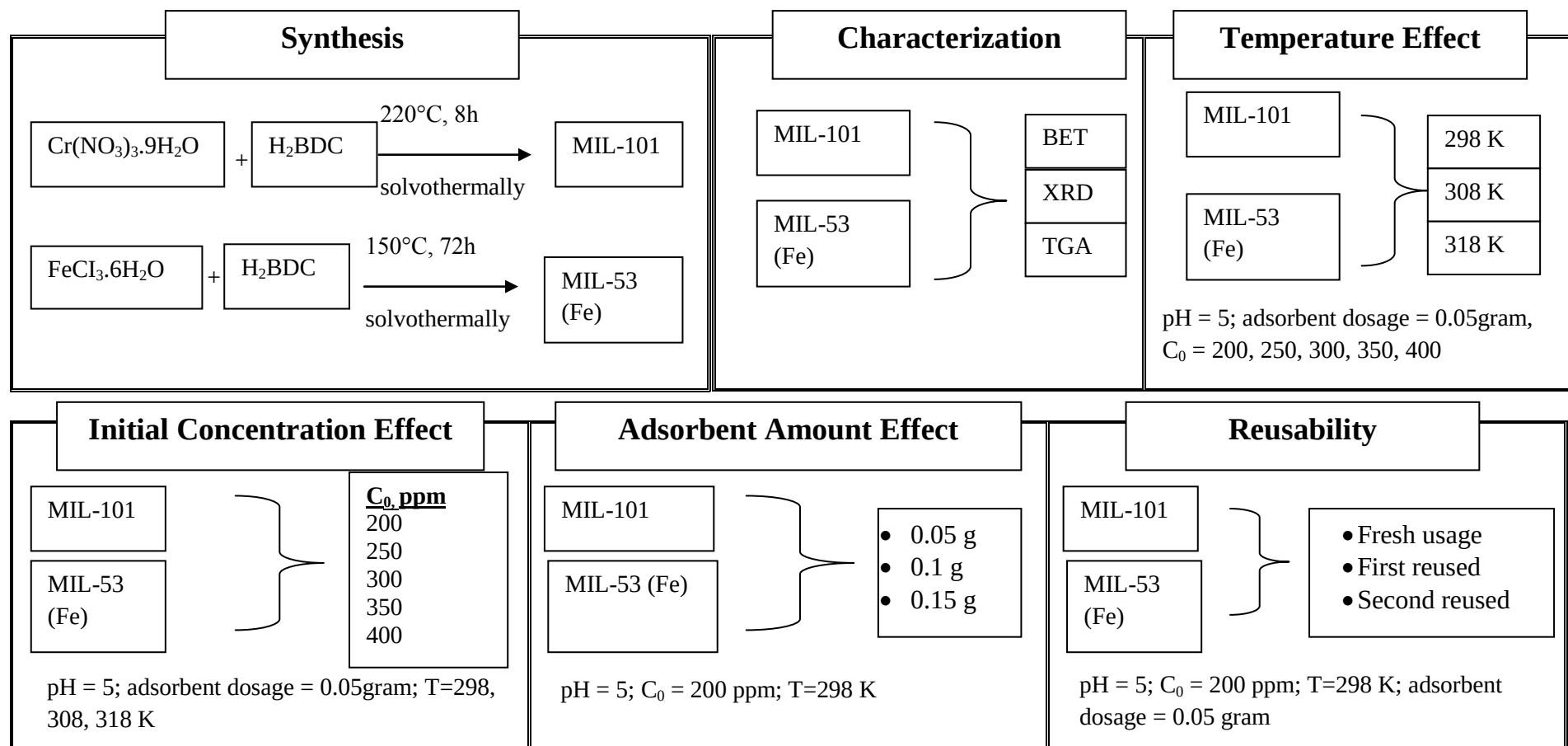


Figure 4.4 The experimental schedule for adsorption of Toluene

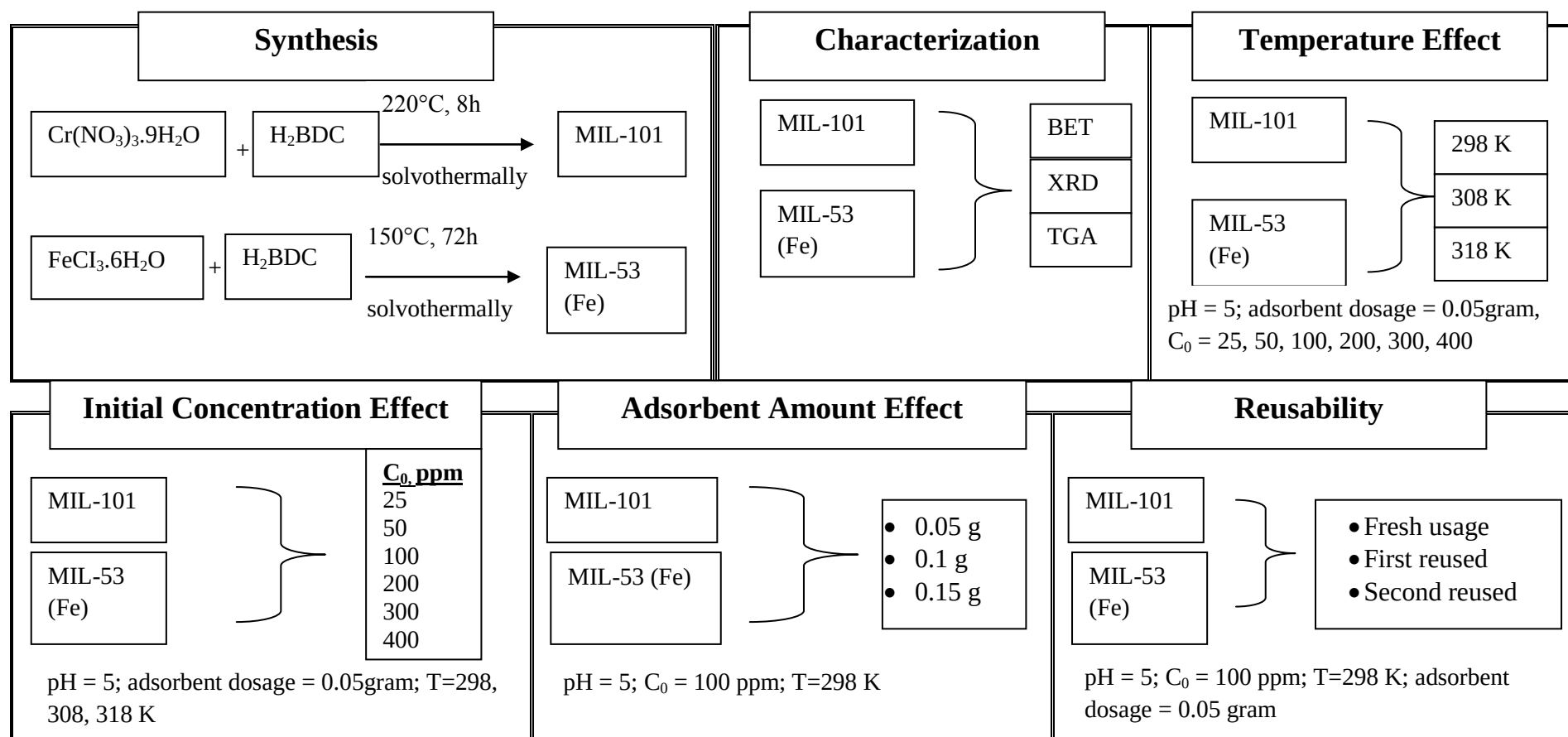


Figure 4.5 The experimental schedule for adsorption of Nitrobenzene

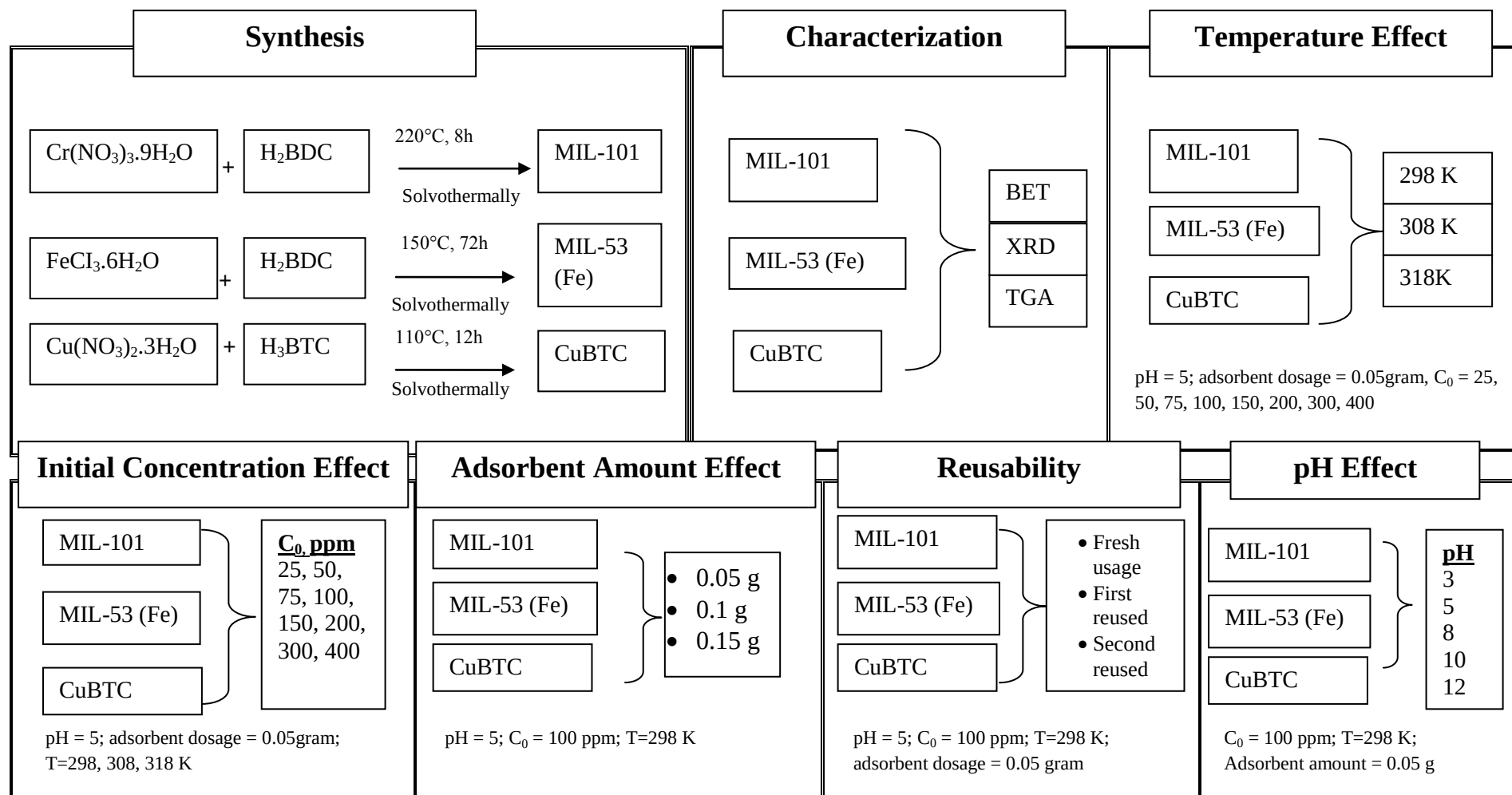


Figure 4.6 The experimental schedule for adsorption of Methyl red

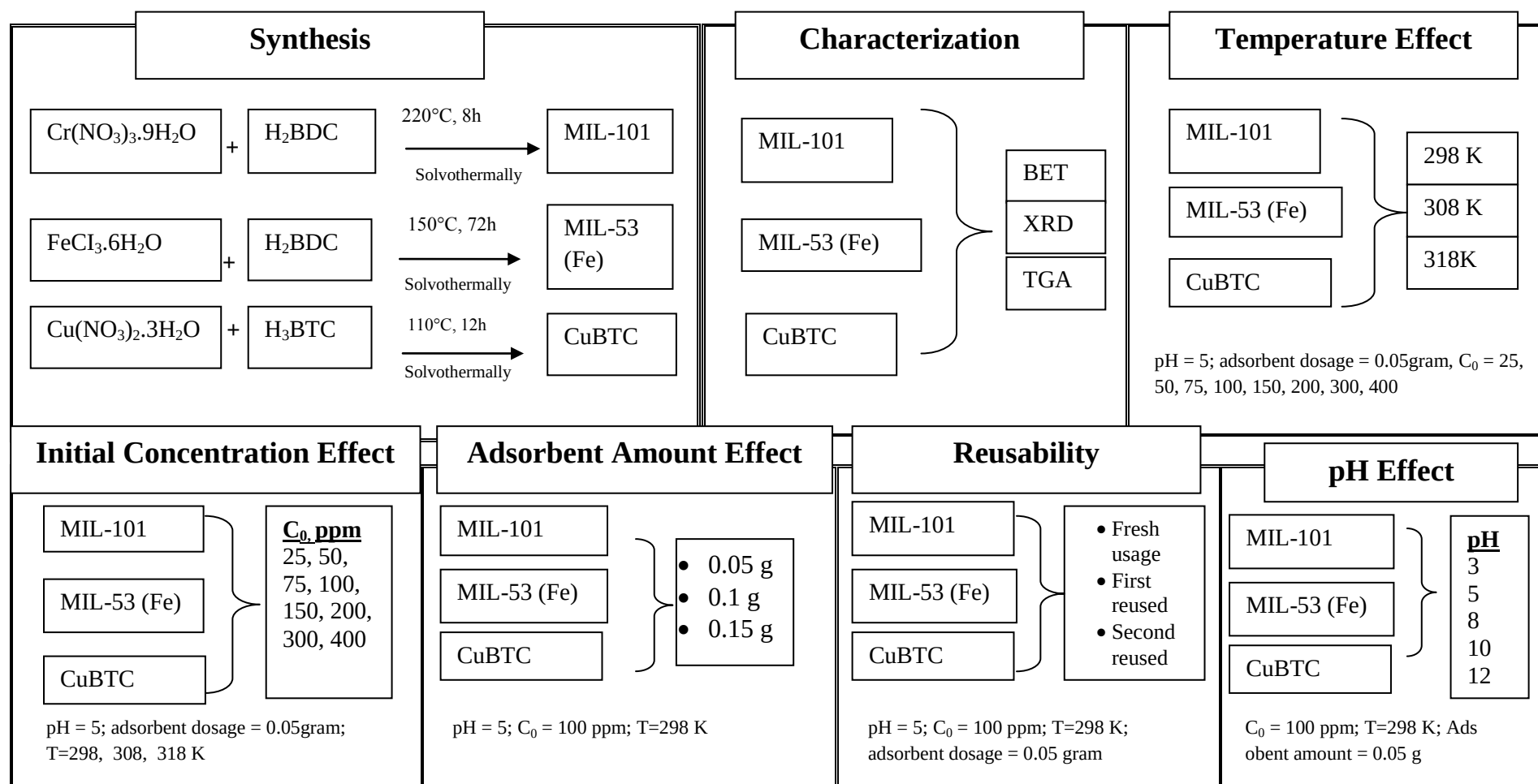


Figure 4.7 The experimental schedule for adsorption of Methyl orange

Table 4.4 Operating conditions for the adsorption of toluene

Toluene Adsorption				
Adsorbent	T (K)	C₀ (ppm)	Adsorbent amount (gram)	Reusability
MIL-101	298	200	0.05	Fresh
		250		
		300		
		350		
		400		
	308	200	0.05	Fresh
		250		
		300		
		350		
		400		
	318	200	0.05	Fresh
		250		
		300		
		350		
		400		
MIL-53 (Fe)	298	200	0.05	Fresh
			0.1	
			0.15	
			0.05	Fresh
				First reused
				Second reused
	298	200	0.05	Fresh
	308	200	0.05	Fresh
	318	200	0.05	Fresh
	298	200	0.05	Fresh
			0.1	
			0.15	
			0.05	Fresh
				First reused
				Second reused

Table 4.5 Operating conditions for the adsorption of nitrobenzene

Nitrobenzene Adsorption				
Adsorbent	T (K)	C₀ (ppm)	Adsorbent amount (gram)	Reusability
MIL-101	298	25	0.05	Fresh
		50		
		100		
		200		
		300		
		400		
	308	25	0.05	Fresh
		50		
		100		
		200		
		300		
		400		
	318	25	0.05	Fresh
		50		
		100		
		200		
		300		
		400		
	298	100	0.05	Fresh
			0.1	
			0.15	
	298	100	0.05	Fresh
				First reused
				Second reused

Table 4.5 Operating conditions for the adsorption of nitrobenzene (continued)

Nitrobenzene Adsorption				
Adsorbent	T (K)	C₀ (ppm)	Adsorbent amount (gram)	Reusability
MIL-53 (Fe)	298	25	0.05	Fresh
		50		
		100		
		200		
		300		
		400		
	308	25	0.05	Fresh
		50		
		100		
		200		
		300		
		400		
	318	25	0.05	Fresh
		50		
		100		
		200		
		300		
		400		
	298	100	0.05 0.1 0.15	Fresh
	298	100	0.05	Fresh First reused Second reused

Table 4.6 Operating conditions for the adsorption of methyl red

Methyl Red Adsorption					
Adsorbent	T (K)	C₀ (ppm)	Adsorbent amount (gram)	Reusability	pH
MIL-101	298	25	0.05	Fresh	5
		50			
		75			
		100			
		150			
		200			
		300			
		400			
	308	25	0.05	Fresh	5
		50			
		75			
		100			
		150			
		200			
		300			
		400			
	318	25	0.05	Fresh	5
		50			
		75			
		100			
		150			
		200			
		300			
		400			
	298	100	0.05	Fresh	5
			0.1		
			0.15		
	298	100	0.05	Fresh	5
				First reused	
				Second reused	
	298	100	0.05	Fresh	3
					5
					8
					10
					12

Table 4.6 Operating conditions for the adsorption of methyl red (continued)

Methyl Red Adsorption					
Adsorbent	T (K)	C₀ (ppm)	Adsorbent amount (gram)	Reusability	pH
MIL-53 (Fe)	298	25	0.05	Fresh	5
		50			
		75			
		100			
		150			
		200			
		300			
		400			
	308	25	0.05	Fresh	5
		50			
		75			
		100			
		150			
		200			
		300			
		400			
	318	25	0.05	Fresh	5
		50			
		75			
		100			
		150			
		200			
		300			
		400			
	298	100	0.05	Fresh	5
			0.1		
			0.15		
	298	100	0.05	Fresh	5
				First reused	
				Second reused	
	298	100	0.05	Fresh	3
					5
					8
					10
					12

Table 4.6 Operating conditions for the adsorption of methyl red (continued)

Methyl Red Adsorption					
Adsorbent	T (K)	C₀ (ppm)	Adsorbent amount (gram)	Reusability	pH
CuBTC	298	25	0.05	Fresh	5
		50			
		75			
		100			
		150			
		200			
		300			
		400			
	308	25	0.05	Fresh	5
		50			
		75			
		100			
		150			
		200			
		300			
		400			
	318	25	0.05	Fresh	5
		50			
		75			
		100			
		150			
		200			
		300			
		400			
	298	100	0.05	Fresh	5
			0.1		
			0.15		
	298	100	0.05	Fresh	5
				First reused	
				Second reused	
	298	100	0.05	Fresh	3
					5
					8
					10
					12

Table 4.7 Operating conditions for the adsorption of methyl orange

Methyl Orange Adsorption					
Adsorbent	T (K)	C₀ (ppm)	Adsorbent amount (gram)	Reusability	pH
MIL-101	298	25	0.05	Fresh	5
		50			
		75			
		100			
		150			
		200			
		300			
		400			
	308	25	0.05	Fresh	5
		50			
		75			
		100			
		150			
		200			
		300			
		400			
	318	25	0.05	Fresh	5
		50			
		75			
		100			
		150			
		200			
		300			
		400			
	298	100	0.05	Fresh	5
			0.1		
			0.15		
	298	100	0.05	Fresh	5
				First reused	
				Second reused	
	298	100	0.05	Fresh	3
					5
					8
					10
					12

Table 4.7 Operating conditions for the adsorption of methyl orange (continued)

Methyl Orange Adsorption					
Adsorbent	T (K)	C₀ (ppm)	Adsorbent amount (gram)	Reusability	pH
MIL-53 (Fe)	298	25	0.05	Fresh	5
		50			
		75			
		100			
		150			
		200			
		300			
		400			
	308	25	0.05	Fresh	5
		50			
		75			
		100			
		150			
		200			
		300			
		400			
	318	25	0.05	Fresh	5
		50			
		75			
		100			
		150			
		200			
		300			
		400			
	298	100	0.05	Fresh	5
			0.1		
			0.15		
	298	100	0.05	Fresh	5
				First reused	
				Second reused	
	298	100	0.05	Fresh	3
					5
					8
					10
					12

Table 4.7 Operating conditions for the adsorption of methyl orange (continued)

Methyl Orange Adsorption					
Adsorbent	T (K)	C₀ (ppm)	Adsorbent amount (gram)	Reusability	pH
CuBTC	298	25	0.05	Fresh	5
		50			
		75			
		100			
		150			
		200			
		300			
		400			
	308	25	0.05	Fresh	5
		50			
		75			
		100			
		150			
		200			
		300			
		400			
	318	25	0.05	Fresh	5
		50			
		75			
		100			
		150			
		200			
		300			
		400			
	298	100	0.05	Fresh	5
			0.1		
			0.15		
	298	100	0.05	Fresh	5
				First reused	
				Second reused	
	298	100	0.05	Fresh	3
					5
					8
					10
					12

4.7. Esterification Studies

The catalytic activities of sulphated MOF samples were tested in the esterification of acetic acid with different alcohols.

Experiments were performed in a reactor which placed on a magnetic heater stirrer and consisted of a 500 ml flash fitted with condenser to prevent loss of material during experiment. Also to prevent concentration gradients across the reaction mixture vigorous stirring was employed at 500 rpm. In experiments an electrical heater with magnetic stirrer (IKA RTC CL) was used to heat the reaction mixture. The temperature was controlled by a temperature controller. The samples were taken at the end of experiment (approximately 8 hours) for gas chromatographic analysis. And the parameters investigated in esterification reaction are shown in Table 4.8 and 4.9.



Figure 4.8 The photograph of batch reactor

The photograph and schematic diagram of experimental set-up are shown in Figures 4.8 and 4.9.

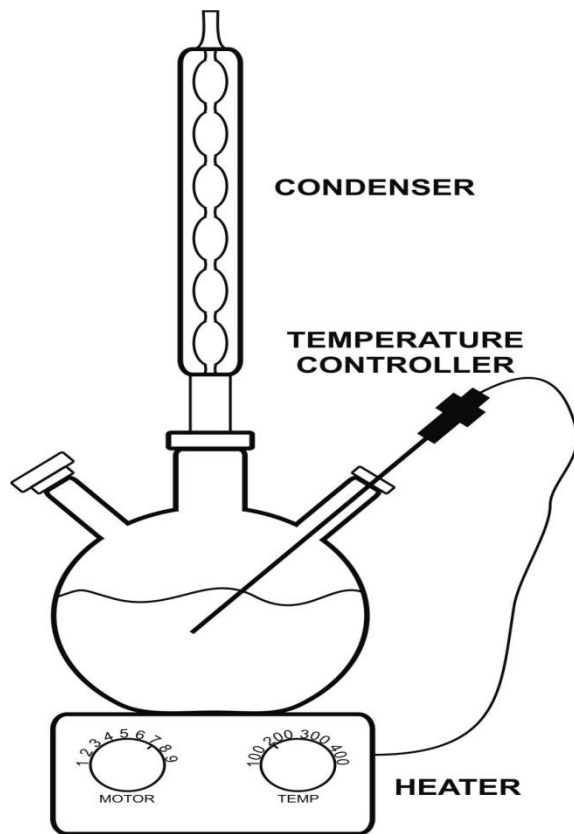


Figure 4.9 The schematic diagram of batch reactor

The experimental schedule is given in Figure 4.10 and 4.11.

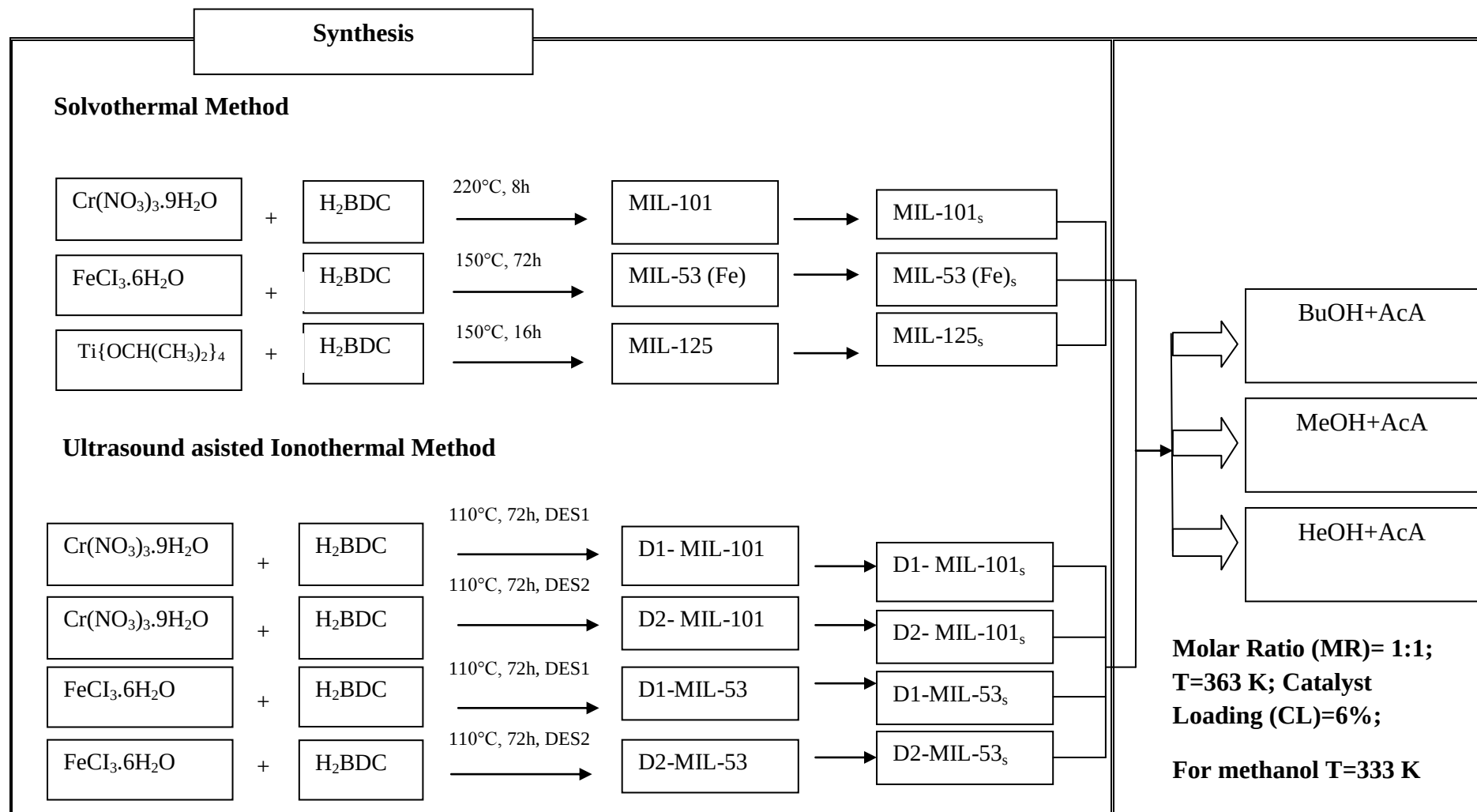


Figure 4.10 The experimental Schedule for esterification reaction

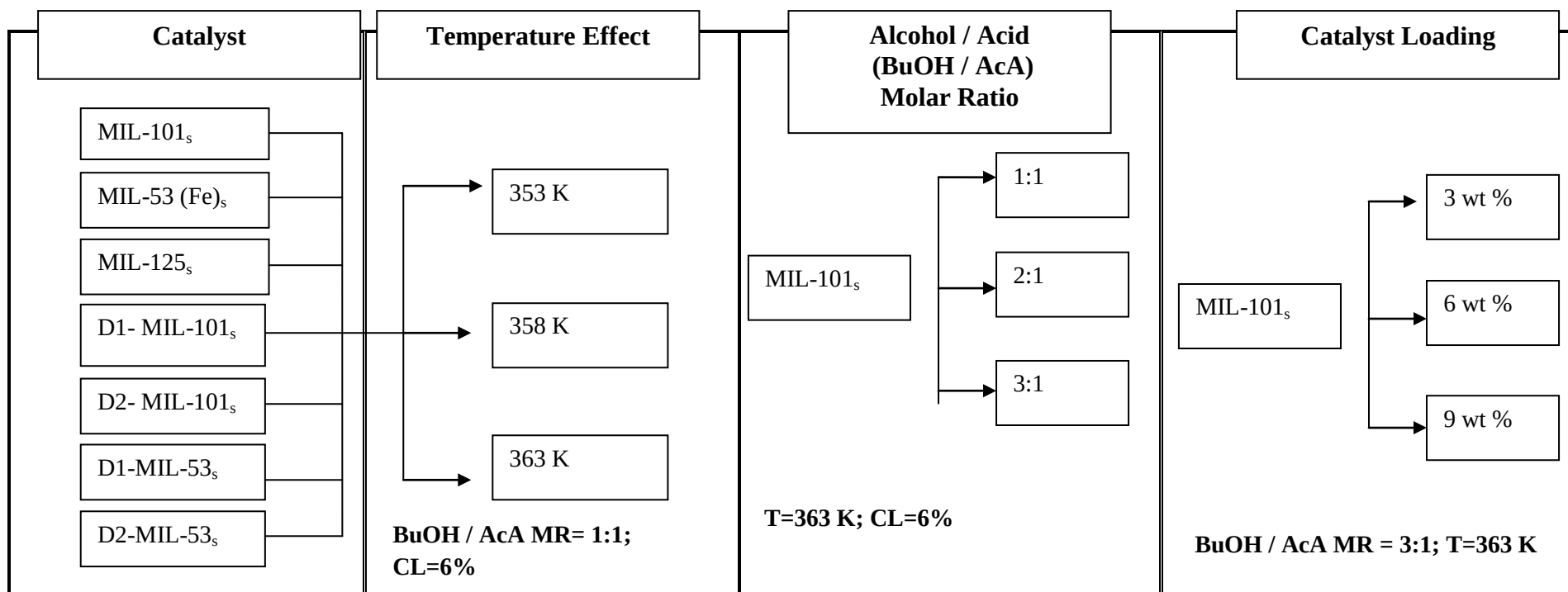


Figure 4.11 The experimental schedule for the effects at operating condition

Table 4.8 Parameters for esterification of acetic acid catalyzed by MIL-101_s

MIL-101_s			
Temperature Effect (K)	Catalyst loading (wt %)	Alcohol Effect	Alcohol-Acid Ratio (BuOH-AcA)
353 358 363	6 %	Butanol	1:1
363	3 % 6 % 9 %	Butanol	3:1
363	6 %	Butanol	1:1 2:1 3:1
363	6 %	Butanol Methanol Hexanol	3:1

Table 4.9 Parameters for esterification of acetic acid catalyzed by other MOFs

MIL-53 (Fe)_s			
Temperature Effect (K)	Catalyst loading (wt %)	Alcohol Effect	Alcohol-Acid Ratio (BuOH-AcA)
353 358 363	6 %	Butanol	1:1
363	6 %	Butanol Methanol Hexanol	3:1
MIL-125_s			
Temperature Effect (K)	Catalyst loading (wt %)	Alcohol Effect	Alcohol-Acid Ratio (BuOH-AcA)
353 358 363	6 %	Butanol	1:1
363	6 %	Butanol Methanol Hexanol	3:1
D1-MIL-101_s			
Temperature Effect (K)	Catalyst loading (wt %)	Alcohol Effect	Alcohol-Acid Ratio (BuOH-AcA)
353 358 363	6 %	Butanol	1:1
363	6 %	Butanol Methanol Hexanol	3:1

Table 4.9 Parameters for esterification of acetic acid catalyzed by other MOFs (continued)

D2-MIL-101_s			
Temperature Effect (K)	Catalyst loading (wt %)	Alcohol Effect	Alcohol-Acid Ratio (BuOH-AcA)
353 358 363	6 %	Butanol	1:1
363	6 %	Butanol Methanol Hexanol	3:1
D1-MIL-53 (Fe)_s			
Temperature Effect (K)	Catalyst loading (wt %)	Alcohol Effect	Alcohol-Acid Ratio (BuOH-AcA)
353 358 363	6 %	Butanol	1:1
363	6 %	Butanol Methanol Hexanol	3:1
D2-MIL-53 (Fe)_s			
Temperature Effect (K)	Catalyst loading (wt %)	Alcohol Effect	Alcohol-Acid Ratio (BuOH-AcA)
353 358 363	6 %	Butanol	1:1
363	6 %	Butanol Methanol Hexanol	3:1

4.7.1. Effect of Temperature

Temperature effect was investigated for MIL-101_s, MIL-53 (Fe)_s, MIL-125_s, D1-MIL-101_s, D2-MIL-101_s, D1-MIL-53 (Fe)_s, and D2-MIL-53 (Fe)_s. The esterification of acetic acid with butanol was studied at three different temperatures; 80, 85 and 90 °C, to investigate the effect of temperature. These experiments were carried out at an alcohol to acid molar ratio of 1, catalyst loading of 6 wt % and stirrer speed of 500 rpm.

Table 4.10 Effect of temperature

Constant parameters 6 % catalyst loading Molar ratio of BuOH:AcA 1:1	Temperature Effect (°C)		
	80	85	90

4.7.2. Effect of Catalyst Loading

Catalyst loading effect was investigated for MIL-101_s. Catalyst loadings were selected as 3, 6 and 9 wt % and other parameters were kept constant at temperature of 90 °C, alcohol to acid molar ratio of 1 and stirrer speed of 500 rpm.

Table 4.11 Effect of catalyst loading

Constant parameters 90 (°C) Molar ratio of BuOH:AcA 3:1	Catalyst Loading		
	3 %	6 %	9 %

4.7.3. Effect of Molar Ratio of Alcohol to Acetic Acid

Another parameter affecting the performance of esterification reaction is molar ratio of alcohol to acetic acid. The molar ratio effect was investigated for MIL-101_s. The initial molar ratio was varied as 1, 2 and 3 while the other parameters were kept constant. Effect of initial molar ratio on the yield of esterification was performed at a temperature of 90 °C, catalyst loading of 6 wt %, and stirrer speed of 500 rpm.

Table 4.12 Effect of molar ratio

Constant parameters 90 (°C) 6 % catalyst loading	Alcohol-Acid Ratio (BuOH:AcA)		
	1:1	2:1	3:1

4.7.4. Effect of Alcohol

The alcohol effect was investigated for MIL-101_s, MIL-53 (Fe)_s, MIL-125_s, D1-MIL-101_s, D2-MIL-101_s, D1-MIL-53 (Fe)_s, and D2-MIL-53 (Fe)_s. Another parameter affecting the performance of esterification reaction is alcohol type. Esterification of acetic acid with butanol, methanol and hexanol were carried out at 90 °C, catalyst loading of 6 wt %, and stirrer speed of 500 rpm.

Table 4.13 Effect of alcohol

Constant parameters 90 (°C), 6 % Molar ratio of BuOH:AcA 3:1	Alcohol Effect		
	Butanol	Methanol	Hexanol

4.8. Analysis

Analyses of adsorption studies were performed with UV-spectra (Figure 4.12) and the analyses of the samples were performed on Agilent 7890A chromatograph (Figure 4.13) for esterification reaction. Figure 4.14 and 4.15 shows UV spectrum of adsorbates and GC chromatogram for the esterification of acetic acid with butanol.

The gas chromatograph column was HP-FFAP connected with flame ionization detector to detect the compounds in the same run. Hydrogen was used as carrier gas. The temperature program of gas chromatographic analysis was given as follows: waiting 3 min at 60°C; heating from 60 to 180°C at a rate of 5°C/min; waiting for 3 min at 180°C. From gas chromatographic analysis, the conversion of limiting reactant (acetic acid) was calculated.



Figure 4.12 The photograph of UV spectra used in adsorption experiments

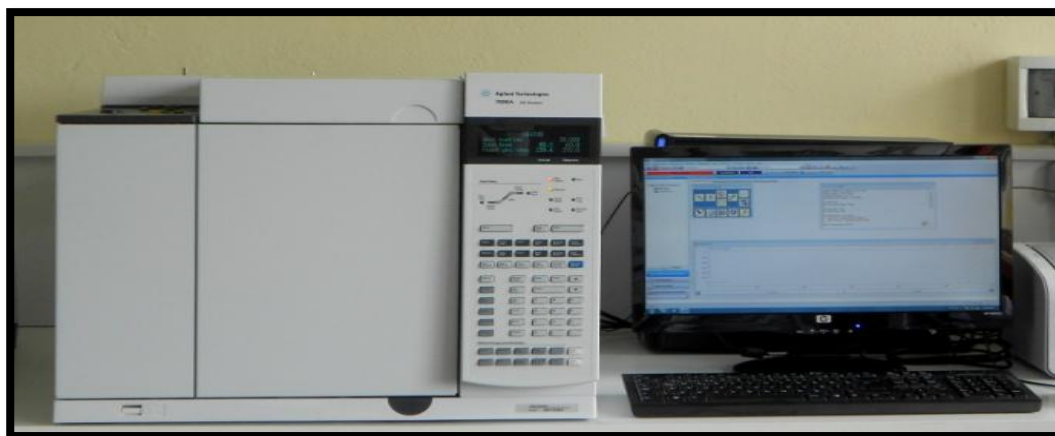


Figure 4.13 The photograph of Gas Chromatography

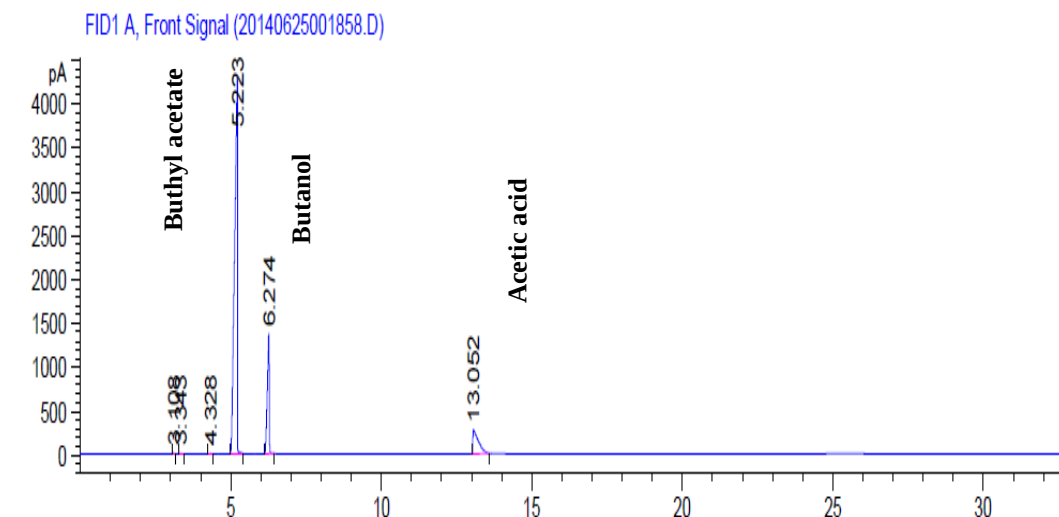


Figure 4.14A sample chromatogram for the esterification of acetic acid with butanol

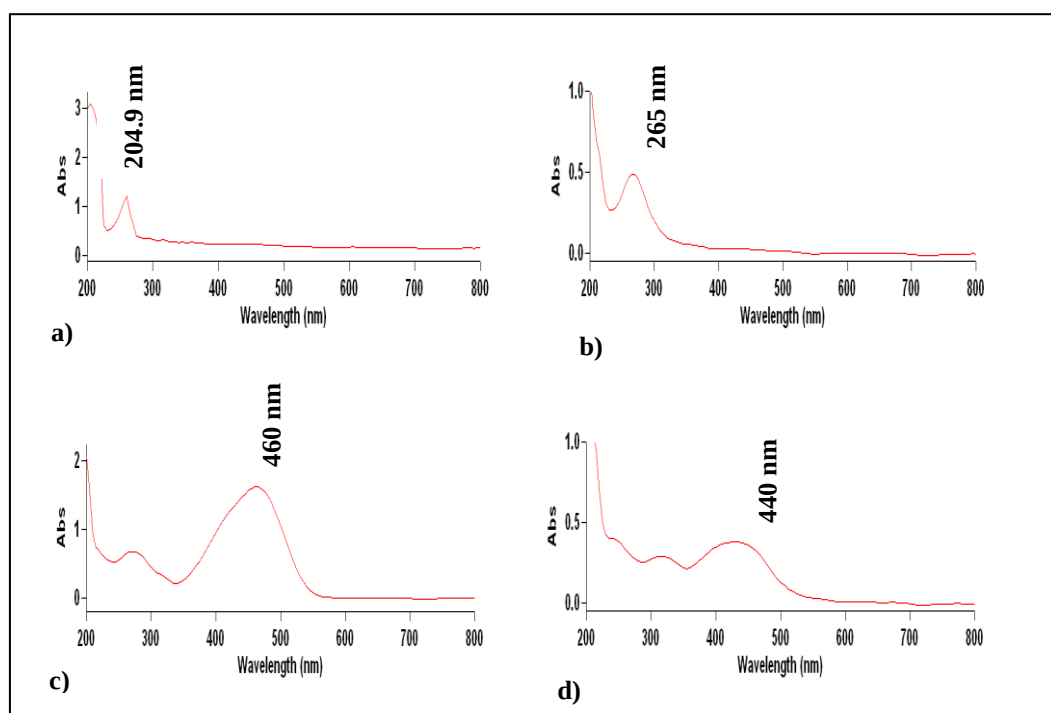


Figure 4.15 UV spectrum of a) toluene b) nitrobenzene c) methyl orange d) methyl red.

5. RESULTS AND DISCUSSION

5.1. Characterization of MOF's

5.1 Characterization of MOF's

The synthesized MOFs are characterized using XRD, BET and TGA analysis. The textural and structural properties of metal organic frameworks based on Cr, Fe, Ti and Cu obtained. Also, the effect of sulfation and the synthesis method are studied.

MIL-101

Figure 5.1 shows the crystal structure of the MIL-101. The diffraction peaks matched well with previous papers for MIL-101 (Chen et al., 2012; Ferey et al., 2005; Haque et al., 2011).

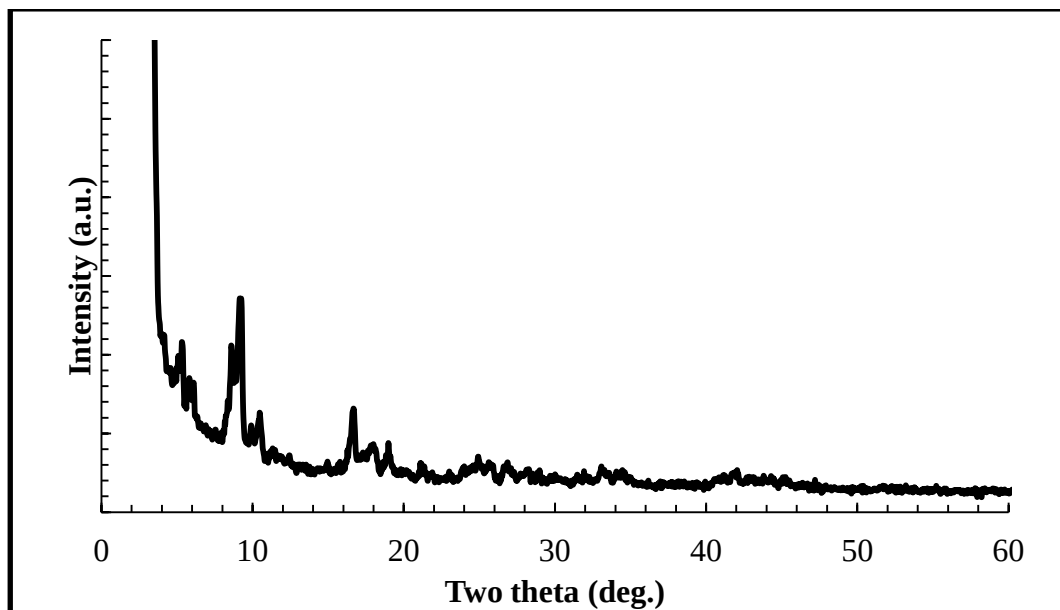


Figure 5.1 XRD pattern of MIL-101

Figure 5.2 shows the N₂ adsorption isotherms of MIL-101 at 77 K and the specific surface areas were evaluated with the Brunauer–Emmett–Teller (BET) and Langmuir methods. N₂ sorption isotherm is of Type I with uptakes at $P/P_0 \sim 0.1$ and at $P/P_0 \sim 0.2$ where P is gas pressure and P_0 is saturation pressure.

The BET and Langmuir surface area, pore volume and adsorption average pore width of MIL-101 are found as 3193.99 m²/g, 4389.11 m²/g, 1.52 cm³/g and

19.08 Å, respectively. These values are close to the reported values for MIL-101 (Chen et al., 2012; Lin et al., 2014). Suresh et.al.(2014) found the surface area of MIL-101 as 2563 m²/g by hydrothermal method. To our knowledge, the highest BET surface area reported for any crystalline or amorphous solid (4500 m²/g) was obtained with MOF-177. In literature, the surface area of MIL-101 changes between 1000-3500 m²/g range because of the presence of variable amounts of free terephthalic acid outside and within the pores (Ferey, 2005).

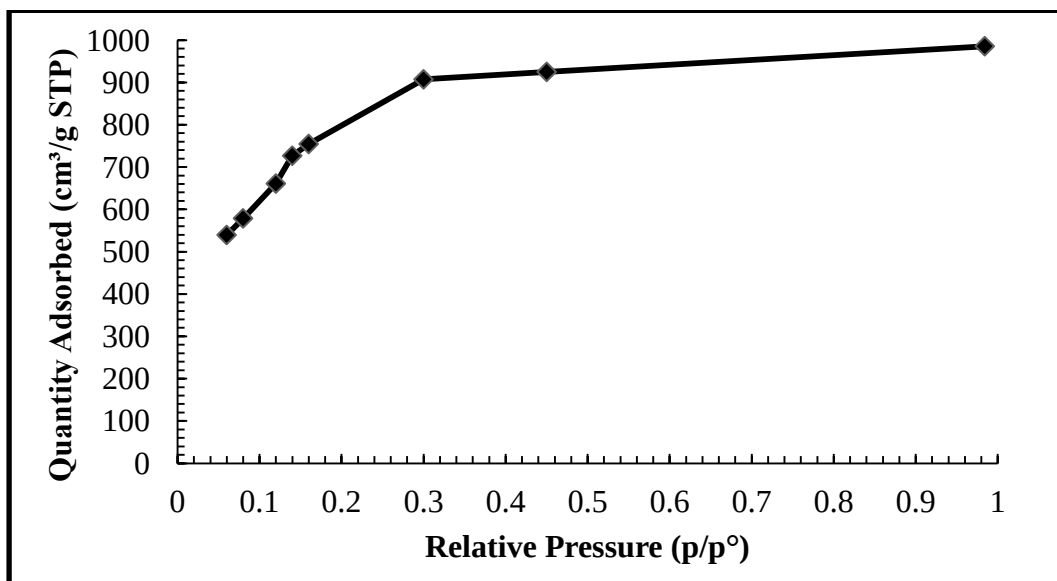


Figure 5.2 N₂ adsorption of MIL-101

The TGA profile shows that MIL-101 is stable up to 400°C (Figure 5.3) and a 3-7% weight loss between 50 and 100°C results from water evaporation for MOFs.

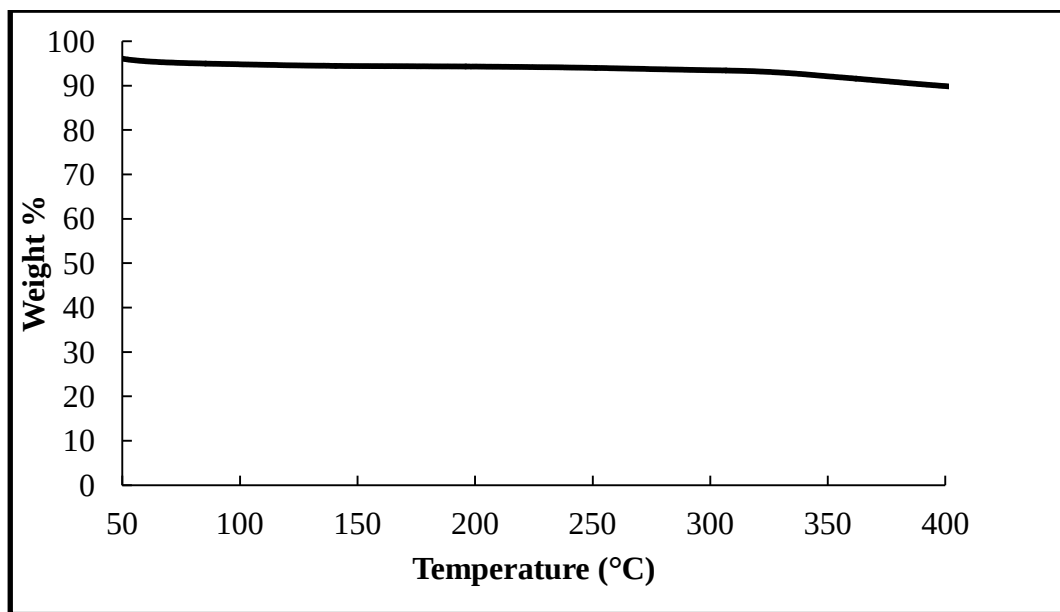


Figure 5.3 TGA profile of MIL-101

MIL-53 (Fe)

Figure 5.4 shows the crystal structure of the MIL-53(Fe). In the pattern of the sample, the main diffraction peaks appearing at 2Θ of 9.24, 12.7, 17.66, 18.24, 18.58, 25.52, 27.32, 29.8, 30.28, 36.18 are identical to those reported for the MIL-53(Fe) phase (Millange et al., 2002; Loiseau et al., 2004). The pattern of MIL-53(Fe) showed a flat background and high intensities, indicating high crystallinity of the samples.

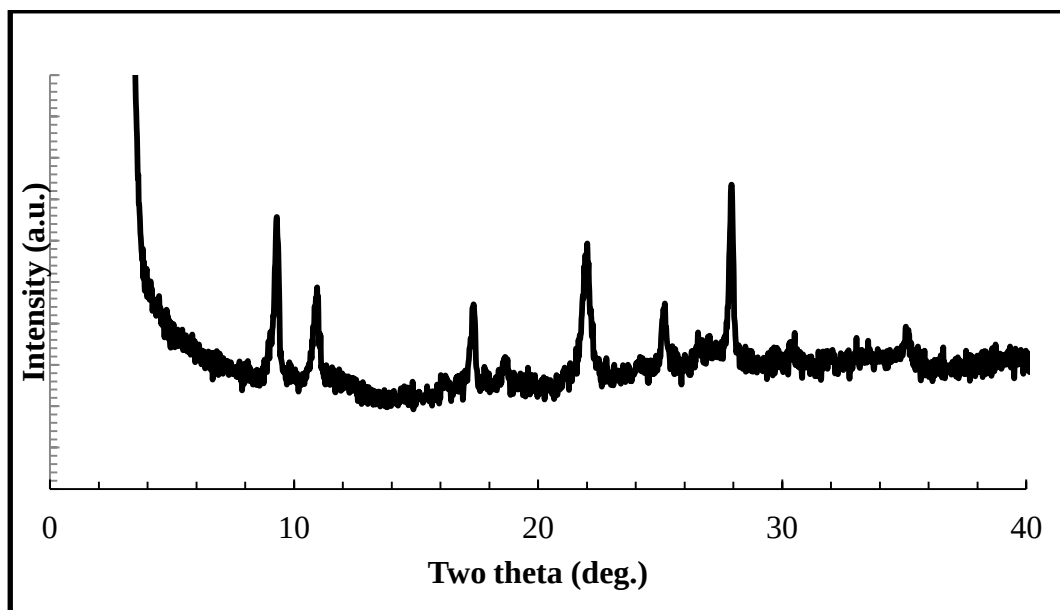


Figure 5.4 XRD pattern of MIL-53 (Fe)

Figure 5.5 shows the N₂ adsorption isotherms of MIL-53 at 77 K and the specific surface areas were evaluated with the Brunauer–Emmett–Teller (BET) and Langmuir methods. The BET and Langmuir surface area pore volume and adsorption average pore width of MIL-53 are found as 23.15 m²/g, 33.05 m²/g, 0.056 cm³/g and 98.13 Å. Due to the closed pores for N₂ at 77 K, flexible MIL-53(Fe) exhibit no accessible porosity (Xie et al., 2014).

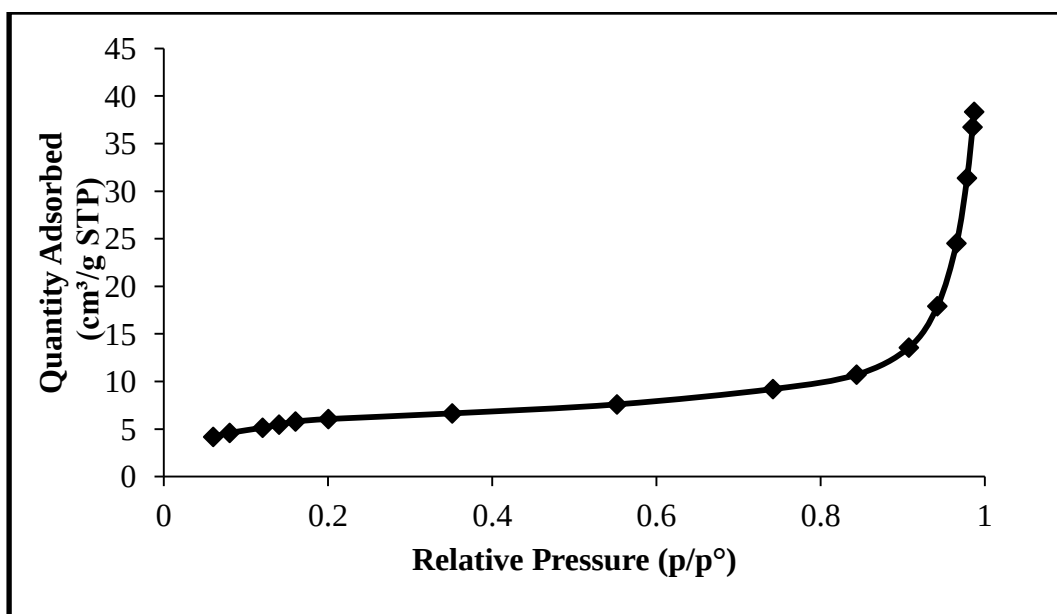


Figure 5.5 N₂ adsorption of MIL-53

The TGA profile shows that MIL-53 (Fe) is stable up to 270° C (Figure 5.6) and a 7% weight loss between 50 and 100° C results from water evaporation for MOFs. The weight loss of MOFs, occurred between, 270 and 400° C for MIL-53 (Fe) respectively which may result from the framework decomposition (Millange et al., 2010).

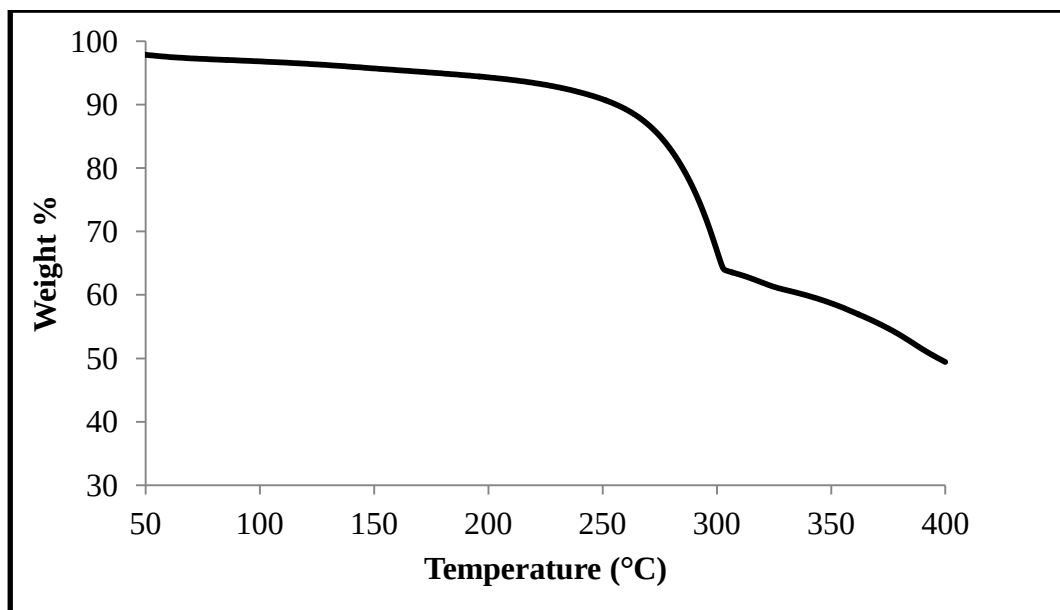


Figure 5.6 TGA profile of MIL-53 (Fe)

CuBTC

The powder X-ray diffraction for this material was shown in Figure 5.7. The XRD pattern of the sample was identical and in good agreement with previous papers CuBTC (Chowdhury et al., 2009; Feng et al., 2013). The small variations in peak intensities can be due to a difference in degree of hydration. The sample shows good crystallinity and synthesized is also very pure since no additional peaks for any foreign impurity is seen in the pattern.

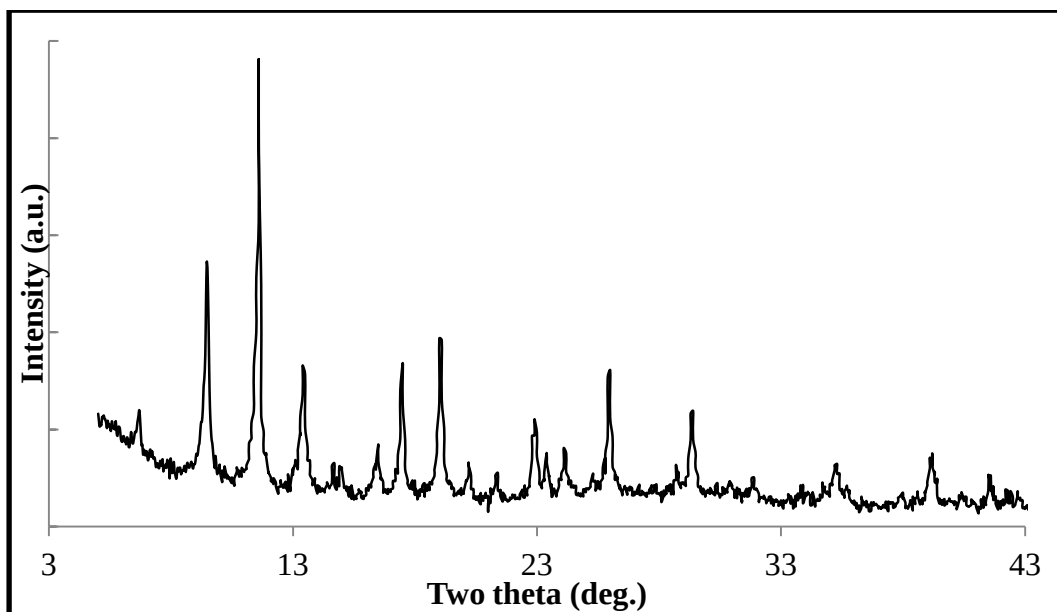


Figure 5.7 XRD patterns of CuBTC

Figure 5.8 shows the N_2 adsorption isotherms of CuBTC at 77 K and the specific surface areas were evaluated with the Brunauer–Emmett–Teller (BET) and Langmuir methods. The shape of N_2 adsorption isotherm is in good agreement with previous paper (Feng et al., 2013).

The estimated BET and Langmuir surface area of CuBTC are $523.33 \text{ m}^2/\text{g}$ and $689.33 \text{ m}^2/\text{g}$, respectively. And the estimated pore volume and adsorption average pore width are $0.39 \text{ cm}^3/\text{g}$ and $29.88 \text{ \AA}$. These values are close to the reported values for CuBTC (Chui et al., 1999; Wang et al). In literature, the surface area of CuBTC changes between $600\text{--}1500 \text{ m}^2/\text{g}$ range because of using different purification process such as basic filtration methods or soxhlet extraction methods for removal of DMF within the pores.

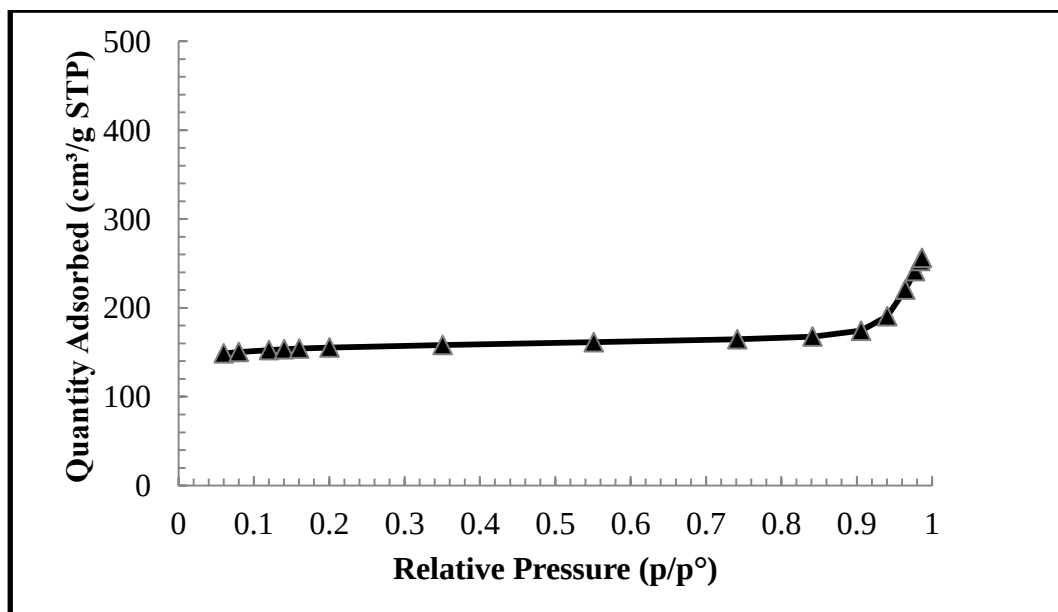


Figure 5.8 N₂ adsorption of CuBTC

The TGA profile shows typical weight loss pattern for the Cu-BTC MOF and complete degradation of CuBTC starts around 290⁰C and by 400⁰C the degradation is complete. In the range between 25-125⁰C the weight loss is purely due to removal of moisture and trapped methanol and between 125⁰C to 275⁰C where the weight remains fairly constant, is stable zone. Thus, for any experimentation using Cu-BTC, the system temperature should be regimentally maintained to be between 125-275⁰C. Figure 5.9 shows the TGA profile. (Chowdhury et al., 2009).

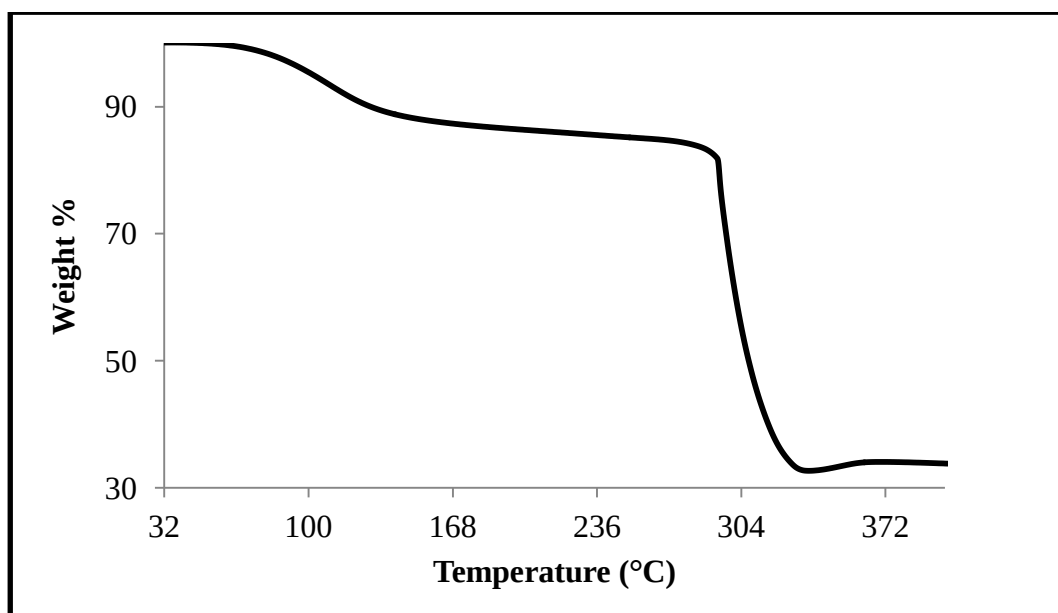


Figure 5.9 TGA profile of CuBTC

MIL-125

Figure 5.10 shows the crystal structure of the MIL-125. The pattern of MIL-125 is consistent with those reported in the literatures (Kim et al., 2013; Vermoortele et al., 2011), demonstrating that this MOF is successfully prepared. Additionally, no traces of characteristic peaks corresponding to bulk titanium dioxide phases, such as anatase (27° , 36° , 55°) and rutile (48°), are observed in the diffraction pattern of MIL-125(Ti). This result indicates that the framework of MIL-125(Ti) consists of small titanium oxide clusters in the absence of bulky aggregated titanium oxide species.

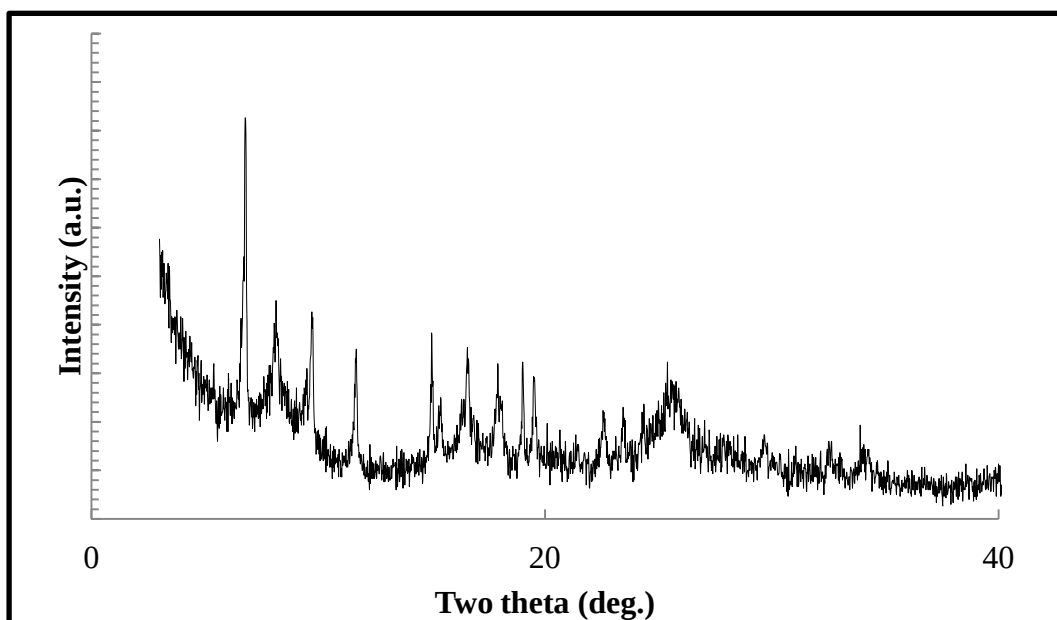


Figure 5.10 XRD pattern of MIL-125

Figure 5.11 shows the N_2 adsorption isotherms of MIL-53 at 77 K and the specific surface areas were evaluated with the Brunauer–Emmett–Teller (BET) and Langmuir methods. The BET and Langmuir surface area pore volume and adsorption average pore width of MIL-53 are found as $265 \text{ m}^2/\text{g}$, $367 \text{ m}^2/\text{g}$, $0.30 \text{ cm}^3/\text{g}$ and $46.7 \text{ \AA}$.

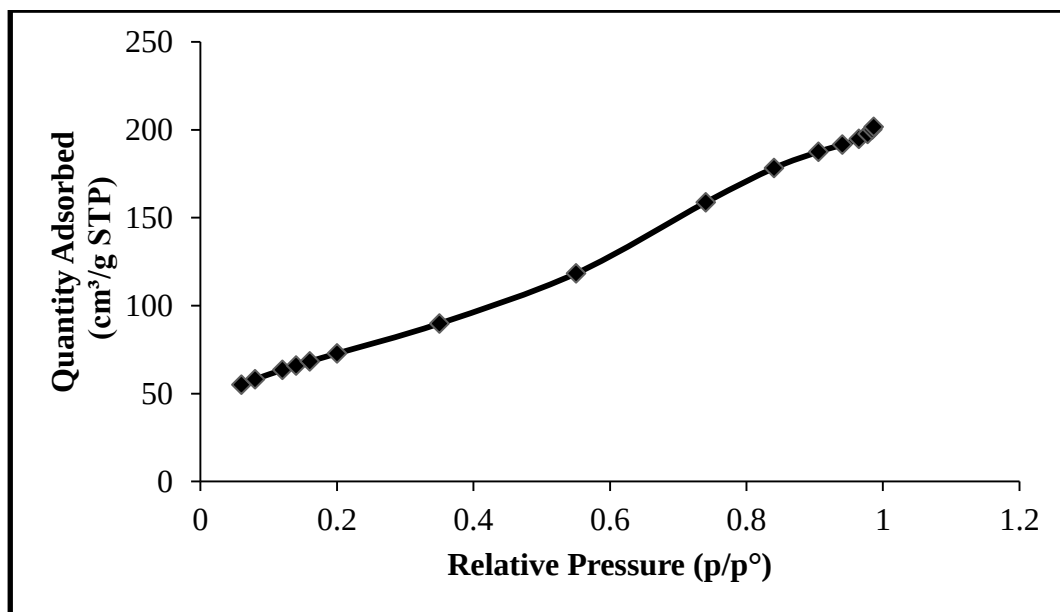


Figure 5.11 N_2 adsorption of MIL-125

D1-MIL-101

Figure 5.12 shows the crystal structure of the D1-MIL-101 synthesized by ultrasound assisted ionothermal method.

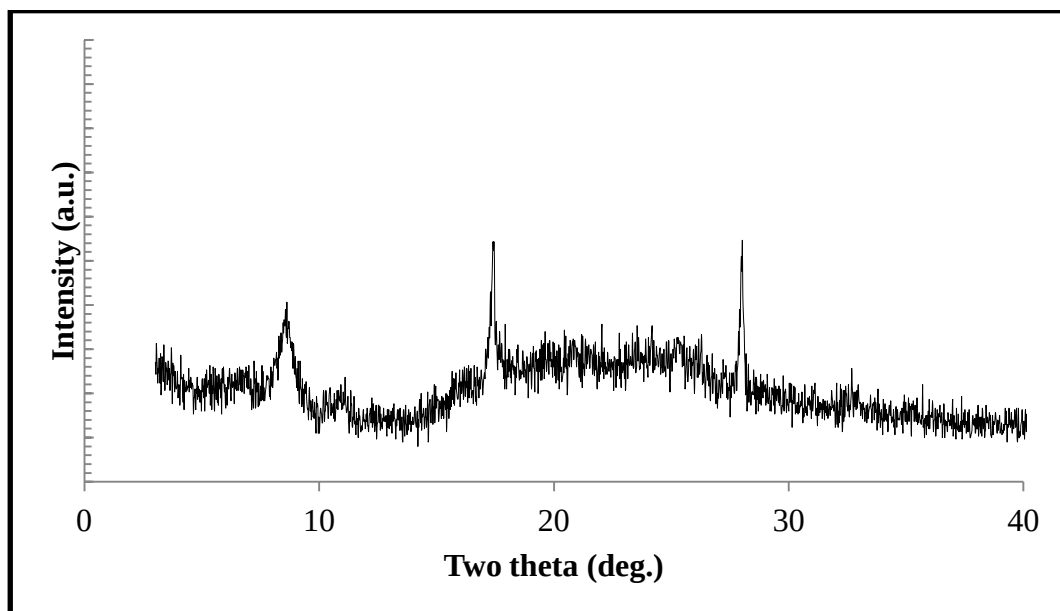


Figure 5.12 XRD patterns of D1-MIL-101

Nitrogen sorption experiments of D1-MIL-101 sample reveals typical Type-I sorption behavior confirming the permanent porosity of compound (Figure 5.13). The estimated BET, Langmuir surface area of sample, pore volume and

average pore width are 118 m²/g and 161, and the estimated pore volume is 0.057 cm³/g and 19.25 Å.

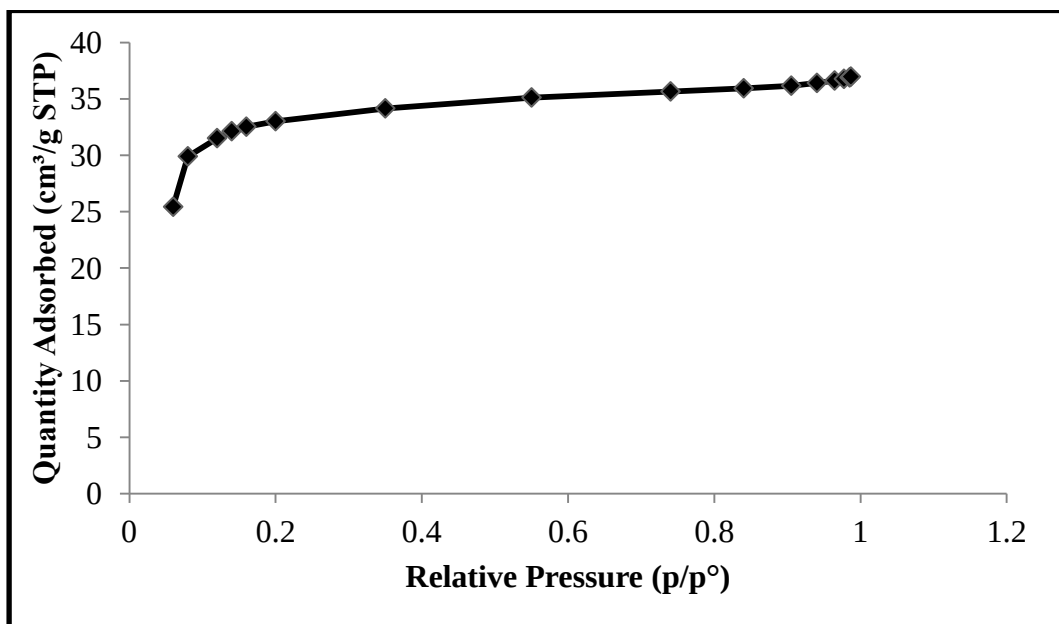


Figure 5.13 N₂ adsorption of D1-MIL-101 and D1-MIL-101

The thermal stability of D1-MIL-101 was confirmed by the TGA. As shown in Figure 5.14, the two-step weight changes are observed while increasing the temperature; the weight change occurs near 250 °C due to the decomposition of the network.

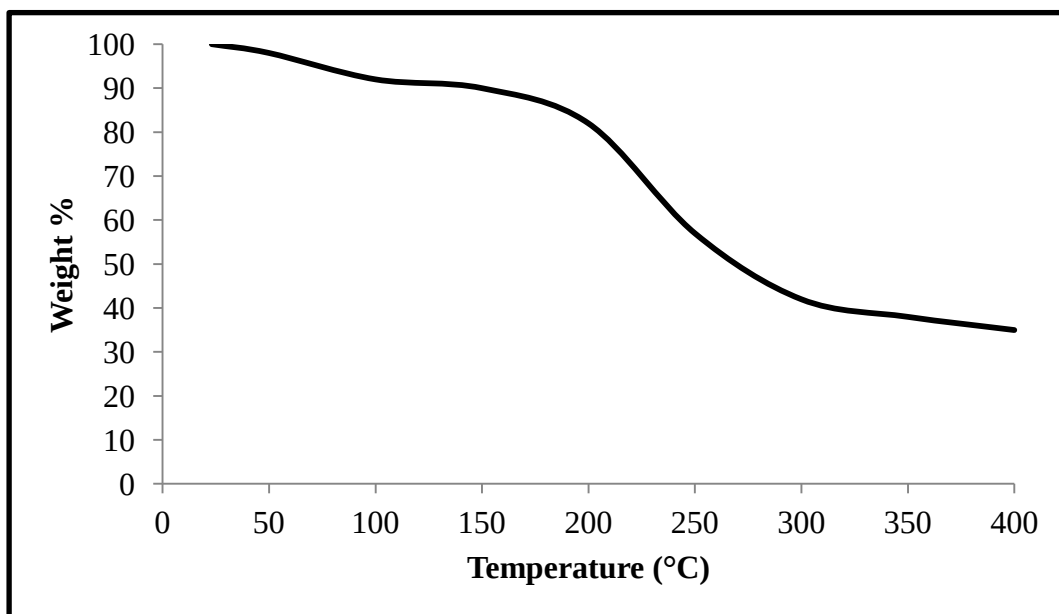


Figure 5.14 TGA profile of D1-MIL-101

D2-MIL-101

Figure 5.15 shows the crystal structure of the D2-MIL-101 synthesized by ultrasound assisted ionothermal method. D2-MIL-101 shows amorphous structure.

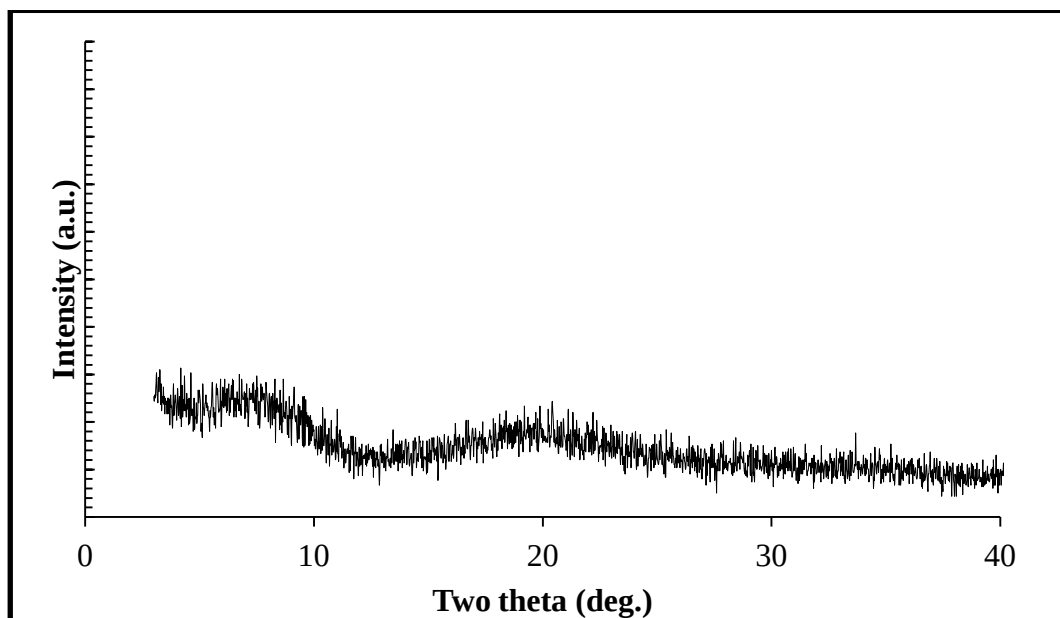


Figure 5.15 XRD patterns of D2-MIL-101

Nitrogen sorption experiments of D2-MIL-101 sample shows Type-III sorption behavior having a weak adsorbate-adsorbent interactions (Figure 5.16). The BET and Langmuir surface area, pore volume and adsorption average pore width of D2-MIL-101 are found as 12.94 m²/g, 17.94 m²/g, 0.022 cm³/g and 63.17 Å, respectively.

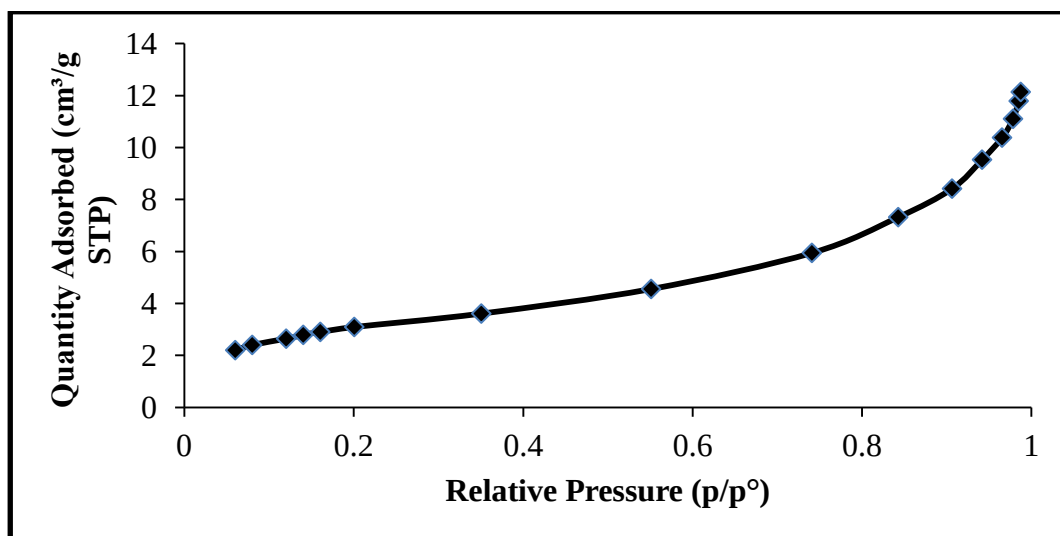


Figure 5.16 N₂ adsorption of D2-MIL-101

D1-MIL-53

The crystallinity of D1-MIL-53 was determined by powder X-ray diffraction measurements (Figure 5.17). The typical peaks of MIL-53 are obtained at 2θ of 9.24, 12.7, 17.66, 18.24, 18.58, 25.52, 27.32, 29.8, 30.28, 36.18 for the ionothermal synthesis of MIL-53.

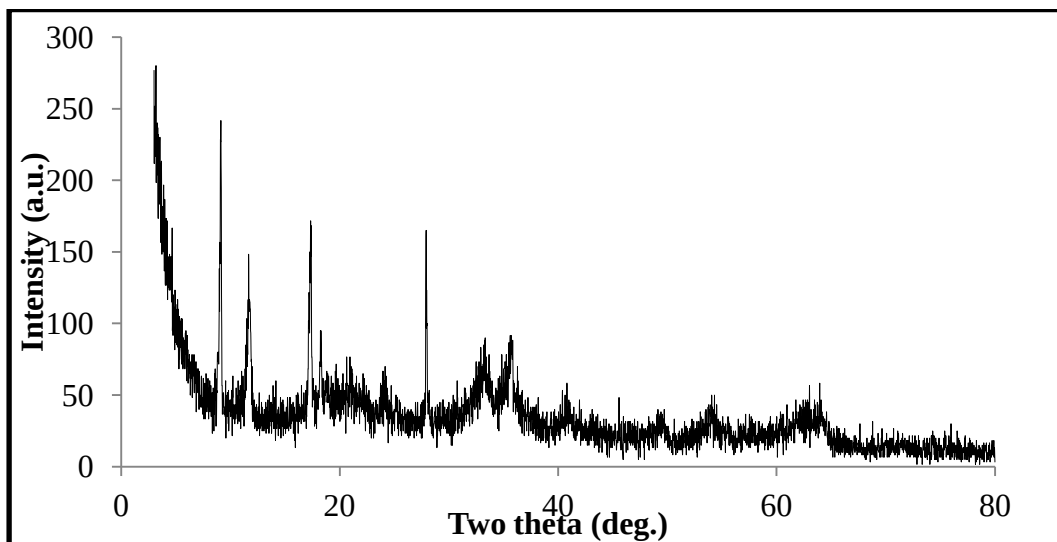


Figure 5.17 XRD patterns of D1-MIL-53

Nitrogen sorption experiments of D1-MIL-53 sample shows Type-II or III sorption behavior indicating of physical adsorption of gases by non-porous solids. In this class of isotherm monolayer coverage is followed by multilayering at high relative pressures. The BET and Langmuir surface area, pore volume and adsorption average pore width of D1-MIL-53 are found as 16.74 m²/g, 23.38 m²/g, 0.039 cm³/g and 93.015 Å, respectively.

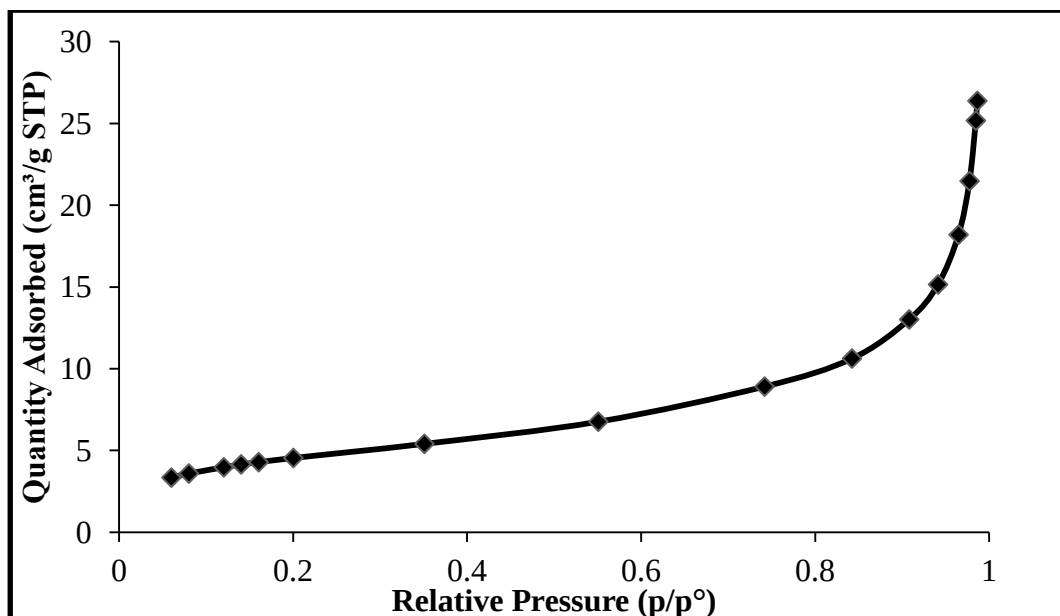


Figure 5.18 N₂ adsorption of D1-MIL-53

The TGA profile shows typical weight loss pattern for the D1-MIL-53 and complete degradation of D1-MIL-53 starts around 300°C and by 400°C the degradation is complete. Figure 5.19 shows the TGA profile of D1-MIL-53.

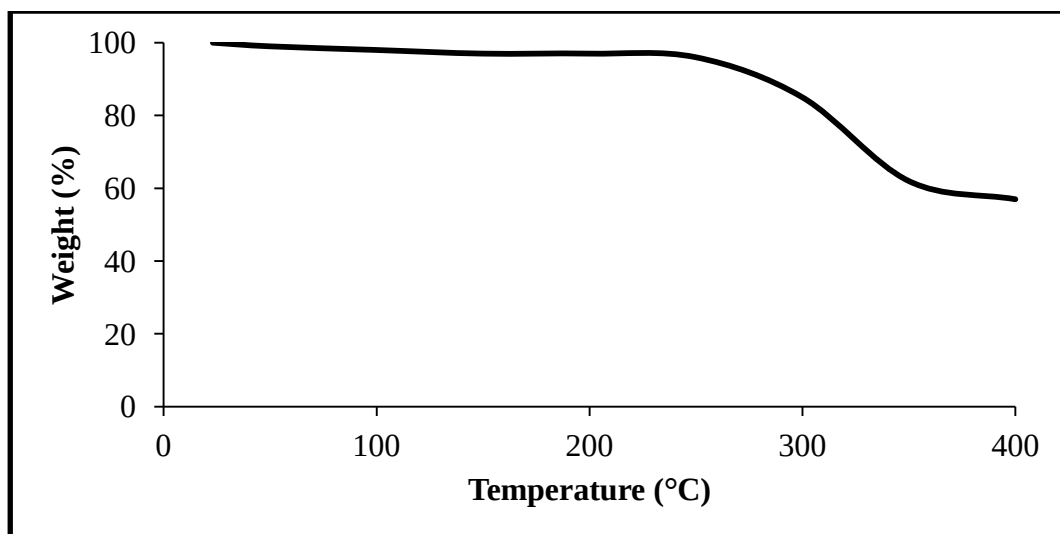


Figure 5.19 TGA profile of D1-MIL-53

D2-MIL-53

Figure 5.20 shows the crystal structure of the D2-MIL-53 synthesized by ultrasound assisted ionothermal method.

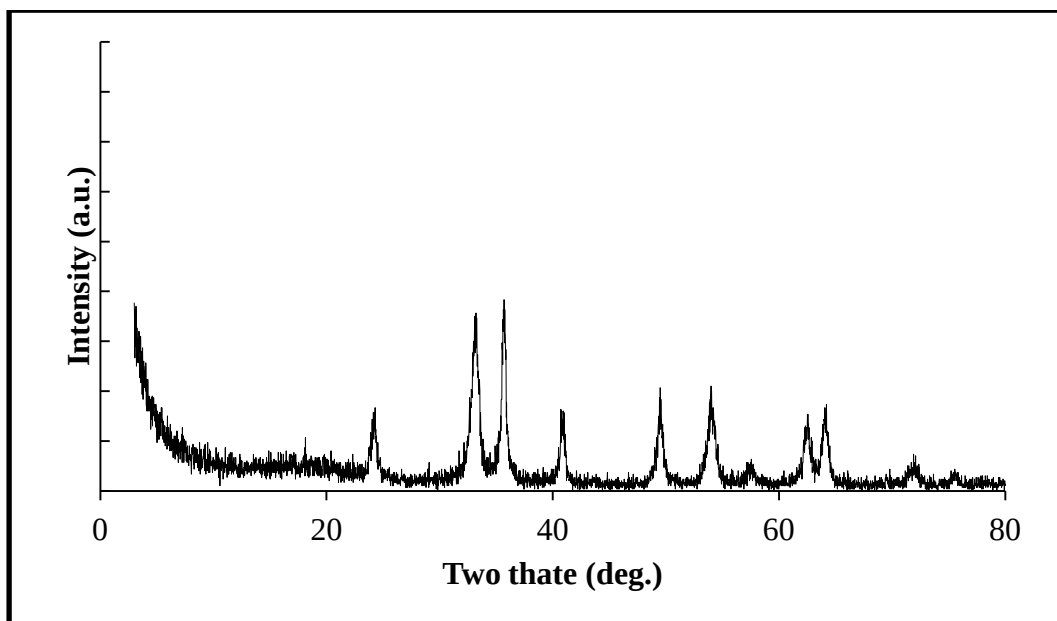


Figure 5.20 XRD patterns of D2-MIL-53

N_2 adsorption of D2-MIL-53 samples isotherm is plotted in Figure 5.21. This isotherm is also like the Type II or III which shows the weak adsorbate adsorbent relation. The BET and Langmuir surface area, pore volume and adsorption average pore width of D2-MIL-53 are found as $63.61 \text{ m}^2/\text{g}$, $88.3 \text{ m}^2/\text{g}$, $0.134 \text{ cm}^3/\text{g}$ and $83.95 \text{ \AA}$, respectively.

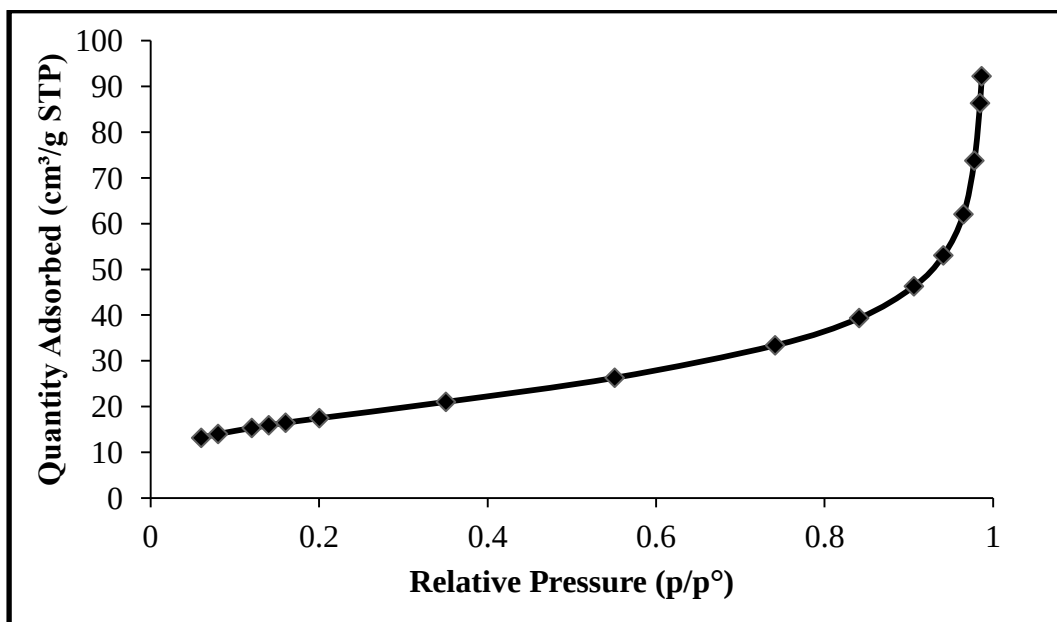


Figure 5.21 N_2 adsorption of D2-MIL-53

Figure 5.22 shows the TGA profile of D2-MIL-53. As shown in Figure 22, the weight loss occurs between 250-400°C by 5%.

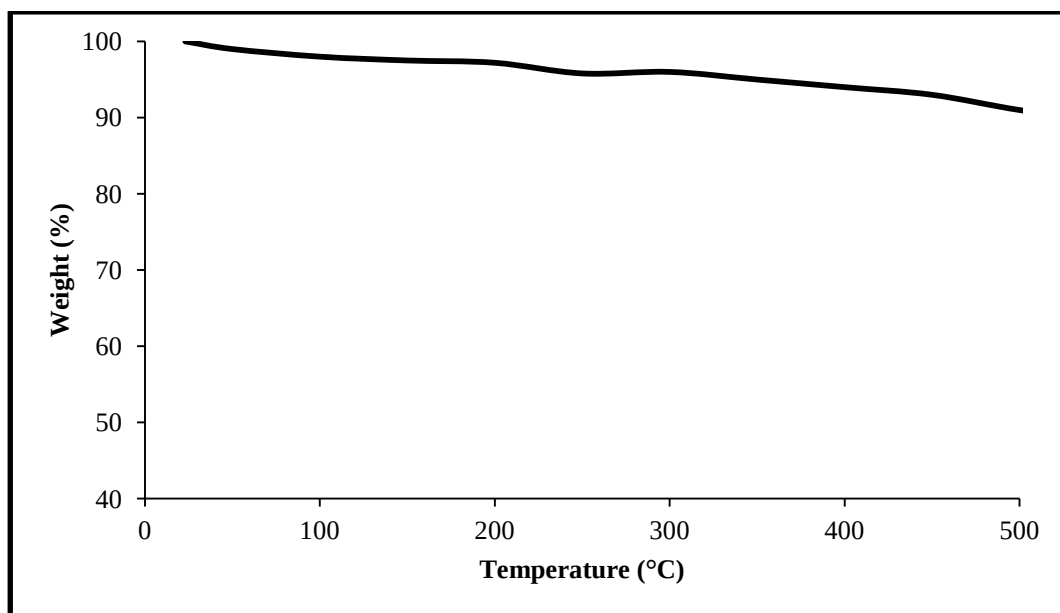


Figure 5.22 TGA profile of D2-MIL-53

The textural and structural analysis of sulfonated MOFs

The synthesized MOFs are sulfated to increase the acidity of the catalysts. The change in the structure of MOFs are observed by TGA, XRD and BET analysis.

MIL-101s

Figure 5.23 shows the crystal structure of the MIL-101s.

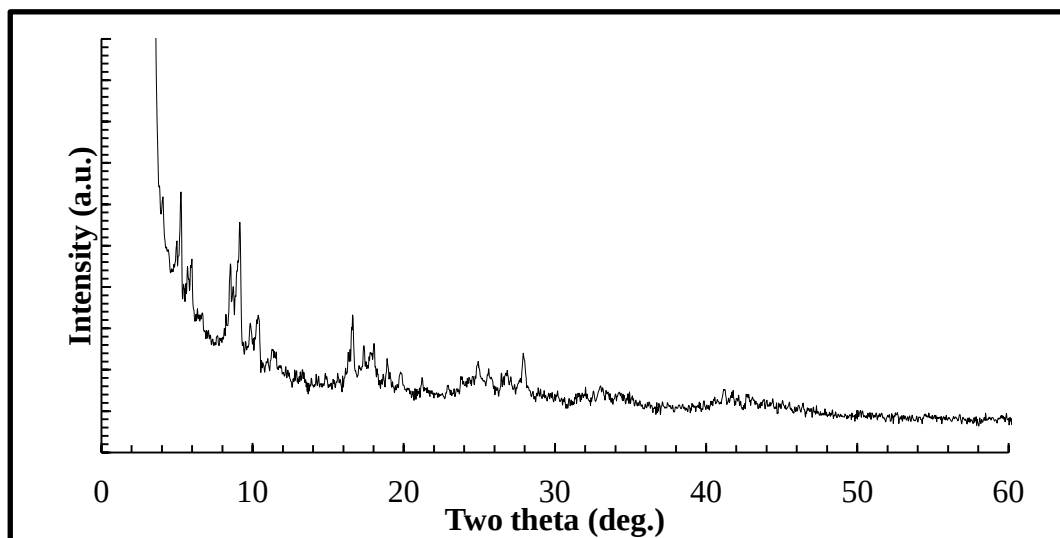


Figure 5.23 XRD patterns of MIL-101s

Figure 5.24 shows the N₂ adsorption isotherms of MIL-101s at 77 K and the specific surface areas were evaluated with the Brunauer–Emmett–Teller (BET) and Langmuir methods. The BET and Langmuir surface area, pore volume and adsorption average pore width of MIL-101s are found as 608.52 m²/g, 841.21 m²/g, 0.32 cm³/g and 21.10 Å, respectively.

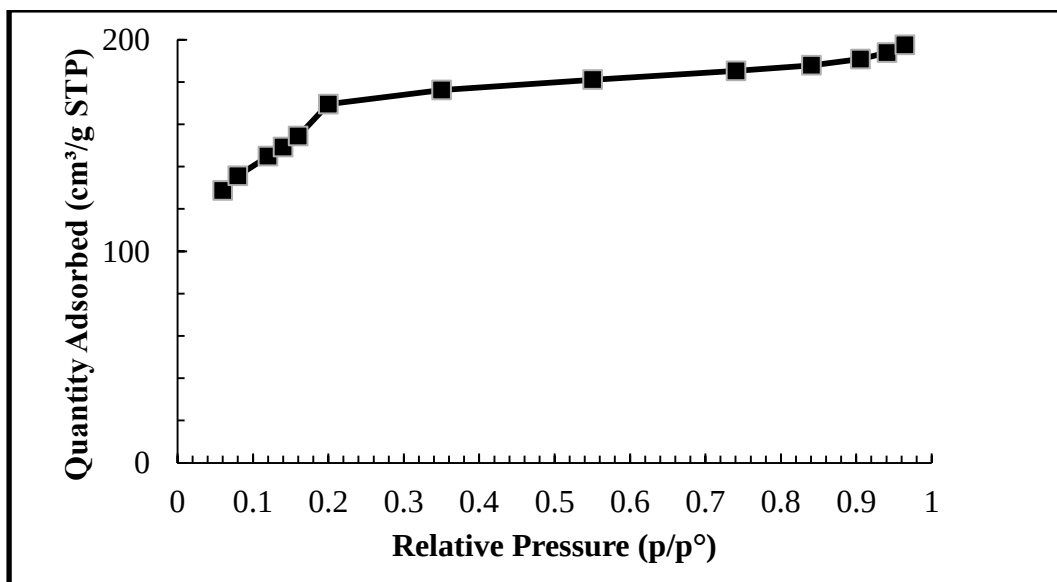


Figure 5.24 N₂ adsorption of MIL-101s

The TGA profile shows that MIL-101s is stable up to 380° C (Figure 5.25) and a 10 % weight loss between 50 and 100° C results from water evaporation for MIL-101s.

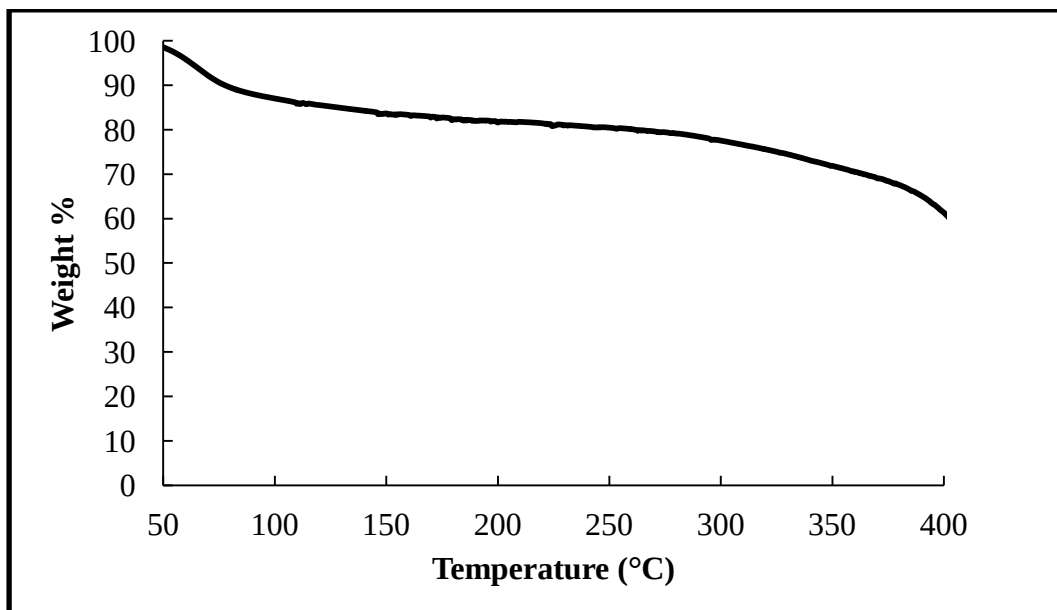


Figure 5.25 TGA profile of MIL-101s

MIL-53 (Fe)s

Figure 5.26 shows the crystal structure of the MIL-53s.

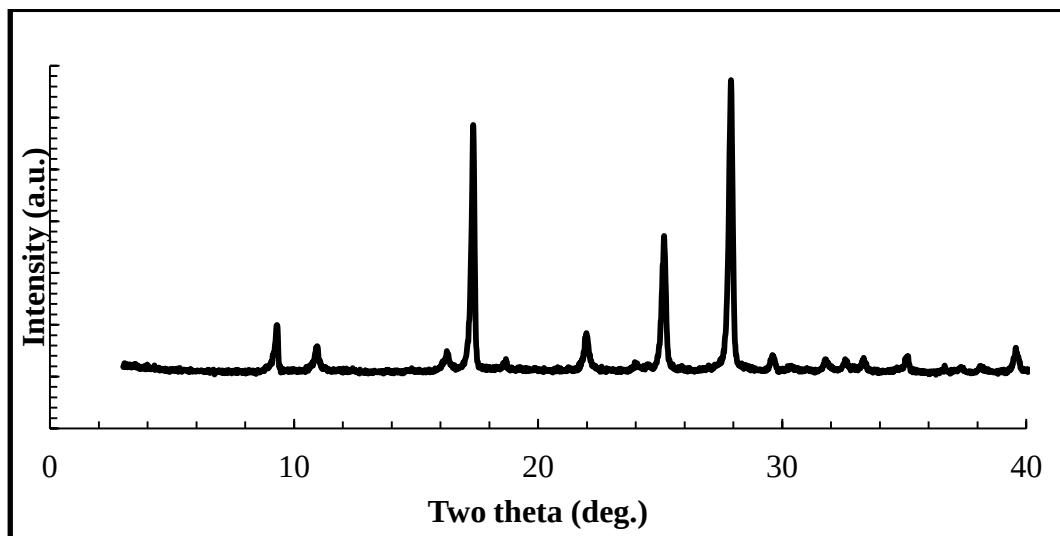


Figure 5.26 XRD patterns of MIL-53 (Fe)s

Figure 5.27 shows the N₂ adsorption isotherms of MIL-101s at 77 K and the specific surface areas were evaluated with the Brunauer–Emmett–Teller (BET) and Langmuir methods. The BET and Langmuir surface area, pore volume and adsorption average pore width of MIL-53s are found as 4.98 m²/g, 7.79 m²/g, 0.012 cm³/g and 98.03 Å, respectively.

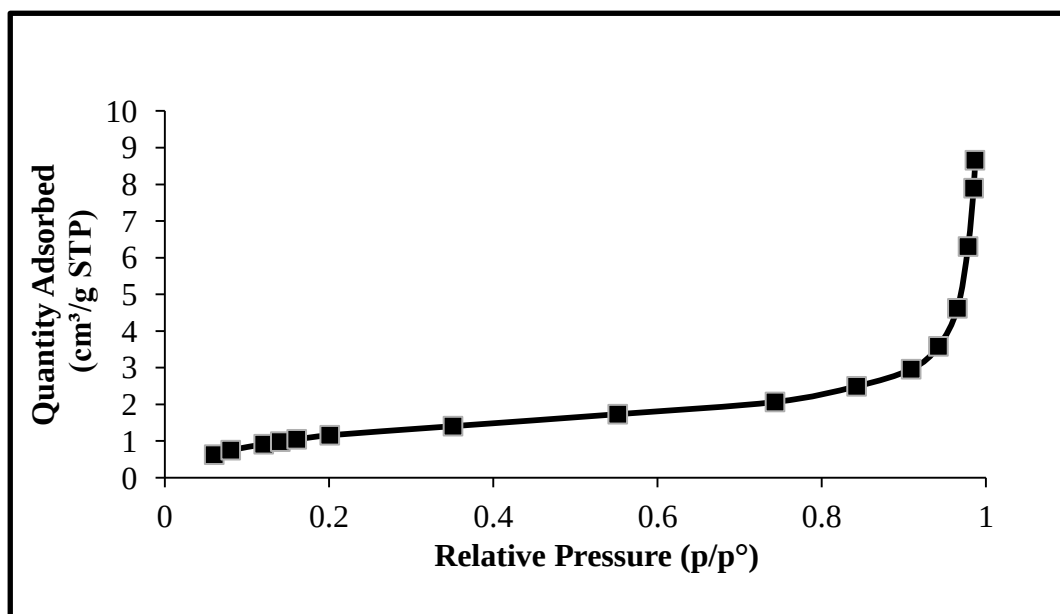


Figure 5.27 N₂ adsorption of MIL-53 (Fe)s

The TGA profile shows that MIL-53(Fe)s is stable up to 300° C (Figure 5.28). The weight loss of MOFs, occurred between, 300 and 400° C for MIL-53(Fe)s which may result from the framework decomposition.

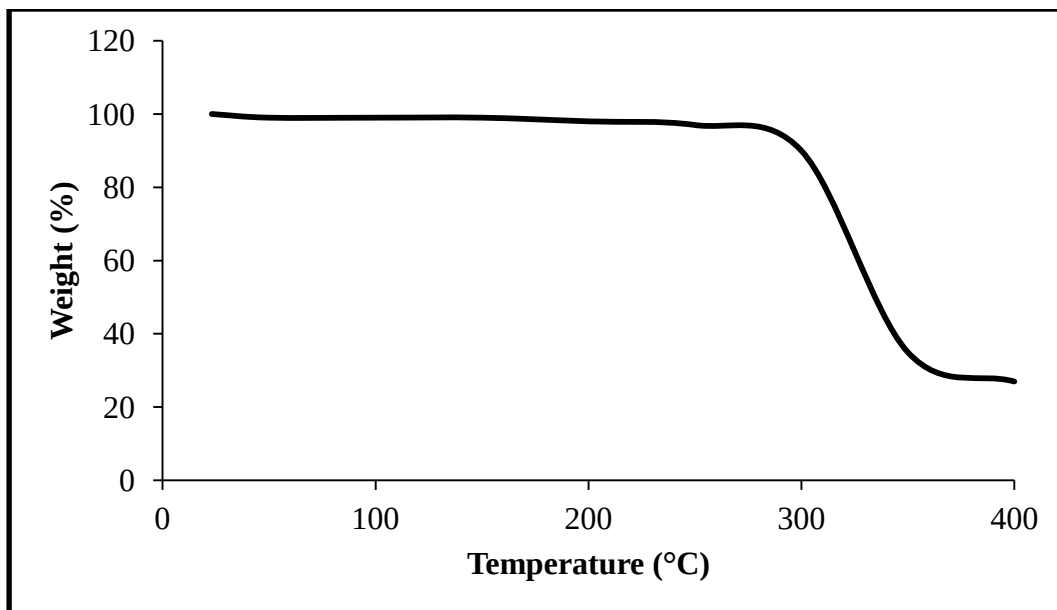


Figure 5.28 TGA profile of MIL-53 (Fe)s

MIL-125s

Figure 5.29 shows the crystal structure of the MIL-125s.

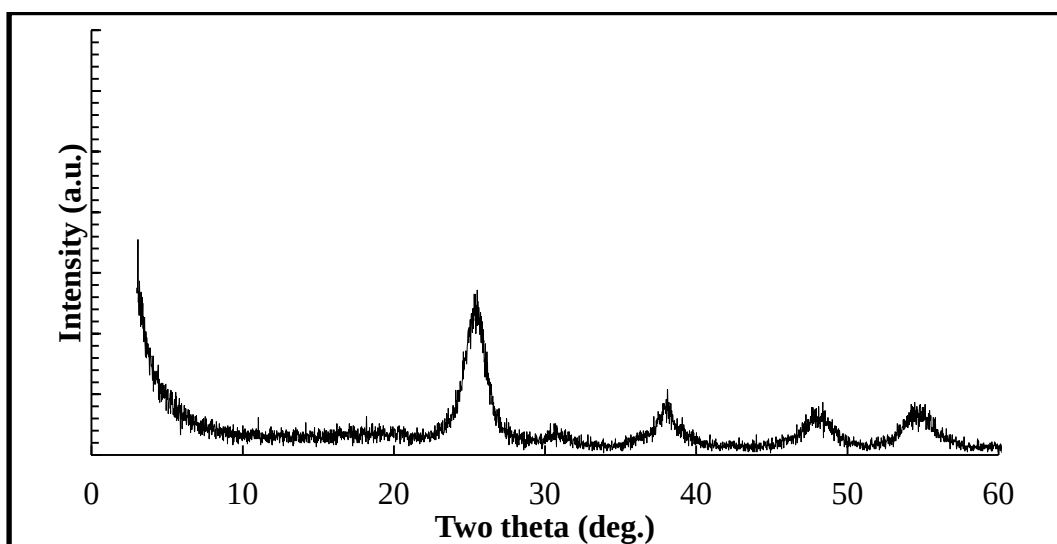


Figure 5.29 XRD patterns of MIL-125s

Figure 5.30 shows the N₂ adsorption isotherms of MIL-125s at 77 K and the specific surface areas were evaluated with the Brunauer–Emmett–Teller (BET) and Langmuir methods. The BET and Langmuir surface area, pore volume

and adsorption average pore width of MIL-125s are found as $215.3\text{ m}^2/\text{g}$, $300\text{ m}^2/\text{g}$, $0.263\text{ cm}^3/\text{g}$ and $48.86\text{ \AA}$, respectively.

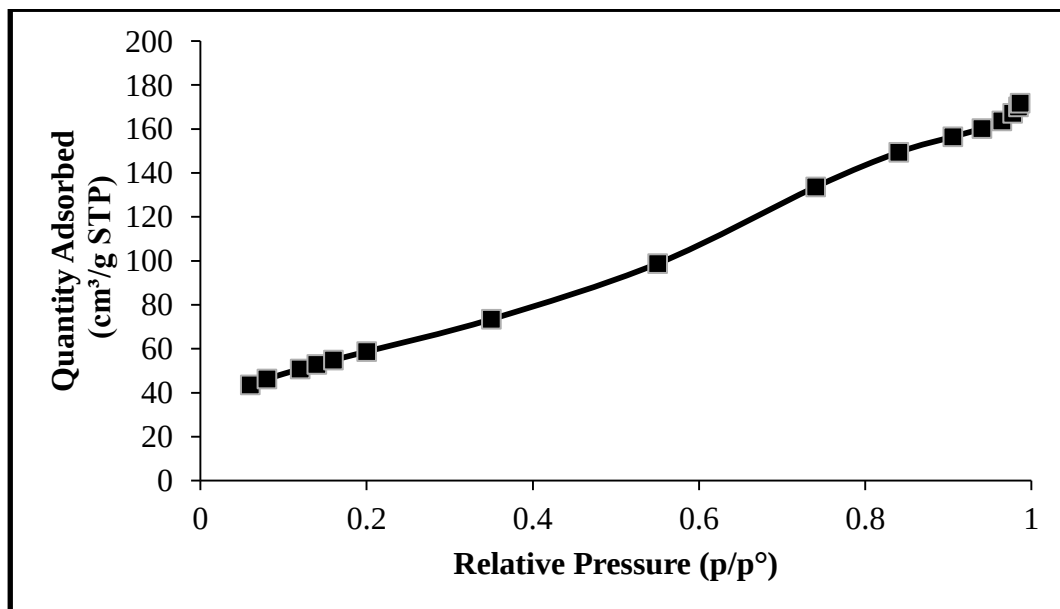


Figure 5.30 N_2 adsorption of MIL-125s

D1- MIL-101s

Figure 5.31 shows the crystal structure of the D1-MIL-101s.

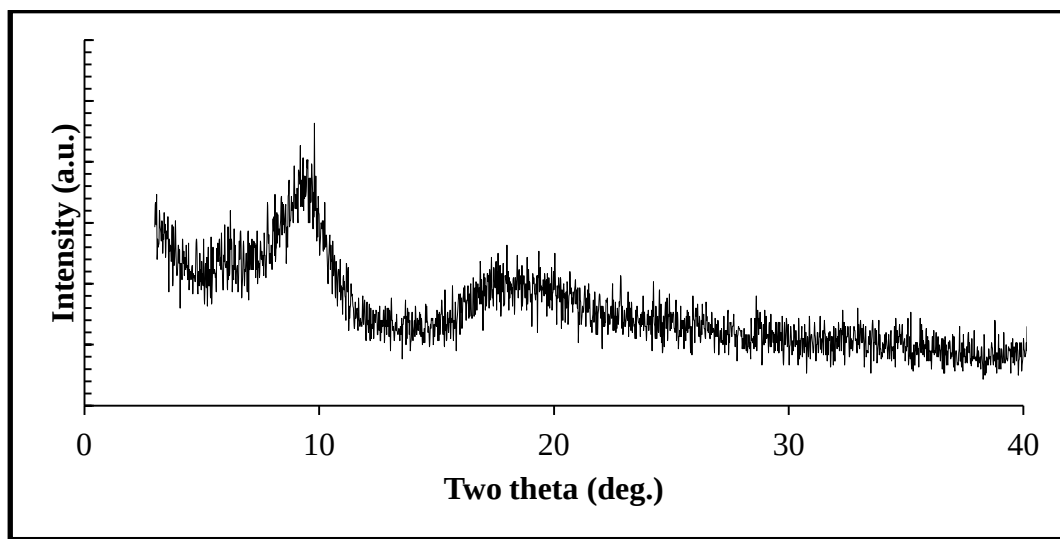


Figure 5.31. XRD patterns of D1-MIL-101s

The TGA profile shows that D1-MIL-101s is stable up to 400° C (Figure 32) The weight loss of MOFs, between 250- 400° C results from the framework decomposition.

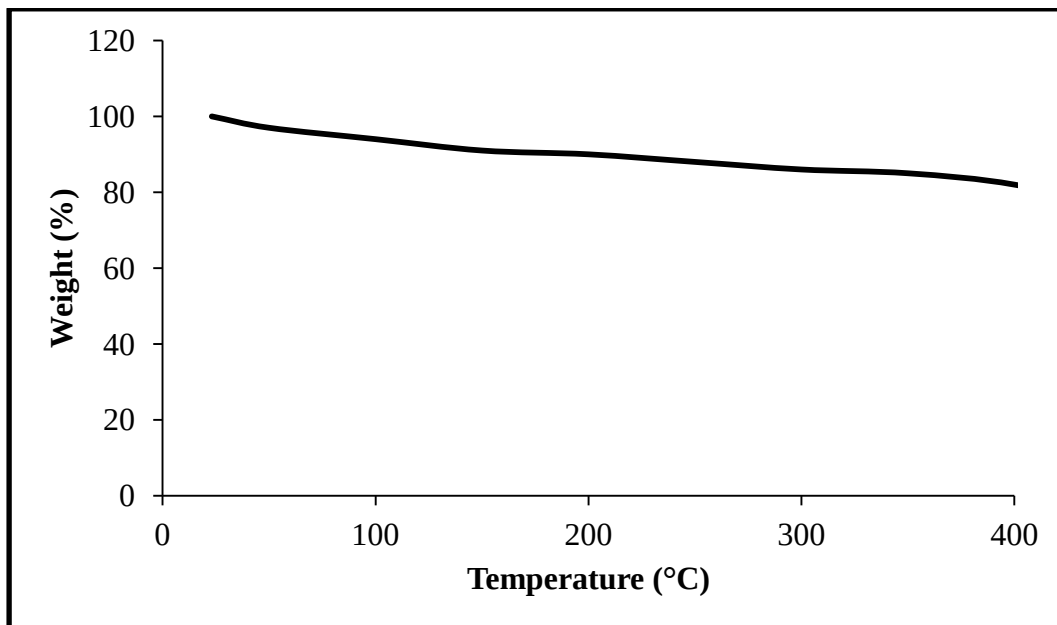


Figure 5.32 TGA profile of D1-MIL-101s

D2-MIL-101s

Figure 5.33 shows the crystal structure of the D2-MIL-101s.

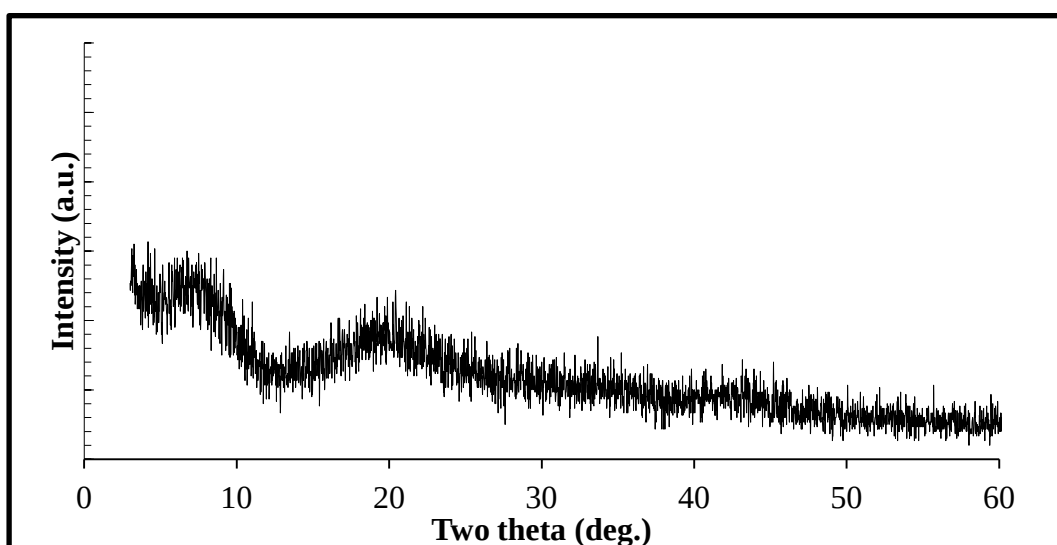


Figure 5.33 XRD patterns of D2-MIL-101s

Figure 5.34 shows the N₂ adsorption isotherms of D2-MIL-101s at 77 K and the specific surface areas were evaluated with the Brunauer–Emmett–Teller (BET) and Langmuir methods. The BET and Langmuir surface area, pore volume and adsorption average pore width of D2-MIL-101s are found as 11.54 m²/g, 16.26 m²/g, 0.018 cm³/g and 69.23 Å, respectively.

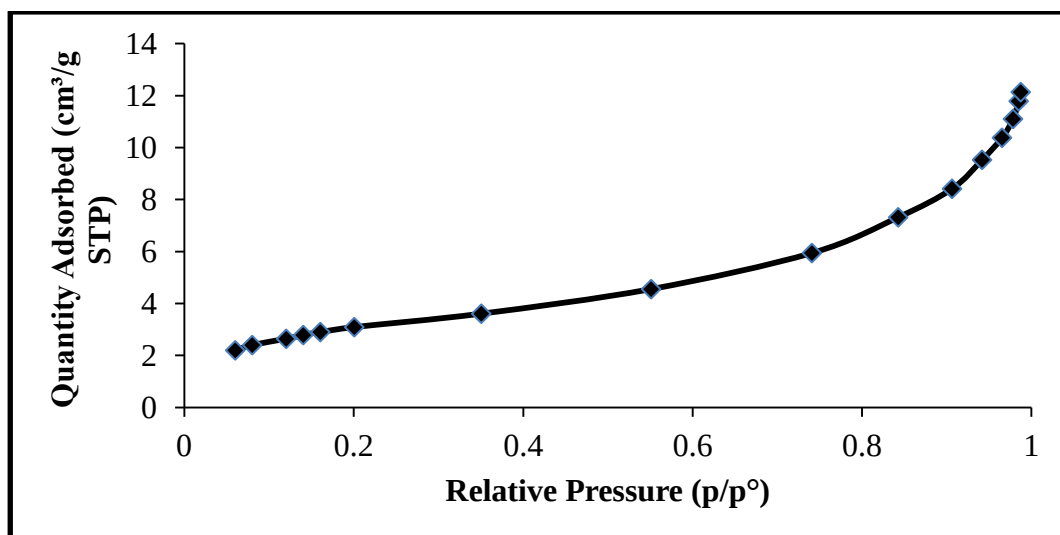


Figure 5.34 N₂ adsorption of D2-MIL-101s

D1-MIL-53s

Figure 5.35 shows the crystal structure of the D1-MIL-53s.

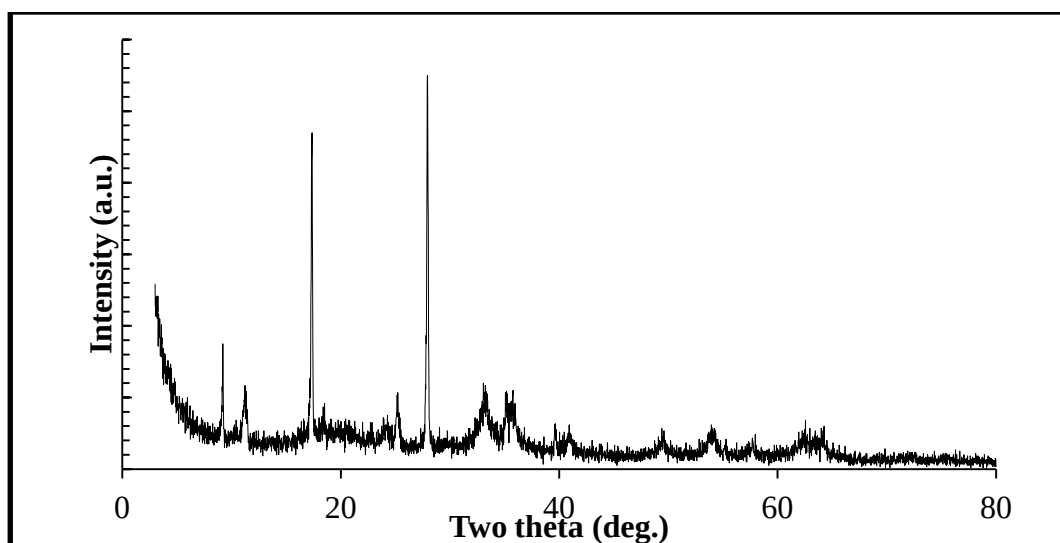


Figure 5.35 XRD patterns of D1-MIL-53s

Figure 5.36 shows the N_2 adsorption isotherms of D1-MIL-53s at 77 K and the specific surface areas were evaluated with the Brunauer–Emmett–Teller (BET) and Langmuir methods. The BET and Langmuir surface area, pore volume and adsorption average pore width of MIL-101s are found as $12.13 \text{ m}^2/\text{g}$, $17.32 \text{ m}^2/\text{g}$, $0.021 \text{ cm}^3/\text{g}$ and $70.94 \text{ \AA}$, respectively.

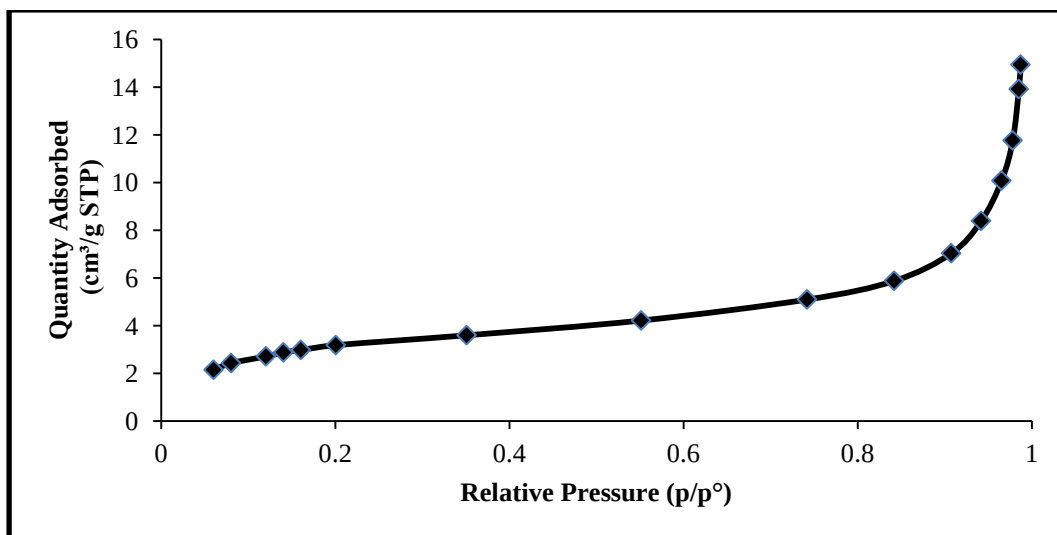


Figure 5.36 N_2 adsorption of D1-MIL-53s

D2-MIL-53s

Figure 5.37 shows the crystal structure of the D2-MIL-53s.

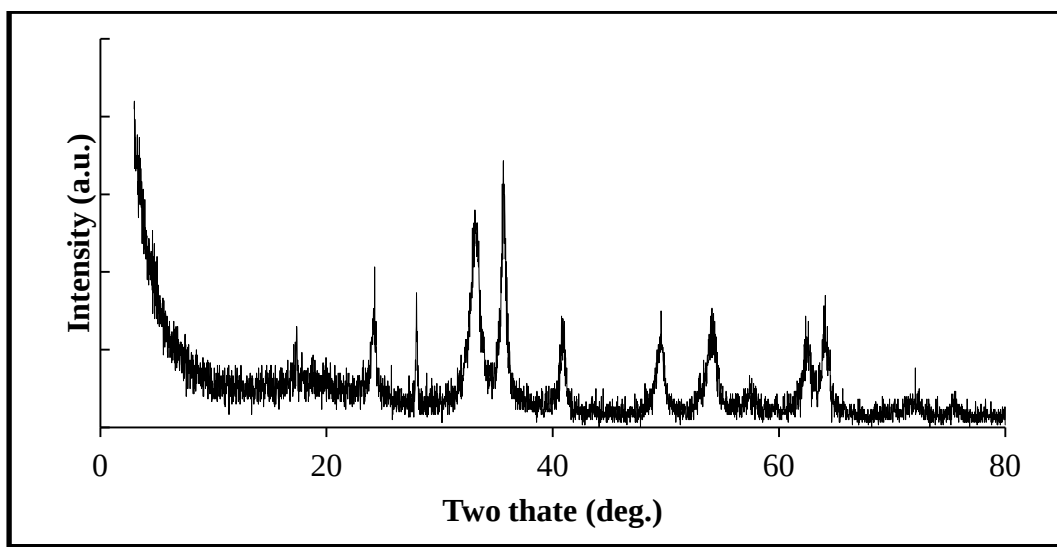


Figure 5.37 XRD patterns of D2-MIL-53s

Figure 5.38 shows the N₂ adsorption isotherms of D2-MIL-53s at 77 K and the specific surface areas were evaluated with the Brunauer–Emmett–Teller (BET) and Langmuir methods. The BET and Langmuir surface area, pore volume and adsorption average pore width of D2-MIL-53s are found as 12.1 m²/g, 16.25 m²/g, 0.018 cm³/g and 63 Å, respectively.

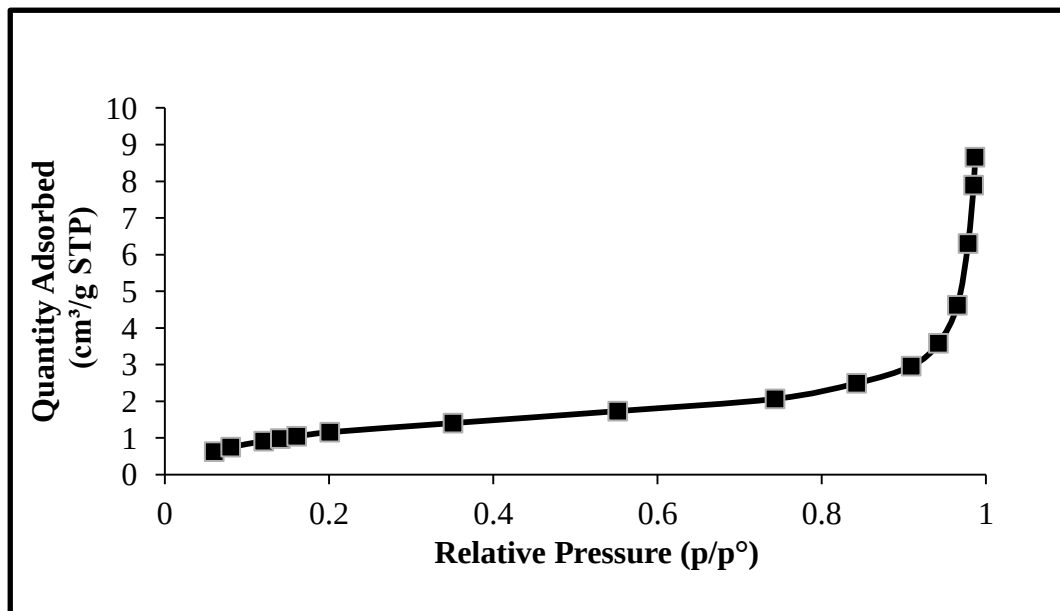


Figure 5.38 N₂ adsorption of D2-MIL-53s

Effect of sulfonation

MIL-101, MIL-53, MIL-125, D1-MIL-101, D2-MIL-101, D1-MIL-53 and D2-MIL-53 were sulfonated to increase the acidity. As shown from the analysis;

- the crystal structures of MOFs doesn't show any difference after sulfation except MIL-125 and D1-MIL-101. In XRD pattern of MIL-125s, the characteristic peaks related to titanium are not observed. This may come from the interaction between sulfur and titanium compounds. In XRD pattern of D1-MIL-101s, the peaks are disappeared at 17 and 28° after sulfation. Generally frameworks are preserved after sulfation.
- N₂ adsorption at 77 K is depicted for all samples. In the case of all MOFs, nitrogen adsorption reveals a decrease in the specific surface area significantly, while the shape of the isotherm remains unchanged after sulfation. A large decrease in the pore size of all synthesized MOFs caused by the volume of the sulfoxy acid groups after sulfation.

- Generally, all MOFs show high thermal stability but for sulfated samples, degradation of MOFs begins at lower temperatures.

Effect of synthesis method

In solvothermal method, solvents are used to synthesize metal organic framework. By accounting environmental effect, the ionothermal method is applied to produce MOF. In ionothermal method, MIL-101 and MIL-53 are synthesized by using two different deep eutectic solvents (ChCl-urea and ChCl-dimethyl urea). As shown from the analysis;

- The crystal structures are almost the same for samples obtained by both methods.
- MOFs produced by eutectic solvents give less surface area and pore volume.
- The thermal stability of the samples obtained from solvothermal and ionothermal are high but for some samples degradation of MOFs obtained by ionothermal method begins at lower temperatures.

5.2. Liquid Phase Adsorption onto Metal Organic Frameworks

In this study, MIL-101 (Cr), CuBTC and MIL-53 (Fe) were used to adsorb methyl red and methyl orange in liquid phase and also MIL-101 (Cr) and MIL-53 (Fe) were used to adsorb toluene and nitrobenzene in liquid phase.

5.2.1. Adsorption of Methyl Red onto MIL-101, MIL-53 and CuBTC

In liquid phase adsorption of methyl red, the effects of temperature, initial concentration, adsorbent amount, contact time and pH were investigated and also reusability of MIL-101, MIL-53 and CuBTC was studied. The adsorption kinetics, mechanism, isotherms were searched and thermodynamic constants were calculated.

5.2.1.1. Adsorption kinetics

To understand the adsorption mechanism, the pseudo-first-order and pseudo-second-order kinetic model (Ho and McKay 1999) were studied. These models are given by the following equation;

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (5.1)$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5.2)$$

where q_e is amount adsorbed at equilibrium (mg/g),

q_t is amount adsorbed at time t (mg/g),

t is adsorption time (min), k_1 the rate constant of pseudo-first-order kinetic (min^{-1}), and

k_2 is the rate constant of the pseudo-second-order kinetic ($\text{g}/(\text{mg} \cdot \text{min})$),

The initial adsorption rate, h ($\text{mg}/(\text{g} \cdot \text{min})$), is calculated by using eq. 3;

$$h = k_2 q_e^2 \quad (5.3)$$

Sorption kinetics is an important characteristic for evaluating the efficiency of sorption. The kinetic behaviour of this process was studied at pH 5 and 298, 308 and 318 K using four different initial MR concentrations (Figure 5.39-5.41). Figure 5.39-5.41 which represents the kinetics of MR adsorption onto MIL-101, CuBTC and MIL-53 (Fe), indicates that the process occurs in two phases: an initial rapid phase followed by a slower phase that ultimately reaches equilibrium. The initial high rate of MR sorption is most likely due to the greater availability of binding sites near the surface of the adsorbents. The sorption capacity increases with an increase in the initial MR concentration, but the time required to reach equilibrium appears to be almost independent of the initial concentration.

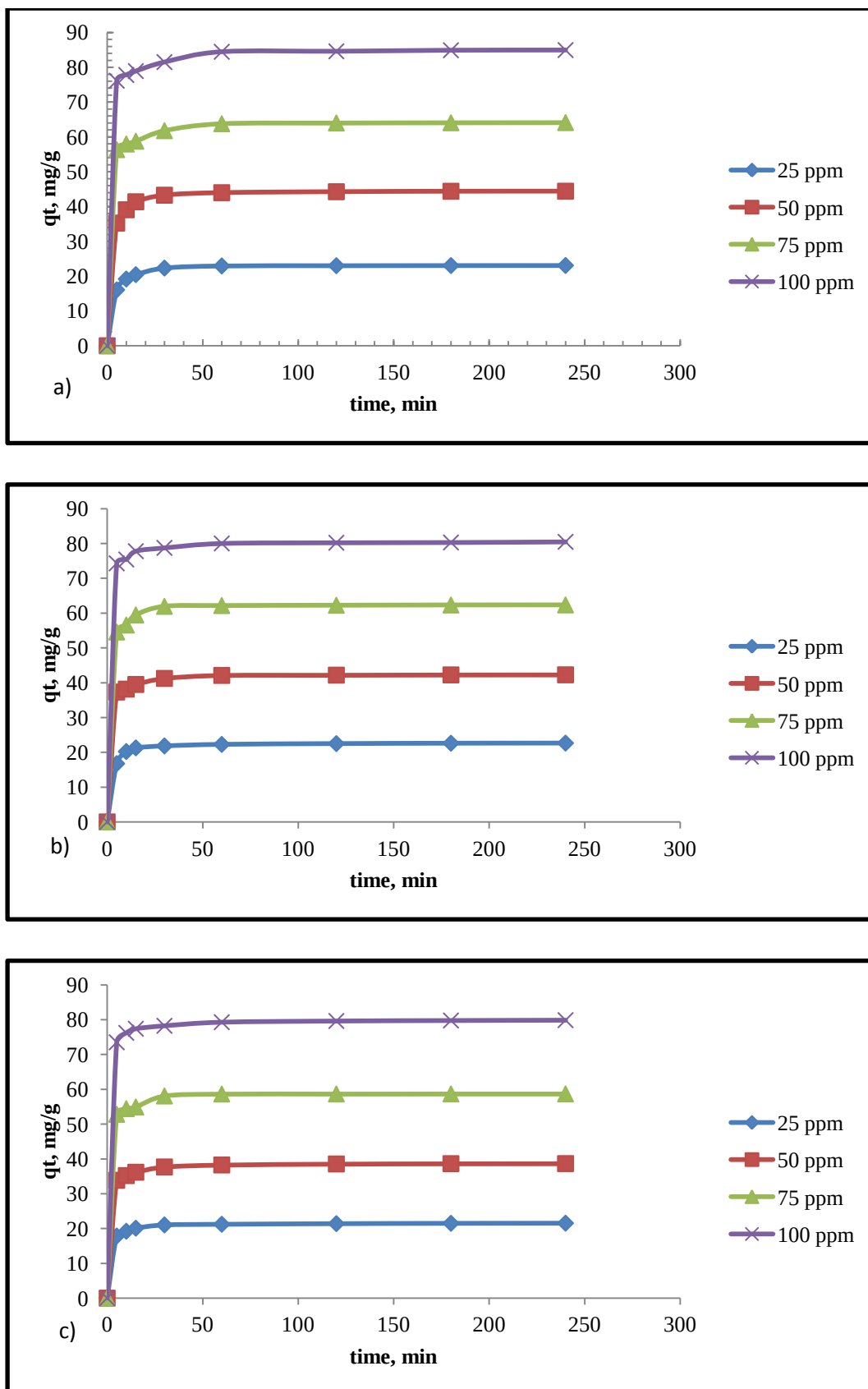


Figure 5.39 Effect of contact time on the adsorption of MR on MIL-101 at different temperature of (a) $T=298$ K; (b) $T=308$ K; (c) $T=318$ K.

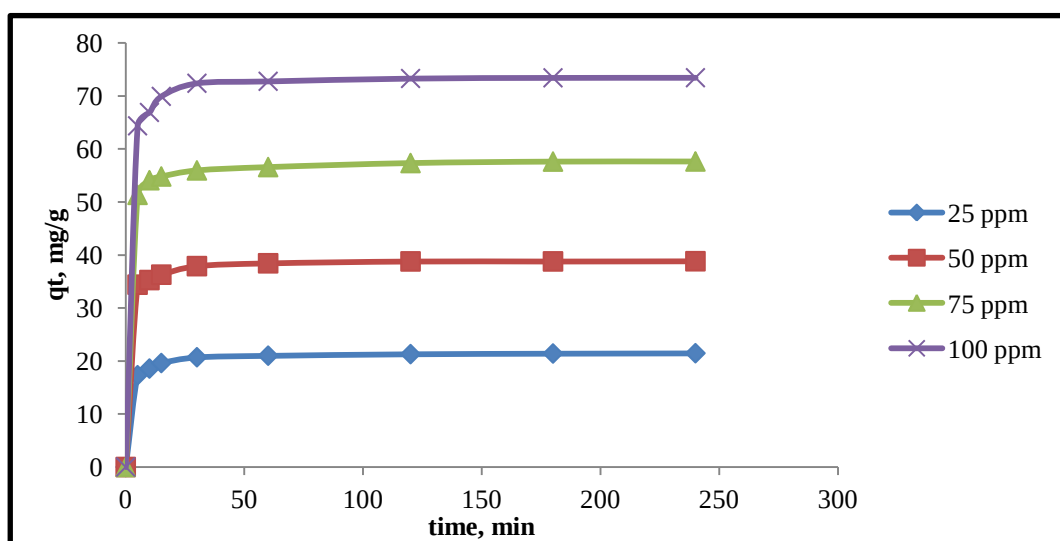
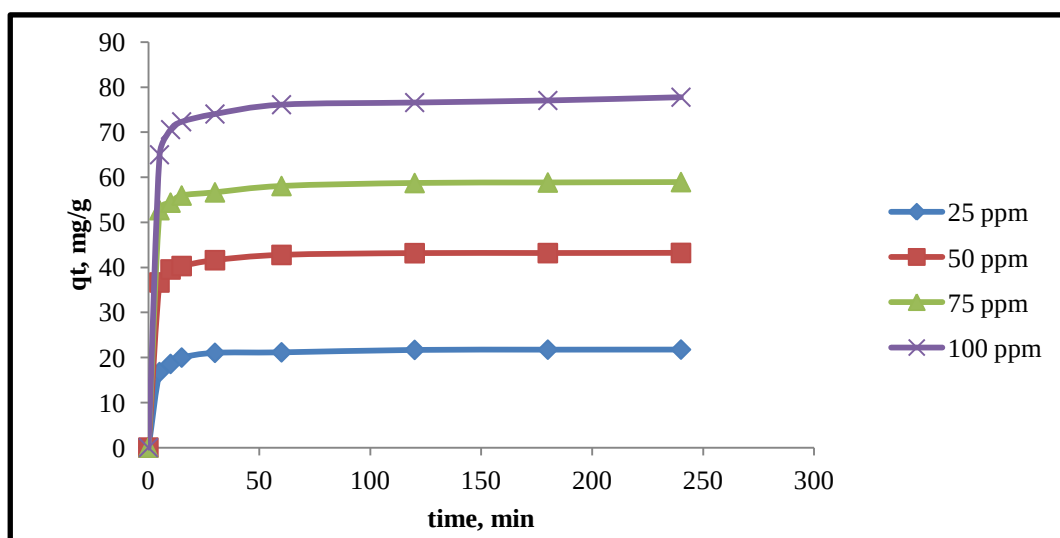
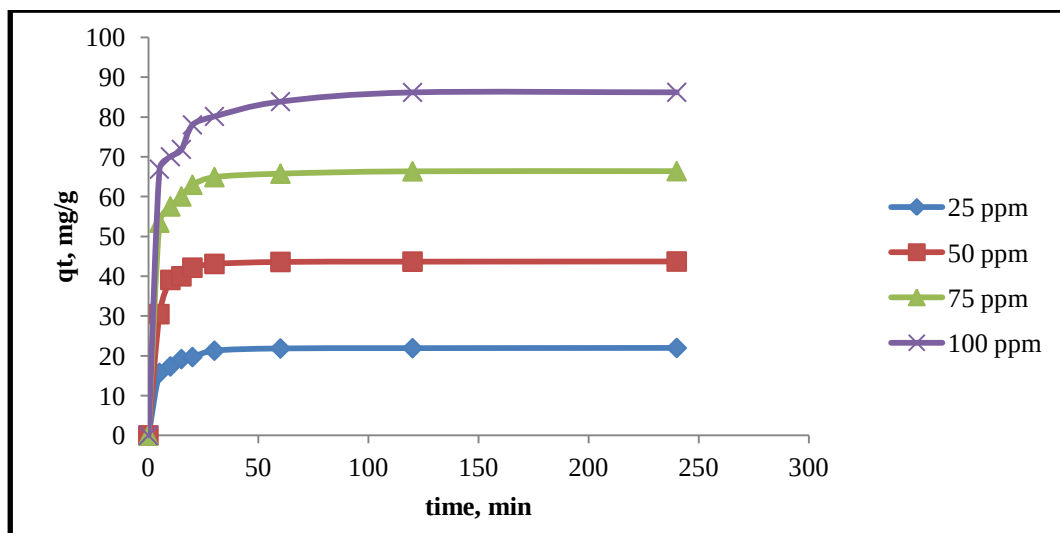


Figure 5.40 Effect of contact time on the adsorption of MR on CuBTC at different temperature of (a) $T=298$ K; (b) $T=308$ K; (c) $T=318$ K.

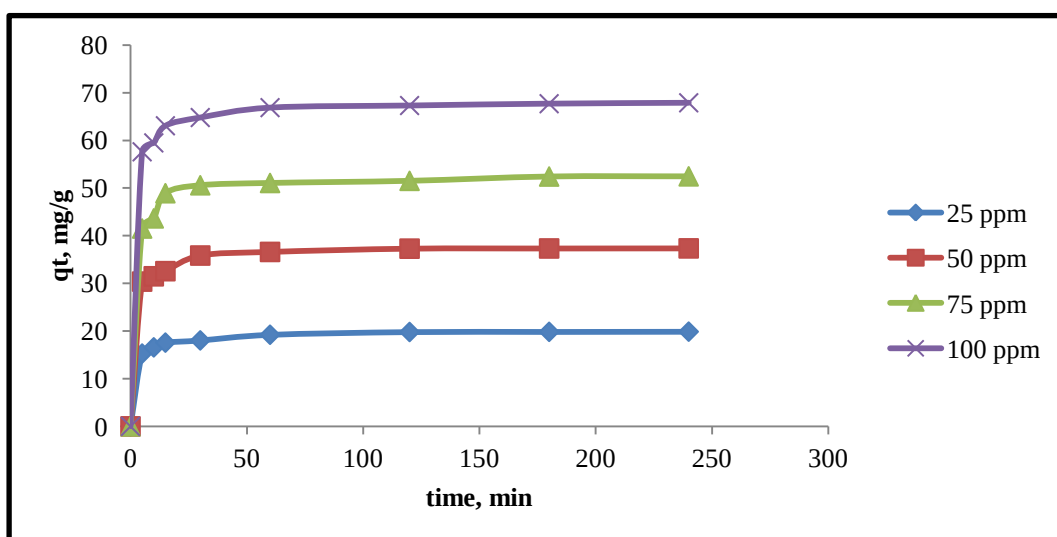
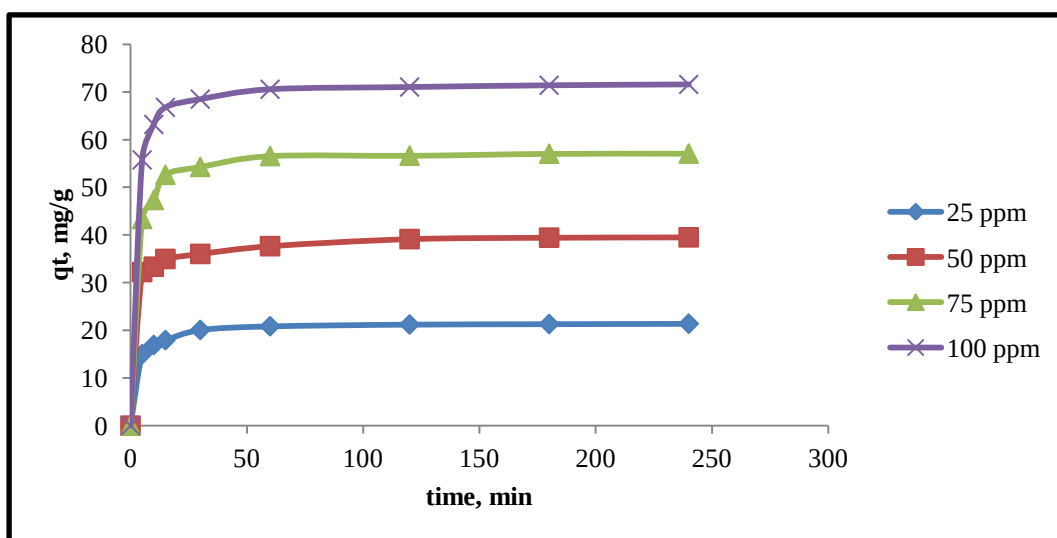
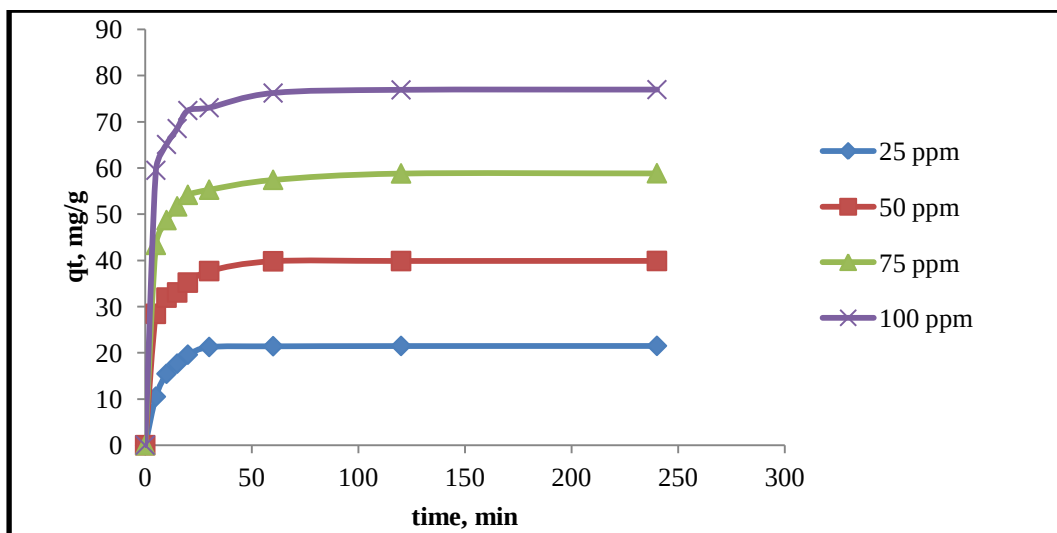


Figure 5.41 Effect of contact time on the adsorption of MR on MIL-53 (Fe) at different temperature of (a) $T=298$ K; (b) $T=308$ K; (c) $T=318$ K.

Pseudo-First-Order Kinetic Model (Lagergren Equation)

Pseudo first order kinetic model equation was given in eq. 5.1

And linearized form of this model equation is;

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5.4)$$

Where;

q_e is amount adsorbed at equilibrium (mg/g),

q_t is amount adsorbed at time t (mg/g),

t is adsorption time (min),

k_1 is the rate constant of pseudo-first-order kinetic (min^{-1}).

The rate constant k_1 is determined from the slope of the plot of $\ln(q_e - q_t)$ versus contact time (t) (Lagergren, 1898). Figure 5.42-5.44 shows the plots of pseudo-first-order kinetics of MR adsorption onto MIL-101, CuBTC and MIL-53 (Fe) at three different temperature ($T = 298, 308$ and 318K).

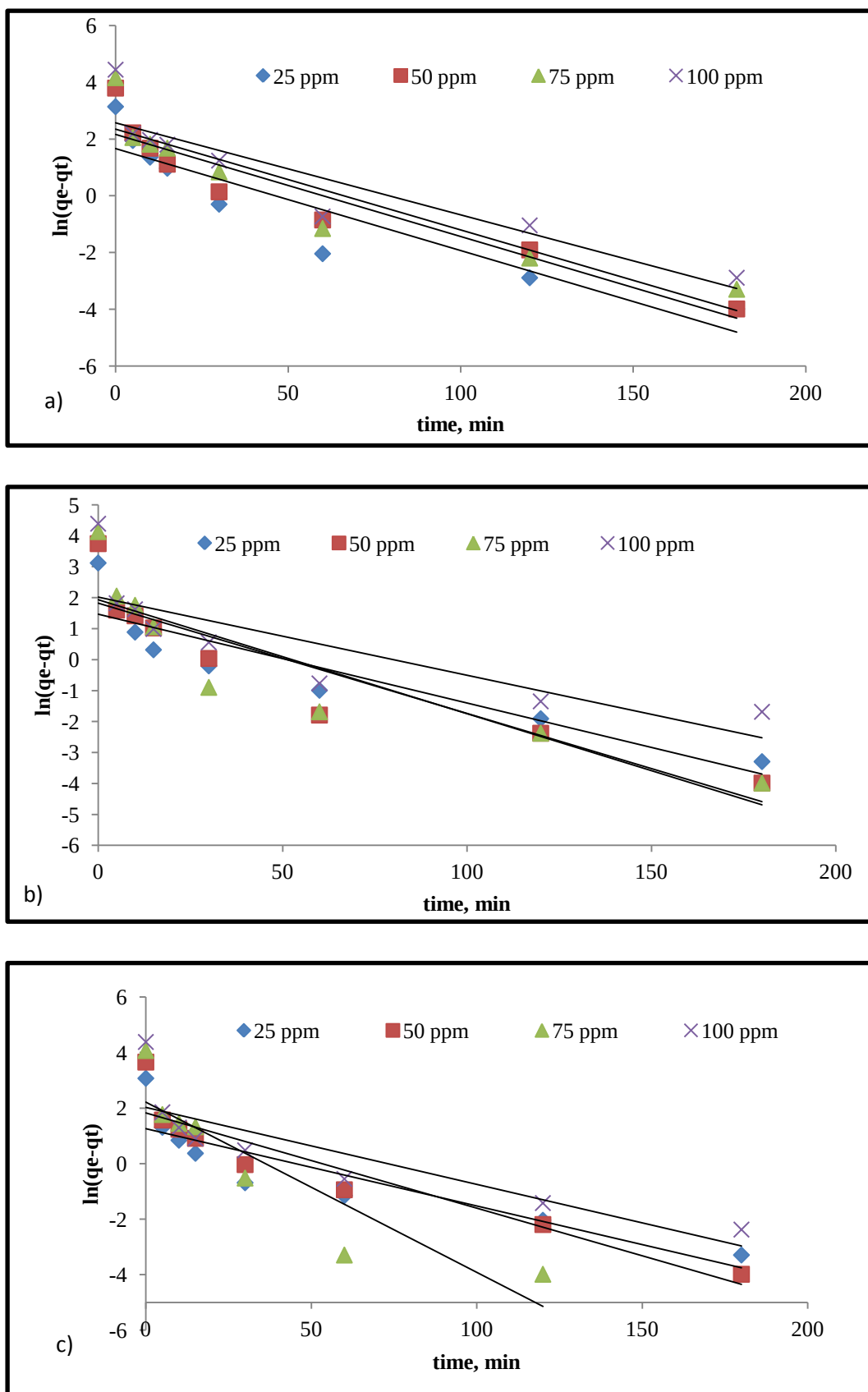


Figure 5.42 Plots of pseudo-first-order kinetics of MR adsorption onto MIL-101: (a) T = 298 K; (b) T = 308 K; (c) T = 318 K

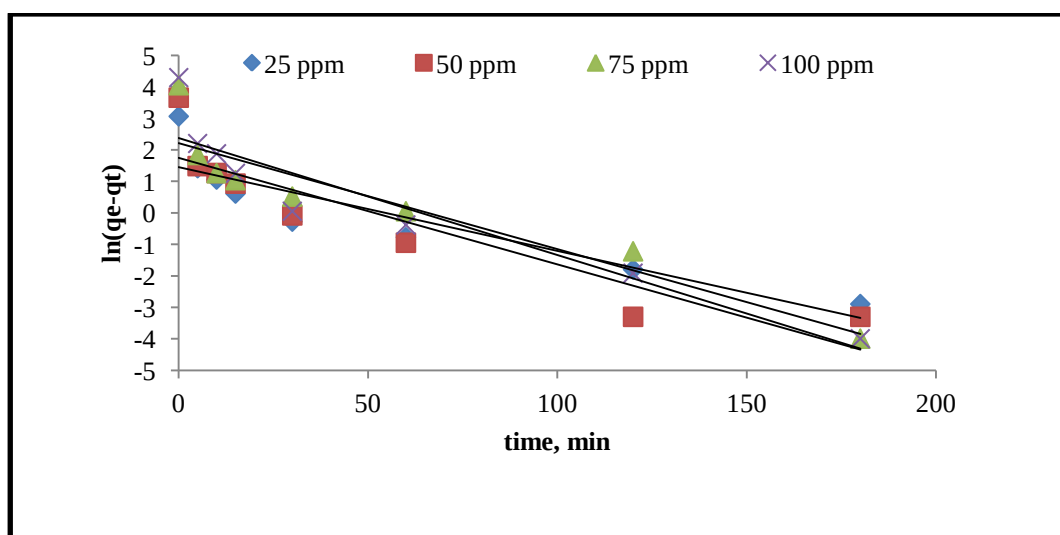
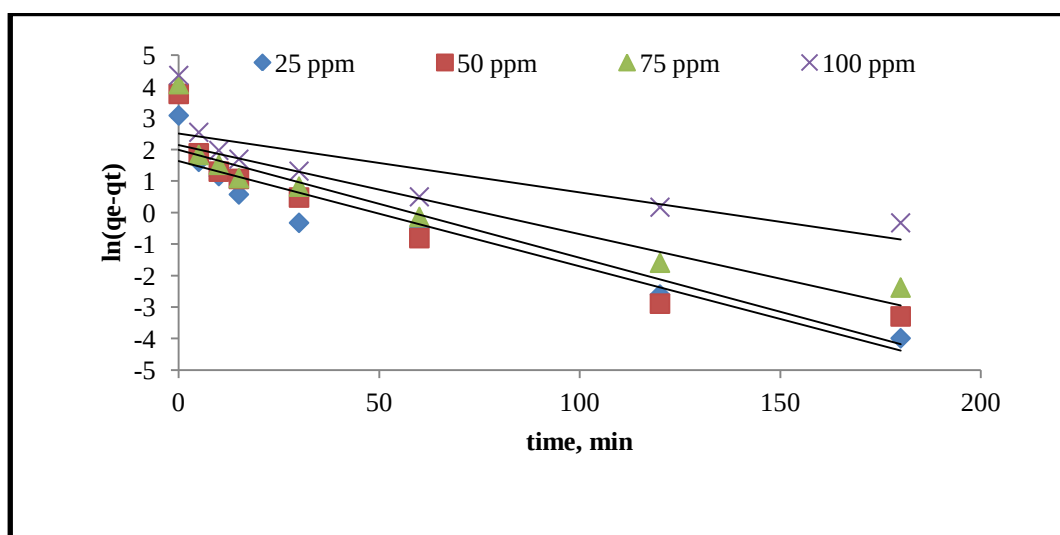
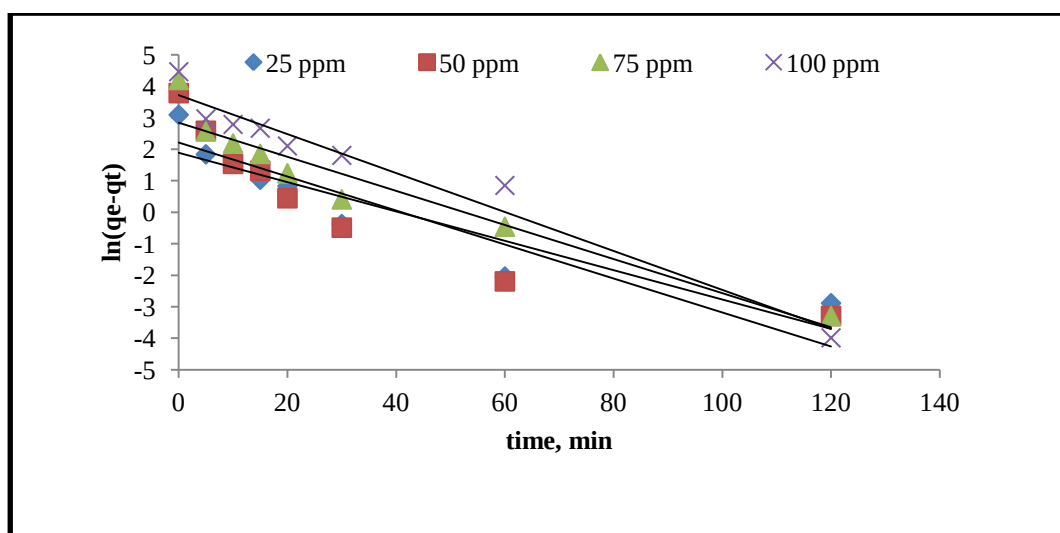


Figure 5.43 Plots of pseudo-first-order kinetics of MR adsorption onto CuBTC: (a) $T = 298\text{ K}$; (b) $T = 308\text{ K}$; (c) $T = 318\text{ K}$

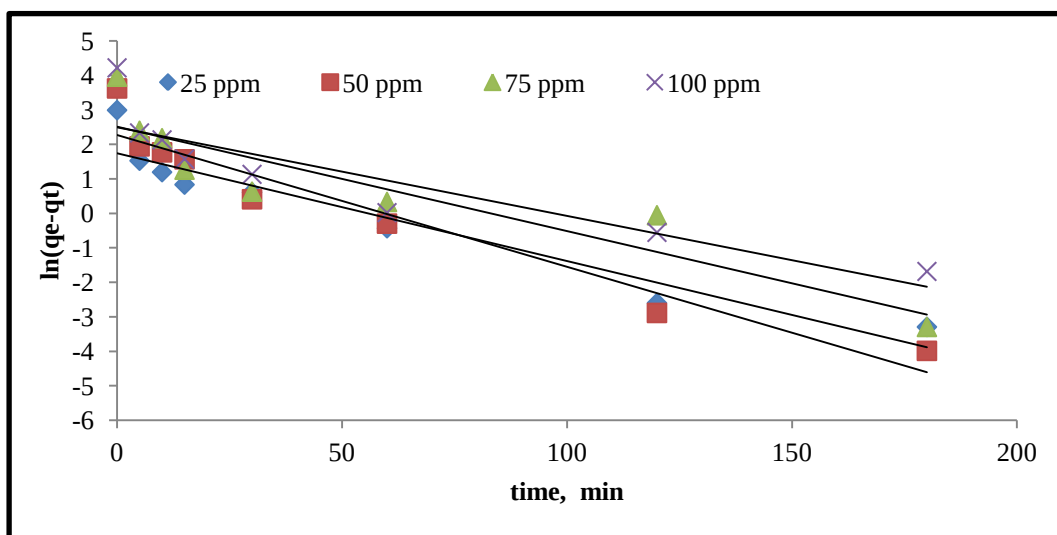
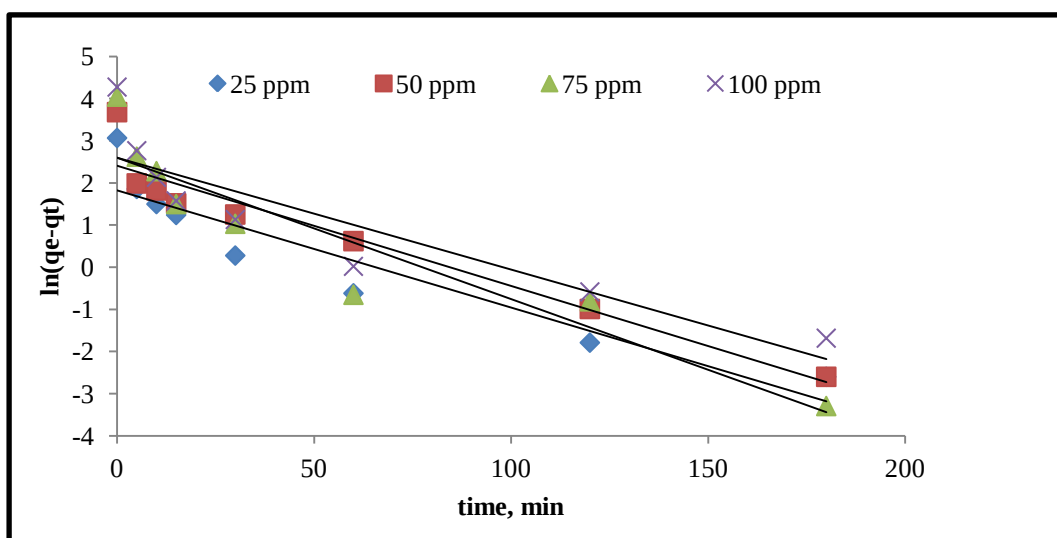
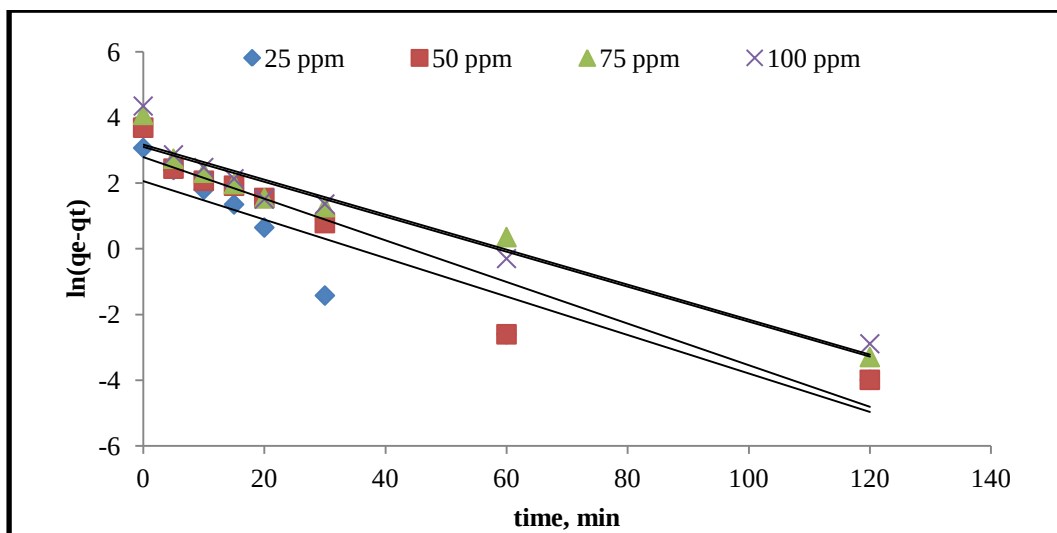


Figure 5.44 Plots of pseudo-first-order kinetics of MR adsorption onto MIL-53 (Fe): (a) $T = 298$ K; (b) $T = 308$ K; (c) $T = 318$ K

Pseudo- Second- Order Kinetic Model

Pseudo second order kinetic model equation was given in equation 5.2.

And linearized form of this model equation is;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5.5)$$

Where;

q_e is amount adsorbed at equilibrium (mg/g),

q_t is amount adsorbed at time t (mg/g),

t is adsorption time (min), and

k_2 is the rate constant of the pseudo-second-order kinetic (g/mg/min).

The rate constant k_2 is determined from the slope and intercept of the plot of t/q_t versus contact time (t).

Figure 5.45-5.47 show the plots of pseudo-second-order kinetics of MR adsorption onto MIL-101, CuBTC and MIL-53 (Fe) at three different temperature ($T = 298, 308$ and $318K$).

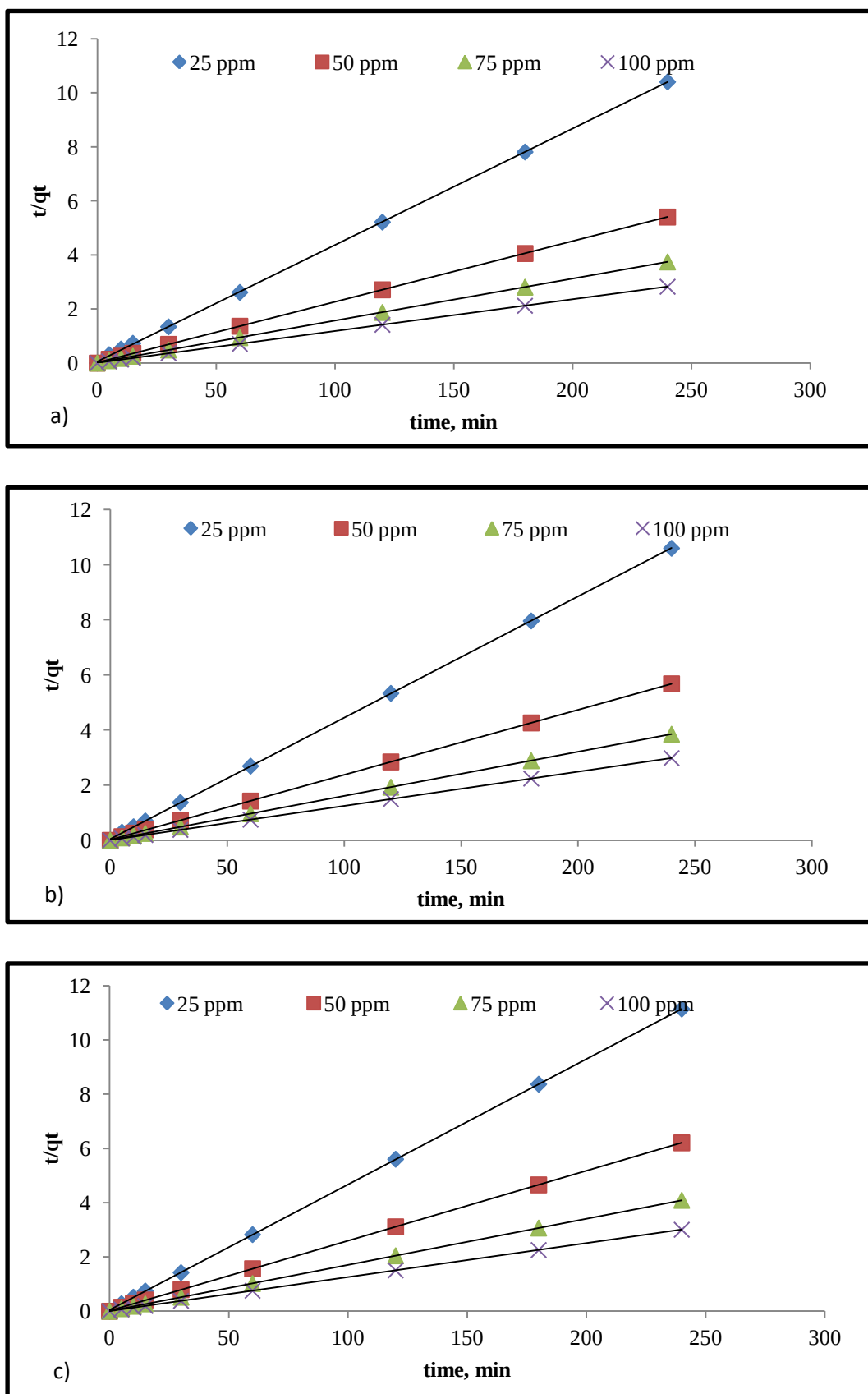


Figure 5.45 Plots of pseudo-second-order kinetics of MR adsorption onto MIL-101: (a) T = 298 K; (b) T = 308 K; (c) T = 318 K

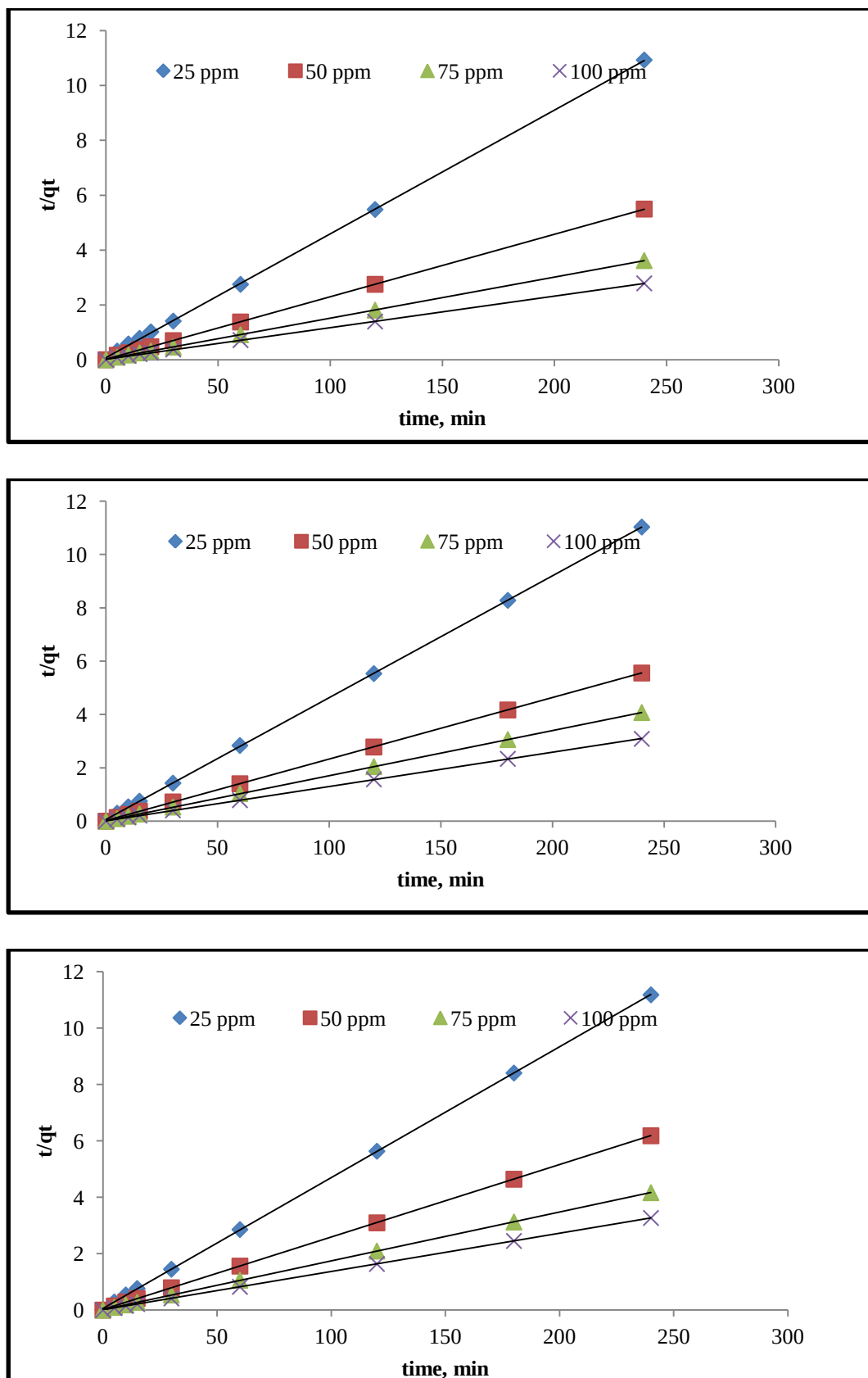


Figure 5.46 Plots of pseudo-second-order kinetics of MR adsorption onto CuBTC: (a) $T = 298 \text{ K}$; (b) $T = 308 \text{ K}$; (c) $T = 318 \text{ K}$

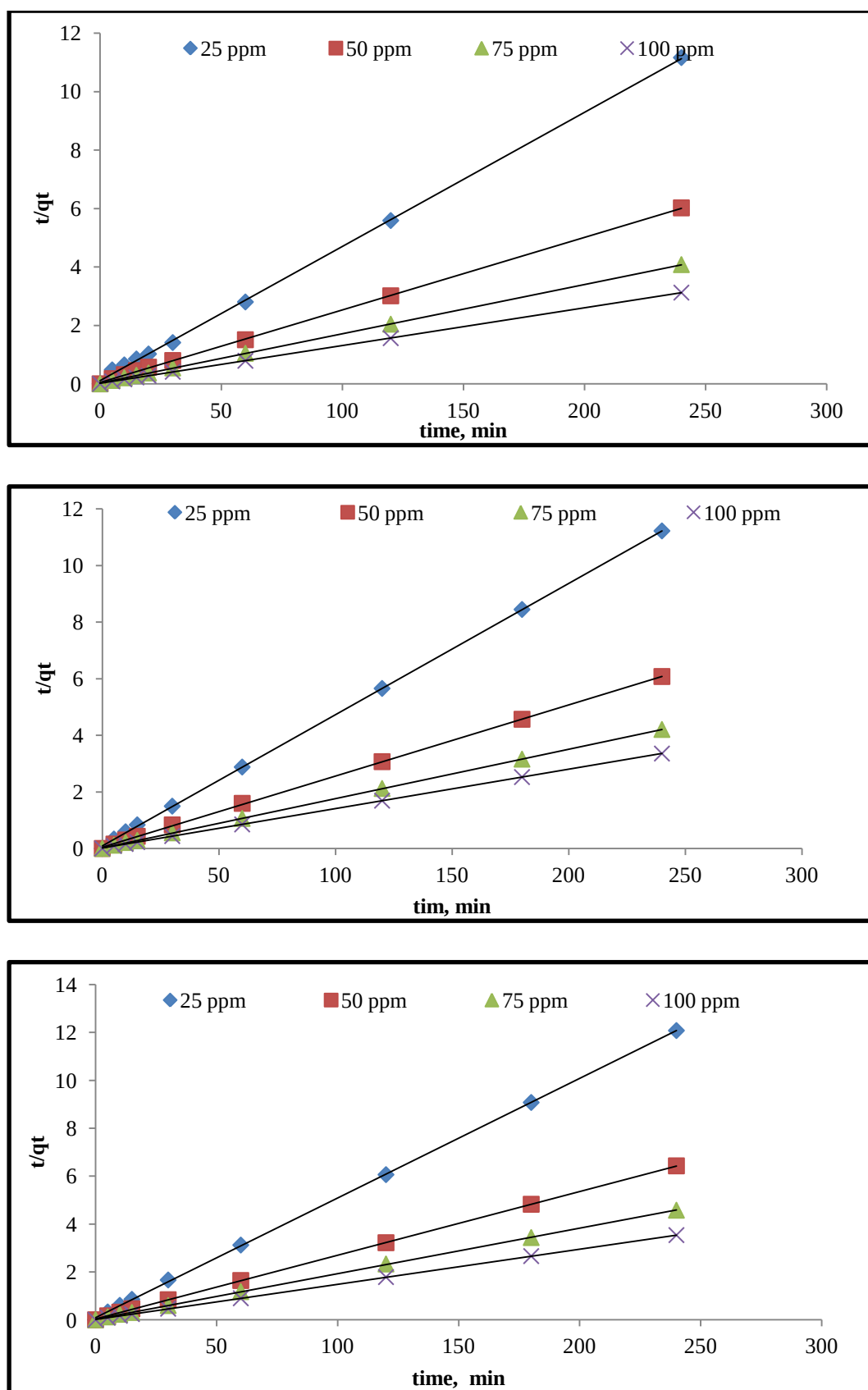


Figure 5.47 Plots of pseudo-second-order kinetics of MR adsorption onto MIL-53 (Fe): (a) T = 298 K; (b) T = 308 K; (c) T = 318 K

Figure 5.39, 5.40 and 5.41 show the adsorption kinetic experiments of MR onto three different adsorbents were conducted at different temperature (298, 308, and 318 K).

Table 5.2-5.4 describes the pseudo- first-order and pseudo-second-order kinetic (Figure 5.42-5.47) parameters for different temperatures. As shown in Table 5.2-5.4 and Figure 5.42-5.44, the correlation coefficient of pseudo first order kinetic model is extremely low. However, the correlation coefficient values of pseudo second order kinetic model are close to the unity ($R^2 > 0.999$) of MR. This result shows the pseudo-second-order model fits the experimental data quite well for the adsorption of MR onto MIL-101, CuBTC and MIL-53 (Fe).

With the increase of the temperature, rate constant increased, that means the initial adsorption rate increased with increasing temperature. However, at a constant temperature, k_2 decreased with the initial concentration of MR (Table 5.2-5.4) indicating the chemisorption between adsorbate and adsorbents. Besides the rate constant is generally depended on the surface area and pore volume (Hasan et al., 2012). In this study, obtained results support this case because k_2 values are in order of MIL-53 < CuBTC < MIL-101 suggests potential applications of MOFs with large surface area and pore volume in dye removal.

Figure 5.39-5.41 also shows the effect of adsorption time on the adsorption of MR. The adsorption equilibrium was reached within 1 h after initiation. Because, early in the time of adsorption, there are numerous vacant surface sites for adsorption and with time the number of vacant sites available decreases and adsorption sites become saturated (Osta et al., 2012; Hasan et al., 2012).

5.2.1.2. Adsorption Mechanism

The sorption processes under isothermal condition basically can be divided into three sequential steps including external diffusion, boundary layer diffusion, and intra-particle diffusion. For MR adsorption of three MOFs, MR molecules in the aqueous solution diffused to the outside surface of sorbents and then passed through the boundary layer to the inside surface. Finally, these molecules were removed by interacting with adsorbents after entering into the framework via intra-particle diffusion. Generally, the sorption rate in the initial phase is controlled by boundary layer diffusion, while intra-particle diffusion plays a decisive role close to the end of the sorption. The pseudo-first-order model and pseudo-second order equation cannot analyze the diffusion mechanism, so the intra- particle diffusion model was used, with the equation being the following:

$$q_t = k_i t^{1/2} + I \quad (5.6)$$

k_i (mg/(g min^{1/2})) is the intra-particle diffusion rate constant, and I (mg/g) is the coefficient associated with the thickness of boundary layer. If $I = 0$, intra-particle diffusion is the only rate-limiting step, otherwise, both intra-particle diffusion and boundary layer diffusion are the rate-limiting steps.

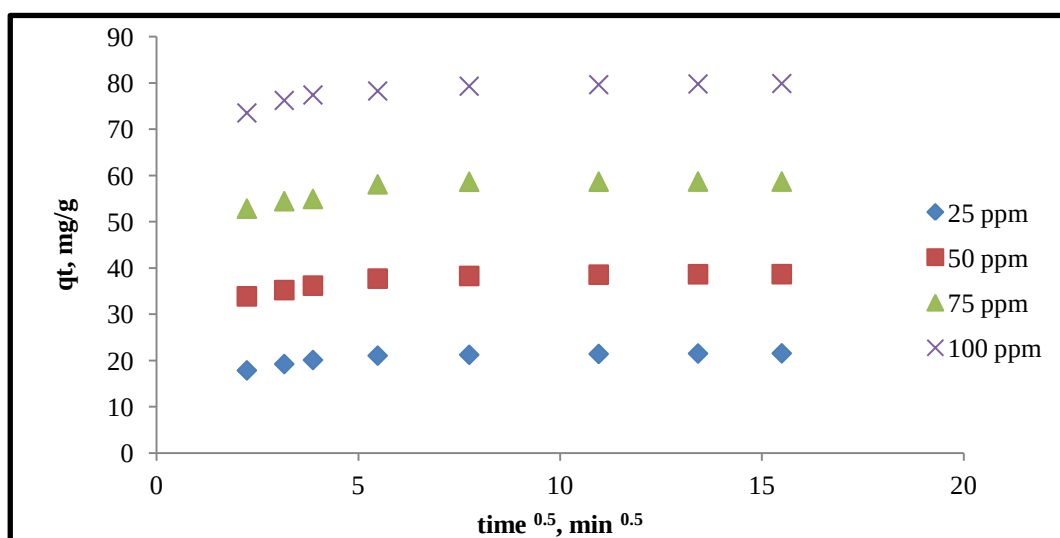
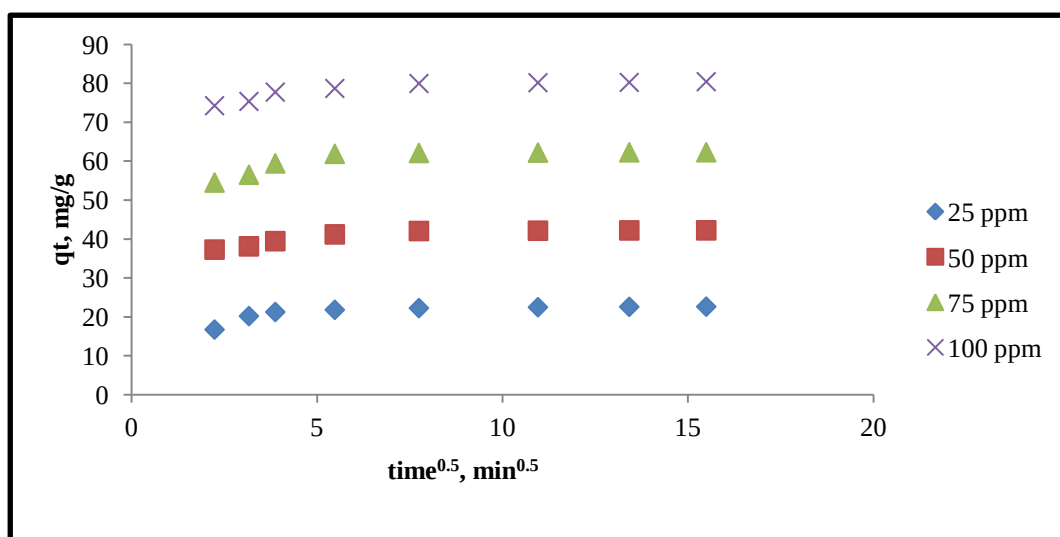
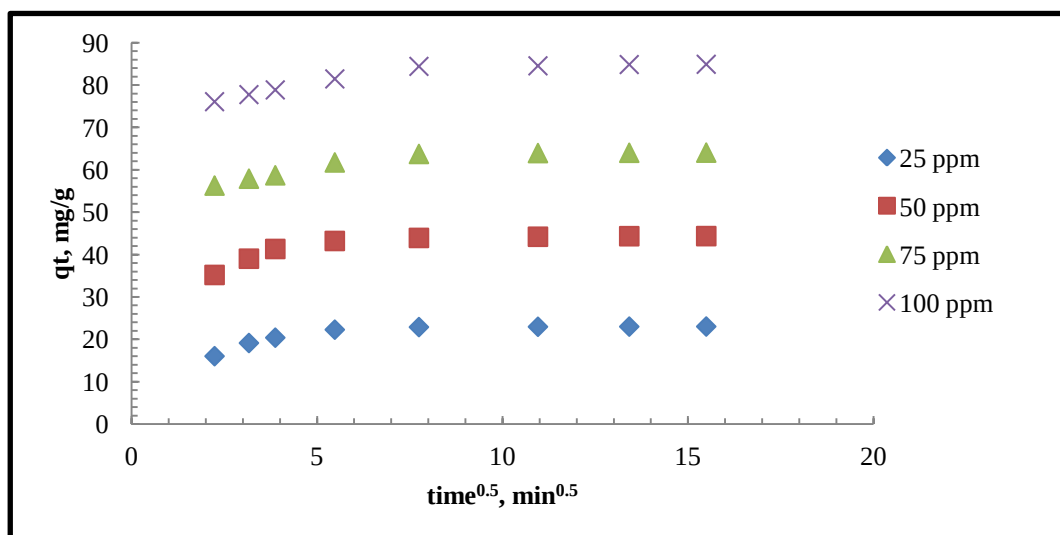


Figure 5.48 Diffusion model plot for the adsorption of MR on MIL-101 at different initial concentrations: (a) T = 298 K; (b) T = 308 K; (c) T = 318 K.

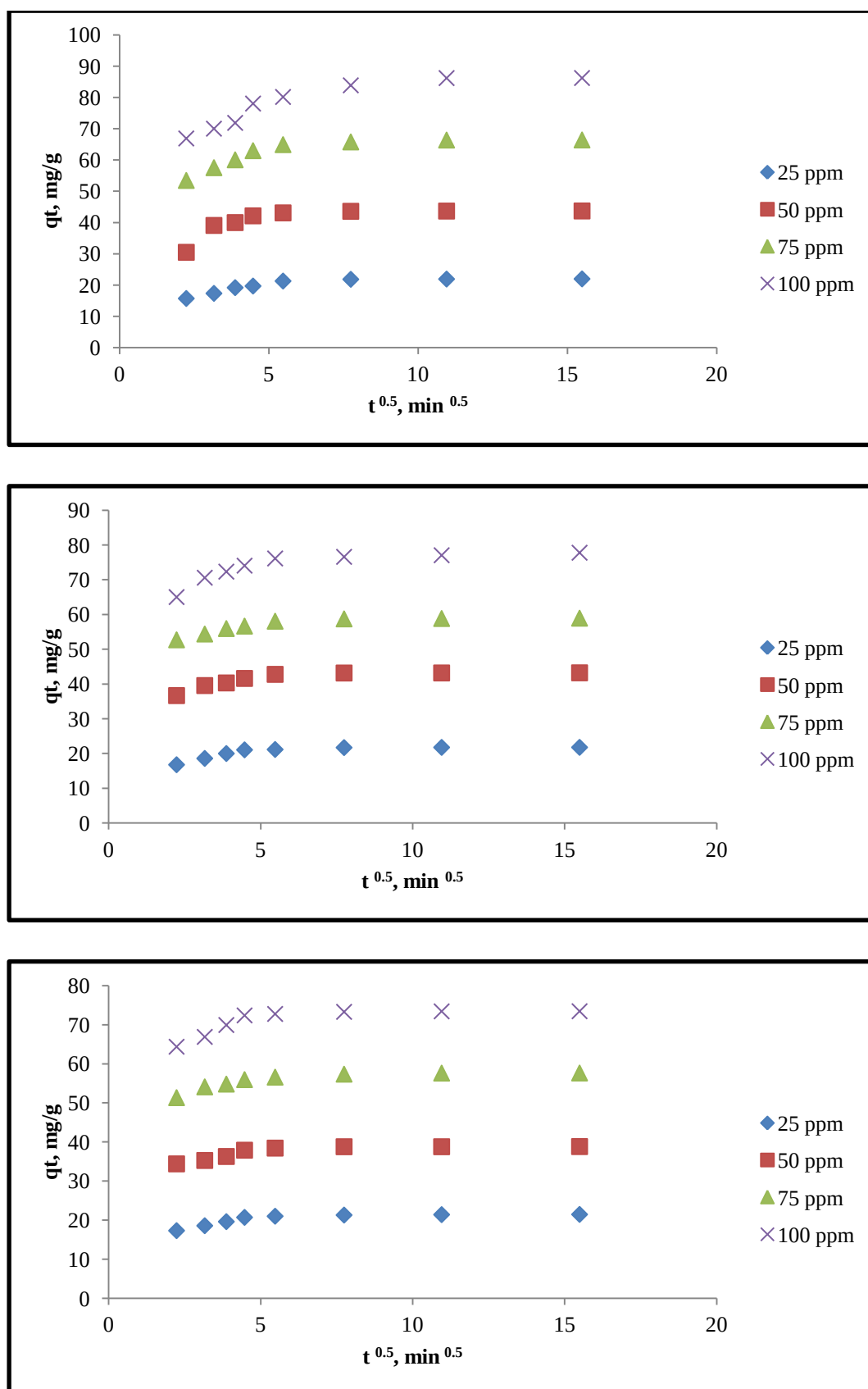


Figure 5.49 Diffusion model plot for the adsorption of MR on CuBTC at different initial concentrations: (a) $T = 298 \text{ K}$; (b) $T = 308 \text{ K}$; (c) $T = 318 \text{ K}$.

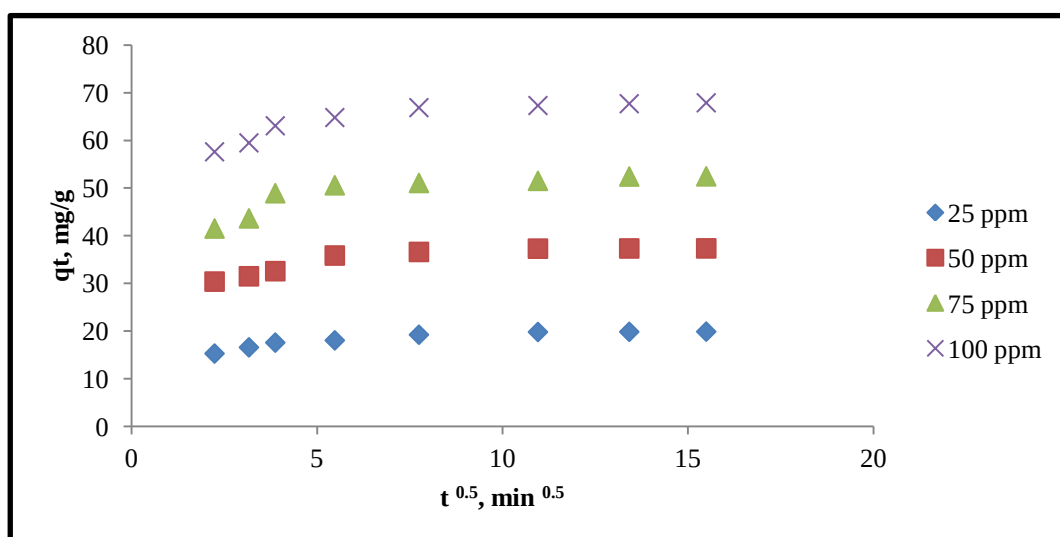
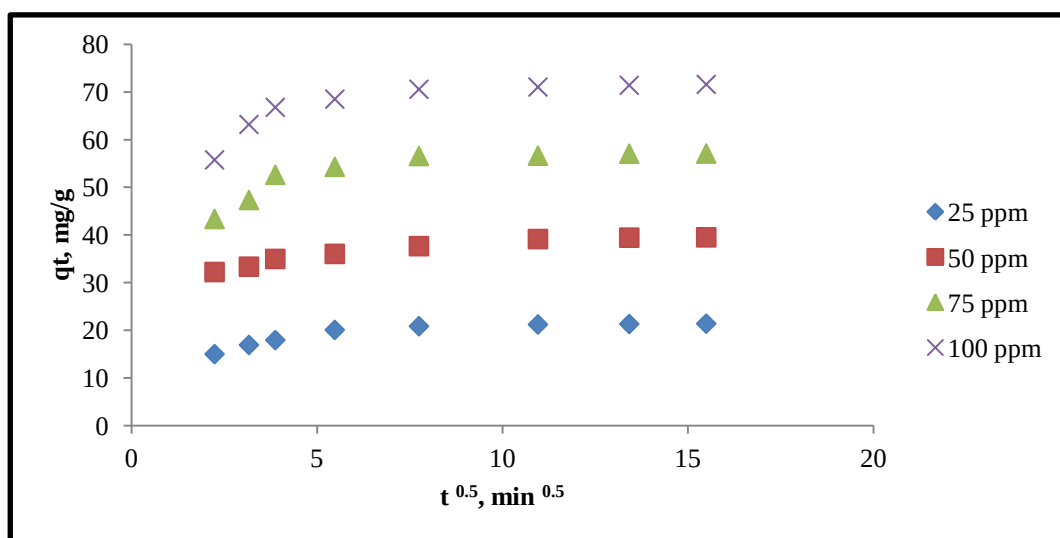
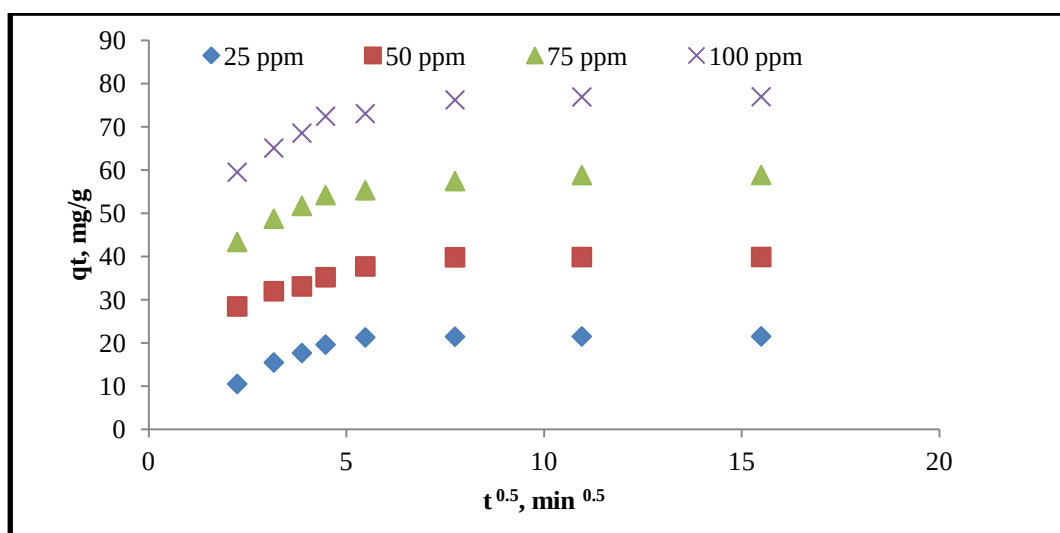


Figure 5.50 Diffusion model plot for the adsorption of MR on MIL-53 (Fe) at different initial concentrations: (a) $T = 298\text{ K}$; (b) $T = 308\text{ K}$; (c) $T = 318\text{ K}$.

As shown in Figures 5.48-5.50, the adsorption process had two phases. This situation suggested that the adsorption process proceeded by surface sorption and intraparticle diffusion. The initial part was a boundary-layer effect while the second linear part was due to intraparticle or pore diffusion which proved that the sorption rate in the initial phase was mainly controlled by boundary layer diffusion, and intra-particle diffusion was fast. While with the increase in the adsorption time, intra-particle diffusion plays a more and more important role in rate-limiting. When sorption equilibrium was reaching, particle intra-diffusion was the main factor affecting the sorption rate. The intraparticle diffusion model constants are given in Table 5.2-5.4. These constants were calculated from slope and intercept of second linear part of Figure 5.48-5.50.

5.2.1.3. Adsorption Isotherm

Adsorption isotherms for MR on MIL-101, CuBTC and MIL-53 (Fe) were studied with different initial concentrations (25–400 ppm) at 298, 308, and 318 K (Figure 5.51). The Langmuir and Freundlich adsorption models were applied for the fitting of the experimental data to understand the interaction between MR and selected MOFs. The following equations are Langmuir and Freundlich model equations;

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (5.7)$$

$$q_e = K_F C_e^{1/n} \quad (5.8)$$

where Q_0 is the maximum adsorption capacity, b is a constant related to the free energy of the adsorption. K_F (mg S/g adsorbent) and n are the Freundlich constants.

Nonlinear curve fitting analysis method in MATLAB programme was also adapted to calculate the parameters of Langmuir and Freundlich isotherm models. Correlation coefficient values are found from the following equation:

$$R^2 = \frac{\sum(q_{e,calc} - \bar{q}_{e,exp})^2}{\sum(q_{e,calc} - \bar{q}_{e,exp})^2 + \sum(q_{e,calc} - q_{e,exp})^2} \quad (5.9)$$

where, $q_{e,calc}$ (mg/g) is amount of MR on the surface of adsorbents at equilibrium time t , obtained from the Langmuir or Freundlich isotherm models; $q_{e,exp}$ (mg/g) is amount of MR on the surface of adsorbents at equilibrium time t , obtained from experiments; and $\bar{q}_{e,exp}$ (mg/g) is average of $q_{e,exp}$.

The parameters and the correlation coefficient values calculated from these two models are listed in Table 5.5. It can be seen from figure 5.51 and table 5.5, the adsorption isotherms are fitted well by the Langmuir model for MR adsorption onto two different MOFs at different temperatures. According to these results, it can be said that the adsorption of MR onto MOFs was a typical monomolecular-layer adsorption. The Q_0 values for the adsorption of MR on different adsorbents are given in Table 5.5

In this study, n values (Freundlich constant) are greater than unity (Table 5.5). If the n value is greater than unity, the isotherm can be classified as L-type, reflecting a high affinity between adsorbate and adsorbent and is indicative of chemisorptions. In addition, the Langmuir constant b and the Freundlich constant, K_F , which is related to the adsorption capacity, show an opposite trend with temperature. indicating that MR adsorption onto MOFs is an exothermic reaction (Boparai et al., 2011).

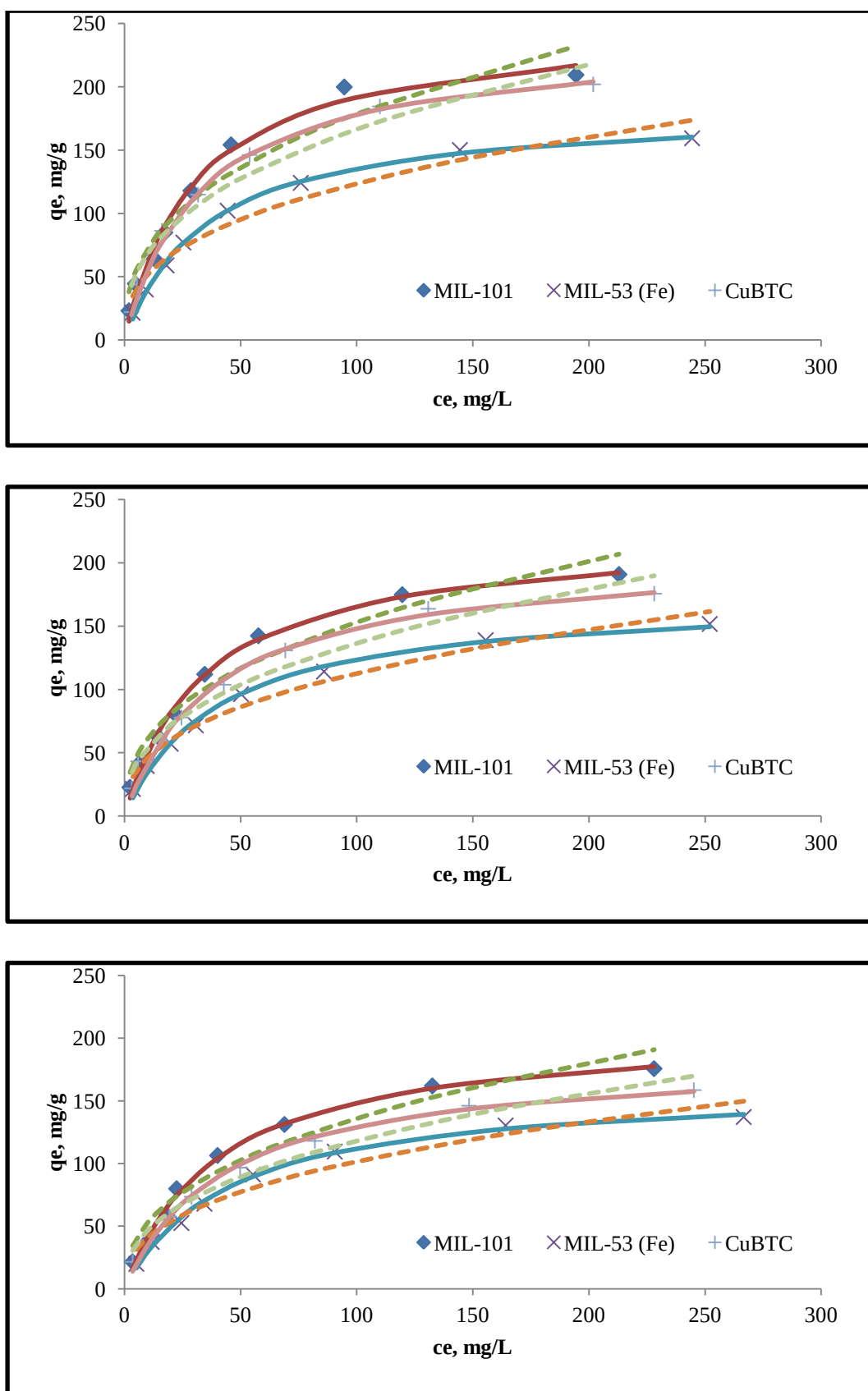


Figure 5.51 Adsorption isotherms for MR adsorption onto the three adsorbents at different temperature: a) $T=298$ K, b) $T=308$ K, c) $T=318$ K. The solid and dashed lines show the calculated results derived from Langmuir and Freundlich isotherm methods respectively.

Table 5.1 The Q_0 values for the adsorption of MR on different adsorbents. (Comparison of adsorption capacity of the MOFs with other adsorbents)

Adsorbent	Q_0 (mg/g)	Reference
MIL-101	251.4	This study
CuBTC	237.9	This study
MIL-53 (Fe)	183.5	This study
Modified zeolite	7	Ioannou, Z., et al.,2013
Commercial activated charcoal	30	Ioannou, Z., et al.,2013
Activated carbon	40.49	Santhi, T., et al., 2010
NaOH modified activated carbon	206.08	Isiuku et al., 2014

It can be said from Table 5.1 MOFs show excellent adsorption capacity for MR removal when compared with the other adsorbents. Although MIL-53 (Fe) has a very small surface area, the maximum adsorption capacity for MR is greater than the other adsorbents because of its breathing feature.

5.2.1.4. Adsorption Thermodynamic

The thermodynamic parameters Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were calculated from the adsorption of MR onto selected MOFs at different temperatures.

The Gibbs free energy change ΔG can be calculated by the following equation:

$$\Delta G^0 = -RT \ln b \quad (8)$$

The enthalpy change ΔH can be obtained by using the van't Hoff equation:

$$\ln b = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (9)$$

where R is the gas constant (8.314 J/mol/K), T the temperature (K), b is Langmuir adsorption constant (L/mol) calculated from intercept of Langmuir isotherm. According to the van't Hoff equation, the van't Hoff plot of $\ln b$ against

$1/T$ was plotted (Figure 5.52), then the enthalpy change (ΔH) and entropy change (ΔS) were obtained from the ($-\text{slope} \times R$) and ($\text{intercept} \times R$) of the van't Hoff plot respectively.

The negative ΔH° indicates that the adsorption process of MR onto MOFs is exothermic. The negative ΔG° suggests that the adsorption process is spontaneous. The positive entropy change, ΔS , indicates the increased randomness at the solid/solution interface during the adsorption process. In other words, in this study the number of desorbed water molecules was larger than that of the adsorbed MR molecules (MR is bigger compared with water; therefore, several water molecules may be desorbed by the adsorption of one MR molecule) (Haque et al., 2010; Leng et al., 2014). Therefore, the driving force for MR adsorption (negative ΔG) onto MOFs is due to both enthalpy effect and entropy effect. All values obtained from the adsorption thermodynamic section were shown in Table 5.6.

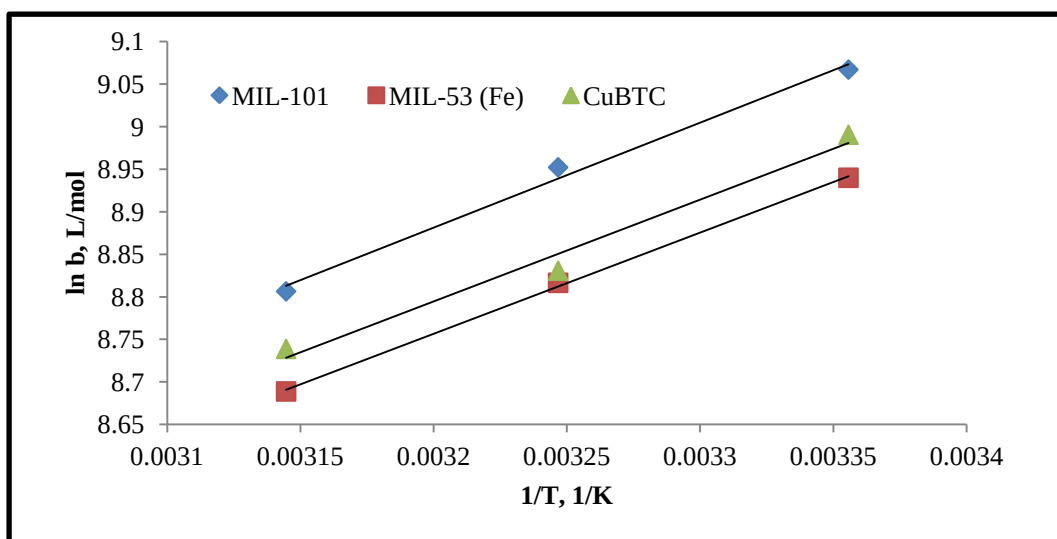


Figure 5.52 van't Hoff plots to get the ΔH and ΔS of the MR adsorption on the different MOFs

5.2.1.5. Effect of regeneration of MOFs

Reusability of adsorbents is an important parameter. In this study, the reusability of MIL-101, CuBTC and MIL-53 (Fe) was evaluated after washing with water and ethanol (100 mL ethanol and water for 1 gram MOF) at least three times. As shown in Figure 5.53 desorption of these three MOFs was achieved and

it can be said these MOFs have excellent regeneration ability in the adsorptive removal of MR from water.

5.2.1.6. Effect of adsorbent dosage

The effect of the adsorbent dosage on adsorption capacity was also investigated. As shown in Figure 5.54, the adsorbed amount of MR increased with increasing adsorbent amounts until 0.1 g. This is explained as when the adsorbent dose increased, more surface area will be available so more active sites will also be available for adsorption of MR. Further increase of the adsorbent amounts doesn't have any effect on the adsorption rate of MR.

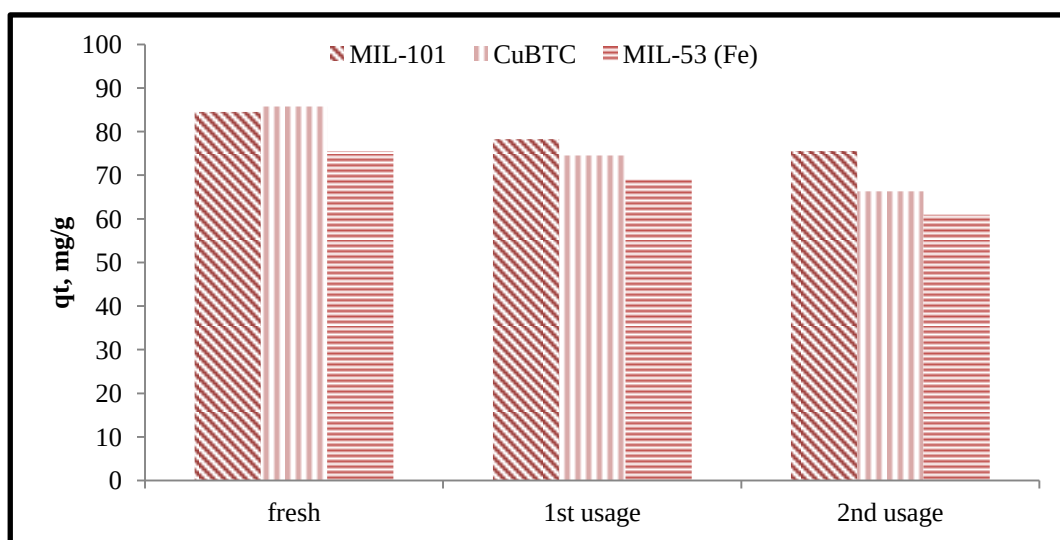


Figure 5.53 The reuse of MOFs on MR adsorption (concentration 100 ppm, T = 298 K).

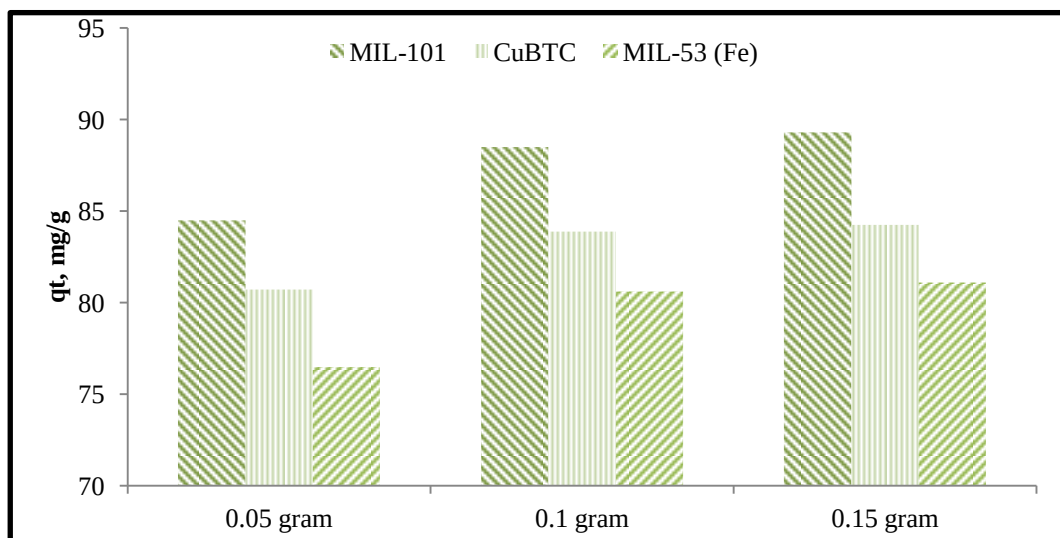


Figure 5.54 Effect of adsorbent dosage (concentration 100 ppm, T = 298 K).

5.2.1.7. Effect of pH

The adsorption of a dye usually depends highly on the pH value of the dye solution. In this work, the pH value effect on the adsorption was carried out at 298 K and 100 ppm. the pH value (2–12) of the solution was adjusted with NaOH or HCl solution. As shown in Figure 5.55, the adsorbed amounts decreased with increasing pH value of the MR solution which is quite similar to previous reports (Haque et al., 2010; Chen et al., 2012). The decreasing of adsorbed MR with increasing pH might be owing to the fact that the amount of positive charges of adsorbents decreased with increasing pH. When the pH value increased to value of 12, the amount of adsorption was zero. Therefore, the mechanism of MR adsorption on different MOFs may be explained with a simple electrostatic interaction between MR and the MOFs. However, other mechanism like π - π interaction (Haque et al., 2011) between benzene rings of MOFs and MR and also breathing effect of MIL-53 (Fe) cannot be ruled out.

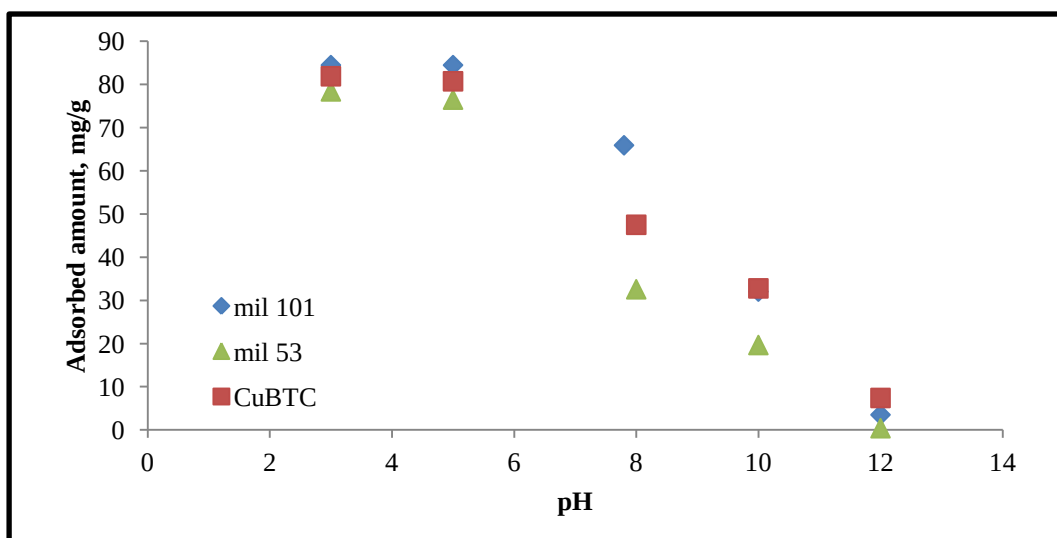


Figure 5.55 Effect of pH on MR adsorption onto three MOFs (concentration 100 ppm, T = 298 K).

Table 5.2 Kinetic constants of MR adsorption onto MIL-101

		Pseudo first order kinetic constants			Pseudo second order kinetic constants			Intraparticle diffusion model		
	C_0 (mg/L)	$q_{e,exp}$ (mg/g)	k_1 (g/(mgmin))	R^2	k_2 (g/(mgmin))	R^2	h (mg/(g.min))	k_i (mg / (g.min ^{1/2}))	I (mg/g)	R^2
T=298 K	25	23.06	0.0359	0.857	0.0312	0.999	16.806	0.0169	22.804	0.965
	50	44.39	0.0360	0.888	0.0239	0.999	47.619	0.0564	43.569	0.916
	75	64.09	0.0355	0.860	0.0189	0.999	78.740	0.0407	63492	0.932
	100	84.93	0.0324	0.840	0.0152	1.000	111.111	0.0675	83.901	0.942
T=308 K	25	22.64	0.0287	0.832	0.0440	0.999	22.730	0.0487	21.930	0.948
	50	42.25	0.0356	0.846	0.0236	1.000	42.370	0.0226	41.921	0.975
	75	62.33	0.0368	0.791	0.0160	1.000	62.500	0.0249	61.963	0.970
	100	80.46	0.0252	0.676	0.0124	1.000	80.650	0.0567	79562	0.973
T=318 K	25	21.53	0.0278	0.804	0.0521	1.000	24.330	0.0412	20.926	0.955
	50	38.64	0.0343	0.876	0.0354	1.000	53.191	0.0508	37.914	0.889
	75	58.66	0.0614	0.822	0.0340	1.000	117.647	0.0051	58.592	0.935
	100	79.85	0.0277	0.740	0.0289	1.000	185.185	0.0742	78.742	0.964

Table5.3 Kinetic constants of MR adsorption onto CuBTC

		Pseudo first order kinetic constants			Pseudo second order kinetic constants			Intraparticle diffusion model		
	C_0 (mg/L)	$q_{e,exp}$ (mg/g)	k_1 (g/(mgmin))	R^2	k_2 (g/(mgmin))	R^2	h (mg/(g.min))	k_i (mg /(g.min ^{1/2}))	I (mg/g)	R^2
T=298 K	25	21.96	0.0466	0.851	0.0272	0.995	13.351	0.0577	21.173	0.628
	50	43.68	0.0540	0.826	0.0235	0.999	45.248	0.0515	42.984	0.618
	75	66.39	0.0541	0.917	0.0173	0.999	72.992	0.1412	64.447	0.765
	100	86.19	0.0618	0.959	0.0108	0.999	71.428	0.5644	78.486	0.737
T=308 K	25	21.75	0.0335	0.902	0.0360	0.995	17.271	0.0774	20.662	0.782
	50	43.20	0.0343	0.861	0.0282	0.999	52.910	0.0553	42.411	0.784
	75	58.92	0.0283	0.817	0.0224	0.999	78.740	0.1100	57.324	0.864
	100	77.75	0.0187	0.660	0.0144	0.999	86.956	0.2063	74.415	0.957
T=318 K	25	21.46	0.0265	0.829	0.0394	0.995	18.315	0.0599	20.579	0.936
	50	38.81	0.0338	0.829	0.0364	0.999	55.248	0.0478	38.13	0.760
	75	57.62	0.0336	0.867	0.0245	0.999	81.967	0.1391	55.631	0.880
	100	73.42	0.0371	0.874	0.0222	0.999	120.481	0.0888	72.157	0.846

Table 5.4 Kinetic constants of MR adsorption onto MIL-53 (Fe)

	C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo first order kinetic constants		Pseudo second order kinetic constants		Intraparticle diffusion model			
			k_1 (g/(mgmin))	R^2	k_2 (g/(mgmin))	R^2	h (mg/(g.min))	k_i (mg/(g.min ^{1/2}))	I (mg/g)	R^2
T=298 K	25	21.50	0.0585	0.847	0.0189	0.995	8.984	0.0214	21.204	0.719
	50	39.87	0.0633	0.917	0.0130	0.999	21.141	0.174	37.575	0.491
	75	58.85	0.0532	0.950	0.0101	0.999	35.587	0.3331	54.294	0.749
	100	76.94	0.0532	0.939	0.0097	0.999	58.823	0.334	72.426	0.613
T=308 K	25	21.39	0.0278	0.879	0.0204	0.997	10.764	0.0683	20.382	0.912
	50	39.50	0.0285	0.919	0.0131	0.988	21.645	0.2379	36.094	0.837
	75	57.07	0.0335	0.875	0.0107	0.998	44.052	0.0756	55.925	0.874
	100	71.57	0.0265	0.806	0.0095	0.999	65.359	0.1343	69.536	0.991
T=318 K	25	19.87	0.0312	0.916	0.0238	0.994	11.086	0.0812	18.714	0.777
	50	37.33	0.0382	0.931	0.0168	0.973	27.932	0.093	36.022	0.747
	75	52.44	0.0303	0.842	0.0142	0.950	39.215	0.1982	49.492	0.924
	100	67.87	0.0257	0.805	0.0121	0.991	64.935	0.1348	65.821	0.992

Table 5.5 Adsorption isotherms of MR adsorption onto MOFs

MOFs	T (K)	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
		b (L/mg)	Q ₀ (mg/g)	R ²	Kf (mg/g(L/mg) ^{1/n})	n	R ²
MIL-101	298	0.0321	251.4	0.986	29.35	2.548	0.927
	308	0.0286	223.8	0.994	24.65	2.521	0.951
	318	0.0247	208.8	0.994	20.59	2.439	0.942
CuBTC	298	0.0298	237.9	0.991	29.51	2.592	0.953
	308	0.0254	206.9	0.985	23.84	2.567	0.960
	318	0.0231	185.3	0.995	19.94	2.509	0.970
MIL-53 (Fe)	298	0.0283	183.5	0.997	21.53	2.635	0.947
	308	0.0250	173.1	0.993	18.85	2.574	0.971
	318	0.0220	163.0	0.995	16.50	2.533	0.945

Table 5.6 Adsorption thermodynamics constants of MR adsorption onto MOFs

MOFs	T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol/K)	R^2
MIL-101	298	-22.46	-10.25	42.04	0.9924
	308	-22.92			
	318	-23.28			
CuBTC	298	-22.27	-9.94	41.31	0.9817
	308	-22.61			
	318	-23.10			
MIL-53 (Fe)	298	-22.15	-9.89	41.18	0.9992
	308	-22.58			
	318	-22.97			

5.2.2. Adsorption of Methyl Orange onto MIL-101, MIL-53 (Fe) and CuBTC

In liquid phase adsorption of methyl orange, the effects of temperature, initial concentration, adsorbent amount, contact time and pH were investigated and also reusability of MIL-101, MIL-53 and CuBTC was studied. The adsorption kinetics, mechanism, isotherms were searched and thermodynamic constants were calculated.

5.2.2.1. Adsorption kinetics

To understand the adsorption mechanism of MO adsorption onto three MOFs, the pseudo-first-order (5.1) and pseudo-second-order kinetic model (5.2) were studied. The initial adsorption rate, h (mg / (g min)), is also calculated by using eq. 5.3.

The kinetic behaviour of this process was studied at pH 5 and 298, 308 and 318 K using four different initial MO concentrations (Figure 5.56-5.58). Figure 5.56-5.58 which represents the kinetics of MO adsorption onto MIL-101, CuBTC and MIL-53 (Fe), indicates that the process occurs in two phases: an initial rapid phase followed by a slower phase that ultimately reaches equilibrium. The initial high rate of MR sorption is most likely due to the greater availability of binding sites near the surface of the adsorbents.

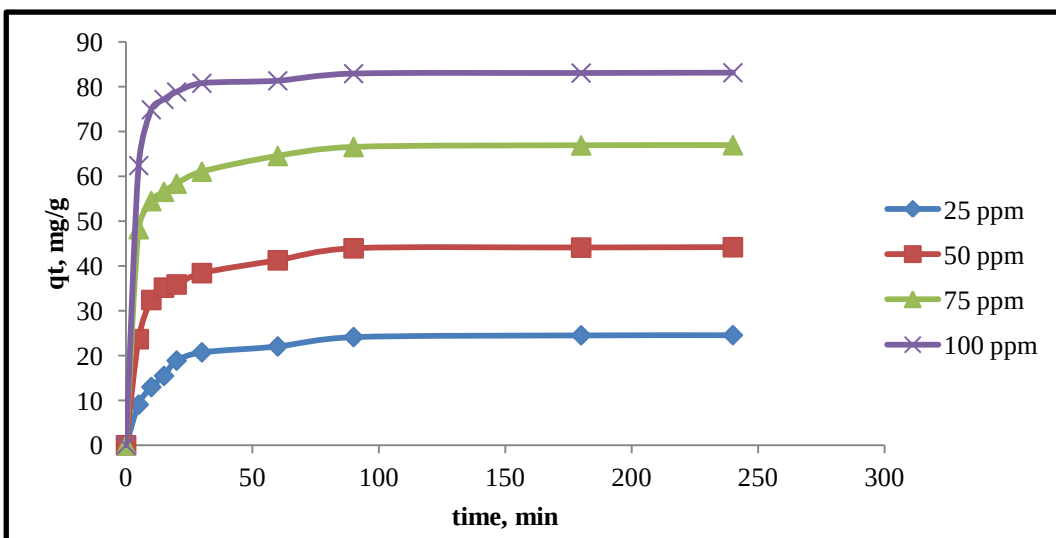
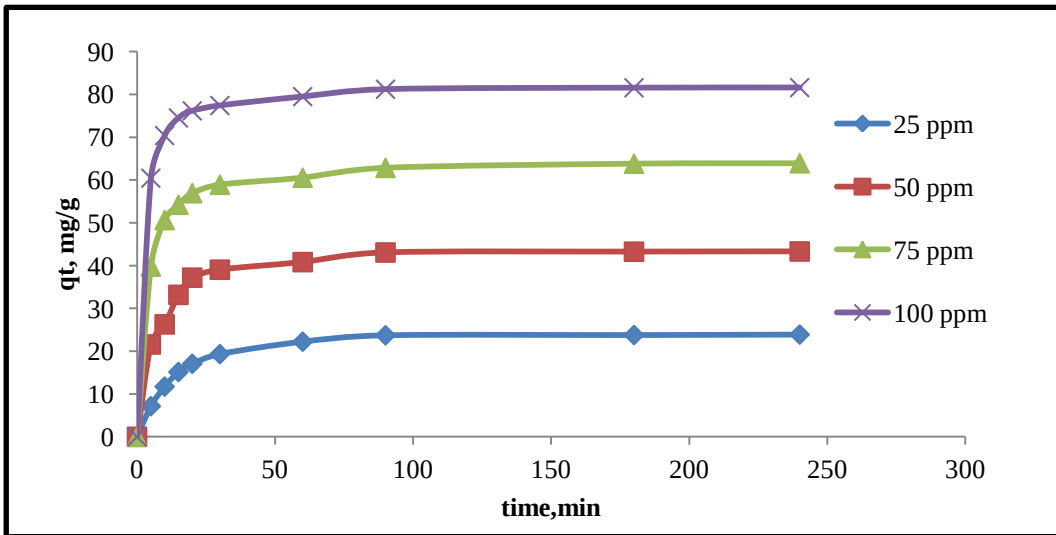
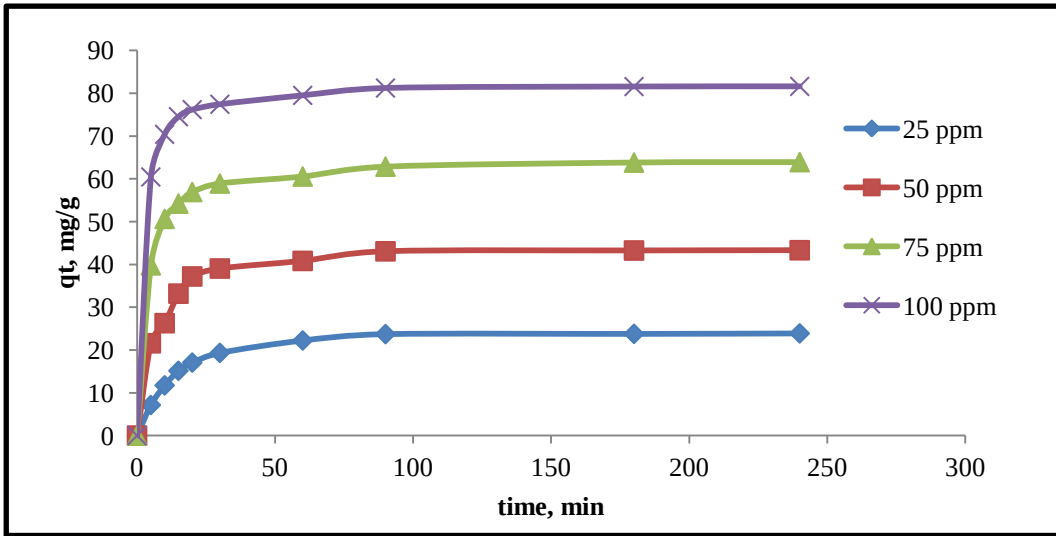


Figure 5.56 Effect of contact time on the adsorption of MO on MIL-101 at different temperature of (a) $T=298$ K; (b) $T=308$ K; (c) $T=318$ K.

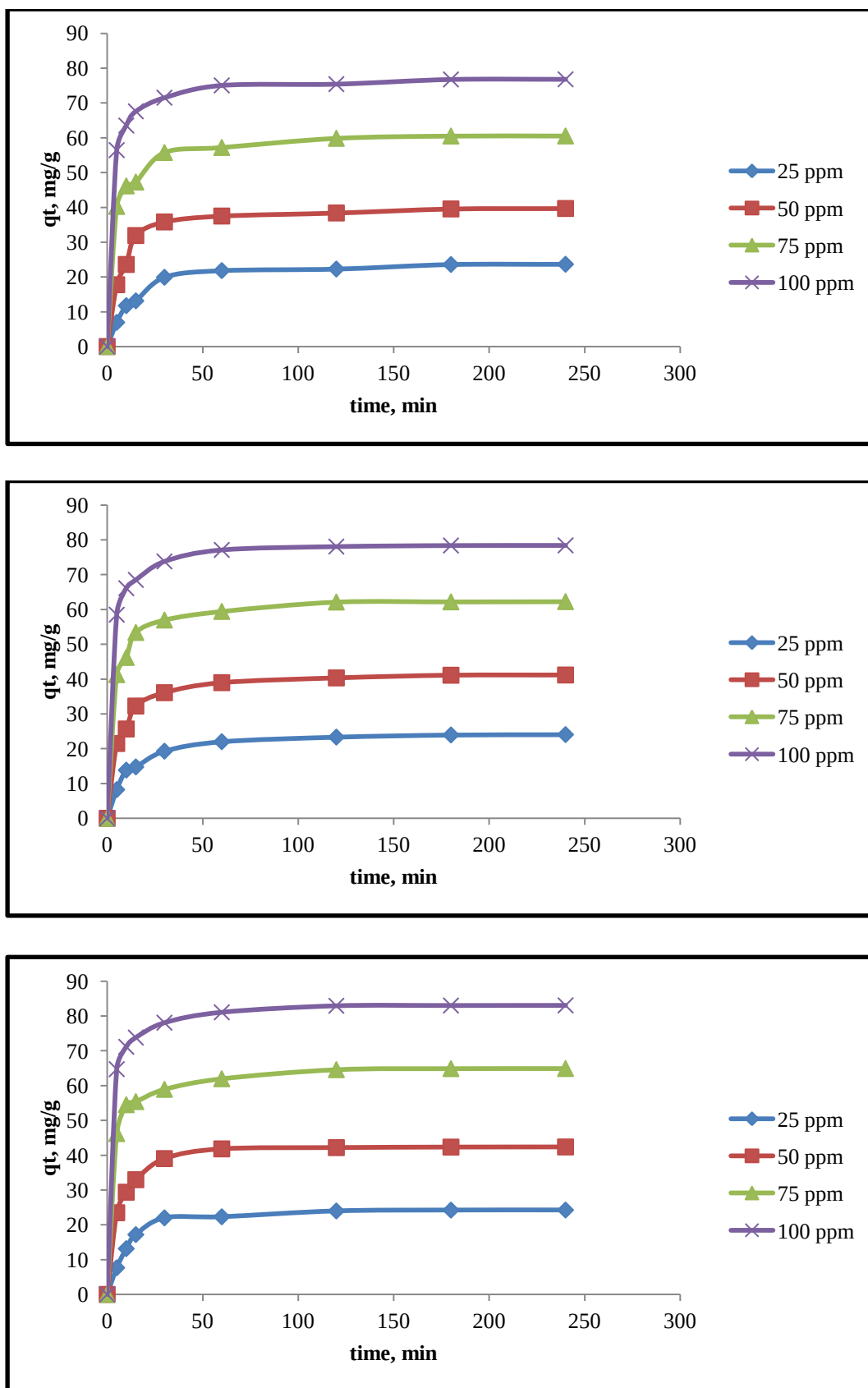


Figure 5.57 Effect of contact time on the adsorption of MO on CuBTC at different temperature of (a) T=298 K; (b) T=308 K; (c) T=318 K.

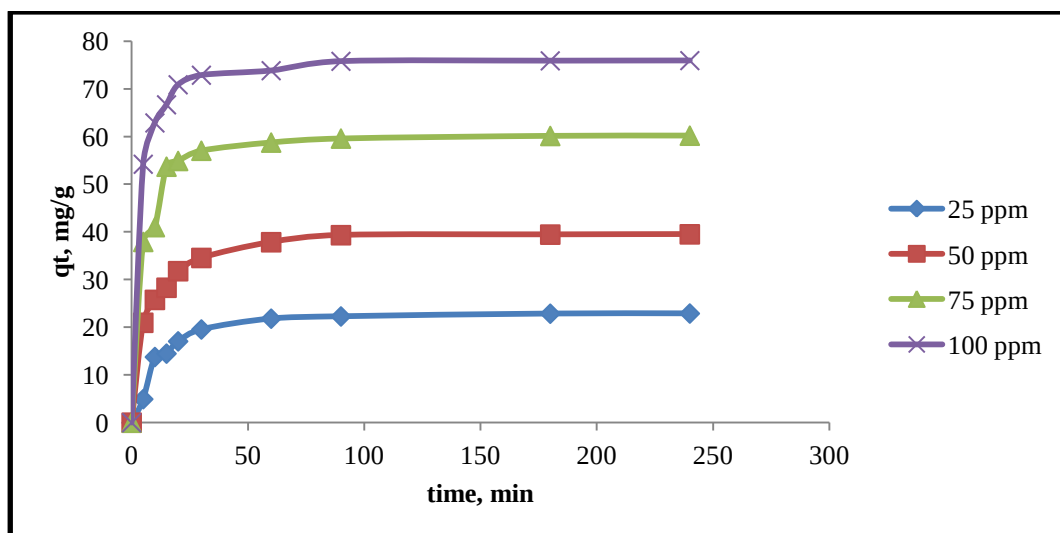
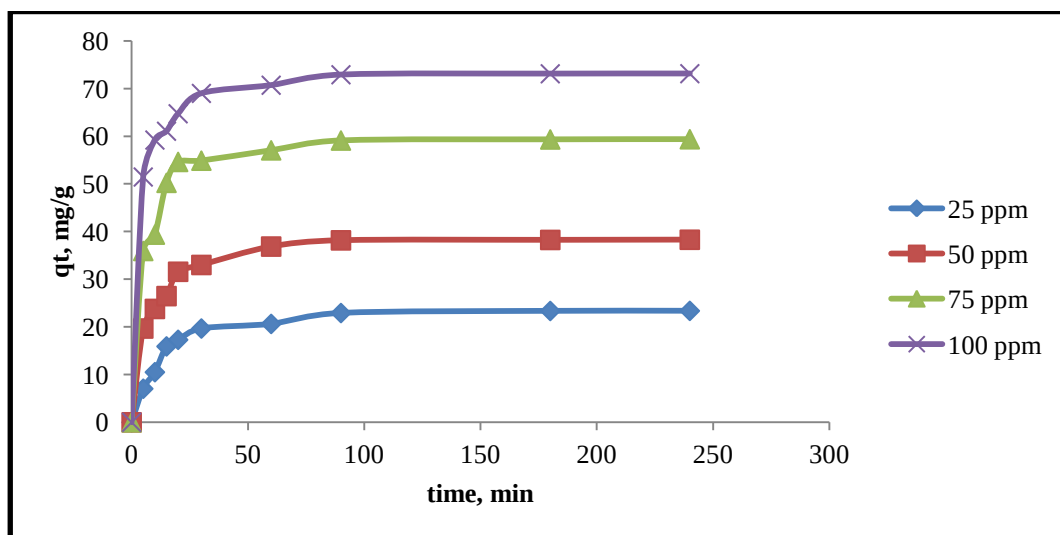
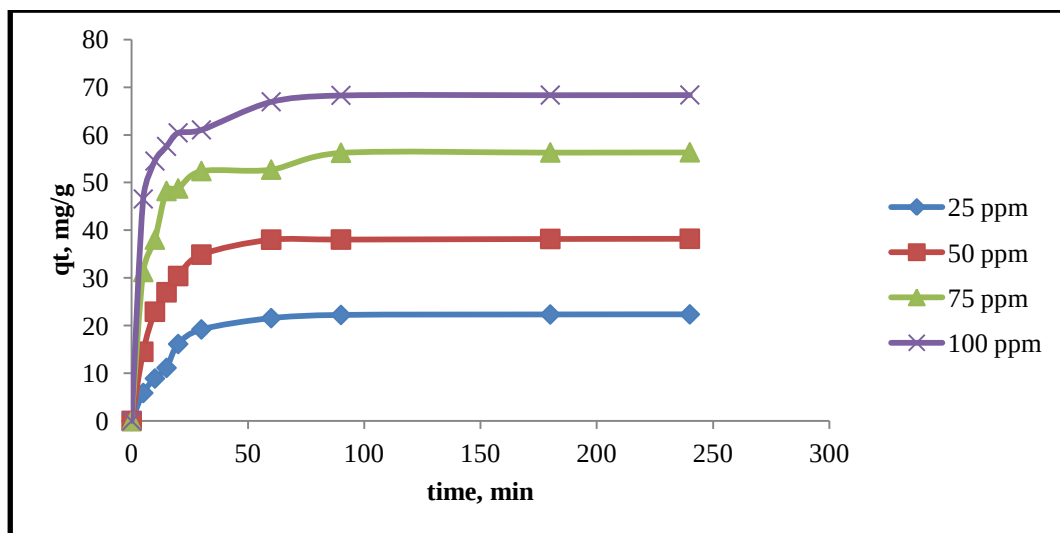


Figure 5.58 Effect of contact time on the adsorption of MO on MIL-53 (Fe) at different temperature of (a) T=298 K; (b) T=308 K; (c) T=318 K.

Pseudo-First-Order Kinetic Model (Lagergren Equation)

Pseudo first order kinetic model equation (5.1) was applied and the equation was linearized (5.4) to calculate the rate constant k_1 (First order kinetic constants)

The rate constant k_1 is determined from the slope of the plot of $\ln(q_e - q_t)$ versus contact time (t) (Lagergren, 1898).

Figure 5.59-5.61 shows the plots of pseudo-first-order kinetics of MR adsorption onto MIL-101, CuBTC and MIL-53 (Fe) at three different temperature ($T = 298$, 308 and 318K).

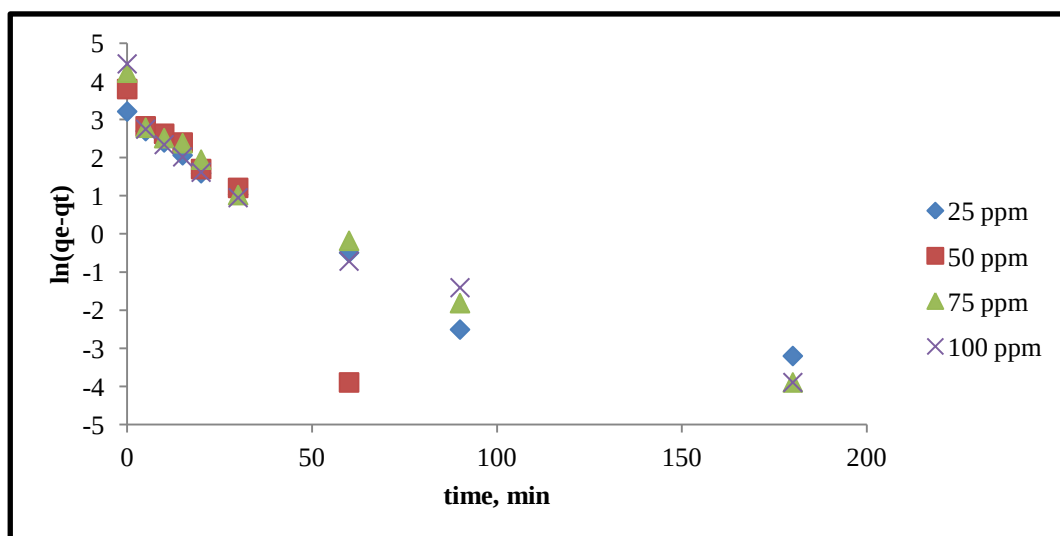
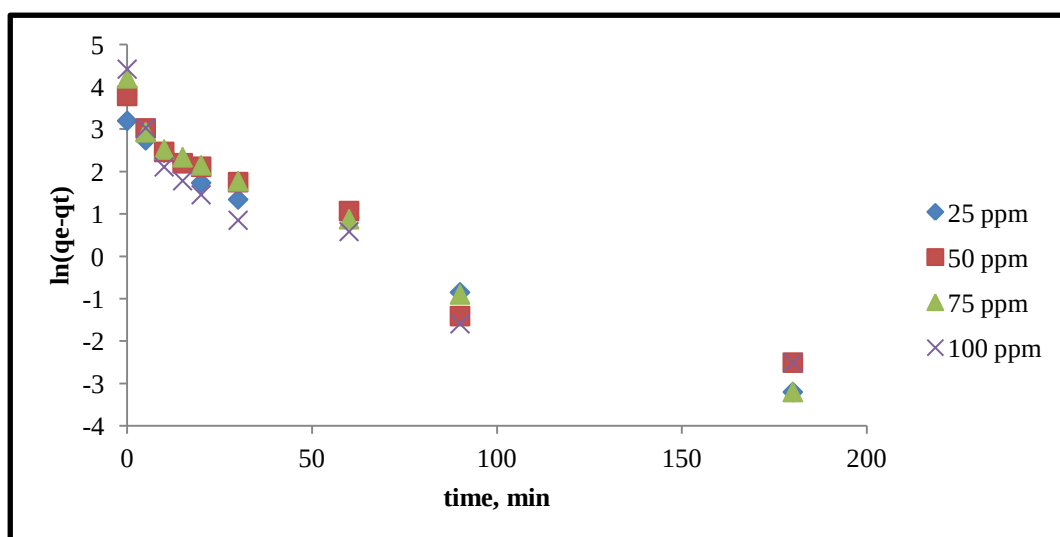
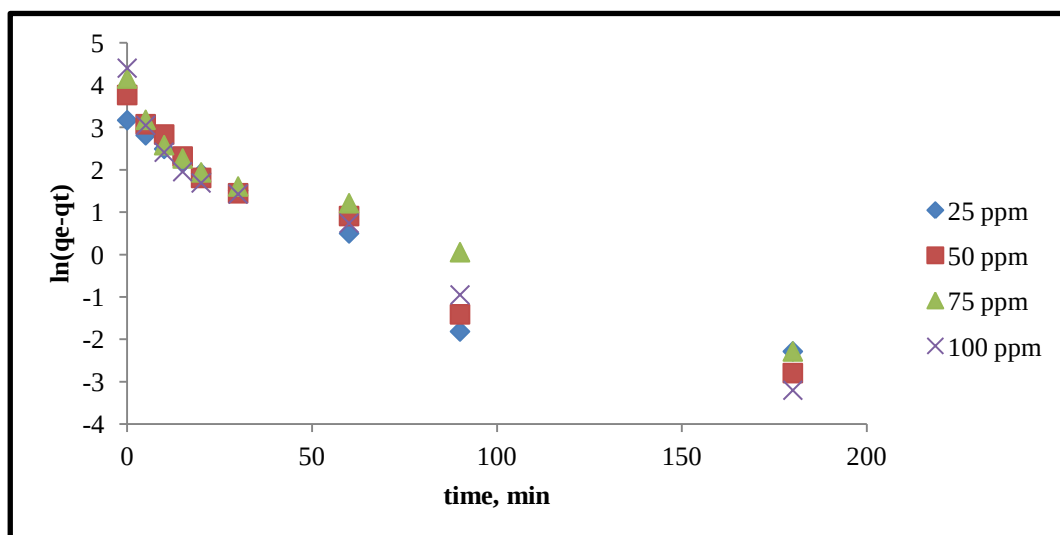


Figure 5.59 Plots of pseudo-first-order kinetics of MO adsorption onto MIL-101: (a) $T = 298\text{ K}$; (b) $T = 308\text{ K}$; (c) $T = 318\text{ K}$.

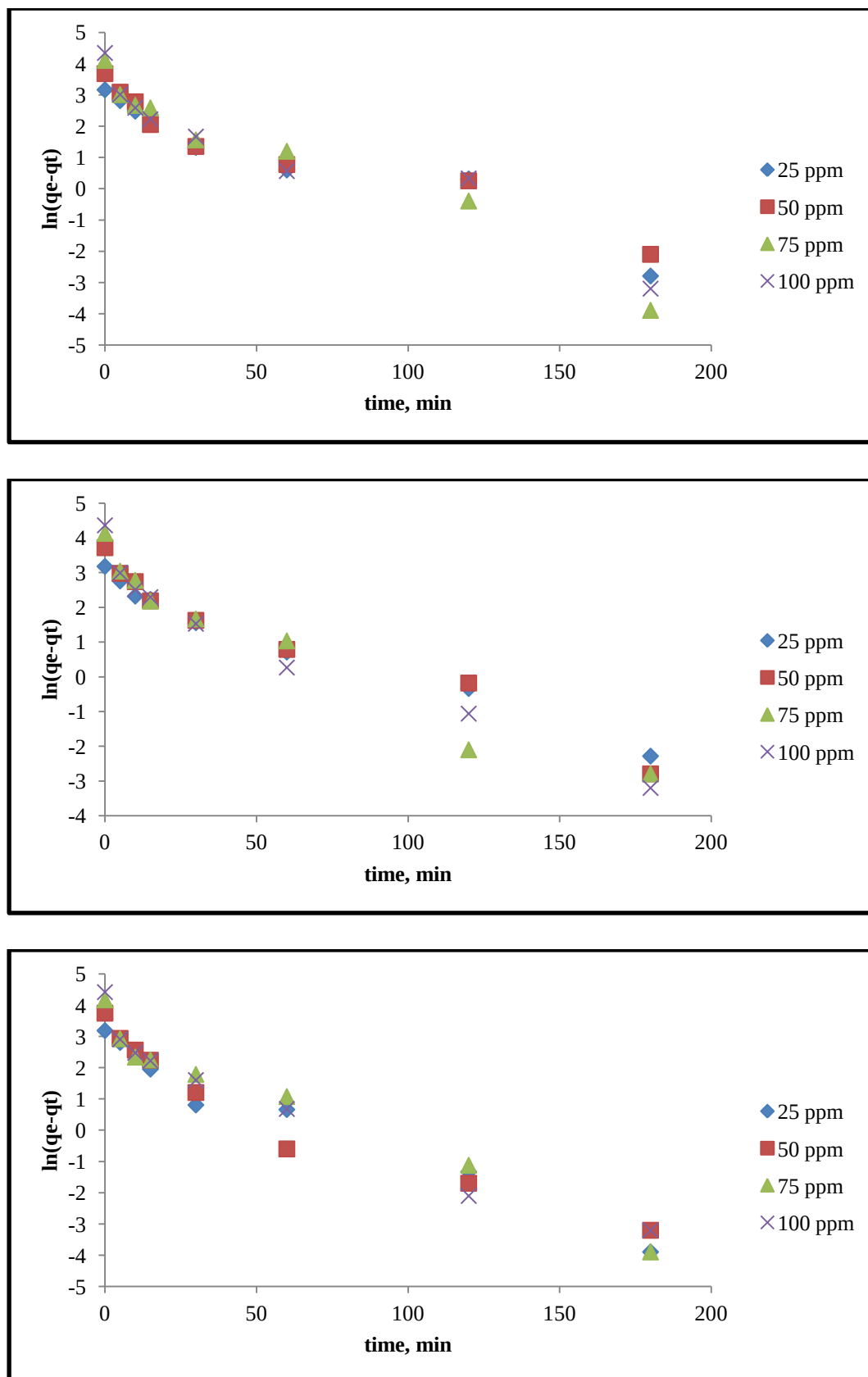


Figure 5.60 Plots of pseudo-first-order kinetics of MO adsorption onto CuBTC: (a) $T = 298 \text{ K}$; (b) $T = 308 \text{ K}$; (c) $T = 318 \text{ K}$.

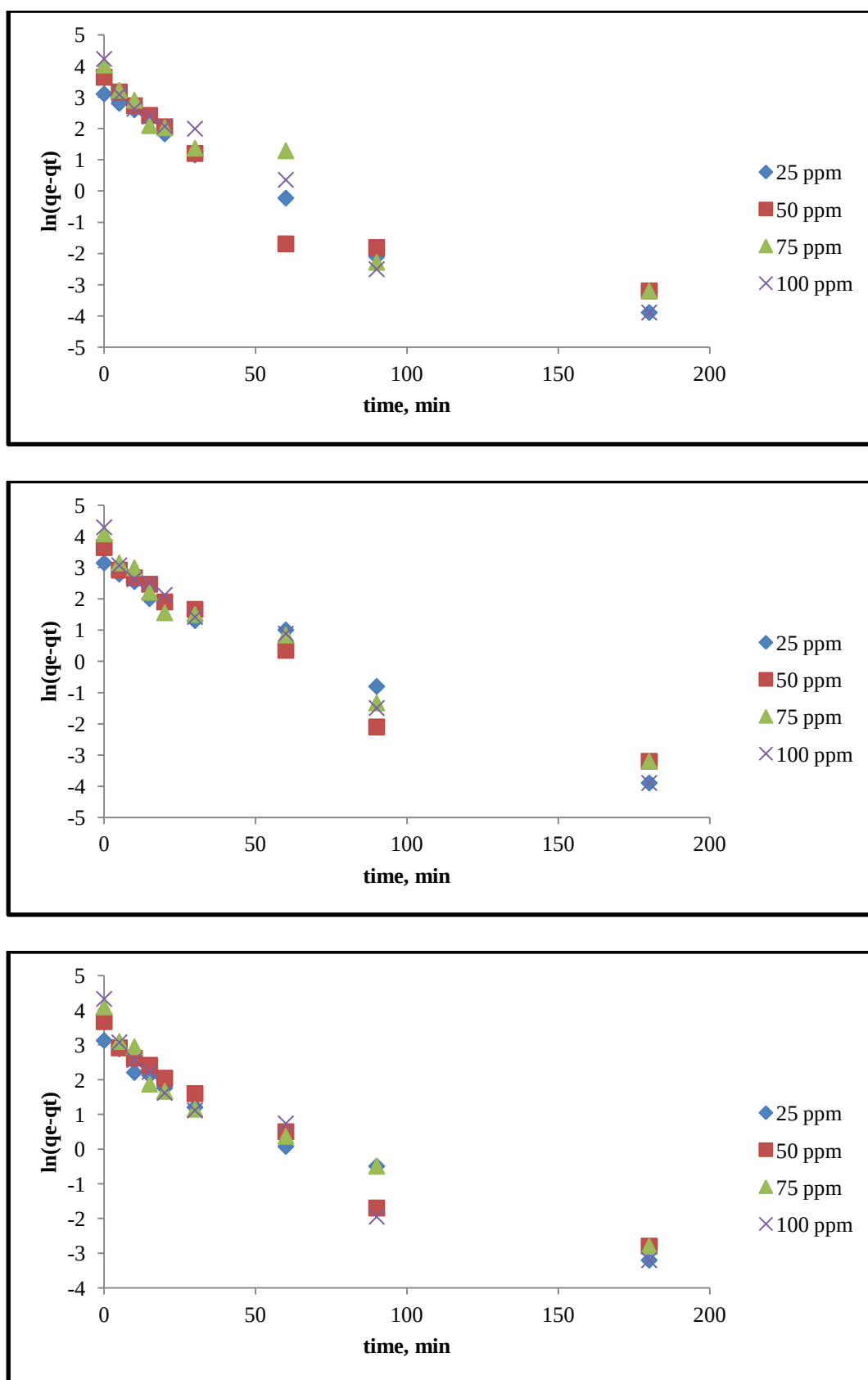


Figure 5.61 Plots of pseudo-first-order kinetics of MO adsorption onto MIL-53 (Fe): (a) $T = 298$ K; (b) $T = 308$ K; (c) $T = 318$ K

Pseudo- Second- Order Kinetic Model

Pseudo second order kinetic model equation (5.2) was applied and the equation was linearized (5.5) to calculate the rate constant k_2 (second order kinetic constants)

The rate constant k_2 is determined from the intercept of the plot of t/q_t versus contact time (t).

Figure 5.62-5.64 shows the plots of pseudo-second-order kinetics of MO adsorption onto MIL-101, CuBTC and MIL-53 (Fe) at three different temperature ($T = 298, 308$ and 318K).

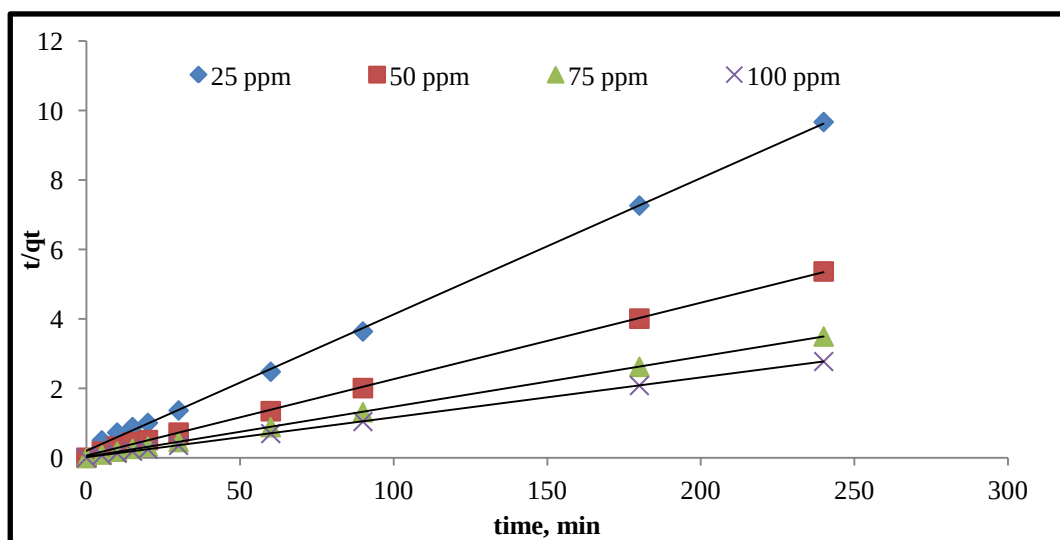
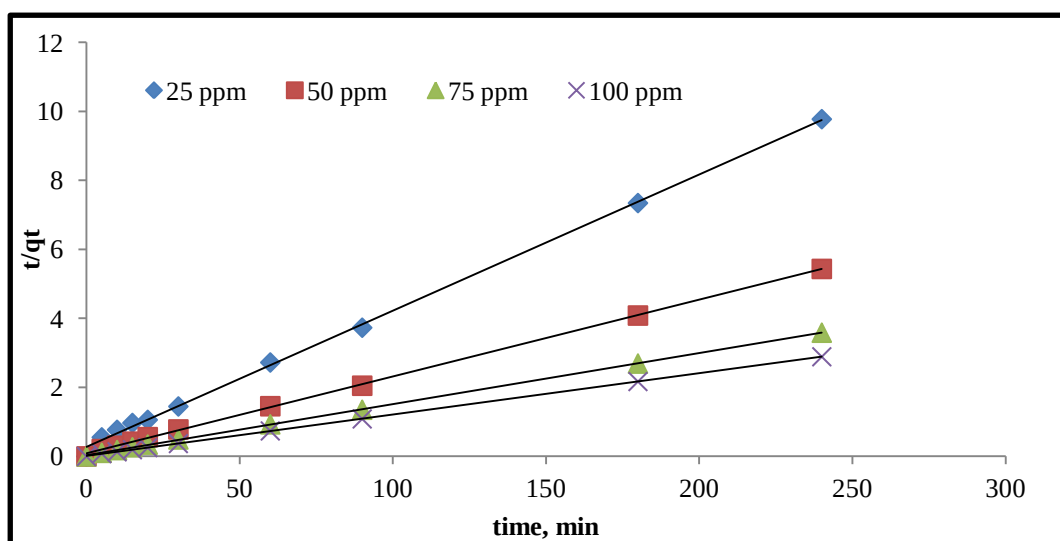
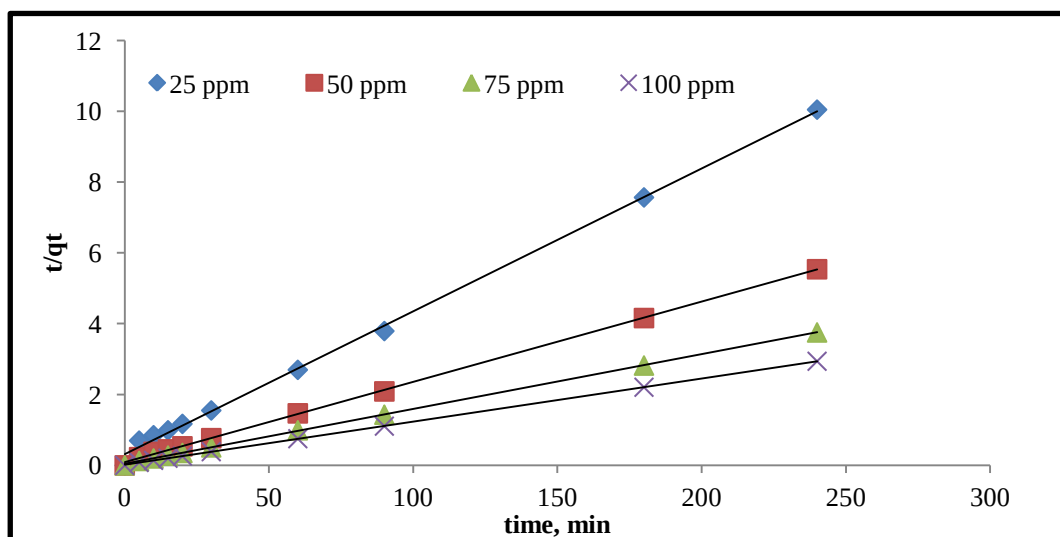


Figure 5.62 Plots of pseudo-second-order kinetics of MO adsorption onto MIL-101: (a) $T = 298$ K; (b) $T = 308$ K; (c) $T = 318$ K

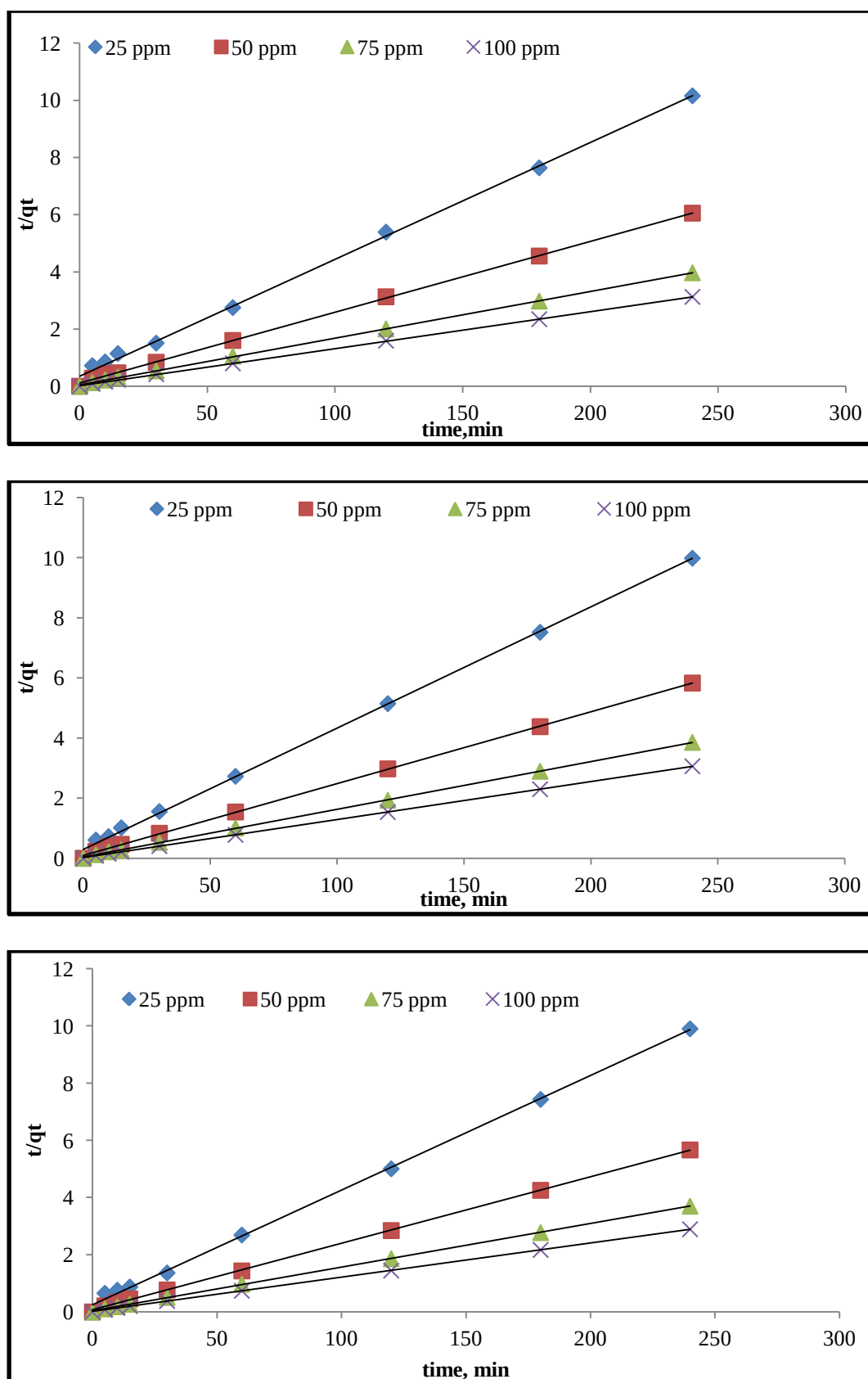


Figure 5.63 Plots of pseudo-second-order kinetics of MO adsorption onto CuBTC: (a) $T = 298$ K; (b) $T = 308$ K; (c) $T = 318$ K

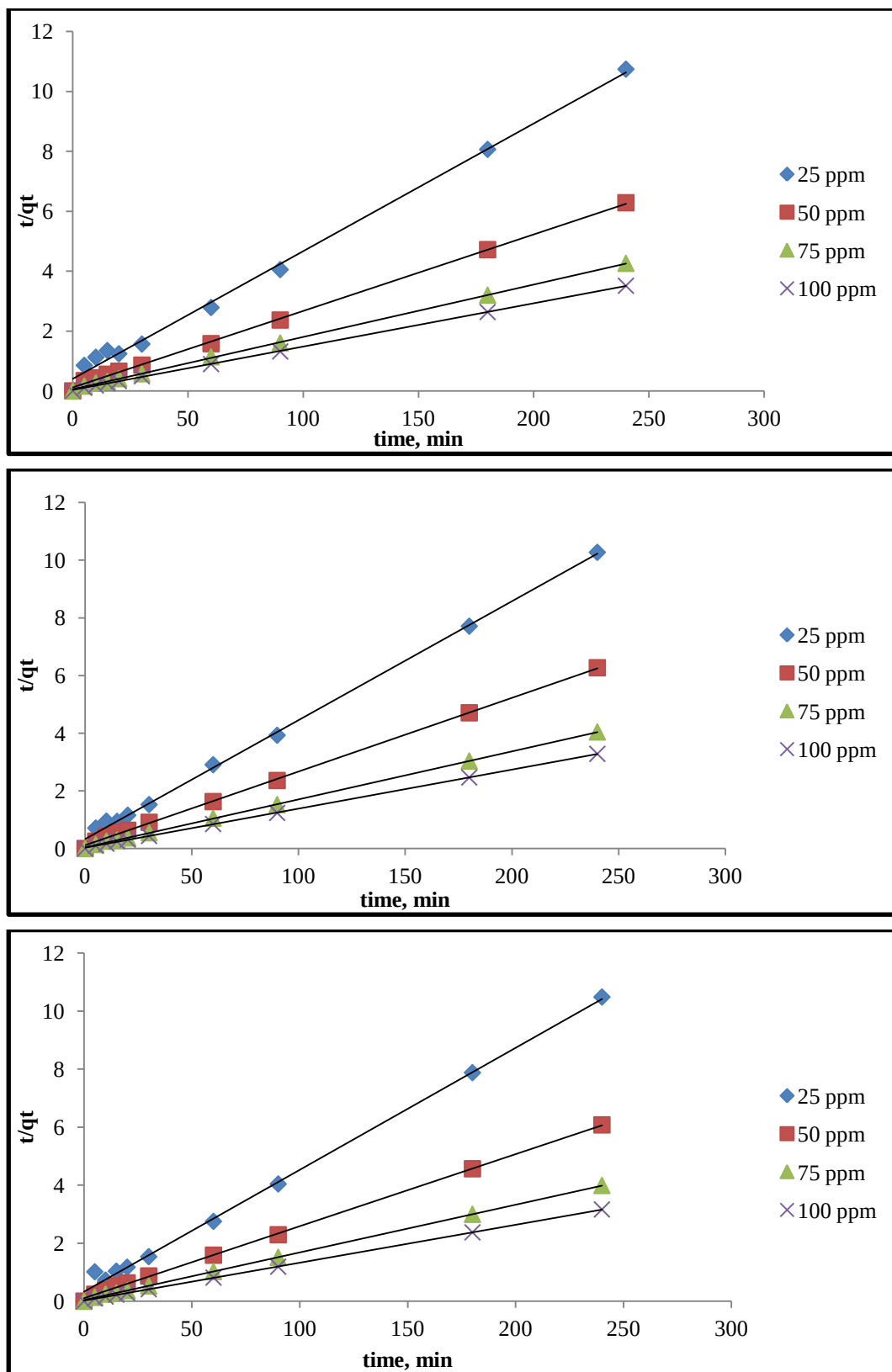


Figure 5.64 Plots of pseudo-second-order kinetics of MO adsorption onto MIL-53 (Fe): (a) T = 298 K; (b) T = 308 K; (c) T = 318.

Figure 5.56-5.58 show the effect of contact time on the adsorption and kinetic experiment of methyl orange (MO) on three different MOFs (MIL-101,

CuBTC and MIL-53 (Fe)) at 298, 308 and 318 K. The adsorption equilibrium was reached within 1 h after initiation. Because, early in the time of adsorption, there are numerous vacant surface sites for adsorption and with time the number of vacant sites available decreases and adsorption sites become saturated.

To understand the adsorption mechanism, the pseudo-first-order (5.1) and pseudo-second-order kinetic model (5.2) was studied. For this purpose, MO was adsorbed at various times up to 2h.

Figure 5.59-5.61 shows the pseudo first order, second order kinetic plots. The values of k_1 , k_2 and the regression coefficient are provided in Table 5.8-5.10. It can be seen from these figures and Table 5.8-5.10. The correlation coefficient values of pseudo second order kinetic model are close to the unity ($R^2 > 0.999$) of MO.

The first order equation did not apply for all contact times and was only applicable over the initial 0-30 min sorption period. In many cases, the pseudo-first-order rate model does not fit the entire range of contact time well and is generally applicable to only the initial stage of the sorption process. A similar trend was observed by Ho and McKay (Ho and McKay et al.,) for dyes on peat particles: The pseudo-first-order model represented the initial, rapid sorption stages well but could not be applied for the entire sorption process.

The best-fit model was selected based on the criteria:

The linear correlation coefficient (R^2) values for the concentrations tested in this work.

The values obtained by the pseudo-second-order model (Figure 5.62 – 5.64) agreed well with experimental data and can be used to explain the MO adsorption on MOFs; MIL-101, CuBTC and MIL-53 (Fe). The resultant values from these calculations are given in Table 5.8-5.10.

With the increase of the temperature, rate constant increased, that means the initial adsorption rate increased with increasing temperature. Besides, at a constant temperature, k_2 increased with the initial concentration of MO (Table 5.8-5.10). And also the rate constant is generally depended on the surface area and pore volume (Hasan et al., 2012). In this study, obtained results support this case

because k_2 values are in order of MIL-53 (Fe) < CuBTC < MIL-101 suggests potential applications of MOFs with large pore volume in dye removal.

5.2.2.2. Adsorption Mechanism

To identify the adsorption mechanism Weber and Morris intraparticle diffusion model (4) was applied.

As shown in Figure 5.65 – 5.67 the adsorption process had two phases. This situation suggested that the adsorption process proceeded by surface sorption and intra-particle diffusion. The initial part was a boundary layer effect while the second linear part was due to intra-particle or pore diffusion. The values of k_{id} and C were obtained from the second linear portion [36]. Table 5.8-5.10 shows the calculated intra-particle diffusion parameters for the adsorption process. Slope of second line is higher for higher initial concentration, which corresponds to an enhanced diffusion of adsorbate. This is due to the greater driving force at higher initial concentration. The intercept values show the measure of the boundary layer thickness.

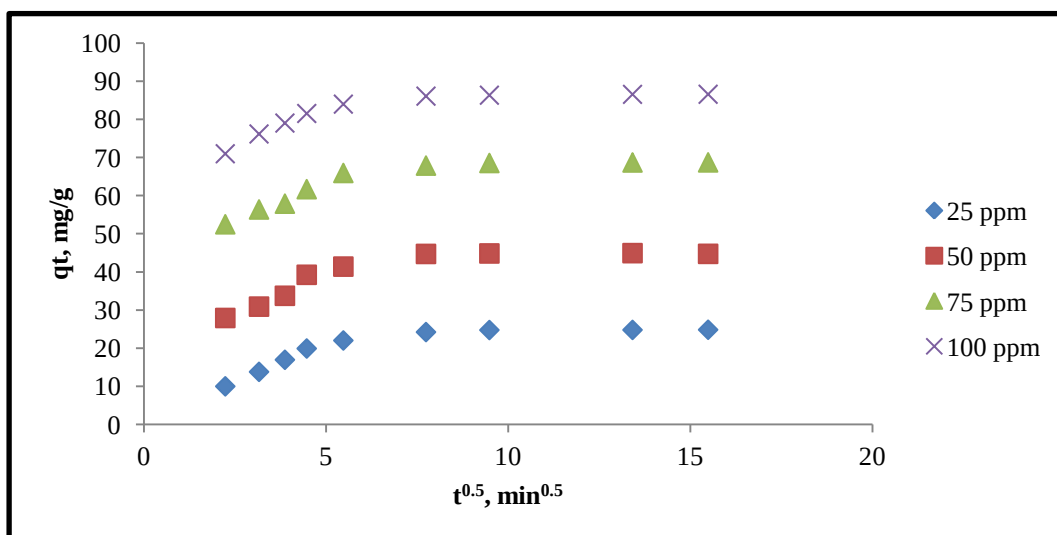
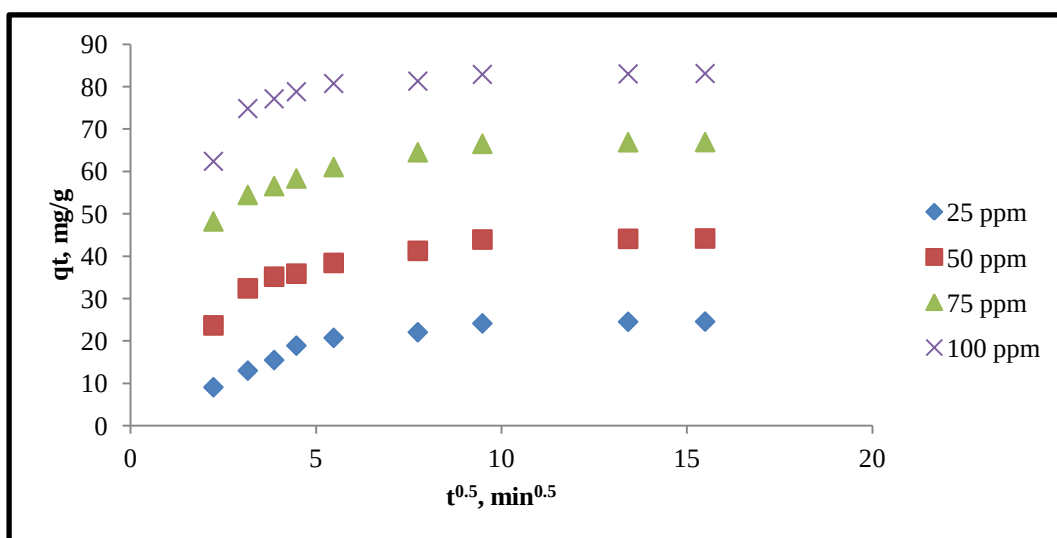
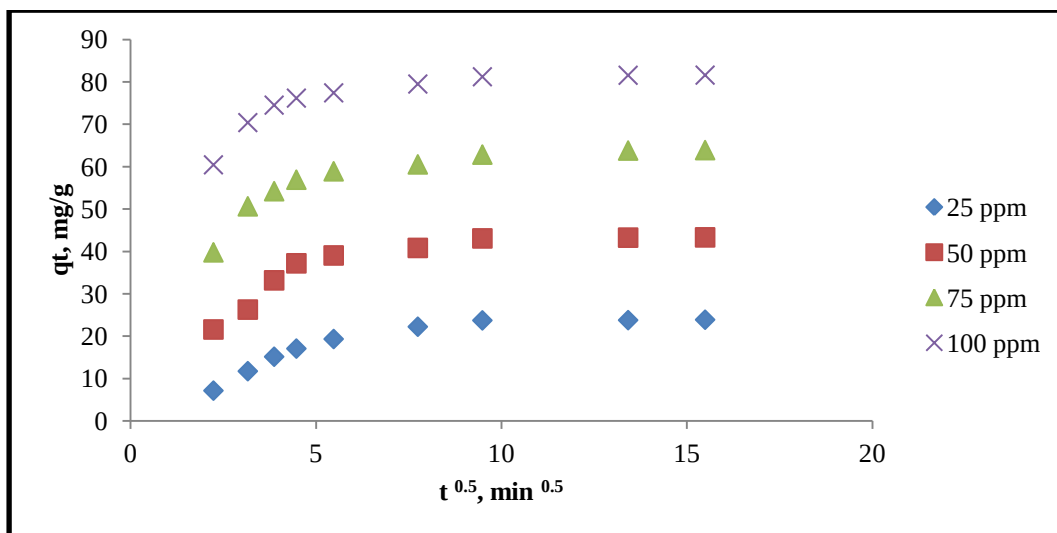


Figure 5.65 Diffusion model plot for the adsorption of MO on MIL-101 at different initial concentrations: (a) T = 298 K; (b) T = 308 K; (c) T = 318 K.

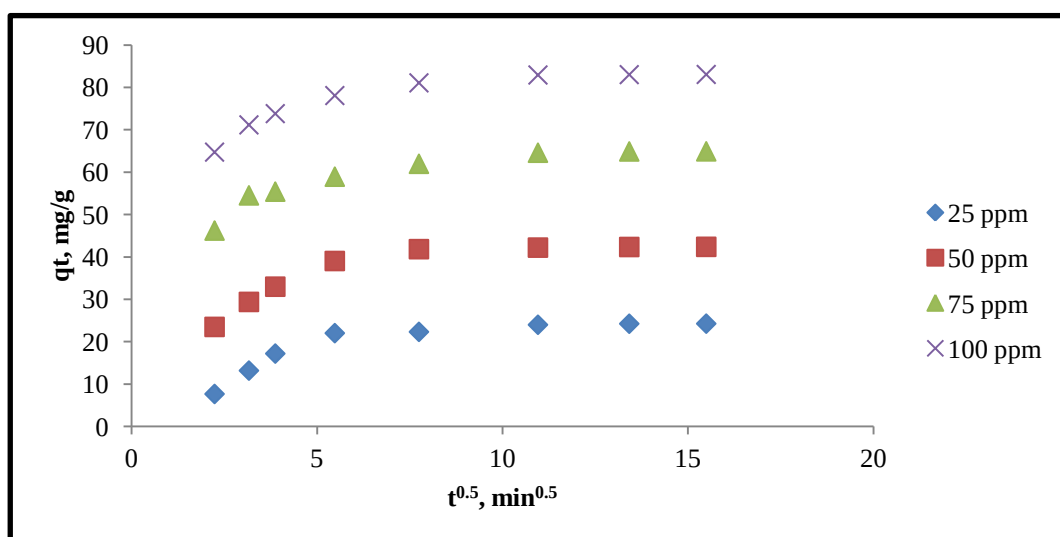
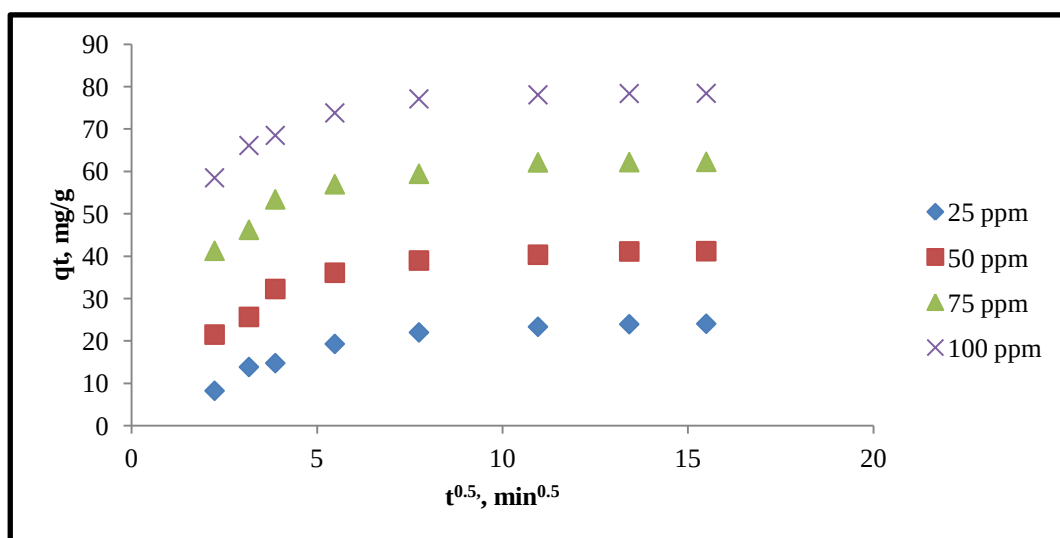
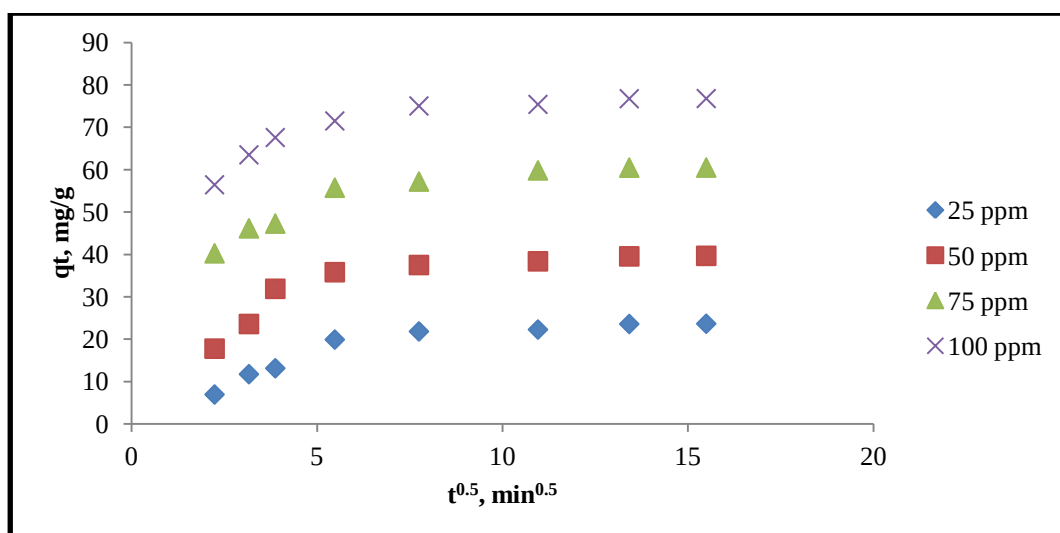


Figure 5.66 Diffusion model plot for the adsorption of MO on CuBTC at different initial concentrations: (a) T = 298 K; (b) T = 308 K; (c) T = 318 K.

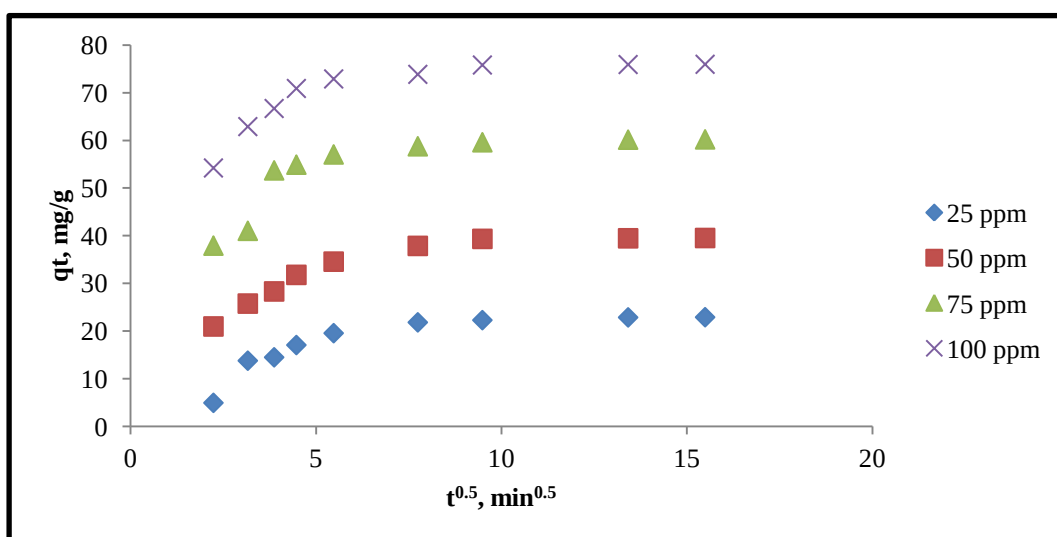
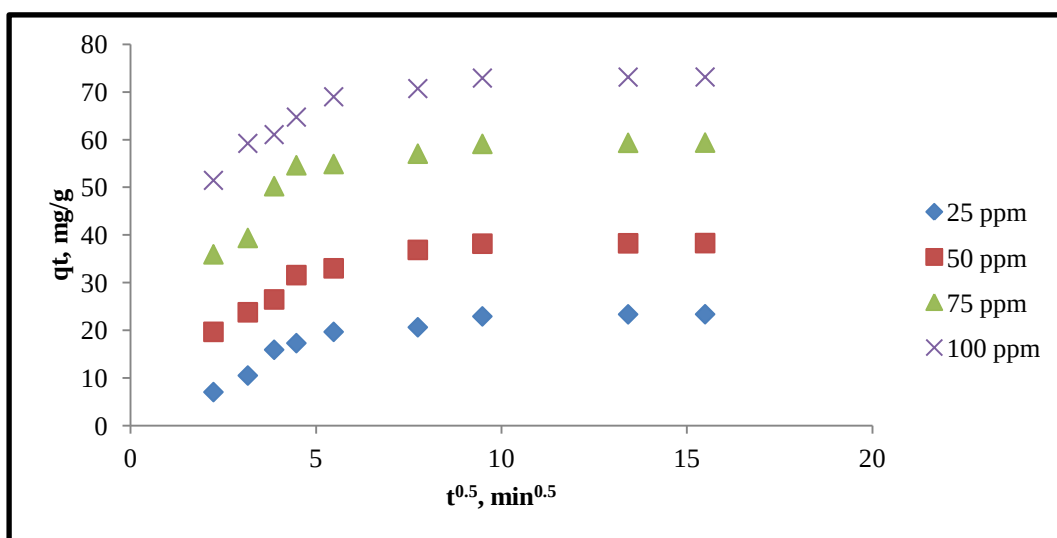
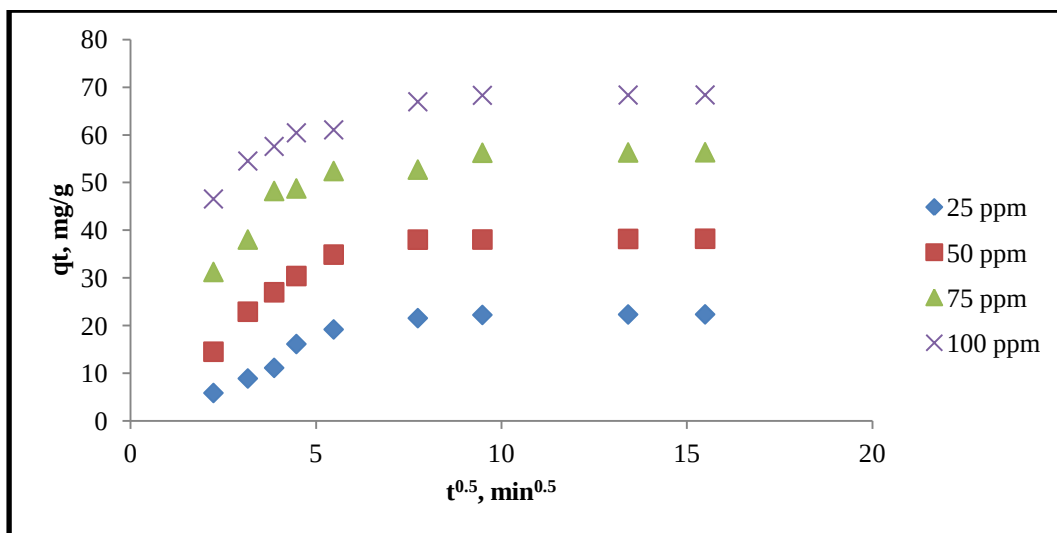


Figure 5.67 Diffusion model plot for the adsorption of MO on MIL-53 (Fe) at different initial concentrations: (a) T = 298 K; (b) T = 308 K; (c) T = 318 K.

5.2.2.3. Adsorption Isotherms

Adsorption isotherms for MO on MOFs were studied with different temperature at 298, 308 and 318 K (Figure 5.68). The Langmuir and Freundlich adsorption models (5,6) were applied for the fitting of the experimental data.

Nonlinear curve fitting analysis method in MATLAB programme was also adapted to calculate the parameters of Langmuir and Freundlich isotherm models. Correlation coefficient values are found from Equation 7.

The parameters and the correlation coefficient values calculated from these two models are listed in Table 5.11. It can be seen that, while the adsorption isotherms of MO are fitted well by the Langmuir model.

In this study, n values (Freundlich constant) are greater than unity (Table 5.11). Hence it can be said; the isotherm can be classified as L-type, reflecting a high affinity between adsorbate and adsorbent and is indicative of chemisorption. In addition, when temperature increases, the Langmuir constant b and the Freundlich constant, K_F , also increases, indicating that MO adsorption onto MOFs are endothermic process [37].

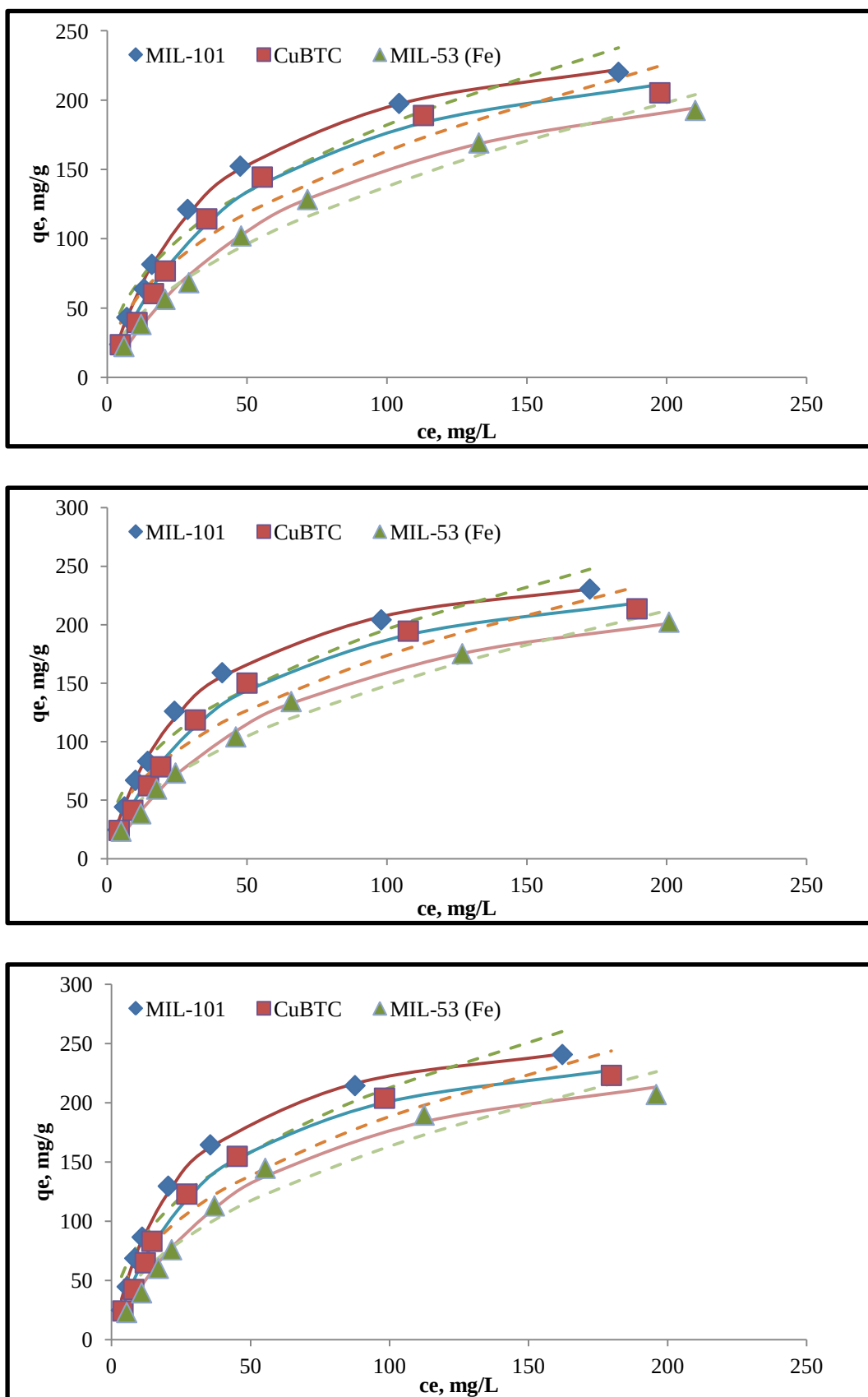


Figure 5.68 Adsorption isotherms for MO adsorption onto the three adsorbents at different temperature: a) $T=298$ K, b) $T=308$ K, c) $T=318$ K. The solid and dashed lines show the calculated results derived from Langmuir and Freundlich isotherm methods respectively.

Table 5.7 The Q_0 values for the adsorption of MO on different adsorbents. (Comparison of adsorption capacity of the MOFs with other adsorbents)

Adsorbent	qm (mg/g)	Reference
MIL-101	279.4	This study
CuBTC	272.3	This study
MIL-53 (Fe)	272.1	This study
MWCNTs	66.6 mg/g	Zhu et al., (2010)
activated carbon obtained from <i>Phragmites australis</i> (PAAC)	238.1 mg/g	Chen et al., (2010)
MWCNTs	52.86 mg/g	Yao et al., (2011)

It can be said from Table 5.7 MOFs show excellent adsorption capacity for MO removal when compared with the other adsorbents which have smaller surface area.

5.2.2.4. Adsorption thermodynamics

The thermodynamic parameters Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were calculated from the adsorption of MO onto MOFs at different temperatures.

The Gibbs free energy change ΔG can be calculated by Equation 8. The enthalpy change ΔH can be obtained by using the van't Hoff Equation 9.

The positive ΔH° indicates that the adsorption process of MO onto MOFs is endothermic. The negative ΔG° suggests that the adsorption process is spontaneous. The positive entropy change, ΔS , shows the increased randomness at the solid/solution interface during the adsorption process. In other words, in this study the number of desorbed water molecules was larger than that of the adsorbed molecules. Therefore, the driving force for MO adsorption (negative ΔG) onto MOFs is due to both enthalpy effect and entropy effect. All values obtained from the adsorption thermodynamic section were shown in Table 5.12.

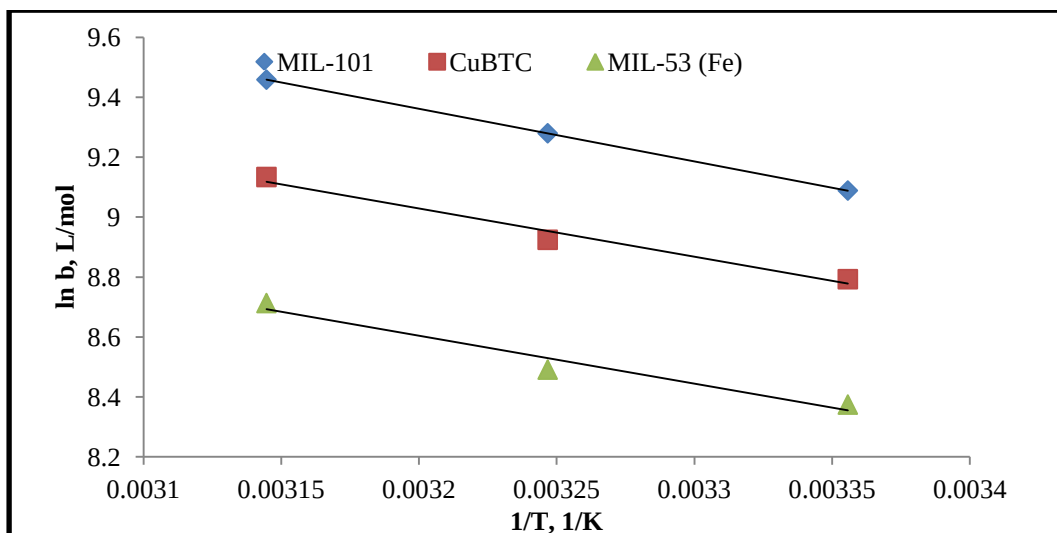


Figure 5.69 van't Hoff plots to get the ΔH and ΔS of the MR adsorption on the different MOFs

5.2.2.5. Effect of regeneration of MOFs

In this study, the reusability of MOFs was evaluated after washing with ethanol, acetone and water at least three times. It is seen from Figure 5.70; MOFs have excellent regeneration ability in the adsorptive removal of MO from water.

5.2.2.6. Effect of adsorbent dosage

The effect of the adsorbent dosage on adsorption capacity was also investigated. As shown in Figure 5.71, the adsorbed amount of MO increased with increasing adsorbent amounts until 0.1 g. This is explained as when the adsorbent dose increased, more surface area will be available so more active sites will also be available for adsorption of MO. Further increase of the adsorbent amounts doesn't have any effect on the adsorption rate of MO.

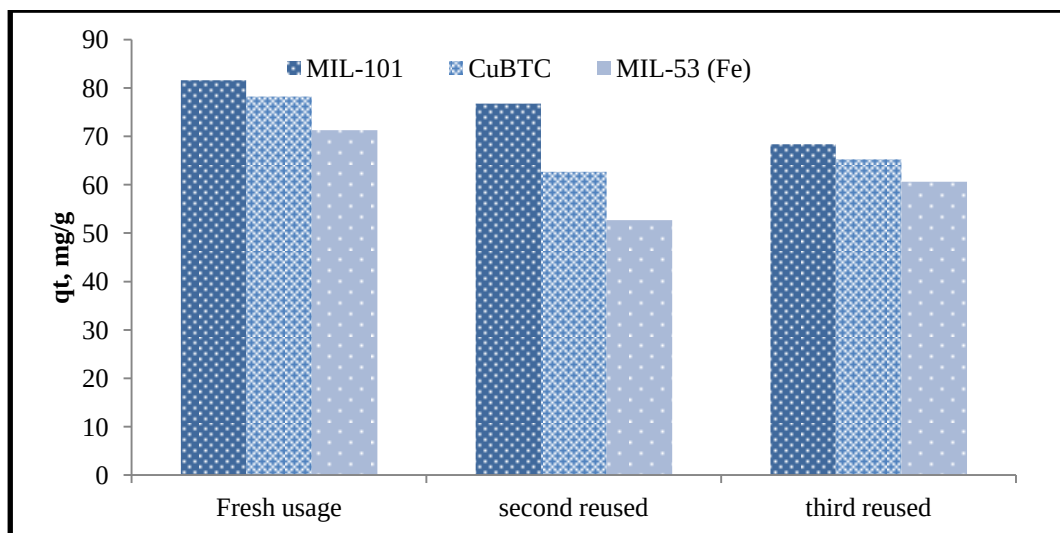


Figure 5.70 The reuse of MOFs on MR adsorption (concentration 100 ppm, $T = 298$ K).

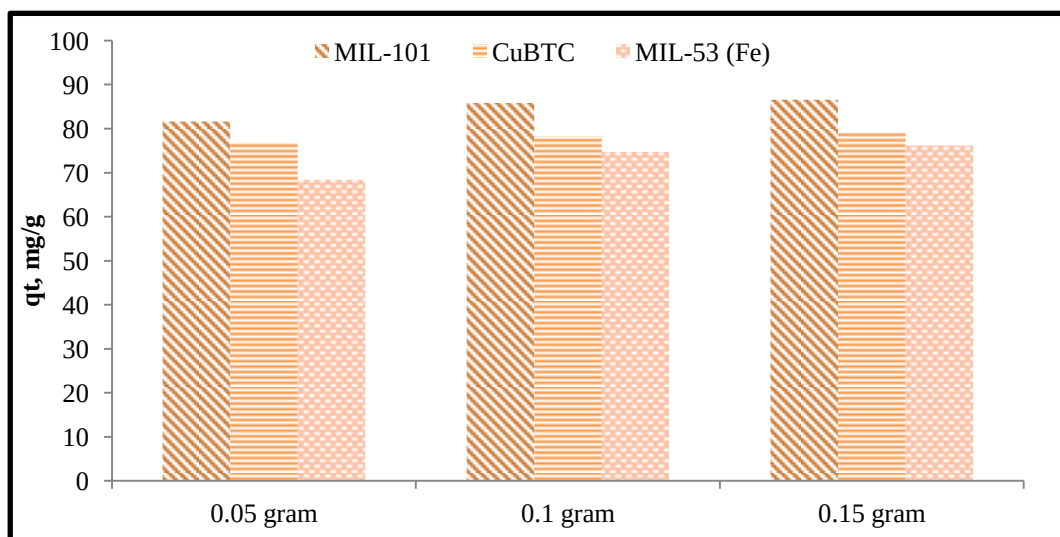


Figure 5.71 Effect of adsorbent dosage (concentration 100 ppm, $T = 298$ K).

5.2.2.7. Effect of pH

The adsorption of a dye usually depends highly on the pH value of the dye solution. In this work, the pH value effect on the adsorption was carried out at 298 K and 100 ppm. The pH value (2–12) of the solution was adjusted with NaOH or HCl solution. As shown in Figure 5.72, the adsorbed amounts decreased with increasing pH value of the MO solution which is quite similar to previous reports (Haque et al., 2010; Chen et al., 2012). The decreasing of adsorbed MO with increasing pH might be owing to the fact that the amount of positive charges of adsorbents decreased with increasing pH. When the pH value increased to value

of 12, the amount of adsorption was zero. Therefore, the mechanism of MO adsorption on different MOFs may be explained with a simple electrostatic interaction between MR and the MOFs. However, other mechanism like π - π interaction (Haque et al., 2011) between benzene rings of MOFs and MO and also breathing effect of MIL-53 (Fe) cannot be ruled out.

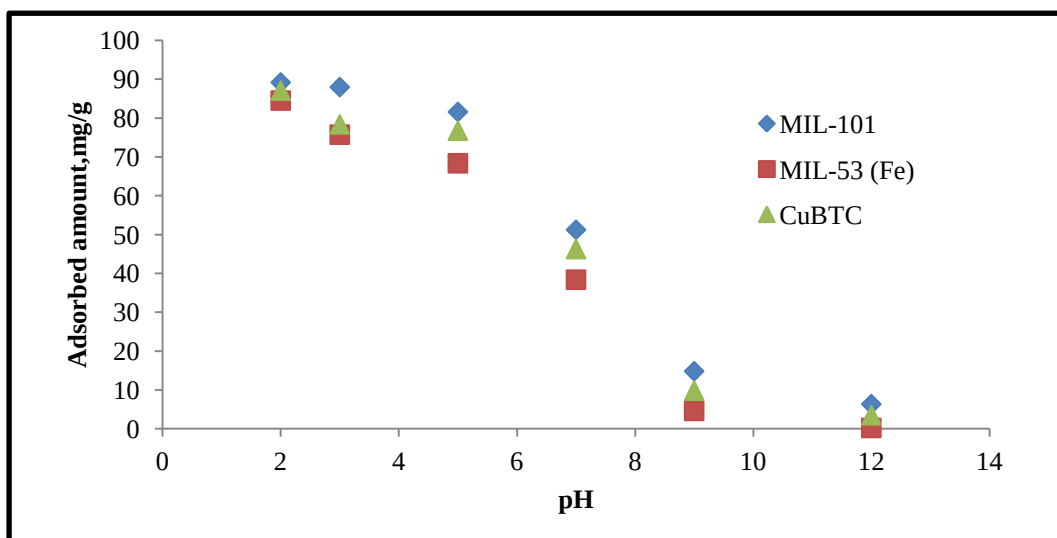


Figure 5.72 Effect of pH on MO adsorption (concentration 100 ppm, T = 298 K).

In this study, dyes (MR and MO) adsorption from waste water was studied. MIL-101, MIL-53 (Fe) and CuBTC were synthesized and the adsorption interaction between these MOFs and dyes in an aqueous solution was studied. The structural characteristics, surface area, and thermal analysis of the synthesized MOFs were carried out by XRD, TGA and BET methods.

The adsorption capacity for dyes is depended on the pore size. In this study, obtained results support this case because maximum adsorption capacity values are in order of MIL-53 (Fe) < CuBTC < MIL-101 suggests potential applications of MOFs with large pore volume in dye removal. Although MIL-53 (Fe) has not high surface area but its flexible structure leads to high adsorption capacity toward dyes.

The adsorption mechanism of dyes may be explained with;

- Electrostatic interaction between acidic anionic dyes (MR and MO) and the adsorbents,
- π - π interaction between benzene rings of MOFs and dyes,
- And also breathing effect of MIL-53 (Fe).

Because electrostatic interaction is important for dye removal, lower pH values were found to be more favourable for adsorption of dyes on MOF. The equilibrium adsorption and kinetics data could be fitted well by the Langmuir isotherm model and pseudo-second-order kinetic model, respectively. The adsorption rate constants for dyes adsorption increased with increasing temperature. And the results of the adsorption thermodynamics revealed that the adsorption of MR by selected MOF was a spontaneous and exothermic process, and for MO adsorption by selected MOFs was also spontaneous and endothermic process. To summarize, it was found that the adsorption rate and capacity is dependent on the pore volume and surface area and flexible structure of the adsorbents indicated MOFs having these properties can be potential adsorbents for removal of dye from wastewater.

Table 5.8 Kinetic constants of MO adsorption onto MIL-101

	C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo first order kinetic constants		Pseudo second order kinetic constants		Intraparticle diffusion model			
			k_1 (g/(mgmin))	R^2	k_2 (g/(mgmin))	R^2	h (mg/(g.min))	k_i (mg/(g.min ^{1/2}))	I (mg/g)	R^2
T=298 K	25	23.87755	0.032	0.8828	0.005173	0.9981	3.169572	0.1697	21.44	0.5878
	50	43.30612	0.0355	0.9198	0.005706	0.9995	11.0742	0.2602	39.606	0.5931
	75	63.89796	0.0311	0.9279	0.00616	0.9998	25.64103	0.3905	58.26	0.7839
	100	81.59184	0.0368	0.9147	0.008755	1	58.82353	0.23	78.306	0.6725
T=308 K	25	24.55102	0.0344	0.9744	0.005766	0.9987	3.695492	0.2732	20.655	0.6603
	50	44.16327	0.0338	0.9105	0.006006	0.9996	12.07729	0.3022	39.866	0.5792
	75	66.91837	0.0374	0.9506	0.006638	0.9999	30.30303	0.2619	63.184	0.6592
	100	83.08163	0.0334	0.8165	0.011339	1	78.74016	0.1873	80.401	0.6045
T=318 K	25	24.81633	0.0373	0.8789	0.00768	0.999	4.97265	0.0639	23.896	0.6201
	50	44.71429	0.1225	0.9601	0.008	0.9996	16.52893	0.0057	44.715	0.449
	75	68.69388	0.0421	0.9239	0.008713	0.9999	42.01681	0.0918	67.379	0.6819
	100	86.55102	0.0411	0.8984	0.011704	1	88.49558	0.0614	85.654	0.9033

Table 5.9 Kinetic constants of MO adsorption onto CuBTC

	C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo first order kinetic constants		Pseudo second order kinetic constants		Intraparticle diffusion model			
			k_1 (g/(mgmin))	R^2	k_2 (g/(mgmin))	R^2	h (mg/(g.min))	k_i (mg (g.min ^{1/2}))	I (mg/g)	R^2
T=298 K	25	23.63265	0.0288	0.9293	0.004729	0.9978	2.827255	0.2624	19.698	0.9042
	50	39.65306	0.0274	0.9134	0.005653	0.9993	9.191176	0.3006	35.183	0.9537
	75	60.4898	0.0377	0.955	0.005814	0.9998	21.88184	0.4302	54.369	0.8359
	100	76.77551	0.0332	0.8974	0.007204	0.9999	43.29004	0.2563	72.929	0.8866
T=308 K	25	24.04082	0.0278	0.976	0.005559	0.9988	3.405995	0.27	20.113	0.9192
	50	41.16327	0.0316	0.9576	0.005841	0.9997	10.22495	0.2957	36.869	0.9238
	75	62.2449	0.0368	0.9423	0.006499	0.9998	25.70694	0.3517	57.309	0.7236
	100	78.40816	0.0363	0.9405	0.008229	0.9999	51.02041	0.1708	759.52	0.8757
T=318 K	25	24.2449	0.0363	0.9718	0.006468	0.9986	4.022526	0.2482	20.734	0.7926
	50	42.36735	0.0366	0.9285	0.007845	0.9996	14.45087	0.072	41.316	0.9172
	75	64.89796	0.0387	0.9667	0.007203	0.9998	30.76923	0.3746	59.618	0.7742
	100	83.04082	0.0385	0.9414	0.008324	0.9999	57.80347	0.2483	79.55	0.7378

Table 5.10 Kinetic constants of MO adsorption onto MIL-53 (Fe)

	Pseudo first order kinetic constants				Pseudo second order kinetic constants			Intraparticle diffusion model		
	C_0 (mg/L)	$q_{e,exp}$ (mg/g)	k_1 (g/(mgmin))	R^2	k_2 (g/(mgmin))	R^2	h (mg/(g.min))	k_i (mg / (g.min ^{1/2}))	I (mg/g)	R^2
T=298 K	25	22.34694	0.0409	0.9448	0.004452	0.9956	2.453386	0.0855	21.126	0.6443
	50	38.20408	0.0396	0.8382	0.005446	0.999	8.375209	0.0253	37.816	0.9846
	75	56.34694	0.0394	0.8778	0.005714	0.9996	18.65672	0.3682	51.156	0.5305
	100	68.36735	0.0442	0.9148	0.00641	0.9998	30.4878	0.1468	66.291	0.5565
T=308 K	25	23.36735	0.0377	0.9825	0.005161	0.998	3.040438	0.2979	19.13	0.6549
	50	38.28571	0.0387	0.9142	0.00581	0.9994	8.865248	0.148	36.18	0.5808
	75	59.36735	0.038	0.922	0.006206	0.9997	22.52252	0.2459	55.873	0.6084
	100	73.12245	0.0422	0.9481	0.006532	0.9999	35.84229	0.255	69.513	0.5896
T=318 K	25	22.89796	0.0339	0.9693	0.005339	0.9967	3.026634	0.1398	20.852	0.9286
	50	39.5102	0.036	0.9156	0.005937	0.9995	9.65251	0.1729	37.042	0.6033
	75	60.20408	0.0339	0.9693	0.00725	0.9998	26.95418	0.1756	57.648	0.8612
	100	75.93878	0.0386	0.881	0.008172	0.9999	47.61905	0.2167	72.867	0.5657

Table 5.11 Adsorption isotherms of MO adsorption onto MOFs

MOFs	T (K)	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
		b (L/mg)	Q ₀ (mg/g)	R ²	K _f (mg/g(L/mg) ^{1/n})	n	R ²
MIL-101	298 K	0.02705	267.1	0.997	23.78	2.262	0.941
	308 K	0.03275	271.3	0.997	27.55	2.346	0.938
	318 K	0.03917	279.4	0.996	31.51	2.41	0.928
CuBTC	298 K	0.02012	264.6	0.994	18.89	2.135	0.936
	308 K	0.02295	268.9	0.994	21.23	2.191	0.934
	318 K	0.02830	272.3	0.995	24.98	2.279	0.929
MIL-53	298 K	0.01324	264.4	0.998	12.4	1.910	0.976
	308 K	0.01488	268.5	0.997	14.13	1.956	0.978
	318 K	0.01858	272.1	0.994	17.65	2.069	0.936

Table 5.12 Adsorption thermodynamics constants of MO adsorption onto MOFs

MOFs	T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol/K)	R^2
MIL-101	298	-22.52	14.58	124.50	1.000
	308	-23.76			
	318	-25.01			
CuBTC	298	-21.78	13.40	117.95	0.977
	308	-22.85			
	318	-24.15			
MIL-53	298	-20.75	13.30	114.09	0.962
	308	-21.74			
	318	-23.04			

5.2.3. Adsorption of Nitrobenzene onto MIL-101 and MIL-53 (Fe)

In liquid phase adsorption of nitrobenzene, the effects of temperature, initial concentration, adsorbent amount and contact time were investigated and also reusability of MIL-101 and MIL-53 was studied. The adsorption kinetics, mechanism, isotherms were searched and thermodynamic constants were calculated.

5.2.3.1. Adsorption kinetics

Figure 5.73 and 5.74 show the effect of contact time on the adsorption and kinetic experiment of Nitrobenzene (NB) on two different MOFs (MIL-101 and MIL-53 (Fe)). The pseudo-first-order (5.1) and pseudo-second-order kinetic model (5.2) was studied.

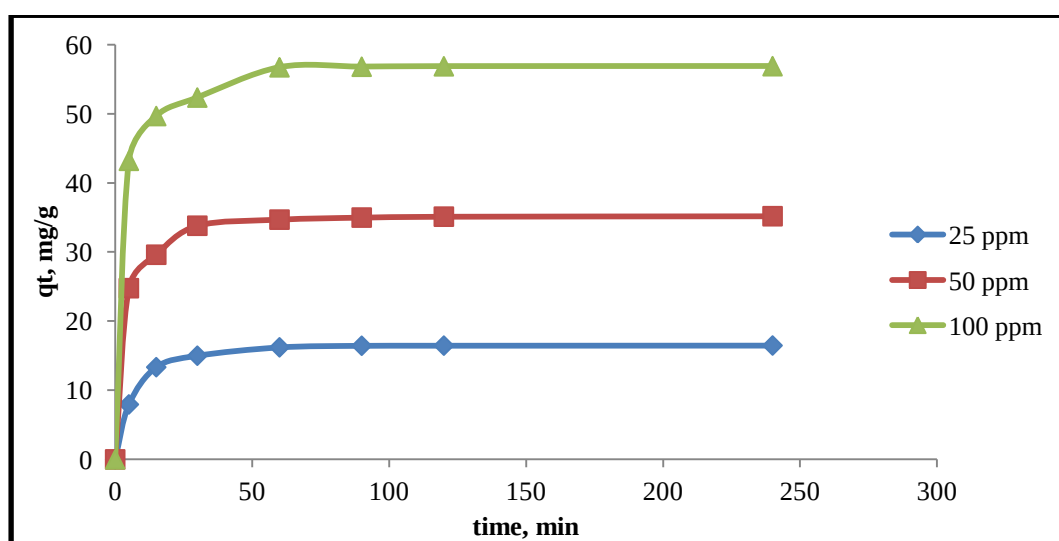
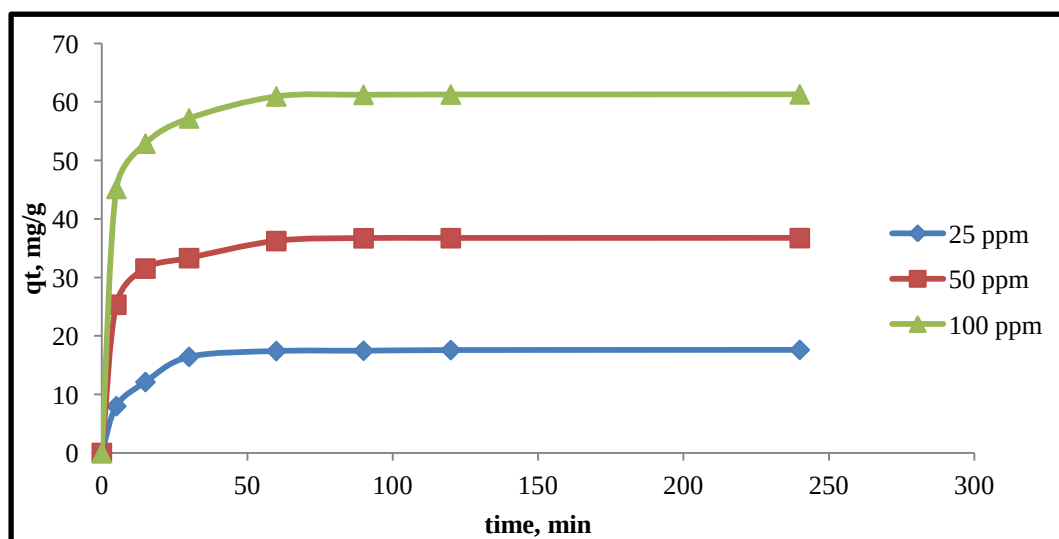
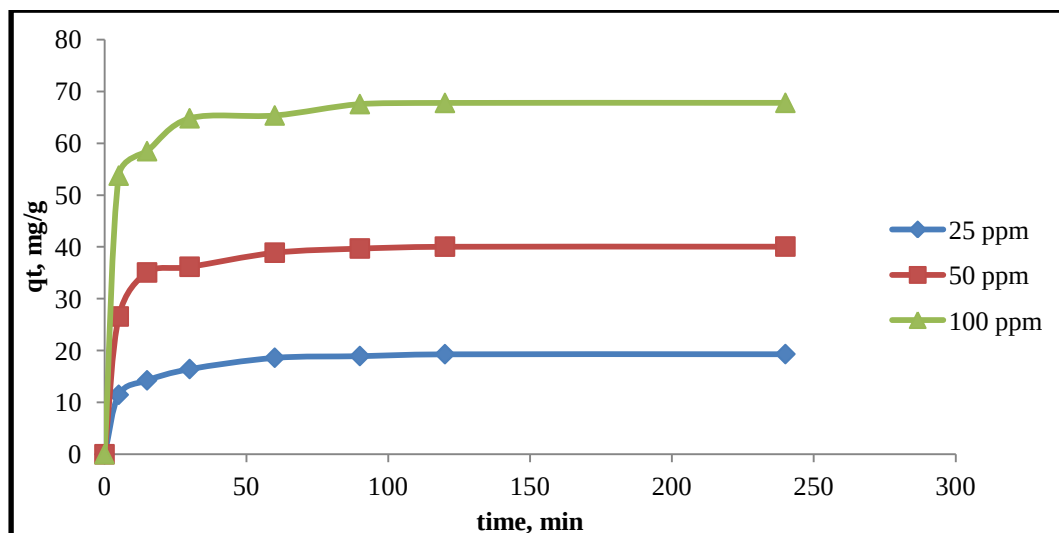


Figure 5.73 Effect of contact time on the adsorption of NB on MIL-101 at different temperature of (a) T=298 K; (b) T=308 K; (c) T=318 K.

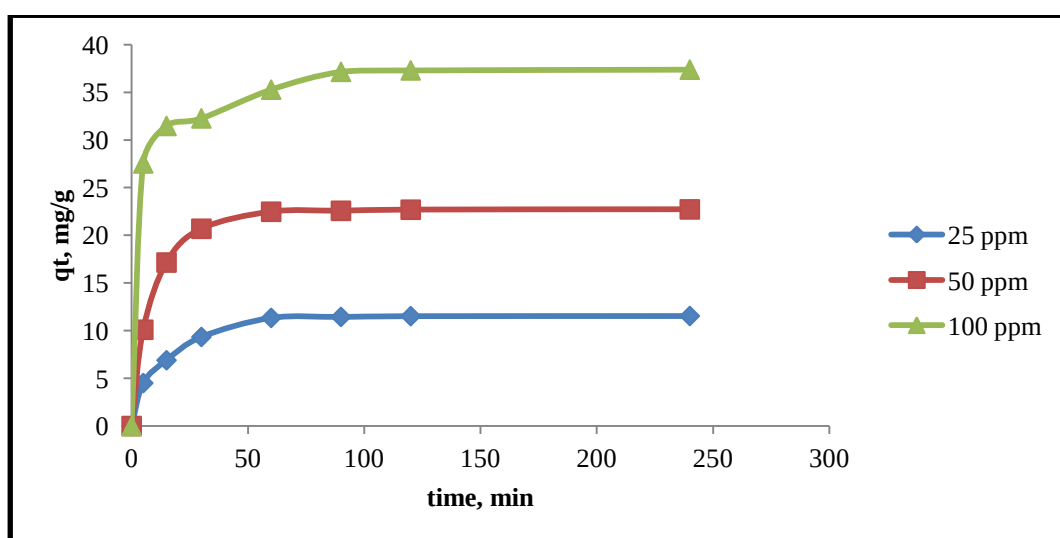
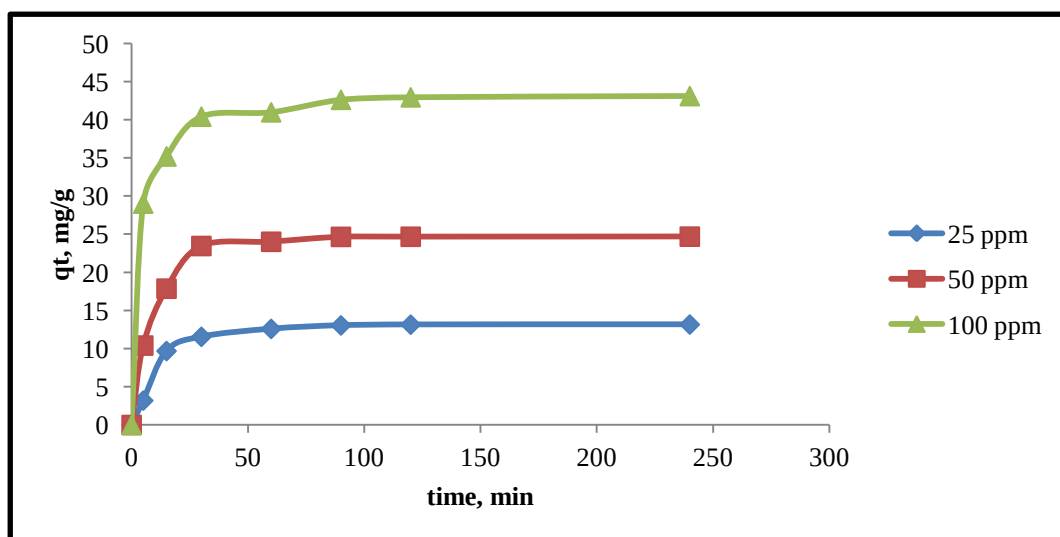
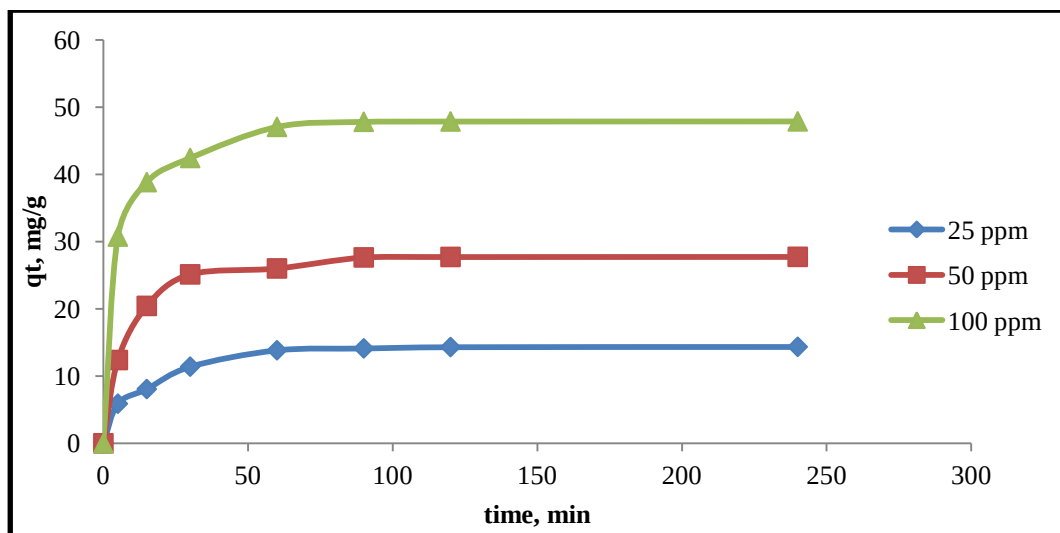


Figure 5.74 Effect of contact time on the adsorption of NB on MIL-53 (Fe) at different temperature of (a) $T=298$ K; (b) $T=308$ K; (c) $T=318$ K.

Pseudo-First-Order Kinetic Model (Lagergren Equation)

Pseudo first order kinetic model equation (5.1) was applied and the equation was linearized (5.4) to calculate the rate constant k_1 (First order kinetic constants)

The rate constant k_1 is determined from the slope of the plot of $\ln(q_e - q_t)$ versus contact time (t) (Lagergren, 1898).

Figure 5.75-5.76 shows the plots of pseudo-first-order kinetics of MR adsorption onto MIL-101 and MIL-53 (Fe) at three different temperature ($T = 298, 308$ and 318K).

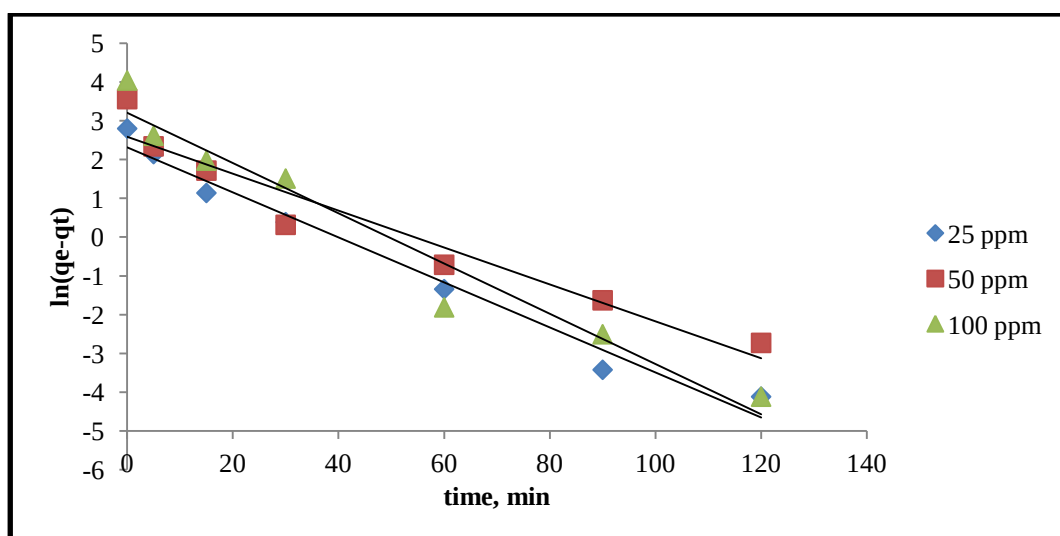
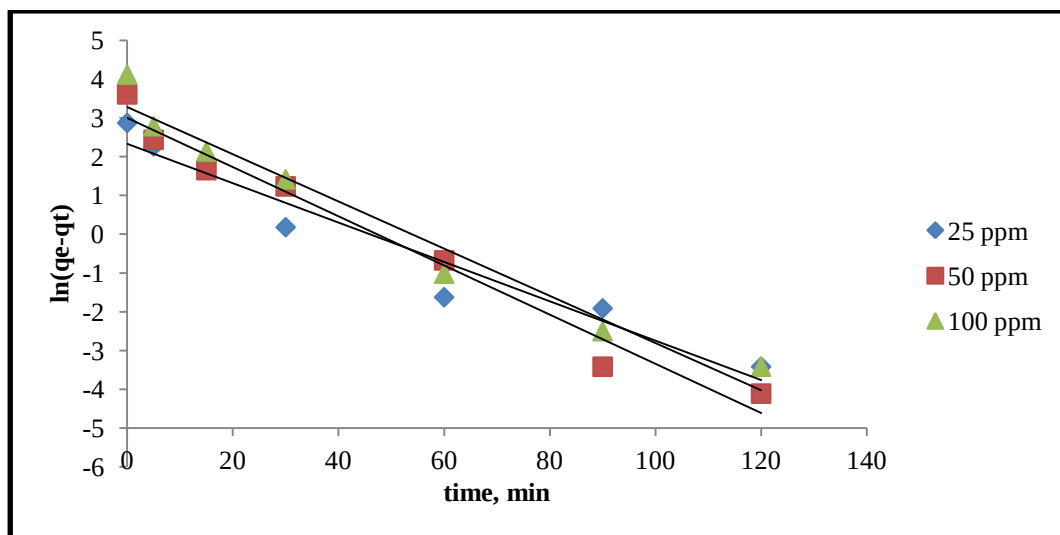
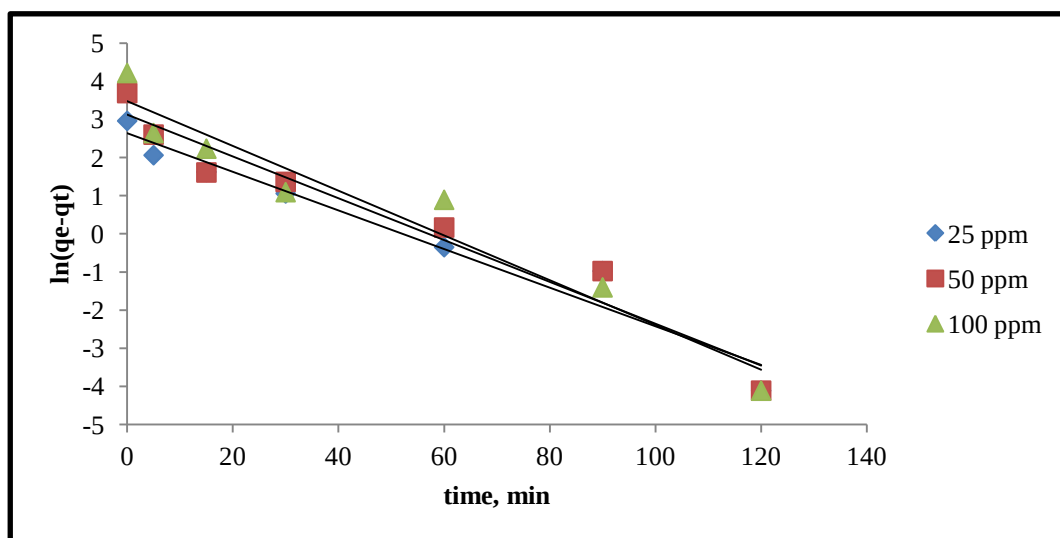


Figure 5.75 Plots of pseudo-first-order kinetics of NB adsorption onto MIL-101: (a) $T = 298\text{ K}$; (b) $T = 308\text{ K}$; (c) $T = 318\text{ K}$.

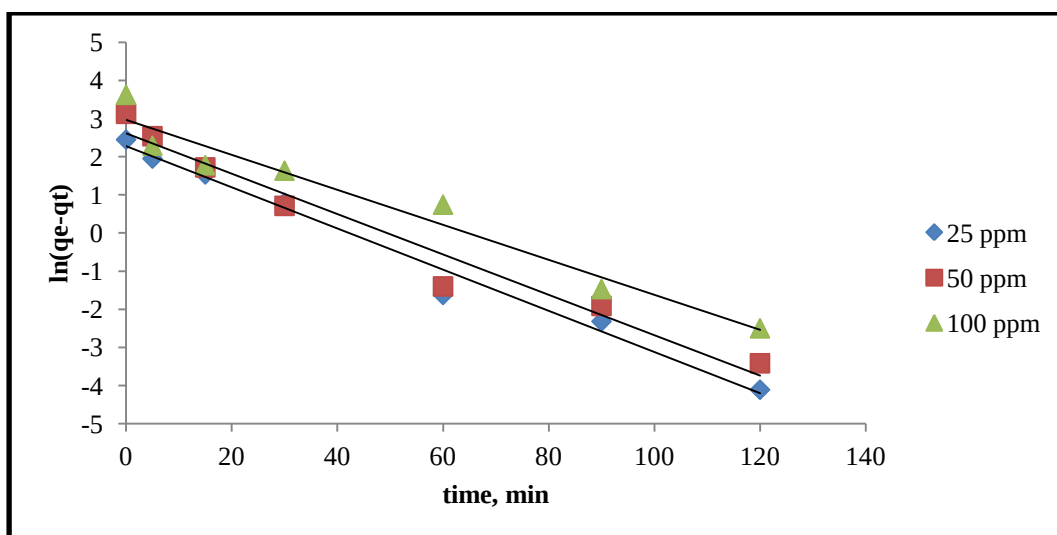
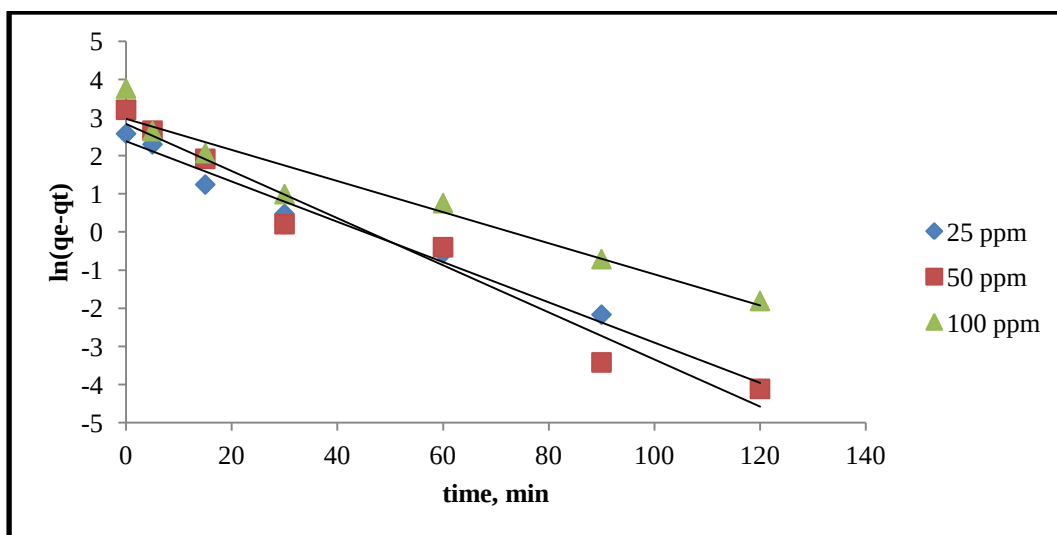
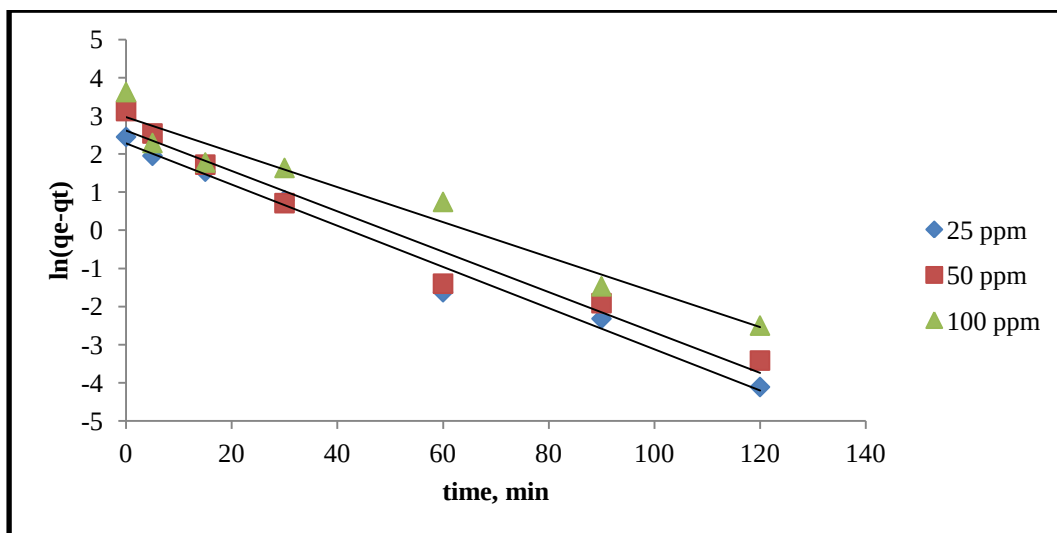


Figure 5.76 Plots of pseudo-first-order kinetics of NB adsorption onto MIL-53 (Fe): (a) $T = 298\text{ K}$; (b) $T = 308\text{ K}$; (c) $T = 318\text{ K}$

Pseudo- Second- Order Kinetic Model

Pseudo second order kinetic model equation (5.2) was applied and the equation was linearized (5.5) to calculate the rate constant k_2 (second order kinetic constants)

The rate constant k_2 is determined from the intercept of the plot of t/q_t versus contact time (t).

Figure 5.77-5.78 shows the plots of pseudo-second-order kinetics of MO adsorption onto MIL-101 and MIL-53 (Fe) at three different temperature ($T = 298, 308$ and 318K).

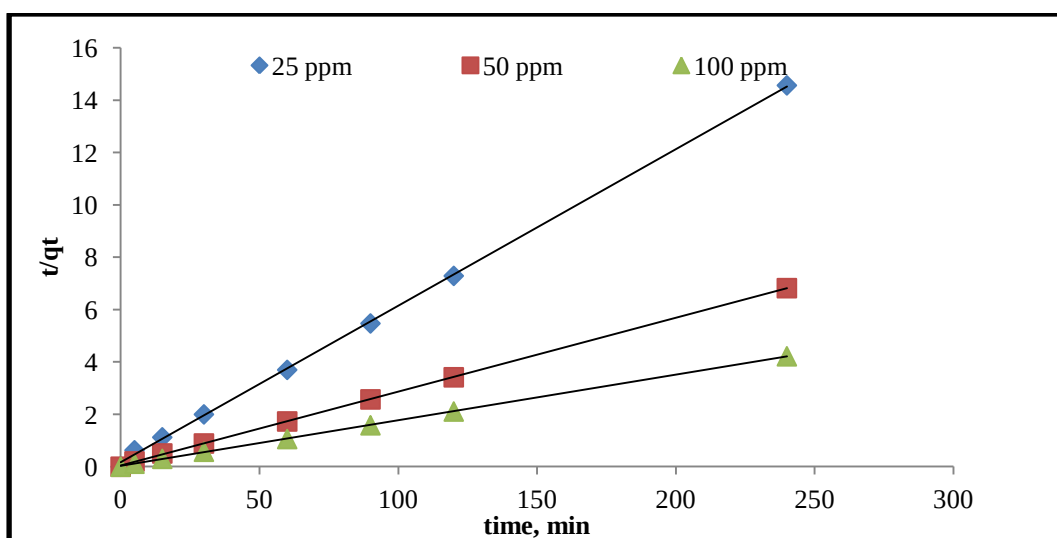
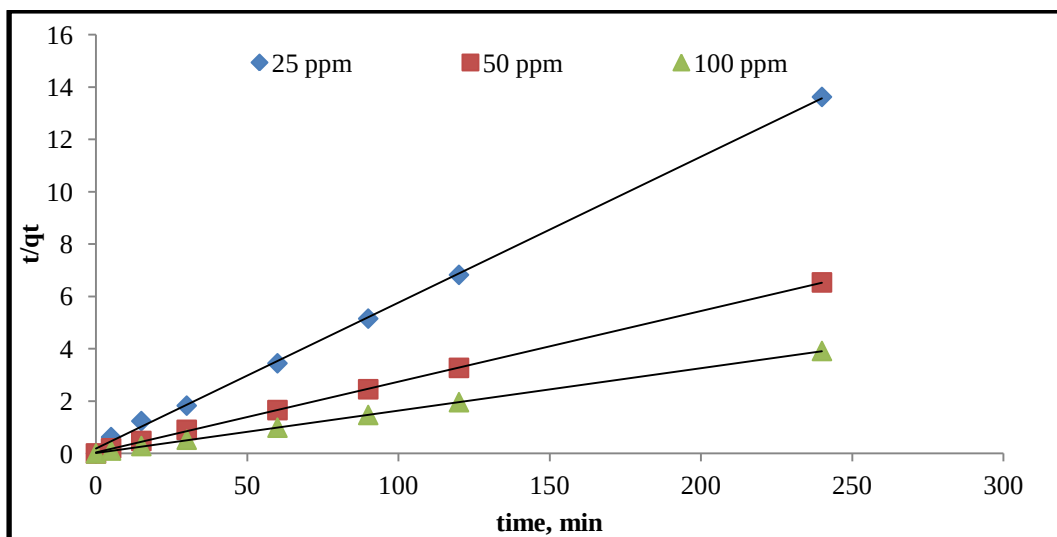
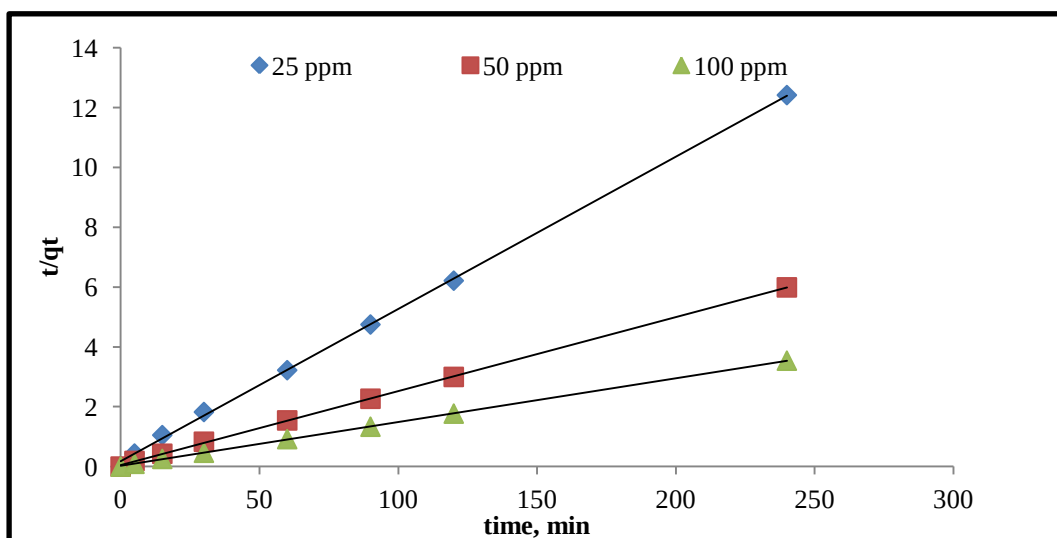


Figure 5.77 Plots of pseudo-second-order kinetics of NB adsorption onto MIL-101: (a) $T = 298\text{ K}$; (b) $T = 308\text{ K}$; (c) $T = 318\text{ K}$

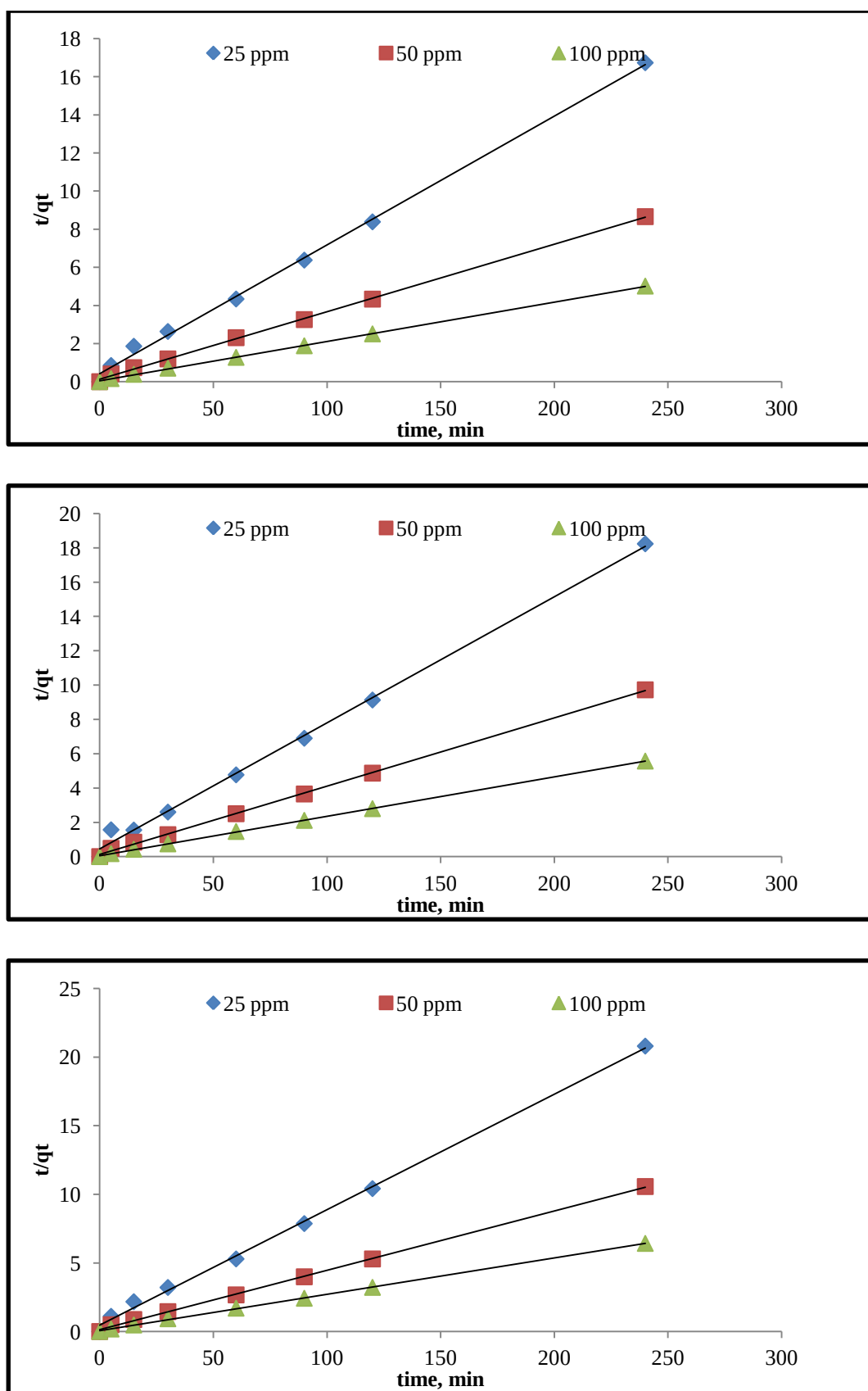


Figure 5.78 Plots of pseudo-second-order kinetics of NB adsorption onto MIL-53 (Fe): (a) $T = 298\text{ K}$; (b) $T = 308\text{ K}$; (c) $T = 318\text{ K}$

Figure 5.73 and 5.74 show the adsorption kinetic experiments of NB onto two different adsorbents were conducted at different temperature (298, 308, and 318 K). Figure 5.73-5.74 also show the effect of contact time on the adsorption of NB. The adsorption equilibrium was reached within 1 h after initiation. Because, early in the time of adsorption, there are numerous vacant surface sites for adsorption and with time the number of vacant sites available decreases and adsorption sites become saturated (Osta et al., 2012; Hasan et al., 2012).

Figure 5.75 - 5.78 shows the pseudo first order, second order kinetic plots. The correlation coefficient values of pseudo second order kinetic model are close to the unity ($R^2 > 0.999$) of NB. Also the q_e values obtained from the experiment is very close to the calculated q_e values from this model. These results show the pseudo-second-order model fits the experimental data quite well for the adsorption of NB onto MIL-101 and MIL-53 (Fe). The constants of the model and initial rates are listed in Table 5.14 and 5.15. Table 5.14 and 5.15 describes the pseudo- first-order and pseudo-second-order kinetic (Figure 5.75-5.78) parameters for different temperatures.

With the increase of the temperature, rate constant increased, that means the initial adsorption rate increased with increasing temperature. However, at a constant temperature, k_2 decreased with the initial concentration of NB (Table 5.14-5.15). Besides the rate constant is generally depended on the pore volume and surface area (Hasan et al., 2012). In this study, obtained results support this case because k_2 values are in order of MIL-53 < MIL-101 suggests potential applications of MOFs with large pore volume in NB removal.

5.2.3.2. Adsorption Mechanism

For NB adsorption onto two MOFs, NB molecules in the aqueous solution diffused to the outside surface of sorbents and then passed through the boundary layer to the inside surface. Finally, these molecules were removed by interacting with adsorbents after entering into the framework via intra-particle diffusion. Generally speaking, the sorption rate in the initial phase was controlled by boundary layer diffusion, while intra-particle diffusion plays a decisive role close to the end of the sorption.

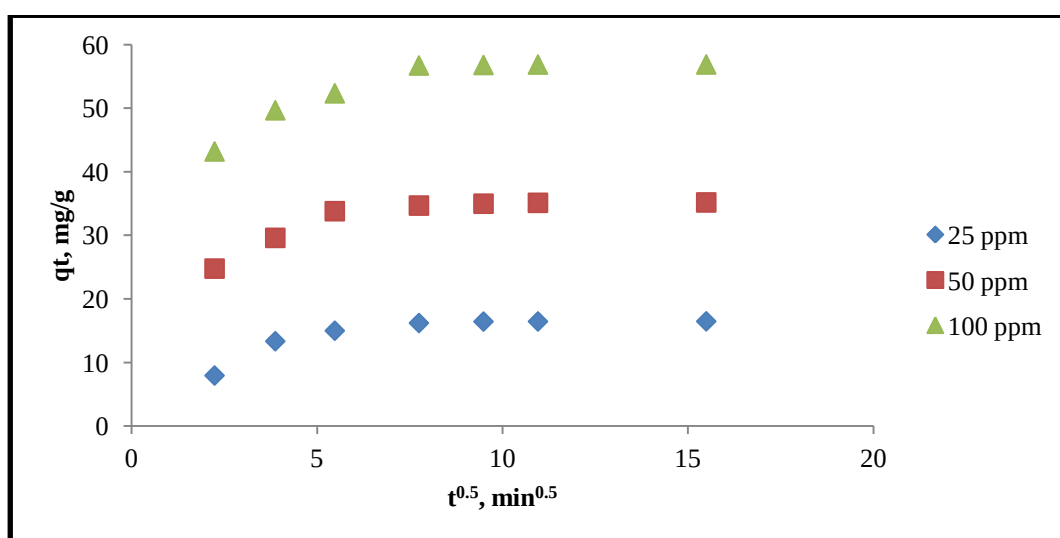
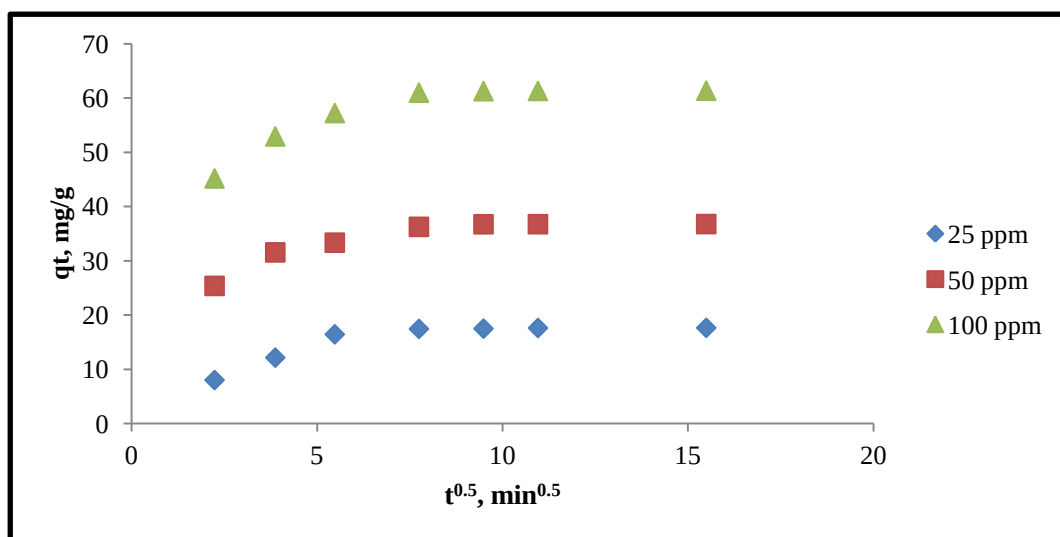
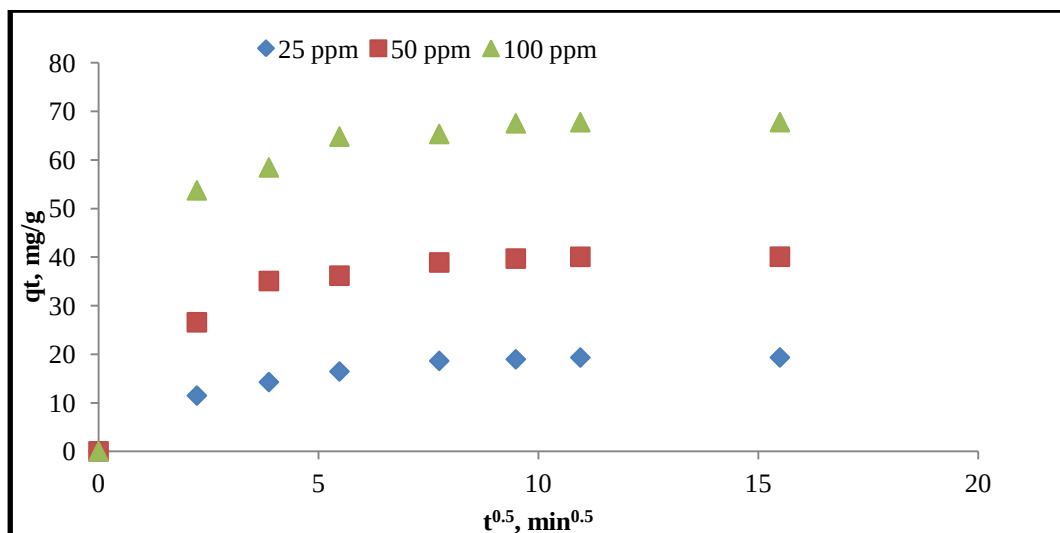


Figure 5.79 Diffusion model plot for the adsorption of NB on MIL-101 at different initial concentrations: (a) $T = 298 \text{ K}$; (b) $T = 308 \text{ K}$; (c) $T = 318 \text{ K}$.

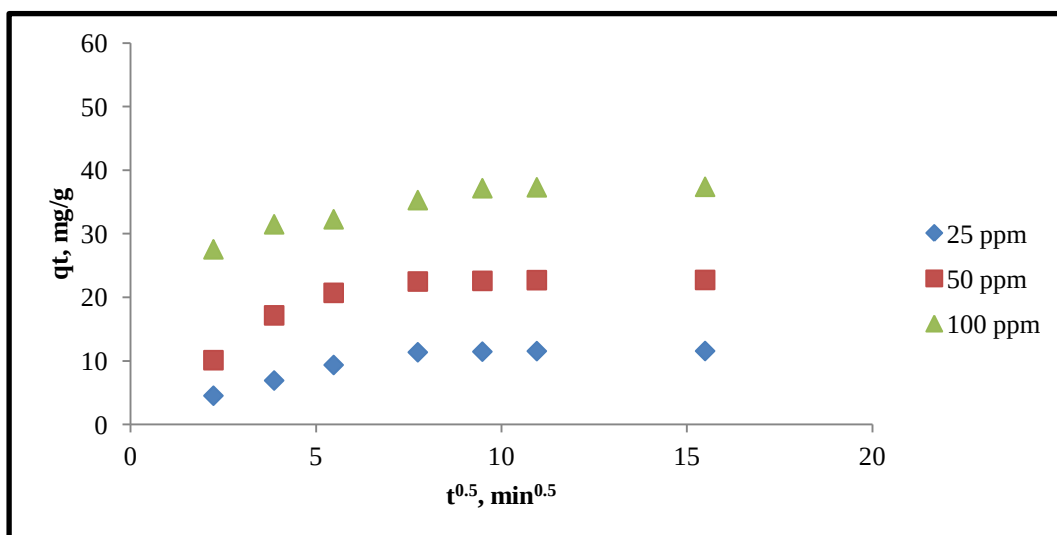
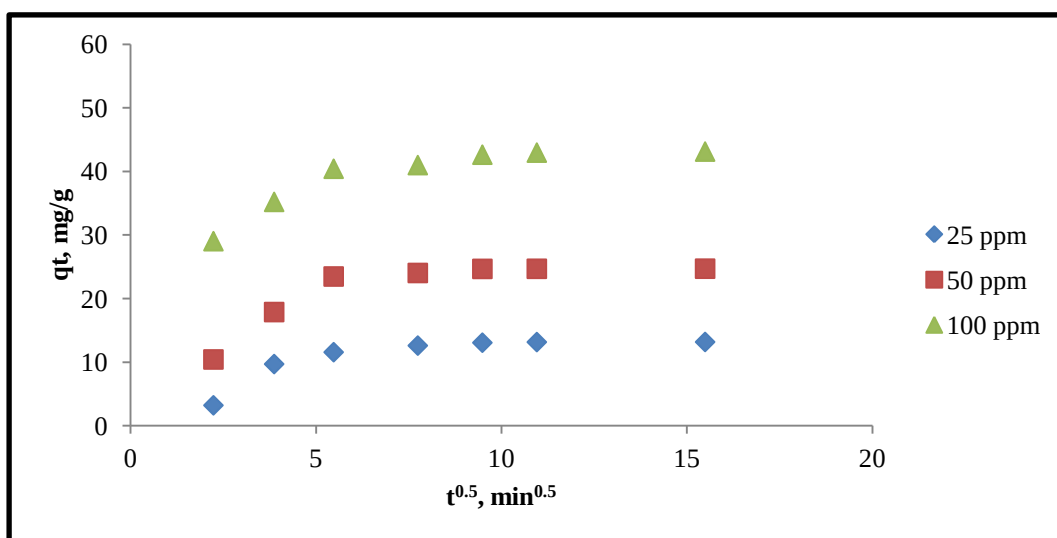
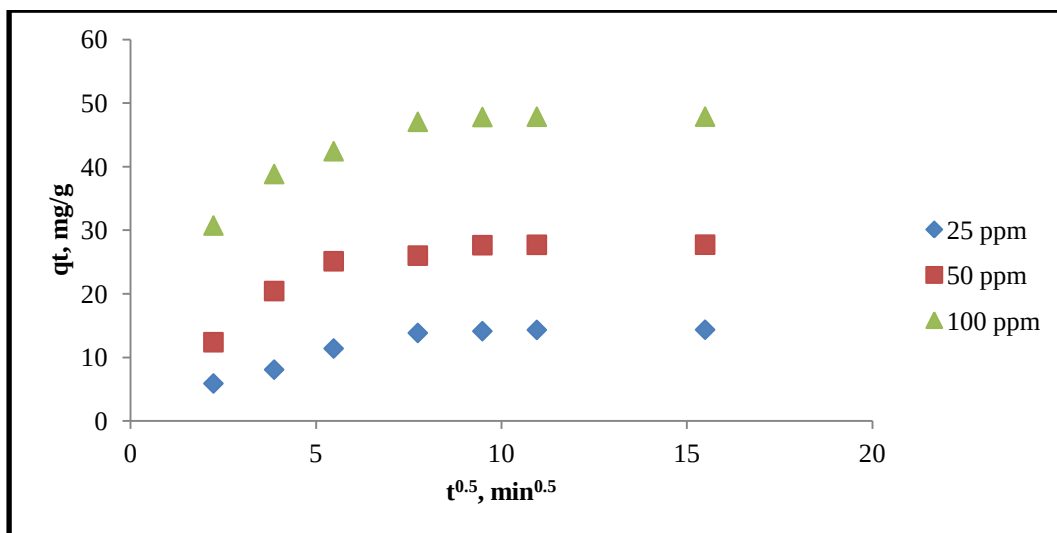


Figure 5.80 Diffusion model plot for the adsorption of NB on MIL-53 (Fe) at different initial concentrations: (a) T = 298 K; (b) T = 308 K; (c) T = 318 K.

As shown in Figure 5.79 and 5.80, the adsorption process had two phases. This situation suggested that the adsorption process proceeded by surface sorption and intraparticle diffusion. The initial part was a boundary-layer effect while the second linear part was due to intraparticle or pore diffusion which proved that the sorption rate in the initial phase was mainly controlled by boundary layer diffusion, and intra-particle diffusion was fast. While with the increase in the adsorption time, intra-particle diffusion plays a more and more important role in rate-limiting. When sorption equilibrium was reaching, particle intra-diffusion was the main factor affecting the sorption rate.

5.2.3.3. Adsorption Isotherms

Adsorption isotherms for NB on MOFs including MIL-101 and MIL-53 (Fe) were studied with different initial concentrations (25-400) at three different temperatures (298, 308 and 318 K) (Figure 5.81). The Langmuir and Freundlich adsorption models (4, 5) were applied for the fitting of the experimental data. The following equations are Langmuir and Freundlich model equations.

Nonlinear curve fitting analysis method in MATLAB programme was also adapted to calculate the parameters of Langmuir and Freundlich isotherm models.

The parameters and the correlation coefficient values calculated from these two models are listed in Table 5.16. It can be seen that, the adsorption isotherms of NB are followed by the Langmuir model.

The Langmuir constant b and the Freundlich constant, K_F decrease with increasing temperature indicating that NB adsorption onto MOFs are exothermic reaction.

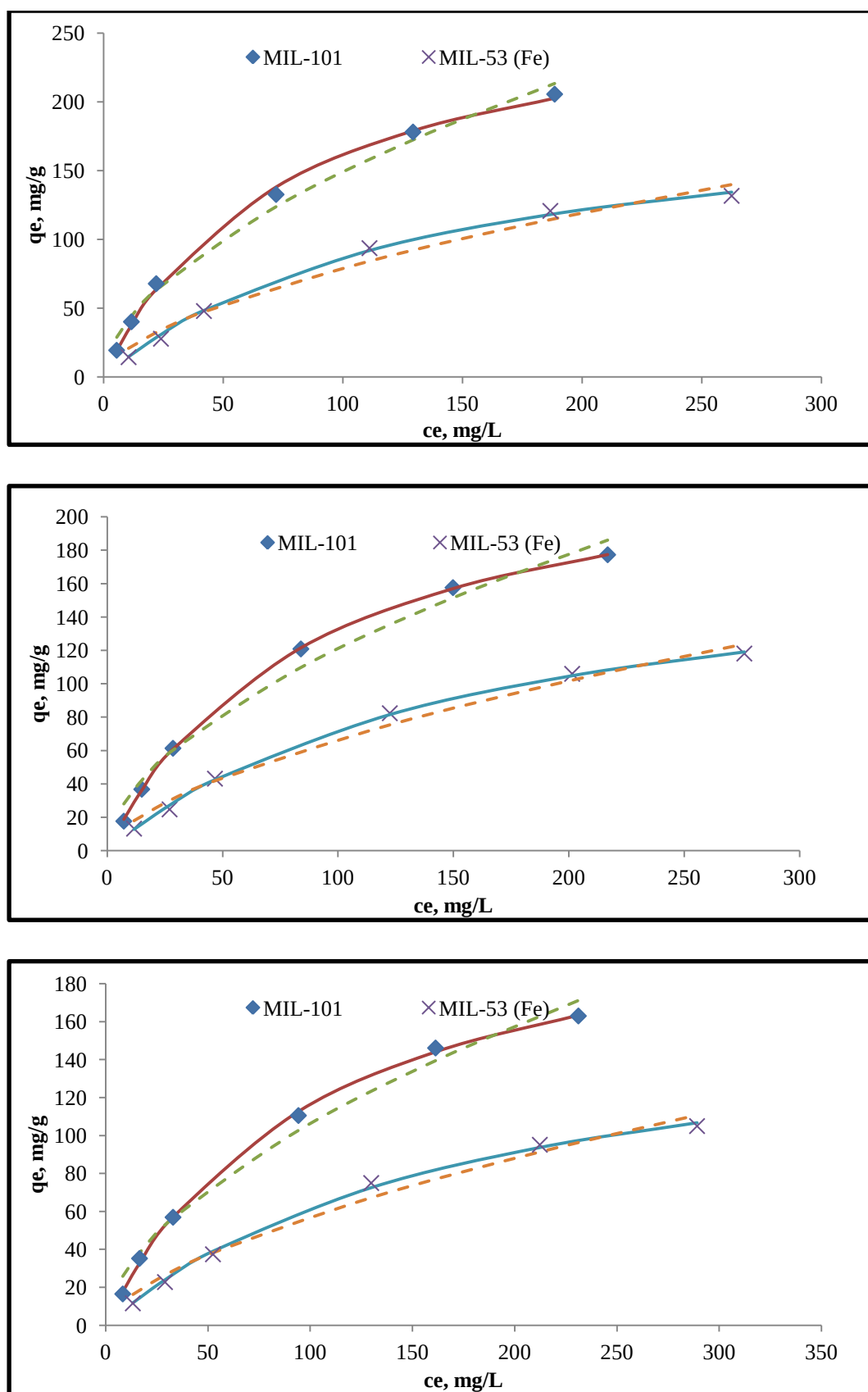


Figure 5.81 Adsorption isotherms for NB adsorption onto the two adsorbents at different temperature: a) $T=298$ K, b) $T=308$ K, c) $T=318$ K. The solid and dashed lines show the calculated results derived from Langmuir and Freundlich isotherm methods respectively.

Table 5.13 The Q_0 values for the adsorption of NB on different adsorbents. (Comparison of adsorption capacity of the MOFs with other adsorbents)

Adsorbent	Q_0 (mg/g)	Surface Area (m^2/g)	Reference
MIL-101	285.5	3193.99	This study
MIL-53 (Fe)	203.2	23.16	This study
MIL-53(Al) obtained was	610	1235	Patil et al., 2011
organoclays	100	5.12	Patel et al
Modified activated carbons	1443.53	926.4	Liu et al
activated carbon(S-23)	550.8	1250	Reungoat et al
faujasite	267.2	750	Reungoat et al

There was no correlation between the nitrobenzene uptake and the surface area of the materials (Table 5.13), that is, the surface area of the material is not the main criteria for its uptake of nitrobenzene. The high uptake in modified activated carbon is mainly good development of mesopores along with presence of micropores. It has been established that for the adsorption of organic molecules in activated carbon the presence of mesopores along with micropores enhances their adsorption capacity especially for large molecules. The increased number of mesopores can reduce the length of the diffusion path to the micropores, accelerate the pore diffusion of nitrobenzene molecules, and decrease the resistance to diffusion. The NB adsorption capacity of MIL-101 and MIL-53(Fe) is lower than that of activated carbon although MIL-101 has larger surface area; this may be due to nonexistence of mesopores in MIL-101. Thanks to the breathing features of the MIL-53 (Fe) structure, NB enters the pores easily. Its maximum adsorption capacity (Q_0) for NB is nearly closed to that of MIL-101.

5.2.3.4. Adsorption thermodynamics

According to van't hof plot (Figure 5.82), the ΔH° is negative indicates that the adsorption process of NB onto MOFs is exothermic. The negative ΔG° suggests that the adsorption process is spontaneous. The positive entropy change, ΔS , indicates the increased randomness at the solid/solution interface during the adsorption process. All values obtained from the adsorption thermodynamic section were shown in Table 5.17.

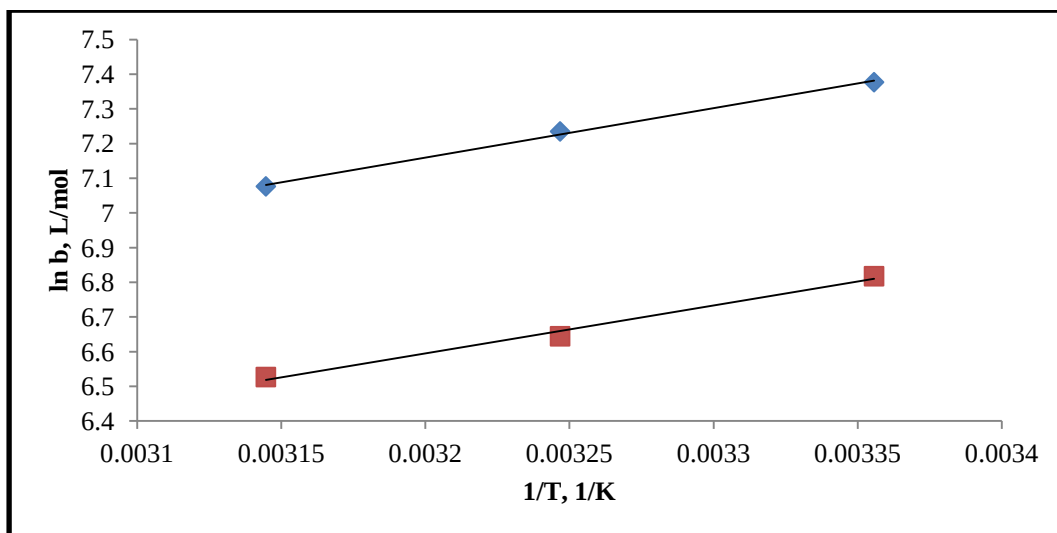


Figure 5.82 van't Hoff plots to get the ΔH and ΔS of the NB adsorption on the different MOFs

5.2.3.5. Effect of regeneration of MOFs

The reusability of MIL-101 and MIL-53 (Fe) were evaluated after washing with methanol, acetone and water at least three times. It is seen from Figure 5.83, MIL-101 have excellent regeneration ability in the adsorptive removal of aromatic compounds from water.

5.2.3.6. Effect of adsorbent dosage

As shown in Figure 5.84, the adsorbed amount of NB increased with increasing adsorbent amounts until 0.1 g but the further increase of the adsorbent amounts doesn't have any effect on the adsorption rate of NB.

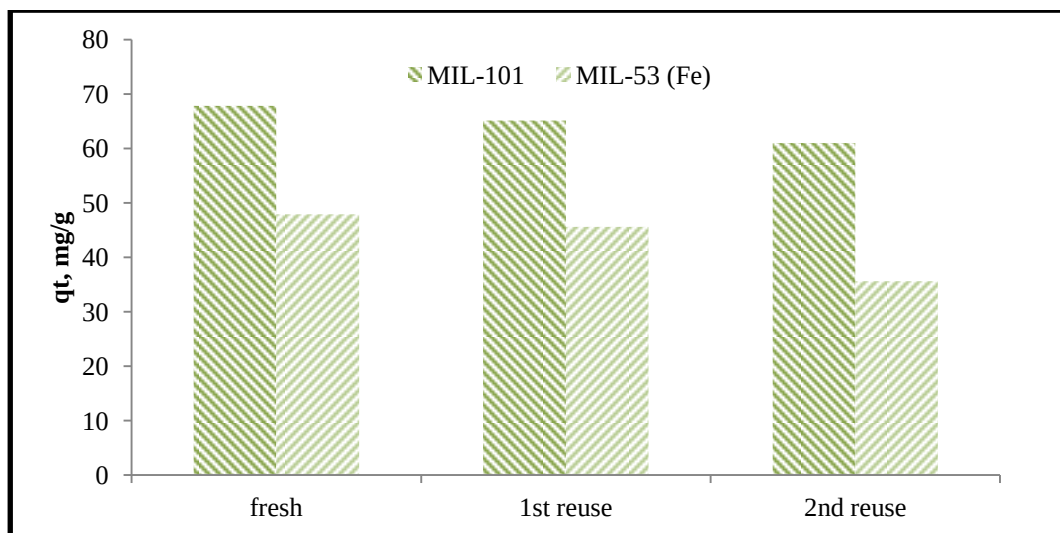


Figure 5.83 The reuse of MOFs on NB adsorption (concentration 100 ppm, $T = 298$ K).

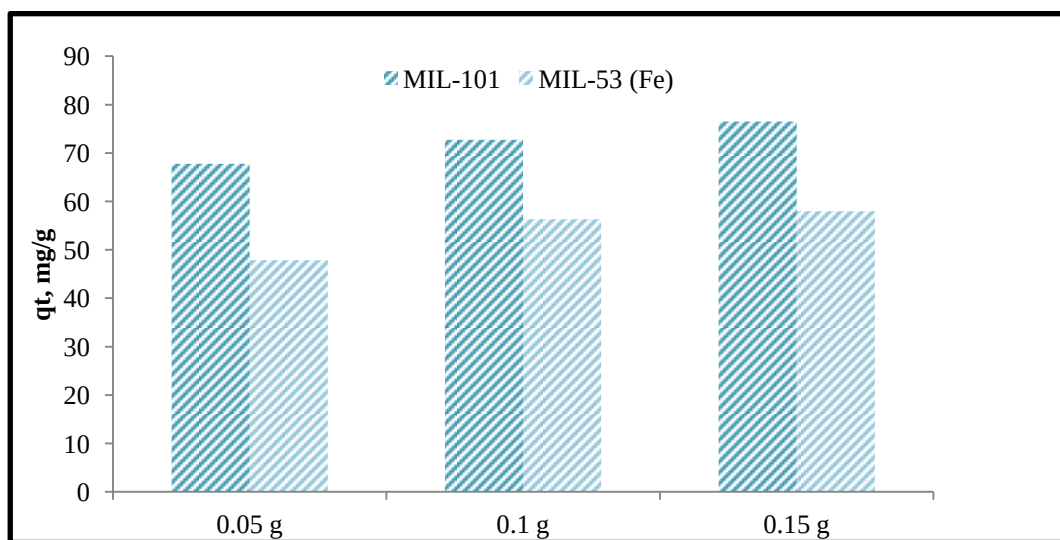


Figure 5.84 Effect of adsorbent dosage (concentration 100 ppm, $T = 298$ K).

Table 5.14 Kinetic constants of NB adsorption onto MIL-101

	C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo first order kinetic constants		Pseudo second order kinetic constants			Intraparticle diffusion model		
			k_1 (g/(mgmin))	R^2	k_2 (g/(mgmin))	R^2	h (mg/(g.min))	k_i (mg / (g.min ^{1/2}))	I (mg/g)	R^2
T=298 K	25	19.327	0.0507	0.9522	0.0149	0.9996	5.757	0.5101	14.039	0.8684
	50	40.065	0.0548	0.9472	0.0124	0.9999	20.449	0.7083	32.735	0.9032
	100	67.786	0.0587	0.9416	0.0104	0.9999	48.543	0.6057	61.267	0.8945
T=308 K	25	17.622	0.0507	0.9478	0.0162	0.9991	5.249	0.2043	15.510	0.7963
	50	36.737	0.0634	0.9737	0.0155	0.9998	21.276	0.6197	30.527	0.7972
	100	61.311	0.0609	0.9655	0.0117	0.9999	44.843	0.7294	54.025	0.7518
T=318 K	25	16.475	0.0580	0.9780	0.0222	0.9986	6.218	0.2660	13.790	0.8142
	50	35.180	0.0476	0.9335	0.0190	0.9998	23.923	0.2398	32.629	0.9173
	100	56.885	0.0648	0.9568	0.0130	0.9998	42.553	0.7991	48.959	0.7153

Table 5.15 Kinetic constants of NB adsorption onto MIL-53 (Fe)

	C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo first order kinetic constants		Pseudo second order kinetic constants			Intraparticle diffusion model		
			k_1 (g/(mgmin))	R^2	k_2 (g/(mgmin))	R^2	h (mg/(g.min))	k_i (mg / (g.min ^{1/2}))	I (mg/g)	R^2
T=298 K	25	14.344	0.0547	0.9849	0.0109	0.9989	2.403	0.0588	13.510	0.6969
	50	27.721	0.0540	0.9656	0.0094	0.9993	7.530	0.1689	25.422	0.4400
	100	47.868	0.0475	0.9721	0.0090	0.9998	21.413	0.0816	46.753	0.4646
T=308 K	25	13.163	0.0528	0.9884	0.0121	0.9966	2.242	0.0601	12.332	0.5461
	50	24.688	0.0618	0.9663	0.0119	0.9991	7.530	0.0660	23.788	0.4452
	100	43.114	0.0407	0.9389	0.0104	0.9998	19.723	0.2259	39.951	0.5877
T=318 K	25	11.540	0.0540	0.9847	0.0151	0.9961	2.135	0.0232	11.210	0.7259
	50	22.721	0.0530	0.9654	0.0136	0.9987	7.256	0.0300	22.287	0.7842
	100	37.377	0.0459	0.9547	0.0107	0.9995	15.313	0.2115	34.465	0.4907

Table 5.16 Adsorption isotherms of NB adsorption onto MOFs

MOFs	T (K)	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
		b (L/mg)	Q ₀ (mg/g)	R ²	K _f (mg/g(L/mg) ^{1/n})	n	R ²
MIL-101	298	0.0129	285.5	0.9978	10.960	1.765	0.9893
	308	0.0112	250.0	0.9999	9.357	1.799	0.9817
	318	0.0096	237.0	0.9990	7.714	1.756	0.9845
MIL-53	298	0.0074	203.2	0.9978	5.213	1.693	0.9757
	308	0.0062	188.2	0.9989	4.002	1.638	0.9836
	318	0.0055	173.3	0.9979	3.242	1.605	0.9802

Table 5.17 Adsorption thermodynamics constants of NB adsorption onto MOFs

MOFs	T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol/K)	R ²
MIL-101	298	-18.27	-11.82	21.67	0.9975
	308	-18.52			
	318	-18.70			
MIL-53	298	-16.89	-11.47	18.11	0.9918
	308	-17.01			
	318	-17.25			

5.2.4. Adsorption of Toluene onto MIL-101 and MIL-53 (Fe)

In liquid phase adsorption of toluene, the effects of temperature, initial concentration, adsorbent amount, and contact time were investigated and also reusability of MIL-101 and MIL-53 was studied. The adsorption kinetics, mechanism isotherms were searched and thermodynamic constants were calculated.

5.2.4.1. Adsorption kinetics

Figure 5.85 and 5.86 show the effect of contact time on the adsorption and kinetic experiment of toluene on two different MOFs including MIL-101 and MIL-53 (Fe). The adsorption equilibrium was reached within 1 h after initiation. To understand the adsorption mechanism, the pseudo-first-order (5.1) and pseudo-second-order kinetic model (5.2) was studied. For this purpose, MO was adsorbed at various times up to 2h.

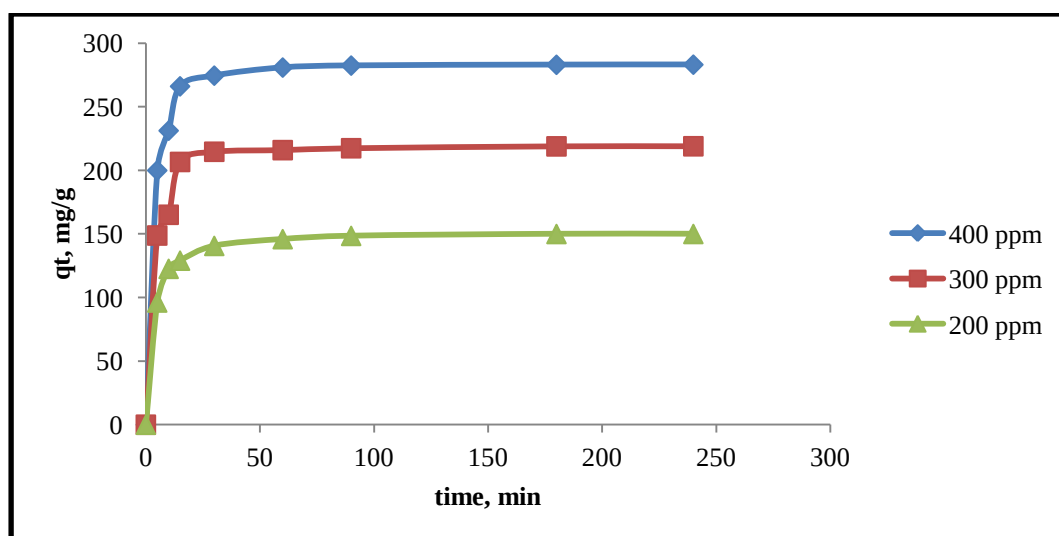
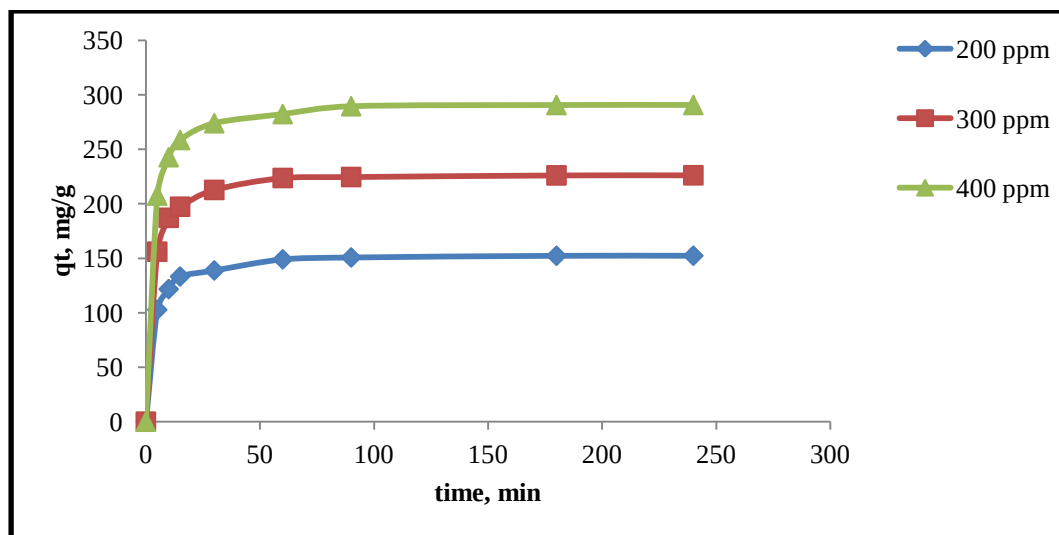
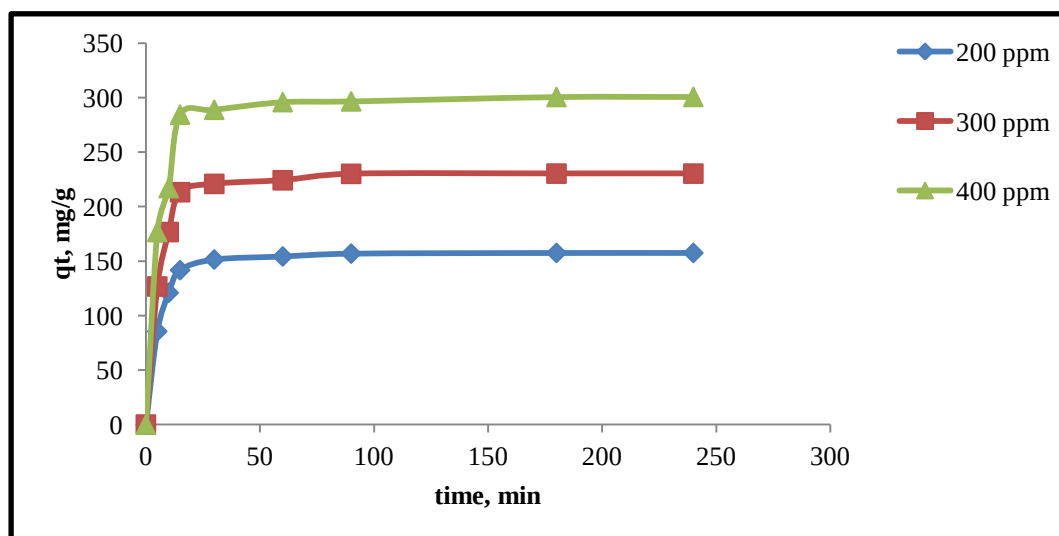


Figure 5.85 Effect of contact time on the adsorption of toluene on MIL-101 at different temperature of (a) $T=298$ K; (b) $T=308$ K; (c) $T=318$ K.

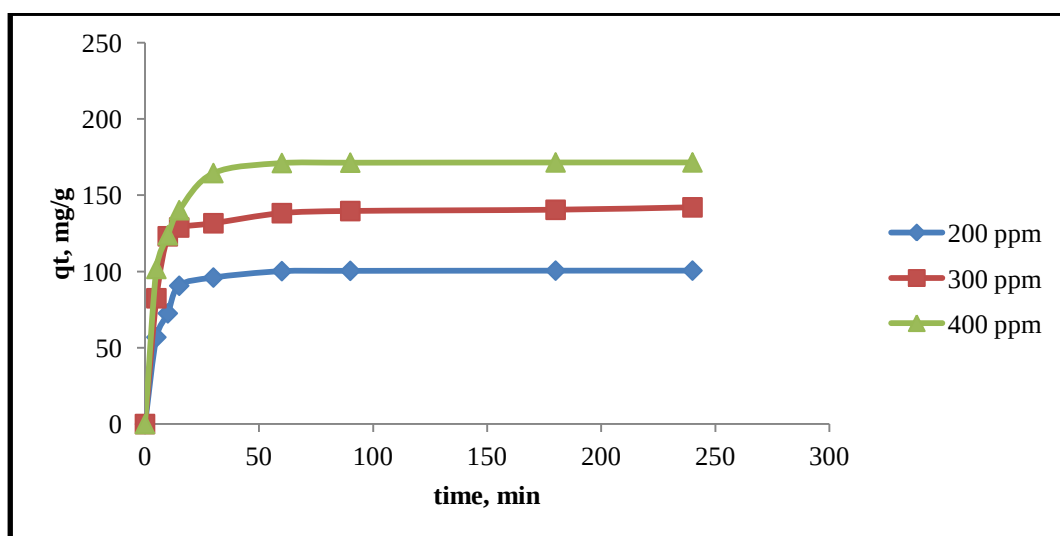
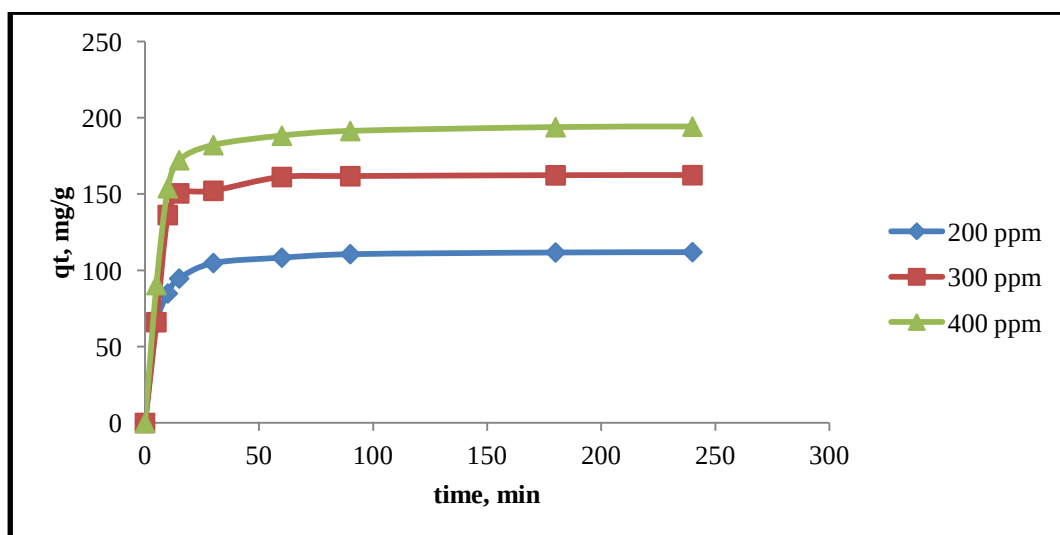
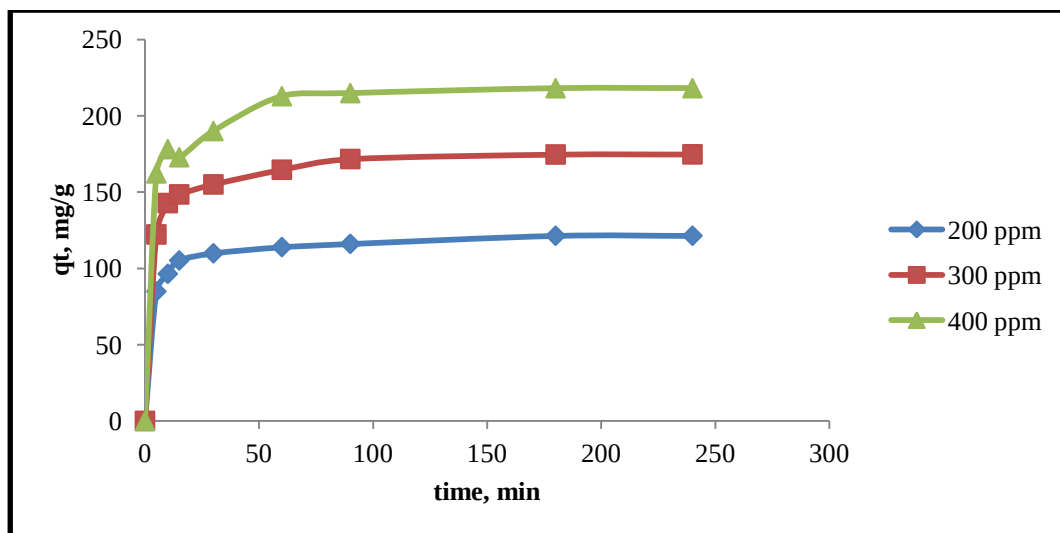


Figure 5.86 Effect of contact time on the adsorption of toluene on MIL-53 (Fe) at different temperature of (a) $T=298$ K; (b) $T=308$ K; (c) $T=318$ K.

Pseudo-First-Order Kinetic Model (Lagergren Equation)

Pseudo first order kinetic model equation (5.1) was applied and the equation was linearized (5.4) to calculate the rate constant k_1 (First order kinetic constants)

The rate constant k_1 is determined from the slope of the plot of $\ln(q_e - q_t)$ versus contact time (t) (Lagergren, 1898).

Figure 5.87-5.88 shows the plots of pseudo-first-order kinetics of MR adsorption onto MIL-101 and MIL-53 (Fe) at three different temperature ($T = 298, 308$ and 318K).

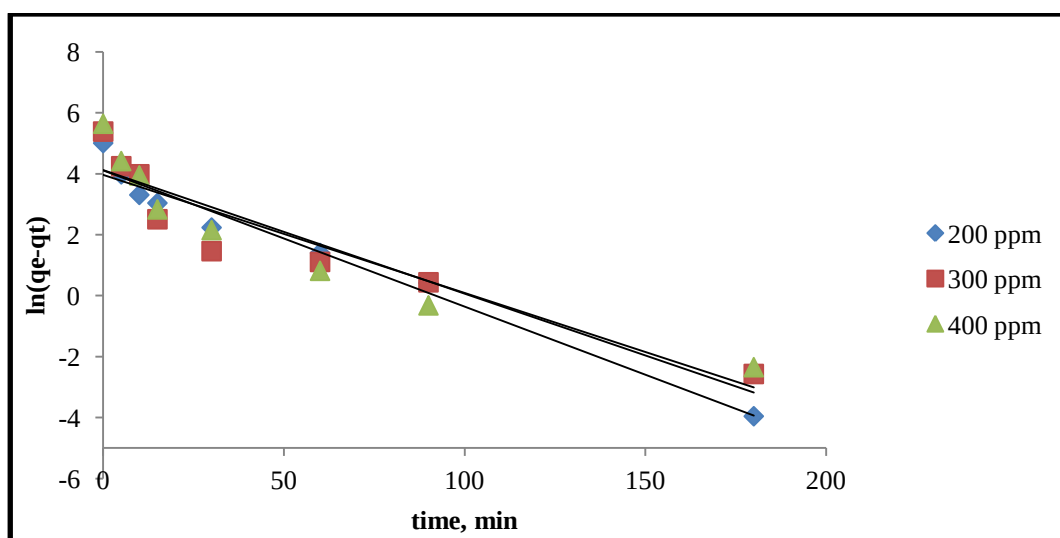
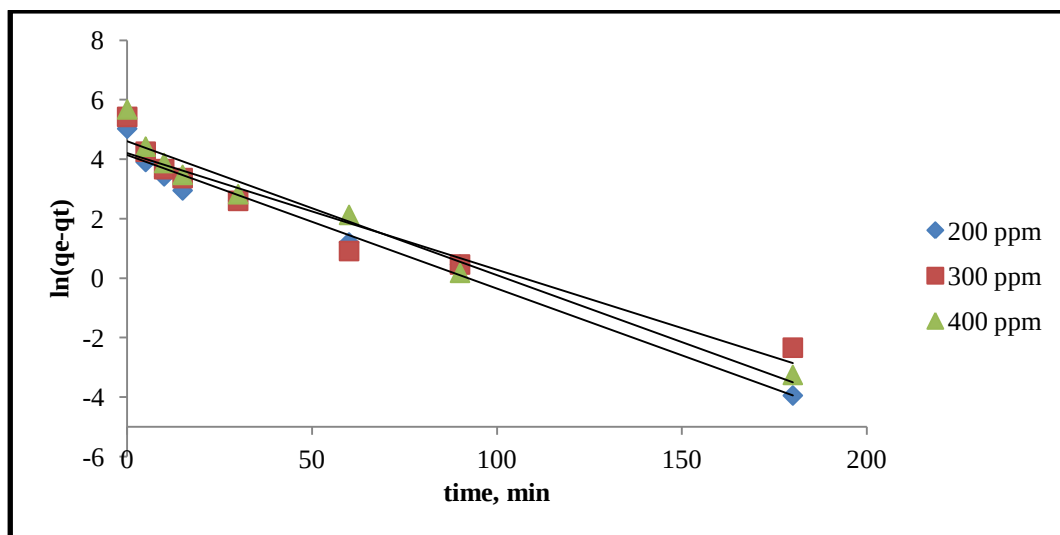
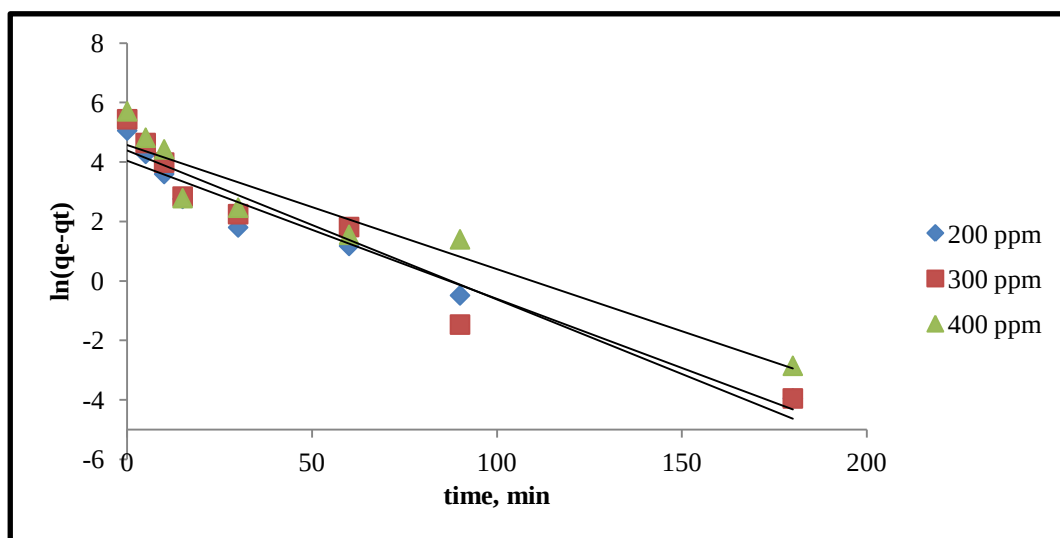


Figure 5.87 Plots of pseudo-first-order kinetics of toluene adsorption onto MIL-101: (a) $T = 298$ K; (b) $T = 308$ K; (c) $T = 318$ K

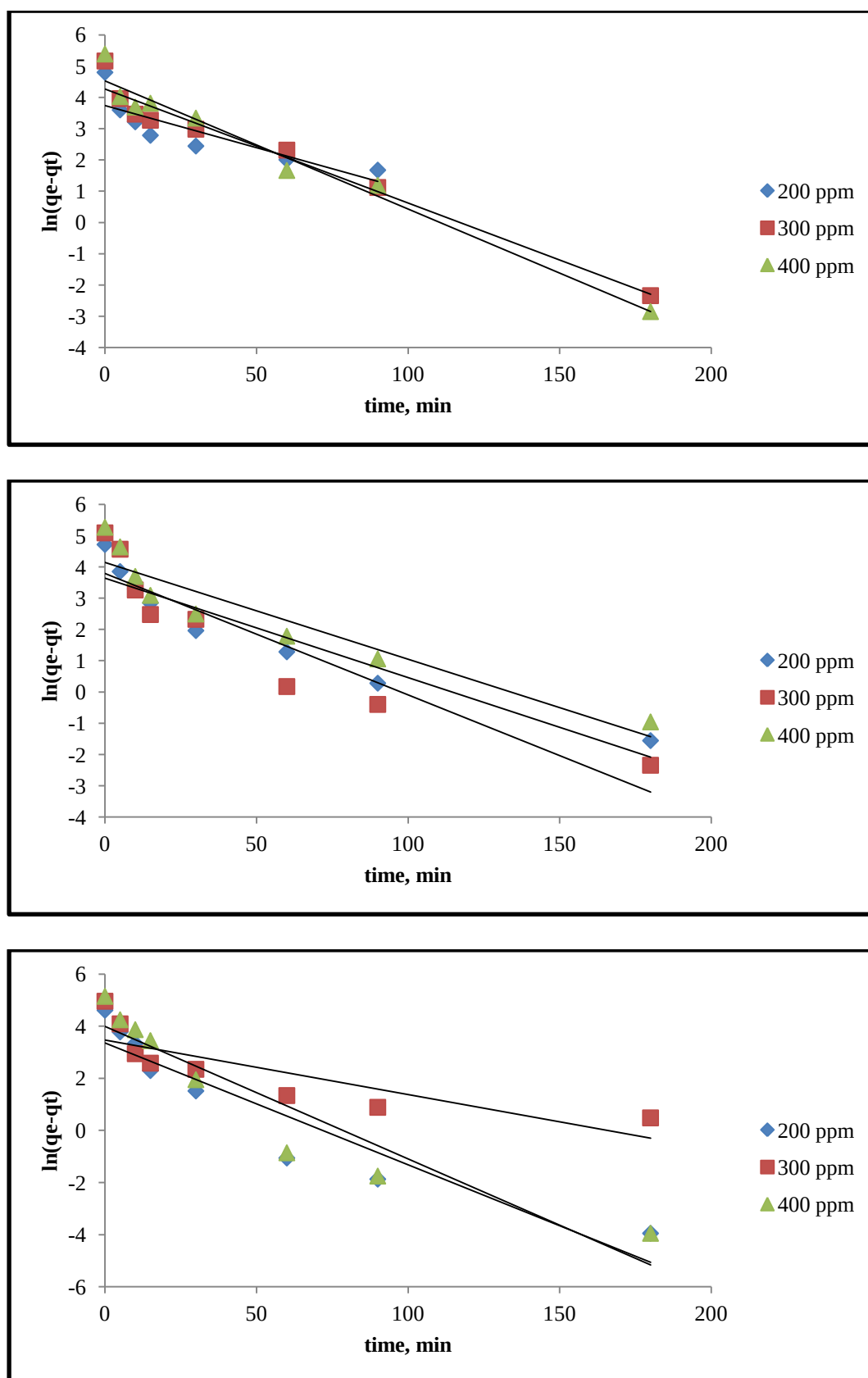


Figure 5.88 Plots of pseudo-first-order kinetics of toluene adsorption onto MIL-53 (Fe): (a) $T = 298\text{ K}$; (b) $T = 308\text{ K}$; (c) $T = 318\text{ K}$

Pseudo- Second- Order Kinetic Model

Pseudo second order kinetic model equation (5.2) was applied and the equation was linearized (5.5) to calculate the rate constant k_2 (second order kinetic constants)

The rate constant k_2 is determined from the intercept of the plot of t/q_t versus contact time (t).

Figure 5.89-5.90 shows the plots of pseudo-second-order kinetics of MO adsorption onto MIL-101 and MIL-53 (Fe) at three different temperature ($T = 298, 308$ and 318K).

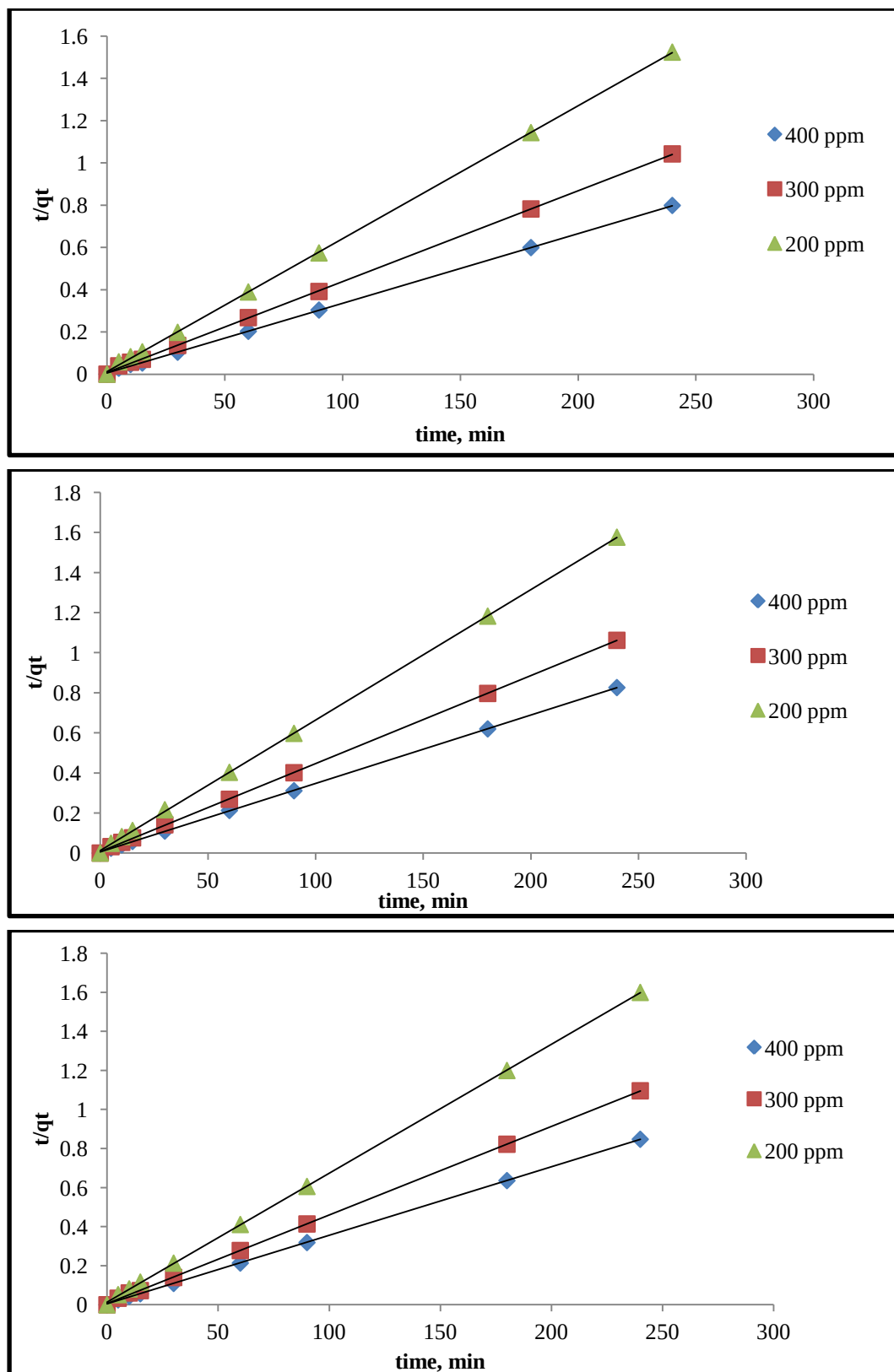


Figure 5.89 Plots of pseudo-second-order kinetics of toluene adsorption onto MIL-101: (a) $T = 298\text{ K}$; (b) $T = 308\text{ K}$; (c) $T = 318\text{ K}$

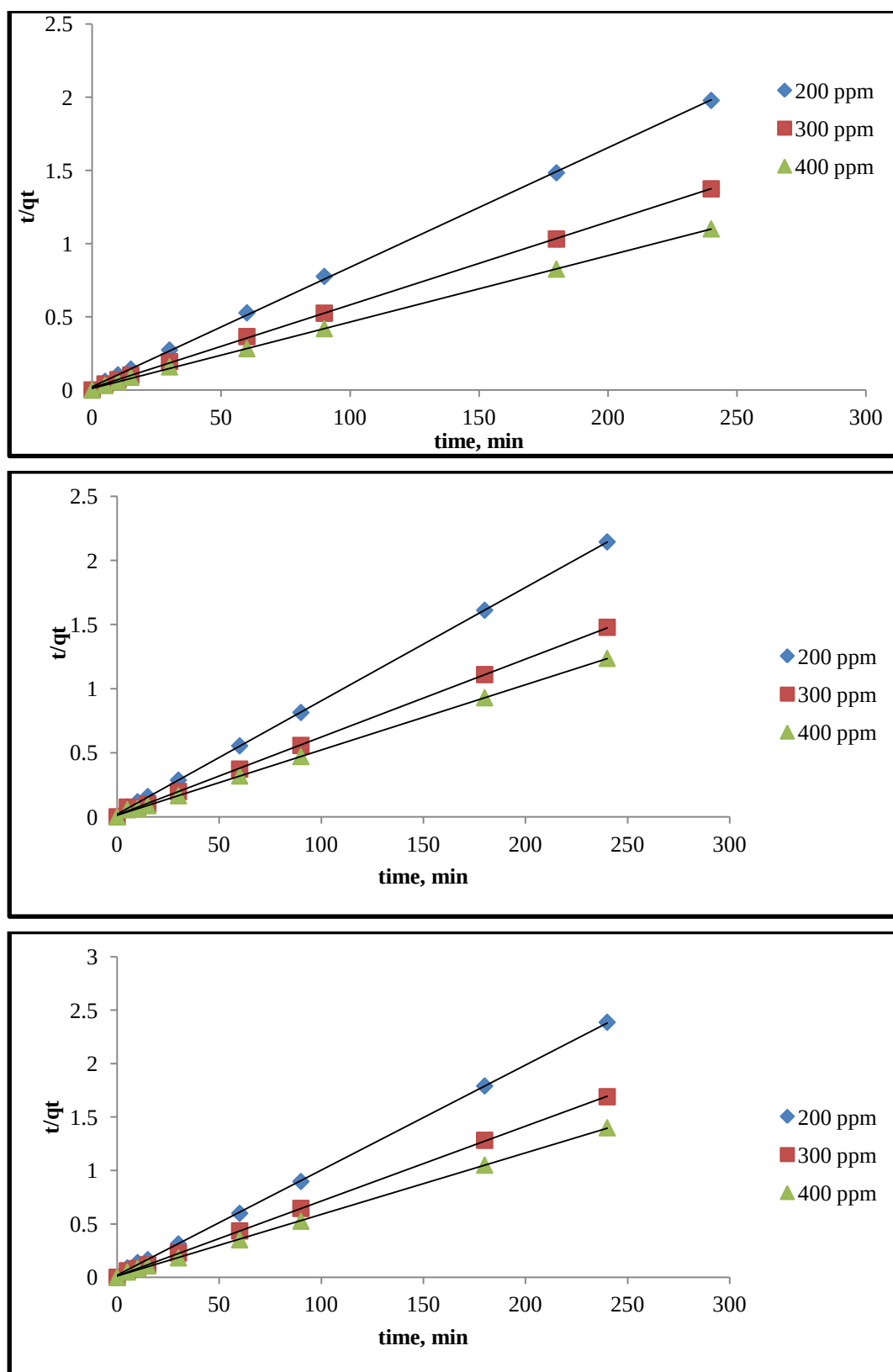


Figure 5.90 Plots of pseudo-second-order kinetics of toluene adsorption onto MIL-53 (Fe): (a) $T = 298$ K; (b) $T = 308$ K; (c) $T = 318$ K

Figure 5.85 and 5.86 show the adsorption kinetic experiments of toluene onto MIL-101 and MIL-53 (Fe) were conducted at different temperature (298, 308, and 318 K). These figure also shows the effect of contact time on the adsorption of MR. The adsorption equilibrium was reached within 1 h after initiation. Because, early in the time of adsorption, there are numerous vacant surface sites for adsorption and with time the number of vacant sites available decreases and adsorption sites become saturated (Osta et al., 2012; Hasan et al., 2012).

Figure 5.87-5.90 shows the pseudo first order, second order kinetic plots. The correlation coefficient values of pseudo second order kinetic model are close to the unity ($R^2 > 0.999$) of toluene. This result shows the pseudo-second-order model fits the experimental data quite well for the adsorption of toluene onto MOFs. The constants of the model and initial rates are listed in Table 5.19, 5.20.

With the increase of the temperature, rate constant increased, that means the initial adsorption rate increased with increasing temperature. However, at a constant temperature, k_2 decreased with the initial concentration of toluene (Table 5.19-5.20). Besides the rate constant is generally depended on the surface area and pore volume (Hasan et al., 2012). In this study, obtained results support this case because k_2 values are in order of MIL-53 < MIL-101 suggests potential applications of MOFs with large pore volume and surface area in toluene removal.

5.2.4.2. Adsorption Mechanism

Molecules in the aqueous solution diffused to the outside surface of sorbents and then passed through the boundary layer to the inside surface. Finally, these molecules were removed by interacting with adsorbents after entering into the framework via intra-particle diffusion. Generally speaking, the sorption rate in the initial phase was controlled by boundary layer diffusion, while intra-particle diffusion plays a decisive role close to the end of the sorption.

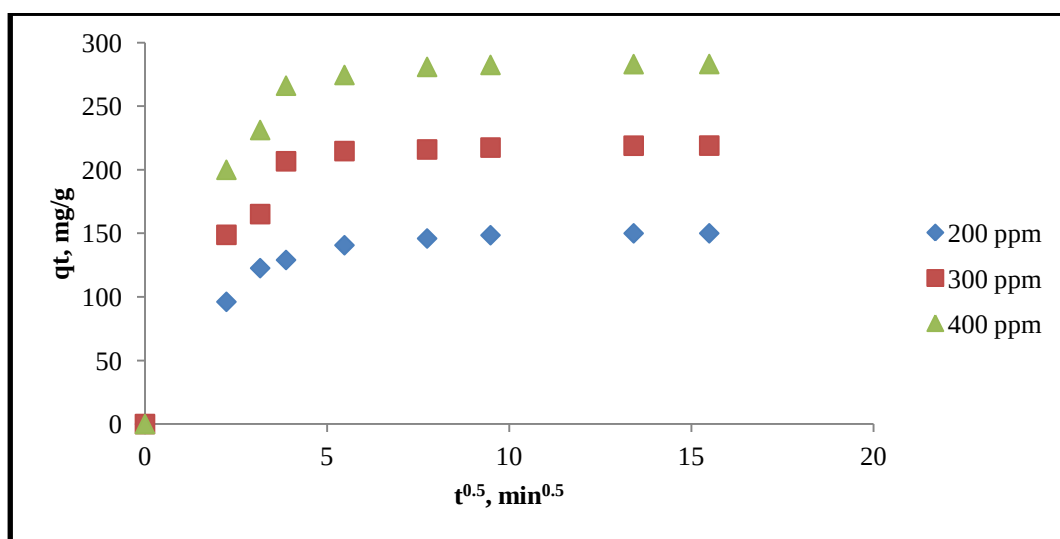
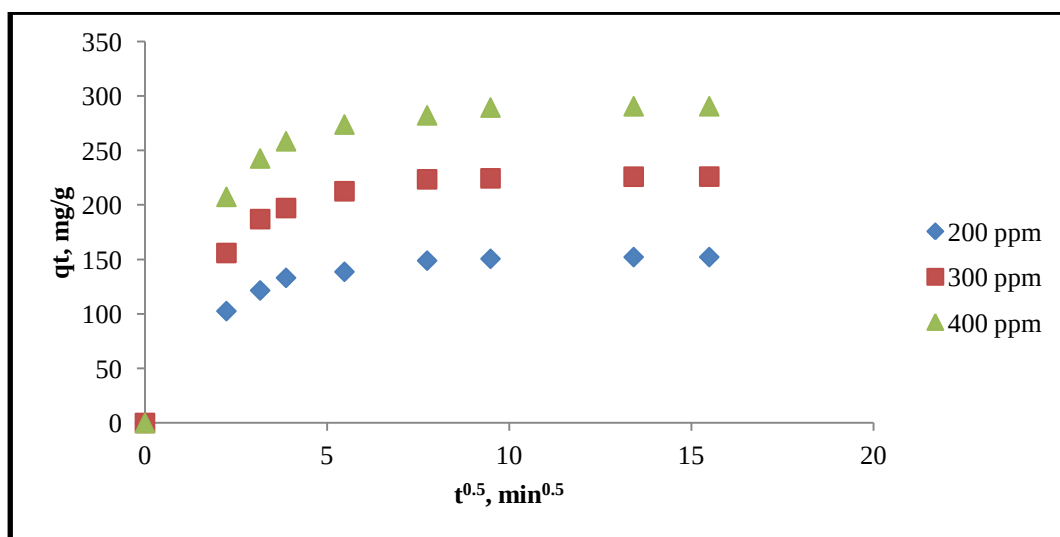
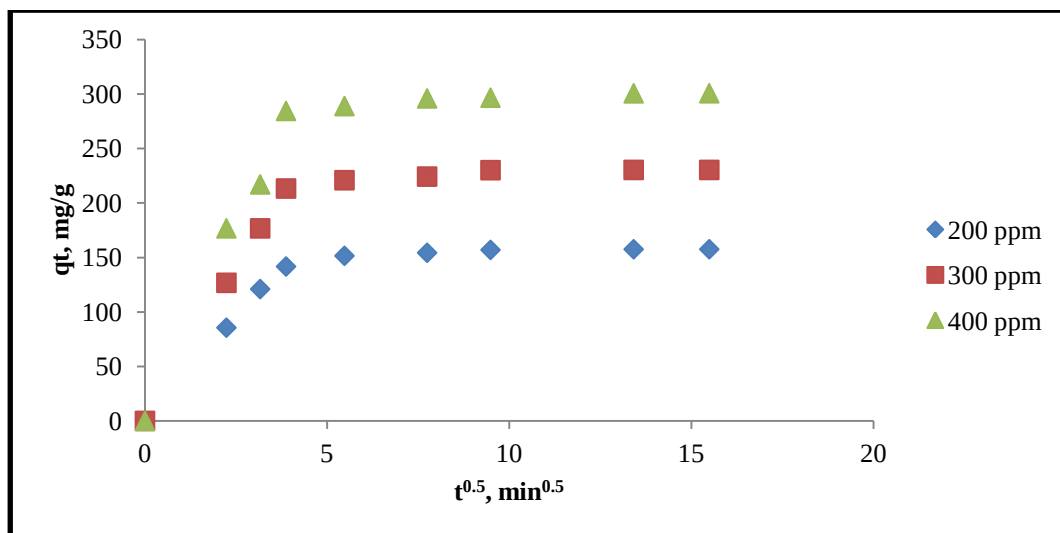


Figure 5.91 Diffusion model plot for the adsorption of toluene on MIL-101 at different initial concentrations: (a) $T = 298 \text{ K}$; (b) $T = 308 \text{ K}$; (c) $T = 318 \text{ K}$.

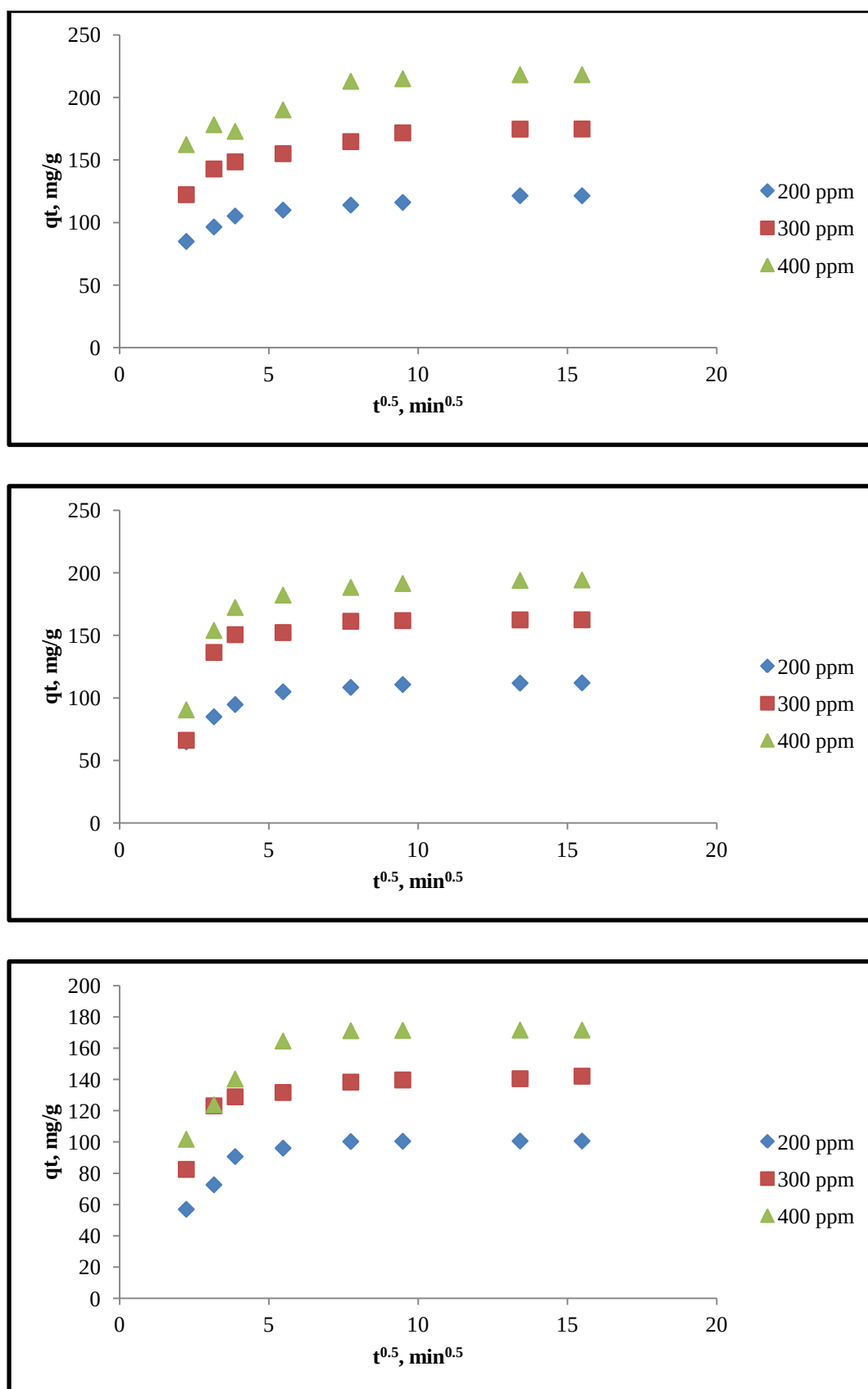


Figure 5.92 Diffusion model plot for the adsorption of toluene on MIL-53 (Fe) at different initial concentrations: (a) $T = 298 \text{ K}$; (b) $T = 308 \text{ K}$; (c) $T = 318 \text{ K}$.

As shown in Figure 5.91 and 5.92, the adsorption process had two phases. This situation suggested that the adsorption process proceeded by surface sorption and intraparticle diffusion. The initial part was a boundary-layer effect while the second linear part was due to intraparticle or pore diffusion which proved that the sorption rate in the initial phase was mainly controlled by boundary layer diffusion, and intra-particle diffusion was fast. While with the increase in the adsorption time, intra-particle diffusion plays a more and more important role in rate-limiting. When sorption equilibrium was reaching, particle intra-diffusion was the main factor affecting the sorption rate.

5.2.4.3. Adsorption Isotherms

Adsorption isotherms for toluene on MOFs (MIL-101 and MIL-53 (Fe)) were studied with different initial concentration (200-400 ppm) at different temperature (298, 308 and 318 K) (Figure 5.93). The Langmuir and Freundlich adsorption models (5,6) were applied for the fitting of the experimental data

Nonlinear curve fitting analysis method in MATLAB programme was also adapted to calculate the parameters of Langmuir and Freundlich isotherm models.

The parameters and the correlation coefficient values calculated from these two models are listed in Table 5.21. The adsorption isotherms of toluene are fitted well by the Freundlich model.

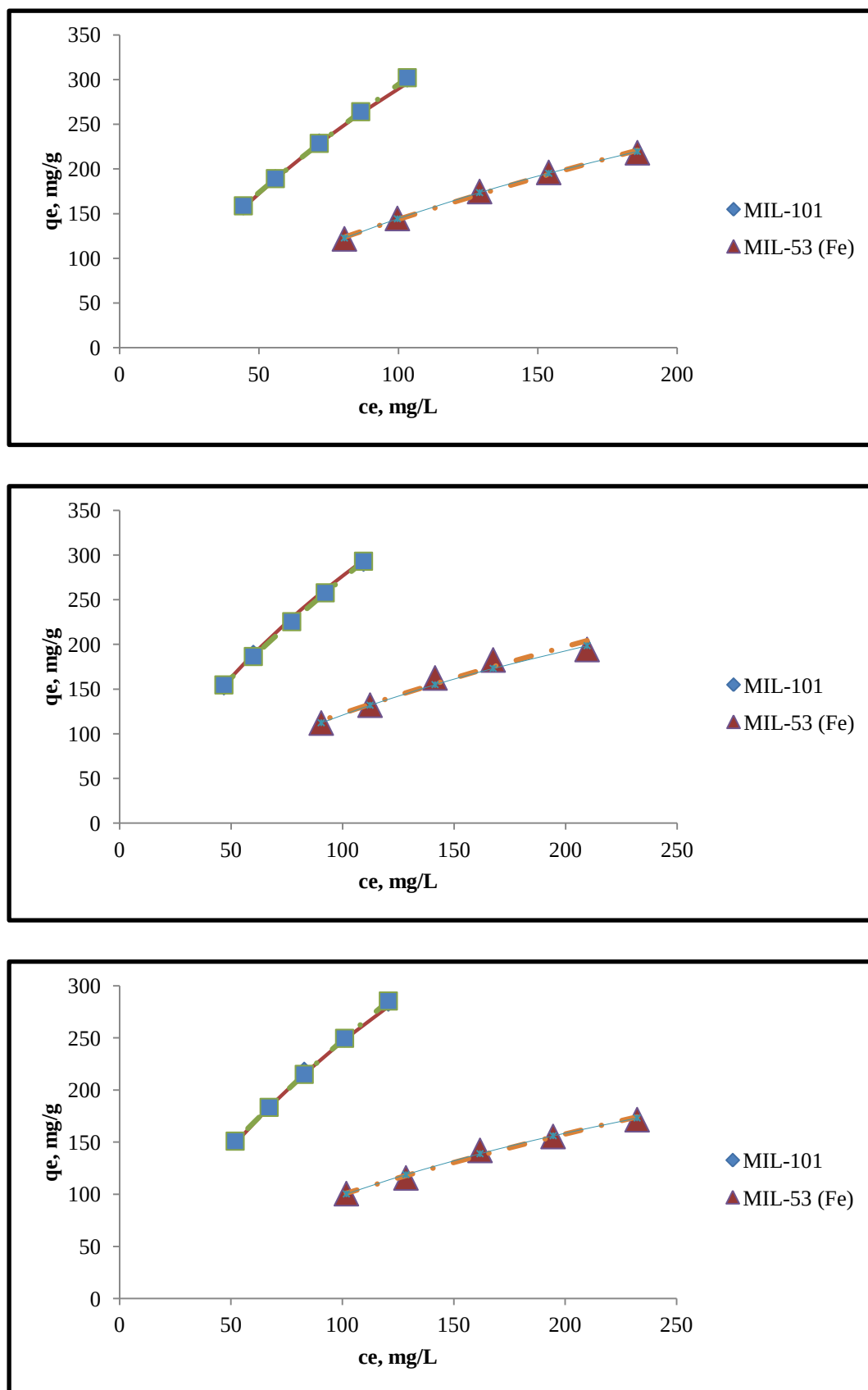


Figure 5.93 Adsorption isotherms for toluene adsorption onto the two adsorbents at different temperature: a) $T = 298$ K, b) $T = 308$ K, c) $T = 318$ K. The solid and dashed lines show the calculated results derived from Langmuir and Freundlich isotherm methods respectively.

Table 5.18 The Q_0 values for the adsorption of toluene on different adsorbents. (Comparison of adsorption capacity of the MOFs with other adsorbents)

Adsorbent	Q_0 (mg/g)	Surface Area (m^2/g)	Reference
MIL-101	909.09	3193.99	This study
MIL-53 (Fe)	555.55	23.16	This study
Commercial clay	247.98	59.87	Bedin et al., 2013
Organoclay	137.75	6.23	Bedin et al., 2013
Molecular sieve	45	414.17	Yu et al., 2012
F-400, Activated carbon	279.16	863.66	Wibowo et al., 2007

It can be said from Table 5.18 MIL-101 and MIL-53 (Fe) have higher toluene adsorption capacity than the other adsorbents. This result indicates MIL-101 having large surface area and MIL-53 (Fe) with flexible structure show excellent adsorption capacity for toluene

5.2.4.4. Adsorption thermodynamics

According to van't Hoff plot (Figure 5.94), the ΔH° is negative indicates that the adsorption process of NB onto MOFs is exothermic. The negative ΔG° suggests that the adsorption process is spontaneous. The positive entropy change, ΔS , indicates the increased randomness at the solid/solution interface during the adsorption process. All values obtained from the adsorption thermodynamic section were shown in Table 5.22.

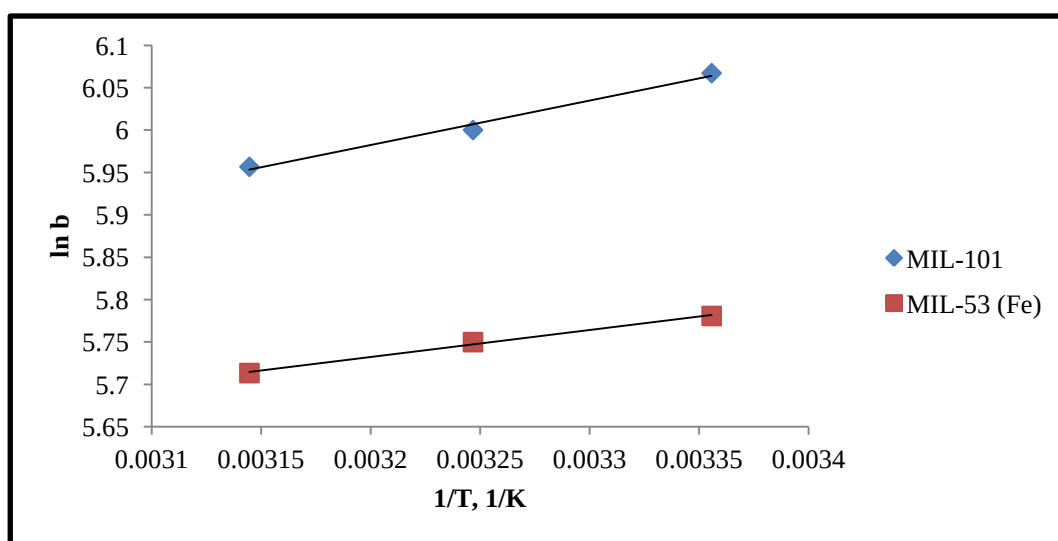


Figure 5.94 van't Hoff plots to get the ΔH and ΔS of the toluene adsorption on the different MOFs

5.2.4.5. Effect of regeneration of MOFs

The reusability of MIL-101 and MIL-53 (Fe) were evaluated after washing with methanol, acetone and water at least three times. It is seen from Figure 5.95 MOFs have excellent regeneration ability in the adsorptive removal of aromatic compounds from water.

5.2.4.6. Effect of adsorbent dosage

The effect of the adsorbent dosage on adsorption capacity was also investigated. As shown in Figure 5.96, the adsorbed amount of toluene increased with increasing adsorbent amounts until 0.1 g. With the further increase of the adsorbent amounts doesn't have any effect on the adsorption rate of toluene.

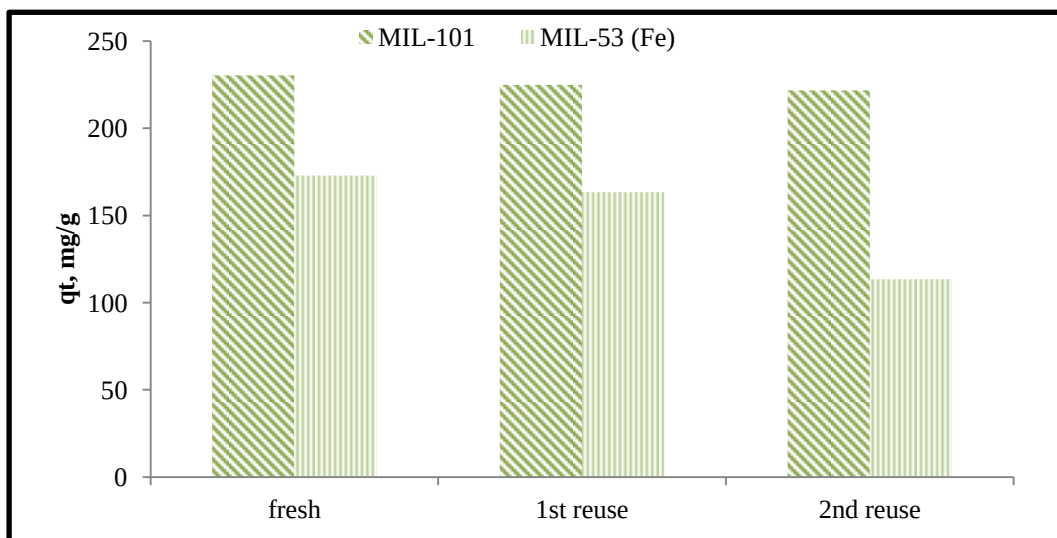


Figure 5.95 The reuse of MOFs on toluene adsorption (concentration 100 ppm, $T = 298$ K).

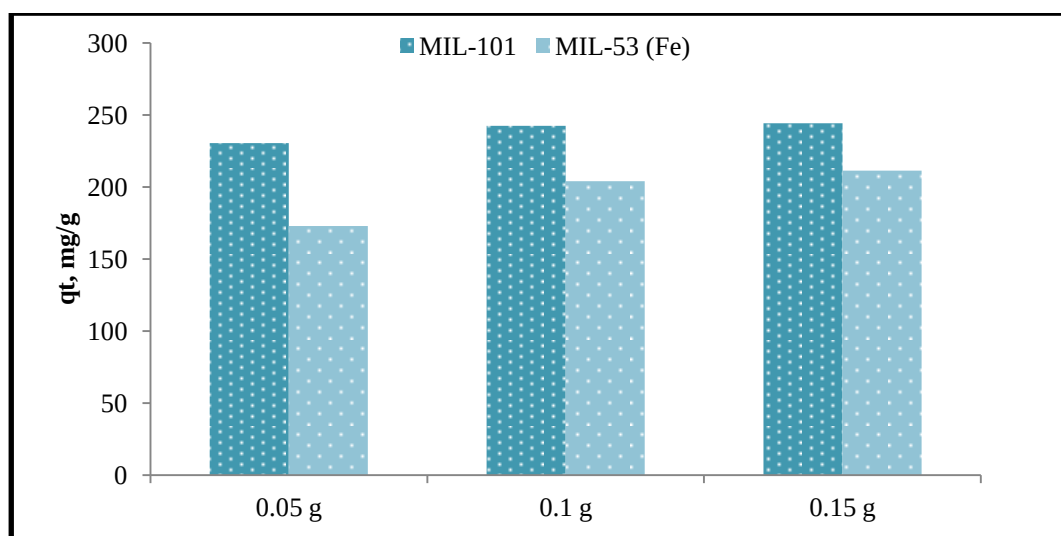


Figure 5.96 Effect of adsorbent dosage (concentration 100 ppm, $T = 298$ K).

Table 5.19 Kinetic constants of toluene adsorption onto MIL-101

		Pseudo first order kinetic constants			Pseudo second order kinetic constants			Intraparticle diffusion model		
	C_0 (mg/L)	$q_{e,exp}$ (mg/g)	k_1 (g/(mgmin))	R^2	k_2 (g/(mgmin))	R^2	h (mg/(g.min))	k_i (mg / (g.min ^{1/2}))	I (mg/g)	R^2
T=298 K	25	157.5192	0.0465	0.9568	0.003101	0.9998	78.125	2.489	134.54	0.8582
	50	230.3077	0.0501	0.9314	0.002175	0.9998	117.6471	2.7815	203.6	0.9575
	100	300.6538	0.0418	0.9152	0.001702	0.9998	156.25	2.2919	276.23	0.9401
T=308 K	25	152.25	0.0449	0.9752	0.003201	0.9992	75.75758	3.2994	120.96	0.9579
	50	226.0769	0.0392	0.9308	0.002689	0.9993	138.8889	4.8244	182.43	0.8811
	100	290.6154	0.045	0.9662	0.002102	0.9994	181.8182	5.2443	241.14	0.9488
T=318 K	25	150.0385	0.0447	0.9724	0.003325	0.9992	76.33588	3.2908	119.18	0.8869
	50	219.0192	0.0388	0.8789	0.003068	0.9993	151.5152	1.7162	202.3	0.7777
	100	283.1923	0.0406	0.8835	0.002917	0.9994	238.0952	2.8775	256.9	0.9200

Table 5.20 Kinetic constants of toluene adsorption onto MIL-53 (Fe)

		Pseudo first order kinetic constants			Pseudo second order kinetic constants			Intraparticle diffusion model		
	C_0 (mg/L)	$q_{e,exp}$ (mg/g)	k_1 (g/(mgmin))	R^2	k_2 (g/(mgmin))	R^2	h (mg/(g.min))	k_i (mg /(g.min ^{1/2}))	I (mg/g)	R^2
T=298 K	25	121.3654	0.027	0.7213	0.003113	0.9997	46.2963	1.0361	106.22	0.9425
	50	174.7115	0.0365	0.9635	0.002288	0.9998	70.42254	1.1746	157.85	0.7727
	100	218.1154	0.041	0.9713	0.001808	0.9997	89.28571	0.7035	207.85	0.9349
T=308 K	25	111.9615	0.0318	0.9096	0.003602	0.9998	46.51163	0.4244	105.78	0.8255
	50	162.4038	0.0389	0.8663	0.002584	0.9994	69.44444	0.1514	160.17	0.9388
	100	194.2308	0.031	0.8895	0.00197	0.9997	75.75758	0.7358	183.44	0.9000
T=318 K	25	100.5769	0.0468	0.8865	0.004875	0.9998	50.76142	0.0421	99.961	0.8766
	50	142.0385	0.0209	0.686	0.003657	0.9998	74.62687	0.4332	135.08	0.9336
	100	171.5192	0.0509	0.8935	0.002649	0.9997	78.74016	0.0509	170.78	0.8532

Table 5.21 Adsorption isotherms of toluene adsorption onto MOFs

MOFs	T (K)	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
		b (L/mg)	Q ₀ (mg/g)	R ²	Kf (mg/g(L/mg) ^{1/n})	n	R ²
MIL-101	298	0.0046	909.09	0.9983	8.772	1.310	0.9993
	308	0.0043	909.09	0.9914	8.544	1.328	0.9974
	318	0.0041	833.33	0.9918	7.663	1.325	0.9982
MIL-53 (Fe)	298	0.0035	555.55	0.9954	5.810	1.435	0.9956
	308	0.0034	476.19	0.9873	5.208	1.456	0.9689
	318	0.0032	400.00	0.9947	4.702	1.507	0.9904

Table 5.22 Adsorption thermodynamics constants of toluene adsorption onto MOFs

MOFs	T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol/K)	R ²
MIL-101	298	-15.03	-4.36	35.77	0.9882
	308	-15.36			
	318	-15.74			
MIL-53 (Fe)	298	-14.32	-2.64	39.18	0.9954
	308	-14.72			
	318	-15.10			

5.3. Usage of MOFs as Catalysts

Esterification of butanol, methanol and hexanol with acetic acid was investigated in a batch reactor as explained in Section 4.2.

In this study, MIL-53 (Fe)s, MIL-125s, D1-MIL-101s, D2-MIL-101s, D1-MIL-53s, D2-MIL-53s and MIL-101s were used for the esterification of acetic acid as catalysts. The preparation and characterization of these catalysts were explained in Section 4.2-4.4 and Section 5.1, respectively. In this study,

- ❖ The catalytic activities MIL-53 (Fe)s, MIL-125s, D1-MIL-101s, D2-MIL-101s, D1-MIL-53s, D2-MIL-53s and MIL-101s were tested in the liquid phase esterification of acetic acid.
- ❖ The most effective catalyst was selected among specified catalysts.
- ❖ The effects of operating conditions including temperature, time, catalyst loading and molar ratio of alcohol to acid were studied.
- ❖ The effect of sulfation on the catalytic activities of catalysts was investigated.
- ❖ The effect of chain length of alcohol was achieved.
- ❖ Reusability of catalysts and catalyst leaching were studied.

To calculate conversion of limiting reactant which is acetic acid and the molar amounts of components in batch reactor experiments, samples were taken and analyzed by Gas Chromatography (GC) at the end of 7 hours. The calculation of conversion is explained in Appendix I part.

5.3.1. Esterification of Acetic Acid Catalyzed by MIL-53(Fe)s

Firstly, the esterification of acetic acid with methanol, butanol and hexanol was carried out catalyzed by MIL-53(Fe)s. Then by using the same catalyst effect of temperature, sulfation and reusability studies were performed for the esterification of acetic acid with butanol.

Effect of Alcohol

Steric effect influences the rate of esterification. Therefore, the chain length and branching of acid and alcohol is important for esterification. The yield

of ester is increasing with decreasing the length of alcohols and acids. Many authors observed similar results in their previous works (Mantri et al., 2005).

In this study hexanol and butanol were compared at 363 K, catalyst loading of 6 wt %, alcohol to acid initial molar ratio of 1 and stirrer speed of 500 rpm. As expected, the higher acetic acid conversions were achieved for the esterification of acetic acid with butanol. As the length of chain increases, the conversion values decreases because of the difficulty of performing esterification reaction.

Methanol experiments were conducted at 333 K because of its low boiling point. Figure 5.97 shows the effect of alcohols on acetic acid conversion. Normally, the highest conversion is expected in the use of methanol but it is difficult to compare conversion values of these three alcohols. As shown from Figure 5.97, the conversion of acetic acid in methyl acetate synthesis is closer to that of butyl acetate synthesis, although the reaction temperature of methyl acetate production is lower than the temperature of butyl acetate synthesis by 30°C.

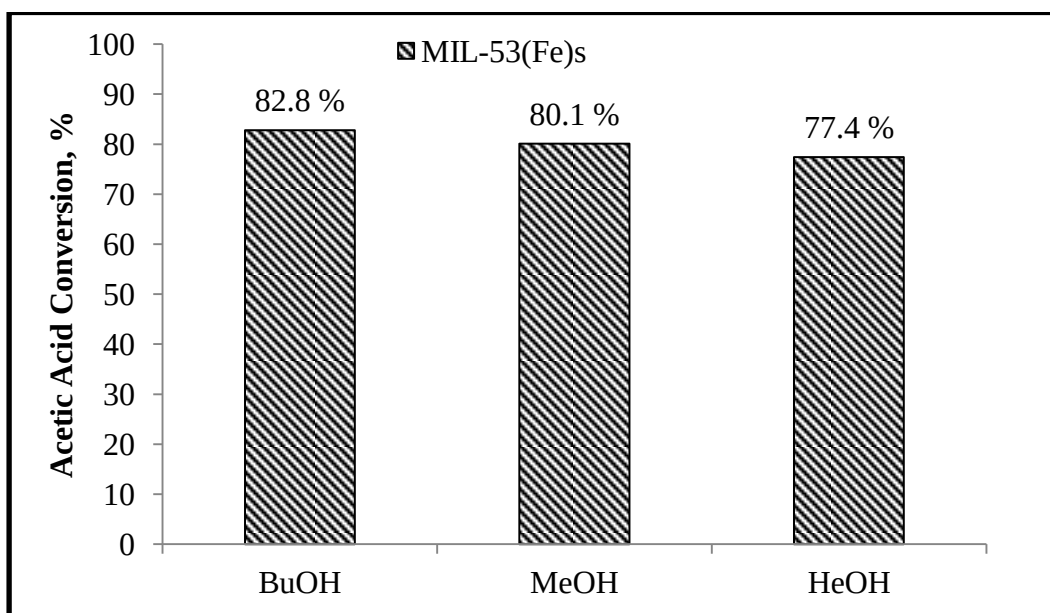


Figure 5.97 Effect of alcohol type on conversion of acetic acid by using MIL-53 (Fe)s.

Effect of Temperature

The effect of temperature on the conversion of acetic acid was investigated by changing temperature as 353, 358 and 363 K, other conditions were kept

constant at catalyst loading of 6 wt %, butanol to acid initial molar ratio of 1 and stirrer speed of 500 rpm.

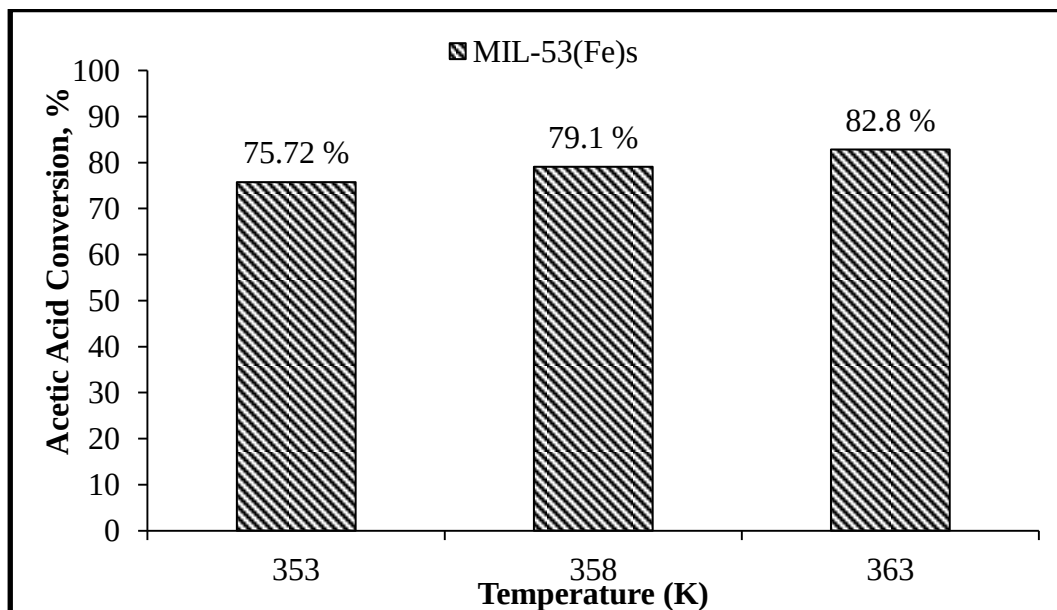


Figure 5.98 Effect of temperature on acetic acid conversion by using MIL-53 (Fe)s.

Figure 5.98 shows the effect of temperature on acetic acid conversion. After 7 hours conversion values of acetic acid for butyl acetate synthesis catalyzed by MIL-53 (Fe)s were found as 75.72 %, 79.1% and 86.8 % at 353, 358 and 363 K, respectively. Temperature increases the number of collisions between the molecules, so conversion increases as expected. (Sert and Atalay, 2010). Similar results were obtained in other works (Teo and Saha, 200 ; Delgado et al., 2007; Altıokka and Ödeş, 2009; Ali et al., 2011).

Effect of Sulfation of MIL-53 (Fe)s

As explained before, the rate of esterification reaction depends on the acidity of the catalyst. To increase the acidity of synthesized MOFs, sulfation of MOFs was conducted. To observe the effect of sulfation, experiments were investigated before and after sulfation. Figure 5.99 shows the effect of sulfation of catalyst. The experiments were carried out at 363 K, 6wt % of catalyst loading, 1:1 acid alcohol molar ratio and 500rpm. As shown from Figure 5.61, sulfation increases the catalytic activity of catalyst for the esterification of acetic acid with butanol. The conversion of acetic acid increases from 45.7% to 82.8% after sulfation.

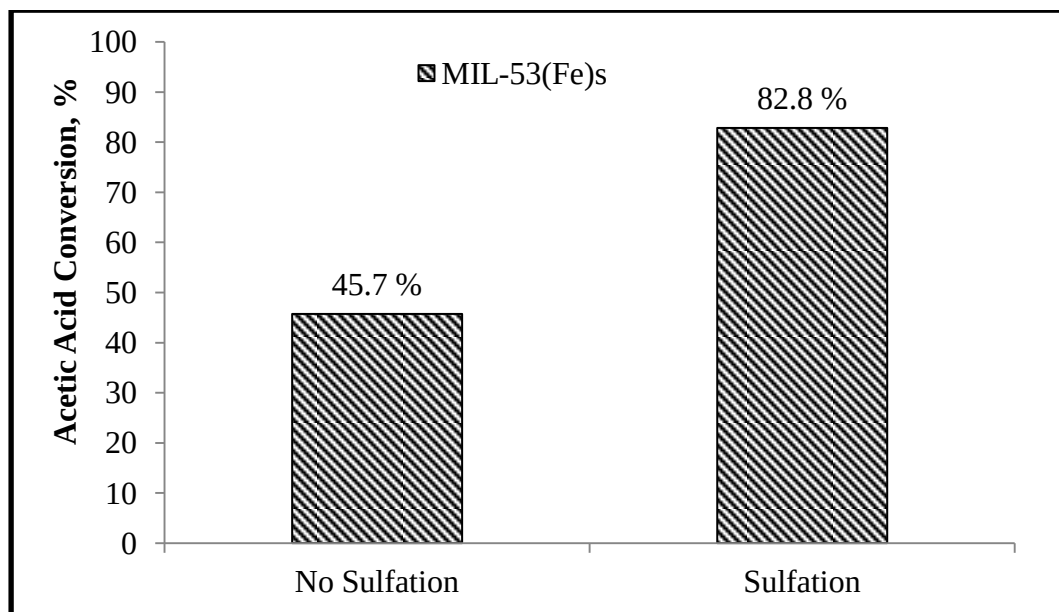


Figure 5.99 Effect of sulfation on conversion of acetic acid by using MIL-53 (Fe)s at 363 K, 6 wt% catalysts loading, 1:1 alcohol acid ratio.

Reusability of MIL-53 (Fe)s

Using heterogeneous catalysts would offer several advantages. Reusability is one of them. The catalyst could be separated from the reaction mixture by simple filtration, and could be reused without a significant degradation in catalytic activity.

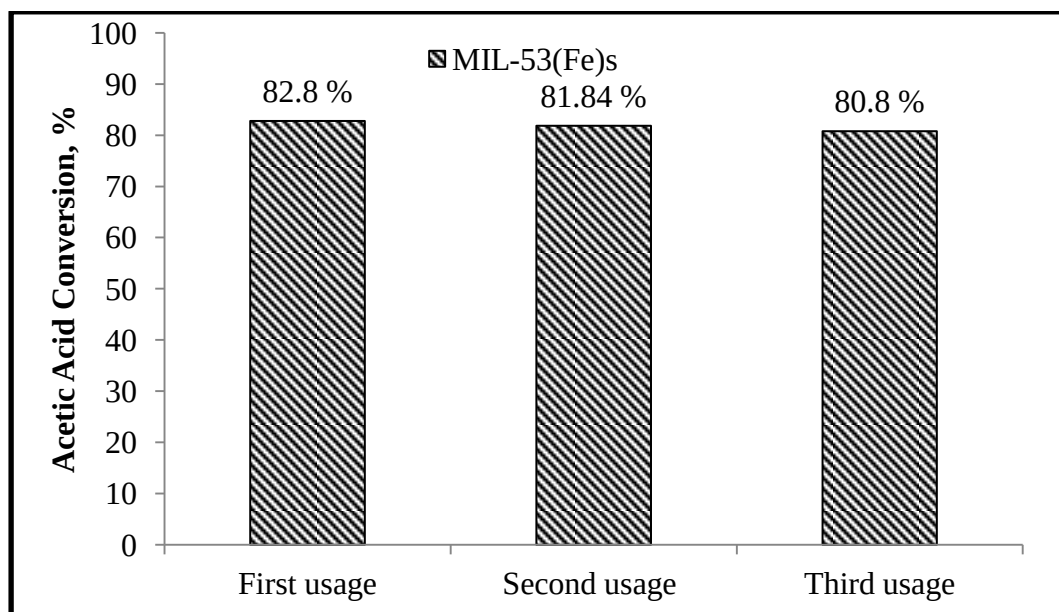


Figure 5.100 Reusability of MIL-53 (Fe)s at 363 K, 6 wt% catalysts loading, 1:1 alcohol acid ratio.

The reusability experiments were carried out at 363 K, 6wt % of catalyst loading, 1:1 acid alcohol molar ratio and 500rpm. Figure 5.62 shows the effect of reusability of catalyst

Another important concept in heterogenous catalyst is catalyst leaching. The reaction mixture was analysed by Atomic Absorption Spectroscopy, there is no Fe is observed.

5.3.2. Esterification of Acetic Acid Catalyzed by MIL-125s

Effect of Alcohol

Esterification reaction of acetic acid with hexanol and butanol were compared at 363 K, catalyst loading of 6 wt %, alcohol to acid initial molar ratio of 1 and stirrer speed of 500 rpm. Methanol experiments were conducted at 333 K because of its low boiling point. Figure 5.101 shows the effect of alcohols on acetic acid conversion. It is seen that the conversion of acetic acid with butanol was higher than that of hexanol. Indeed, it is expected that the conversion must be high when methanol is used as alcohol in esterification reaction. Because the length of chain increases, the conversion values decreases due to the difficulty of performing esterification reaction. However, the experiments were conducted at 333 K with methanol. Hence the comparing of methanol with other alcohols is difficult. Although the experiments, methanol was used were conducted 30°C lower than that of with other alcohols, the conversion of acetic acid in methyl acetate synthesis close to that of butyl acetate synthesis.

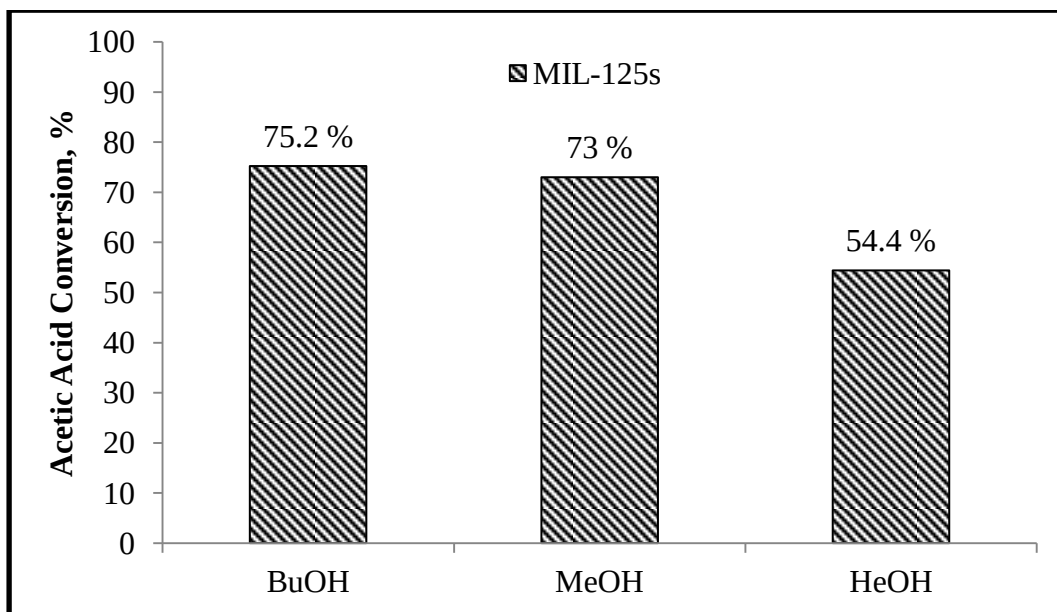


Figure 5.101 Effect of alcohol type on conversion of acetic acid by using MIL-125s.

Effect of Temperature

The effect of temperature on the conversion of acetic acid was investigated by changing temperature as 353, 358 and 363 K, other conditions were kept constant at catalyst loading of 6 wt %, butanol to acid initial molar ratio of 1 and stirrer speed of 500 rpm.

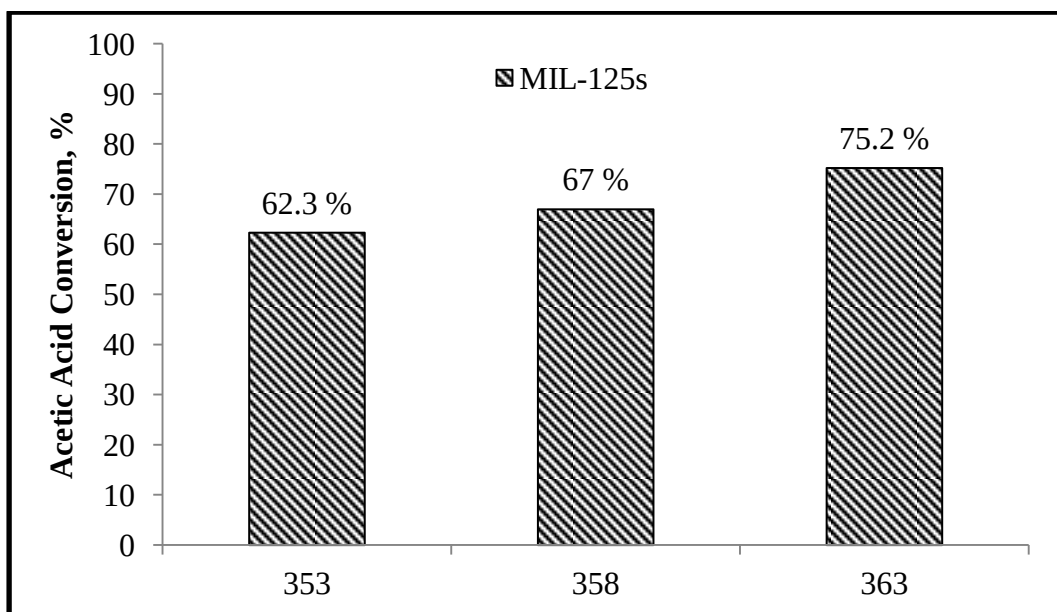


Figure 5.102 Effect of temperature on acetic acid conversion by using MIL-125s.

Figure 5.102 shows the effect of temperature on acetic acid conversion. After 7 hours experiments, conversions using MIL-125 as catalyst were found as 62.3 %, 67 % and 75.2 % at 353, 358 and 363 K, respectively.

Effect of Sulfation of MIL-125s

To observe the effect of sulfation of MIL-125s, the experiments were investigated before and after sulfation. Figure 5.103 shows the effect of sulfation of catalyst. The experiments were carried out at 363 K, 6wt % of catalyst loading, 1:1 acid alcohol molar ratio and 500rpm of stirred. The conversion of acetic acid increases from 55.74% to 75.2% after sulfation. It is concluded that sulfation increases the acidity of MIL-125.

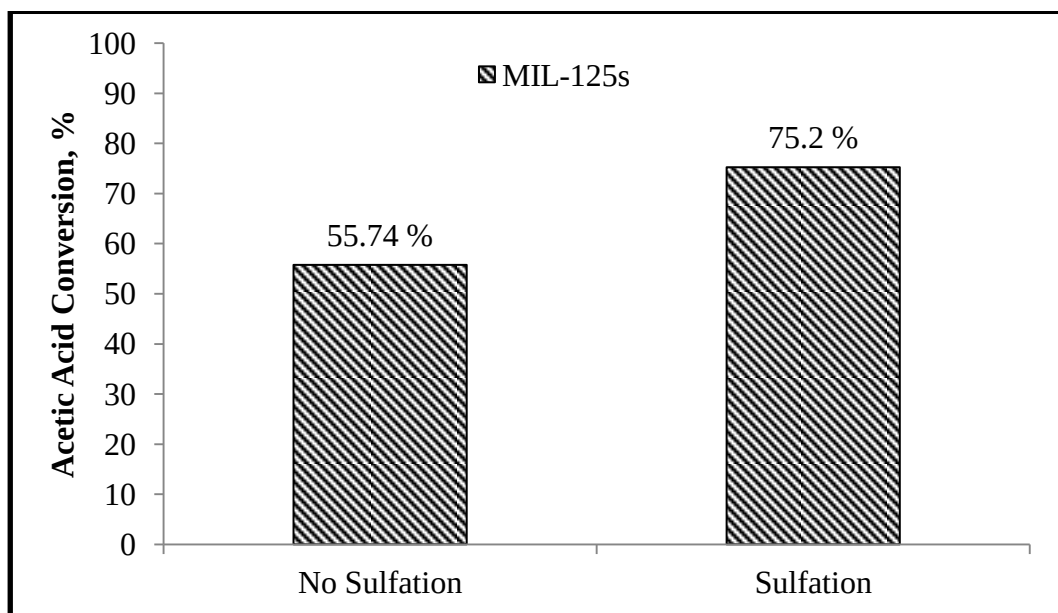


Figure 5.103 Effect of sulfation on conversion of acetic acid by using MIL-125s at 363 K, 6 wt% catalysts loading, 1:1 alcohol acid ratio.

Reusability of MIL-125s

MIL-125s was separated from the reaction mixture by simple filtration, and was reused without a significant degradation in catalytic activity.

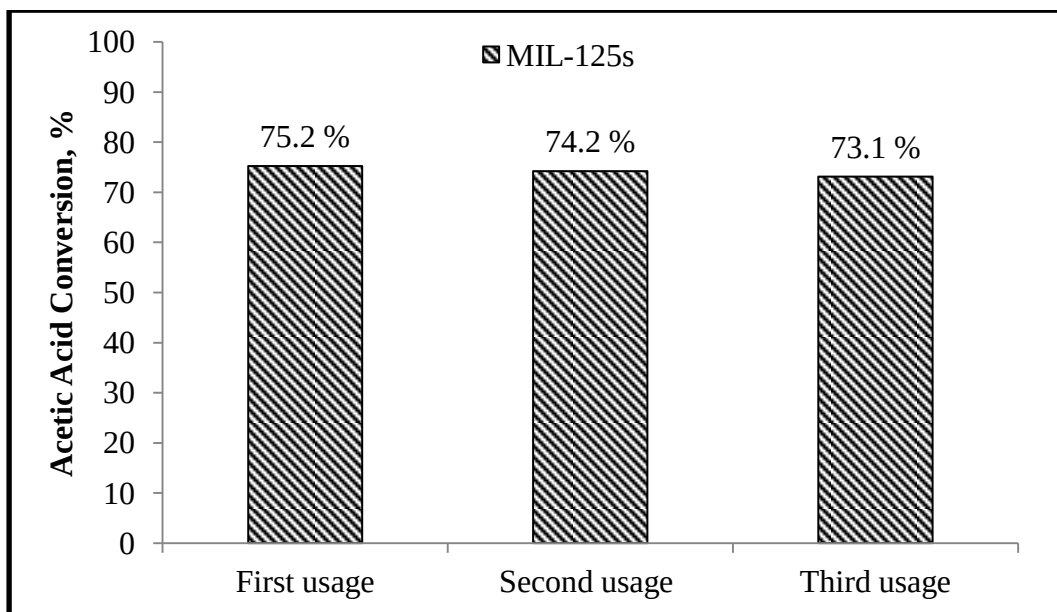


Figure 5.104 Reusability of MIL-125s at 363 K, 6 wt% catalysts loading, 1:1 alcohol acid ratio.

The reusability experiments were carried out at 363 K, 6wt % of catalyst loading, 1:1 acid alcohol molar ratio and 500rpm. Figure 5.104 shows the reusability of catalyst. After third usage, the conversion of acetic acid decreased by 2.1 % when compared to conversion obtained by fresh catalyst.

The catalyst leaching was investigated, the reaction mixture was analysed by Atomic Absorption Spectroscopy, there is no any Ti detected.

5.3.3. Esterification of Acetic Acid Catalyzed by D1-MIL-101s

Effect of Alcohol

In this study hexanol and butanol were compared at 363 K, catalyst loading of 6 wt %, alcohol to acid initial molar ratio of 1 and stirrer speed of 500 rpm. Methanol experiments were conducted at 333 K because of its low boiling point. Figure 5.105 shows the effect of alcohols on acetic acid conversion. It is seen that as the length of the chain increases, the conversion values decreases.

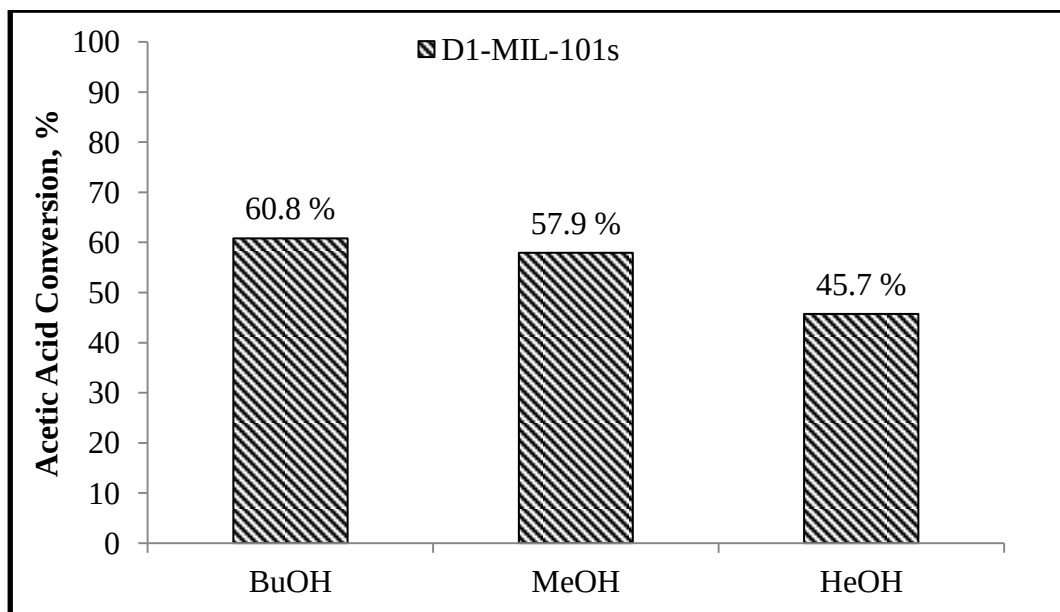


Figure 5.105 Effect of alcohol type on conversion of acetic acid by using D1-MIL-101s.

Effect of Temperature

The effect of temperature on the conversion of acetic acid was investigated by changing temperature as 353, 358 and 363 K, other conditions were kept constant at catalyst loading of 6 wt %, alcohol butanol to acid initial molar ratio of 1 and stirrer speed of 500 rpm.

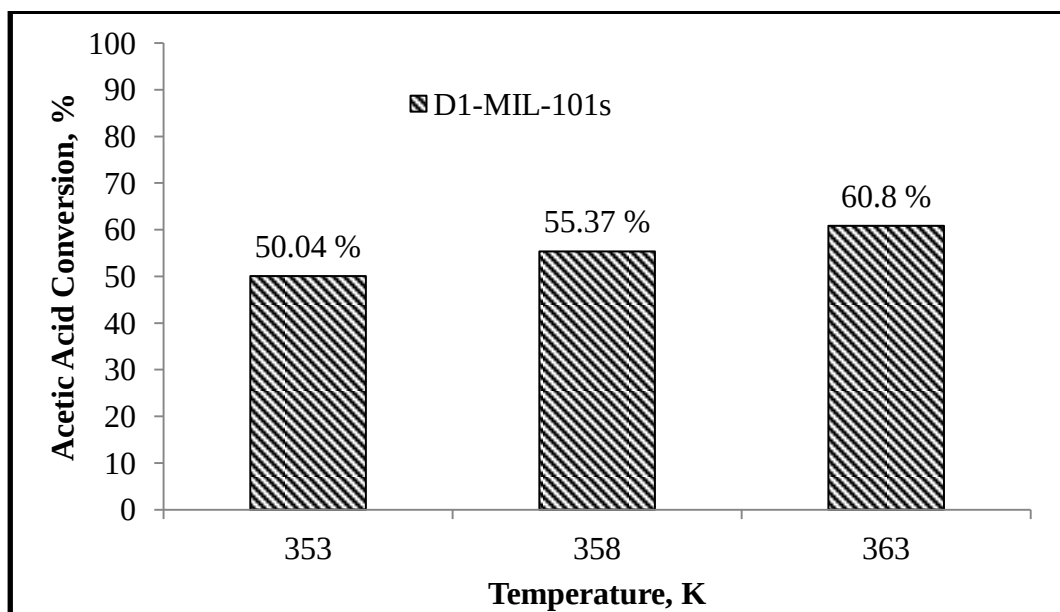


Figure 5.106 Effect of temperature on acetic acid conversion by using D1-MIL-101s.

Figure 5.106 shows the effect of temperature on acetic acid conversion. After 7 hours, conversions using D1-MIL-101s as catalyst were found as 50.04 %, 55.37 % and 60.8 % at 353, 358 and 363 K, respectively.

Effect of Sulfation of D1-MIL-101s

To increase the acidity of D1-MIL-101s was conducted. Effect of sulfation were carried out at 363 K, 6wt % of catalyst loading, 1:1 acid alcohol molar ratio and 500rpm. The conversion of acetic acid increases from 46.3 % to 60.8 % after sulfation for D1-MIL-101s. This result shows the importance of acidity of catalyst in esterification reactions. Sulfation increases the conversion by 14.5 %.



Figure 5.107 Effect of sulfation on conversion of acetic acid by using D1-MIL-101s at 363 K, 6 wt% catalysts loading, 1:1 alcohol acid ratio.

Reusability of D1-MIL-101s

Using heterogeneous catalysts would offer several advantages. Reusability makes the catalyst more effective. The catalyst could be separated from the reaction mixture by simple filtration, and could be reused without a significant degradation in catalytic activity.

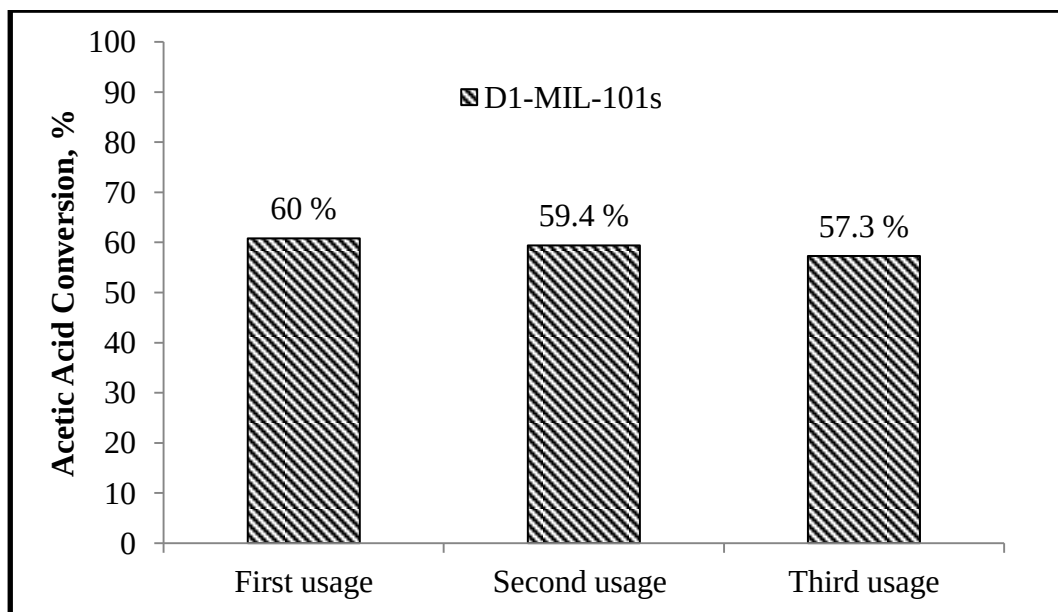


Figure 5.108 Reusability of D1-MIL-101s at 363 K, 6 wt% catalysts loading, 1:1 alcohol acid ratio.

Figure 5.108 shows the effect of reusability of catalyst. The experiments were carried out at 363 K, 6wt % of catalyst loading, 1:1 acid alcohol molar ratio and 500rpm. After third usage, the conversion of acetic acid decreased by 2.7 %.

Another important concept in heterogenous catalyst is catalyst leaching. The reaction mixture was analysed by Atomic Absorption Spectroscopy, there is no any Cr detected.

5.3.4. Esterification of Acetic Acid Catalyzed by D2-MIL-101s

Effect of Alcohol

In this study hexanol and butanol were compared at 363 K, catalyst loading of 6 wt %, alcohol to acid initial molar ratio of 1 and stirrer speed of 500 rpm. Methanol experiments were conducted at 333 K because of its low boiling point. Figure 5.109 shows the effect of alcohols on acetic acid conversion.

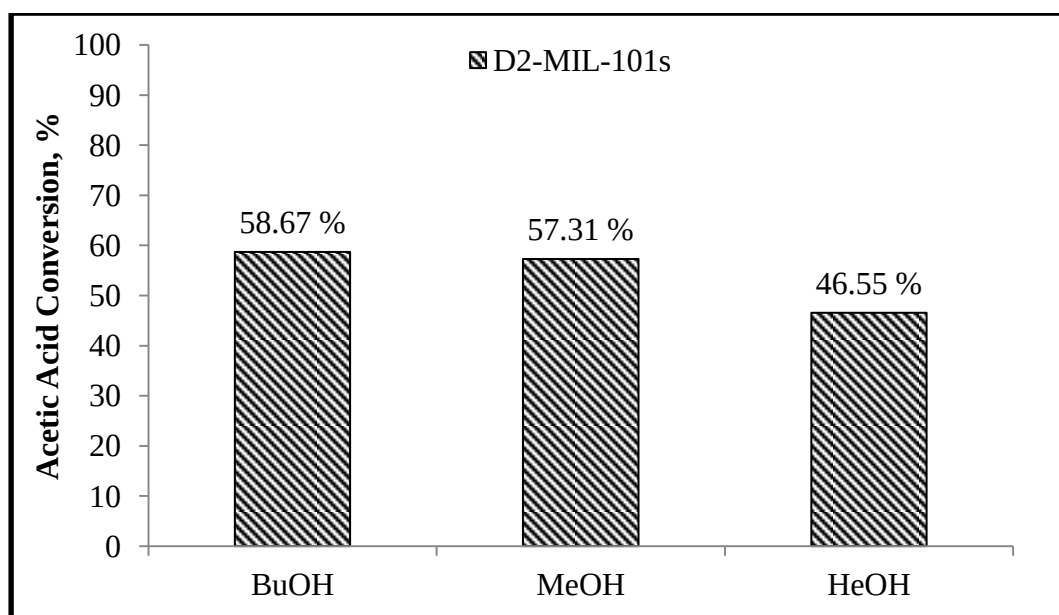


Figure 5.109 Effect of alcohol type on conversion of acetic acid by using D2-MIL-101s.

As shown from figure 5.109, as the chain length of alcohol decreases, the conversion increases.

Effect of Temperature

Temperature of the reaction mixture is crucial for determining the kinetic model. The effect of temperature on the conversion of acetic acid was investigated by changing temperature as 353, 358 and 363 K, other conditions were kept constant at catalyst loading of 6 wt %, butanol to acid initial molar ratio of 1 and stirrer speed of 500 rpm.

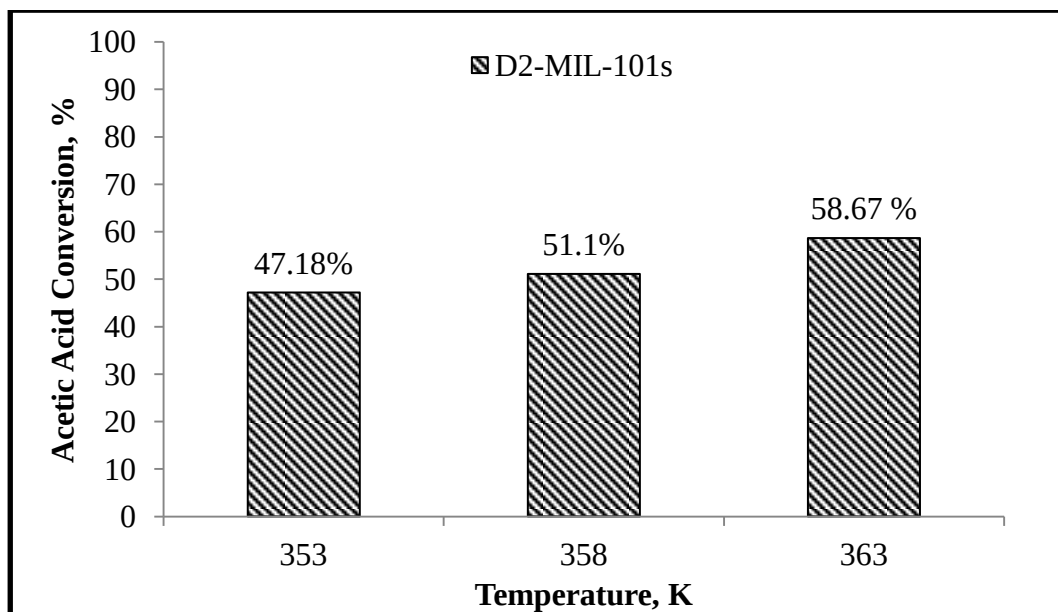


Figure 5.110 Effect of Temperature on acetic acid conversion by using D2-MIL-101s.

Figure 5.72 shows the effect of temperature on acetic acid conversion. After 7 hours experiments, conversions using D2-MIL-101s as catalyst were found as 47.18 %, 51.1% and 58.69 % at 353, 358 and 363 K, respectively.

Effect of Sulfation of D2-MIL-101s

To increase the yield of ester, sulfation of MOFs was conducted. To observe the effect of sulfation, experiments were investigated before and after sulfation. Figure 5.111 shows the effect of sulfation of catalyst. The experiments were carried out at 363 K, 6wt % of catalyst loading, 1:1 acid alcohol molar ratio and 500rpm. The conversion of acetic acid increases from 44.1 % to 58.67 % after sulfation for D2-MIL-101s.

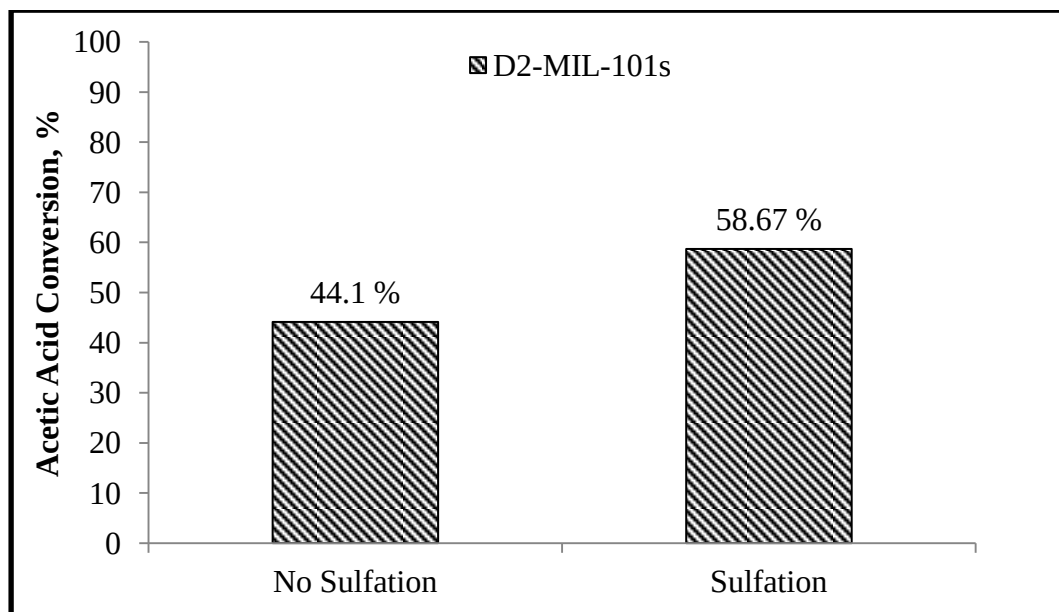


Figure 5.111 Effect of sulfation on conversion of acetic acid by using D2-MIL-101s at 363 K, 6 wt% catalysts loading, 1:1 alcohol acid ratio.

Reusability of D2-MIL-101s

Reusability is one of the advantages of heterogeneous catalysts. Using heterogeneous catalysts would offer several advantages. The catalyst could be separated from the reaction mixture by simple filtration, and could be reused without a significant degradation in catalytic activity.

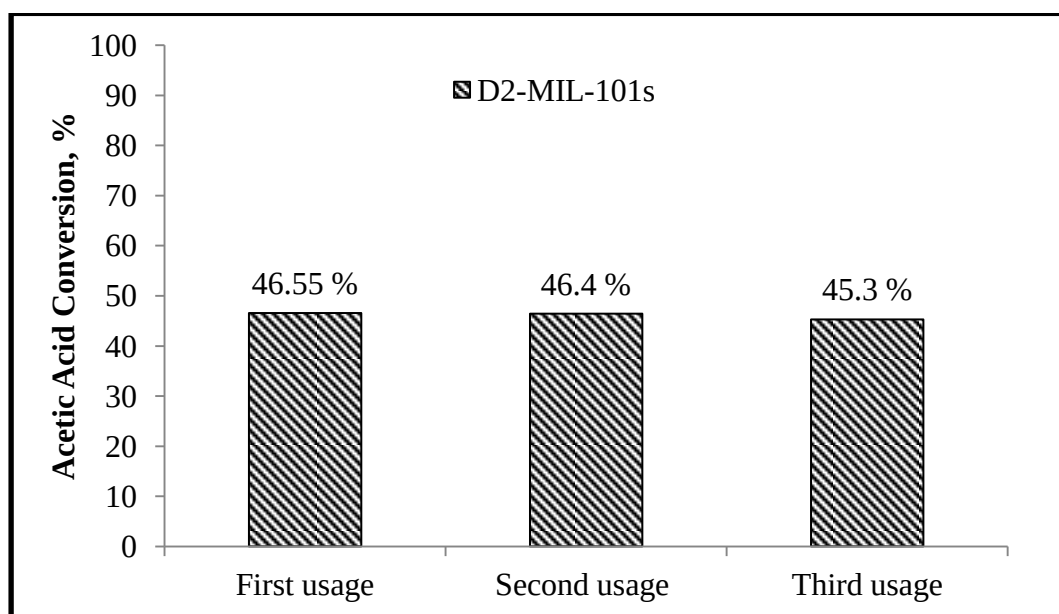


Figure 5.112 Reusability of D2-MIL-101s at 363 K, 6 wt% catalysts loading, 1:1 alcohol acid ratio.

Figure 5.112 shows the effect of reusability of catalyst. The experiments were carried out at 363 K, 6wt % of catalyst loading, 1:1 acid alcohol molar ratio and 500rpm. The conversion of acetic acid decreases by 1.25 % after third use.

Another important concept in heterogenous catalyst is catalyst leaching. The reaction mixture was analysed by Atomic Absorption Spectroscopy, there is no any Cr detected.

5.3.5. Esterification of Acetic Acid Catalyzed by D1-MIL-53s

Effect of Alcohol

In this study hexanol and butanol were compared at 363 K, catalyst loading of 6 wt %, alcohol to acid initial molar ratio of 1 and stirrer speed of 500 rpm. Metanol experiments were conducted at 333 K because of its low boiling point. Figure 5.113 shows the effect of alcohols on acetic acid conversion.

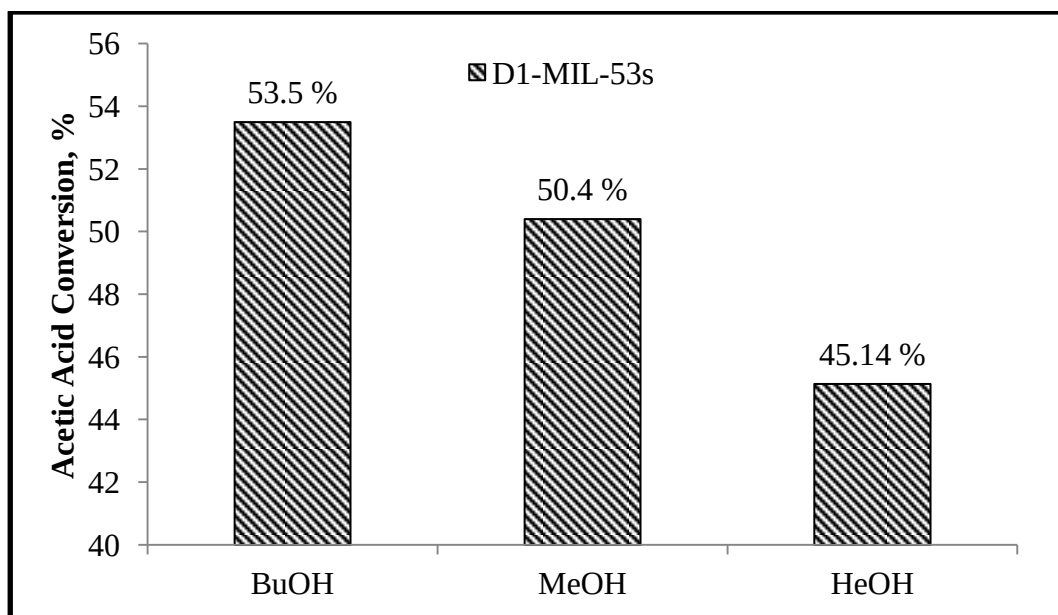


Figure 5.113 Effect of alcohol type on conversion of acetic acid by using D1-MIL-53s

Effect of Temperature

The effect of temperature on the conversion of acetic acid was investigated by changing temperature as 353, 358 and 363 K, other conditions were kept

constant at catalyst loading of 6 wt %, butanol to acid initial molar ratio of 1 and stirrer speed of 500 rpm.

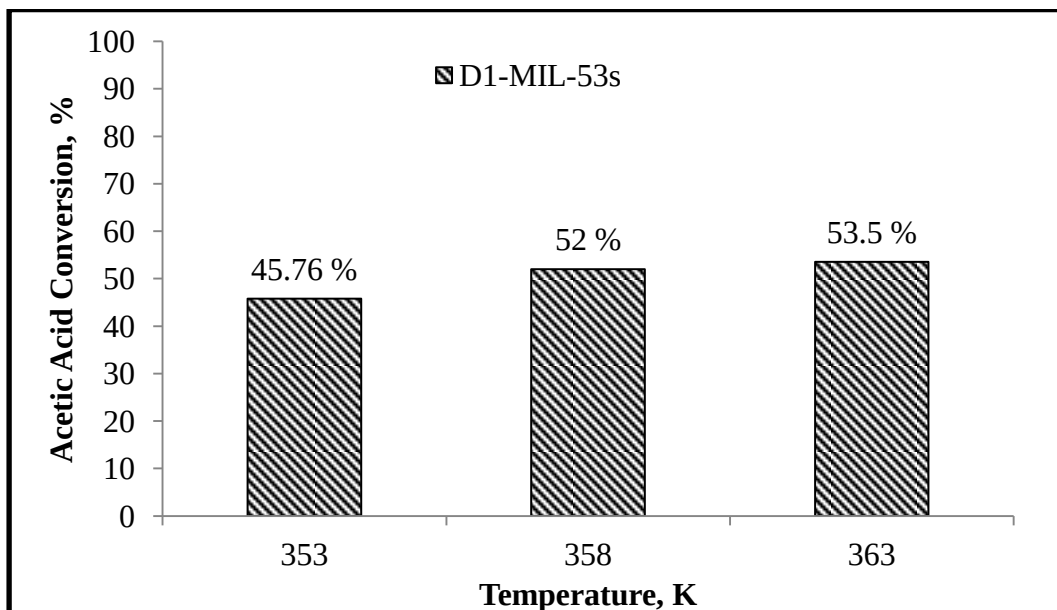


Figure 5.114 Effect of Temperature on acetic acid conversion by using D1-MIL-53s.

Figure 5.114 shows the effect of temperature on acetic acid conversion. After 7 hours experiments, conversions using D1-MIL-53s as catalyst were found as 45.76 %, 52% and 53.5 % at 353, 358 and 363 K, respectively.

Effect of Sulfation of D1-MIL-53s

To increase the acidity of D1-MIL53 was conducted. To observe the effect of sulfation, experiments were investigated before and after sulfation. Figure 5.115 shows the effect of sulfation of catalyst. The experiments were carried out at 363 K, 6wt % of catalyst loading, 1:1 acid alcohol molar ratio and 500rpm. The conversion of acetic acid increases from 36 % to 53.5 % after sulfation.

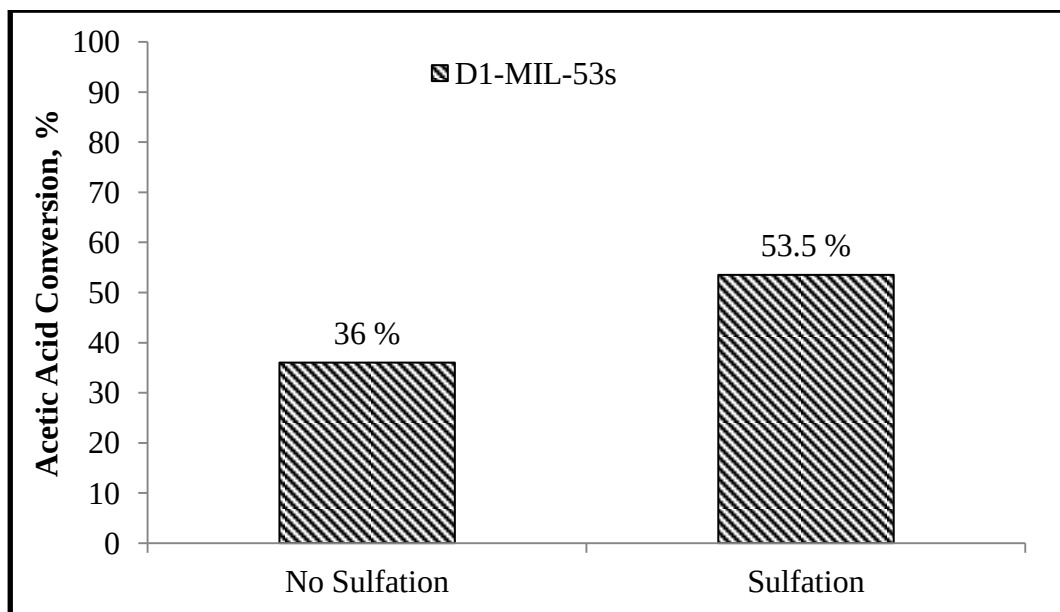


Figure 5.115 Effect of sulfation on conversion of acetic acid by using D1-MIL-53s at 363 K, 6 wt% catalysts loading, 1:1 alcohol acid ratio.

Reusability of D1-MIL-53s

Reusability was tested at 363 K, 6wt % of catalyst loading, 1:1 acid alcohol molar ratio and 500rpm.

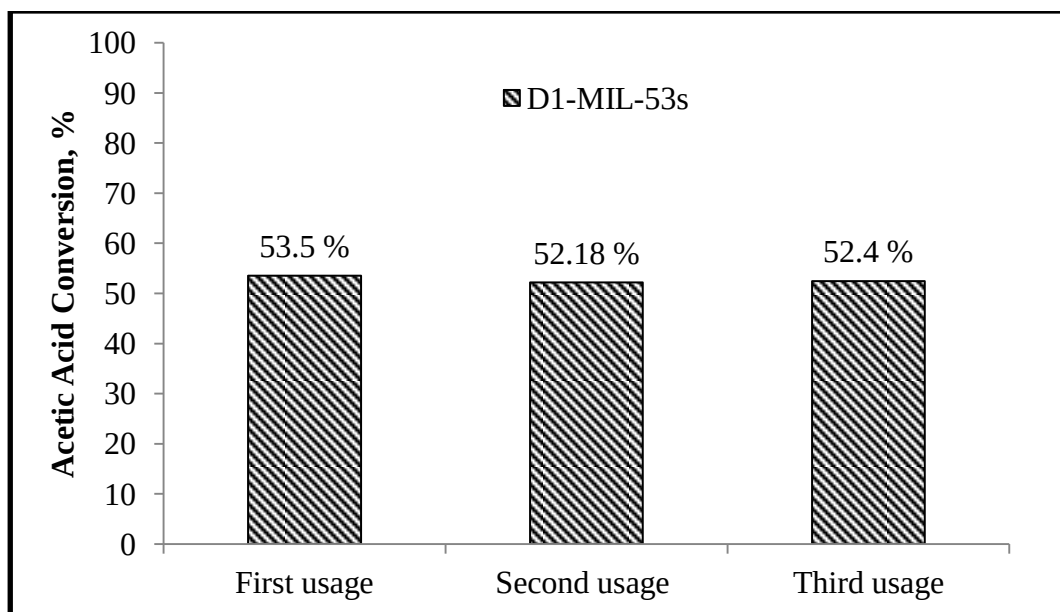


Figure 5.116 Reusability on conversion of acetic acid by using D1-MIL-53s at 363 K, 6 wt% catalysts loading, 1:1 alcohol acid ratio.

The conversion of acetic acid decreases by 1.4 %. The reaction mixture was analysed by Atomic Absorption Spectroscopy, there is no any Fe detected.

5.3.6. Esterification of Acetic Acid Catalyzed by D1-MIL-53s

Effect of Alcohol

In this study hexanol and butanol were compared at 363 K, catalyst loading of 6 wt %, alcohol to acid initial molar ratio of 1 and stirrer speed of 500 rpm. Methanol experiments were conducted at 333 K because of its low boiling point. Figure 5.117 shows the effect of alcohols on acetic acid conversion.

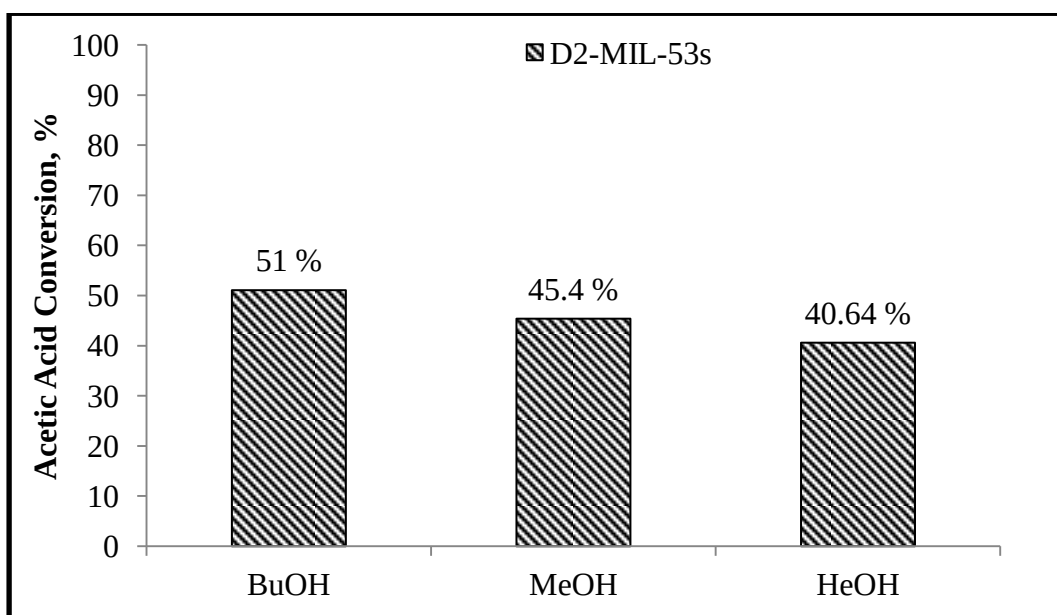


Figure 5.117 Effect of alcohol type on conversion of acetic acid by using D2-MIL-53s.

Effect of Temperature

The effect of temperature on the conversion of acetic acid was investigated by changing temperature as 353, 358 and 363 K, other conditions were kept constant at catalyst loading of 6 wt %, butanol to acid initial molar ratio of 1 and stirrer speed of 500 rpm.

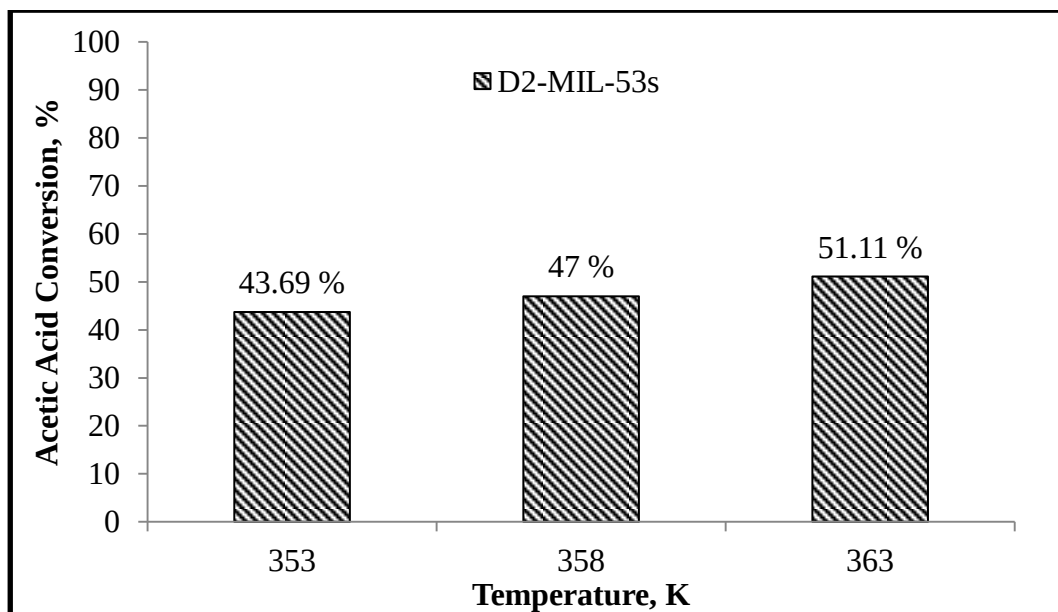


Figure 5.118 Effect of temperature on acetic acid conversion by using D2-MIL-53s.

Figure 5.118 shows the effect of temperature on acetic acid conversion. After 7 hours experiments, conversions using D2-MIL-53s as catalyst were found as 43.69 %, 47% and 51.11 % at 353, 358 and 363 K, respectively.

Effect of Sulfation of D2-MIL-53s

To increase acidity, sulfation of D2-MIL-53 was conducted. To observe the effect of sulfation, experiments were investigated before and after sulfation. Figure 5.119 shows the effect of sulfation of catalyst. The experiments were carried out at 363 K, 6wt % of catalyst loading, 1:1 acid alcohol molar ratio and 500rpm. The conversion of acetic acid increases from 26.7 % to 51.11 % after sulfation.

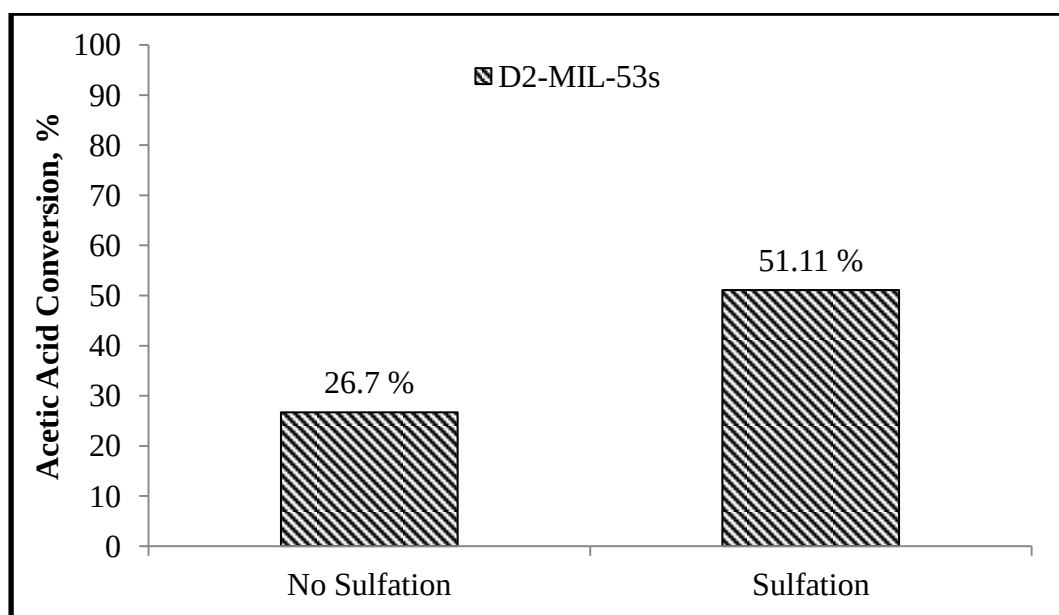


Figure 5.119 Effect of sulfation on conversion of acetic acid by using D2-MIL-53s at 363 K, 6 wt% catalysts loading, 1:1 alcohol acid ratio.

Reusability of D2-MIL-53s

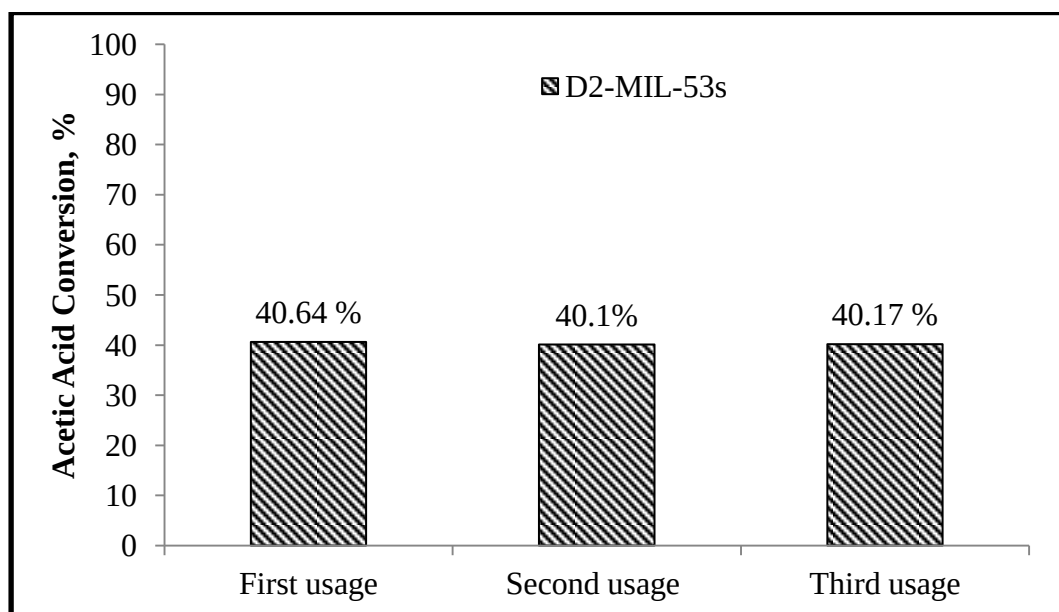


Figure 5.120 Reusability of D2-MIL-53s at 363 K, 6 wt% catalysts loading, 1:1 alcohol acid ratio.

Figure 5.120 shows reusability of catalyst. The experiments were carried out at 363 K, 6wt % of catalyst loading, 1:1 acid alcohol molar ratio and 500 rpm of stirrer speed. It can be seen from figure no contribution from homogeneous catalysis of active species leaching into the liquid phase was detected.

5.3.7. Esterification of Acetic Acid Catalyzed by MIL-101s

Among the seven sulfated MOFs, **MIL-101s** shows the highest catalytic activity because of having highest surface area and pore volume. Figure 5.121-123 show the conversion values of acetic acid for all catalysts.

Firstly, the effect of alcohol was searched by using methanol, butanol and hexanol catalyzed by MIL-101s. The effects of important operating parameters such as; temperature, time, catalyst loading, molar ratio were investigated and also effect of sulfation on the conversion of acetic acid was studied for the esterification of acetic acid with butanol. The reusability and leaching of MIL-101s were carried out for the same reaction.

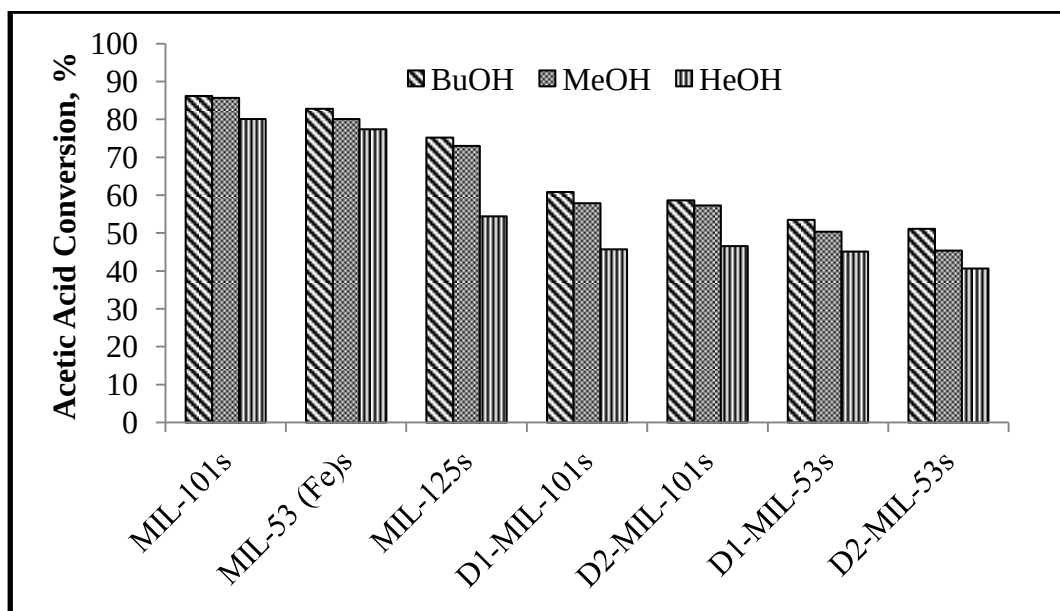


Figure 5.121 Conversion values of acetic acid at 363 K for all catalysts

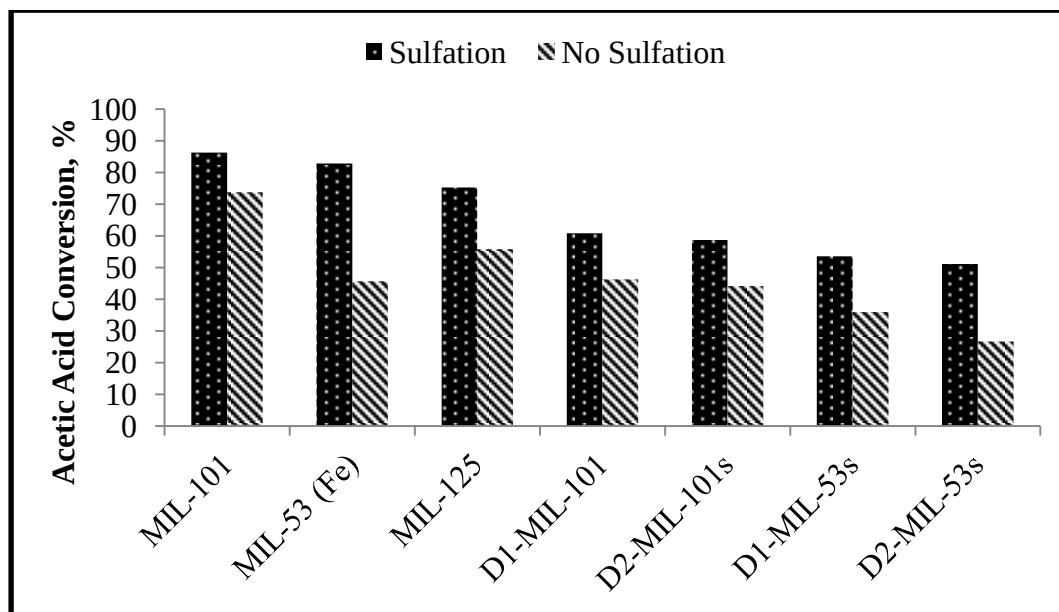


Figure 5.122 Conversion values of acetic acid at 363 K for all catalysts before and after sulfonation

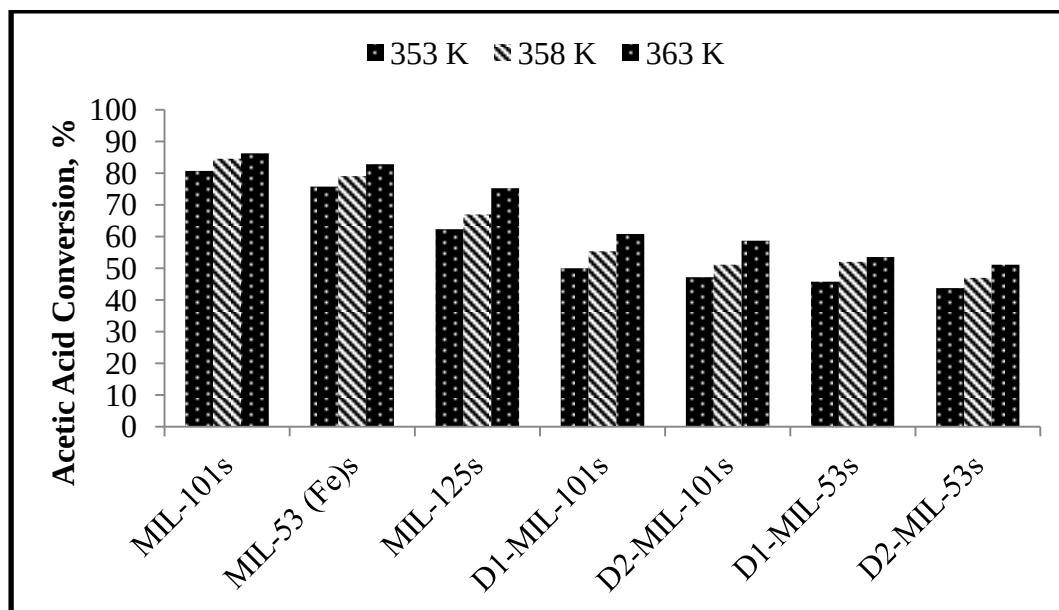


Figure 5.123 Conversion values of acetic acid at different temperature for all catalysts

Effect of Alcohol

In this study hexanol and butanol were compared at 363 K, catalyst loading of 6 wt %, alcohol to acid initial molar ratio of 1 and stirrer speed of 500

rpm. Metanol experiments were conducted at 333 K because of its low boiling point. Figure 5.124 shows the effect of alcohols on acetic acid conversion.

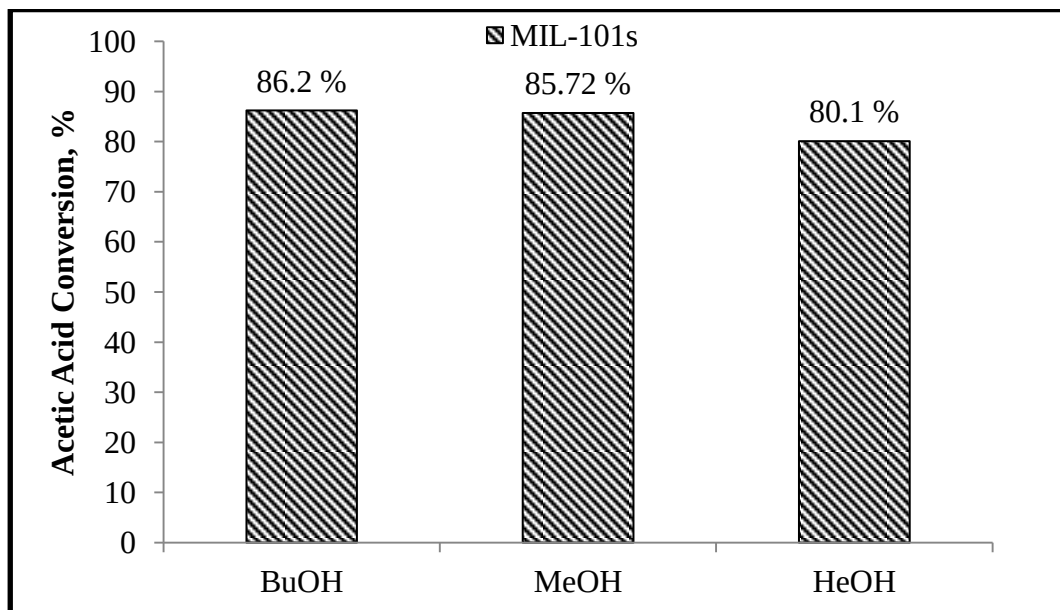


Figure 5.124 Effect of alcohol type on conversion of acetic acid by using MIL-101s.

The same trend was observed for this catalyst, the conversion of acetic acid (86.6%) is higher in butyl acetate synthesis than the conversion (80.1%) in hexyl acetate synthesis at the same temperature.

Effect of Temperature

The effect of temperature on the conversion of acetic acid was investigated by changing temperature as 353, 358 and 363 K, other conditions were kept constant at catalyst loading of 6 wt %, butanol to acid initial molar ratio of 1 and stirrer speed of 500 rpm.

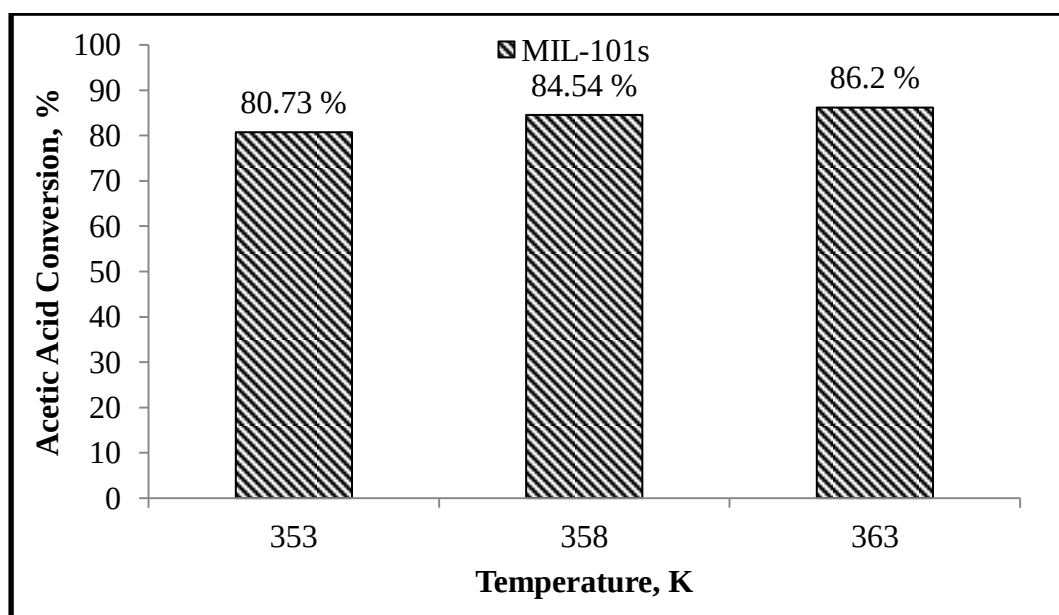


Figure 5.125 Effect of temperature on acetic acid conversion by using MIL-101s.

Figure 5.125 shows the effect of temperature on acetic acid conversion. After 7 hours, conversion values of acetic acid for butyl acetate synthesis catalyzed by MIL-101 were found as 80.73 %, 84.54% and 86.2 % at 353, 358 and 363 K, respectively.

Effect of Catalyst Loading

Experiments were carried out with catalyst loading of 3 wt %, 6 wt % and 9 wt % to examine the effect of catalyst loading. These experiments were studied at 363 K with a reactant ratio 3:1. The results are given in Figure 5.126. As shown in the figure, acetic acid conversion is increased with increasing of catalyst loading due to increment in the number of acid sites .

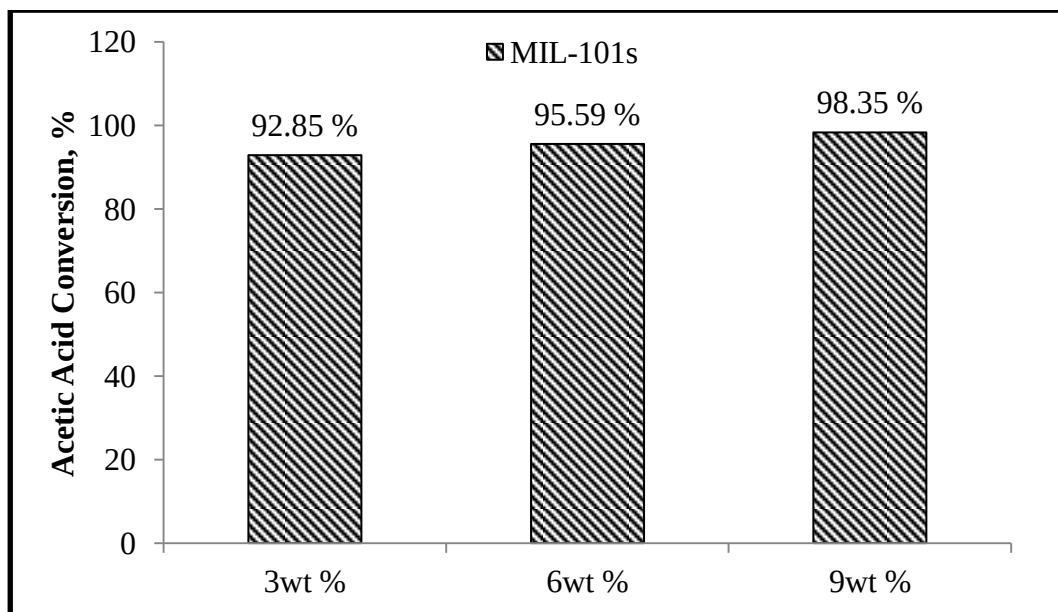


Figure 5.126 Effect of catalyst loading on conversion of acetic acid by using MIL-101s at 363 K and 3:1 alcohol acid ratio.

As the reaction rate is directly related to the number of resin functional groups; catalyst concentration makes a positive effect in conversion. The increase in conversion is more significant when the catalyst concentration is raised from 6 to 9 wt %. Final conversions of acetic acid were calculated as 92.85 %, 95.59 % and 98.35 % at catalyst loadings of 3, 6 and 9 wt%, respectively. Many authors observed similar results in their previous works (Chen et al., 1999; Yadav and Kulharni, 2000; Sanz and Gmehling, 2006; Ali and Merchant, 2009).

Effect of Initial Molar Ratio

Since the esterification is an equilibrium reaction, the equilibrium might be shifted towards the products by using excess reactant. Therefore, it is logical to use one of the reactants in excess amount by considering the stoichiometry of the reaction. Since alcohols like methanol and ethanol have reasonable costs and they are easier to be found, these alcohols are used in excess amounts for esterification. However, it is not a preferred method for the esterification of long chain fatty acids with long chain fatty alcohols, because both the acid and the alcohol used in these reactions are expensive reagents.

To investigate the effect of the initial molar ratio of butanol to acetic acid on the conversion, the initial molar ratio was changed as 1:1, 2:1 and 3:1 at a

temperature of 363 K, catalyst loading of 6 wt %, and stirrer speed of 500 rpm. According to previous studies, it is known that, alcohol to acid initial molar ratio is directly related to conversion in esterification reactions (Ali et al., 2007; Qu et al., 2009; Brahmkhatri and Patel, 2012, Pappu et al., 2013). The results are given in Figure 5.127. It can be seen that the conversion of acetic acid increases with increasing the initial molar ratio of alcohols to acetic acid. This result shows that conversion of acetic acid can be effectively enhanced by using a large excess of alcohols.

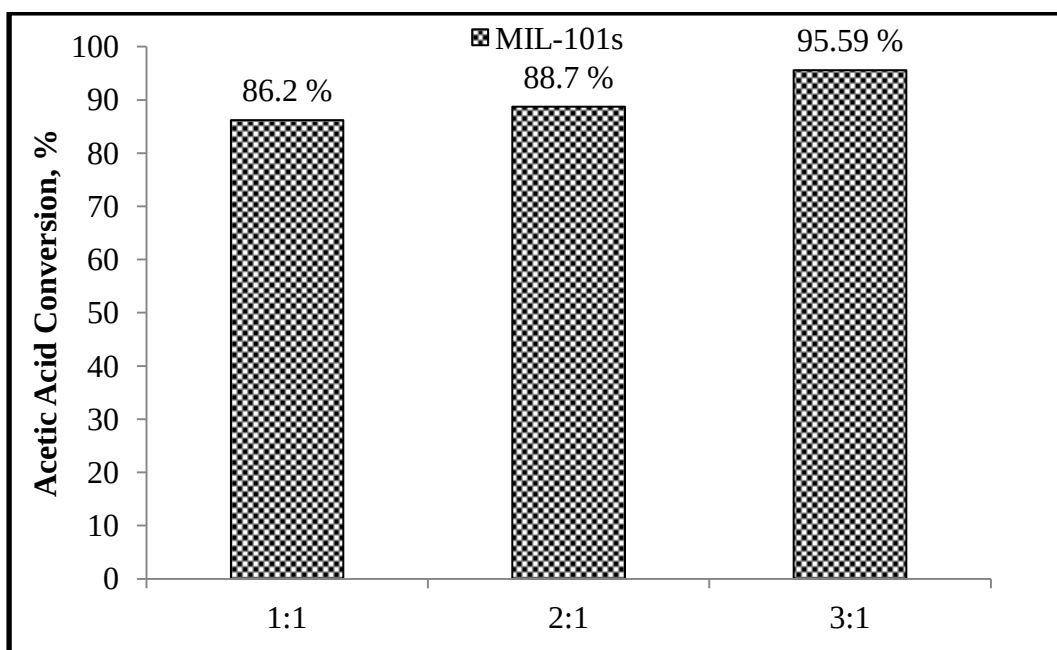


Figure 5.127 Effect of molar ratio of alcohol to acetic acid on conversion of acetic acid by using MIL-101s at 363 K, 6 wt% catalysts loading.

Effect of Sulfonation of MIL-101s

To increase the acidity of catalyst, sulfonation of MOFs was conducted. To observe the effect of sulfation, experiments were investigated before and after sulfation. Figure 5.126 shows the effect of sulfation of MIL-101s. The experiments were carried out at 363 K, 6wt % of catalyst loading, 1:1 acid alcohol molar ratio and 500rpm. As shown from figure, the conversion of acetic acid increases from 73.71% to 86.2% after sulfation.

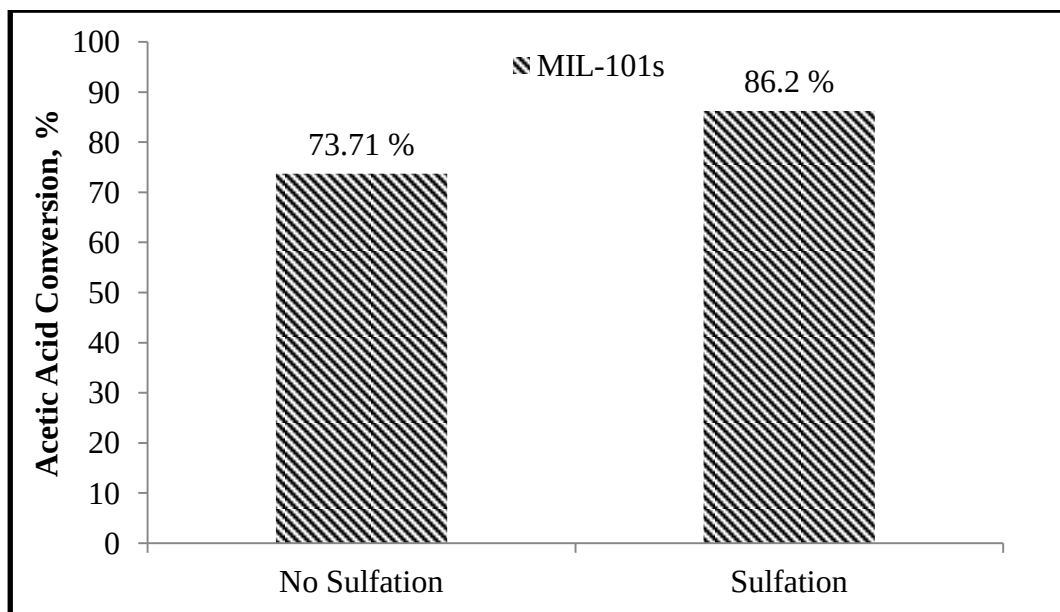


Figure 5.128 Effect of sulfation on conversion of acetic acid by using MIL-101s at 363 K, 6 wt% catalysts loading, 1:1 alcohol acid ratio.

Reusability of MIL-101

The catalyst could be separated from the reaction mixture by simple filtration, and could be reused without a significant degradation in catalytic activity.

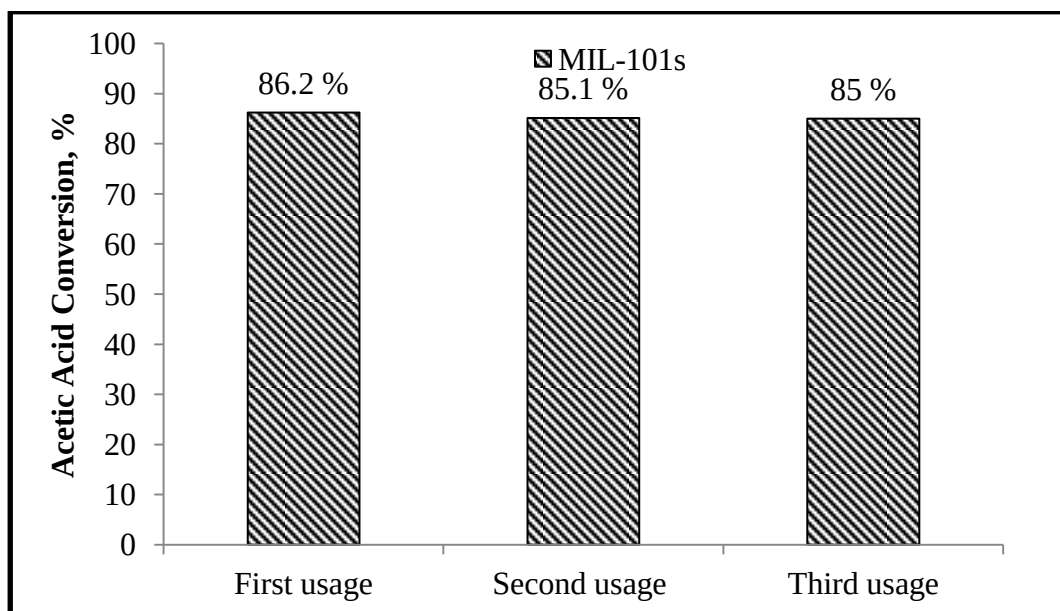


Figure 5.129 Reusability of MIL-101s at 363 K, 6 wt% catalysts loading, 1:1 alcohol acid ratio.

The experiments were carried out at 363 K, 6wt % of catalyst loading, 1:1 acid alcohol molar ratio and 500 rpm. Figure 5.129 shows the reusability of catalyst. MIL-101s is effective and reusable for the liquid phase esterification reactions.

Another important parameter in heterogeneous catalysis is catalyst leaching. After AAS analysis of the reaction mixture, there is no any amount of Cr in the reaction mixture.

5.3.8. Esterification of Acetic Acid in the non catalyzed reaction

Esterification reactions proceed with or without a catalyst. However, esterification reaction without catalyst is slower because rate depends on the autoprotolysis of the carboxylic acid. Therefore, esterification should be occurred with help of an acid catalyst that acts as a proton donor to the carboxylic acid. Figure 5.130 shows the conversion of acetic acid without catalyst. The conversion achieved in the non-catalyzed reaction was 21, 20.5, 18.7% by using butanol, methanol and hexanol, respectively. The experiments were carried out at 363 K, 1:1 alcohol acid molar ratio for same reaction time (7 hours). (For methanol, experiment was conducted at 333 K).

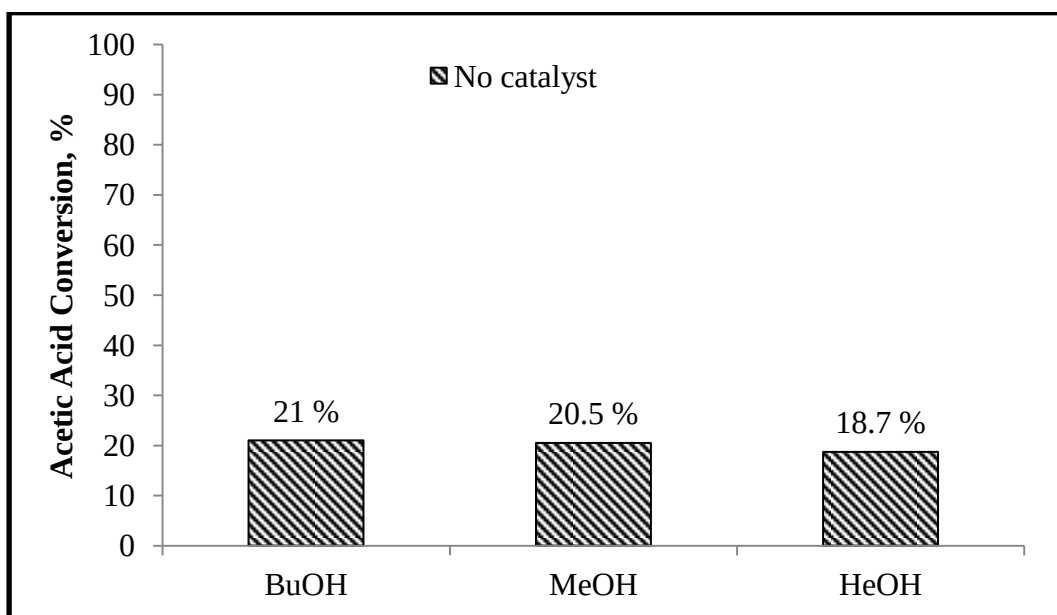


Figure 5.130 Acetic acid conversion without catalyst at 363 K, 1:1 molar ratio.

Table 5.23 shows the studies about esterification of acetic acid with butanol by using different catalysts.

Table 5.23 Comparison of conversion of acetic acid with butanol

Catalyst	Operating Conditions	Conversion, %	Reference
No Catalyst	MR:1:1, 363 K, 6wt % CL	21	This study
MIL-101s	MR:1:1, 363 K, 6wt % CL	86.2	This study
MIL-53s	MR:1:1, 363 K, 6wt % CL	82.8	This study
MIL-125s	MR:1:1, 363 K, 6wt % CL	75.2	This study
D1-MIL-101s	MR:1:1, 363 K, 6wt % CL	60.8	This study
D2-MIL-101s	MR:1:1, 363 K, 6wt % CL	58.67	This study
D1-MIL-53s	MR:1:1, 363 K, 6wt % CL	53.5	This study
D2-MIL-53s	MR:1:1, 363 K, 6wt % CL	51.11	This study
Amberlyst 15	MR:1:1, 343 K, 2wt % CL	65 %	Sert, E. and Atalay F., 2010
Dowex-50	MR:1:1, 363 K, 1wt % CL	67 %	Zaidoon et al., 2011
WMNLR-400 c Manganese nodule leached residue (MNLR)	MR:1:10, 363 K, 2 wt % CL	48.7	Dash and parida, 2007

6. CONCLUSION

In the first part of experiments, synthesis of metal organic frameworks, MIL-101, MIL-53 (Fe), MIL-125, CuBTC, D1-MIL-101, D2-MIL-101, D1-MIL-53, D2-MIL-53, was achieved.

In the second part, adsorptive removal of aromatic organics and dyes was studied. From the adsorption kinetic results, the pseudo second order kinetic model was fitted well by experimental results for all adsorbates.

With the increase of the temperature, rate constant increased, that means the initial adsorption rate increased with increasing temperature. Besides, at a constant temperature, k_2 increased with the initial concentration of MO, and decreased with the initial concentration of MR, toluene and NB that means MO adsorption is endothermic, the others are exothermic processes. This results are supported by thermodynamic adsorption studies. And also the rate constant is generally depended on the pore size (Hasan et al., 2012). In this study, obtained results support this case because k_2 values are in order of MIL-53 (Fe) < CuBTC < MIL-101 suggests potential applications of MOFs with large pore size in adsorptive removal.

Due to the pseudo first order and second order kinetic models are not sufficient to understand the adsorption mechanism, intraparticle diffusion model was applied. As shown in Figures 5.14 and 5.16, the adsorption process had two phases. This situation suggested that the adsorption process proceeded by surface sorption and intraparticle diffusion. Because of the intercept of second linear part is not zero, it can be said intraparticle diffusion is not only rate limiting step.

Adsorption isotherm was also investigated for all adsorbates. Adsorption isotherm data is important to predict and compare adsorption performance, as the sorption isotherm represents the equilibrium relationship between the solute in solution and the sorbate retained in the sorbent at a given temperature. The model parameters often provide information about the mechanisms of sorption, surface properties of the sorbent and affinity between the sorbate and sorbent. Langmuir and Freundlich adsorption isotherms model were applied. These models were adjusted by nonlinear regression by using MATLAB software and Langmuir was

found more suitable for adsorption of nitrobenzene, methyl red and methyl orange experimental results. According to these results, it can be said that the adsorption of MR onto MOFs was a typical monomolecular-layer adsorption. Freundlich model was more suitable for only toluene adsorption results.

In this study, n values (Freundlich constant) are greater than unity (Table 5.3). If the n value is greater than unity, the isotherm can be classified as L-type, reflecting a high affinity between adsorbate and adsorbent and is indicative of chemisorptions. In addition, the Langmuir constant b and the Freundlich constant, K_F , which is related to the adsorption capacity, show an opposite trend with temperature indicating that MR adsorption onto MOFs is an exothermic reaction.

Adsorption thermodynamic studies were also investigated and the negative ΔH° indicates that the adsorption process onto MOFs is exothermic. The negative ΔG° suggests that the adsorption process is spontaneous. The positive entropy change, ΔS , indicates the increased randomness at the solid/solution interface during the adsorption process. In other words, in this study the number of desorbed water molecules was larger than that of the adsorbed molecules. Therefore, the driving force (negative ΔG) onto MOFs is due to both enthalpy effect and entropy effect.

Effect of regeneration of MOFs and effect of adsorbent dosage were also studied. It can be said these MOFs have excellent regeneration ability in the adsorptive removal. Adsorbed amount of adsorbates increases with increasing adsorbent amounts until 0.1 g. This is explained as when the adsorbent dose increased, more surface area will be available so more active sites will also be available for. Further increase of the adsorbent amounts doesn't have any effect on the adsorption rate.

The adsorption of a dye usually depends highly on the pH value of the dye solution. Therefore for adsorptive removal of dyes, pH effect was also investigated and it was found the adsorbed amounts decreased with increasing pH value of the dye solution which is quite similar to previous reports (Haque et al., 2010; Chen et al., 2012). The decreasing of adsorbed MR with increasing pH might be owing to the fact that the amount of positive charges of adsorbents

decreased with increasing pH. When the pH value increased to value of 12, the amount of adsorption was zero.

When compared the other adsorbents, MOFs were found as effective adsorbents due to large surface area and high pore volume and although MIL-53 (Fe) has a very small surface area, its flexible structure make it the material of choice for adsorption studies.

The adsorption mechanism of organic aromatics and dyes may be explained with;

- Electrostatic interaction between acidic anionic dyes (MR and MO) and the adsorbents,
- π - π interaction between benzene rings of MOFs and aromatics and dyes,
- And also breathing effect of MIL-53 (Fe).

To summarize, it was found that the adsorption rate and capacity is dependent on the pore size and flexible structure of the adsorbents indicated MOFs having these properties can be potential adsorbents for removal of aromatics and dyes from wastewater.

In the third part, the esterification of acetic acid with different alcohols was performed by conventional batch process.

In this study, MIL-53 (Fe)s, MIL-125s, D1-MIL-101s, D2-MIL-101s, D1-MIL-53s, D2-MIL-53s and MIL-101s were used for the esterification of acetic acid as catalysts. The preparation these catalysts were explained in Section 4.2-4.4 and Section 5.3, respectively.

- ❖ The catalytic activities MIL-53 (Fe)s, MIL-125s, D1-MIL-101s, D2-MIL-101s, D1-MIL-53s, D2-MIL-53s and MIL-101s were tested in the liquid phase esterification of acetic acid.
- ❖ The most effective catalyst was selected among specified catalysts.
- ❖ The effects of operating conditions including temperature, catalyst loading and molar ratio of alcohol to acid were studied.

- ❖ The effect of sulfation on the catalytic activities of catalysts was investigated.
- ❖ The effect of chain length of alcohol was achieved.
- ❖ Reusability of catalysts and catalyst leaching were studied.

To calculate conversion of limiting reactant which is acetic acid and the molar amounts of components in batch reactor experiments, samples were taken and analyzed by Gas Chromatography (GC) at the end of 7 hours.

Firstly, the esterification of acetic acid with methanol, butanol and hexanol was carried out catalyzed by MOFs. Then by using the same catalyst, effect of temperature, sulfation and reusability studies were performed for the esterification of acetic acid with butanol.

Among the seven sulfated MOFs, **MIL-101s** shows the highest catalytic activity because of having highest surface area.

The effect of temperature on the conversion of acetic acid was investigated by changing temperature as 353, 358 and 363 K, other conditions were kept constant at catalyst loading of 6 wt %, butanol to acid initial molar ratio of 1 and stirrer speed of 500 rpm. After 7 hours, conversion values of acetic acid for butyl acetate synthesis catalyzed by MIL-101 were found as 80.73 %, 84.54% and 86.2 % at 353, 358 and 363 K, respectively.

Reusability of catalyst is important for economic and environmental aspects. For this purpose the reusability experiments were carried out at 363 K, 6wt % of catalyst loading, 1:1 acid alcohol molar ratio and 500rpm. and it was seen that conversion change is negligible. Therefore, the catalyst turned out to be reusable. Another important concept in heterogenous catalyst is catalyst leaching. The reaction mixture was analysed by Atomic Absorption Spectroscopy, there is no any Fe, Cr or Ti observed.

Experiments were carried out with catalyst loading of 3 wt %, 6 wt % and 9 wt % to examine the effect of catalyst loading. These experiments were studied at 363 K with a reactant ratio 3:1. As the reaction rate is directly related to the number of resin functional groups; catalyst concentration makes a positive effect

in conversion. The increase in conversion is more significant when the catalyst concentration is raised from 6 to 9 wt %. Final conversions of acetic acid were calculated as 92.85 %, 95.59 % and 98.35 % at catalyst loadings of 3, 6 and 9 wt%, respectively. Many authors observed similar results in their previous works (Chen et al., 1999; Yadav and Kulharni, 2000; Sanz and Gmehling, 2006; Ali and Merchant, 2009).

To investigate the effect of the initial molar ratio of butanol to acetic acid on the conversion, the initial molar ratio was changed as 1:1, 2:1 and 3:1 at a temperature of 363 K, catalyst loading of 6 wt %, and stirrer speed of 500 rpm. According to previous studies, it is known that, alcohol to acid initial molar ratio is directly related to conversion in esterification reactions (Ali et al., 2007; Qu et al., 2009; Brahmkhatri and Patel, 2012, Pappu et al., 2013). It can be seen that the conversion of acetic acid increases with increasing the initial molar ratio of alcohols to acetic acid. This result shows that conversion of acetic acid can be effectively enhanced by using a large excess of alcohols.

Sulfation was applied to synthesized MOFs to increase the acidity. To observed the effect of sulfation, experiments were carried out before and after sulfation. Sulfation decreases the surface area, pore volume and thermal stability but increases the conversion of acetic acid because of acidity increment. For example, the conversion of acetic acid increases from 73. 71 % to 86.2 % after sulfation for MIL-101.

The highest conversion is achieved as 98.35 % at a temperature of 363 K, molar ratio of 3:1 and catalyst loading of 9 wt %.

Esterification reactions proceed with or without a catalyst. However, esterification reaction without catalyst is slower because rate depends on the autoprotolysis of the carboxylic acid. Therefore, esterification should be occurred with help of an acid catalyst that acts as a proton donor to the carboxylic acid. The conversion achieved in the non-catalyzed reaction was 21, 20.5, 18.7% by using butanol, methanol and hexanol, respectively. The experiments were carried out at 363 K, 1:1 alcohol acid molar ratio. (For methanol, experiment was conducted at 333 K).

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RESUME

Bornova/İZMİR

email: esra.yilmaz@ege.edu.tr**Personel Informations**

Nationally: T.C.

Place of Birth: Sivas

Date of Birth: 1989

Driving Licence: B (2010)

Education

- 2012 - 2015 Ege University, Chemical Engineering (Master Degree)
- 2007 - 2012 Ege University, Chemical Engineering
- 2003 - 2007 Rahmi Kula Anatolian High School
- 2000 - 2003 23 Nisan Elementary Middle School

Experiance

- Intern Engineer (14.06.2010 – 15.07.2010)
PETROFER Endüstriyel Yağlar San. ve Tic. A.Ş., İzmir, Laboratory Internship
- Intern Engineer (14.06.2011-15.07.2011)
Petkim Petrokimya Holding A.Ş., Aliğa, İZMİR, Plant Internship
- Research Assistant at Çankırı Karatekin University Chemical Engineering Department (04.12.2013---)

Projects and Achievements

2nd Degree of Chemical Engineering Department

Diploma Project:

- **TÜBİTAK Project:** Searching for thermodynamic equilibrium in the esterification of Acrylic Acid with three different alcohols which are butanol, iso-butanol and hexanol

Design Project:

- Design of a cumene production plant
- Design of a continuous distillation column for a multicomponent component mixture
- Design of a pumping system using solar energy
- Design of a billboard by using cholesteric liquid crystals
- Design of a compressor driven by a geothermal energy based turbine
- Design of a fire extinguisher
- Design of ethyl benzene production plant

Seminar and Courses

- Sustainable Production and Consumption Seminar, 2009, İzmir
- Time Management and SWOT Analysis Seminar, 2009, İzmir
- Entrepreneurism and Applications of Entrepreneurism, 2012, İzmir
- Being a good engineer - Being a good manager, 2012, İzmir

Computer Skills

- MS-Office Programs (Word, Excel, Powerpoint)
- ASPEN Plus
- IntelliCAD
- MATLAB

- Polymath

Publications

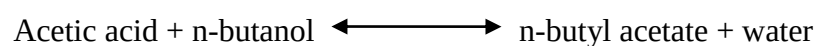
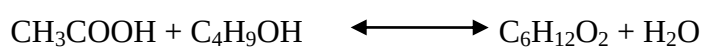
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- 2015, E. Yılmaz, E. Sert, F.S. Atalay, “Removal of Aromatic Organic Compounds using MIL-101” under review.
- 2015, E. Yılmaz, E. Sert, F.S. Atalay, “Synthesis and characterization of ferrous metal organic frameworks and usage in esterification reaction” Porous and Powder Materials 2015 (PPM 2015).

APPENDIX

Calculation of Conversions

To calculate conversion of acetic acid to buthyl acetate, the weight percentages of butanol, acetic acid and buthyl acetate in the reaction medium were measured by GC analysis.

The reaction and the molar amounts of components according to reaction stoichiometry are as follows;



	MW (g/mol)	Initial	Final
Acetic Acid, A	60.05	$N_{A,0}$	$N_{A,0} (1-x)$
Butanol, B	74.12	$N_{B,0}$	$N_{B,0} - N_{A,0}x$
Buthyl Acetate, C	116.17	-	$N_{A,0}x$
Water, D	18	-	$N_{A,0}x$

wA : weight percent of acetic acid

wC : weight percent of buthyl acrylate

$$\frac{wA}{wC} = \frac{N_{A,0}(1 - X)mol(60.05g/mol)}{N_{A,0}Xmol (116.17 g/mol)} \quad A.1$$

$$\frac{wA}{wC} = \frac{(1 - X)}{X(116.17)} \quad A.2$$

According to Eqn (A.2) conversions of acetic acid were calculated at every time intervals for all runs.