DOKUZ EYLÜL UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCIES

INVESTIGATION OF APPLICABILITY OF CLAY MINERALS IN WASTEWATER TREATMENT

by

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December, 2007

İZMİR

INVESTIGATION OF APPLICABILITY OF CLAY MINERALS IN WASTEWATER TREATMENT

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M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"INVESTIGATION OF APPLICABILITY OF CLAY MINERALS IN WASTEWATER TREATMENT"** completed by **ÇİĞDEM KÜÇÜKSELEK** under supervision of **Assoc.Prof.Dr. DENİZ DÖLGEN** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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INVESTIGATION OF APPLICABILITY OF CLAY MINERALS IN WASTEWATER TREATMENT

ABSTRACT

Clay minerals are natural, colloidal materials which have ion exchange capacity and adsorption properties. In environmental engineering clay minerals are used generally as adsorbance and ion exchanger in order to treat both water and wastewater, and as an impermeable layer in order to prevent groundwater contamination in landfill areas.

The aim of this study was to utilize the clay minerals in wastewater treatment. Hence, kaolinite is used as an adsorbent to remove certain metals (i.e. Cu, Fe, Ni, Zn) from aqueous solutions. Synthetic and industrial wastewaters were used in batch adsorption experiments. In the experiments, the effects of the pH, particle size, adsorbent dosage, contact time, and initial concentrations on metal removal were investigated. Experimental results were showed that kaolinite is a very strong adsorbent. Metal uptake was strongly affected from the pH of the metal solution. The maximum Cu, Ni and Zn adsorption were observed at pH 10. Copper concentration was reduced from 1000 µg/L to 5 µg/L yielding 99.4% removal efficiency. The maximum efficiency for Ni and Zn ions were 98% and 97% respectively. However, highest iron ion adsorption was obtained at pH 5 yielding 99% efficiency. Although, adsorption efficiency was not significantly affected from the particle size, the smallest particle size, i.e. 0.053 mm was determined as an effective diameter for the kaolinite. Required adsorbent doses were 0.1 g/L for copper and zinc ions. Relatively higher doses were required for nickel and iron adsorption. In addition, metal uptakes were accomplished very quickly. 15 minutes contact time was enough for the effective metal removal. Besides, adsorption kintecis were evaluated. Adsorption data for copper, iron and nickel was fitted to Freudlich equation which exhibits that physical adsorption mechanism is effective in the process.

Keywords: Adsorption, clay minerals, heavy metals, kaolinite, wastewater treatment.

KİL MİNERALLERİNİN ATIK SU ARITIMINDA UYGULANABİLİRLİĞİNİN ARAŞTIRILMASI

ÖZ

Kil mineralleri iyon değiştirme kapasitesi ve adsorpsiyon özelliği olan doğal koloidal maddelerdir. Çevre mühendisliğinde genellikle su ve atıksu arıtmak için adsorbans ve iyon değiştirici olarak, katı atık depolama sahalarında ise geçirimsiz tabaka olarak yeraltı suyu kirliliğinin önlenmesi için kullanılırlar.

Bu çalışmanın amacı, kil minerallerini atık su arıtımında kullanmaktır. Bu amaçla kaolin sucul ortamlardan bakır, demir, nikel ve çinko gibi bilinen metalleri gidermek için adsorban olarak kullanılmıştır. Sentetik ve endüstriyel atıksular kesikli adsorpsiyon deneylerinde kullanılmıştır. Deneylerde, metal giderim verimlerine pH'ın, partikül boyutunun, adsorban dozunun, temas süresinin ve giriş konsantrasyonun etkisi araştırılmıştır. Deneysel sonuçlar kaolinin çok güçlü bir adsorban olduğunu göstermiştir. Metal alımı pH parametresinden etkilenmiştir. Maksimum Cu, Ni ve Zn adsorpsiyonu pH 10'da elde edilmiştir. Bakır derişimi 1000 µg/L'dan 5 µg/L mertebesine inmiş ve %99.4 oranında giderim verimi sağlanmıştır. Nikel ve çinko iyonları için maksimum verim sırasıyla %98 ve %97% olarak elde edilmiştir. Demir iyonları için ise maksimum verim pH 5'de sağlanmış, %99 oranında demir giderimi elde edilmiştir. Adsorpsiyon verimi partikül boyutundan fazla etkilenmemekle birlikte kullanılan en küçük partikül büyüklüğünde (0.053 mm) en yüksek performans elde edilmiştir. Bakır ve çinko iyonları için etkin adsorbent dozu 0.1 g/L olarak belirlenmiştir. Nikel ve demir adsorpsiyonunda ise nisbeten daha yüksek dozlarda adsorban kullanılması gerekmiştir. Bunlara ek olarak, metal alımı çok hızlı gerçekleşmiştir. Etkili metal giderimi için 15 dakikalık temas süresi yeterli bulunmuştur. Ayrıca, adsorpsiyon kinetikleri incelenmiştir. Bakır, demir ve nikel iyonu adsorpsiyonun Freundlich izotermine uyduğu belirlenmiş olup bu durum süreçte fiziksel adsorpsiyon mekanizmasının etkili olduğu şeklinde açıklanmıştır.

Anahtar sözcükler: Adsorpsiyon, ağır metaller, atıksu arıtımı, kaolin, kil mineralleri

CONTENTS

CHAPTER ONE
INTRODUCTION

Clay minerals are natural, heterogeneous, fine-grained and colloidal particles having a diameter less than 0.002mm. Clay minerals are composed mainly of silicon, oxygen, alumina, magnesium, iron and hydroxide. Lots of scientist classifies clay minerals according to composition and structure. The characterististics common to all clay minerals derive from their chemical composition, layered structure, and size.

Clay mineral particles are commonly too small and this means small volume of clay particles has a large surface area. Large surface area, the ion exchange capacity, swelling and adsorption properties of clay minerals are commercial values. In addition to this, particle size and grain shape are main properties that affect the usage of clay minerals. Because of these values clay minerals are used many industries. Generally clay minerals are used in ceramics, paper, rubber, medical, paint, detergents, cosmetics, oil and cement industries.

Clay minerals usage is increased day by day, and in paralelly clay minerals usage in environmental engineering is increased day by day. Clay minerals are used to removal of organic matter, drug residual, heavy metals, color and lots of pollutant from the wastewaters due to their adsorption and ion exchange capacity. In addition to wastewater treatment usage of clay minerals, they are also used in solid waste management as impermeable layer instead of geomembrane in landfill areas. Clay minerals are also used in treatment plant sludges management.

Heavy metals are ubiquitous in the environment and pass through to water cycle with rainfalls, geological phenomenons, animal and human activities. Concentration of heavy metals in water cycle is increasing day by day with developed industrilizations. Copper, iron, nickel and zinc are detected in contaminated waters. These heavy metals generated metal plating, metal mining, metallurgical industry, smelting, porcelain industry, inorganic chemical industry, dye manufacture, textile

manufacture, petroleum refining, paint manufacture, pigment manufacture, wire drawing and foundries.

All the organisms need trace amounts of heavy metal in order to survive. Moreover, if heavy metals uptake over dose, acute and chronic disorder occurs in animal and human. Lots of researchers interested to remove toxic heavy metals from wastewater and lots of method have been used for this aim. A few of them are chemical precipitation, ion exchange, ultrafiltration, reverse osmosis and adsorption. However, all the options are so expensive except adsorption. Owing to the fact that adsorption is cheaper than the other alternatives this method is researched continuously by a lot of researcher with a passion. In these researchs different kinds of adsorbents for examples, activated carbon, clay minerals, agricultural by-produts and industrial by-products have been tried to heavy metals and the other pollutants' removal. Also in this thesis kaolinite which is a kind of clay mineral is tested as an adsorbent for adsorption of some heavy metals which are copper, iron, nickel and zinc from wastewater. The main purposes of choosing kaolinite as an adsorbent are its low price, easy to gain and it is a natural adsorbent.

Two types of wastewaters which were synthetic and industrial wastewaters were used for adsorption experiments. During the batch adsorption experiments with using synthetic wastewater, the effects of the pH, particle size, adsorbent dosage, contact (agitation) time, and initial concentrations on Cu, Fe, Ni, Zn removal were investigated separately. According to results of synthetic wastewaters adsorption experiments, industrial wastewaters were coordinated suitable pH, particle size and contact time. So, effect of adsorbent dosage was observed in industrial wastewaters. In addition to this, adsorption isotherms (Freundlich isotherm and Langmuir isotherm) are determined. According to experiments results, kaolinite is a very strong adsorbent for removing heavy metal ions from aqueous solutions.

In the thesis literature survey is placed in Chapter Two. In this chapter clay minerals and adsorption are mentioned. Chapter Three includes experimental studies. In Chapter Three preparation of kaolinite, heavy metals solutions, and the adsorption

of synthetic and industrial wastewater experiments are represented. Result and discussion with their interpretations for each heavy metal ions are present separetly in Chapter Four. The last conclusion and the recommendation are placed in Chapter Five.

CHAPTER TWO
LITERATURE SURVEY

2.1 Clay Minerals

2.1.1 Definition of Clay Minerals

Clay has two definitions. According to the clay mineralogist, a clay mineral is a layer silicate mineral (also called a phyllosilicate) or other mineral which imparts plasticity and which hardens upon drying or firing. The word "clay" is also used to refer to a particle size in a soil or sediment. The term is used in the U.S. and by the International Society of Soil Science for a rock or mineral particle in the soil having a diameter less than 0.002 mm (2 microns) (Barton and Karathanasis, 2002) whereas sedimentologists classify particles smaller than 0.004 mm as clay (ACMS, n.d.).

In practice, the term clay implies a natural, earthy, fine-grained material which develops plasticity when mixed with a limited amount of water. By plasticity is meant the property of the moistened material to be deformed under the application of pressure, with the deformed shape being retained when the deforming pressure is removed. Chemical analyses of clays show them to be composed essentially of silica, alumina and water frequently with appreciable quantities of iron, alkalies and alkaline earths.

2.1.2 Formation of Clay Minerals

Clay minerals refers to a group of hydrous aluminosilicates that predominate the clay-sized (<2 μm) fraction of soils. These minerals are similar in chemical and structural composition to the primary minerals that originate from the Earth's crust; however, transformations in the geometric arrangement of atoms and ions within their structures occur due to weathering. Primary minerals form at elevated temperatures and pressures, and are usually derived from igneous or metamorphic rocks. Inside the Earth these minerals are relatively stable, but transformations may

occur once exposed to the ambient conditions of the Earth's surface. Although some of the most resistant primary minerals (quartz, micas, and some feldspar) may persist in soils, other less resistant minerals (pyroxenes, amphiboles, and a host of accessory minerals) are prone to breakdown and weathering, thus forming secondary minerals. The resultant secondary minerals are the culmination of either alteration of the primary mineral structure or neoformation through precipitation or recrystallization of dissolved constituents into a more stable structure. These secondary minerals are often referred to as phyllosilicates because, as the name implies (Greek: *phyllon,* leaf), they exhibit a platy or flaky habit, while one of their fundamental structural units is an extended sheet of SiO_4 tetrahedra (Barton and Karathanasis, 2002).

2.1.3 Structure of Clay Minerals

The basic crystal structure of clay minerals is comprised of layers, a sandwich of one or two silicon dioxide sheets with one aluminum oxide or magnesium oxide sheet. Clay mineralogy, or the classification of clay minerals, is based on the precise structure of this layer, whether there are two sheets or three, and what is the composition of the octahedral sheet.

There are two types of sheet: tetrahedral (silicate) and octahedral. Tetrahedral sheets are made up of silicon (Si^{4+}) and oxygen (O_2^-). In the silica sheet, the basic unit is the silica tetrahedron. In this unit the silicon atom is bonded to 4 oxygen atoms. Each tetrahedron shares 3 of its 4 oxygens to form a hexagonal structure, as shown in Figure 2.1.

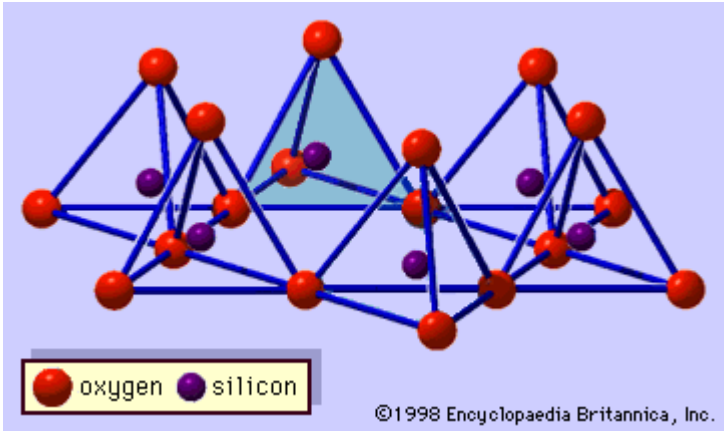

Figure 2.1 Structure of a tetrahedral sheet

Octahedral sheets are made up of hydroxide (OH^-) and either aluminium (Al^{+3}) or magnesium (Mg^{+2}). An octahedral sheet is referred to as dioctahedral if it contains aluminium and trioctahedral if it contains magnesium. In the alumina or magnesium sheet, the basic unit is the octahedron. This unit is usually formed by aluminum or magnesium and hydroxide ions. The aluminum or magnesium atom is bonded to 6 oxygen atoms. Each octahedron shares all 6 oxygen atoms to form a hexagonal structure, shown in Figure 2.2.

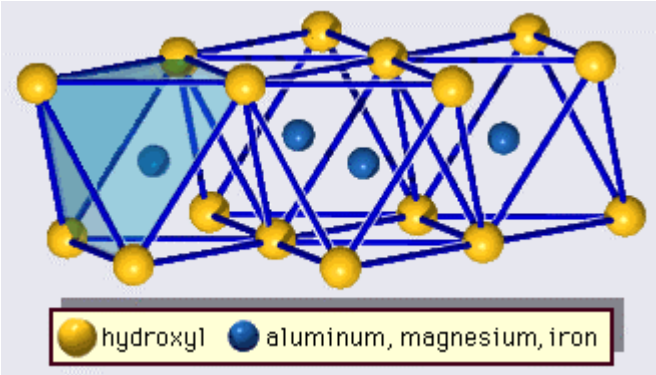

Figure 2.2 Structure of an octahedral sheet

These sheets combine in various ways to produce clay structures. They combine by sharing oxygen atoms to form a chemically bonded layer. Some minerals have layers comprised of two sheets (one tetrahedral and one octahedral), while others have layers comprised of three sheets (one octahedral sandwiched between two tetrahedral layers). For example, kaolinite is made up of one tetrahedral sheet plus

one octahedral sheet (1:1 layer), while smectite and illite are made up of two tetrahedral sheets and one octahedral sheet (2:1 layer). The space between layers is known as the interlayer space. The interlayer space may contain positive ions known as cations (for example, potassium K^{+}). Different clay minerals contain different cations in the interlayer space.

2.1.4 Classification of Clay Minerals

Clay minerals are classified by Grim and Güven in 1978 as two main titles on the basis of their structure and composition. The first title is amorphous and the other title is crystalline. Crystalline group is divided into four, which are two-layer type, three layer types, regular mixed-layer types and the chain structure types. Two-layer type clay minerals sheet structure is composed of units of one layer of silica tetrahedrons and one layer of alumina octahedrons. Three-layer type clay minerals sheet structure is composed of two layers of silica tetrahedrons and one central dioctahedral or trioctahedral layer. Regular mixed–layer type clay minerals ordered stacking of alternate layers of different types. Hornblende–like chains of silica tetrahedrons linked together by octahedral groups of oxygen and hydroxyls containing Al^{+3} and Mg^{+2} atoms are made chain structure type clay minerals. Kaolninite and halloysite group clay minerals are placed in two-layer type. Three-layer clay minerals include montmorillonite and illite group clay minerals. Chlorite group clay minerals belonged to regular mixed–layer types. Attapulgite, sepiolite and palygorskite are placed in chain structure type clay minerals.

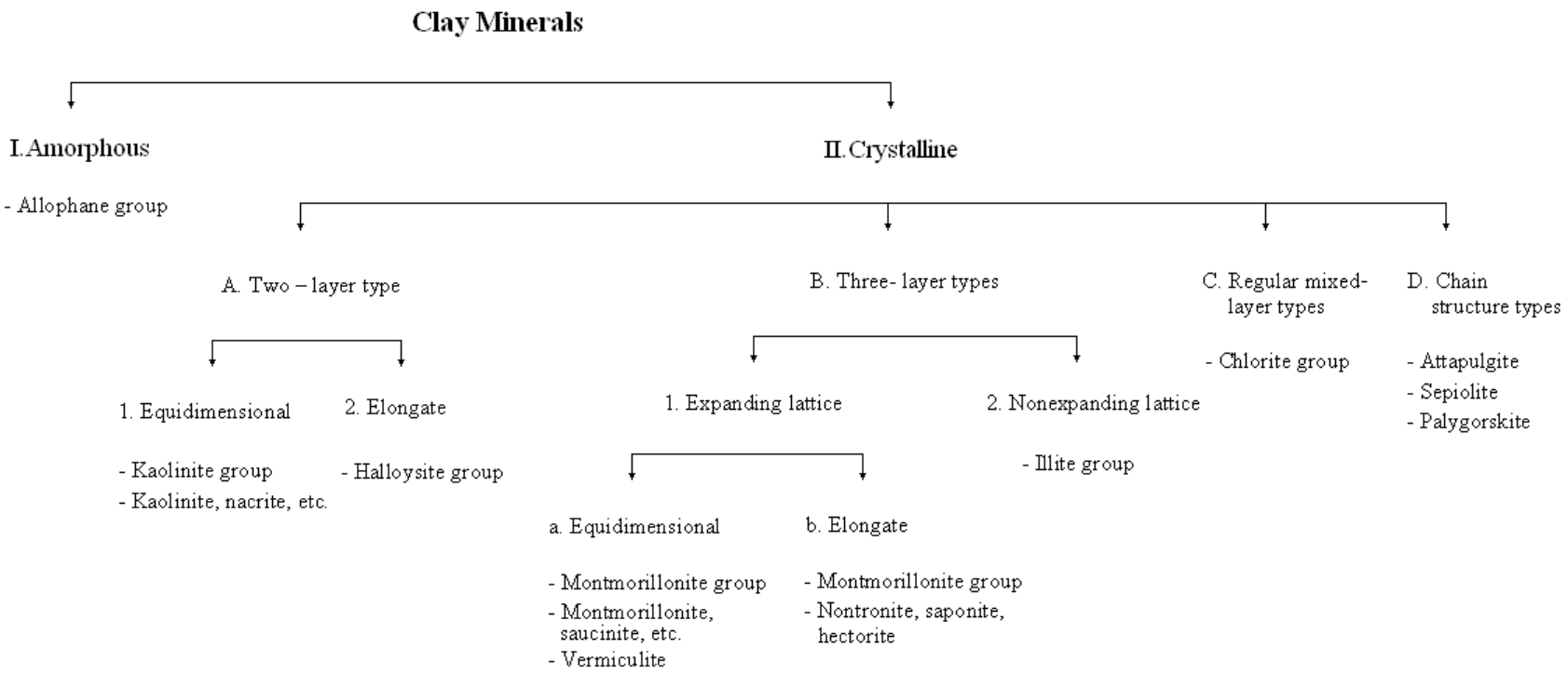

Figure 2.3 Classification of Clay Minerals

According to the U.S. Bureau of Mines, clays are categorized into six groups. The categories are kaolin, ball clay, fire clay, bentonite, fuller's earth, and common clay and shale. Kaolin, or china clay, is defined as a white, claylike material composed mainly of kaolinite, which is a hydrated aluminum silicate ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), and other kaolin-group minerals. Kaolin has a wide variety of industrial applications including paper coating and filling, refractories, fiberglass and insulation, rubber, paint, ceramics, and chemicals. Ball clay is plastic, white-firing clay that is composed primarily of kaolinite and is used mainly for bonding in ceramic ware, primarily dinnerware, floor and wall tile, pottery, and sanitary ware. Fire clays are composed primarily of kaolinite, but also may contain several other materials including diaspore, burley, burley-flint, ball clay, and bauxitic clay and shale. Because of their ability to withstand temperatures of 1500°C or higher, fire clays generally are used for refractories or to raise vitrification temperatures in heavy clay products. Bentonite is a clay composed primarily of smectite minerals, usually montmorillonite, and is used largely in drilling muds, in foundry sands, and in pelletizing taconite iron ores. Fuller's earth is defined as a nonplastic clay or claylike material that typically is high in magnesia and has specialized decolorizing and purifying properties. Fuller's earth, which is very similar to bentonite, is used mainly as absorbents of pet waste, oil, and grease. Common clay is defined as a plastic clay or claylike material with a vitrification point below 1100°C. Shale is a laminated sedimentary rock that is formed by the consolidation of clay, mud, or silt. Common clay and shale are composed mainly of illite or chlorite, but also may contain kaolin and montmorillonite (EPA, 1995).

Another classification of clay minerals is up to swelling property of clay minerals. Clays are thus divided into swelling and non-swelling type mineral. Swelling clays are called smectities. Non-swelling clays are illite, chlorite and kaolinite.

2.1.5 Physical and Chemical Properties of Clay Minerals

The characterististics common to all clay minerals derive from their chemical composition, layered structure, and size. The commercial value of clay depends

primarily on its physical properties such as plasticity, strength, shrinkage, vitrification range, refractoriness, fired color, porosity and absorption. Clay mineral particles are commonly too small for measuring precise optical properties. Their small size means that a small volume of clay particles has a large surface area. This large surface area makes available many reactive sites of exchange of ions in a small volume of soil. Besides, small grain size of clays gives more viscous suspensions which increase the density of the solutions. Specific gravities of most clay minerals are within the range from 2 to 3.3. Their hardness generally falls below 2 $^{1}/_{2}$, except for antigorite, whose hardness is reported to be 2 $^{1}/_{2}$–3 $^{1}/_{2}$.

Clay minerals all have a great affinity for water. Water molecules are strongly attracted to clay mineral surfaces. When a little clay is added to water, is becoming a slurry forms because the clay distributes itself evenly throughout the water. This property of clay is used by the paint industry to disperse pigment (color) evenly throughout a paint. Without clay to act as a carrier, it would be difficult to evenly mix the paint base and color pigment. A mixture of a lot of clay and a little water results in a mud that can be shaped and dried to form a relatively rigid solid. These properties exploited by potters and the ceramics industry to produce plates, cups, bowls, pipes, and so on. Environmental industries use both these properties to produce homogeneous liners for containment of waste. The process by which some clay minerals swell when they take up water is reversible. Swelling clay expands or contracts in response to changes in environmental factors. Hydration and dehydration can vary the thickness of a single clay particle by almost 100 percent (for example, a 10Å-thick clay mineral can expand to 19.5Å in water (Velde, 1995). Houses, offices, schools, and factories built on soils containing swelling clays may be subject to structural damage caused by seasonal swelling of the clay portion of the soil.

The ion-exchange properties of the clay minerals are extremely important because they determine the physical characteristics and economic use of the minerals. Depending on deficiency in the positive or negative charge balance of mineral structures, clay minerals are able to adsorb certain cations and anions retain them around the outside of the structural unit in an exchangeable state, generally without

affecting the basic silicate structure. These adsorbed ions are easily exchanged by other ions. The exchange reaction differs from simple sorption because it has a quantitative relationship between reacting ions. Exchange capacities vary with particle size, perfection of crystallinity, and nature of the adsorbed ion; hence, a range of values exists for a given mineral rather than a single specific capacity. With certain clay minerals such as imogolite, allophane, and to some extent kaolinite that have hydroxyls at the surfaces of their structures, exchange capacities also vary with the pH of the medium, which greatly affects dissociation of the hydroxyls. Under a given set of conditions, the various cations are not equally replaceable and do not have the same replacing power. Calcium, for example, will replace sodium more easily than sodium will replace calcium. Sizes of potassium and ammonium ions are similar, and the ions are fitted in the hexagonal cavities of the silicate layer. Vermiculite and vermiculitic minerals preferably and irreversibly adsorb these cations and fix them between the layers. Heavy metal ions such as copper, zinc, and lead are strongly attracted to the negatively charged sites on the surfaces of the 1:1 layer minerals, allophane and imogolite, which are caused by the dissociation of surface hydroxyls of these minerals.

The solubility of the clay minerals in acids varies with the nature of the acid and its concentration, the acid-to-clay ratio, the temperature, the duration of treatment, and the chemical composition of the clay mineral attacked. In general, ferromagnesian clay minerals are more soluble in acids than their aluminian counterparts. Incongruent dissolutions may result from reactions in a low-acid-concentration medium where the acid first attacks the adsorbed or interlayer cations and then the components of the octahedral sheet of the clay mineral structure. When an acid of higher concentration is used, such stepwise reactions may not be recognizable, and the dissolution appears to be congruent. One of the important factors controlling the rate of dissolution is the concentration in the aquatic medium of the elements extracted from the clay mineral. Higher concentration of an element in the solution hinders to a greater degree the extractions of the element. In alkaline solutions, a cation-exchange reaction first takes place, and then the silica part of the

structure is attacked. The reaction depends on the same variables as those stated for acid reactions.

High-temperature reactions of clay minerals are important for certain industries such as ceramic science and industry. When heated at temperatures beyond dehydroxylation, the clay mineral structure may be destroyed or simply modified, depending on the composition and structure of the substance. In the presence of fluxes, such as iron or potassium, fusion may rapidly follow dehydroxylation. In the absence of such components, particularly for aluminous dioctahedral minerals, a succession of new phases may be formed at increasing temperatures prior to fusion.

Smectite, vermiculite, and other expansible clay minerals can accommodate relatively large, inorganic cations between the layers. Because of this multivalency, the interlayer space is only partially occupied by such inorganic cations that are distributed in the space like islands. Hydroxy polymers of aluminum, iron, chromium, zinc, and titanium are known examples of the interlayering materials. Most of these are thermally stable and hold as pillars to allow a porous structure in the interlayer space. The resulting complexes, often called pillared clays, exhibit attractive properties as catalysts namely, large surface area, high porosity, regulated pore size, and high solid acidity. On the other hand, cationic organic molecules, such as certain aliphatic and aromatic amines, pyridines, and methylene blue, may replace inorganic exchangeable cations present in the interlayer of expansible minerals. Polar organic molecules may replace adsorbed water on external surfaces and in interlayer positions. Ethylene glycol and glycerol are known to form stable specific complexes with smectites and vermiculites. The formation of such complexes is frequently utilized for identifying these minerals. As organic molecules coat the surface of a clay mineral, the surface of its constituent particles changes from hydrophilic to hydrophobic, thereby losing its tendency to bind water. Consequently, the affinity of the material for oil increases, so that it can react with additional organic molecules. As a result, the surface of such clay materials can accumulate organic materials. Some of the clay minerals can serve as catalysts for reactions in which one organic substance is transformed to another on the mineral's surface. Some of these organic

reactions develop particular colours that may be of diagnostic value in identifying specific clay minerals. Organically clad clay minerals are used extensively in paints, inks, and plastics.

2.1.6 General Uses of Clay Minerals

From prehistoric times, clay has been indispensable in architecture, in industry, and in agriculture. As a building material, it is used in the form of brick, either sun-dried (adobe) or fired. Clays are also of great industrial importance, e.g., in the manufacture of tile for wall and floor coverings, of porcelain, china, and earthenware, and of pipe for drainage and sewage. Highly absorbent, bentonite is much used in foundry work for facing the molds and preparing the molding sands for casting metals. The less absorbent bentonites are used chiefly in the oil industry, e.g., as filtering and deodorizing agents in the refining of petroleum and, mixed with other materials, as drilling muds to protect the cutting bit while drilling. Other uses are in the making of fillers, sizings, and dressings in construction, in clarifying water and wine, in purifying sewage, and in the paper, ceramics, plastics, and rubber industries. Clay, being almost impermeable to water, is also used where natural seals are needed, such as in the cores of dams, or to seal landfills against toxic seepage.

2.1.6.1. Industrial and Agricultural Applications

Clays have a tremendous number of miscellaneous industrial uses (manufacturing of paper, refractories, rubber, sanitary wear, fire clay, firebricks, construction materials, cosmetics, etc.), and for each application a distinct type with particular properties such as swelling properties, cation exchange and adsorbing capacity, etc. are important. In addition, particle size and grain shape are main properties that affect the usage of clay minerals.

In the paper industry, kaolin as clay mineral is used both as a filler in the bulk of the paper and to coat its surface. Kaolin's whiteness, opacity, large surface area and low abrasivity make it an ideal raw material for paper production. When kaolin is

used as a pigment, it is divided broadly into filler and paper coating grade clays based on their brightness and viscosity. Kaolin is used in plastics to provide smooth surfaces, dimensional stability and resistance to chemical attack, to conceal fiber reinforcement patterns and to reduce shrinkage and cracking during polymer compounding and shape forming. Refractory materials are produced from natural materials, combinations of compounds and minerals, such as kaolin, which are used to build structures subjected to high temperatures, ranging from simple to sophisticated products, e.g. from fireplace brick linings to re-entry heat shields for the space shuttle. In kaolin hydrous or calcinated forms, kaolin can improve the optical, mechanical and rheological properties of paint. Kaolin improves the strength, abrasion resistance and rigidity to rubber. The fiberglass which is used as a strengthener in a multitude of applications requires the use of kaolin for its manufacture. Besides, kaolin allows for the strengthening of the fibers integrated into the material. Kaolin converts to mullite and glass when fired to temperatures exceeding 1000° C. It is used in ceramic industry in formulations described as white wares, which consists of tableware, sanitary ware, and wall and floor tiles. It provides strength and plasticity in the shaping of these products and reduces the amount of pyroplastic deformation in the process of firing (Ima-Europe, n.d.).

Bentonite is used as a bonding material in the preparation of moulding sand for the production of iron, steel and non-ferrous casting. The unique properties of bentonite yield green sand moulds with good flowability, compactability and thermal stability for the production of high quality castings. Bentonite is used as a binding agent in the production of iron ore pellets. Through this process, iron ore fines are converted into spherical pellets, suitable as feed material in blast furnaces for pig iron production, or in the production of direct reduction iron. Bentonite in civil engineering applications is traditionally used as a thixotropic, support and lubricant agent in diaphragm walls and foundations, in tunnelling, in horizontal directional drilling and pipe jacking. Bentonite, due to its viscosity and plasticity, is also used in portland cement and mortars. It is used as an animal feed supplement, as a pelletising aid in the production of the animal feed pellets, as well as a flowability aid for unconsolidated feed ingredients such as soy meal. It is also used as an ion exchanger

for improvement and conditioning of the soil. When thermally treated, it can be used as a porous ceramic carrier for various herbicides and pesticides. Laundry detergents and liquid hand cleansers/soaps rely on the inclusion of bentonite, in order to remove the impurities in solvents and to soften the fabrics (Ima-Europe, n.d).

Characteristics of bricks vary according to mineral variation of soil, mixture style and baking conditions during brick production. Determination of the suitability of clay mines around Tokat region in brick manufacture is investigated by Karaman et al., 2005. Chemical and mechanical characteristics of raw material are obtained and the suitability of this raw material for brick and tile production is determined. Raw material includes chlorite and illite which are clay mineral. According to the results, it is determined that the raw material used in brick and tile industry is suitable. In addition, it was also determined that the samples taken for perforated bricks produced in 17 factories showed the characteristic which was mentioned in standards in terms of compressive strength, unit weight, freezing and thawing, harmful manias and calcium content.

Lightweight concrete production is accomplished by utilizing lightweight aggregate or chemical foaming agents in concrete. Both concrete types have advantageous insulation characteristics in structures because of the air gaps in their structure. Natural zeolite is a kind of alumina silicate mineral that contains high amounts of SiO_2 and Al_2O_3. It improves the binding effect in cement based structures reacting with $Ca(OH)_2$ like other pozzolanic materials fly ash and silica fume. Due to its porous silicate structure, zeolite shows similar strength and hardness properties though more lightweight. The natural zeolite is used for aerated concrete (lightweight concrete) production by Topçu et al., 2005. They found that lightweight concrete density is decreased by zeolit ratio and 25% of the zeolite ratio is obtained as most efficient ratio.

Another usage of clay minerals is the pet food industry. Hydrated sodium calcium aluminosilicate (HSCAS) is phyllosilicate clay and selectively adsorbs aflatoxins.

Therefore, has been commonly used as an anticaking agent in animal feeds (Bingham et al., 2004).

2.1.6.2 Environmental Applications

Recently, clays have become important for various aspects of environmental science and remediation. Dense smectite clays can be compacted as bentonite blocks to serve as effective barriers to isolate radioactive wastes. Various clays may absorb various pollutants including organic compounds (such as atrazine, trifluraline, parathion, and malathion) and inorganic trace metals (such as copper, zinc, cadmium and mercury) from soils and groundwater. Clay is also used as an effective barrier in landfills and mine tailing ponds to prevent contaminants from entering the local groundwater system (Encyclopædia Britannica, Inc., n.d.). As research continues, clay minerals are playing an increasing role in solving environmental problems.

Clay minerals have been used to remove various pollutants from the wastewaters due to their adsorption and ion exchange capacity. In this context, the recent literature is investigated extensively and summarized below.

2.1.6.3 Organic Matter Removal

The effluent concentrations of certain organic matters like phenol, lignin, polyethylenimine, NH_4-N, etc. are restricted by regulations and thus they have to be controlled before the discharge. Clay minerals due to their adsorption and ion exchange capacity have been investigated by various researchers in order to remove organic matters from wastewater. For example, the efficiency of sepiolite for phenol and lignin removals is investigated by Uğurlu et al., 2003. For optimum conditions, i.e. low pH, 1 hour of adsorption time, small particle size, activation temperature at 120^{o}C, 80% of phenol and lignin removal are obtained.

The removal of nitrogen in the form of ammonium ions N-NH_4^+ from aqueous solutions using clinoptilolite and bentonite is investigated by Rosic et al., 2000.

Alkaline and acid modification of natural clay was performed. The highest removal efficiency value for $N\text{-}NH_4$ (61.1 wt%) was achieved with the natural zeolite at the lowest used initial concentration, i.e. at a concentration of 100 mg $N\text{-}NH_4$/l. When the initial concentration of ammoniacal nitrogen increasing, the removal efficiency decrease.

Kaolinite is used by Hasçakır and Dölgen (2005) in wastewater treatment to remove organic matter. High treatment performance was obtained especially, when the kaolinite was used as coagulant aid. For domestic wastewater, maximum treatment efficieny (i.e. 82% COD removal) is obtained when alum and kaolinite is used as coagulant and coagulant aid, respectively. For industrial wastewater (printing processes of cardboard manufacturing), 99% of COD is removed when ferric chloride was used as coagulant and kaolinite was used as coagulant aid. Besides the organic matter, solid matter (SS), oil-grease, turbidity, and color parameter are efficiently removed by kaolinite.

Adsorption of l-lysine (amino acid) onto montmorillonite is investigated by Parbhakar et al., 2007. The reaction products were studied using X-ray diffraction, chemical analysis and infrared spectroscopy. Lysine adsorption is first dominated by cation exchange and then by adsorption of electrically neutral lysine (as a zwitterion), as indicated by chemical and FTIR evidence. At the maximum concentration, lysine displaces only ~1/3 of the original interlayer cations.

Kuleyin and Ergun (2005) studied NH_4-N removal from leachate using clinoptilolite. Treatment of clinoptilolite by NaCl at 70^oC resulted with increased removal efficiency.

Adsorption of polyethylenimine which is cationic polymer (PEI) on bentonite clays is investigated in the aqueous solution by Öztekin et al., 2001. The apparent adsorption and the true adsorption rates was found and compared for all bentonite clays. The adsorption of PEI for all system was observed as very rapid. Equilibrium was attained within 5 min. Retention of PEI on three sample clays were determined

as 42%, 62% and 82%. In conclusion, the adsorption of positively charged PEI is very strong on the negatively charged clay.

2.1.6.4 Drug Residuals Removal

Trimethoprim (TMP) is among the most important antibacterial agents (synthetic antibiotics) used in human and veterinary medicine. The adsorption of Trimethoprim (TMP) on montmorillonite KSF was studied under different conditions (pH, ionic strength, temperature) by Bekçi Z. 2005. The results indicate that a pH value of 5.04 is optimum value for the adsorption of TMP on KSF. According to results of Langmuir and Freundlich equation, the adsorption capacity values raised as the solution temperature and ion strength decreased.

The adsorption of the drug, Promethazine hydrochloride onto montmorillonite K10 was studied under different temperatures, ionic strength and pH levels is investigated by Gereli G., 2005. Kinetic and thermodynamic parameters were calculated. The results show that the adsorption decreases with the increase of temperature. The adsorption of promethazine hydrochloride was strongly dependent on pH and ionic strength. According to the results, montmorillonite K10 can be used as excipient for promethazine hydrochloride and oral adsorbent in the case of promethazine hydrochloride poisonings.

2.1.6.5 Heavy Metals Removal

The removal Mn(II), Co(II), Ni(II), andCu(II) from aqueous solution by using a raw kaolinite is investigated by Yavuz et al., 2003. Results indicate that kaolinite shows the following absorption affinity order for metal ions: Cu(II)> Ni(II)>Co(II)>Mn(II) andsorption of copper, nickel, cobalt and manganese ions on kaolinite conformed to the linear form of Langmuir adsorption equation. Langmuir Cm constants for each metal were found as 0.446 mg/g (Mn), 0.919 mg/g (Co), 1.669 mg/g (Ni), 10,787 mg/g (Cu) at 251 ^{o}C, respectively.

Gupta and Bhattacharyya (2006) used kaolinite, montmorillonite and their poly(oxo zirconium) and tetrabutylammonium derivatives for removing Cd(II) from aqueous solution. Batch adsorption studies were carried out under various Cd(II) concentrations, amount of clay adsorbents, pH, interaction time and temperature. The uptake of the metal was initially very fast, but gradually slowed down indicating diffusion into the interior of the adsorbent particles. Adsorption was poor in strongly acidic solution but was improved in alkaline medium and continuously increased with rise in pH. Montmorillonite is almost five times more effective in adsorbing Cd(II) than kaolinite.

Sharma and friends (2007) used wollastonite for removing of Cr(VI) from industrial effluents. The removal of chromium is found to be concentration dependent. The removal increased from 47.4 to 69.5% by decreasing the concentration from 2.0×10^{-4} to 0.5×10^{-4} M at pH 2.5, 0.01 M $NaClO_4$ ionic strength, 100 μm adsorbent particle diameter and 30 °C temperature. Rate of uptake of Cr(VI) was found to be 3.0×10^{-2} min^{-1} under optimum conditions.

Use of clinoptilolite for heavy metals removal from wastewaters is investigated by Çağın et al., 2005. Cu (II) and Ni (II) removal with Bigadiç clinoptilolite was under investigation. In isoterm studies, ion exchange was determined to be the dominant mechanism in clinoptilolite-metal solution interactions. In addition to ion exchange, adsorption, dissolution of clinoptilolite and especially in the case of Cu(II) removal surface precipitation were discussed as other possible mechanisms. 36% efficient was gained without conditioning, 70% and 74% efficient were gained with conditioning in a day and a week, respectively. Conditioning process did not supply a significant success at heavy metal removal.

Removal of Cu^{+2} and Zn^{+2} from aqueous solutions by sorption on the montmorillonite modified with sodium dodecylsulfate (SDS) was investigated by Lin and Juang (2002). Experiments were carried out as a function of solution pH, solute concentration, and temperature (25–55 ◦C). The sorption of metal ions on modified clay was rapid during the first 10 min and the equilibrium was attained within 2 h.

The Dubinin–Kaganer Radushkevick model was adopted to describe the single-solute sorption isotherms. The pseudo-first-order rate constants for Zn^{+2} and Cu^{+2} sorption were found to be 6.64×10^{-4} and 3.14×10^{-3} min^{-1}, respectively at 25 ^{o}C.

Vieira dos Santos and Masini (2007) used vermiculite as a low cost adsorbent for treatment of wastewater from a coatings industry containing Cd(II), Pb(II) and Cu(II). Determination of metal cation concentrations in solution was made by continuous flow anodic stripping voltammetry. Adsorption data was fitted by Freundlich isotherms, as well as by partition constants at pH 4, 5 and 6. It is found that pH 4: Cu(II)<Cd(II)<Pb(II); pH 5: Cu(II)□Cd (II)<Pb(II); pH 6: Cd(II)<Cu(II)<Pb(II). Extraction percentages were found around of 76% at pH 6.5 for Cd(II), Pb(II) and Cu(II). However, this efficiency is lower than that predicted by Freundlich parameters for Pb(II) and Cu(II), but it is higher than that predicted for Cd(II).

The removal of cadmium pollution from waste water in packed columns on sepiolite and diatomite by adsorption is investigated by Koçyiğit et al., 2001. Diatomite and beige sepiolite have been used as adsorbents. As the result of the study, adsorption capacities, of beige sepiolite and diatomite were determined as 5.42 mg cadmium/g adsorbent, 4.99mg cadmium/g adsorbent respectively.

2.1.6.6. Color Removal

The adsorption of textile dye acid red 57 with using sepiolite has been examined by Alkan et al., 2004. Batch adsorption tests of acid red 57 from aqueous sepiolite solutions have been investigated as a function of parameters such as pH, ionic strength and temperature. Adsorption equilibrium was reached within 1 h. The removal of acid red 57 decreases with pH from 3 to 9 and temperature from 25 to 55 °C whereas it increases with ionic strength from 0 to 0.5 mol l^{-1}.

The adsorption capacity of zeolite (clinoptilolite) mineral has been examined by Fakı et al., with the aim of identifying the ability of zeolite to remove reactive azo

dye with a brand name Everzol Yellow 3RS H/C which is used in dying process of the textile industry. The adsorption experiments were realized in the fixed bed column reactor, each run consisted of modifying zeolite wiyh HTAB in the column followed by removal of color from the modified zeolite bed. Optimization studies were realized on 25 cm zeolite bed show that 3g/l of HTAB dosage showed the best performance.

2.1.6.7 Other

Some researchers have also studied on radioactive waste removal by clay minerals. Treatment of liquid radioactive waste by using bentonite, kaolinite, and diatomite minerals is investigated by Kam et al., 2005. Significant increment in decontamination factor (DF) of chemical precipitation process was obtained in the case of minerals are used as an additive. In addition, liquid decontamination studies were carried out by direct filtration methods. In these studies it was determined that up to 95% of radioactivity was retarded by clay minerals. As a result, most of the clay minerals are able to absorb radioisotopes and thus clays can be successfully used for decontamination of liquid waste.

Hameed (2007) used activated clay as adsorbent for the kinetics of 2,4,6-trichlorophenol (TCP) which has been commonly used as pesticide, herbicide, wood, leather and glue preservatives since the 1930s. Experiments were carried out as a function of solution pH (2-12), solute concentration (30-220mg/l), and temperature (30–50 ◦C). The adsorption dependent on pH, contact time and temperature. The maximum adsorption of TCP was at pH 2–6.

To improve of dewatering capacity of oily sludges with using conditioners, such as bentonite, fly ash and gypsum, were examined by Küçükselek, in 2005. CST and SRF reduction could be achieved lower than 50% with using bentonite, fly ash and gypsum.

Prymnesium parvum Carter (Haptophyceae) is a toxic algal species commonly found in low salinity lakes (e.g. in Israel), and in the mesohaline waters of the Baltic Sea. Sengco and friends (2005) used some clay minerals (kaolinite, bentonite and illite) for removing this fish-killing microalga. The addition of polyaluminum chloride (PAC, at 5 ppm) improved removal efficiency. Removal efficiency also varied with *P. parvum* concentration, reaching a maximum level at the lowest cell concentration (1×103 cells/mL).

Effect of mineral materials and cations on activated and alum sludge settling was investigated by Piirtola et al., 1999. Bentonite, clinoptilolite, montmorillonite, acid modified magnesium silicate, and a blend of talc and chlorite are used as minerals in batch settling tests. The impact of mineral materials on alum sludge filterability was tested by capillary suction time (CST) measurements. Mineral materials, except bentonite and test sand, improved activated and alum sludge settling by 21-47% based on sludge volume when a dosage of 3g/l was used.

2.1.6.8 Clay Minerals Utilization in Solid Waste Management

Environmentally, certain type of clays are the material of choice in protecting the local environment and ground in the construction and rehabilitation of landfill sites. Clay is used for the production of Geosynthetic Clay Liners (GCLs), where it is sandwiched between two geosynthetic liners. The main purpose of a clay barrier is to retard the movement of fluids into the surrounding medium. In addition to acting as a containing barrier that protects aquifers, clay (especially bentonite) is used to treat the contaminated water. Because, addition of the bentonite results in suspended solid removal and heavy metal adsorption. On the other hand, clay can be utilized as an impermeable layer instead of geomembrane in landfill areas

Utilization of kaolinite and zeolite liners in sanitary landfills is investigated by Koyuncu et al., 2003. Different kaolinite/zeolite mixtures were used in the experiments. Optimum kaolinite and zeolite ratio was found as 0.2. The mixture was contaminated by various pollutants such as Na, Ca, Pb, Cu. Consequently, the

mixture of K/Z 0.2 is ascertained as highly adsorptive and recommended as liner materials in landfills.

The mixture of bentonite/zeolite usage in landfill is investigated by Güney et al., 2001. Zeolite and bentonite was mixed with ratios 90% and 10%, respectively. The mixture having low permeability is found as efficient in heavy metal removal.

2.2 Adsorption

2.1.1 Definitions

Adsorption is a process that collects soluble substances from solution on an interface or surface (Metcalf & Eddy, 1991, p. 314). The process can occur between liquid-liquid, gas-liquid, gas-solid or liquid-solid interfaces. The adsorbate is the substance that is being removed from liquid phase at the interface. The adsorbent is the solid, liquid, or gas phase onto which the adsorbate accumulates (Metcalf & Eddy, 2003, p.293).

The application of adsorption technology for pollution control usually deals with the control of organic compounds (VOC's, pesticides, PCB's, phenolics, and complex synthetic organics), inorganic compounds (heavy metals, reduced sulfur gases, and chlorine), taste, odour, and dyes.

The adsorption process takes place in three steps: macrotransport, microtransport, and sorption. Macrotransport involves the movement of the adsorbate (e.g., organic matter) through the water to the liquid/solid interface by the advection and diffusion. Microtransport involves the diffusion of the organic material through the macropore system of the solid adsorbent, such as activated carbon, to the adsorption sites in the micropores and the solid adsorbent. Although adsorption also occurs on the surface of the solid adsorbent and in the macropores (pores with widths exceeding about 50 nm) and mesopores (pores widths between 2 nm and 50 nm), the surface area of these parts of most solid adsorbents is so extremely small (see Fig.2.4.) compared

with the surface area of the micropores (pores with widths not exceeding about 2 nm) that the amount of material adsorbed there is usually considered negligible (Metcalf & Eddy, 2003, p.293).

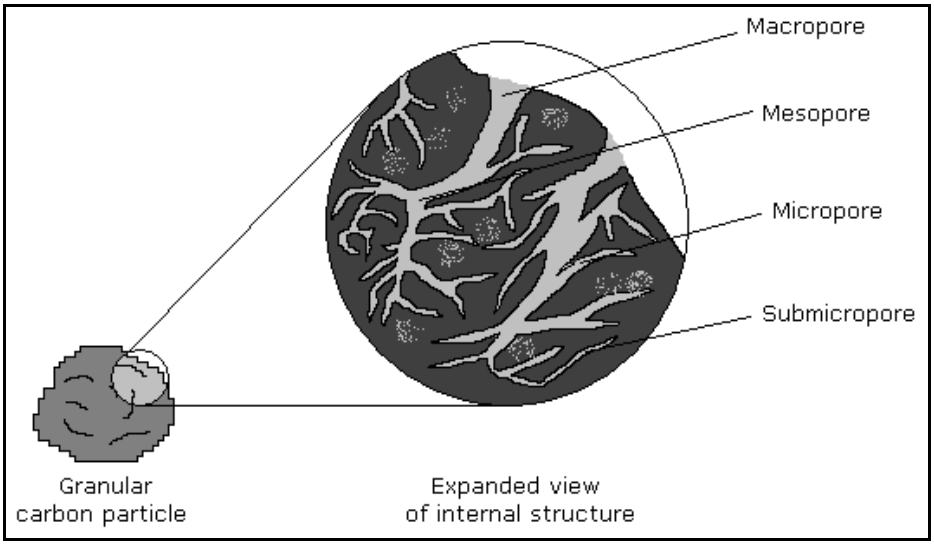

Figure 2.4 Macropore, mesopore, micropore, and submicropore adsorption sites on activated carbon (Metcalf & Eddy, 2003, p.293).

2.2.2 Adsorption Mechanisms

Adsorption mechanisms are generally categorized as either physical adsorption, chemisorption, or electrostatic adsorption. Physical adsorption is the results of intermolecular forces of attraction between molecules of the solid (adsorbent) and the substance adsorbed (adsorbate). Van der Waals forces are effective in physical adsorption. It is predominant at low temperature and is characterized by a relatively low energy of adsorption. If the adsorbate undergoes chemical interaction with the adsorbent, it is called chemical adsorption, activated adsorption or chemisorption. It exhibits high energy of adsorption (Weber, W. J., 1972. p, 205). Electrostatic adsorption involves the adsorption of ions through Coulombic forces, and is normally referred to as ion exchange, which is addressed separately in the ion exchange modules. In liquids, interactions between the solute and the solvent also play an important role in establishing the degree of adsorption (FRTR, n.d.).

The principal characteristics of the physical and chemical adsorption are discussed in the Table 2.1.

Table 2.1 Typical characteristics of adsorption process (Gereli, 2005, p.2).

Characteristics	Physical Adsorption	Chemical Adsorption
Binding force	Due to physical force of attraction, thus this process is also called as van der Waal's adsorption	Due to chemical forces or bonding, thus this process is also called as activated adsorption.
Saturation uptake	Multilayer phenomena	Single layer phenomena
Activation Energy	No activation energy involved	May be involved
Temperature Range (over which adsorption occurs)	Adsorption is appreciable at lower temperature below boiling point of adsorbate	Adsorption can take place even at higher temperature
Nature of sorbate	Amount of adsorbate removed depends more on adsorbate than on adsorbent	Depends on both adsorbent and adsorbate
Crystallographic specificity	Virtually independent of surface atomic geometry	Marked variation between crystal planes
Heat of adsorption	1 Kcal/mole	50 - 100 Kcal/mole

2.2.3 Factors Influencing Adsorption

- Surface area can be defined as that portion of the total area that is available for adsorption. A large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surfaces (Bekçi, 2005 p.3).
- For organic molecules the followings have been found: adsorption of a solute is inversely proportional to its solubility in the solvent. The greater is the solubility, the stronger the solute-solvent bond and the small the extent of adsorption - Lundelius's rule (Bekçi, 2005, p.6). For a homologous series of solutes in water, adsorption usually increases with increase of carbon atoms. Adsorption is

minimum for the charge species and maximum for neutral species. Decreasing adsorption with increasing ionization has been found for many organic acids (Oskay, 2003, p.4).

- Adsorption reaction is exothermic so adsorption increases with decreasing temperature (Oskay, 2003, p.4).
- Because hydrogen and hydroxide ions are adsorbed quite strongly, the adsorption of other ions is influence by the pH of the solution. In general, adsorption of typical organic pollutant from water is increased with decreasing pH. (Weber, W. J., 1972. p, 229).
- The nature of adsorbent has effect on rate and capacity of adsorption (Weber, W. J., 1972. p, 230). As long as the compounds are structurally simple, adsorption is at minimum for the charged species and at a maximum for the neutral species. As compounds become more complex, the effect of ionization becomes of decreasing important.

2.2.4 Adsorption Equilibrium and the Adsorption Isotherm

Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). There are three types of isothermal adsorption are used to explain the adsorption process, i.e. Langmuir, Freundlich and BET isotherms.

2.2.4.1 Langmuir Isotherm

One of the simplest and most widely used isotherms is the Langmuir isotherm that was originally derived from adsorption kinetics by equating the rates of adsorption and desorption onto a flat surface. The Langmuir isotherm equation assumes that fixed individual sites exist on the surface of the adsorbent, each of these sites being capable of adsorbing one molecule, resulting in a layer one molecule thick over the entire carbon surface. The Langmuir model also assumes that the surface is homogeneous; the energy of adsorption is equal for all adsorption sites, all sites adsorb the adsorbate equally.

Equilibrium is reached when the rate of adsorption of molecules onto the surface is the same as the rate of desorption of molecules from the surface. The rate at which adsorption proceeds is proportional to the driving force, which is difference between the amount adsorbed at a particular concentration and the amount that can be adsorbed at that concentration. At the equilibrium concentration this difference is zero (Metcalf & Eddy, 2003, p.1144).

Langmuir adsorption is defined in the following equation:

$$\frac{C_e}{q_e} = \frac{1}{ab} + \frac{1}{a} C_e$$

where C_e (mg/L) equilibrium concentration of adsorbate in solution after adsorption, q_e (mg/g) the amount adsorbed at equilibrium, a (mg/g) is a temperature independent equilibrium constant related to maximum adsorption capacity (capacity parameter), b (L/mg) temperature dependent equilibrium constant related to energy of adsorption (affinity parameter). The adsorption affinity of the adsorbent for adsorbate can be assessed by comparing the constant, b. A high b value indicates that the adsorbent has a high affinity for adsorbate and vice versa. Figure 2.5 shows the graphical representation of Langmuir isotherm.

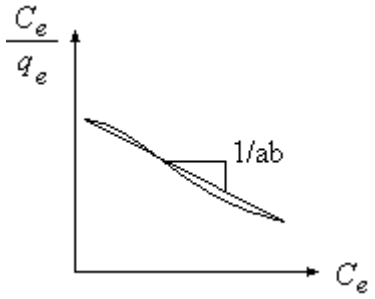

Figure 2.5 Graphical representation of Langmuir isotherm

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which describes the type of isotherm and is defined by following equation.

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

where, b (l/mg) is the Langmuir constant and C_0 (mg/l) the initial concentration of solute. R_L indicates the type of isotherm as follows:

Table 2.2 Equilibrium parameter, R_L (Kutlu, 2005, p.36-37)

Value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

2.2.4.2 Freundlich Isotherm

The Fruendlich isotherm equation assumes that the adsorbent has a heterogeneous surface composed of adsorption sites with different adsorption potentials. This equation assumes that each class of adsorption site adsorbs molecules, as in the Langmuir equation. The Fruendlich isotherm equation is the most widely used equation in adsorption from aqueous solution.

In other words, for Freundlich isotherms to be valid, the adsorption must be purely a physical process with no change in the configuration of the molecules in the adsorbed state (Kutlu, 2005, p.35).

According to the Freundlich equation, the amount adsorbed increases infinitely with increasing concentration or pressure. This equation is, therefore, unsatisfactory for high coverages. At low concentration, it does not reduce to the linear isotherm (Kutlu, 2005, p.35).

Freundlich proposed the equation:

$$q_e = x/m = K_F C_e^{1/n}$$

where C_e (mg/l) is the equilibrium concentration, q_e (mg/g) the amount adsorbed at equilibrium, and K_F and n is the constants that can be related to the adsorption capacity and the adsorption intensity, respectively. If 1/n is less than 1, it indicates a

favourable adsorption. If 1/n is much lower than 1, it indicates superior activity (Erden, 2003, p.17).

The Freundlich equation is basically empirical but is often useful as a means for data description. Data are usually fitted to the logarithmic form of equation. The linear form of Freundlich equation is presented below. Values of K_F and n may be calculated by plotting log q_e versus log C. The slope is equal to 1/n and the intercept is equal to log K_F. Figure 2.6 shows the graphical representation of Freundlich isotherm.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

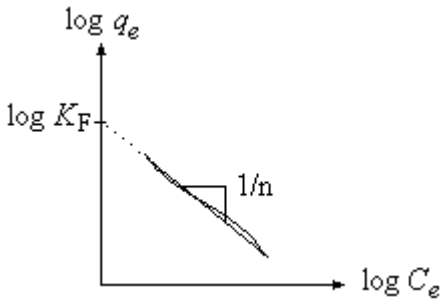

Figure 2.6 Graphical representation of Freundlich isotherm

2.2.4.3 BET Isotherm

In 1938, Brunauer, Emmett, and Teller showed how to extend Langmuir's approach to multilayer adsorption, and their equation has come to be known as the BET equation. The basic assumptions are that each molecule in the first adsorbed layer is considered to provide one site for the second and subsequent layers, that the molecules in the second and subsequent layers, which are in contact with other sorbate molecules rather than with the surface of the adsorbent are considered to behave essentially as the saturated liquid, while the equilibrium constant for the first layer of molecules in contact with the surface of the adsorbent is different. (Kutlu, 2005, p.37)

The BET equation assumes that the energy required to adsorb the first particle layer is adequate to hold the monolayer in place. The adsorption process can be described as adsorbed molecules on the surface sites and attachment of molecules to sites where occupied by adsorbed molecules. The resulting equation for the BET equilibrium isotherm is:

$$q_e = \frac{B\,C\,Q^0}{(C_s - C)[1 + (B - 1)(C / C_s)]} \tag{2.5}$$

whereas Cs saturation concentration of the solute, C measured concentration in solution at equilibrium, Q^0 number of moles of solute adsorbed per unit weight of adsorbent in forming complete monolayer on the surface, qe number of moles of solute adsorbed per unit weight at concentration C, and B is the constant expressive of the energy of the interaction with the surface.

2.2.5 Principle Adsorbents

The adsorbents are used usually in the form of spherical pellets, rods, moldings or monoliths with hydrodynamic diameter between 0.5 and 10 mm. They must have high abrasion resistance, high thermal stability and small micropore diameter, which results in higher exposed surface area and hence high capacity of adsorption. The adsorbents must also have a distinct macropore structure which enables fast transport of the gaseous vapours. Different types of industrial adsorbents generally fall into three classes:

- Oxygen-containing compounds are hydrophilic and polar, including materials such as silica gel and zeolites.
- Carbon-based compounds are hydrophobic and non-polar, including materials such as activated carbon.
- Polymer-based compounds are polar or non-polar functional groups in a porous polymer matrix.

All over the world activated carbon is the most popular and most usable adsorbent in wastewater treatment. Activated carbon is high quality, but it is very expensive material. Altough its cost inefficiency lots of researcher used activated carbon for removing pollutants from the aqueous solution.

Aber and friends (2007) studied that the removal of acid orange 7 (AO7) by powdered activated carbon from aqueous solutions with initial concentrations of 150 ppm to 350 ppm and initial pH values of 2 to 10.5 at 25°C. The maximum removal efficiency of acid orange 7 (AO7) was 96.24% for initial concentration of 150 ppm and at pH = 2.8, and minimum removal efficiency was 48.05% for initial concentration of 350 ppm and at pH = 5.8.

Adsorption of zinc(II) from an aqueous solution onto activated carbon is investigated by Ramos et al., 2002. Adsorption isotherms were measured experimentally for Zn(II) adsorption onto commercial activated carbons C, F-400, F-300 and Centaur HSL in a batch adsorbent experiments. The effects of carbon type and solution pH on adsorption isotherms were evaluated in this work. Nearly three times as much Zn(II) adsorbed onto C carbon as on the other three carbon types. The adsorption isotherm for Zn(II) was dependent on solution pH since Zn(II) did not adsorb to carbon below pH 2, and the adsorption isotherm increased as pH increased from 3 to 7. The adsorption isotherm of Zn(II) on C carbon was temperature independent while on F-400 the isotherm showed unusual behavior as temperature increased.

Removal of arsenic, iron and manganese with using Fe^{+3} impregnated granular activated carbon and granular activated carbon compared by Mondal, Balomajumder and Mohanty in 2007. The effects of shaking time, pH, and temperature on the percentage removal of As(T), As(III), As(V), Fe^{+2}, Fe^{+3}, and Mn were tested. Under the experimental conditions, the optimum removal of As(T), As(III), As(V), Fe, and Mn are 95.5%, 93%, 98%, 100%, and 41%, respectively, when GAC-Fe is used. For GAC these values are 56%, 41%, 71%, 99%, and 98%.

Activated carbon is very expensive adsorbent and because of this, a lot of researchers studied ability of low cost adsorbents for removing various pollutions from wastewater. Some examples are presented under four main title is following:

- Minerals
- Agricultural by-products
- Industrial waste and by-product
- Other

2.2.5.1 Minerals

Different kinds of mineral are used as adsorbent for removing pollutants. Generally clay minerals which are kaolinite, bentonite, zeolite, montmorillonite, sepiolite, clinoptilolite, illite, diatomite and vermiculite are preferred as low cost adsorbent due to their easy to ability.

The ability of natural zeolite clinoptilolite and bentonite to remove Pb(II) from aqueous solutions has been investigated by Inglezakis et al., 2007. Adsorption tests of Pb(II) were carried out using a solution concentration of 1,036 ppm at initial pH = 4, and solid to liquid ratio of 2 g/100 mL. The effects of agitation speed (0, 100, 200, 500 rpm), temperature (28°C, 45°C, 60°C) and particle size (2.5–5.0 mm, dust) were examined. The removal of Pb(II) using bentonite reached 100% at ambient temperature and mild agitation (100 rpm), while it was approximately 90% at 60°C without agitation. On the other hand, the highest removal level reached by clinoptilolite was 55%.

Kyanite, is a triclinic crystalline mineral like other aluminosilicates has been used as an adsorbent for the removal of heavy metals, such as Ni(II), Zn(II), Cr(VI) and Cu(II) from electroplating wastewater is investigated by Ajmal et al., 2001. Adsorption studies of Cu(II), Zn(II), Ni(II) and Cr(VI) using Kyanite as an adsorbent have shown the percent adsorption in the order of Cu(II) > Ni(II) > Cr(VI) > Zn(II).

The degree (%) of adsorption increases with increase in adsorbent dose (0.2–1 g) and decrease in particle size of Kyanite.

Adsorption of methylene blue onto clay from Erzurum district was investigated by Gürses et al., 2003. The adsorption time, initial concentration of methylene blue, and temperature of adsorption were chosen as parameters for adsorption of dyestuff onto clay. It was observed that the adsorption capacity decreases with increasing temperature and adsorption equilibrium was attained within 1 hour.

Kaolinite and montmorillonite are used by Gupta and Bhattacharyya (2007) for the immobilization of Pb(II), Cd(II) and Ni(II) on clays in aqueous medium through the process of adsorption under a set of variables (concentration of metal ion, amount of clay, pH, time and temperature of interaction). Langmuir and Freundlich showed good fits with the experimental data. Kaolinite and montmorillonite have considerable Langmuir monolayer capacity with respect to Pb(II), Cd(II) and Ni(II), the values being in the range of 6.8–11.5 mg/g (kaolinite) and 21.1–31.1 mg/g (montmorillonite). The Freundlich adsorption capacity follows a similar order. Adsorption increases with pH till the metal ions are precipitated out as metal hydroxides.

The effectiveness of surfactant-modified bentonite in removing humic acid from wastewaters was evaluated by Anirudhan and Ramachandran in 2007. Hexadecyl trimethylammonium (HDTMA) chloride was used to modify the bentonite. Modified bentonite exhibits very high adsorption potential for humic acid and at pH 3.0 more than 99% removal was achieved from an initial concentration of 25 μmol/l.

Vermiculite was applied as adsorbent for removal of cadmium, zinc, manganese, and chromium from aqueous solutions by Fonseca, Oliveira and Arakaki 2006. Parameters such as time of reaction, effect of pH and cation concentration were investigated. The quantity of adsorbed cations was 0.50, 0.52, 0.60, and 0.48 mmol g^{-1} of Cd^{2+}, Mn^{2+}, Zn^{2+}, and Cr^{3+}, respectively.

2.2.5.2 Agricultural By-products

Lots of agricultural by-products terminated, instead to terminate their economic value they can be used as adsorbents for removing many pollutants. These agricultural by-products are mandarin peelings, sunflower seed shells, lentil shells, wheat shells, rice shells, walnut shells, exhausted coffee, tea waste, nut, groundnut husk and peanut husk. In addition to this, wood particles or their components, e.g., cellulose, sawdust, wood chips, wood ash pine bark, pine cones and pine needles, leaf compost, tree fern, have also been used in the wastewater treatment.

Adsorption of Cu ions on sawdust is studied by Ajmal et al., 1998. The researchers also studied the effects of salinity on the removal of Cu(II) ions. The maximum removal efficiency is gained at pH 6, 500 mg sawdust dose and 100µ sawdust particle size. Salinity effect can be inferred that the Cu(II) may be effectively removed even from highly saline medium.

There is little literature available on the use of coffee ground as adsorbents. Extensive investigations have been carried out on the adsorbent capacity of coffee grounds of aluminum ions. Coffee grounds are documented to adsorb large amounts of aluminum ions as well as other miscellaneous heavy metals (Adeyiga et al, 1998).

Orhan and Büyükgüngör (1993) used waste tea, Turkish coffee, exhausted coffee, nut and walnut shells as adsorbents to remove heavy metals from wastewater. Batch studies showed that these adsorbents exhibit a good adsorption potential for Al (III) metal ions. The adsorption ratios of Al (III) were as 98, 99, 96, 99.5 and 96% for waste tea, Turkish coffee, exhausted coffee, nut and walnut shells, respectively.

Tree fern, which is an agriculture product, is used to remove heavy metal ions, such as Zn(II), Cu(II) and Pb(II), from aqueous solutions is researched by Ho et al., 2002. The maximum sorption capacities of metal ions onto tree fern were 7.58 mg/g for Zn(II), 10.6 mg/g for Cu(II) and 39.8 mg/g for Pb(II). It was noted that an increase in temperature resulted in a higher metal loading per unit weight of the

adsorbent. Decreasing the particle sizes of tree fern led in an increase in the metal uptake per unit weight of the adsorbent.

Leaf compost was tested as a suitable sorbent since there are studies that show certain kinds of leaves and bark provide a surface for heavy metals to adsorb onto (Adeyiga et al, 1998; Sharma and Forster, 1994). Unfortunately, since the composition of the leaf compost is not known, there are variable ranges of adsorption available for the different leaves or wood species that could be in the compost (Adeyiga et al, 1998). This means the effectiveness of the leaf compost will be quite variable as well, depending on the seasonal species found in the compost at any given time in any given part of the compost. The mechanism that compost leaves remove heavy metals with is not clearly understood; a significant contribution is presumed to come from the leaf mold found growing on composted leaves. Leaf mold has been studied to have favourable kinetics and the adsorbance capacity to reduce heavy metals in solution, such as chromium, nickel, copper, zinc and cadmium (Sharma and Forster, 1994). The chemi-sorbant adsorption has a second order reaction rate, which means that at low heavy metal concentrations, leaf mold efficiently and speedily reduces the soluble heavy metal content. Leaf compost also has bark in it, which can be an effective sorbent because of its high tannin content. Ion exchange takes place as metal cations displace adjacent phenolic hydroxyl groups on the tannin, forming a chelate (Randal et al, 1974). One problem with tannin-containing materials, however, is the discoloration of the water from the phenols, which can interfere with the metal analysis instrument readings. Overall, leaf based wastewater treatment methods are fast, with absorption reaching equilibrium in less than 30 minutes (Adeyiga et al, 1998).

Carbon prepared from peanut husks (PHC) has been used for the adsorption of Pb^{+2}, Zn^{+2}, Ni^{+2} and Cd^{+2} is investigated by Ricordel et al., 2001. It can be observed that the Pb^{+2} was the most rapidly removed from solution, followed by Zn^{+2} and Ni^{+2} and finally Cd^{+2} which was adsorbed the most slowly. In excess of 98% of Pb^{+2} were removed, 87, 83 and 75% removal have been found in the case of Zn^{+2}, Ni^{+2} and Cd^{+2}, respectively.

Removal of dyestuffs from a synthetic wastewater with using granular and powdered activated carbon, zeolite, wood chips and wood ash by adsorptive biodegradation was investigated by Karapınar Kapdan and Kargı in 2000. The adsorption capacity of wood ash was found to be comparable with powdered activated carbon. Operation of activated sludge unit with the addition of wood ash at different sludge ages (Θc=3-30 days) resulted in maximum decolorization effciency of E = 37% at a sludge age of Θc=20 day.

Adsorption of copper and lead ions onto tea waste from aqueous solutions was studied by Amarasinghe and Williams in 2007. The adsorption capacity was highest at solution pH range 5–6. The adsorbent to solution ratio and the metal ion concentration in the solution affect the degree of metal ion removal. Highest metal uptake of 48 and 65 mg/g were observed for Cu and Pb, respectively. Pb showed higher affinity and adsorption rate compared to Cu under all the experimental conditions. Kinetic studies revealed that Pb and Cu uptake was fast with 90% or more of the adsorption occurring within first 15–20 min of contact time.

Al-Asheh and Duvnjak (1997) investigated that sorption of Pb, Cd, Ni and Cu adsorption on pine bark. Bark is able to sorb the following metals in the indicated order (mass basis): Pb^{+2} > Cd $^{+2}$> Cu^{+2}> Ni^{+2}, from their aqueous solutions. In addition to this bark can be re-utilized several times for further adsorption processes without regeneration is found in this study.

Cellulose, a natural polymer, was used as an adsorbent for the adsorption of Cu(II) ions from the aqueous solutions of copper sulfate pentahydrate ($CuSO_4$. $5H_2O$) is investigated by Acemioğlu and Alma in 2001. When the concentration of copper sulfate pentahydrate solution is increasing, the amount of Cu(II) ions adsorbed per unit of adsorbent increased.

Removal of the synthetic anionic dye Reactive Black 5 (RB5) from aqueous solutions with using sunflower seed shells and mandarin peelings was investigated by Osma et al., 2007. Sunflower seed shells led to a percentage of dye removal

higher than mandarin peelings 85% and 71% after 210 min, respectively, for an initial RB5 concentration of 50 mg L−1 and an initial pH of 2.0.

Silver impregnated groundnut husk carbon and groundnut husk carbon were tested for the removal of chromium(VI) is researched by Dupey and Gopal 2007. 97% of hexavalent chromium was removed at pH 3 within 5 h. Silver impregnated groundnut husk carbon demonstrates the better adsorption capacity (11.399 mg/g) compared to groundnut husk carbon (7.0104 mg/g) In fact, for the removal of complete chromium, silver impregnated groundnut husk carbon is better than groundnut husk carbon.

Utilization of coffee residues binding with clay as adsorbent for removal of heavy metal ions in solution is studied by Boonamnuayvitaya et al., 2004. Factors affecting the adsorption such as pyrolysis temperature, weight ratio of coffee-residue to clay and particle size were investigated in the present preliminary study on the adsorption of metal ions. The pyrolysis temperature of 500 ^{o}C, weight ratio of coffee residue to clay of 80:20, and particle size diameter of 4 mm were found to be the suitable conditions. At this condition, the adsorption capacities increased in the order of Cd^{+2} >Cu^{+2} >Pb^{+2} >Zn^{+2} >Ni^{+2}.

Removal of copper (II) from aqueous solution by different adsorbents such as shells of lentil, wheat, and rice was investigated by Aydın, Bulut, Yerlikaya, 2007. The maximum adsorption capacities for Cu (II) on lentil shells, wheat shells and rice shells adsorbents at 293, 313 and 333K temperature were found to be 8.977, 9.510, and 9.588; 7.391, 16.077, and 17.422; 1.854, 2.314, and 2.954mg g^{-1}, respectively.

2.2.5.3 Industrial Wastes and By-products

Industrial waste and by-products are increasing day by day with developing of indusrilization. These waste and by-product can be used as adsorbents instead of terminating. Fired coal fly ash, wheat bran, eggshells, red mud, electric furnace slag

and grape bagasse which are industrial waste and by-product, are used as adorbents for removing pollutants from aqueous solutions.

Eggshell is a food processing by-product. The calcified eggshell and its ground powder used as adsorbents for removal of two different dyestuffs which are cationic basic blue 9 and anionic acid orange 51 from aqueous solution is studied by Tsai et al., 2007. The adsorption capacity of acid orange 51 onto eggshell is significantly smaller than that onto eggshell powder, which is in line with their pore properties (i.e., 1 vs. 21 m^2/g). The adsorption potential for basic blue 9 onto the ground eggshell powder is far lower than that for acid orange 51.

Fired coal fly ash, which is a solid by-product that is produced in power plants worldwide in million of tones, is shaped into pellets and used for removal of copper and cadmium ions from wastewaters is investigated by Papandreou et al., 2007. The adsorption capacities of pellets for copper and cadmium were 20.92 and 18.98 mg/g. Researchers proposes an efficient and simple stabilization process of the utilized adsorbent is a safe disposal in industrial landfills and eliminating the risk of pollution for groundwater and other natural water receivers.

Removing procion orange with waste red mud was investigated in different initial dye concentrations, agitation time, adsorbent dosage, and pH by Namasivayam et al., in 2002. Maximum removal of %82 of the dye was observed at pH 2.0. Desorption studies showed that maximum desorption occurred at a pH of 11.

Grape bagasse generated in the wine production process. Cd and Pb ions removal with using grape bagasse is researched by Farinella, Matos and Arruda in 2007. Maximum adsorption was found to occur at pH 7.0 and 3.0 for Cd(II) and Pb(II), respectively, and a contact time of 5 min was required to reach equilibrium for both metals. The adsorption capacities were found to be 0.479 and 0.204 mmol g^{-1} for Cd(II) and Pb(II), respectively. The results showed that grape bagasse could be employed as a low-cost alternative adsorbent for effluent treatment.

The adsorption of Reactive Blue 19 (RB 19), Reactive Red 195 (RR 195) and Reactive Yellow 145 (RY 145) onto wheat bran, generated as a by-product material from flour factory, was studied by Çiçek et al., 2007. The adsorption of RB 19, RR 195 and RY 145 onto wheat bran increased with increasing temperature and initial dye concentration while the adsorbed RB 19, RR 195 and RY 145 amounts decreased with increasing initial pH and adsorbent concentration. Adsorption capacities of wheat bran for RB 19, RR 195 and RY 145 dyes were obtained as 117.6, 119.1 and 196.1 mg/g at 60 ^{o}C, respectively. It was observed that the reactive dye adsorption capacity of wheat bran decreased in the order of RY 145 >RB 19 >RR 195.

The fly ash is a major byproduct generated in coal-based thermal power plants and has good potential for use as an adsorbent. Matheswaran and Karunanithi (2007) used fly ash as adsorbent for the removal of Chrysoidine R which is an azo dye, are used for producing majority of textile dyestuffs and also synthetic formulations in many industries. In a batch experiments effect of contact time, pH (2, 4, 6 and 8) initial concentration of the dye (400, 600, 800 and 1000 mg L−1), amount of the adsorbent (125, 250, 375 and 500 mg L−1), and temperature (303, 313, 323 and 333 K) on adsorption are observed. Maximum removal efficiency is gained at pH 4, 303 K and 250 mg/l initial dye concentration. The percentage removal of the dye was increased with increasing the amount of adsorbent loading.

Electric furnace slag (EFS) which is an industrial by-product is used as an adsorbent to remove Pb^{+2} and Cu^{+2} from industrial effluents is investigated by Curkovic et al., 2001. Respectively 26.2, 28.6, 31.8 mg Cu^{+2} and 25.4, 27.5, 30.6mg Pb^{+2} were taken up by 1.00 g of electric furnace slag at temperatures of 293, 303 and 313 K.

2.2.5.4 Other

Lots of researcher investigated alternative adsorbents like alum residuals, silica gel, chitosan, low-rank coal, wood charcoal, brick powder, animal bone, animal charcoal, fish bone charcoal, sheep manure waste.

Kandah is studied that Zn ions removal with using sheep manure waste in 2001. Sheep manure waste is collected from one specific farm and utilized adsorption studies. The adsorption experiments were performed under various conditions such as different adsorbent particle size (0.064–1.0 mm), Zn^{+2} initial concentration (20–150 ppm), shaking time (1–300 min), pH (1–6), and adsorbent concentration (2–30 g/l). About 10 g/l of sheep manure waste (0.064mm in diameter) was found to be enough to remove 93.3% of 100 ppm Zn^{+2} from 50 ml aqueous solution after 1 h. The optimum pH value was found to be at 4.

Mortula and Gagnon (2007) investigate the effectiveness of alum residuals, which were generated during drinking water treatment for adsorption of phosphorus from aquaculture process water. Batch and fixed bed column tests were conducted. Experimental results observed phosphorus removal of 94–99% using an alum residuals concentration of 4–16 g/l. Effluent pH levels for both batch and fixed bed column tests were within range of 6–9 and the effluent BOD5 was below 30 mg/l for most of the samples.

Silica gel is a synthetic amorphous polymer with silanol groups on the surface allowing metal adsorption. Adsorption of Pb(II) and Cu(II) onto a grafted silica and non-modified silica are studied by Chiron et al., 2003. Maximum adsorption capacities of the grafted silica towards Pb(II) and Cu(II) are determined 0.184 mmol Pb(II) g^{-1} and 0.261 mmol Cu(II) g^{-1} and compared to those of non-modified silica respectively, 0.019 and 0.036 mmol g^{-1}.

Batch adsorption studies were carried out by Nemade et al., 2002 to determine the fluoride removal efficiency for fly ash, brick powder, wood charcoal, animal charcoal, fish bone charcoal, etc. Among them, the fish bone charcoal showed a comparatively higher fluoride removal than other adsorbents.

The effectiveness of animal bones (AB) to adsorb zinc from aqueous solution was tested by Banat, Al-Asheh, Mohai, 2000. It was noted that an increase in the zinc concentration, temperature, and initial pH of the metal solution resulted in an

increase in the metal uptake per unit weight of the adsorbent. The decrease in the particle size of the adsorbent resulted in an increase in the metal uptake per unit weight of the adsorbent.

The removal of heavy-metal ions from aqueous solutions containing low-to-moderate levels of contamination using Beypazarı low-rank coal was investigated by Karabulut et al., 2000. Adsorption reached equilibrium in 20 min and the optimum pH was measured to be 4.0. The maximum adsorption capacities of the metal ions from their single solutions were 1.62 mg for Cu(II) and 1.20 mg for Zn(II) per g of coal. The order of affinity based on a weight uptake by coal was as follows Cu(II)>Zn(II).

The adsorption of Cu(II) ions onto chitosan is a natural polymer and cross-linked chitosan beads were tested by Ngah, Endud and Mayanar (2002). Chitosan beads were cross-linked with glutaraldehyde (GLA), epichlorohydrin (ECH) and ethylene glycol diglycidyl ether (EGDE) in order to obtain sorbents that are insoluble in aqueous acidic and basic solution. The uptakes of Cu(II) ions on chitosan beads were 80.71 mg Cu(II) /g chitosan, on chitosan-GLA beads were 59.67 mg Cu(II) /g chitosan-GLA, on chitosan-ECH beads were 62.47 mg Cu(II) /g chitosan-ECH and on chitosan-EGDE beads were 45.94 mg Cu(II) /g chitosan-EGDE.

The list of the various types of adsorbents is presented in Table 2.3 by evaluating the recent literature.

Table 2.3 The list of the various adsorbents used in wastewater treatment (Kumar et al., 2004).

Adsorbent	**Adsorbate**	**Reference**	**Remarks**
Powdered activated carbon	Distillery Spent wash	Sekar and Murthy (1998)	Removal of 18% is noted and when spent was pretreated with poly-electrolyte as a flocculating agent, the color removal was increased up to 99%.
Powdered activated carbon	Synthetic dye wastewater of Disperse-red-60	Yeh and Thomas (1995)	95-98% of COD removal for 25-200 ppm & 88-98% for various particle sizes. Freundlich, Langmuir, Dziubek & Kowals adsorption isotherms fit well. Film-pore double resistance diffusion model describes the mass transfer. External film mass transfer coefficient increases with

			decrease in particle size.
Powdered activated carbon, Activated alumina, Molecular Sieves & Diatomite	Disperse-red-60	Yeh and Adrian Thomas (1995)	Decrease in particle size gave only a minor improvement for activated alumina, finer molecular sieve materials reduce the dosage requirement by half. Performance of adsorbents are as PAC> Activated alumina> molecular sieve.
Granular Activated carbon [Industrial grade; Laboratory grade]	Catechol	Mahesh et al. (1998)	Equilibrium studies showed that IGGAC has the maximum adsorption capacity. Diffusion studies showed that initial part of the adsorption is attributed to external mass transfer effects followed by intraparticle diffusion.
Fly Ash [Coal]	Petrochemical Effluent (Raw)	Kapadia et al. (2000)	Adsorption dose of 3-3.5% shows significant color removal. Contact period of 30-40 minutes gives optimum removal.
Powdered activated carbon, Granular Activated carbon, Carbon soot, Fly ash	Petrochemical Effluent (Raw)	Kapadia et al. (2001)	Batch studies show that flyash also reduces suspended solids, ammonical nitrogen, COD, and nitrophenol apart from color. Efficiencies of adsorbents in decreasing order PAC>Carbon soot>GAC> Flyash.
Fly ash I& II	Malachite green, Methylene blue.	Mall and Upadhyay (1998)	Maximum color removal was attained with flyash containing high carbon content. Column studies show the applicability of BDST theory.
Bagasse pith, Orange peel, Sawdust, Eichornia shoot & root	Malachite green	Sharma et al. (1999)	PH Studies shows that there exists some chemical interaction between adsorbent and adsorbate. Efficiency in decreasing order Eichornia root>Eichornia shoot>Orange peel>Saw dust>Bagasse.
Activated carbon, Natural clay, Bagasse pith, Maize cob.	Astrazone Blue, Maxillon Red, Telon Blue.	Nassar and Geundi (1991)	Activated carbon has maximum adsorption capacity. Cost analysis showed that Natural clay, bagasse pith &maize cob were economically attractive than activated carbon.
Lignite	Cr (IV).	Balasub-ramanim et al. (1998)	Kinetic showed the applicability or Lagergren model. The datas tend to follow first order rate kinetics.
Chitin	Direct Scarlet. B	Annadurai G. (1998)	Diffusion studies showed adsorption mechanism involves an initial rapid uptake of dye due to surface adsorption followed by intraparticle diffusion.

Rice bran based activated carbon	Direct Red 31, Acid Black 1 & Acid Blue 16	Sankar et al. (1999)	Maximum removal is seen at acidic pH and 20-30 degree C. The enthalpy value show that adsorption is a physical phenomena
Natural clay	Basic Red 22	Nassar and Magdy (1999)	Mass transfer study showed thar external mass transfer is the only rate-controlling step.
Carbonized wood	Astrazone Blue	McKay and McConvey (1981)	Mass transfer study showed thar external mass transfer is the only rate-controlling step.
Peatv	Telon Blue (Acid)	McKay and Allen(1980)	Temperature has the most pronounced effect on mass transfer.
Peat	Astrazone Blue BG	McKay and Ho (1998)	Pseudo second order mechanism has been explained.
Chitosan	Verofix Red	Annadurai, Krishnan (1997)	The datas tend to follow First order kinetics
Jack fruit peel (Carbonized by chemical method)	Malachite green	Inbaraj and Sulochana (2002)	Equilibrium datas tend to follow Freundlich, Langmuir & Redlich Peterson isotherms. Desorption studies show that adsorption is a chemical phenomena.
Blast furnace dust & Slag	Raw Paper mill effluent	Das and Patnaik (2001)	COD removal efficiency of BFD is significantly better than Basic slag.
Activated carbon	Deorlene Yellow, Telon Blue, Victoria Blue	McKay (1982)	Batch study shows that addition of salt in the form of NaSo4 increases the rate of adsorption.
Activated carbon	Deorlene Yellow, Telon Blue.	McKay (1982)	Column studies show the applicability of BDST theory.
Activated carbon	Deorlene Yellow, Telon Blue, Victoria Blue, Disperse Blue	McKay (1983)	Diffusion study show that intraparticle diffusion is not a rate controlling step.
Activated carbon	Deorlene Yellow, Telon Blue, Victoria Blue, Disperse Blue	McKay (1983)	Mass studies show that resistance to external mass transfer is mainly controlled by initial conc. And adsorbent dosage.
Activated carbon	Telon Blue, Deorlene Yellow	McKay (1984)	Homogenous solid phase diffusion coefficient had been estimated using Two resistance mass transfer model.
Lignite	Maxilon Red, Astrazone Yellow	Allen et al. (1989)	Equilibrium dats tend to follow Freundlich, Langmuir & Redlich Peterson isotherms. The equilibrium isotherm

			exhibited deviates from the theory.
Fly ash	Copper (Synthetic)	Kapadia et al. (2000)	Maximum efficiency was at the pH of 6.0. The fly ash treatement raises the pH of effluent.
Coal Fly ash	Cadmium (Synthetic)	De (2001)	100% removal is seen at lower initial conc. of 3 mg/l.
Bagasse, Fly ash	Copper & Lead (Synthetic)	Rao et al. (2001)	Adsorption capacity decrease in the order Fly ash > Bagasse> PAC for the removal of copper ions and PAC > Bagasse >Fly ash for removal of lead ions under optimum conditions.
Rice husk Fly ash (Boiler feed)	Magenta	Rai et al. (2000)	When compared to other adsorbents Chitin has the maximum adsorbent potential, Nickel shows more preference for adsorption sites of chitin than Zinc.
Chitin, Saw dust, Clay, Fly ash	Zinc & Nickel ions	Vis-wanathan et al.	When compared to other adsorbents Chitin has the maximum adsorbent potential, Nickel shows more preference for adsorption sites of chitin than Zinc.

CHAPTER THREE
EXPERIMENTAL STUDY

3.1 Materials and Methods

3.1.1 Preparation of Kaolinite

Kaolinite ($Al_2Si_2O_5(OH)_4$), available in the Aksaray, was used as adsorbent. In the experiments, the refined kaolinite used as high performance filler minerals especially in paint, natural latex and rubber was obtained from Kızıldağ Madencilik Company. The properties of kaolinite are summarized in Table 3.1. In the study, the kaolinite was screened through sieves and it was separated into size fractions with particle size; <53µm, 106µm-212µm, 212µm-1.18mm, 1.18mm-2.36mm and 2.36mm-4.75mm. After screening, kaolinite were washed de-ionized water and then were dried at 103 ^oC for 24 hours. Kaolinite samples were kept in the desiccators throughout the experiments.

Table 3.1 Physical and chemical properties of the kaolinite used in the experiments

Chemical Analysis	(%)	Physical Properties	Values
SiO_2	≤50.00	Brightness (Elrepho R 457)	85±2
Al_2O_3	≥30.00	Yellowish	6±1
Fe_2O_3	≤0.50	Humidity (at 105^oC)	≤%7
TiO_2	≤0.60	pH	6.5-8.0
K_2O	≤3.30	Surface Area	15-25 m^2/g
CaO+MgO	≤1.00	Total Density	0.50-0.60 g/cm^3
Na_2O	0.15	Appearance	Powder

3.1.2 Preparation of Standard Heavy Metal Solution and Glassware

Analytical grade chemicals were used in all experiments and all standard solutions were stored in refrigerator. Glassware was soaked in dilute H_2SO_4, and rinsed with de-ionized water. The glassware was oven dried and then cooled to room temperature prior to use.

3.1.2.1 Copper Solution

Standard solution for copper numbered as 1.19786.0500 by Merck was used in the experiments. Standard solutions concentration is 1000 ppm. This stock solution was appropriately diluted to obtain the concentrations (i.e. 1, 5, 10, 100, 500 ppm Cu^{+2}).

3.1.2.2 Iron Solution

Standard solution for iron numbered as 1.19781.0500 by Merck was used in the experiments. Standard solutions concentration is 1000 ppm. This stock solution was appropriately diluted to obtain the concentrations (i.e. 1, 5, 10, 100, 500 ppm Fe^{+2}).

3.1.2.3 Nickel Solution

Standard solution for nickel numbered as 1.19792.0500 by Merck was used in the experiments. Standard solutions concentration is 1000 ppm. This stock solution was appropriately diluted to obtain the concentrations (i.e. 1, 5, 10, 100, 500 ppm Ni^{+2}).

3.1.2.4 Zinc Solution

Standard solution for zinc numbered as 1.19806.0500 by Merck was used in the experiments. Standard solutions concentration is 1000 ppm. This stock solution was appropriately diluted to obtain the concentrations (i.e. 1, 5, 10, 100, 500 ppm Zn^{+2}).

3.1.3 Analytical Methods

In the study, the concentration of heavy metals in the solutions was determined by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy) using standard methods 3120B. pH was measured using a NEL 890 pH meter. A rotary shaker was used to mix the samples. Shaker which is designed and produced by a local manufacturer is used in the experiments. Sigma S-16 model centrifuge was used for centrifugation.

3.2 Batch Adsorption Studies

3.2.1 Adsorption Experiments Using Synthetic Solutions

Adsorption experiments were carried out at room temperature by shaking the synthetic wastewater-kaolinite mixtures on a shaker. The experiments were conducted for 24 hours until adsorption reached equilibrium. Then, the suspensions were centrifuged at 5000 rpm for 15 min in Sigma S-16 model centrifuge at the same temperature. Liquid phases were separated and equilibrium concentration was determined by ICP-OES. Difference between initial concentration and equilibrium concentration is equal to the portion adsorbed. During the experiments, the effects of the pH, particle size, adsorbent dosage, contact (agitation) time, and initial concentrations of Cu, Fe, Ni, Zn were investigated separately.

Langmuir and Freundlich adsorption isotherms were used for determination of the adsorption characteristics of the adsorbents, isotherm constant, and regression coefficient for both isotherms.

3.2.1.1 The Effect of pH

In order to investigate the effect of pH on heavy metal adsorption with kaolinite, metal solutions of 100 ml in volume and 10 ppm in concentration were used at pH ranging from 2 to 12. In the experiments, kaolinite content was kept constant (1 g/l) and their size was lower than 53μm. The agitation time was determined as to be 1 hour at 100 rpm. Following to shaking, the samples were centrifuged at 5000 rpm for 15 min for liquid phase separation, and reserved in the refrigerator for analysis. Samples were acidified prior to measurement of the metals by ICP-OES.

3.2.1.2 The Effect of Particle Size

Following to optimum pH determination for each metal solution, the effect of particle size on metal adsorption was investigated. Metal solutions of 100 ml in

volume and 10 ppm in concentration were used in the experiments. Adsorbent, i.e. kaolinite used in the experiments was separated into five particle size. Particle sizes were determined according to ASTM mesh no. Particle sizes used in the experiments were <53µm (mesh no: 270), 106µm-212µm (mesh no: 140-70), 212µm-1.18mm (mesh no: 70-16), 1.18mm-2.36mm (mesh no: 16-8), and 2.36mm- 4.75mm (mesh no: 8-4). During the experiments, adsorbent content was kept constant (1 g/l) and their size was lower than 53µm. The agitation time was determined as to be 1 hour at 100 rpm. Following to shaking, the samples were centrifuged at 5000 rpm for 15 min for liquid phase separation, and reserved in the refrigerator for analysis. Samples were acidified prior to measurement of the metals by ICP-OES.

3.2.1.3 The Effect of Adsorbent Dose

In order to determine the optimum kaolinite dosage, solutions with an initial metal concentration of 10 ppm were used at optimum pH value. The agitation time was determined as to be 1 hour at 100 rpm. The amount of kaolinite added to the solutions varied between 0.1 and 100 g/l. Following to shaking, the samples were centrifuged d at 5000 rpm for 15 min for liquid phase separation, and reserved in the refrigerator for analysis. Samples were acidified prior to measurement of the metals by ICP-OES.

3.2.1.4 The Effect of Contact (Agitation) Time

In order to determine the equilibrium time for kaolinite, various agitation periods were experienced. The effect of time on removal efficiency was investigated by using the previously determined optimum values of pH, kaolinite dosage and size. In the experiments, solutions with an initial metal concentration of 10 ppm were used. In the study, samples were shaken at different time periods varying between 5 min. and 24 hours. Centrifuged samples at 5000 rpm reserved in the refrigerator for analysis. Samples were acidified prior to measurement of the metals by ICP-OES.

3.2.1.5 The Effect of Initial Concentration

The effect of initial metal concentration on adsorption was also determined in the study. Metal solutions of 100 ml were used at optimum conditions (i.e. optimum pH, adsorbent dosage, adsorbent size, and contact time). Various metal concentrations ranging from 1 to 500 mg/l were used to determine the optimum metal concentration. Finally, centrifuged samples at 5000 rpm reserved in the refrigerator for analysis. Samples were acidified prior to measurement of the metals by ICP-OES.

3.2.2 Adsorption Experiments Using Industrial Wastewater Samples

Following to the adsorption studies with synthetic wastewater, industrial wastewater samples were used in the study. Industrial wastewater samples were obtained from an automotive side industry and an automotive industry. Samples were taken from the inlet of the wastewater treatment plants. Because of the industrial wastewaters pH 7-8 caustic (NaOH) was used to obtain alkaline condition for Cu, Ni, and Zn experiments whereas sulphuric acid (H_2SO_4) was used to acidify the samples for Fe experiments.

Adsorption experiments were carried out at room temperature by shaking the wastewater-kaolinite mixtures on a shaker. Metal solutions of 100 ml were used at optimum pH conditions obtained from previous studies. In the experiments, kaolinite dosages were between 0.01 and 5g/l. The experiments were conducted until adsorption reached equilibrium. Then, the suspensions were centrifuged at 5000 rpm for 15 min in Sigma S-16 model centrifuge at the same temperature. Liquid phases were separated and equilibrium concentration was determined by ICP-OES.

CHAPTER FOUR
RESULTS AND DISCUSSION

In the presented study, the adsorption characteristics of kaolinite were investigated for the ions of copper, iron, nickel and zinc. The effect of pH, particle size, contact time, adsorbent doze and metal ion concentrations were examined and the results obtained from the batch adsorption studies were discussed.

4.1 Adsorption Characteristics of Kaolinite for Copper Ions

4.1.1 Effect of pH

The pH of solution is the most important variable affecting metal ions adsorption. Adsorption of Cu(II) was studied over the pH range of 1.5–12. The adsorbent dose and initial metal ion concentration were 1g/l and 10 mg/l, respectively. The results obtained from batch experiments are presented in Table 4.1. The solution pH had a dramatic effect on the adsorption of Cu(II) onto kaolinite. The highest removal efficiency (99.4 %) was obtained at pH > 10. At lower pH values (pH < 5.0), the adsorption efficiency was decreased. The low adsorption observation at low pH values, was explained due to increase in positive charge (protons) density on the surface sites and thus, electrostatic repulsion occurred between the metal ions and the edge groups with positive charge on the surface (Evans et al., 2002; Lai et al., 2002; Alkan, Doğan, 2001). In an alkaline medium, the surface of kaolinite becomes negatively charged and electrostatic repulsion decreases with raising pH due to reduction of positive charge density on the sorption edges thus resulting in an increase metal adsorption. A similar theory was proposed by several earlier workers for metal adsorption on different adsorbent (Srivastava et al., 2006; Bhattacharya et al., 2006; Feng et al., 2004). A considerable increase in the adsorption was occurred at pH 7-10 and the maximum Cu(II) adsorption was observed at pH 10. Thus, pH value was selected as 10 to be the optimum pH for further studies.

Table 4.1 The effect of pH on copper ions removal

pH	1.5	2.0	3.0	5.0	7.0	10.0	12.0
Ce(µg/l)	1000	1000	1000	1000	149.6	5.59	13.27

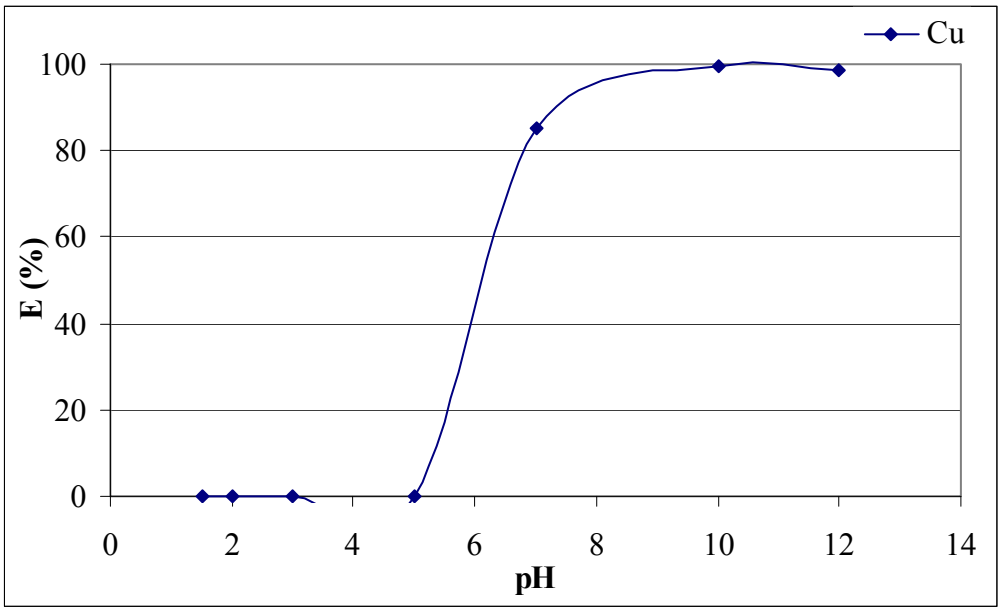

Figure 4.1 The effect of pH on copper removal efficiency.

4.1.2 Effect of Particle Size

Particle size is an important factor in adsorption kinetics because it determines the time required for transport within the pores to adsorption sites. In the experiments, a sample of kaolinite was sieved to various sizes (2.36-4.75, 1.18-2.36, 0.212-1.18, 0.106-0.212, less than 0.053 mm of diameter). The effect of the particle size on Cu (II) removal was studied and the measured values of the residual concentration of Cu (II) in solution relating to various sizes are presented in Table 4.2. According to the particle size distribution one may conclude that kaolinite sample looks more like powder than grain. Adsorption efficiency derived from the initial and residual concentrations are calculated and plotted versus particle size in Figure 4.2. As seen in Figure 4.2, particle sizes used in the experiments were quite effective thus adsorption efficiencies were not significantly affected from the varied particle sizes. Banat et al. (2000) stated that the increase in the sorption capacity is attributed to the increase in the external surface area of the sorbent available for adsorption. Thus, in this study,

the most effective particle size is determined as <0.053mm due to its larger surface area.

Table 4.2 The effect of kaolinite particle size on copper ions removal

Particle Size (mm)	< 0.053	0.106 – 0.212	0.212 – 1.18	1.18 – 2.36	2.36 – 4.75
Ce (µg/l)	15.04	14.49	17.34	50.20	52.13

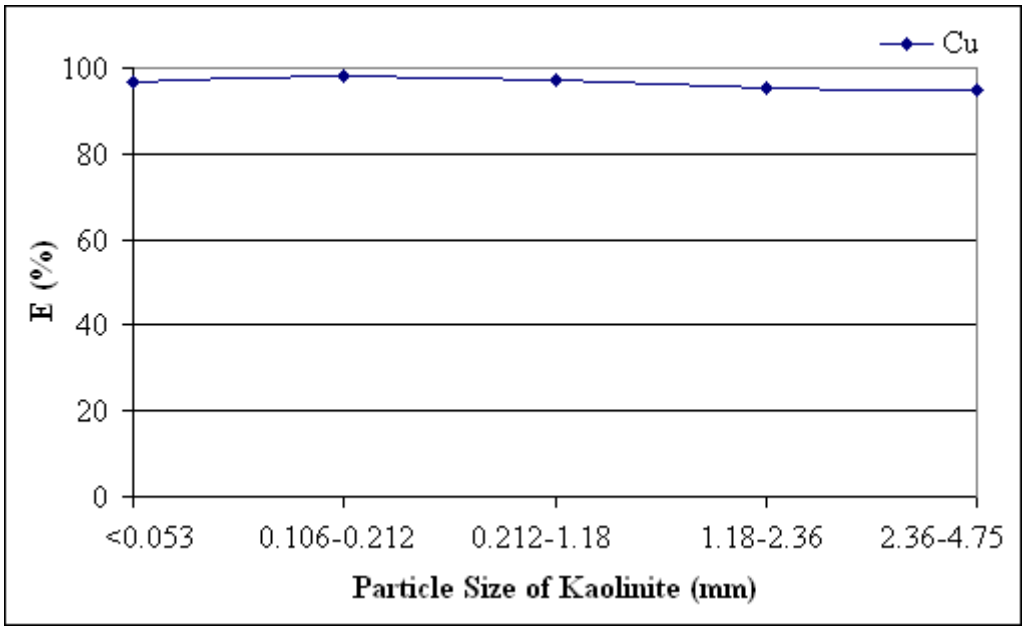

Figure 4.2 The effect of the particle size of kaolinite on copper removal efficiency.

4.1.3 Effect of Adsorbent Dosage

Adsorbent dosage is an important parameter because this determines the capacity of an adsorbent for a given initial concentration of the adsorbate at the operating conditions. In the experiments, the adsorbent doses were varied from 0.01 to 100 g/l with initial Cu(II) concentration of 10 mg/l. The results obtained from the batch experiments are summarized in Table 4.3 and the effect of adsorbent dosage on the adsorption of Cu(II) ions is shown in Fig. 4.3. As seen from Figure 4.3, Cu (II) ions were effectively removed from the solution even at small adsorbent doses. When the adsorbent dosage was increased from 0.01 to 0.5 g/l, the adsorption percentage was raised from 94 to 99%. The increase in the adsorption percentage with rise in

adsorbent dosage is due to increase in active sites on the adsorbent and thus making easier penetration of the metal ions to the sorption sites. The highest removal efficiency was obtained at 50 g/l kaolinite (removal efficiency is 99.79%). However, the adsorption percentage of Cu (II) ions was almost over 98% for 0.1 g/l adsorbent dosage. Therefore, the amount of kaolinite was selected as 0.1 g/l for further adsorption experiments.

Table 4.3 The effect of kaolinite dosage on copper ions removal

Dosage of Kaoline (g/l)	0.01	0.05	0.1	0.5	1.0	5.0	10	50	100
Ce (µg/l)	60.98	45.91	27.34	12.23	8.539	4.988	4.304	3.847	4.015

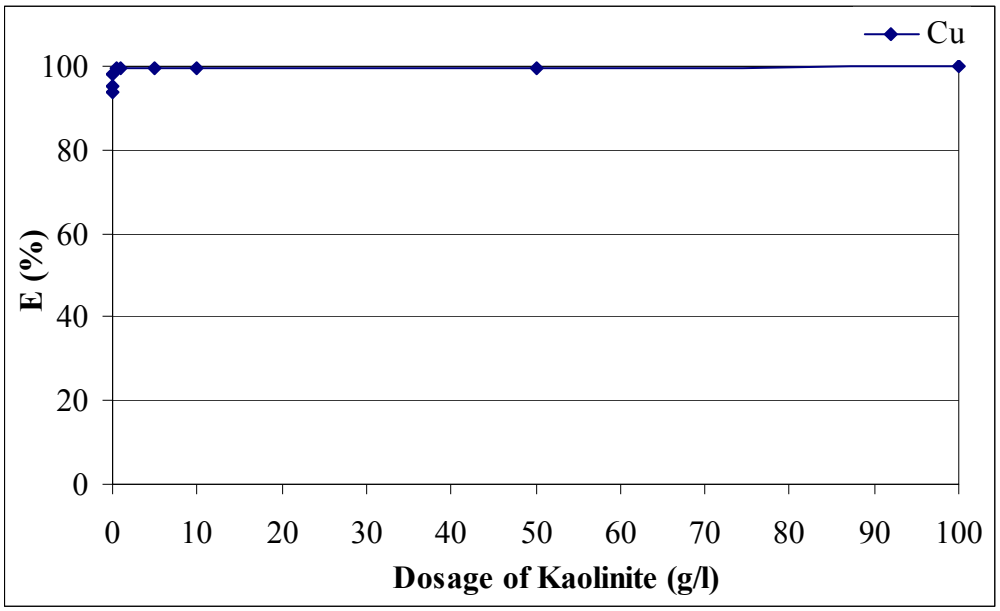

Figure 4.3 The effect of dosage of kaolinite on copper removal efficiency

4.1.4 Effect of Contact Time

The effect of agitation time on the adsorption of metal ions by the kaolinite was studied in the study. The flasks were shaken for different time intervals in a temperature-controlled shaker. The adsorption percentages of Cu(II) ions as a function of shaking time are given in Table 4.4 and schematically drawn in Fig. 4.4.

Time required for attaining equilibrium for Cu (II) ions was about 5 min. Maximum adsorption was attained as 98% for Cu(II) ion.

Table 4.4 The effect of contact time on copper ions removal

Θ (min)	5	15	30	45	60	120	180	1440
Ce(µg/l)	12.43	17.78	17.10	12.70	20.35	9.68	19.82	32.99

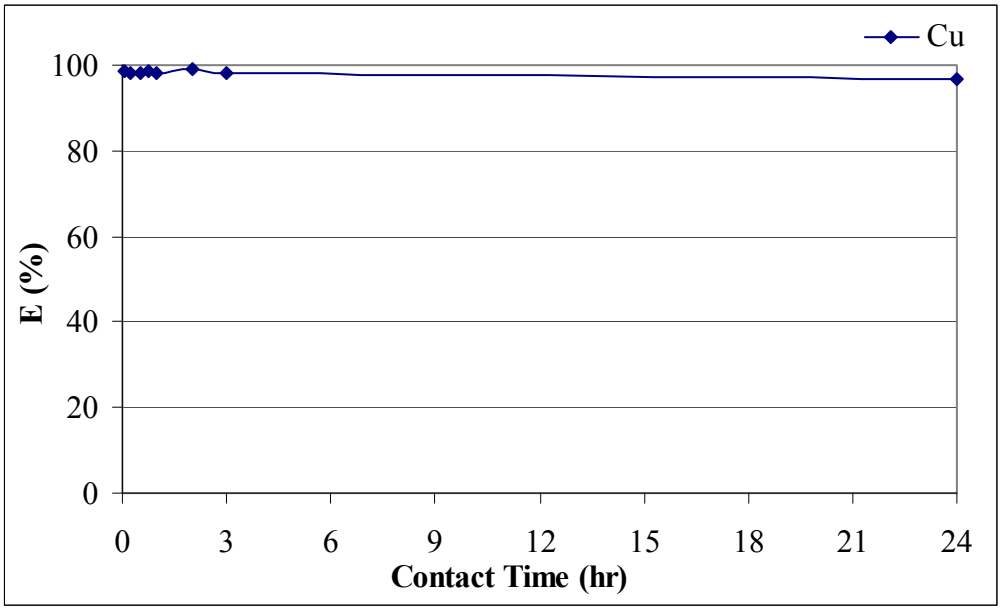

Figure 4.4 The effect of contact time on copper removal efficiency.

4.1.5 Effect of Initial Concentration

Heavy metal ions adsorption capacities of kaolinite are presented as a function of initial concentration of Cu(II) ions within aqueous solution in Table 4.5. The amount of metal ions adsorbed per gram of kaolinite increased with the increase of initial metal ions concentration (see Fig.4.5). An increase in the initial metal concentration led to an increase in the amount of metal ion adsorbed onto kaolinite. This may be attributed to an increase in the driving force of the concentration gradient with the increase in the initial Cu (II) concentration. Apparently, the initial Cu (II) concentration plays an important role in affecting the adsorption capacity of Cu onto

kaolinite. The results show that a rapid increase in Cu (II) adsorption occurred within 5 min with more than 90% of total Cu adsorption completed in all cases.

Table 4.5 The effect of initial concentration on copper ions removal

Co (mg/l)	1.0	5.0	10	100
Ce (µg/l)	84.47	15.56	12.09	10.44

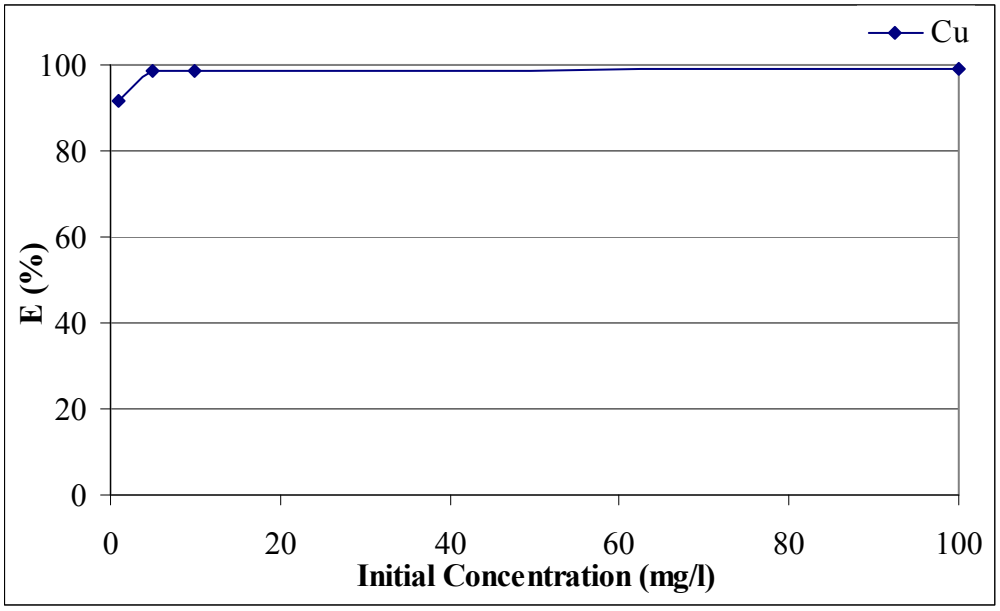

Figure 4.5 The effect of initial concentration on copper removal efficiency.

4.1.6 Batch Isotherm Results

Analysis of the equilibrium data is essential to develop an equation which precisely represents the results and which can be used for design purposes. Various isotherm models have been used for the equilibrium modeling of adsorption systems. The Langmuir model is one of the most widely used models to describe the mineral adsorption process. The Langmuir model assumes that adsorptions occur at specific homogeneous sites on the adsorbent and is used successfully in many monolayer adsorption processes. This model can be written as follows:

$$\frac{Ce}{qe} = \frac{1}{ab} + \left(\frac{1}{a}\right)Ce$$

where *q*e is the equilibrium metal ion concentration on the adsorbent (mg/g), *C*e the equilibrium metal ion concentration in the solution (mg/l), a (mg/g) is a temperature independent equilibrium constant related to maximum adsorption capacity (capacity parameter), b (l/mg) temperature dependent equilibrium constant related to energy of adsorption (affinity parameter). The adsorption affinity of the adsorbent for adsorbate can be assessed by comparing the constant, b. A high b value indicates that the adsorbent has a high affinity for adsorbate and vice versa..

The Freundlich model can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. The Freundlich model in linear form is:

$$\log qe = \log K_F + \frac{1}{n}(\log Ce)$$

where *Kf* is a constant related to the adsorption capacity and 1/*n* is an empirical parameter related to the adsorption intensity, which varies with the heterogeneity of the material.

Fig. 4.6 shows the Freundlich isotherm obtained by plotting log *q*e versus log *C*e values. The values of *Kf* and *n* were found to be 210 and 0.36 for Cu(II) ion. The r^2 value was found to be 0.93 for Cu (II) ion indicating that the Freundlich model was able to adequately to describe the relationship between *q*e and *C*e values.

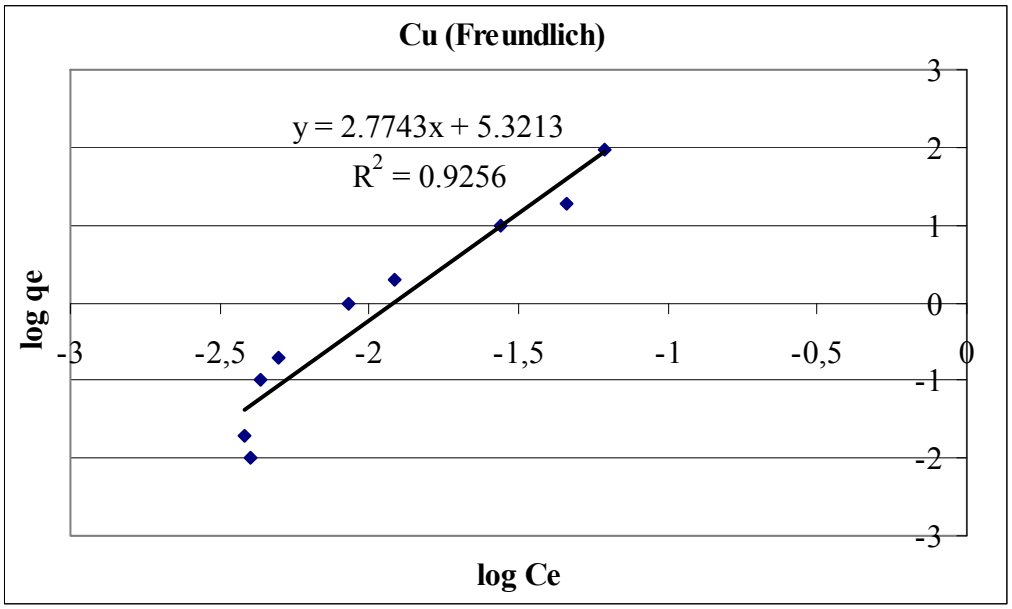

Figure 4.6 Freundlich isotherm of copper

The results obtained from the empirical studies were applied to Langmuir isotherm. The dependence of *Ce*/*q*e from *C*e was obtained by using empirical results. Fig. 4.7 shows the Langmuir isotherms obtained by plotting the 1/*q*e versus 1/*C*e values. The correlation coefficient (r^2) was found to be 0.18 for the adsorption of Cu(II) ion indicating that the equilibrium data did not fit well the Langmuir model.

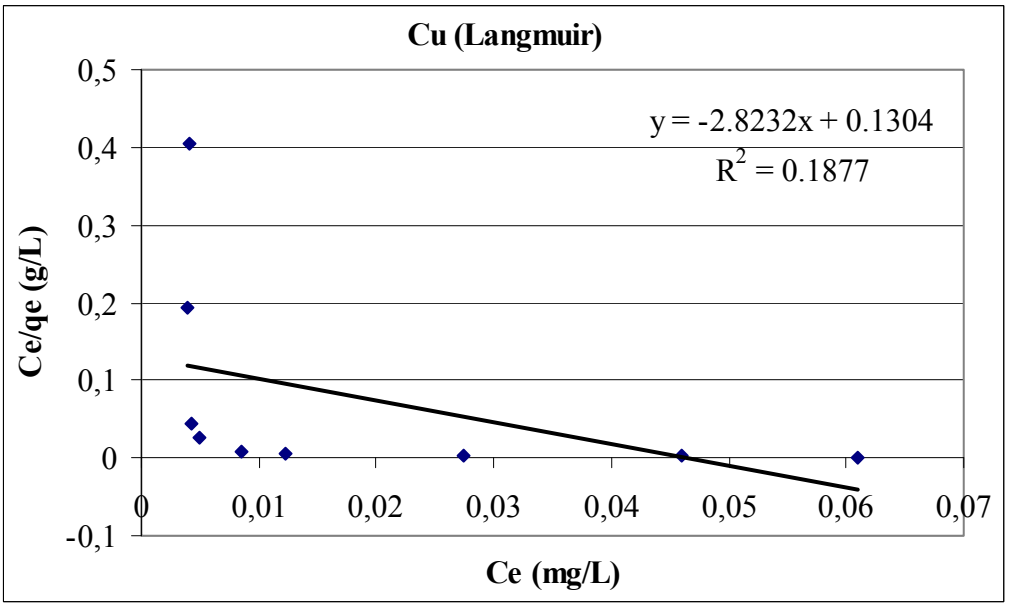

Figure 4.7 Langmuir isotherm of copper.

4.2. Adsorption Characteristics of Kaolinite for Iron Ions

4.2.1 Effect of pH

Solution pH has been identified as the most important variable factor governing metal adsorption. To study the pH effect on the adsorption of kaolinite, metal uptake was studied at pH ranging from 1.5 to 12.0. Metal uptake was strongly affected by pH of the metal solution (Fig.4.8). The maximum adsorption efficiency for Fe ions was 99% at pH 5.0**,** while at pH 2.0 the adsorption capacity of kaolinite was much low, because large quantities of protons compete with metal cations for the adsorption sites. As the pH of solution increases, the number of protons dissociated from actional groups on the surface of kaolinite increases and thus more negative groups for complexation of metal cations are provided.

Table 4.6 The effect of pH on iron ions removal.

pH	1.5	2.0	3.0	5.0	7.0	10.0	12.0
Ce(μg/l)	858.7	1058	441.4	6.342	5.687	20.95	136.5

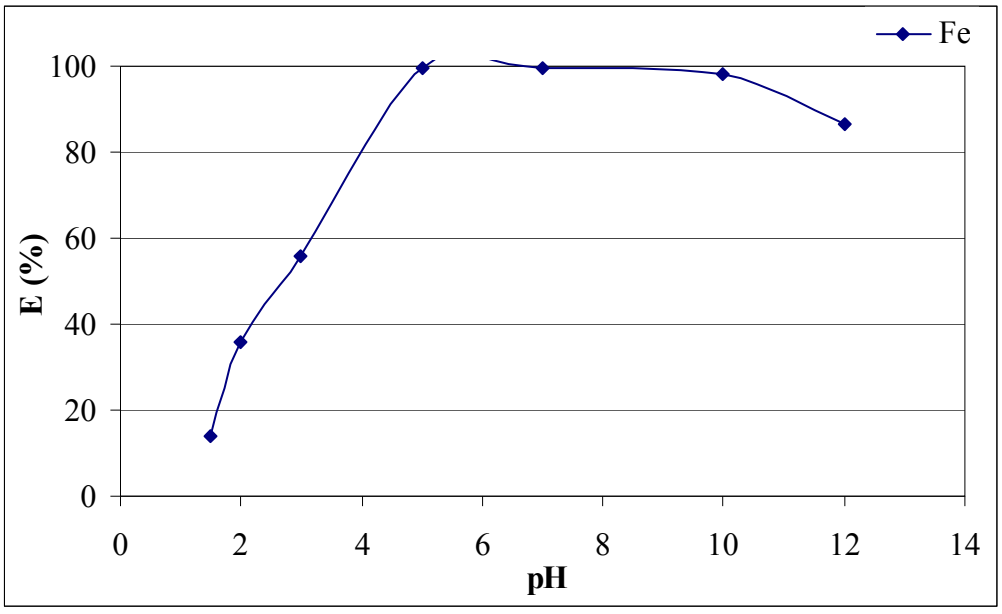

Figure 4.8 The effect of pH on iron removal efficiency.

4.2.2 Effect of Particle Size

In order to determine the particle size effect on adsorption, a sample of kaolinite was sieved to various sizes (2.36-4.75, 1.18-2.36, 0.212-1.18, 0.106-0.212, less than 0.053 mm of diameter). The effect of the particle size on Fe removal was studied and the measured values of the residual concentration of Fe in solution relating to various sizes are presented in Table 4.7. Adsorption efficiency derived from the initial and residual concentrations are calculated and plotted versus particle size in Figure 4.7. As seen in Figure 4.7, particle sizes used in the experiments were quite effective thus adsorption efficiencies were not significantly affected from the varied particle sizes. Approximately, 93% removal efficiency was achieved for each particle size.

Table 4.7 The effect of kaolinite particle size on iron ions removal.

Particle Size (mm)	< 0.053	0.106 – 0.212	0.212 – 1.18	1.18 – 2.36	2.36 – 4.75
Ce (µg/l)	60.05	69.18	57.46	68.16	66.95

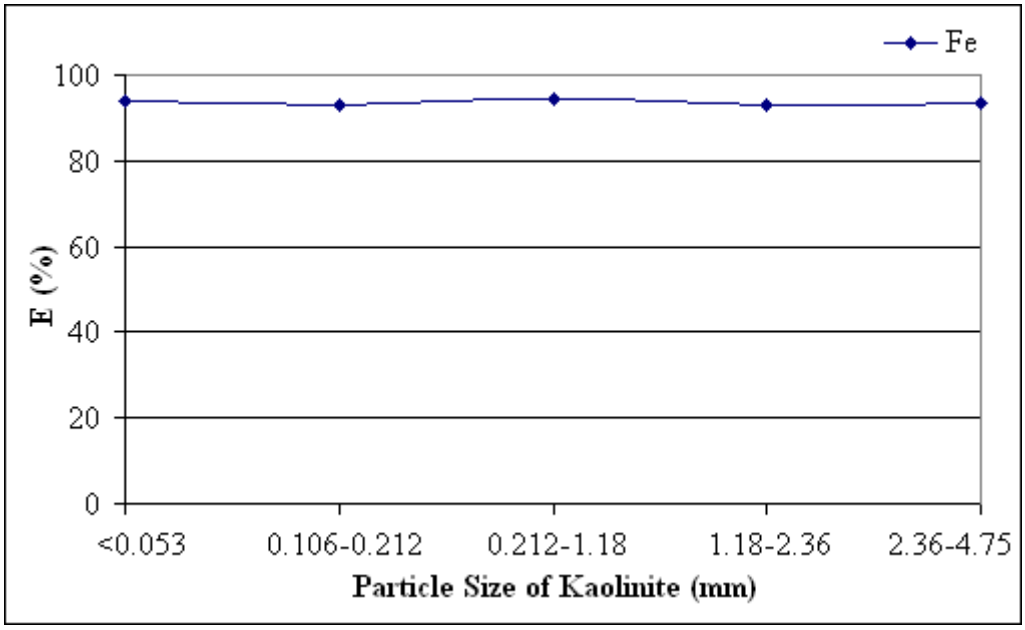

Figure 4.9 The effect of the particle size of kaolinite on iron removal efficiency.

4.2.3 Effect of Adsorbent Dosage

Adsorbent dosage is an important parameter because this determines the capacity of an adsorbent for a given initial concentration of the adsorbate at the operating conditions. The effect of adsorbent dosage on the adsorption of Fe ions is shown in Fig. 4.10. When the adsorbent dosage was increased from 1 to 5 g/l, the adsorption percentage was raised from 72 to 97% for Fe ions. The increase in the adsorption percentage with rise in adsorbent dosage is due to increase in active sites on the adsorbent and thus making easier penetration of the metal ions to the sorption sites. The adsorption percentages of Fe ions were almost over 95% for adsorbent dosage of greater than 5 g/l. Therefore, the amount of kaolinite was selected as 5 g/l for further adsorption experiments. With increasing adsorbent dosage, more surface area is available for adsorption.

Table 4.8 The effect of kaolinite dosage on iron ions removal

Dosage of Kaoline (g/l)	0.1	0.5	1.0	5.0	10	50	100
Ce (µg/l)	404.6	332.4	280.1	32.75	82.66	25.14	28.26

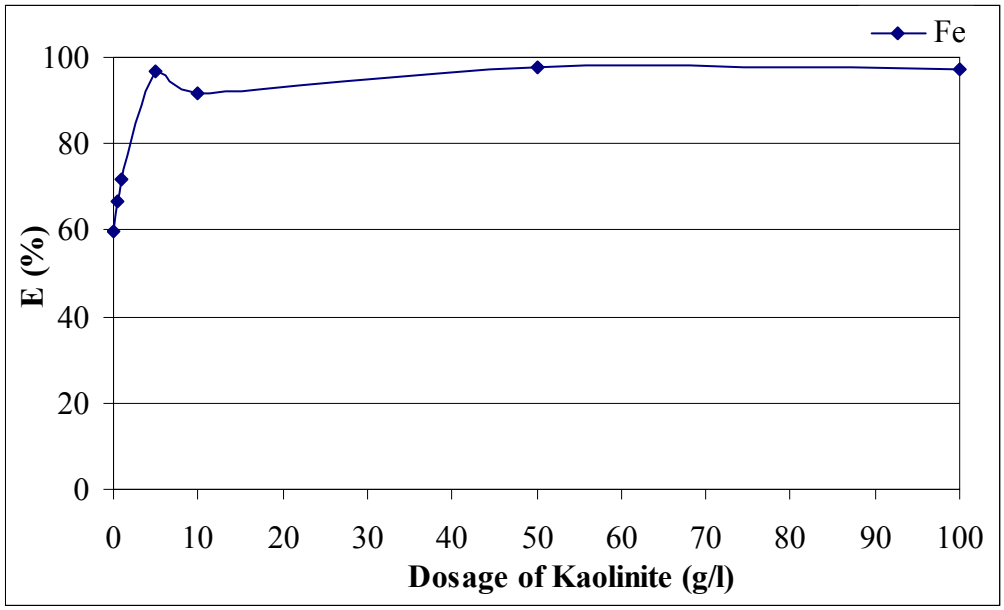

Figure 4.10 The effect of dosage of kaolinite on iron removal efficiency.

4.2.4 Effect of Contact Time

The agitation time was also evaluated as one of the most important factors affecting the adsorption efficiency. By using the previously determined optimum values of pH and particle size, the effect of time on removal efficiency was analyzed. At the study carried out in a batch system, samples were taken at different time periods varying between 5 and 1440 min, and the remaining concentrations were analyzed by ICP-OES. As seen in Figure 4.9 high efficiency for iron adsorption can be obtained at short time periods. The optimum time for iron removal was determined at 15 min. For 15 min agitation time 94% of iron removal is obtained. Since, prolonged agitation was not resulted in higher efficiency 15 min agitation period is used for designing purpose.

Table 4.9 The effect of contact time on iron ions removal

Θ (min)	5	15	30	45	60	120	180	1440
Ce(µg/l)	116.3	59.42	51.81	49.63	52.58	55.35	52.87	58.15

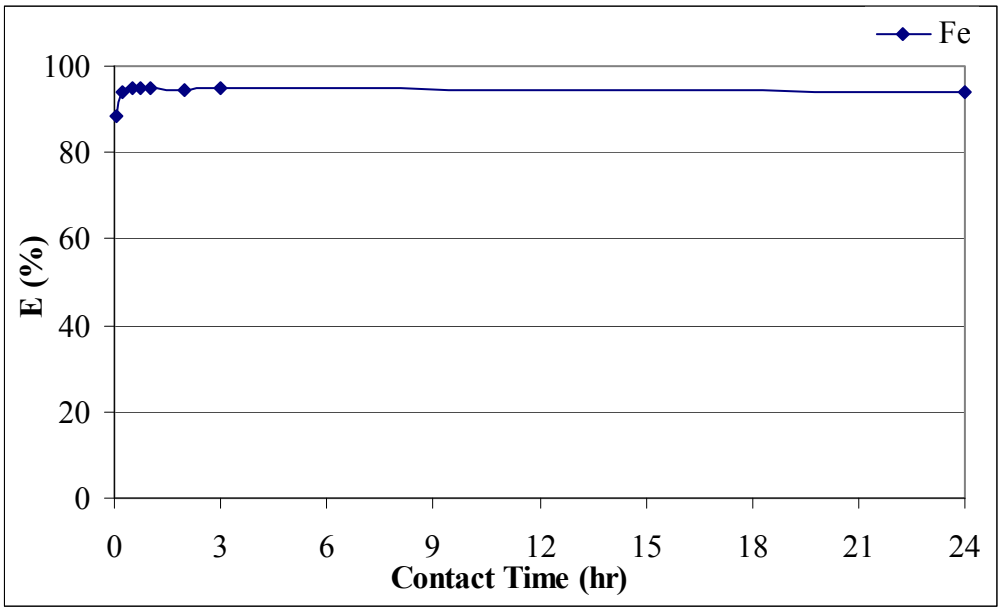

Figure 4.11 The effect of contact time on iron removal efficiency.

4.2.5 Effect of Initial Concentration

Optimum concentrations were determined after experimental studies achieved under various metal concentrations ranging between 1.0 and 100 mg/l. The results obtained from the experimental studies are shown in Fig. 4.10 .The adsorption efficiency increased to a certain level, and remained stable as the concentration increased. Following the saturation on the surface where the adsorption takes place, no more metal ions can be adsorbed.

Table 4.10 The effect of initial concentration on iron ions removal

Co (mg/l)	1.0	5.0	10	100
Ce (µg/l)	586	73.88	48.63	50.01

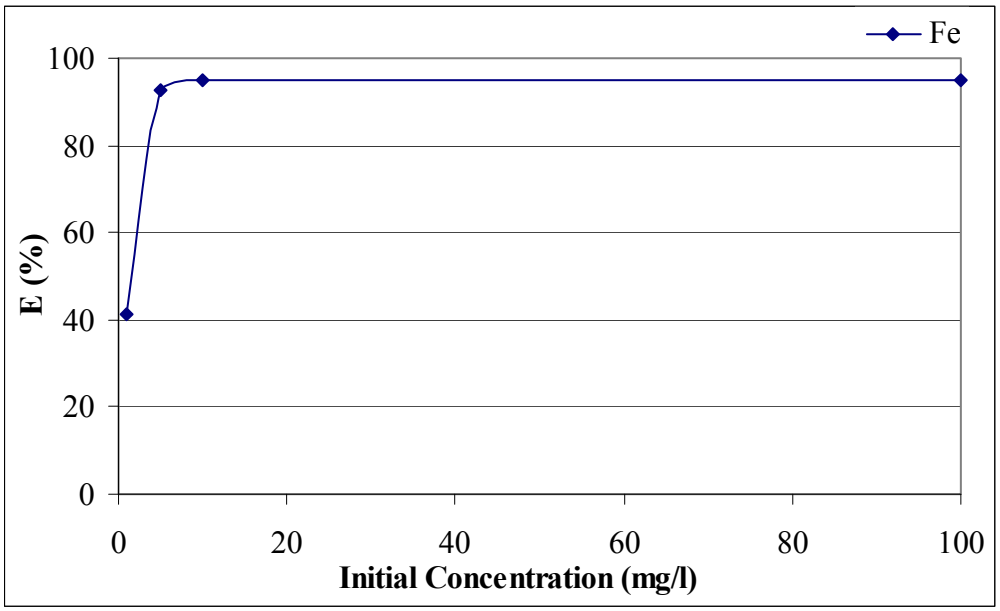

Figure 4.12 The effect of initial concentration on iron removal efficiency.

4.2.6 Batch Isotherm Results

The experimental data corresponding to the isotherms were plotted in Figure 4.13 and 4.14 according to the Freundlich and Langmuir equations. Fig. 4.13 shows the Freundlich isotherm obtained by plotting log *q*e versus log*C*e values. The values of *Kf* and *n* were found to be 11 and 0.59 for iron ion. The r^2 value was found to be 0.82

for Fe ion indicating that the Freundlich model was able to adequately to describe the relationship between *q*e and *C*e values

Fig. 4.14 shows the Langmuir isotherms obtained by plotting the 1/*q*e versus 1/*C*e values. The correlation coefficient (r^2) was found to be 0.36 for the adsorption of Fe ion indicating that the equilibrium data did not fit well the Langmuir model.

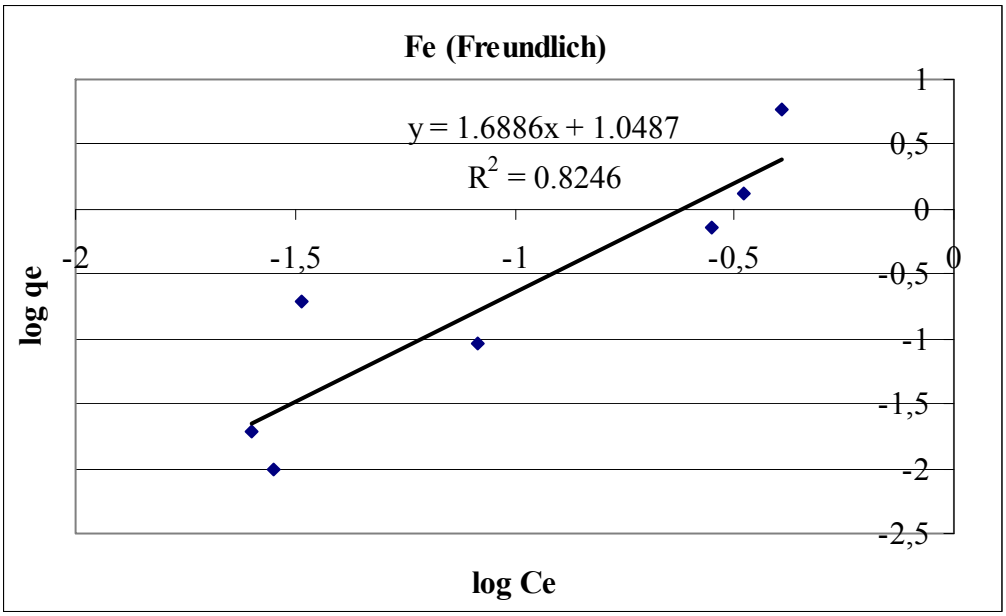

Figure 4.13 Freundlich isotherm of iron.

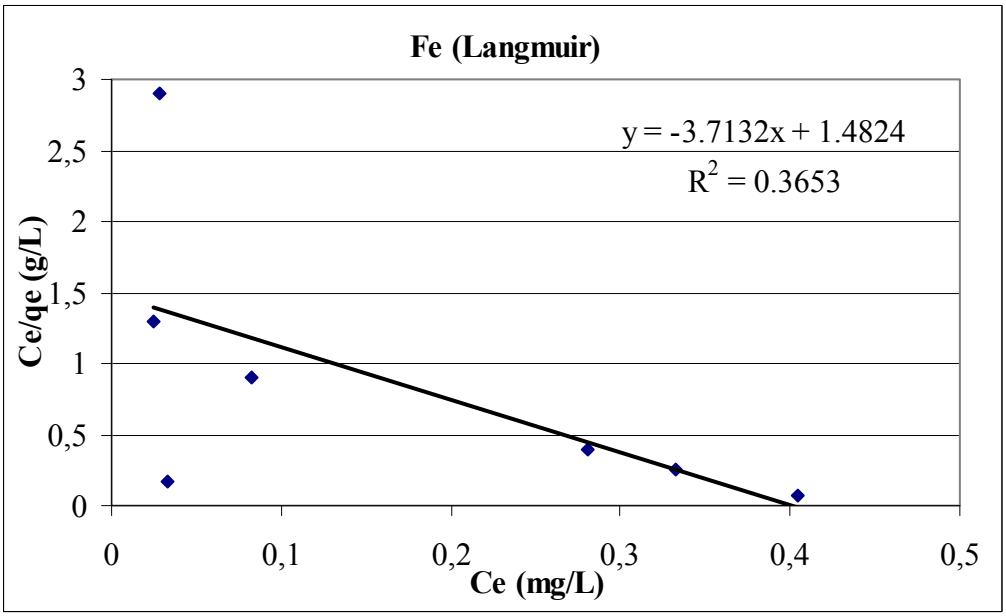

Figure 4.14 Langmuir isotherm of iron

4.3. Adsorption Characteristics of Kaolinite for Nickel Ions

4.3.1 Effect of pH

Ni ion uptake was studied at pH ranging from 3.0 to 12.0. Fig. 4.15 shows the uptake of ionic Ni depends on pH. Ni uptake by kaolinite increased with the increase of solution pH. The maximum adsorption was 98% at pH 10.0, while at pH 3.0 the adsorption capacity of kaolinite was relatively low (82%), because large quantities of protons compete with metal cations for the adsorption sites. As the pH of solution increases, the number of protons dissociated from functional groups on the surface of kaolinite increases and thus more negative groups for complexation of metal cations are provided. On the other hand, decrease in adsorption under pH 7 may be due to occupation of the adsorption sites by anionic species which retards the approach of such ions further toward the sorbent surface.

Table 4.11 The effect of pH on nickel ions removal

pH	3.0	5.0	7.0	10.0	12.0
Ce (µg/l)	183.1	131.1	121.6	15.97	7.558

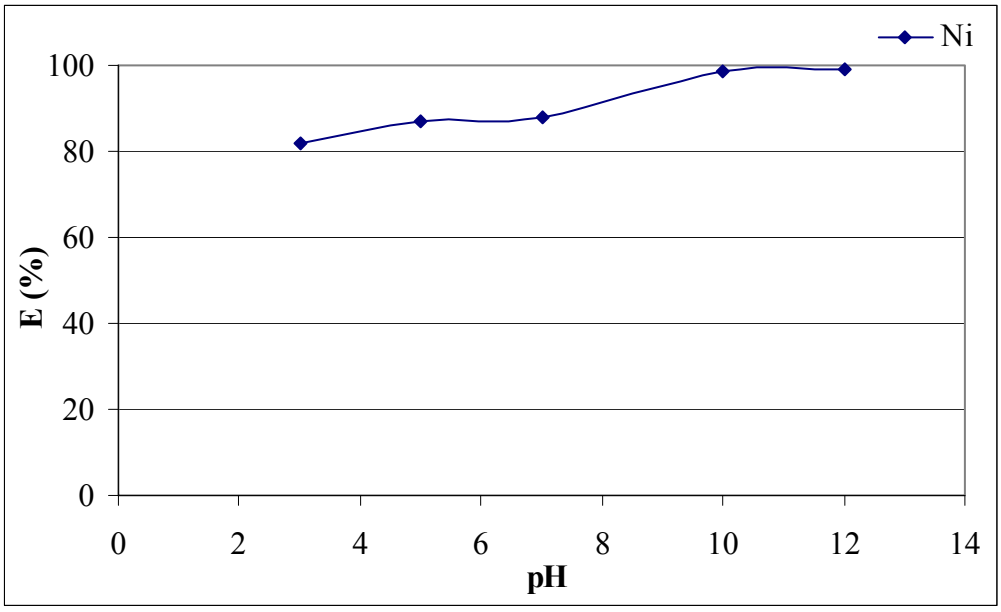

Figure 4.15 The effect of pH on nickel removal efficiency.

4.3.2 Effect of Particle Size

In the experiments, a sample of kaolinite was sieved to various sizes (2.36-4.75, 1.18-2.36, 0.212-1.18, 0.106-0.212, less than 0.053mm of diameter). The effect of the particle size on Ni (II) removal was studied and the measured values of the residual concentration of Ni (II) in solution relating to various sizes are presented in Table 4.12. Adsorption efficiency derived from the initial and residual concentrations are calculated and plotted versus particle size in Figure 4.16. As seen in Figure 4.16, particle sizes used in the experiments were quite effective thus adsorption efficiencies were not significantly affected from the varied particle sizes. Adsorption efficiencies were quite high for each particle size (99% removal). Thus, in this study, the most effective particle size is determined as <0.053mm.

Table 4.12 The effect of kaolinite particle size on nickel ions removal

Particle Size (mm)	< 0.053	0.106 – 0.212	0.212 – 1.18	1.18 – 2.36	2.36 – 4.75
Ce (µg/l)	15	13.5	36.4	13.8	13.9

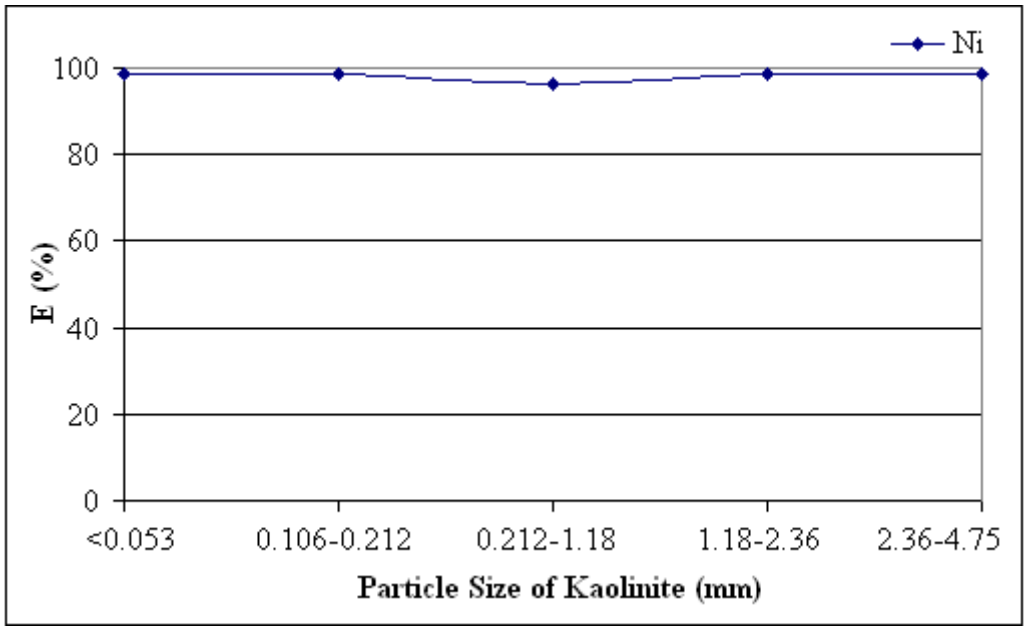

Figure 4.16 The effect of the particle size of kaolinite on nickel removal efficiency.

4.3.3 Effect of Adsorbent Dosage

In the experiments, the adsorbent doses were varied from 0.1 to 100 g/l with initial Ni (II) concentration of 10 mg/l. The results obtained from the batch experiments are summarized in Table 4.13 and the effect of adsorbent dosage on the adsorption of Ni (II) ions is shown in Fig. 4.17. As seen from Figure 4.17, Ni (II) ions were effectively removed from the solution even at small adsorbent doses. When the adsorbent dosage was increased from 0.1 to 100 g/l, the adsorption percentage was raised from 93.7% to 99.8%. The highest removal efficiency was obtained at 100 g/l kaolinite (removal efficiency is 99.8%) while the adsorption percentage of Ni (II) ions was almost over 99.5% for 10 g/l adsorbent dosage. Therefore, considering the cost and operational requirements, the amount of kaolinite was selected as 10 g/l for further adsorption experiments.

Table 4.13 The effect of kaolinite dosage on nickel ions removal

Dosage of Kaoline (g/l)	0.1	0.5	1.0	5.0	10	50	100
Ce (µg/l)	63.3	28.8	29.5	16.8	4.5	2.5	1.9

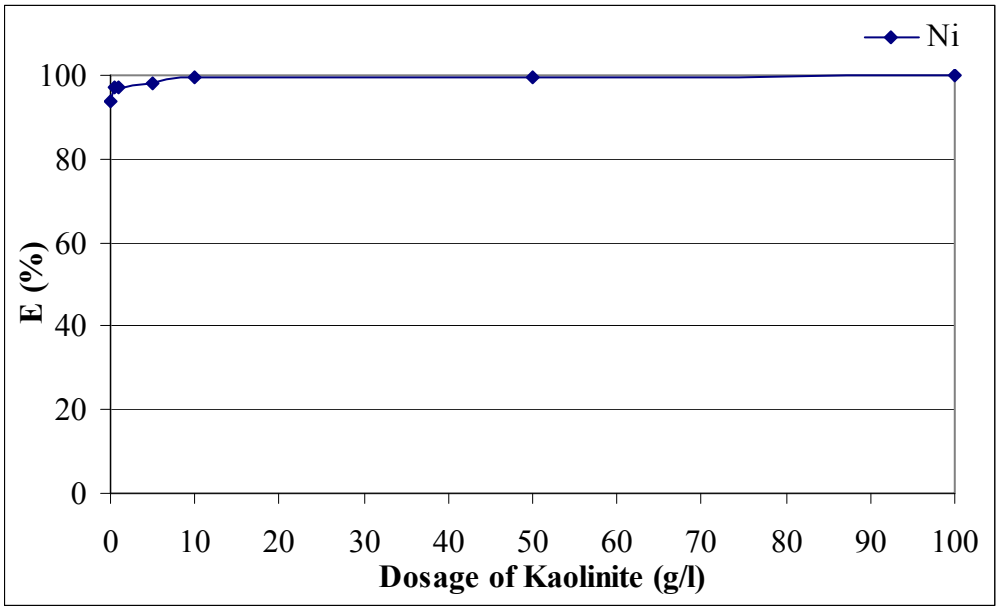

Figure 4.17 The effect of dosage of kaolinite on nickel removal efficiency.

4.3.4 Effect of Contact Time

The agitation time was also evaluated as one of the most important factors affecting the adsorption efficiency. By using the previously determined optimum values of pH and particle size, the effect of time on removal efficiency was analyzed. In the study, samples were taken at different time periods varying between 5 and 1440 min, and the remaining concentrations were analyzed. As seen in Figure 4.18 high efficiency for Ni adsorption can be obtained at very quickly. The optimum time for nickel removal was determined at 5 min. For 5 min agitation time 99% of nickel removal is obtained. Since, prolonged agitation was not resulted in higher efficiency 5 min agitation period is used for designing purpose.

Table 4.14 The effect of contact time on nickel ions removal

Θ (min)	5	15	30	60	120	180	1440
Ce (µg/l)	10.38	5.21	11.98	18.99	11.71	7.76	5.74

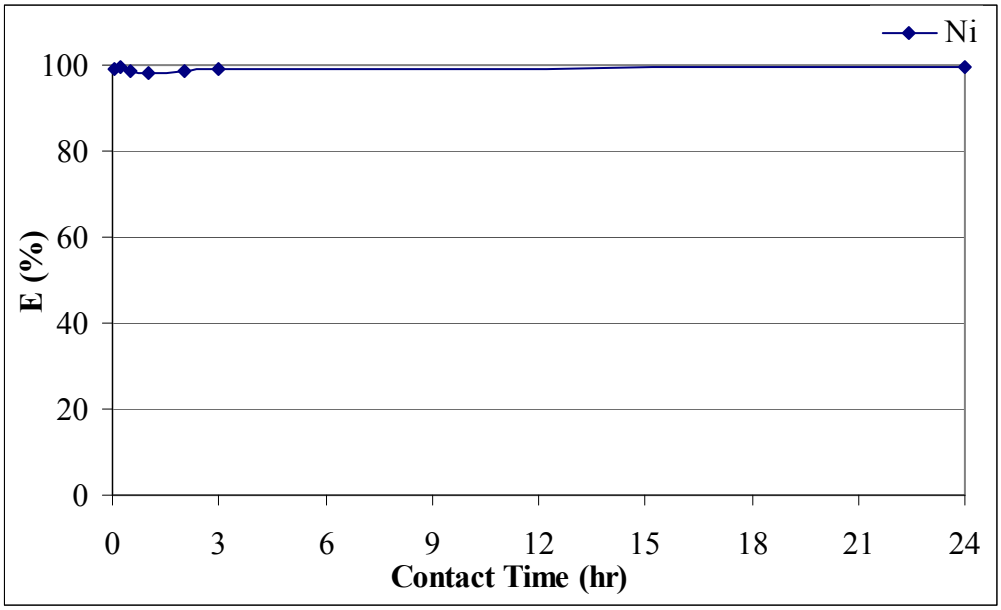

Figure 4.18 The effect of contact time on nickel removal efficiency.

4.3.5 Effect of Initial Concentration

Adsorption capacities of kaolinite are presented as a function of initial concentration of Ni (II) ions within aqueous solution in Table 4.15. Nickel ion adsorption capacity was superior (app. 100%) and the amount of metal ions adsorbed per gram of kaolinite was very high for initial Ni ion concentrations of 1 to 500 mg/l.

Table 4.15 The effect of initial concentration on nickel ions removal

Co (mg/l)	1.0	5.0	10	100	500
Ce (µg/l)	6.74	5.17	3.51	3.68	2.24

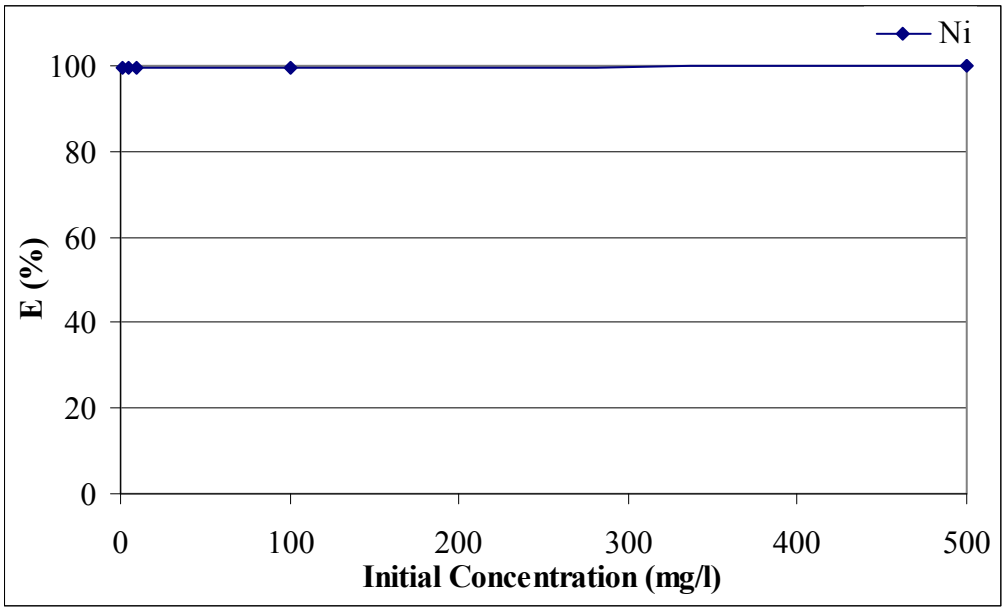

Figure 4.19 The effect of initial concentration on nickel removal efficiency.

4.3.6 Batch Isotherm Results

The experimental data corresponding to the isotherms were plotted in Figure 4.20 and 4.21 according to the Freundlich and Langmuir equations. Fig. 4.20 shows the Freundlich isotherm obtained by plotting log *q*e versus log*C*e values. The values of *Kf* and *n* were found to be 851 and 0.56 for nickel ion. The r^2 value was found to be

0.95 for Ni ion indicating that the Freundlich model was able to adequately to describe the relationship between *q*e and *C*e values

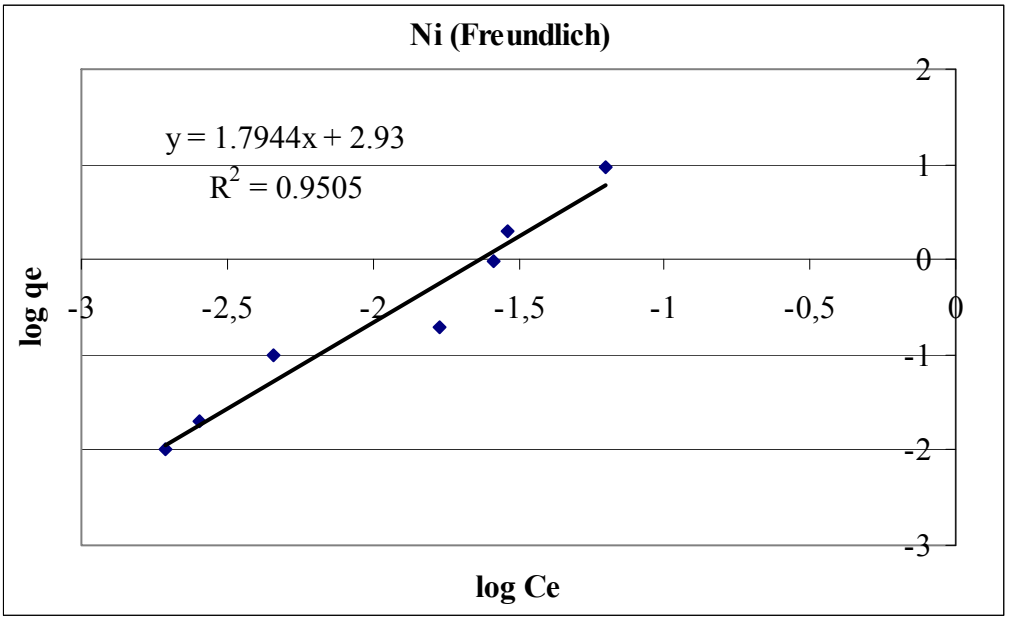

Figure 4.20 Freundlich isotherm of nickel.

Fig. 4.21 show the Langmuir isotherms obtained by plotting the 1/*q*e versus 1/*C*e values. The correlation coefficient (r^2) was found to be 0.50 for the adsorption of Ni ion indicating that the equilibrium data did not fit well the Langmuir model.

Consequently, as can be observed, experimental data were better fitted to the Freundlich equation (R^2=0.95) than to the Langmuir equation and therefore, it is more suitable for the analysis of kinetics. Fitting of the Freundlich isotherm is indicated that adsorption is occurred in a physical process, so, there is not any transfer or sharing of electrons.

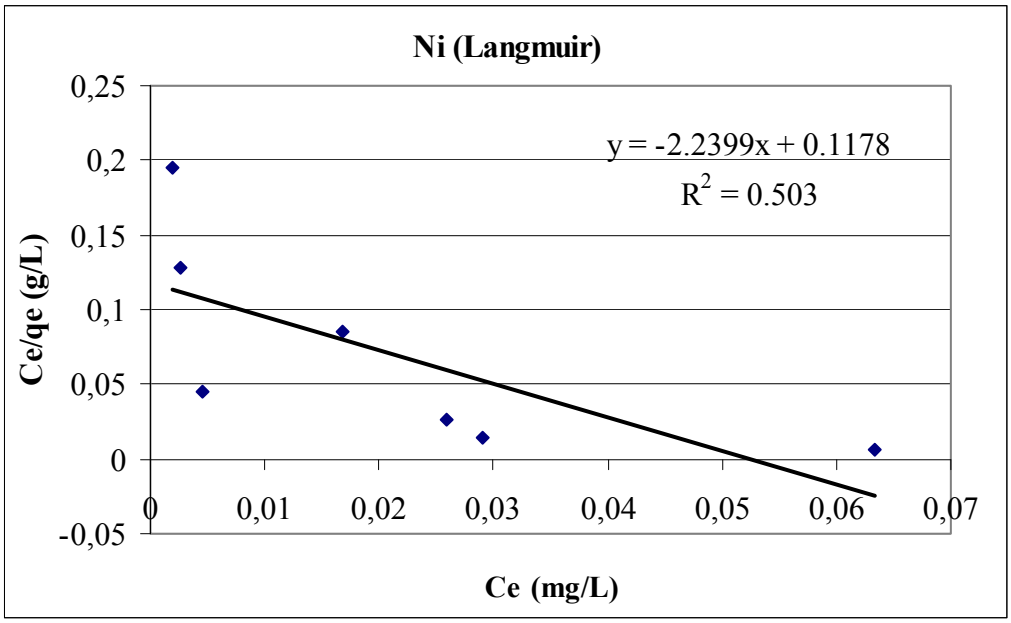

Figure 4.21 Langmuir isotherm of nickel.

4.4 Adsorption Characteristics of Kaolinite for Zinc Ions

4.4.1 Effect of pH

The highest removal efficiency in the zinc adsorption with natural clay was obtained at pH 10. At lower pH values (< 5), adsorption of Zn ions onto kaolinite was not achieved. The low adsorption efficiency at low pH may be explained by the competitive sorption between proton and metal ions. As the solution pH increases, the number of negatively charged sites increases, which favors the sorption of metal cations (Lin and Juang, 2002). The adsorption efficiency was also decreased at pH values greater than 10. In this study, the optimum pH values for the zinc removal were determined as 9-10.

Table 4.16 The effect of pH on zinc ions removal

pH	2.0	3.0	5.0	7.0	10.0	12.0
Ce (µg/l)	1000	1000	1000	660.4	30.97	570.3

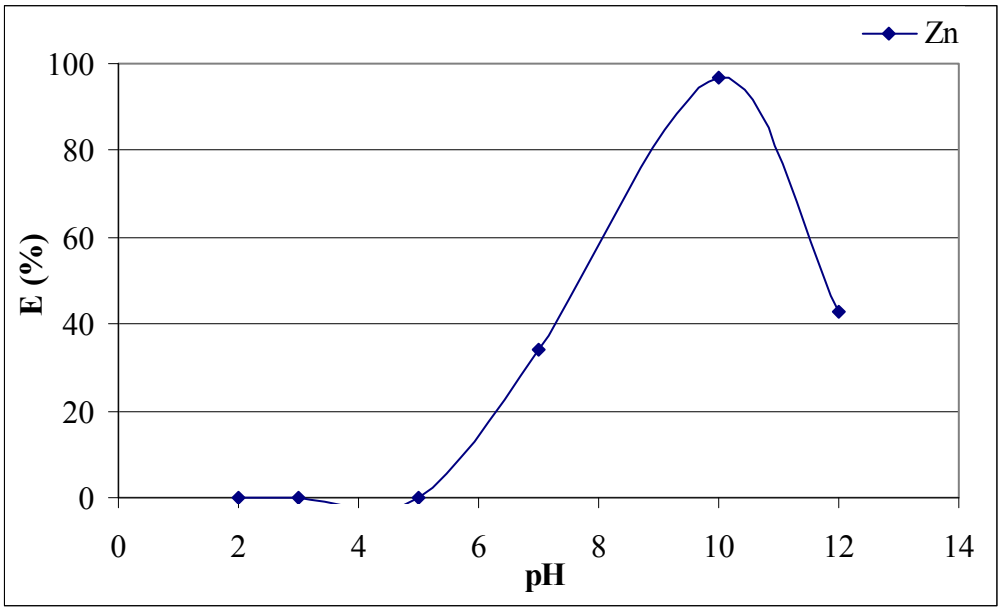

Figure 4.22 The effect of pH on zinc removal efficiency.

4.4.2 Effect of Particle Size

In the experiments, a sample of kaolinite was sieved to various sizes (2.36-4.75, 1.18-2.36, 0.212-1.18, 0.106-0.212, less than 0.053mm of diameter). The effect of the particle size on Zn (II) removal was studied and the measured values of the residual concentration of Zn (II) in solution relating to various sizes are presented in Table 4.17. Adsorption efficiency derived from the initial and residual concentrations are calculated and plotted versus particle size in Figure 4.17. As seen in Figure 4.23, particle sizes used in the experiments were quite effective thus adsorption efficiencies were not significantly affected from the varied particle sizes. Adsorption efficiencies were quite high (> 88%) for each particle size.

Table 4.17 The effect of kaolinite particle size on zinc ions removal

Particle Size (mm)	< 0.053	0.106 – 0.212	0.212 – 1.18	1.18 – 2.36	2.36 – 4.75
Ce (µg/l)	119.1	26.34	28.41	24.25	61.80

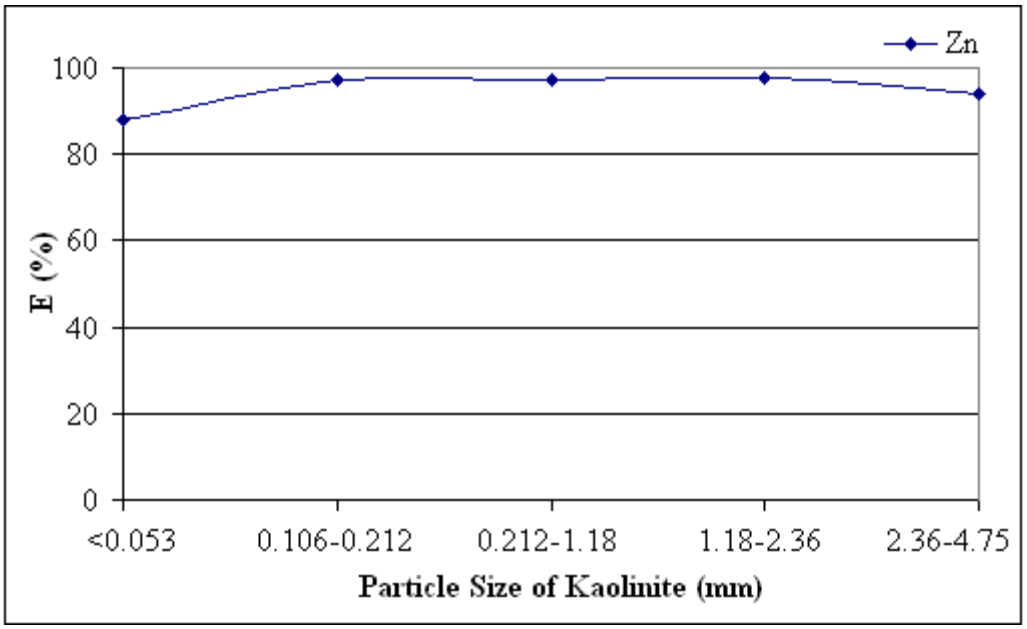

Figure 4.23 The effect of the particle size of kaolinite on zinc removal efficiency.

4.4.3 Effect of Adsorbent Dosage

In the experiments, the adsorbent doses were varied from 0.1 to 100 g/l with initial Zn (II) concentration of 10 mg/l. The results obtained from the batch experiments are summarized in Table 4.18 and the effect of adsorbent dosage on the adsorption of Zn (II) ions is shown in Fig. 4.24. As seen from Figure 4.24, Zn (II) ions were effectively removed from the solution even at small adsorbent doses. For the lowest adsorbent dosage (i.e. 0.1 g kaolinite/l) approximately 98% Zn ion removal was achieved. The adsorption percentage of Zn (II) ions was almost over 93% for other doses thus considering the cost and operational requirements, the amount of kaolinite was selected as 0.1 g/l for further adsorption experiments.

Table 4.18 The effect of kaolinite dosage on zinc ions removal

Dosage of Kaoline (g/l)	0.1	0.5	1.0	5.0	10	50	100
Ce (µg/l)	19.13	36.39	67.95	24.42	10.93	20.69	30.43

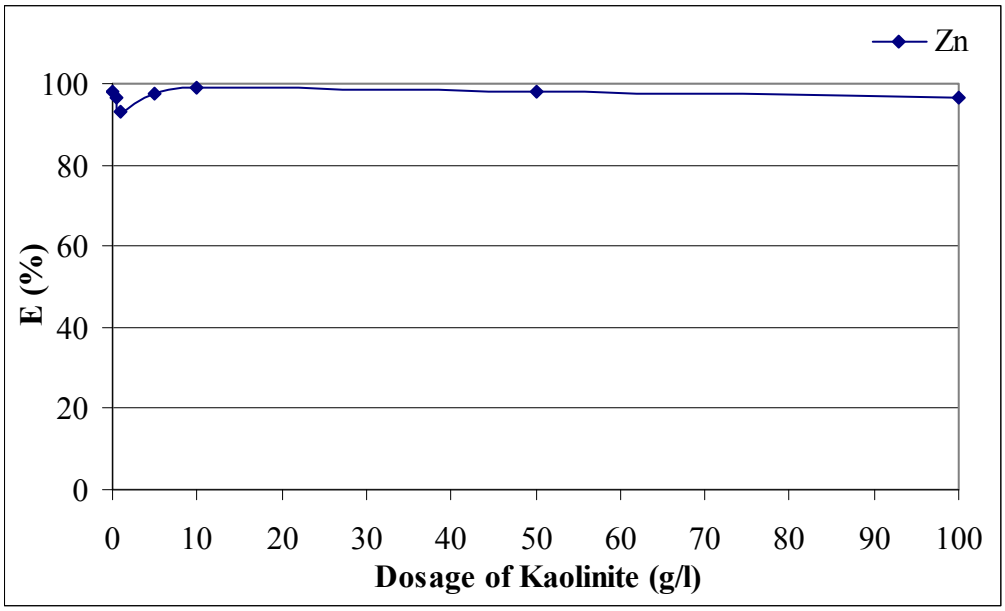

Figure 4.24 The effect of dosage of kaolinite on zinc removal efficiency.

4.4.4 Effect of Contact Time

In the study, samples were taken at different time periods varying between 5 and 1440 min, and the remaining concentrations were analyzed to determine the effect of the agitation time on adsorption efficiency. As seen in Figure 4.25 the highest efficiency for Zn adsorption was obtained within 180 minutes. However, adsorption efficiency was not significantly reduced for the agitation times lower than 180 minutes. For example, 96% Zn removal was achieved at 5 minutes agitation period. Thus, 5 minutes contact period was used in the experiments. On the other hand, adsorption efficiency at the end of the 24 hours was decreased, a slight increase in Zn ion concentration can be attributed to the desorption of Zn ions to the solution.

Table 4.19 The effect of contact time on zinc ions removal

Θ (min)	5	15	30	45	60	120	180	1440
Ce(µg/l)	33.20	25.37	30.70	45.05	18.06	54.87	9.93	178.6

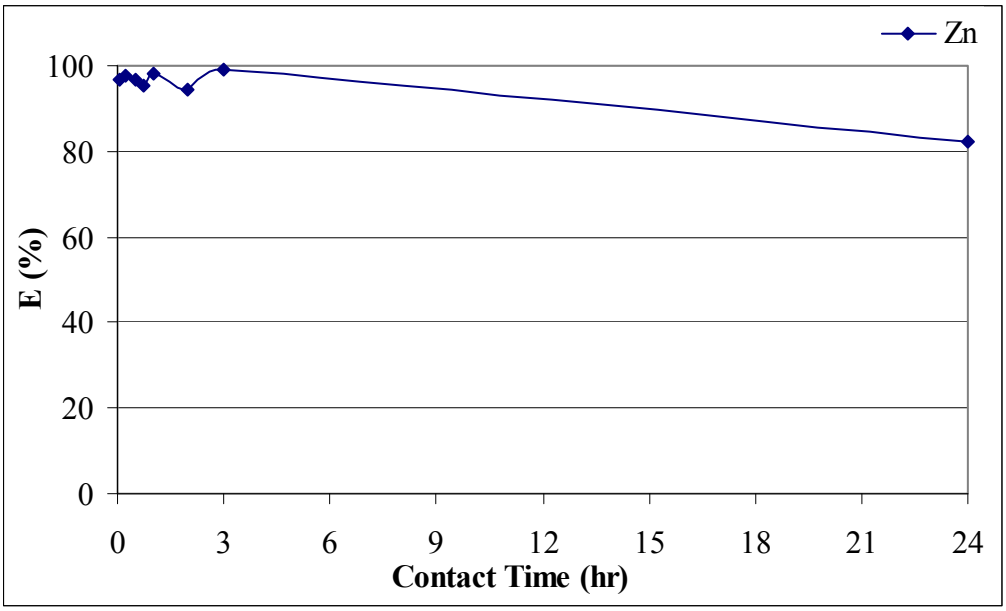

Figure 4.25 The effect of contact time on zinc removal efficiency.

4.4.5 Effect of Initial Concentration

Zinc ions adsorption capacities of kaolinite are presented as a function of initial metal concentration in Table 4.20. For the 1 g Zn/l, app. 93% removal efficiency was obtained. When the initial Zn concentration increased to 5 and 10 mg/l adsorption efficiencies were reduced to 75% and 65%, respectively. An increase in the initial metal concentration led to a decrease in the amount of metal ion adsorbed onto kaolinite. However, when the Zn concentration increased to 100 g/l, 98% removal efficiency was achieved.

Table 4.20 The effect of initial concentration on zinc ions removal

Co (mg/l)	1.0	5.0	10	100
Ce (µg/l)	71.5	252.7	346	15.57

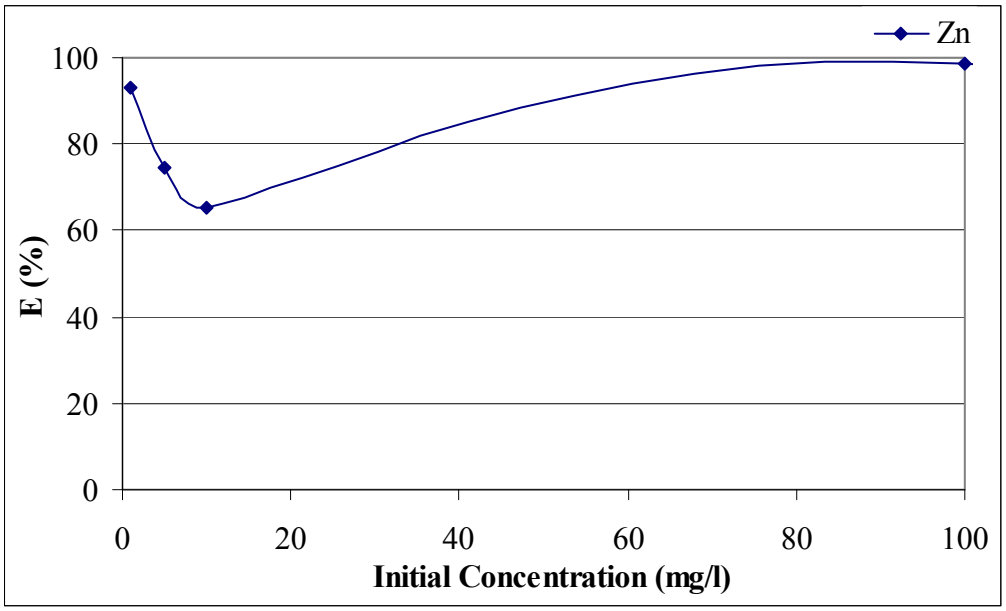

Figure 4.26 The effect of initial concentration on zinc removal efficiency

4.4.6 Batch Isotherm Results

The experimental data corresponding to the isotherms were plotted in Figure 4.27 and 4.28 according to the Freundlich and Langmuir equations. Fig. 4.27 shows the Freundlich isotherm obtained by plotting log *q*e versus log*C*e values. The values of *Kf* and *n* were found to be 813 and 0.31 for zinc ion. The r^2 value was found to be 0.59 for Zn ion indicating that the Freundlich model was adequate to describe the relationship between *q*e and *C*e values

Fig. 4.28 shows the Langmuir isotherms obtained by plotting the 1/*q*e versus 1/*C*e values. The correlation coefficient (r^2) was found to be 0.32 for the adsorption of Zn ion indicating that the equilibrium data did not fit well the Langmuir model.

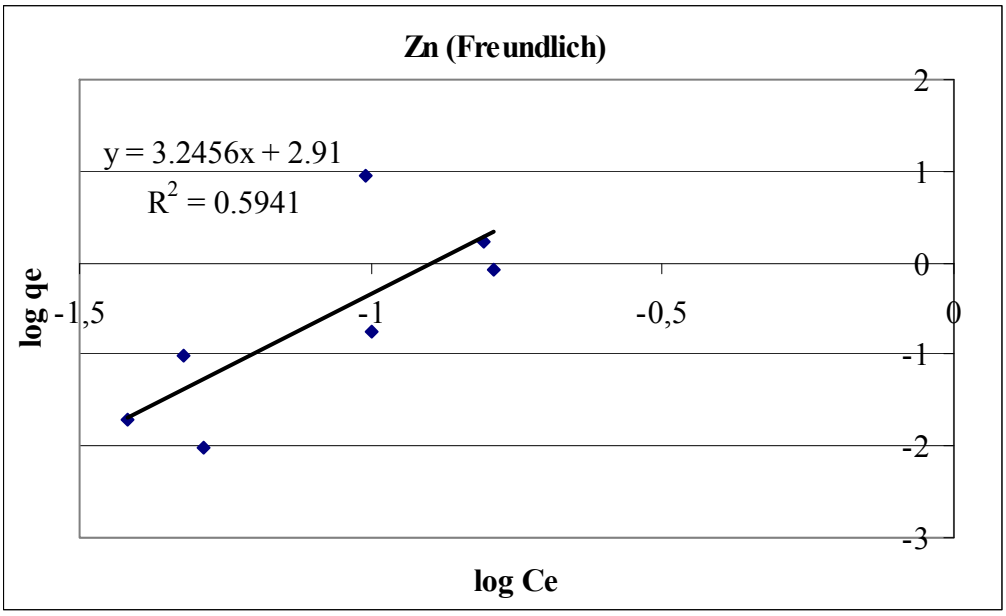

Figure 4.27 Freundlich isotherm of zinc.

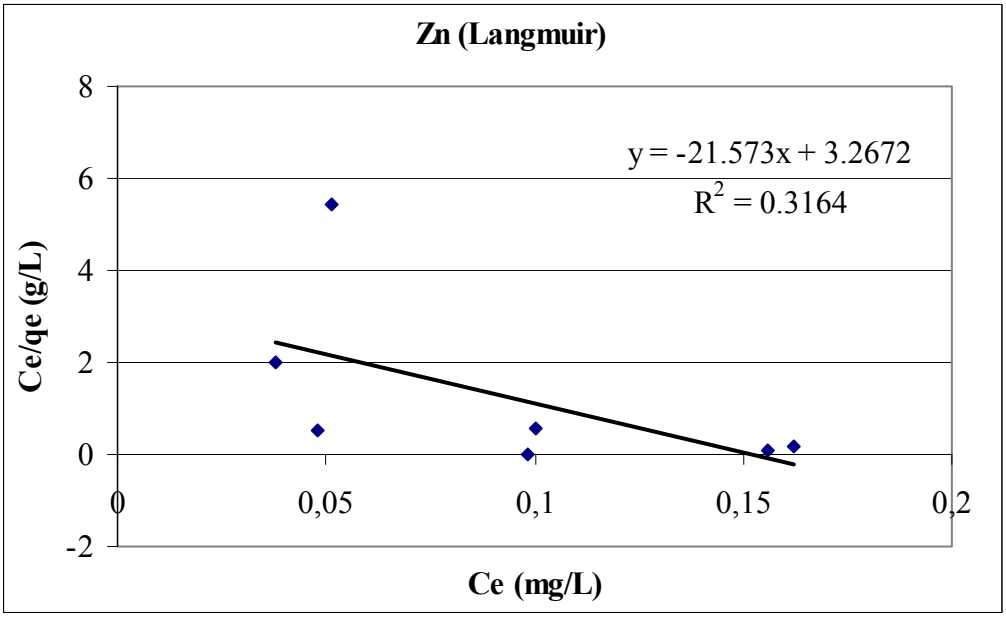

Figure 4.28 Langmuir isotherm of zinc.

4.5 Metal Ion Adsorption from Industrial Wastewater Samples

In this stage, wastewater samples obtained from two different automotive industries (i.e. automotive side industry (ASI) and automotive industry (AI)) were

used. Experimental data (i.e. optimum pH, particle size, contact time, adsorbent dose) obtained from previous studies were utilized for heavy metal removal purpose.

4.5.1 Metal Adsorption from the Automotive Side Industry (ASI) Wastewater

In the experiments, the adsorbent doses were varied from 0.01 to 5.0 g/l. The pH of the solutions was adjusted as 10, 5, 10, and 10 for Cu, Fe, Ni and Zn, respectively. The effective particle size was selected as 0.53 μm in each set. During the experiments, samples were agitated throughout 60 minutes. In Figure 4.29 and 4.30, residual metal ions in the solution after adsorption are presented for various kaolinite doses. Initial copper ion concentration was reduced from 7.84 μg/l to 4.6 for 0.05 g kaolinite/l corresponding 42% removal efficiency. Contrary to copper ions, nickel was effectively adsorbed onto kaolinite. Nickel ions decreased from 22.2 μg/l to 2.6 μg/L yielding 88% removal. The highest adsorption efficiency was obtained for 5 gr/l adsorbent dosage. Although, 5 mg/l was found as most efficient dose, other doses were not resulted significant variations in terms of Ni removal. Figure 4.30 shows the adsorbent dosage effect on Fe and Zn ions removal. Regarding to iron ions removal, 86% of Fe was adsorbed at kaolinite dose of 5 g/l. The lowest Fe removal was 82% and obtained at 0.01 g kaolinite/l dosage. Zinc ion concentration was dramatically reduced from 419.3 μg/l to 13.4 μg/l at 0.01 g kaolinite/l. The adsorption efficiency was not considerably varied for the increasing adsorbent dosages.

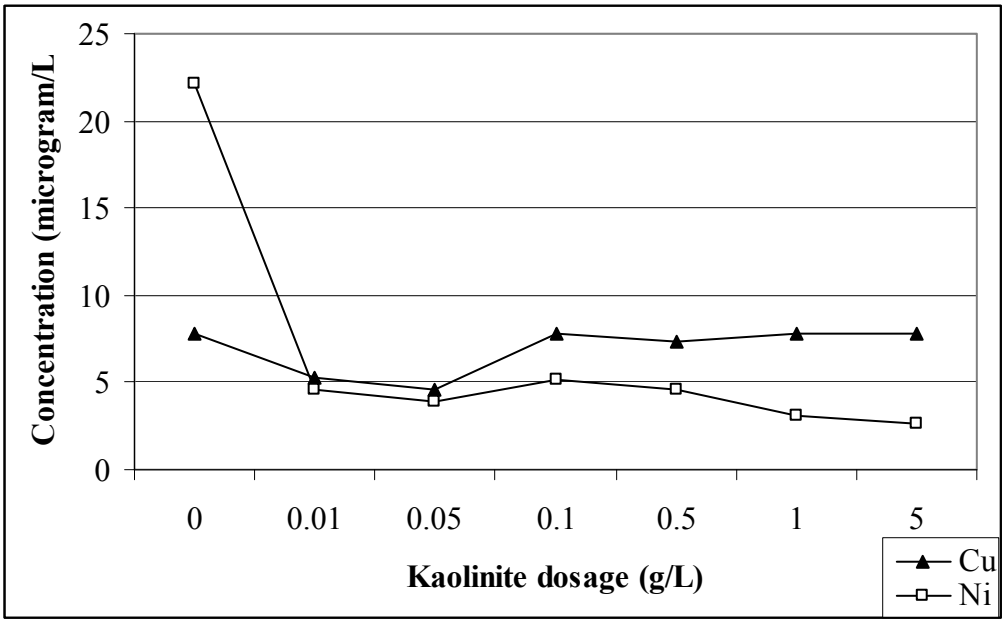

Figure 4.29 The effect of kaolinite dosage on Cu and Ni ions adsorption for ASI wastewater

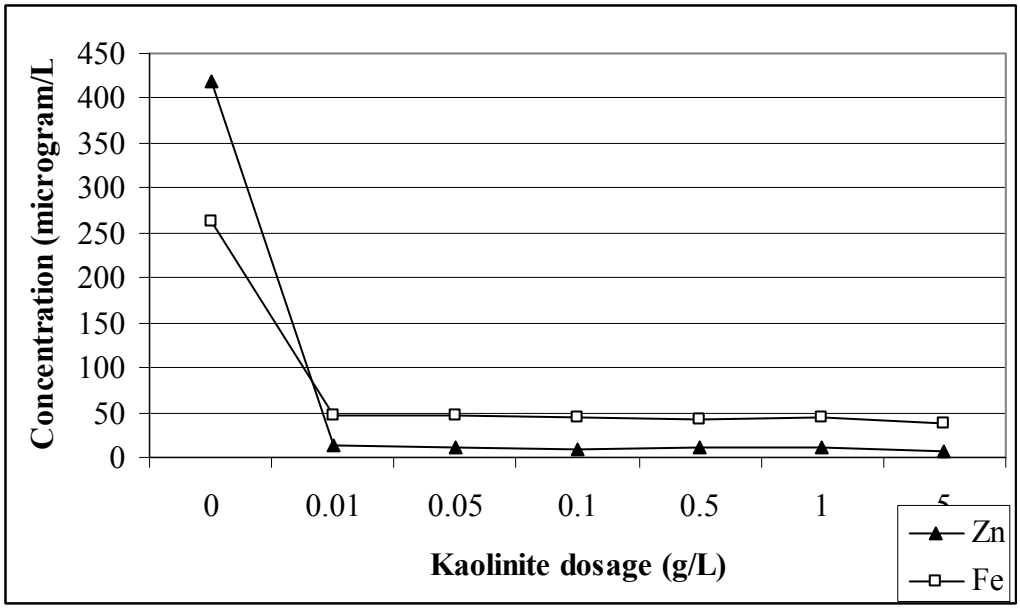

Figure 4.30 The effect of kaolinite dosage on Zn and Fe ions adsorption for ASI wastewater

Fig. 4.31 shows the Freundlich isotherm obtained by plotting log *q*e versus log*C*e values. The values of *Kf* and *n* were found to be 1.05×10^{17} and 0.13 for Cu ion. The r^2 value was found to be 0.56 for Cu ion indicating that the Freundlich model was able to adequately to describe the relationship between *q*e and *C*e values. Fig. 4.32 shows the Langmuir isotherms obtained by plotting the 1/*q*e versus 1/*C*e values. The

correlation coefficient (r^2) was found to be 0.15 for the adsorption of Cu ion indicating that the equilibrium data did not fit well the Langmuir model.

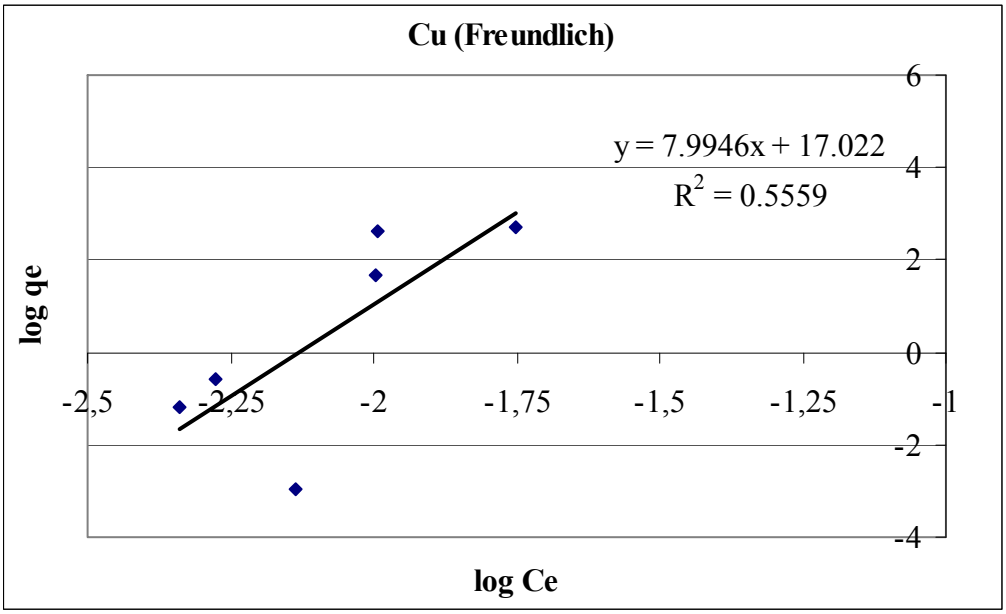

Figure 4.31 Freundlich isotherm of Cu for ASI wastewater

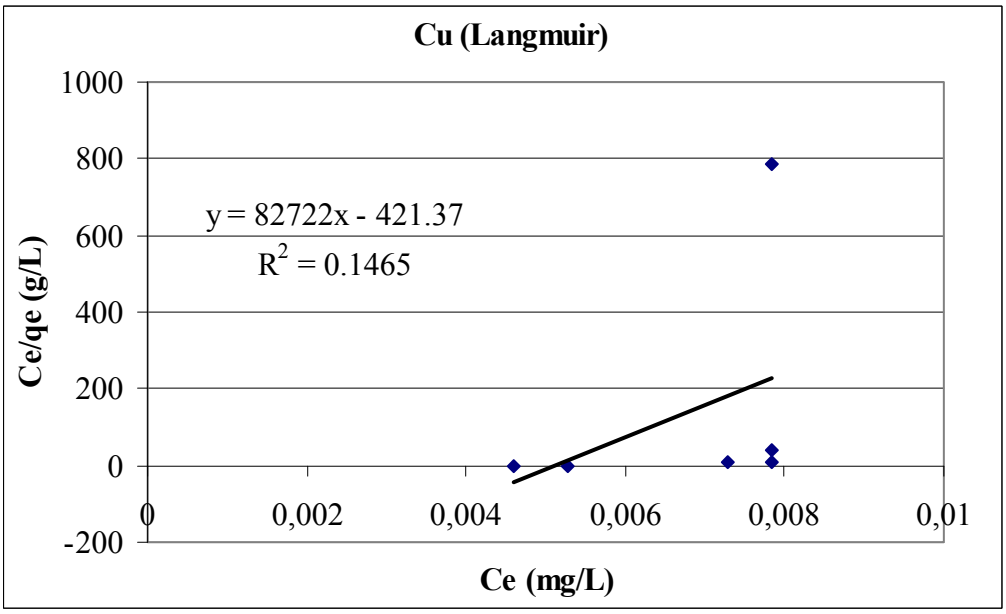

Figure 4.32 Langmuir isotherm of Cu for ASI wastewater

Fig. 4.33 shows the Freundlich isotherm obtained for Fe ions. The values of *Kf* and *n* were found to be 1.28×10^{25} and 0.05 for Fe ion. The r^2 value was found to be

0.86 for Fe ion indicating that the Freundlich model was able to adequately to describe the relationship between *q*e and *C*e values. Fig. 4.34 shows the Langmuir isotherms obtained by plotting the 1/*q*e versus 1/*C*e values. The correlation coefficient (r^2) was found to be 0.91 for the adsorption of Fe ion indicating that the equilibrium data fitted well the Langmuir model.

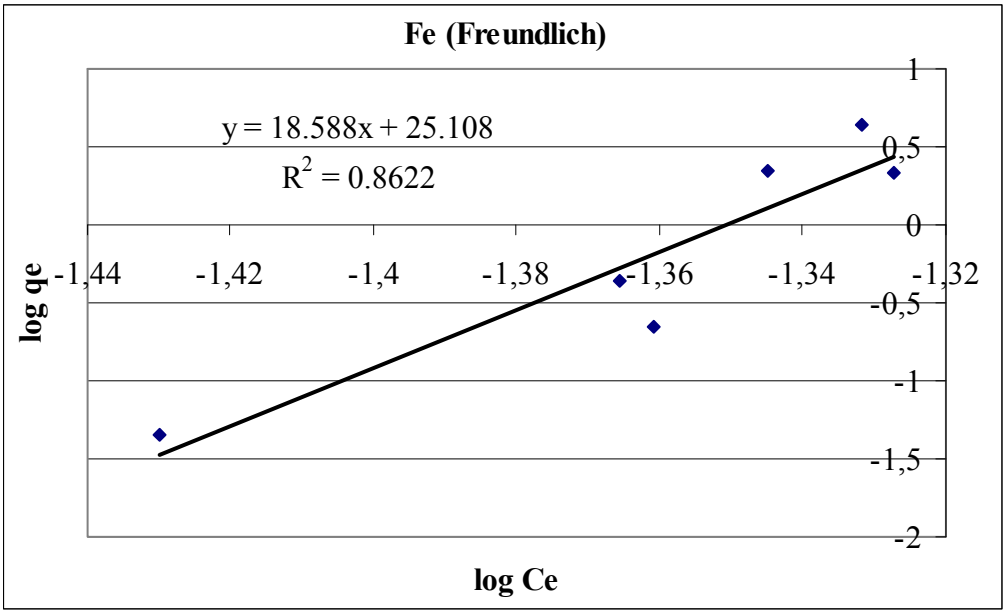

Figure 4.33 Freundlich isotherm of Fe for ASI wastewater.

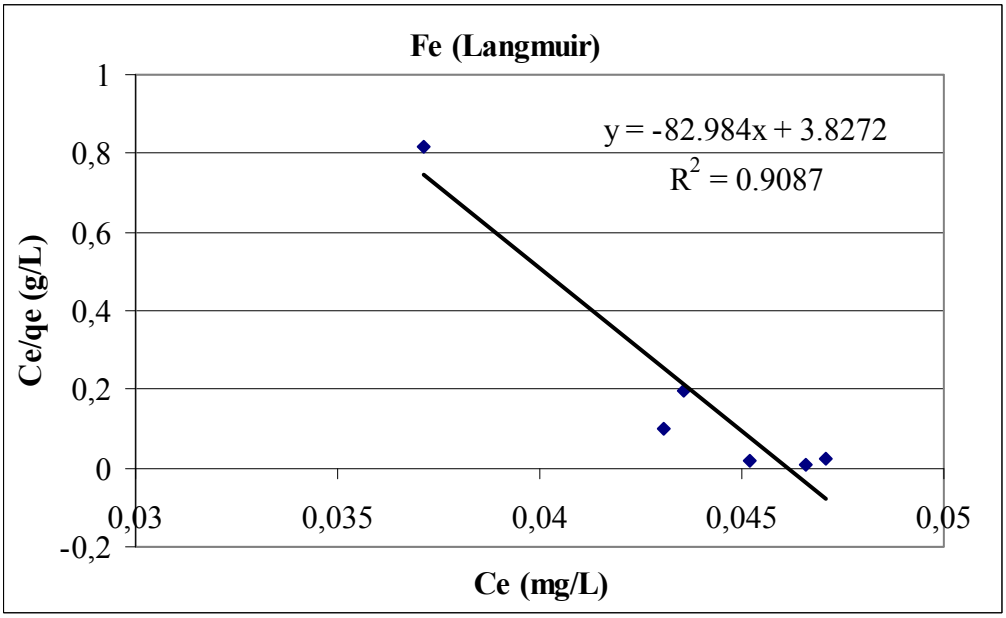

Figure 4.34 Langmuir isotherm of Fe for ASI wastewater.

Fig. 4.35 shows the Freundlich isotherm obtained for Ni ions. The values of *Kf* and *n* were found to be 5.04×10^{13} and 0.16 for Ni ion. The r^2 value was found to be 0.54 for Ni ion indicating that the Freundlich model was able to adequately to describe the relationship between *q*e and *C*e values. Fig. 4.36 shows the Langmuir isotherms obtained by plotting the 1/*q*e versus 1/*C*e values. The correlation coefficient (r^2) was found to be 0.57 for the adsorption of Ni ion indicating that the equilibrium data fitted the Langmuir model, as well.

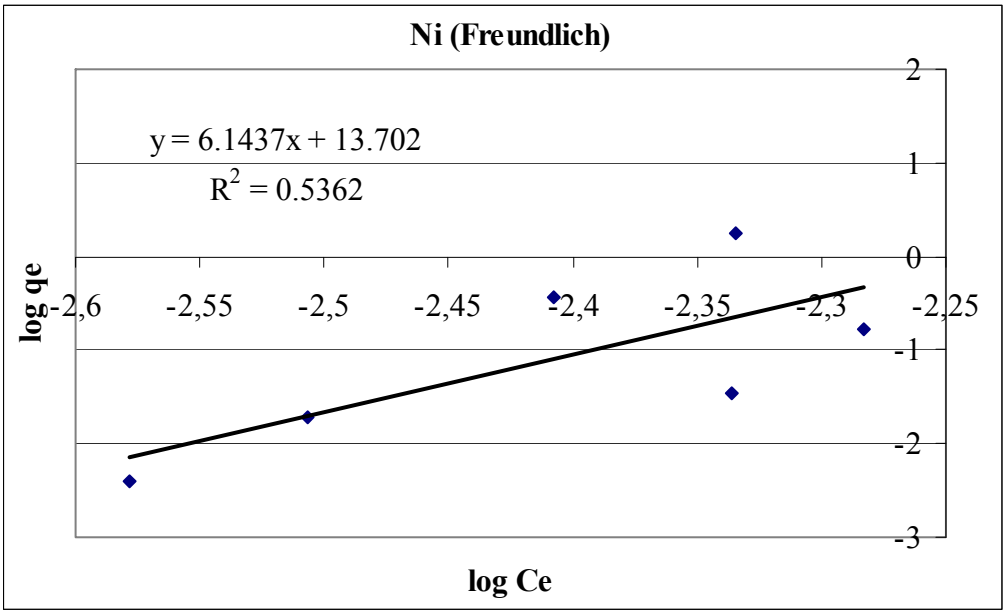

Figure 4.35 Freundlich isotherm of Ni for ASI wastewater.

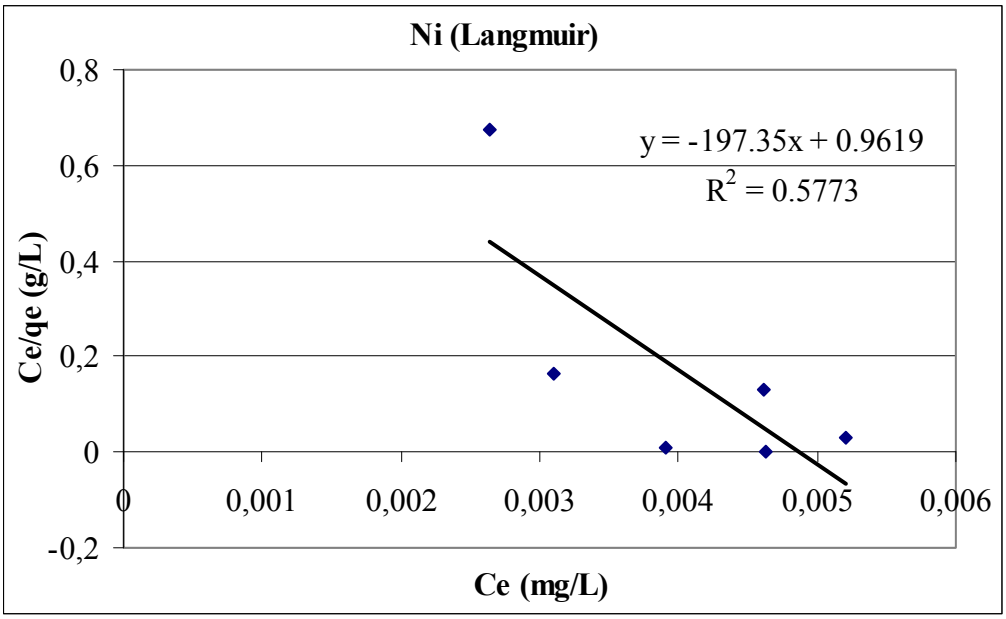

Figure 4.36 Langmuir isotherm of Ni for ASI wastewater.

Fig. 4.37 shows the Freundlich isotherm obtained for Zn ions. The values of *Kf* and *n* were found to be 5.71×10^{17} and 0.11 for Zn ion. The r^2 value was found to be 0.66 for Zn ion indicating that the Freundlich model was able to adequately to describe the relationship between *q*e and *C*e values. Fig. 4.38 shows the Langmuir isotherms obtained by plotting the 1/*q*e versus 1/*C*e values. The correlation coefficient (r^2) was found to be 0.51 for the adsorption of Zn ion indicating that the equilibrium data did not fit well the Langmuir model.

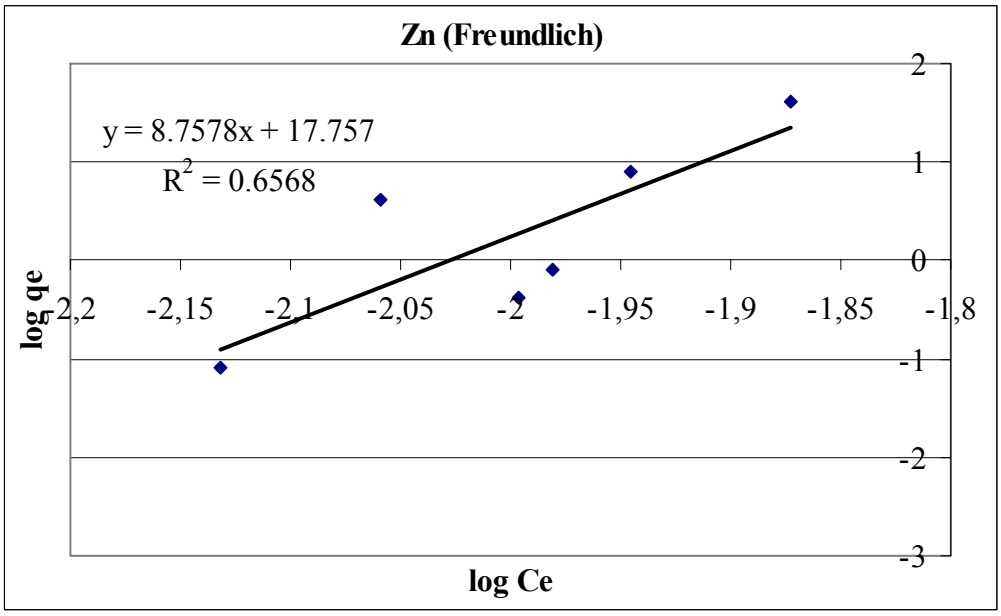

Figure 4.37 Freundlich isotherm of Zn for ASI wastewater.

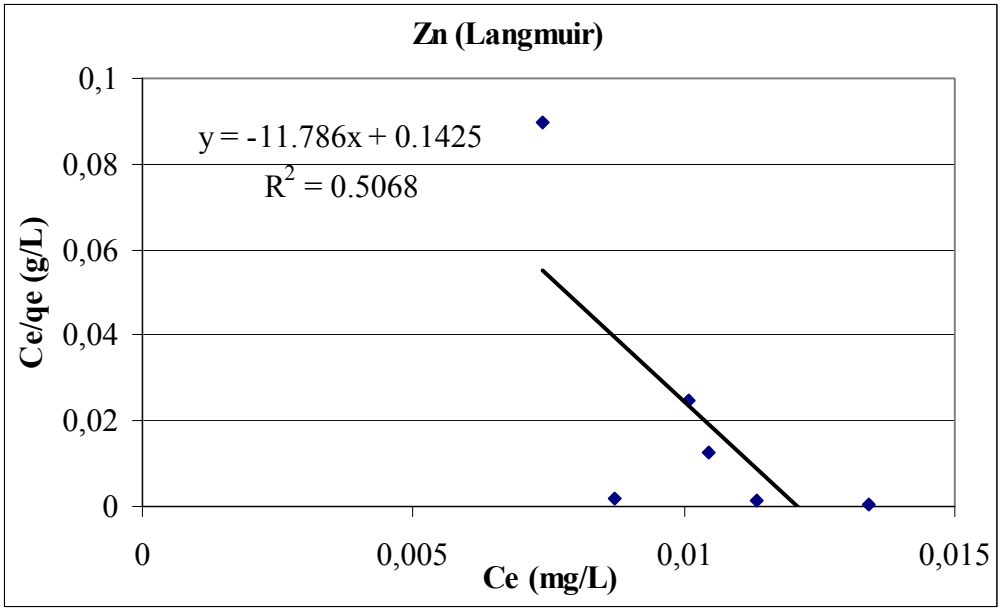

Figure 4.38 Langmuir isotherm of Zn for ASI wastewater.

4.5.2 Metal Adsorption from the Automotive Industry (AI) Wastewater

In the experiments, the adsorbent doses were varied from 0.01 to 5.0 g/l. The pH of the solutions was adjusted as 10, 5, 10, and 10 for Cu, Fe, Ni and Zn, respectively. The effective particle size was selected as 0.53 μm in each set. During the experiments, samples were agitated throughout 60 minutes. In Figure 4.39 and 4.40, residual metal ions in the solution after adsorption are presented for various kaolinite doses. Initial copper ion concentration was reduced from 7.98 μg/l to 4.43 for 0.5 g kaolinite/l corresponding ~45% removal efficiency. Similarly to copper ions, nickel ions decreased from 12.3 μg/l to 5.9 μg/l yielding 52% removal. The highest adsorption efficiency was obtained for 1 gr/l adsorbent dosage. Although, 1 mg/l was resulted in most efficiency in terms of Ni ions, relatively higher removals were obtained at lower kaolinite doses. Figure 4.40 shows the adsorbent dosage effect on Fe and Zn ions removal. Regarding to iron ions removal, 69% of Fe was adsorbed at kaolinite dose of 5 g/l. Zinc ion concentration was dramatically reduced from 1801 μg/L to 69.7 μg/l at 5 g kaolinite/l. The adsorption efficiency was calculated as 96% at 5 g kaolinite dosage/l.

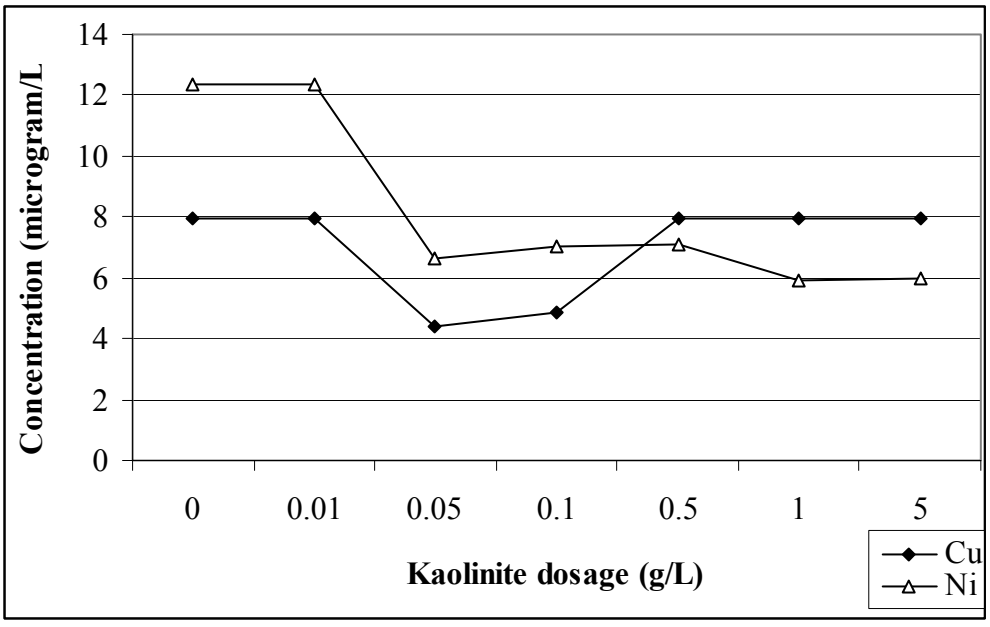

Figure 4.39 The effect of kaolinite dosage on Cu and Ni ions adsorption for AI wastewater

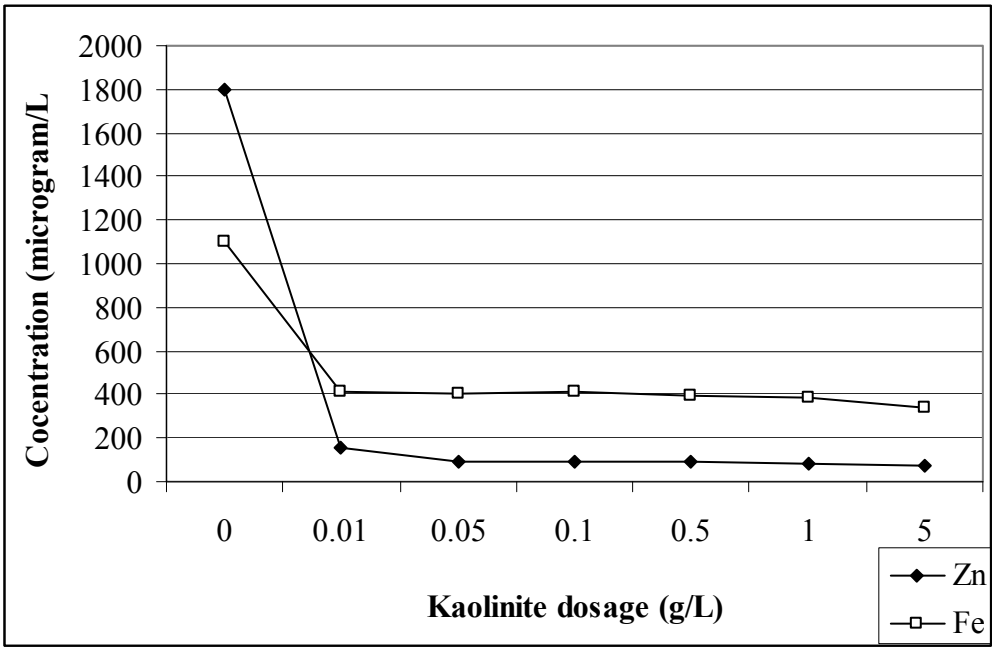

Figure 4.40 The effect of kaolinite dosage on Zn and Fe ions adsorption for AI wastewater

Fig. 4.41 shows the Freundlich isotherm obtained by plotting log *q*e versus log*C*e values. The values of *Kf* and *n* were found to be 98 and 0.27 for Cu ion. The r^2 value was found to be 0.46 for Cu ion indicating that the Freundlich model was not able to adequately to describe the relationship between *q*e and *C*e values. Fig. 4.42 shows the Langmuir isotherms obtained by plotting the 1/*q*e versus 1/*C*e values. The correlation coefficient (r^2) was found to be 0.47 for the adsorption of Cu ion indicating that the equilibrium data did not fit well the Langmuir model.

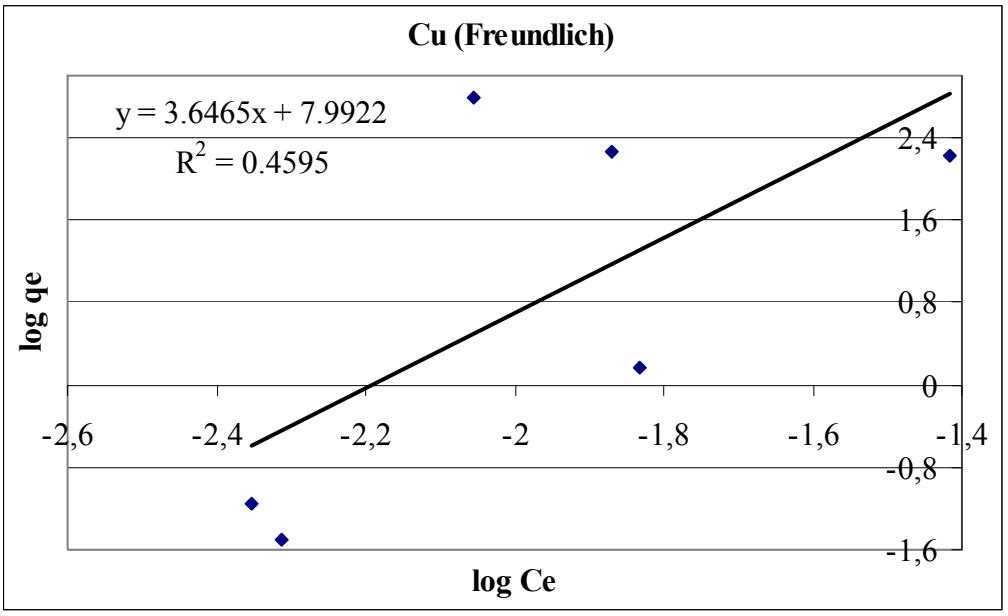

Figure 4.41 Freundlich isotherm of Cu for AI wastewater.

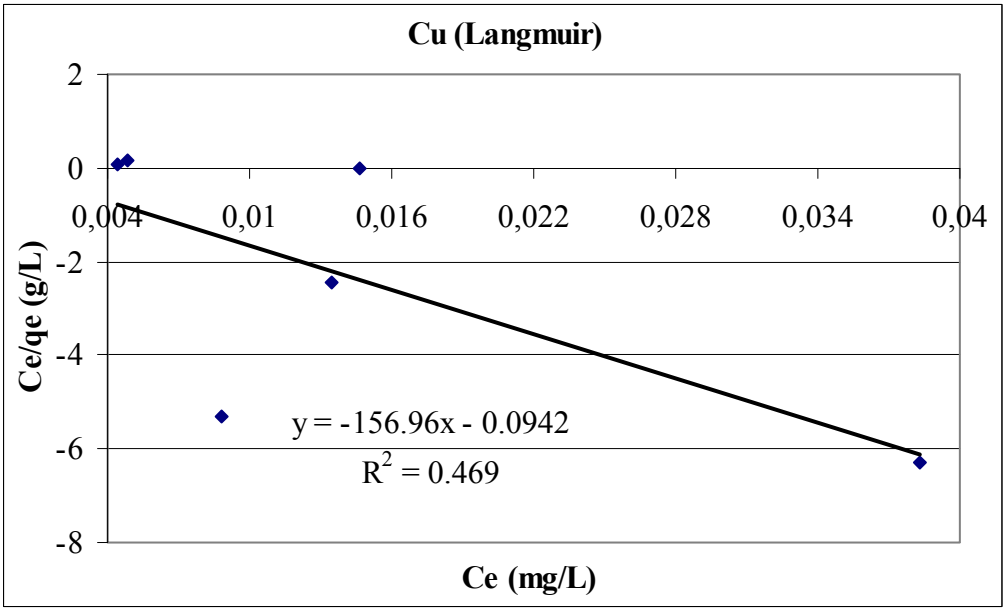

Figure 4.42 Langmuir isotherm of Cu for AI wastewater

Fig. 4.43 shows the Freundlich isotherm obtained for Fe ions. The values of *Kf* and *n* were found to be 2.30×10^{11} and 0.04 for Fe ion. The r^2 value was found to be 0.67 for Fe ion indicating that the Freundlich model was able to adequately to describe the relationship between *q*e and *C*e values. Fig. 4.44 shows the Langmuir isotherms obtained by plotting the 1/*q*e versus 1/*C*e values. The correlation

coefficient (r^2) was found to be 0.99 for the adsorption of Fe ion indicating that the equilibrium data fitted well the Langmuir model.

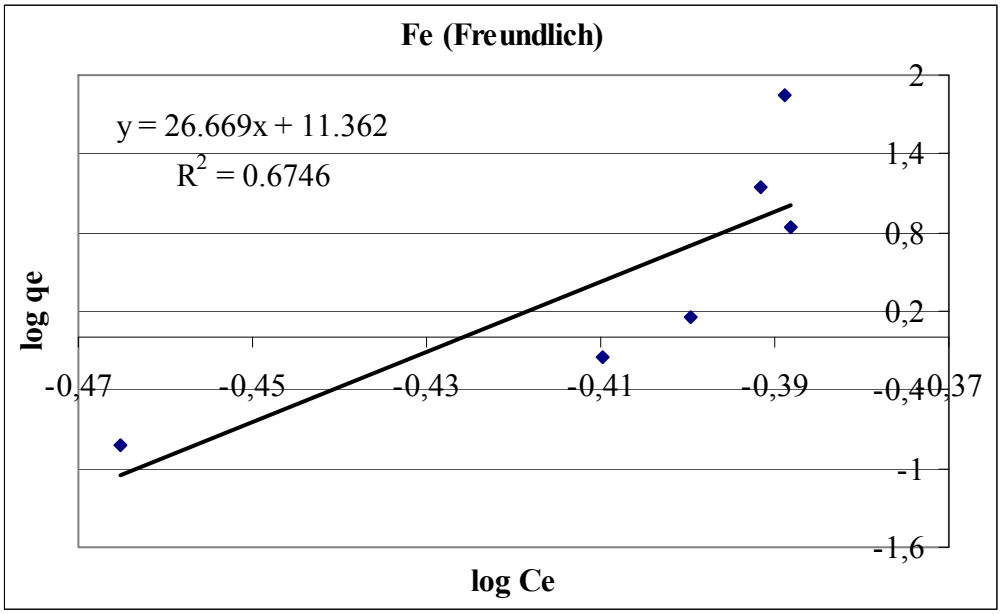

Figure 4.43 Freundlich isotherm of Fe for AI wastewater.

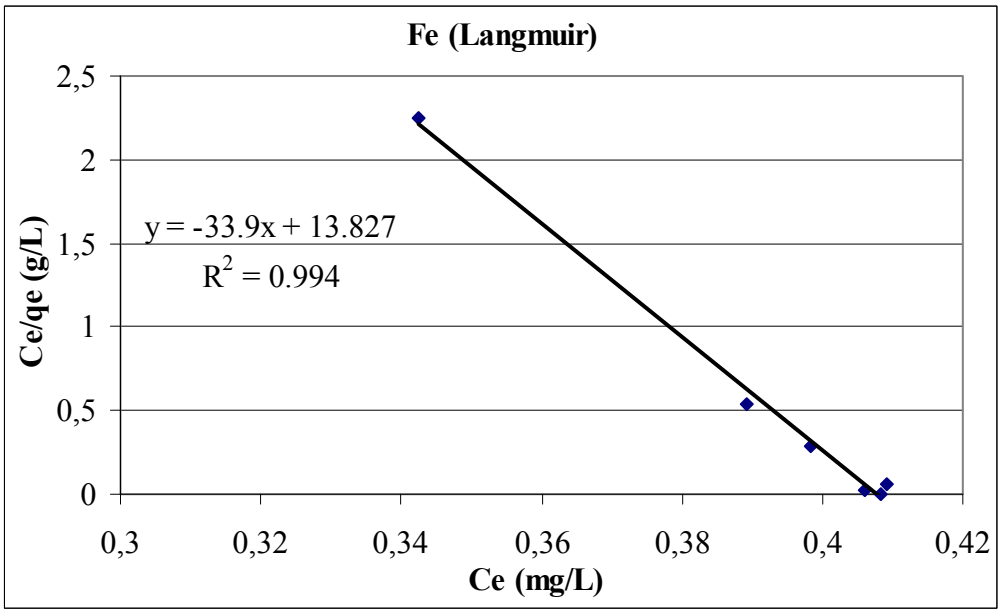

Figure 4.44 Langmuir isotherm of Fe for AI wastewater.

Fig. 4.45 shows the Freundlich isotherm obtained for Ni ions. The values of *Kf* and *n* were found to be 228 and 0.52 for Ni ion. The r^2 value was found to be 0.47

for Ni ion indicating that the Freundlich model was not able to adequately to describe the relationship between *q*e and *C*e values. Fig. 4.46 shows the Langmuir isotherms obtained by plotting the 1/*q*e versus 1/*C*e values. The correlation coefficient (*r*2) was found to be 0.1 for the adsorption of Ni ion indicating that the equilibrium data did not fit well the Langmuir model.

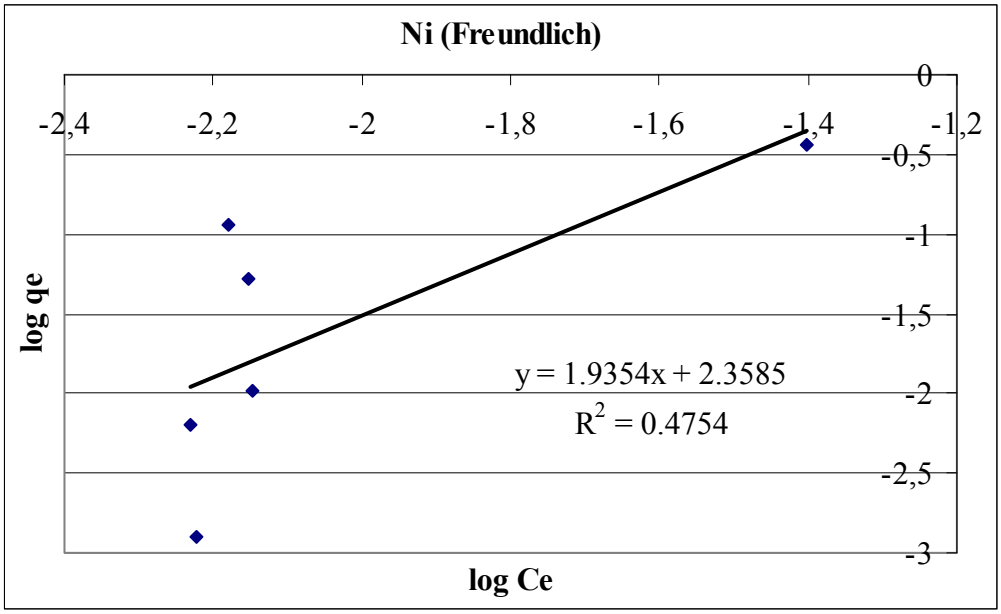

Figure 4.45 Freundlich isotherm for Ni for AI wastewater

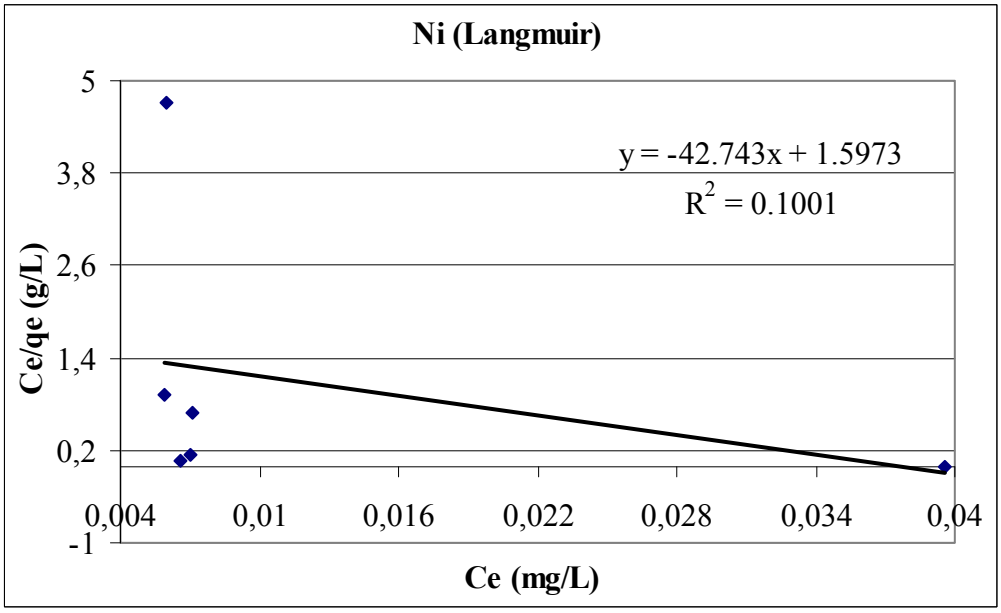

Figure 4.46 Langmuir isotherm for Ni for AI wastewater

Fig. 4.47shows the Freundlich isotherm obtained for Zn ions. The values of *Kf* and *n* were found to be 243 and 0.14 for Zn ion. The r^2 value was found to be 0.81 for Zn ion indicating that the Freundlich model was able to adequately to describe the relationship between *q*e and *C*e values. Fig. 4.48 shows the Langmuir isotherms obtained by plotting the 1/*q*e versus 1/*C*e values. The correlation coefficient (*r*2) was found to be 0.30 for the adsorption of Zn ion indicating that the equilibrium data did not fit well the Langmuir model.

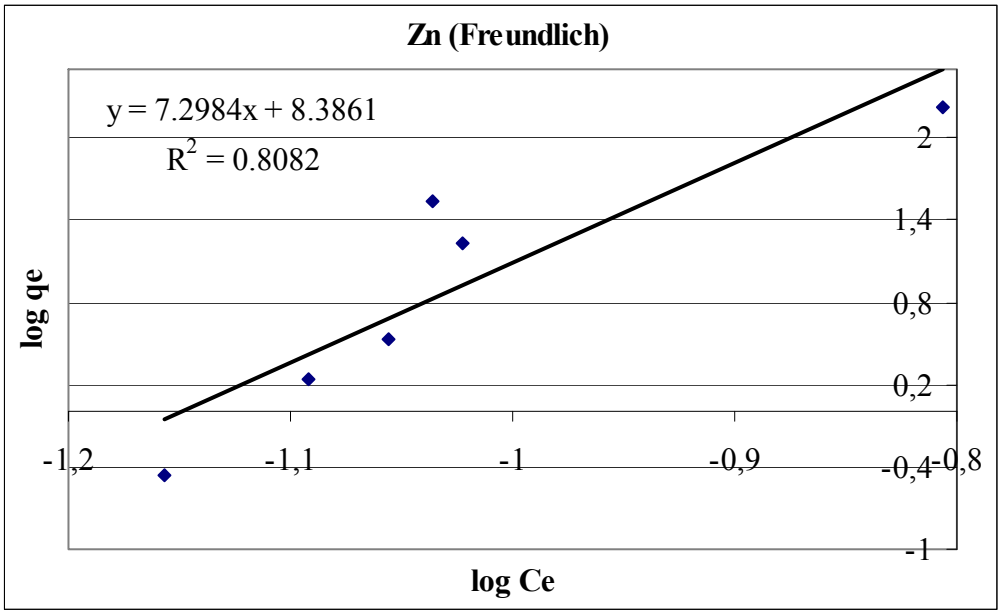

Figure 4.47 Freundlich isotherm for Zn for AI wastewater

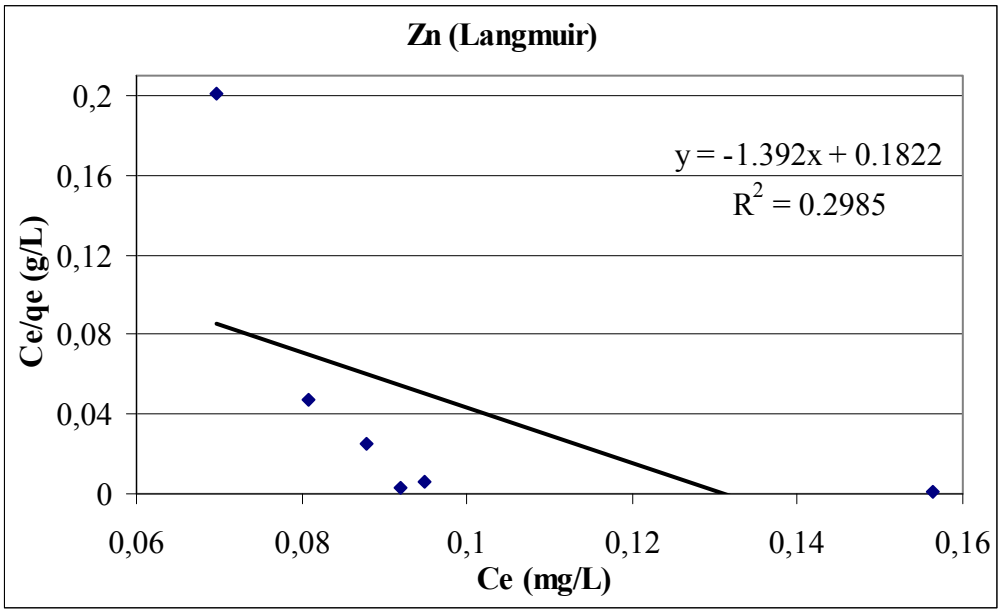

Figure 4.48 Langmuir isotherm for Zn for AI wastewater

CHAPTER FIVE
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study was performed to investigate the applicability of clay minerals in wastewater treatment. For this purpose, kaolinite was obtained from Kızıldağ Madencilik Company. The kaolinite was screened through sieves and it was separated into size fractions with particle size; <53µm, 106-212µm, 212µm-1.18mm, 1.18mm-2.36mm and 2.36mm-4.75mm. Synthetic and industrial wastewaters were used for experiment. Synthetic heavy metal solutions (Cu, Fe, Ni, Zn) were prepared with using standard metal solutions. Industrial wastewater samples were obtained from an automotive side industry and an automotive industry. In the experiments, the effects of the pH, particle size, adsorbent dosage, contact (agitation) time, and initial concentration on Cu, Fe, Ni, Zn removal were investigated separately.

According to experimental results, the conclusion remarks from this study could be given as follows:

- Adsorption of Cu and Fe ions were studied over the pH range of 1.5–12, the adsorption of Ni ions was studied over the pH range of 3-12 and the adsorption of Zn ions was studied over the pH range of 2-12. The maximum Cu (II) adsorption was observed at pH 10. The removal efficiency is 99.4 % at this pH. The maximum adsorption efficiency for Fe ions was 99% at pH 5.0. Ni ions adsorption was 98% at pH 10. The optimum pH value for the zinc removal was determined as 10 and adsorption efficiency is 97%.

- In the experiments, various kaolinite particle sizes (2.36-4.75, 1.18-2.36, 0.212-1.18, 0.106-0.212, less than 0.053 mm of diameter) is used for determining the effect of particle size. Kaolinite particle sizes used in the experiments were quite effective thus adsorption efficiencies were not significantly affected from the varied particle sizes. Adsorption efficiencies

for all heavy metals were quite high > 88% for each particle size. The most effective particle size is determined as <0.053mm for all metal ions.

- In the experiments, the adsorbent doses were varied from 0.01 to 100 g/l for Cu and varied from 0.1 to 100 g/l for Fe, Ni and Zn. 0.1 g/l kaolinite dosage is selected for Cu removal significantly because the removal efficiency is 94% in this dosage. The adsorption percentages of Fe ions were almost over 95% for adsorbent dosage of greater than 5 g/l. For the using 10g kaolinite/l approximately 99.5% Ni ions removal was achieved. The adsorption percentage of Zn (II) was over 98% with using 0.1 g/l adsorbent dosage.

- In order to understand the effect of contact time, samples are shaked at different time periods varying between 5 and 1440 min. Time required for attaining equilibrium for Cu (II) ions was about 5 min and maximum adsorption was attained as 98%. The optimum time for iron removal was determined at 15 min. For 15 min agitation time 94% of iron removal is obtained. The optimum time for nickel removal was determined at 5 min and in this period 99% of nickel removal is obtained. 96% Zn removal was achieved at 5 minutes agitation period.

- To investigate the effect of initial concentration, experimental studies carried out under various metal concentrations ranging between 1.0 and 100 mg/l for Cu, Fe and Zn ions and ranging between 1.0 and 500 mg/l for Ni ions. For all heavy metals; the amount of metal ions adsorbed per gram of kaolinite increased with the increase of initial metal ions concentration.

- The Freundlich isotherm successfully represented the adsorption phenomenon at using synthetic wastewater samples.

- In the experiments, liquid-solid separation by sedimentation was not achieved however centrifugation was worked well. Thus, using of centrifuges for liquid-solid separation is recommended for full scale applications.

5.2 Recommendations

- Although kaolinite gives suitable results, other clay minerals which are bentonite, zeolite, montmorillonite, sepiolite, clinoptilolite, illite, diatomite, vermiculite, etc. can be examined at further researches.

- This kind of study could be carried out with the other heavy metals such as cadmium, chromium, lead, arsenic, mercury, etc.

- The effect of temperature on adsorption experiments can be investigated further research in order to developed applicability of clay minerals on wastewater treatment.

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APPENDICES

Appendices : Kinetic Parameters for Adsorption

Table 1. Kinetic table for Cu

m(g/l)	Co (µg/l)	Ce (µg/l)	qe (mg/g)	log Ce	log qe	Ce/qe (g/l)
0.01	1000	60.98	93.9020	-1.2148	1.9727	0.0006
0.05	1000	45.91	19.0818	-1.3381	1.2806	0.0024
0.1	1000	27.34	9.7266	-1.5632	0.9880	0.0028
0.5	1000	12.23	1.9755	-1.9126	02957	0.0062
1.0	1000	8.539	0.9915	-2.0689	-0.0037	0.0086
5.0	1000	4.988	0.1990	-2.3021	-0.7011	0.0251
10	1000	4.304	0.0996	-2.3661	-1.0019	0.0432
50	1000	3.847	0.0199	-2.4149	-1.7006	0.1933
100	1000	4.015	0.0099	-2.3963	-2.0018	0.4056

Table 2. Kinetic table for Fe

m (g/l)	Co (µg/l)	Ce (µg/l)	qe (mg/g)	log Ce	log qe	Ce/qe (g/l)
0.1	1000	0.40460	5.9540	-0.3929	0.7748	0.068
0.5	1000	0.33240	1.3352	-0.4783	0.1255	0.249
1.0	1000	0.28010	0.7199	-0.5527	-0.1427	0.389
5.0	1000	0.03275	0.1935	-1.4848	-0.7134	0.169
10	1000	0.08266	0.0917	-1.0827	-1.0375	0.901
50	1000	0.02514	0.0195	-1.5996	-1.7100	1.289
100	1000	0.02826	0.0097	-1.5488	-2.0124	2.908

Table 3. Kinetic table for Ni

m (g/l)	Co (µg/l)	Ce (µg/l)	qe (mg/g)	log Ce	log qe	Ce/qe (g/l)
0.1	1000	63.3	9.3666	-1.1983	0.9716	0.0068
0.5	1000	28.8	1.9421	-1.5381	0.2883	0.0149
1.0	1000	29.5	0.9741	-1.5859	-0.0114	0.0266
5.0	1000	16.8	0.1966	-1.7739	-0.7063	0.0856
10	1000	4.5	0.0995	-2.3430	-1.0020	0.0456
50	1000	2.5	0.0199	-2.5952	-1.7001	0.1276
100	1000	1.9	0.0099	-2.7144	-2.0008	0.1949

Table 4. Kinetic table for Zn

m (g/l)	Co (µg/l)	Ce (µg/l)	qe (mg/g)	log Ce	log qe	Ce/qe (g/l)
0.1	1000	19.13	9.0184	-1.008	0.9551	0.0109
0.5	1000	36.39	1.6880	-0.8069	0.2274	0.0924
1.0	1000	67.95	0.8377	-0.7896	-0.0769	0.1938
5.0	1000	24.42	0.1799	-0.9999	-0.7449	0.5559
10	1000	10.93	0.0952	-1.3204	-1.0214	0.5023
50	1000	20.69	0.0192	-1.4189	-1.7167	1.9849
100	1000	34.43	0.0095	-1.2881	-2.0223	5.4226

Table 5.Kinetic table for ASI Cu

m (g/l)	Co (µg/l)	Ce (µg/l)	qe (mg/g)	log Ce	log qe	Ce/qe (g/l)
0.01	7.844	5.282	0.25620	-2.2772	-0.5914	0.0206
0.05	7.844	4.589	0.06510	-2.3383	-1.1864	0.0705
0.1	7.844	7.843	-0.02236	-1.9965	1.6505	784.30
0.5	7.844	7.294	0.00110	-2.137	-2.9586	6.6309
1.0	7.844	7.843	-0.00231	-1.9935	2.6371	7.8430
5.0	7.844	7.843	-0.00198	-1.7506	2.7033	39.215

Table 6. Kinetic table for ASI Fe

m (g/l)	Co (µg/l)	Ce (µg/l)	qe (mg/g)	log Ce	log qe	Ce/qe (g/l)
0.01	263.9	47.06	2.1684	-1.3273	0.3361	0.0217
0.05	263.9	46.59	4.3462	-1.3317	0.6381	0.0107
0.1	263.9	45.19	2.1871	-1.3449	0.3399	0.0207
0.5	263.9	43.09	0.4416	-1.3656	-0.3549	0.0976
1.0	263.9	43.57	0.2203	-1.3608	-0.6569	0.1977
5.0	263.9	37.15	0.0454	-1.4300	-1.3434	0.8192

Table 7. Kinetic table for ASI Ni

m (g/l)	Co (µg/l)	Ce (µg/l)	qe (mg/g)	log Ce	log qe	Ce/qe (g/l)
0.01	22.19	4.631	1.7559	-2.3343	0.2445	0.0026
0.05	22.19	3.911	0.3656	-2.4077	-0.4370	0.0107
0.1	22.19	5.210	0.1698	-2.2832	-0.7701	0.0307
0.5	22.19	4.610	0.0352	-2.3363	-1.4539	0.1311
1.0	22.19	3.108	0.0191	-2.5070	-1.7194	0.1627
5.0	22.19	2.640	0.0039	-2.5784	-2.4078	0.6752

Table 8. Kinetic table for ASI Zn

m (g/l)	Co (µg/l)	Ce (µg/l)	qe (mg/g)	log Ce	log qe	Ce/qe (g/l)
0.01	419.3	0.01341	40.589	-1.8726	1.6084	0.00033
0.05	419.3	0.01134	8.1592	-1.9454	0.9116	0.0014
0.1	419.3	0.00872	4.1058	-2.0595	0.6134	0.0021
0.5	419.3	0.01046	0.8177	-1.9805	-0.0874	0.0128
1.0	419.3	0.01009	0.4092	-1.9961	-0.3881	0.0247
5.0	419.3	0.00739	0.0824	-2.1314	-1.0842	0.0897

Table 9. Kinetic table for AI Cu

m (g/l)	Co (µg/l)	Ce (µg/l)	qe (mg/g)	log Ce	log qe	Ce/qe (g/l)
0.01	7.979	14.68	-0.6701	-1.8333	0.1739	-0.0219
0.05	7.979	4.427	0.0710	-2.3539	-1.1485	0.0623
0.1	7.979	4.868	0.0311	-2.3126	-1.5071	0.1565
0.5	7.979	8.807	-0.0017	-2.0552	2.7799	-5.3054
1.0	7.979	13.49	-0.0055	-1.8699	2.2596	-2.4527
5.0	7.979	38.32	-0.0061	-1.4166	2.2147	-6.2819

Table 10. Kinetic table for AI Fe

m (g/l)	Co (µg/l)	Ce (µg/l)	qe (mg/g)	log Ce	log qe	Ce/qe (g/l)
0.01	1105	408.4	69.660	-0.3889	1.8429	0.0059
0.05	1105	406.0	13.980	-0.3915	1.1455	0.0290
0.1	1105	409.2	6.958	-0.3881	0.8425	0.0588
0.5	1105	398.4	1.4132	-0.3997	0.1502	0.2819
1.0	1105	389.3	0.7157	-0.4097	-0.1453	0.5439
5.0	1105	342.6	0.1525	-0.4652	-0.8168	2.2466

Table 11. Kinetic table for AI Ni

m (g/l)	Co (µg/l)	Ce (µg/l)	qe (mg/g)	log Ce	log qe	Ce/qe (g/l)
0.01	12.33	39.53	-2.7200	-1.4031	-0.4346	-0.0145
0.05	12.33	6.607	0.1145	-2.1799	-0.9413	0.0577
0.1	12.33	7.027	0.0530	-2.1532	-1.2755	0.1325
0.5	12.33	7.118	0.0104	-2.1476	-1.9819	0.6844
1.0	12.33	5.899	0.0064	-2.2292	-2.1917	0.9173
5.0	12.33	5.996	0.0013	-2.2221	-2.8973	4.7213

Table 12. Kinetic table for AI Zn

m (g/l)	Co (µg/l)	Ce (µg/l)	qe (mg/g)	log Ce	log qe	Ce/qe (g/l)
0.01	1801	156.3	164.47	-0.8060	2.2161	0.0009
0.05	1801	92.06	34.179	-1.0359	1.5338	0.0027
0.1	1801	94.97	17.060	-1.0224	1.2319	0.0056
0.5	1801	87.85	3.4263	-1.0563	0.5348	0.0256
1.0	1801	80.93	1.7201	-1.0919	0.2355	0.0471
5.0	1801	69.71	0.3463	-1.1567	-0.4606	0.2013