

**REPUBLIC OF TURKEY**  
**FIRAT UNIVERSITY**  
**THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**



**As (V) REMOVAL FROM AQUEOUS SOLUTIONS**  
**WITH MAGNETIC ACTIVATED CARBON**  
**PREPARED FROM ALMOND SHELL, APRICOT AND PEACH**  
**STONES MIXTURE**

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**Master Thesis**

**Department: Environmental Engineering**

**Supervised By: Prof. Dr. Mehmet ERDEM**

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## ABSTRACT

### **As(V) Removal from Aqueous Solutions with Magnetic Activated Carbon Prepared from Almond Shell, Apricot and Peach Stones Mixture**

Arsenic pollution, which has serious carcinogenic and toxic effects even at very low concentrations, has been a serious problem for public health for a long time. Arsenic pollution in drinking water and water resources in many countries around the world continues to threaten human health.

Arsenic contamination is caused by natural processes such as mineral weathering and dissolution resulting from a change in the geo-chemical environment to a reductive condition and by human activities such as mining wastes, petroleum refining, sewage sludge, agricultural chemicals, ceramic manufacturing industries and coal fly ash. It occurs in the forms of organic (usually occurs less than 1  $\mu\text{g/L}$  in natural conditions) and inorganic in waters. Arsenate (As(V)) is the predominant and stable inorganic arsenic form in the oxygen-rich aerobic environments, while arsenite (As(III)) occurs (above pH 9.3) in reducing anaerobic environments. Owing to epidemiological evidence linking arsenic and cancer, maximum concentration level in drinking water has been limited to 10  $\mu\text{g/L}$  by WHO.

Many treatment technologies have been developed such as oxidation, lime precipitation, coagulation/filtration, adsorption, ion exchange and membrane processes to remove arsenic from water. Among these methods, adsorption method seems to be promising. Activated carbon is the most widely used adsorbent. Particularly, it can be obtained the most suitable adsorbents for different pollutants by modifying its surface properties. In this study; two magnetic activated carbons were prepared from almond shell, apricot and peach stones mixture and used for arsenic removal from aqueous solution. First activated carbon (MAC1) having 375.28  $\text{m}^2/\text{g}$  surface area and 0.2391  $\text{cm}^3/\text{g}$  of total pore volume was prepared from the mixture by direct  $\text{FeSO}_4$  chemical activation. The second one (MAC2) having 396.42  $\text{m}^2/\text{g}$  of surface area and 0.254  $\text{cm}^3/\text{g}$  of total pore volume prepared from a novel activated carbon prepared from the triple mixture by chemical activation with  $\text{ZnCl}_2$ . Both activated carbons were used as adsorbent to remove the arsenic and effects of the some parameters such as pH, adsorbent dosage, contact time and initial arsenic concentration on the arsenic adsorption were examined.

According to results obtained, it has been determined that pH, adsorbent dosage and contact time are important parameter affecting the arsenic adsorption onto both magnetic activated carbons. In order to remove arsenic ions having the concentration of 10 mg/L, the most suitable pH, adsorbent dosage and contact time have been determined as adsorbent dosage of 1.5 g/L and contact time of 60 min for MAC1, pH 4, adsorbent dosage of 1 g/L and contact time of 60 min for MAC2. Under these conditions, 99.31% and 100% of arsenic in the solution have been removed by MAC1 and MAC2, respectively.

**Key Words:** Arsenic; activated carbon; adsorption; agricultural by-products.



## ÖZET

### **Badem Kabuğu ile Kayısı ve Şeftali Çekirdeği Karışımından Hazırlanan Manyetik Aktif Karbonla Sulu Ortamlardan As(V) Giderimi**

Düşük konsantrasyonlarda bile ciddi kanserojen ve toksik etkilere sahip olan arsenik kirliliği uzun zamandan beri insan sağlığı açısından önemli bir problemdir. İçme suyu ve su kaynaklarındaki arsenik kirliliği dünya genelindeki pek çok ülkede insan sağlığını tehdit etmektedir.

Arsenik kirliliği indirgen şartlarda yer kabuğunun jeo-kimyasal değişimlerinin ve minerallerin ayrışması gibi doğal olaylarla, maden endüstrisi atıkları, petrol rafinasyonu, kanalizasyon çamuru, tarımsal ilaçlar, seramik endüstrisi ve kömür uçucu külleri gibi insan faaliyetleriyle üretilen veya oluşturulan kaynaklardan meydana gelir. Sularda organik (doğal şartlarda 1 µg/L'den daha düşük seviyelerde bulunur) ve inorganik bileşikleri halinde bulunur. Oksijence zengin aerobik ortamlarda arsenat yani arseniğin inorganik As(V) formu baskınken, indirgen anaerobik ortamlarda arsenit yani As(III) (pH 9.3'ün üzerinde) formu baskındır. Epidemiyolojik çalışmalarla kanıtlanmış olan arsenik kanser ilişkisi nedeniyle, içme suyundaki maksimum konsantrasyon seviyesi dünya sağlık örgütü tarafından 10 µg/L ile sınırlandırılmıştır.

Arseğinin sulardan giderilmesi amacıyla oksidasyon, kireç çöktürme, koagulasyon/filtrasyon, adsorpsiyon, iyon değiştirme ve membran prosesler gibi birçok arıtma yöntemi geliştirilmiştir. Bu metotlar arasında adsorpsiyon umut verici bir yöntemdir. Aktif karbon en yaygın kullanılan adsorbenttir. Özellikle yüzey özelliklerinin modifikasyonu ile farklı kirleticilerin giderimi için daha uygun ve seçici adsorbentler elde edilebilmektedir.

Bu çalışmada; badem kabuğu ile kayısı ve şeftali çekirdeği karışımından iki farklı manyetik aktif karbon hazırlandı ve sulu çözeltilerden arsenik giderimi için kullanıldı. 375.28 m<sup>2</sup>/g yüzey alanı ve 0.2391 cm<sup>3</sup>/g toplam gözenek hacmine sahip birinci aktif karbon (MAC1), karışımın doğrudan FeSO<sub>4</sub> ile kimyasal aktivasyonu ile hazırlandı. 396.42 m<sup>2</sup>/g yüzey alanı ve 0.254 cm<sup>3</sup>/g toplam gözenek hacmine sahip olan ikinci aktif karbon ise (MAC2), üçlü karışımın ZnCl<sub>2</sub> ile kimyasal aktivasyonu ile elde edilen yeni bir aktif karbondan hazırlandı. Her iki aktif karbon da arsenik adsorpsiyonu için kullanıldı.



Çalışmada arsenik giderimi üzerine pH, adsorbent dozu, temas süresi ve başlangıç arsenik konsantrasyonu gibi parametrelerin etkileri incelendi.

Elde edilen sonuçlara göre; her iki manyetik aktif karbonla sulu ortamlardan arsenik adsorpsiyonu üzerine pH, adsorbent dozu ve temas süresinin önemli parametreler olduğu tespit edilmiştir. 10 mg/L konsantrasyonuna sahip arseniği gidermek için, en uygun pH, adsorbent dozu ve temas süresinin MAC1 için pH'dan bağımsız, 1.5 g/L adsorbent dozu ve 60 dk, MAC2 için ise pH 4, 1 g/L ve 60 dk olduğu belirlenmiştir. Bu şartlar altında, ortamdaki arsenik MAC1 ve MAC2 ile sırasıyla 99.31% ve 100% oranında giderilebilmiştir.

**Anahtar Kelimeler:** Arsenik; aktif karbon; adsorpsiyon; tarımsal yan ürünler.

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## 1. INTRODUCTION

Arsenic is creating potentially serious environmental problems for humans and other living organisms. Arsenic is released and/or transported into environment from natural and anthropogenic sources. It is estimated that the total amount of arsenic in the upper layer of the earth's crust is  $4.01 \times 10^{16}$  kg. It has been reported that the arsenic in the global arsenic cycle is  $3.7 \times 10^6$  ktons in the oceans,  $9.97 \times 10^5$  ktons on land,  $25 \times 10^9$  ktons in sediments and 8.12 ktons in the atmosphere (Choong et al., 2007). For this reason, natural phenomena such as volcanic movements, winds, infiltration from the rocks and forest fires cause the arsenic transportation to environment. The most important anthropogenic arsenic sources are mining activities, fossil fuel burning, and widespread use of arsenic-containing pesticides, ceramics, cement, cosmetics, paint, leather, paper industry and animal feed additive. Arsenic and its compounds are widely used in wood preservatives, glass manufacture, electronics, catalysts, alloys, feed additives and veterinary chemicals. Pigments, insecticides, herbicides and some minerals containing arsenic are major sources of arsenic in natural waters (Kumaresan and Riyazuddin, 2001; Choong et al., 2007; Biswas et al., 2008).

Arsenic occurs in the forms of organic and inorganic in waters (Kirk-Othmer, 1992). The organic arsenic usually occurs less than 1  $\mu\text{g/L}$  in natural conditions. Arsenate (as  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$ ) is the predominant and stable inorganic arsenic form in the oxygen-rich aerobic environments, while arsenite occurs primarily as  $\text{H}_3\text{AsO}_3$  and  $\text{H}_2\text{AsO}_3^-$  (above pH 9.3) in reducing anaerobic environments. Arsenite (As(III)), one of the most abundant inorganic arsenic species in water, is the most toxic form of arsenic and is found in groundwaters (Smedley and Kinniburgh, 2002). Owing to epidemiological evidence linking arsenic and cancer, maximum concentration level in drinking water has been limited to 10  $\mu\text{g/L}$  by WHO.

Many treatment technologies have been developed such as lime precipitation, oxidation, coagulation/filtration, adsorption, ion exchange and membrane processes to remove arsenic from water. Among these methods, adsorption method seems to be promising, easy to apply and cheaper. Activated carbon is the most widely used adsorbent. However, its cost limits widespread use of the activated carbon. Activated carbons are generally produced from the carbonaceous materials with high carbon but low inorganic content and relatively expensive. In order to drop the cost of the activated carbon, cheaper

and readily available precursors such as agricultural and agro-based by-products or waste have been tried recently. A lot of activated carbons with high quality have been prepared from these materials (Dias et al., 2007; Hadi et al., 2015; Yahya et al., 2015). Particularly, it can be obtained the most suitable adsorbents for different pollutants by modifying surface properties of the activated carbons. In the process; the functional groups that are selective for the contaminant to be removed from the water onto the adsorbent surface are suitably bonded. Surface modified adsorbents attract the contaminant to the surface and usually chemically bind to it. As(V) forms insoluble compounds with Fe(III), Fe(II), Zn(II), Cu(II) and Pb(II) ions in waters (Robins, 1985). Particularly Fe(II) and Fe(III) arsenate have low solubility (Khoe et al., 1991) and this compound has recently been the basis of a process developed and successfully demonstrated in a variety of applications (Twidwell et al., 1999). These elements also form selective surfaces for As (V) on the adsorbent surface. For this purpose, some iron oxides have been used as adsorbent for arsenic removal (Sun et al., 1996; Fendorf et al., 1997). In the light of this information, in this study; both iron and zinc magnetic activated carbons prepared from almond shell, apricot and peach stones mixture by chemical activation and chemical precipitation methods and As(V) adsorption ability were tested in batch adsorption experiments.

## **2. ARSENIC**

### **2.1. Chemistry of Arsenic**

Arsenic (As) is a toxic metalloid element. It is not actually a metal but it has some metallic properties. As is a Va group member of the periodic table and it has four valence states:  $-3$ ,  $0$ ,  $+3$  and  $+5$ . It can combine readily with many other elements to form different compounds. Some forms of them are inorganic, which do not contain carbon, and others are organic, which always contain carbon. Generally, As is distributed in more than 200 minerals (Fleischer, 1983). Inorganic compounds of arsenic include halides, hydrides, acids, oxides and sulfides (Kirk-Othmer, 1992). Arsenic trioxide, sodium arsenite and arsenic trichloride are most common trivalent compounds, and arsenic pentoxide, arsenic acid and arsenate salts are common pentavalent arsenic compounds. Most important organic arsenic compounds include arsanilic acid, methylarsonic acid, dimethylarsinic acid and dimethylarsinate (WHO, 2001).

The valence state of  $-3$  and  $0$  occur only rarely in nature. But, As(III) and As(V) compounds are generally found in the environment. Elemental arsenic is not soluble in water but its salts exhibit a wide range of solubilities depending on pH (Figure 2.1) and some environmental conditions. Arsenic's toxicity and mobility has been proved to vary with its chemical form and state of valence. Generally inorganic arsenic compounds are about 100 times more toxic than the organic arsenic compounds (Jain and Ali, 2000).

Arsenic exists in anionic form in the aqueous systems and it has two stable oxidation stages; arsenite, with a valency of  $+3$ , and arsenate, with a valency of  $+5$ . As(III) is the dominant form under reducing conditions; As(V) is generally the stable form in oxygenated conditions.

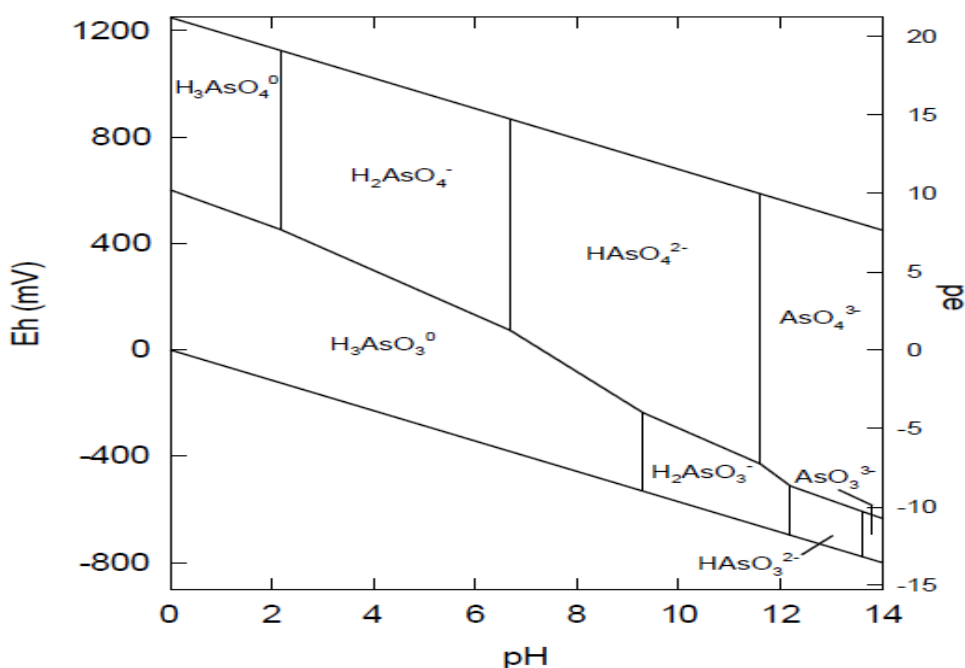
#### **2.1.1. Arsenic Species and Their Mobilities**

Arsenic seldom takes place in the free state and is appeared mostly in mixture and combination with iron, oxygen and sulfur. Arsenic joins with oxygen to produce inorganic forms of arsenite trivalent and arsenate pentavalent in the ground water. Dissimilar other oxyanion-forming elements and heavy metalloids, arsenic can be movement under a broad range of oxidizing and reducing conditions in the range of natural ground waters pH

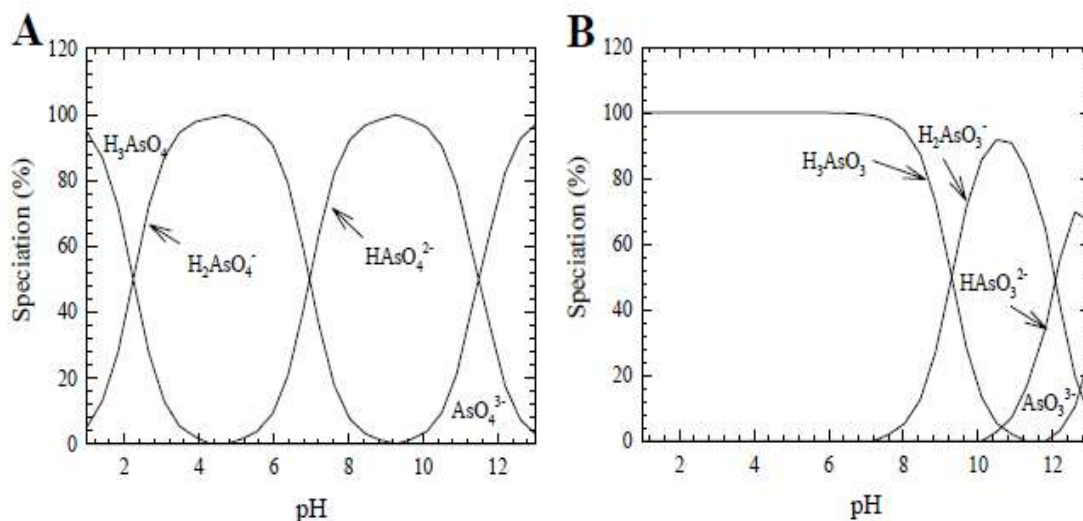
between 6.5 – 8.5. While all other oxyanion-forming elements can be appeared among the  $\mu\text{g/L}$  ranges, arsenic appeared among the  $\text{mg/L}$  levels (Vu et al., 2003).

Arsenic present as the semi-metallic element ( $\text{As}^0$ ) in solution, arsenite ( $\text{As}^{3+}$ ), arsine ( $\text{As}^{3-}$ ), arsenate ( $\text{As}^{5+}$ ) and organic dimethylarsinate (DMAA) and monomethylarsonate (MMAA). The amount of each of those species relies on the nature anthropogenic input and biological activity and the redox conditions. Though, the organic arsenic (methylated) generally occurs under than  $1 \mu\text{g/L}$  at the natural concentrations and in drinking water treatment is not of major significance. Arsenate (as  $\text{HAsO}_4^{2-}$  and  $\text{H}_2\text{AsO}_4^-$ ) is the stable and predominant inorganic arsenic in the oxygen-rich aerobic environments. Belong to the relatively unhurried redox transformation, both of them arsenate and arsenite are often appeared in redox environment (Jang et al., 2003).

Figure 2.1 and 2.2 shows Eh - pH diagram of arsenic in As- $\text{H}_2\text{O}$  system and the proportional change of arsenite and arsenate species in aqueous solution depending on pH. As can be seen, arsenic exist +5 oxidation state under the oxygen-rich aerobic conditions.  $\text{H}_3\text{AsO}_4$  is predominant under pH 2 but it is dissociated to  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$  in the pH range of 2 and 11. The dominant type in the low Eh values is  $\text{H}_3\text{AsO}_3$  with +3 valency and it is stable up to pH 9. At higher pH values, arsenic emerges as  $\text{H}_2\text{AsO}_3^-$ ,  $\text{HAsO}_3^{2-}$ , and  $\text{AsO}_3^{3-}$ . However, it appears that these compounds lost their stability in neutral and acidic conditions (Smedley and Kinniburgh, 2002).



**Figure 2.1.** Eh – pH diagram of arsenic in As- $\text{H}_2\text{O}$  system.



**Figure 2.2.** Proportional change of arsenite and arsenate species in aqueous solution depending on pH.

Arsenic exhibits different toxic properties depending on its oxidation stage. Pentavalent state arsenic is about 60 times less than toxic arsenic in the trivalent state and organic arsenic compounds are about 100 times less than toxic inorganic arsenic compound. The toxicities of the arsenic compounds decrease in the order arsenic hydride ( $AsH_3$ ) > inorganic ( $As^{3+}$ ) > organic ( $As^{3+}$ ) > inorganic ( $As^{5+}$ ) > organic ( $As^{5+}$ ) >  $As^0$ .

### 2.1.2. Arsenic Sources and Its Transportation

Arsenic, the twentieth most abundant element in earth's crust, is an element that can be found in the atmosphere, soil, rocks, natural waters and organisms. Arsenic is released and/or transported into environment from natural and anthropogenic sources. It is estimated that the total amount of arsenic in the upper layer of the earth's crust is  $4.01 \times 10^{16}$  kg. It has been reported that the arsenic in the global arsenic cycle is  $3.7 \times 10^6$  ktons in the oceans,  $9.97 \times 10^5$  ktons on land,  $25 \times 10^9$  ktons in sediments and 8.12 ktons in the atmosphere (Choong et al., 2007). Arsenic is generally distributed in more than 320 minerals (Fleischer, 1983), and it's commonly found in arsenopyrite ( $FeAsS$ ), orpiment ( $As_2S_3$ ), realgar ( $As_2S_2$ ), and pyrite ( $FeS_2$ ) (Smedley et al., 1996). For this reason, natural phenomena such as volcanic movements, winds, infiltration from the rocks and forest fires cause the arsenic transportation to environment.



The most important anthropogenic arsenic sources are mining activities, fossil fuel burning, and widespread use of arsenic-containing pesticides, ceramics, cement, cosmetics, paint, leather, paper industry and animal feed additive. Arsenic and its compounds are widely used in wood preservatives, glass manufacture, electronics, catalysts, alloys, feed additives and veterinary chemicals. Pigments, insecticides, herbicides and some minerals containing arsenic are major sources of arsenic in natural waters (Kumaresan and Riyazuddin, 2001; Choong et al., 2007; Biswas et al., 2008).

Atmospheric arsenic emissions occur from fossil fuels used in thermal power plants and homes. Arsenic in agriculture sector is agricultural medicine, supplementary nutrients and fertilizers. In particular, it is used in the form of calcium arsenate to control weed and insect reproduction in cotton production. It is used in electronic industry as semiconducting materials in the form of metallic arsenic. Arsenic trioxide is used as a color removal and refining agent in the glass industry. It is also used as a timber protectant in forest industry in forms such as chromated copper arsenate and ammonia copper acetate. Therefore, arsenic is released from the places where these chemicals are produced and used to environment.

## **2.2. Arsenic Removal Technologies**

There are several methods for the removal of arsenic from waters. Coagulation, adsorption, ion exchange and membrane processes are widely used as treatment methods.

Arsenic is present generally in ionic pentavalent and nonionic trivalent inorganic forms in ground water in the various proportions depend on the environmental condition of aquifer. In general, arsenic solubility controlled via biological activity, pH, adsorption and redox condition. It has been reported that the all types of the removal technologies show better performance when arsenic is present in pentavalent form. For this reason, pre-oxidation is generally applied to the arsenite containing waters. The most common methods are given below in subheadings (Uddin et al., 2007; Mohan and Pittman, 2007; Nicomel et al., 2016).

### 2.2.1. Oxidation

The chemical form of arsenic is important in the removal of arsenic from waters. Because arsenic in groundwater is generally inorganic As(III) (arsenite), it must first be converted to As(V) (arsenate) form in order to be effectively removed from water (EPA, 2003). The oxidation takes place at the beginning of the purification process by the addition of a suitable oxidant. Oxygen, ozone, free chlorine, hypochlorite, permanganate and solid phase oxidizers are the oxidizing agents used for this purpose. Atmospheric oxygen, hypochlorite and permanganate are commonly used oxidants and the reactions taking place are as follows (Ahmed, 2001);



As (III) can be oxidized with dissolved oxygen but the oxidation rate is low and oxidation does not occur exactly (Wilson et al., 2004). In recent years, it has been observed that air oxidation of dissolved As(III) in the presence of near-UV rays and dissolved iron compounds has been increased by four times without the addition of a chemical oxidant.

One of the most commonly-selected oxidants is the chloride, but if there is a natural organic matter in the water, chlorinated organic compounds may form. Permanganate is a powerful oxidant widely used in iron and manganese removal from water. Potassium permanganate can be used in solid, granular form and its solution.

The oxidation method alone can not provide arsenic removal; the process must be combined by a treatment method such as coagulation, adsorption or ion exchange (Smedley and Kinniburgh, 2002).

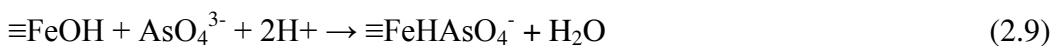
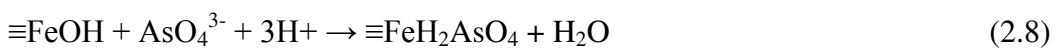
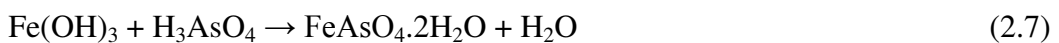
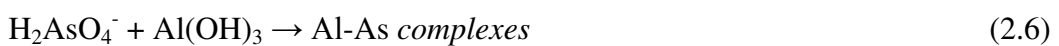
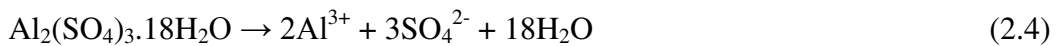
Oxidation/filtration is belonging to precipitation process that is systemized to eliminate naturally occurring manganese and iron in the water. This process gives oxidation for the soluble form of manganese and iron to their insoluble forms that are then eliminated via filtration. Arsenic can be eliminated through two main mechanisms: which include both of them adsorption and co-precipitation. First of all, soluble As(III) and

iron are oxidized after that the As(V) adsorb the iron hydroxide  $\text{Fe}(\text{OH})_2$  precipitates that are finally filtered out of solution. The removing of arsenic effectiveness is strongly depends on the initial arsenic and iron concentrations. Overall, the iron to arsenic mass ratio ought to be at least 20 to 1. Those conditions are usually resulting in a removing arsenic efficiency of 80-90%. With the increasing pH means decreases the arsenic removal (EPA, 2005).

### 2.2.2. Coagulation/Filtration

Coagulation/filtration is a precipitation process. The removal mechanism involves co-precipitation and adsorption of As(V) to a ferric hydroxide  $\text{Fe}(\text{OH})_3$  or aluminum precipitate. As(III) is not effectively remove because of its generally neutral charge under natural pH. Because of As(III) is not easy to removing, usually pre-oxidation is needed. The economics and efficiency of the system are dependent on many factors, including pH, mixing intensity, coagulant dosage and coagulant type. Optimized coagulation-filtration systems are able of achieving more than 90% As(V) removal. Though both iron and aluminum coagulants can removes arsenic, iron coagulants (ferric sulfate  $\text{Fe}_2(\text{SO}_4)_3$  or ferric chloride ( $\text{FeCl}_3$ ) both of them are very effective for removing (EPA, 2005).

The arsenic can be converted into the insoluble form by coagulation using iron and aluminum salts. Iron salts are generally more effective than aluminum salts at arsenic removal. This is due to the fact that some of the aluminum remains soluble while the iron salts are fully converted to the form of particulate iron hydroxide (Wickramasinghe et al., 2004; Jain et al., 2009). Iron hydroxides are also more stable than aluminum hydroxides at pH 5.5-8.5. Optimum pH range for aluminum in coagulation is 5-7 and 5-8 for iron (Başkan and Pala, 2009). Reactions occurring in coagulation for aluminum and iron are given below;



The Al-As and Fe-As complexes formed by adsorption to hydroxide surfaces and/or co-precipitation can be removed by sedimentation / filtration from water.

### **2.2.3. Ion Exchange**

Synthetic ion exchange resins with different functional groups are widely used for the purpose of removing ions from water. The process is a physicochemical process involving an ion exchange between a solid resin and the liquid phase. Resins have acidic or basic groups and show selectivity depending on the contaminant ion species. The process is independent of pH water. The method is widely applied in water softening, nitrate, sulphate and heavy metal removal from water (EPA, 2005).

It is not possible to remove uncharged arsenite by the ion exchange method. For this reason, a preliminary oxidation process should be applied to the arsenic removal from arsenite containing water.

### **2.2.4. Adsorption Process**

It is one of the methods in which developed recently for removal of arsenic. There are many types of adsorptive media to removing arsenic such as activated carbon, manganese and iron coated sand and so on. Activated alumina (AA) is a sorption process, it is a cheap method for removing arsenic, has a good property and large surface area for adsorption that uses granular and porous material with ion exchange characteristics. In drinking water treatment, packed-bed activated alumina adsorption is usually used to remove fluoride and natural organic material. The As(V) removal via adsorption can be accomplished by continuously allow water under pressure via two or more than one beds. Activated alumina media can be disposed or regenerated and replaced with fresh media. When the water allow cross the packed column, the active alumina adsorbed arsenic and other impurities catch by grains. The economics and efficiency of the system are depending on several factors: pre-treatment oxidation of As(III) change to As(V), constituent(s) interference with the adsorption process, and the require for pH changing to lesser than 6.5 (EPA, 2005).

### **2.2.5. Membrane Technology for Removing Arsenic**

Membrane technology is the one of the best technology to arsenic removal in water. Generally, membranes are synthesized materials with the many billions microscopic holes or pores which is doing like a permeable and precision selective barrier, the membrane structure designed for permit and allowing a few constituent pass it, but other materials are does not pass and rejected. The molecules are movement cross along membranes by drive force. There are variety types of membrane technology gave to removing arsenic in water such as reverse osmosis, nanofiltration, ultrafiltration and microfiltration (EPA, 2005).

#### **2.2.5.1. Reverse Osmosis**

Reverse osmosis (RO) is the attractive and well established technology for removing arsenic to small water system. Reverse osmosis is based on pressure-driven membrane separation process can able to arsenic remove from water by means of particle size, hydrophobicity/hydrophilicity and dielectric characteristics. Reverse osmosis also efficiently eliminates another's constituents from water, such as dissolved minerals, salts, color and organic carbon. This process is relatively independent to pH but adversely affected by existence of colloidal substances, although pH changing may be necessary to save the membrane from fouling. This process rejection or exclude ions and the low molecule mass can able to achieve. Despite that, this process can simply be controlled. The rejection of arsenite As(III) was (65-85%) significantly lesser than arsenate As(V) rejection (95%) by using each types of reverse osmosis membranes (Shih, 2005).

#### **2.2.5.2. Nanofiltration**

Nanofiltration membrane is generally acts to separating multivalent ion from monovalent. It is sometime designed as 'loose' reverse osmosis membranes. In generally, those membranes are negative charged and asymmetric at alkaline and neutral media. Brandhuber and Amy in their studied were using three types of nanofiltration membranes for rejection of arsenic. For all the three NF membranes, the rejection of As(III) was between 20-53%, while the rejection of As(V) was higher than 95% (Uddin et al., 2007).

### **2.2.5.3. Ultrafiltration**

It is another technology from different membrane filtrations, using for arsenic removal. It has low pressure driven membrane operation in which colloids, solutes and macromolecules. Forces such as concentration gradients and pressure caused to separate by a semi permeable membrane. It has big size in pores of the membranes. The anions existence in feed solution occurred result from reduce in arsenate As(V) rejection the divalent of anions are demonstrating higher influence monovalent. In the existence divalent cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , As(V) rejection decreased near until to zero. The reduction of rejection arsenate As(V) was belong to the contact and interaction between membrane and solutes (Uddin et al., 2007).

### **2.2.5.4. Microfiltration**

It is a type of physical filtration method and shortened to MF. The particles size in which range between 0.02 – 10  $\mu\text{m}$  can separate in the solvated from a fluid mixture. The solutes and particles retention occurs by adsorption or sieving from the membrane matrix. MF has very large pore compare with others it can able to eliminated colloid and dissolved arsenic species successfully. Also it can able to removing arsenic particulate form in water (Uddin et al., 2007).

### **3. ADSORPTION**

The operation of adsorption is a substance (adsorbate), in a liquid or gas phase, accumulates on the surface of a solid. It's relying on the ability of pore materials with a big surfaces area to selectivity retain compounds on the surface of the solid (adsorbent). There are two kinds of adsorption; one of them is physical and another is chemical adsorptions (Balanay, 2011).

#### **3.1. Physical Adsorption**

The adsorption of physical is achieved through hydrogen binding, Van der Waals force and dipole interaction. It has no electron exchange amid adsorbate and adsorbent. Because it has no activation energy needed for adsorption of physical, the time is required to arrive balance is too little. The adsorption of physical is a non-specific and a reversible operate (Treybal, 1981; Ruthven, 1984; Balanay, 2011).

#### **3.2. Chemical Adsorption**

In the chemical adsorptions, sometimes called chemo-sorption, the adsorbate forms strong localize (example; covalent) bonds at active center on the adsorbent surface. The molecules are not free to go on the surface or among the interface (Balanay, 2011). Chemical adsorption is different from the physical adsorption. These differences are given in Table 3.1.

#### **3.3. Adsorption Mechanisms**

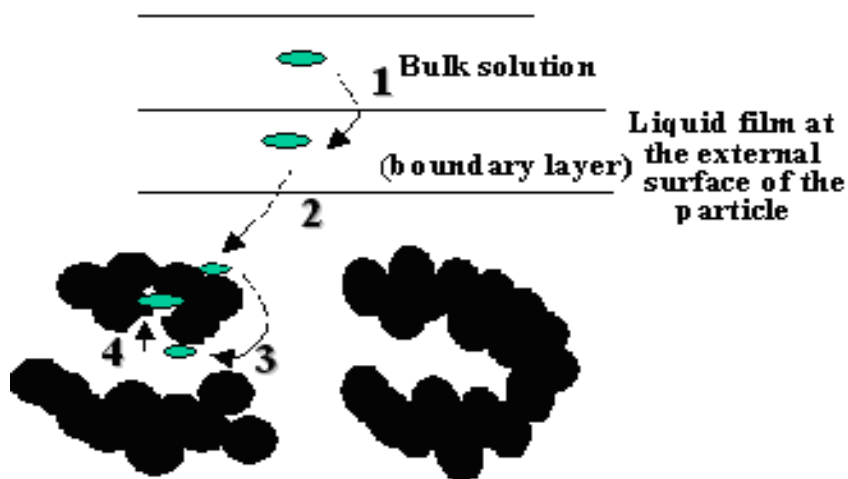
The operation of adsorption and mechanisms consist of the bellowing steps (Figure 3.1):

- 1) Mass transfer of the adsorbate molecules crossways the external border layer in the direction of the solid particle.
- 2) Adsorbate molecules transporting from the surface particle area into the active site areas via dispersion among the pore filled liquid and travel the length of the solid surface of the pores.

- 3) Solute molecule adsorptions on the active site on the interior surface area of the pore.
- 4) Once the molecule adsorbed, it may travel on the surface through surface diffusion (Mohamed, 2011).

**Table 3.1.** Differences between physical adsorption and chemical adsorption (Treybal, 1981; Ruthven, 1984).

| Physical Adsorption                                                                   | Chemical Adsorption                                    |
|---------------------------------------------------------------------------------------|--------------------------------------------------------|
| Molecules are held due to Van Der Waal's forces                                       | Molecules are held due to chemical bond forces.        |
| No surface compound is formed                                                         | Surface compounds are formed                           |
| Heat of adsorption are in the range of 20 – 40 kJ/mol                                 | Heat of adsorption are in the range of 40 – 400 kJ/mol |
| Activation energy are small                                                           | Activation energy are appreciable                      |
| Usually occurs rapidly at low temperatures and decreases with increase in temperature | It can occur at high temperature                       |
| Usually completely reversible                                                         | Often irreversible                                     |
| Not very specific                                                                     | Often highly specific                                  |
| The extent of adsorption is approximately related to the ease of liquification of gas | No such correlation is there                           |
| Form multilayer on the surface of adsorbent                                           | Forms unimolecular layer                               |



**Figure 3.1.** Schematic diagram of adsorption mechanism (Mohamed, 2011).



### 3.4. Parameters Affecting Adsorption

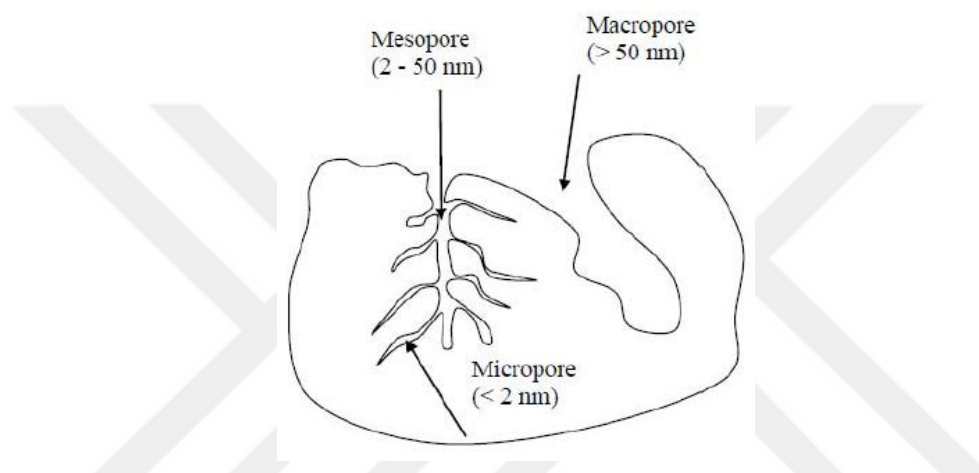
Adsorption is a phenomenon occurring at the interface between a fluid phase with a solid surface. This transition varies depending on the pH, temperature, the properties of the adsorbed material and adsorbents such as surface area, pore structure, type and presence of surface functional groups and contact type. Among these parameters, pH is one of the most important parameters. At the acidic pHs, the surface of the adsorbent becomes more suitable for the adsorption of negatively charged ions as the possibility of positive loading of the surface increases. Unlike, as the surface is negatively charged at high pH, the adsorption of positively charged ions becomes effective.

The amount of adsorbed material is proportional to the specific surface area of the adsorbent. The larger surface area of porous and fine-grained adsorbents increases the adsorption yields. The surface functional groups of the adsorbents also greatly affect the adsorption. The surfaces of the adsorbents can be made more active for the adsorption of positive or negative charged ions with activation. Activation is usually achieved by activating the adsorbents with a strong acid or base or selective reagents.

Specific surface area is also another significant characteristic which determines adsorbent usage and its capability. The entirety surfaces of activated carbon are ranging between 500 till 2000 m<sup>2</sup>/g, quantifies of adsorption sites for molecules to catch. The micro-pores normally give the biggest amount of the interior surface area of the adsorbent and give too many of the entirety pore volume. The entirety numeral of pores, their size and form determine the adsorption capability and still the dynamic of adsorption ratio of adsorbent. The range of pore volume, which is definite according as the International Union of Pure and Applied Chemistry (IUPAC) is given in Table 3.2. And a diagram demonstration of structure porous of adsorbent is showed in Figure 3.2 (Everett, 1972). In spite of many of the adsorption occurs in the micro-pores, the macro and meso-pores play have a significant function in any adsorption operate because they serve as passageway for the adsorbate to arrive micro-pores. Furthermore, the multilayer adsorption just occurs in macro and meso-pores (Mohamed, 2011).

**Table 3.2.** Pore size types of IUPAC.

| Pores             | Pore size, nm                |
|-------------------|------------------------------|
| Ultra micro-pores | Less than 0.7                |
| Super micro-pores | $0.7 < \text{Pore size} < 2$ |
| Micro-pores       | $< 2$                        |
| Meso-pores        | $2 < \text{Pore size} < 50$  |
| Macro-pores       | $> 50$                       |



**Figure 3.2.** Kinds of pores in an adsorbent.

The effect of the temperature on the adsorption depends on the formation of the exotherm or endotherm of the adsorption process. Physical adsorption is usually exothermic and the amount of adsorbed material decreases with increasing temperature in such an adsorption process. But, high temperatures may increase the adsorption efficiencies in chemical adsorption.

The polarity and molecular structure of the adsorbed material may significantly affect the adsorption efficiency. In the cases where the pores of the microporous solid are too small to absorb the molecules of the adsorbed material, the adsorption efficiency is reduced. Especially in adsorption from aqueous solutions, the hydrophilic and hydrophobic properties of the adsorbent used affect the adsorption negatively or positively.

The adsorption rate is controlled either by film or pore diffusion depending on the mixing speed of the system. At low mixing speeds, the liquid film thickness around the particle will be too high and the film diffusion rate will be the limiting factor for adsorption. If sufficient mixture is provided in the system, the film diffusion rate increases

towards the pore diffusion point, which is the rate limiting factor. Therefore, the contact type and conditions are also important parameters to increase the adsorption efficiencies (Mohamed, 2011).

### 3.5. Isotherm Theory and Adsorption Isotherms

Adsorption isotherm is a mathematical model equations used to describe the relationship between the adsorbed materials with absorbent material. An adsorption isotherm is a curve relating the equilibrium concentration of a solute on the surface of an adsorbent,  $q_e$ , to the concentration of the solute in the liquid,  $C_e$ , with which it is in contact. The adsorption isotherm is also an equation relating the amount of solute adsorbed onto the solid and the equilibrium concentration of the solute in solution at a given temperature. According to the (IUPAC) classify adsorption isotherms become six types as explained bellows (Figure 3.3).

I. Type one, also belonged to as Langmuir isotherms, are bowl-shaped with respect to  $P/P^0$ . This isotherm arrives to the greatest adsorption value. The gradient of incline of the isotherm from  $P/P^0$  values of zero to 0.05 indicates the narrow of the micro-pores. Its overall agreed that type one isotherms stand for micro-porous solids with a tiny outside surface area for example zeolite and activated carbon.

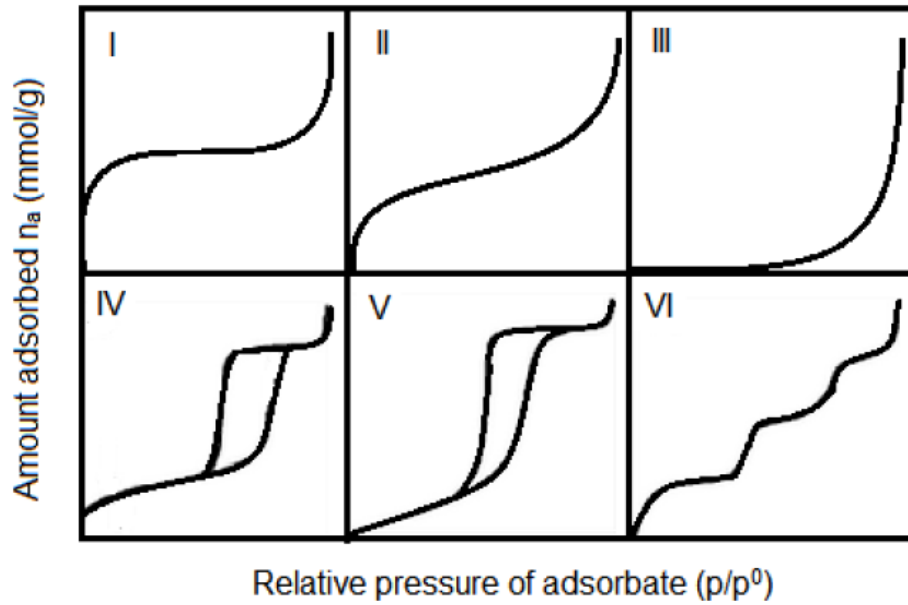
II. Type two isotherms talk about adsorption in the existence of both of them micro-pores and open surface. These isotherms stand for solids that are either macro-porous or non-porous.

III. The isotherms of type three are convex and are typical of adsorption at sites with low down adsorption potential like organic polymeric systems.

IV. The isotherms of type four are same as category three isotherms but include mesoporosity. Activated carbons won't typically present a plateau in the above relation pressure area.

V. The isotherm of type five is properties of a few energy, homogenous and mesoporous solid.

VI. The final of them is the isotherms of type six are properties exceedingly homogenous surface like pyrolytic graphite. Measurement is perform using methane or argon rather than nitrogen ( Ruthven, 1984; Sarıkaya, 1993).



**Figure 3.3.** According to IUPAC, shows the classification isotherm of gas adsorption.

There are several adsorption isotherm models such as Linear, Langmuir, Freundlich, Temkin, Brunauer–Emmett–Teller (BET), Dubinin-Radushkevich and Polanyi for predicting the equilibrium distribution (Ruthven, 1984; Sarıkaya, 1993). However, Langmuir and Freundlich models are most commonly used.

Langmuir adsorption isotherm describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface (Ruthven, 1984; Sarıkaya, 1993). Based upon these assumptions, Langmuir represented the following equation:

$$q_e = q_m b C_e / (1 + b C_e) \quad (3.1)$$

Langmuir adsorption parameters were determined by transforming the Langmuir equation (3.1) into linear form.

$$C_e/q_e = 1/bq_m + C_e/q_m \quad (3.2)$$

Where:

$C_e$ : the equilibrium concentration of adsorbate (mg/L)

$q_e$  = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g)

$q_m$  = maximum monolayer coverage capacity (mg/g)

$b$  = Langmuir isotherm constant (L/mg)

The values of  $q_m$  and  $b$  can be calculated from the slope and intercept of the Langmuir plot of  $C_e$  versus  $C_e/q_e$ .

Freundlich adsorption isotherm is commonly used to describe the adsorption characteristics for the heterogeneous surface. These data often fit the following empirical equation proposed by Freundlich (Ruthven, 1984; Sarıkaya, 1993).

$$q_e = K_F \cdot C_e^{1/n} \quad (3.3)$$

Where;

$q_e$  = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).

$K_F$  = Freundlich isotherm constant (mg/g)

$C_e$  = the equilibrium concentration of adsorbate (mg/L)

$n$  = adsorption intensity

The Freundlich isotherm equation can be written in the linear form as given below:

$$\log q_e = \log K_F + 1/n \log C_e \quad (3.4)$$

The constant  $K_F$  is an approximate indicator of adsorption capacity, while  $1/n$  is a function of the strength of adsorption in the adsorption process. If  $n = 1$  then the partition between the two phases are independent of the concentration. If value of  $1/n$  is below one it indicates a normal adsorption. On the other hand,  $1/n$  being above one indicates cooperative adsorption (Ruthven, 1984; Sarıkaya, 1993).

## **4. ACTIVATED CARBON**

### **4.1. Definition of Activated Carbon**

Activated carbon is a carbonaceous material with a well-developed porous structure and a large surface area. These properties give strong adsorption properties to activated carbon. The surface area of 1 g of commercial activated carbon ranges from about 300 to 2000 m<sup>2</sup>. Activated carbons can be defined as adsorbents whose internal surface area and pore volume are highly improved by the activation process applied to materials with high carbon content. Because of their large surface areas, pore volumes and high adsorption capacities, activated carbons are the most commonly used adsorbents (Everett, 1972).

#### **4.1.1. Properties of Activated Carbons**

#### **4.1.2. Physical Properties**

Activated carbons produced by using various raw materials as starting materials may contain different pores depending on the method of production and the properties of the raw materials used. Different chemical and thermal treatments applied after the activated carbon production improve the pore structure at the beginning and provide new micropores (Gündüzoğlu, 2008). The main component of active carbon is carbon and carbon content of a good activated carbon varies in the range of 85-95%. Also active carbons may contain some other elements such as hydrogen, nitrogen, sulfur, and oxygen in small quantities. On the other hand, it may contain different elements depending on the content of the raw materials used and other chemical substances used in the production/activation processes.

The activated carbon is similar in its properties and structure to graphite. Graphite is formed from flat layers of carbon atoms to form a hexagonal structure. In these layers, three electrons of carbon atoms make covalent bonds, while the remaining electrons are released between bond structures.

The most important physical properties of activated carbon in used are the surface area and porosity. Activated carbon particles have pores in different dimensions. According to IUPAC, these pores are classified as follows (Everett, 1972):

- Micro-pores;  $< 2$  nm
- Meso-pores;  $2 < \text{Pore size} < 50$  nm
- Macro-pores;  $> 50$  nm

The structures that give the carbon adsorption capacity are micro and meso pores. These pores occur throughout the activation process. The size of the pores determines the degree of transition of the molecules of the adsorbed material to the internal adsorption surface. Therefore, the pore size distribution of the adsorbent is another very important adsorption characteristic.

#### **4.1.3. Chemical Properties**

The presence of free electrons (especially polar or polarizable substances) affects the adsorption properties of active carbon. Active carbon contains elements that are chemically bonded to oxygen and hydrogen. These elements come from the raw material or as a result of carbonization which is not ideally realized and make chemical bonding to the surface during activation. Mineral matter, oxygen and hydrogen affect the properties of active carbon. Even small quantities of mineral matter are important in the adsorption of electrolytes and non-electrolytes solutions. The presence of hetero atoms in the active carbon structure constitutes a state of confusion. The oxygen, hydrogen and hetero atoms in the carbonaceous materials form bonds with the carbons. These atoms are attached to carbon atoms can not be fully filled. If the carbon atoms in the crystal lattice are misplaced, these atoms react with hydrogen, oxygen and other atoms to reduce their energy. The complex compounds formed are in the form of four different surface oxides. These are strong carboxylic groups, weak carboxylic groups, phenol groups and carbonyl groups (Pradhan and Sandle, 1999).

The selectivity of activated carbons for adsorption is depended upon their surface chemistry, as well as their pore size distribution (Addoun et al, 2002). Normally, the adsorptive surface of activated carbon is approximately neutral such as that polar and ionic species are less readily adsorbed than organic molecules.

Depending on the starting material used, the active carbons may contain in the range of 1 - 20% of mineral matter. The mineral matter content of the active carbon constitutes some inorganic substances such as silicates, aluminates and trace amounts of calcium, magnesium, iron, potassium, sodium, zinc, lead, copper and vanadium. In the adsorption of

electrolytes and non-electrolytic components from gases and solutions, the mineral matter content of activated carbon plays an important role. Iron, calcium and hydroxides and carbonates of sodium and potassium increase the formation of narrow and elongated micropores; at the same time, it is known that these alkaline earth metal compounds enrich meso pore formation with water vapor activation (Addoun et al., 2002).

#### 4.2. Materials Used for Activated Carbon Production

In the first years of active carbon production, wood, lignite, and peat were used but then it has been started to be used as raw materials in biomass to reduce the cost of raw materials and to evaluate wastes (Table 4.1).

**Table 4.1.** Some materials used or tested in activated carbon production (Dias et al., 2007; Hadi et al., 2015; Yahya et al., 2015).

|                |                         |                      |
|----------------|-------------------------|----------------------|
| Walnut shell   | Lignin                  | Drinking plant waste |
| Grape stalk    | Tea production residues | Date core            |
| Vine shoots    | Cherry stones           | Palm tree / tree     |
| Coconut shell  | Coal                    | Leather sole         |
| Moon core husk | Peanut shell            | Fruit shells         |
| Brass shell    | Wood                    | Seaweed              |
| Hazelnut shell | Leaves                  | Meyan root           |
| Fruit juice    | Rubber waste            | Carbohydrate         |
| Cocoa shell    | Schist oil              | Rubber waste         |
| Pumpkin seeds  | Sewage mud              | Sawdust              |
| Coffee bean    | Grain waste             | Oil                  |
| Peach stones   | Textile wastes          | Peat                 |
| Sugar cane     | Agricultural waste      | Grain                |
| Olive seeds    | Skin wastes             | Lignite              |
| Almond peel    | Flue dust               | Bone                 |
| Fish           | Raw bark                | Blood                |
| Graphite       | Corn cob and corn stalk | Molasses             |

The purpose of active carbon production is to produce higher quality activated carbon by activating high carbon content products. Therefore, raw material selection is very important while active carbon is being produced. The different raw materials with high carbon content high carbon content are generally used. However, the following features should be considered when selecting materials;



- Low inorganic content
- High density and sufficient volatile content
- The stability of supply in the countries
- Potential extent of activation
- Inexpensive material
- Decomposition properties during the storage
- Providing a high quality activated carbon
- Processability of raw materials

When producing activated carbon, it is necessary to have low ash content from the raw material. The carbon ash content increases after the activation process several times during production. In addition, high density and volatile content in the appropriate amount is also very important in the selection of raw materials. By increasing the mechanical strength of high-density active carbon, it also reduces the effects of size reduction that can occur during use. Activated carbons produced from raw materials such as wood and cellulose, which have low density and high volatile content, have large pore volumes and low strength. These carbons are generally used in liquid phase adsorption. Active carbon produced from coconut shells, fruit seeds and other sources with higher density and high volatile content have high resistance and large pore volumes and are used in liquid phase adsorption as well as vapor (gas) phase adsorption. Activated carbons produced from lignite are harder and have smaller pore volumes. It is generally preferred to use such carbon in the purification of waters. The density and hardness of activated carbons produced from bituminous coal are among activated carbons produced from coconut and lignite. They are mostly used in liquid and vapor phase adsorption (Bansal et al., 1988; Dias et al., 2007).

### **4.3. Active Carbon Types**

Active carbon properties are complicated process when classified according to surface characteristics and behavior. Classification by a single property, such as surface area only, does not give sufficient insight into the quality of active carbon. As the adsorbed molecule size changes, the available surface area also changes. However, information on surface area and pore structure can be used for comparison purposes. Active carbons can

also be produced with different properties and are classified according to these properties. These;

- Powdered activated carbons
- Granular activated carbons
- Pellet activated carbons
- Polymer coated activated carbons
- Impregnated activated carbons
- Spherical activated carbons (Bansal and Goyal 2005).

#### **4.4. Production of Activated Carbon**

##### **4.4.1. Physical Activation**

The physical activation process is carried out in two stages, carbonization and activation.

###### **4.4.1.1. Carbonization (Pyrolysis)**

Carbonization is the process of heat treatment of carbonaceous materials, the removal of certain organic substances from the environment, and finally the production of carbon-rich porous solids. It is usually carried out in inert media and at temperatures between 350 and 900 °C. During the carbonization of carbonaceous substances, a large part of the elements (H, N, O and S) other than carbon are removed from the gaseous medium by pyrolytic decomposition. During the process, primarily low molecular weight volatiles are removed. Following this, the formation of light aromatics and finally hydrogen gas is observed. Some carbon-containing materials may also be removed as oxides during the removal of carbon-free parts from within the body. As a result of this process, new bonds are formed and a structure containing a high amount of pores is obtained. Activation is required to increase the surface area of the resulting carbonized product. The properties of the product obtained as a result of the carbonization depend on the heating rate, carbonization temperature and duration, as well as the structure and physical properties of the starting material (Bansal et al., 1988).

#### 4.4.1.2. Activation

Activation is an important process for obtaining active carbon from carbon-containing materials. In the activation process, the pore structure is improved by cleaning the some degradation products formed during the carbonization and filled into the pores by physical and chemical processes applied. Depending on the physical and chemical process applied, the catalytic, electrical and hydrophilic properties of the product can be improved. The activation process is performed in two ways, physical (thermal) and chemical. Physical activation is the heating of the raw material at 800-1000°C and the activation by means of oxidizing gases. The process is also referred to as thermal activation (Dias, et al., 2007).

Carbon-containing raw materials are thermally unstable and thermally decompose when heated at high temperature in a gas atmosphere where oxygen is absent and are separated into liquid, solid and gaseous products. This process is commonly described as pyrolysis. Pyrolysis against an exothermic combustion process is an endothermic process. The most commonly used gases in the activation step are carbon dioxide, water vapor or a mixture of both. Endothermic reactions occurring in the process can be shown as follows:



#### 4.4.2. Chemical Activation

Chemical activation in the production of activated carbon, chemical substances that give rise to oxidizing gases in their heating or decompose organic substances by dehydration are used. Some compounds such as zinc chloride, sulfuric acid, phosphoric acid, alkali metal hydroxides, carbonates, sulphites, sulphates are used as activators in chemical activation (Dias, et al., 2007). The various chemical substances used in the chemical activation process are given in Table 4.2.

**Table 4.2.** Chemical substances used in the chemical activation (Dias et al., 2007; Hadi et al., 2015; Yahya et al., 2015)

|                     |                        |                     |
|---------------------|------------------------|---------------------|
| Zinc chloride       | Dolomite               | Iron chloride       |
| Phosphoric acid     | Manganese coal         | Iron sulphate       |
| Boric acid          | The cyanide            | Sulfuric acid       |
| Potassium hydroxide | Potassium permanganate | Potassium carbonate |
| Sodium chloride     | Manganese dioxide      | Calcium hydroxide   |
| Nitric acid         | Chlorine               | Calcium phosphate   |
| Sodium sulphate     | Sulfur                 | Sodium phosphate    |

Chemical activation is a process involving thermal decomposition and some reaction take place between the raw material and chemical activator. Chemical activation is usually carried out at 350-900°C. In chemical activation, the raw material is first mixed with a suitable chemical activator at certain ratios and is expected to absorb certain of time. Then, the activator is removed from the mixture by washing with an appropriate reagent such as water, hot water, acids or bases. Activation creates large surfaces by separating both the volatile components and removes the activators filled in the pores.

#### **4.5. Uses of Active Carbon**

Activated carbon (AC) is widely used in different industrial applications such as water and wastewater treatment, air and gas filtration, decolorization and deodorization of foods, purification of compounds used in pharmaceutical industry, gas mask making in personal protection, metal recovery, as catalyst in oil refineries and catalyst supporting material (Walker and Weatherley, 2000; Martins et al., 2016). Therefore, the need for AC in the world is on an upswing. The main usages;

- Wastewater treatment
- Unwanted taste, smell, color removal
- Purification of solids and gases
- As catalyst and catalyst support material
- Adsorption processes
- Breathing apparatus and gas masks
- Recovery of volatile solvents
- Medicine
- NBC (nuclear biological chemical) protective clothing and filters

## 5. INVESTIGATIONS ON ARSENIC ADSORPTION

There are a lot of research arsenic removals from water systems with different methods. These researches have been reported in review papers (Mohan and Pittman, 2007; Guan et al., 2012; Sachin et al., 2015; Lata and Samadder, 2016; Nidheesh and Singh, 2017). But the researches that are closely related to the subject of this thesis are summarized in the following table.

**Table 5.1.** Some researches on arsenic removal from waters by adsorption.

| Activated Carbon                                                                            | Adsorbent dosage              | Contact time | pH   | Initial Conc.       | Adsorption yield | Reference              |
|---------------------------------------------------------------------------------------------|-------------------------------|--------------|------|---------------------|------------------|------------------------|
| Powdered activated carbon                                                                   | 1 g                           | 30 min       | 3    | 10 mg/L             | 75 %             | Ansari and Singh, 2006 |
| Fe(III)-Si binary oxide                                                                     | 50 mg                         | 60 min       | 6.4  | 50 mg/L             | 98 %             | Zeng, 2004             |
| Iron oxide/activated carbon magnetic composite                                              | 5.0 g/L                       | 60 min       | 6    | 10 mg/L             | 95.27 %          | Yao et al., 2014       |
| Zirconium polyacrylamide (ZrPACM-43)                                                        | 1.3 g/L                       | 120 min      | 3    | 10 mg/L             | 98.22 %          | Mandal et al., 2013    |
| Nanoparticles of zero valent iron NZVI                                                      | 1 g/L                         | 10 min       | 7    | 1-30 mg/L           | 99.9 %           | Rahmani et al., 2011   |
| Aluminium oxide nanoparticles: mesoporous silica media (SBaE15)                             | 2 g/L                         | 12 min       | 6-8  | 9.96-99.64          | 94 %             | Jang et al., 2003      |
| Aluminum alum                                                                               | 20 mg/L                       | 6 h          | 6.6  | 0.1 mg/L            | 96 %             | Vu et al., 2003        |
| Magnetic composite Fe <sub>3</sub> O <sub>4</sub> Ca(OH) <sub>2</sub>                       | 10 mg                         | 12 h         | 3-10 | 30 mg/L             | -                | Peng et al., 2016      |
| Iron hydroxide / manganese dioxide straw activated carbon Fe-Mn-SAC                         | 1 g/L                         | 24 h         | 3    | 20 mg/L             | 85 %             | Xiong et al., 2017     |
| Multiwall carbon nanotubes MWCNT                                                            | 25 mg                         | 5 min        | 12   | 0.72 µg/L or 2 mg/L | > 95 %           | Aranda et al., 2015    |
| Iron treated activated carbon and zeolite                                                   | 0.1 g                         | 48 h         | 7-11 | 50 µg/L             | 85 %             | Kelly and Tarek, 2005  |
| Iron impregnated sugarcane carbon Fe-SCC                                                    | 0.25 g                        | 30 min       | 7    | 100 µg/L            | 94.5 %           | Roy, 2013              |
| Hydrous iron oxide impregnated Alginate beads                                               | 1 g/L                         | 7 day        | 6    | 10 mg/L             | -                | Sigdel et al., 2016    |
| Powder Activated Carbon PAC, Sodium Hypochlorite SH, Zeolite Z and Aluminum Polychloride AP | 30, 205, 100 mg/L and 50 µg/L | -            | -    | 100 µg/L            | 89.2 %           | Pio et al., 2015       |
| Zerovalent iron, Fe <sup>0</sup>                                                            | 2500 mg/L                     | 30 min       | 5    | 2000 µg/L           | 95 %             | Ramaswami et al., 2001 |

## 6. MATERIALS AND METHODS

### 6.1. Materials

Apricot and peach stones, and almond shell mixture was used as a precursor for activated carbon preparation in this study. The samples were provided from agricultural product markets. Each precursor was washed three times with tap waters to remove dust and other surface impurities and finally deionized water and then, dried at temperature room for 5 days and then at 80°C for 24 hours prior to use. The dried samples were ground by a knife-mill and sieved to get a homogeneous particle sizes. The samples having -30+50 mesh fraction (0.3-0.5 mm) were mixed on the weight ratios of 1/1/1 and this mixture was used as a precursor in the study. This mixture will be called triple mixture in later parts of the thesis.

Different analytical reagents grade chemicals such as  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (Merck1.03965),  $\text{HCl}$  (Merck10.0317),  $\text{NaOH}$  (Merck10.6462),  $\text{Na}_2\text{CO}_3$  (Merck10.6392),  $\text{NaHCO}_3$  (Merck10.6329)  $\text{As(V)}$  (Merck1.19773) were purchased from Merck and used in the study.

### 6.2. Preparation of Magnetic Activated Carbons (MACs)

Two magnetic activated carbons (MAC) were prepared and used in the study. The first MAC was prepared from the triple mixture of agriculture by-product with  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  chemical activation. In the chemical activation, different amounts of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in the range of 5-80 g were dissolved in 200 mL of distilled water, and then 40 g of the precursor was mixed with the  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  solution and impregnated via shaking at 100 rev/min via using a Gallenkamp flask shaker at 25°C for 24h. The impregnated materials were dried at 105°C for 24 h and then pyrolyzed in a cylindrical stainless steel reactor with 15 cm height and 6 cm in diameter under the  $\text{CO}_2$  flow. The reactor was heated from room temperature to the pyrolysis temperature with 20°C/min heating rate. In the pyrolysis temperature, the samples were maintained for 60 min and then cooled down in  $\text{CO}_2$  atmosphere. The reactor contents were evacuated and the activation yield calculated by weighing of the iron loaded activated carbon.

Second magnetic activated carbon was prepared from a novel activated carbon obtained from the triple mixture with  $\text{ZnCl}_2$  chemical activation by Akçakal, 2017. Some

general properties are given in Results and Discussion section. The following procedure was applied to give magnetic properties to the active carbon;

1. 50 g of activated carbon was suspended in 500 ml of purified water,
2. 1300 ml of Fe(III) solution containing 18.5 g of  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  and 150 ml of Fe(II) solution containing 20 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  were prepared and then mixed,
3. Fe(II) and Fe(III) mix solution was slowly added to the activated carbon suspension and stirred for further 30 minutes for good contact.
4. 10 M NaOH solution was added dropwise to the mixture prepared in step 3 until its pH was fixed to about 10-11.
5. The mixture was stirred for a further 60 min after the pH had fixed and aged at 25°C for 24 h, and then filtered.
6. The remaining solid was washed several times with distilled water, then washed with ethanol and then dried at 50°C.

### **6.3. As(V) Adsorption Experiments**

1000 mg/L standard stock solution of arsenate As(V) was used to prepare the experimental solutions in the study. The working solutions were prepared by diluting this solution with ultrapure water. pH adjustments were made by using nitric acid  $\text{HNO}_3$  and sodium hydroxide (NaOH) solutions in different concentrations. All reagents used in the study were in the analytical reagent grade.

Adsorption experiments were carried out in the batch reactors (250 ml erlenmeyer) containing different amounts of activated carbon and 50 ml of As(V) solutions having various pH and concentrations. The reactors were shaken at 150 rev/min via using a GFL flask shaker for contact times ranging between from 5 to 60 min. From the obtained results, contact time, adsorbent dosage and optimum pH were determined for further studies.

Adsorption isotherm studies were carried out with As(V) solutions having variety of concentrations in the ranging of 10-50 mg/L at the condition of adsorbent dosage, pH and contact time optimized.

At the ending of the each contact period, reaction mixtures were filtered and then the final pH of the filtrates was measured via a pH meter. The filtrates were analyzed for As(V) and iron by using Perkin Elmer AAnalyst800 model atomic absorption

spectrophotometer equipped with hydride system. The experiments were performed in duplicate and mean values were taken into account.

#### **6.4. Characterization Tests**

The triple mixture was characterized by proximate analysis, SEM (JEOL/JSM-6510 LV), FTIR (Perkin Elmer Spectrum One) and TG (Perkin Elmer Pyris TG/DTA) analysis. The MACs obtained were characterized by BET surface area, total pore volume and pore size (Micromeritics ASAP 2020), qualitatively surface functional group analysis by FTIR, SEM-EDX for the surface morphology and ash content according as ASTM D3174-73 standard.



## 7. RESULTS AND DISCUSSION

### 7.1. Preparation and Characterization of Magnetic Activated Carbons

#### 7.1.1. Preparation of magnetic activated carbon from the triple mixture with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ chemical activation

In order to get MAC from the low cost triple mixture, some elements that will give magnetic properties to the activated carbon must be incorporated to its structure. The main magnetic low-cost element is iron. It is believed that  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  is both an activating agent in pyrolysis and can also provide magnetic properties to the activated carbon. Therefore,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was used as an activating agent in the study.

In the chemical activation, type and amount of the activation reagent, impregnation conditions and activating temperature are important parameters. In the lots of researches related to activated carbon production from the agricultural by-products, these parameters have been optimized depending on the precursor and activation reagent to be used (Dias et al., 2007; Hadi et al., 2015; Yahya et al., 2015). The duration and temperature of impregnation and activation temperature have generally been selected to be 24 h and 25°C and 700°C, respectively, in the most of these studies. But, the weight ratio of activating agent to precursor, which is named impregnation ratio, has been accepted the most important parameter and examined detailed. Starting from this point, effect of the impregnation ratio (weight ratio of  $\text{FeSO}_4$  to the triple mixture) on the prepared activated carbon was investigated at the constant impregnation time (24 h), temperature (25°C) and activation temperature (700°C) for 60 min. The obtained results are presented in Table 7.1.

Main purpose of the classical activated carbon production is to obtain an AC having big surface area and total pore volume. But, it is desired that magnetic properties of active carbon in addition to these properties should be gained to the sample in the production of magnetic activated carbon. The iron salt used will give the sample a magnetic property by loaded and/or precipitated to its pores and surfaces. For this reason, while the added iron salt will give the sample a magnetic property, it will probably decrease its surface area. The results obtained from experiments carried out at the impregnation rates ranging from 5/40 to 80/40 indeed confirm this expectation (Table 7.1). Total pore volume and BET-surface area raised with the rising impregnation ratio up to 20/40, but they sharply

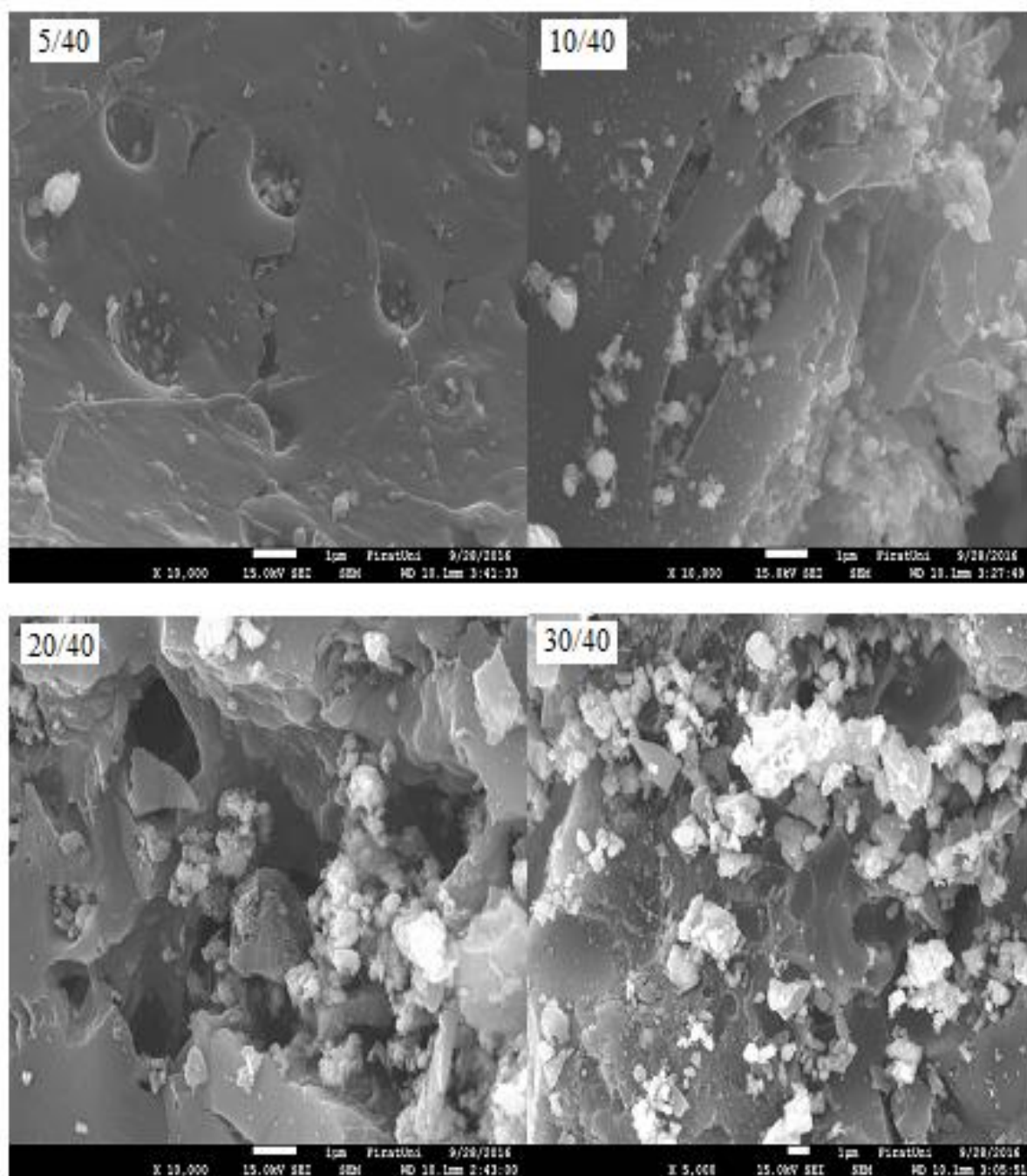
decreased after this ratio. Although it has been reported that the commonly used commercial ACs have surface area in the range of 500-1500 m<sup>2</sup>/g, total pore volume of higher than 0.2-0.6 cm<sup>3</sup>/g and carbon content of 85-95 % (Bansal and Goyal, 2005), it has not been given any information related to the magnetic activated carbons in the literature. Therefore, impregnation ratio of 20/40 which the magnetic activated carbon having the higher BET-surface area and total pore volume could be obtained was selected the most suitable impregnation ratio. The magnetic activated carbon obtained under these conditions has 375.28 m<sup>2</sup>/g BET-surface area, 0.2391 cm<sup>3</sup>/g total pore volume and 2.549 nm pore size. pH<sub>pzc</sub> value of this magnetic activated carbon was determined to be 5.34.

**Table 7.1.** Effect of the impregnation ratio on the magnetic activated carbon preparation from the triple mixture (impregnation time: 24 h; impregnation temperature: 25°C; pyrolysis temperature: 700°C; pyrolysis time: 60 min).

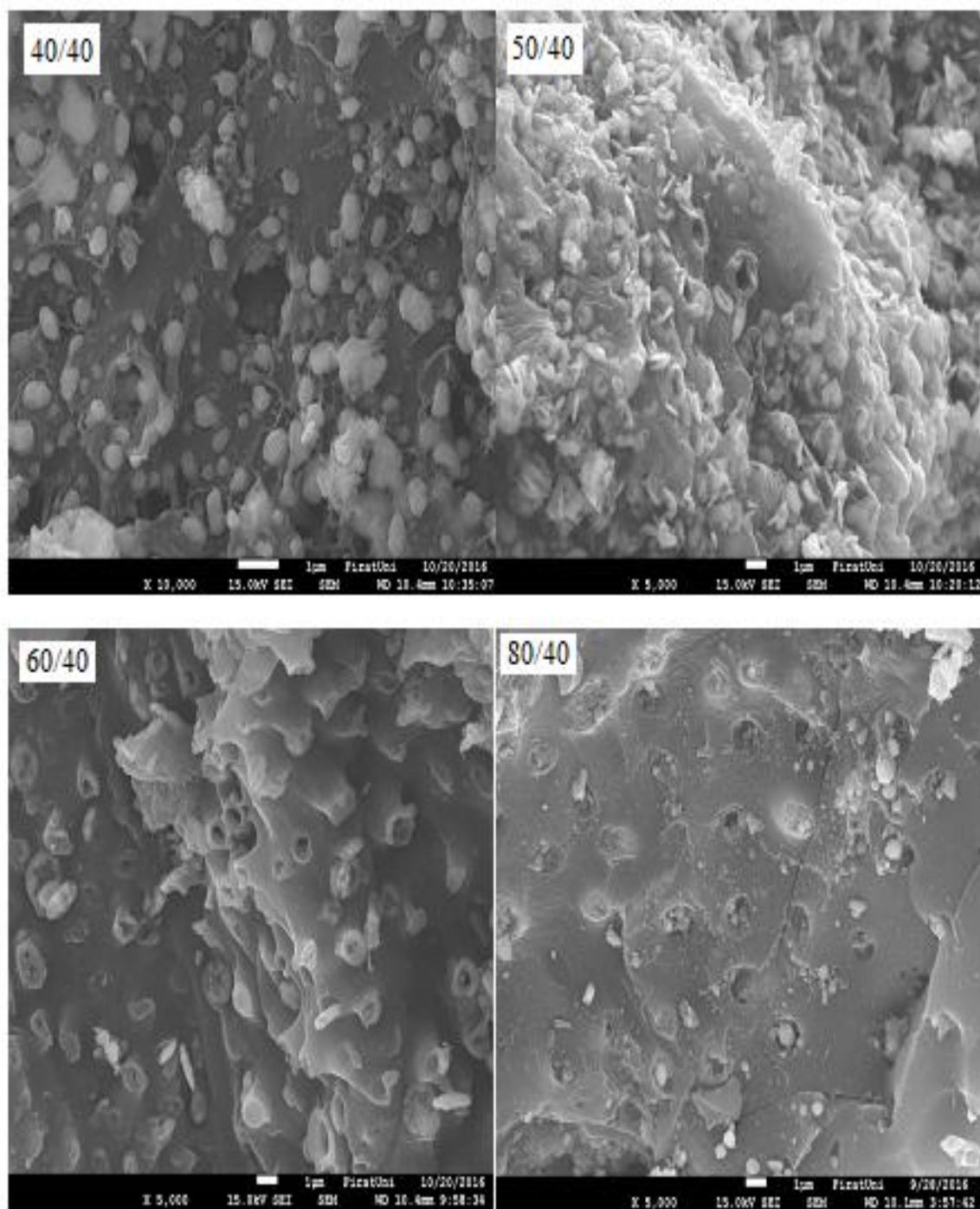
| Impregnation ratio,                   | 5/40   | 10/40  | 20/40         | 30/40  | 40/40  | 50/40  | 60/40  | 80/40  |
|---------------------------------------|--------|--------|---------------|--------|--------|--------|--------|--------|
| BET-surface area, m <sup>2</sup> /g   | 273.98 | 294.74 | <b>375.28</b> | 269.58 | 251.52 | 302.83 | 251.23 | 216.98 |
| Total pore volume, cm <sup>3</sup> /g | 0.168  | 0.185  | <b>0.2391</b> | 0.1296 | 0.1456 | 0.1543 | 0.1432 | 0.1301 |
| Pore size, nm                         | NM     | NM     | <b>2.549</b>  | NM     | NM     | NM     | NM     | NM     |
| pH <sub>pzc</sub>                     | NM     | NM     | <b>5.34</b>   | NM     | NM     | NM     | NM     | NM     |
| Yield, %                              | NM     | NM     | <b>20</b>     | NM     | NM     | NM     | NM     | NM     |

\*NM.: not measured

Figure 7.1 and 7.2 show the SEM images of the MACs obtained from the triple mixture impregnated with various amounts of FeSO<sub>4</sub>. As seen from the SEM images, it has been observed that the sample surfaces have partially pores and cracks up to impregnation ratio of 20/40, but they were covered by the increasing impregnation ratio. This shows that the increased FeSO<sub>4</sub> was covered the whole particle surface and turn into its oxides during impregnation and thus further activation could not be achieved. The EDX results of the magnetic samples given in Table 7.2 also confirm this situation. In particular, the raise in the ratio of oxygen and iron on the sample surface suggests that the surface is covered with an iron oxide layer, which prevents pyrolysis. For that reason, total pore volumes and BET-surface area of the samples were reduced.



**Figure 7.1.** SEM images of magnetic activated carbons obtained from the triple mixture impregnated with FeSO<sub>4</sub> in the range of 5/40-30/40.



**Figure 7.2.** SEM images of magnetic activated carbons obtained from the triple mixture impregnated with  $\text{FeSO}_4$  in the range of 40/40-80/40.

**Table 7.2.** Surface elemental compositions of the magnetic activated samples determined by SEM-EDX.

| Sample       | Weight, %    |              |             |             |
|--------------|--------------|--------------|-------------|-------------|
|              | C            | Fe           | O           | S           |
| 5/40         | 68.00        | 16.05        | 8.24        | 6.74        |
| 10/40        | 72.94        | 12.08        | 7.47        | 7.12        |
| <b>20/40</b> | <b>77.57</b> | <b>10.02</b> | <b>8.89</b> | <b>3.51</b> |
| 30/40        | 70.44        | 13.06        | 9.46        | 6.25        |
| 40/40        | 69.88        | 15.81        | 8.74        | 5.57        |
| 50/40        | 61.54        | 21.00        | 11.68       | 5.78        |
| 60/40        | 54.07        | 23.11        | 15.88       | 6.94        |
| 80/40        | 50.17        | 26.35        | 16.22       | 7.26        |

Surface area is the main important parameter in adsorption. Therefore, the magnetic activated carbon having the higher BET-surface area and total pore volume obtained from the triple mixture activated with  $\text{FeSO}_4$  at the impregnation ratio of 20/40 was selected as the most suitable adsorbent for As(V) adsorption and used in the study. This first magnetic activated carbon was called MAC1 and it will be used as MAC1 in the later sections of the thesis.

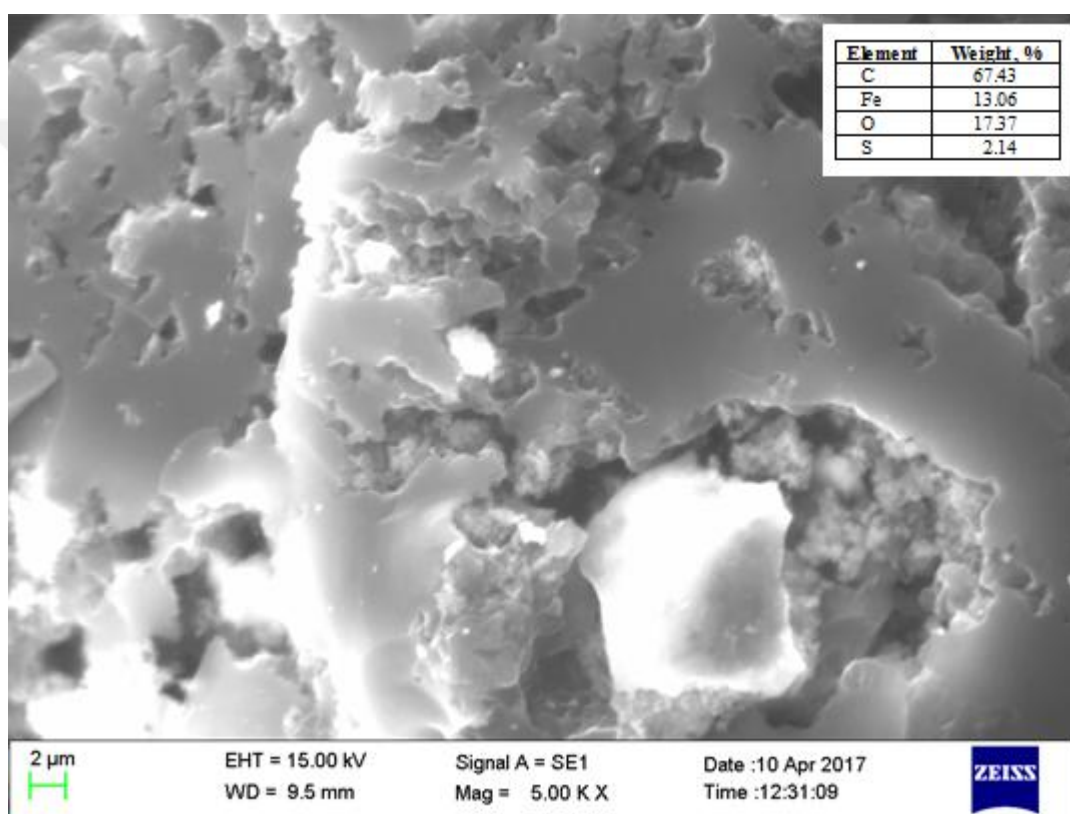
#### **7.1.2. Preparation and Characterization of the Magnetic Activated Carbon from a Novel Activated Carbon**

The second magnetic activated carbon was prepared from a novel activated carbon prepared from the triple mixture by chemical activation with  $\text{ZnCl}_2$ . The novel activated carbon given its characteristics in Table 7.3 has been prepared by Akçakal, 2017. It has a superb surface area and porosity and these properties are upper than those of the most trade AC. This activated carbon was used to prepare MAC with higher surface area. After magnetization procedure applied, it could be obtained a magnetic activated carbon having the BET-surface area of  $396.42 \text{ m}^2/\text{g}$  and total pore volume of  $0.254 \text{ cm}^3/\text{g}$ . The surface area of the obtained activated carbon was found to be higher than that of the magnetic active carbon (MAC1) obtained from directly the  $\text{FeSO}_4$  activation. Figure 7.3 show the SEM micrograph and EDX result of the magnetic activated carbon obtained. It can be seen from the SEM micrographs that the outer surface of the sample is porous surface with cracks, cavities, holes and pores were different sizes. But, its surface is covered with

activating agent. It contains 13.06% iron its surface. This second magnetic activated carbon was called MAC2 and it will be used as MAC2 in the later sections of the thesis.

**Table 7.3.** Some characteristics of the AC used for MAC preparation.

| BET-surface area, m <sup>2</sup> /g | Total pore volume, cm <sup>3</sup> /g | Pore size, Nm | C, %  | pH <sub>pzc</sub> |
|-------------------------------------|---------------------------------------|---------------|-------|-------------------|
| 1618.34                             | 0.7655                                | 1.8920        | 96.19 | 5.80              |



**Figure 7.3.** SEM image and EDX result of the magnetic activated carbons.

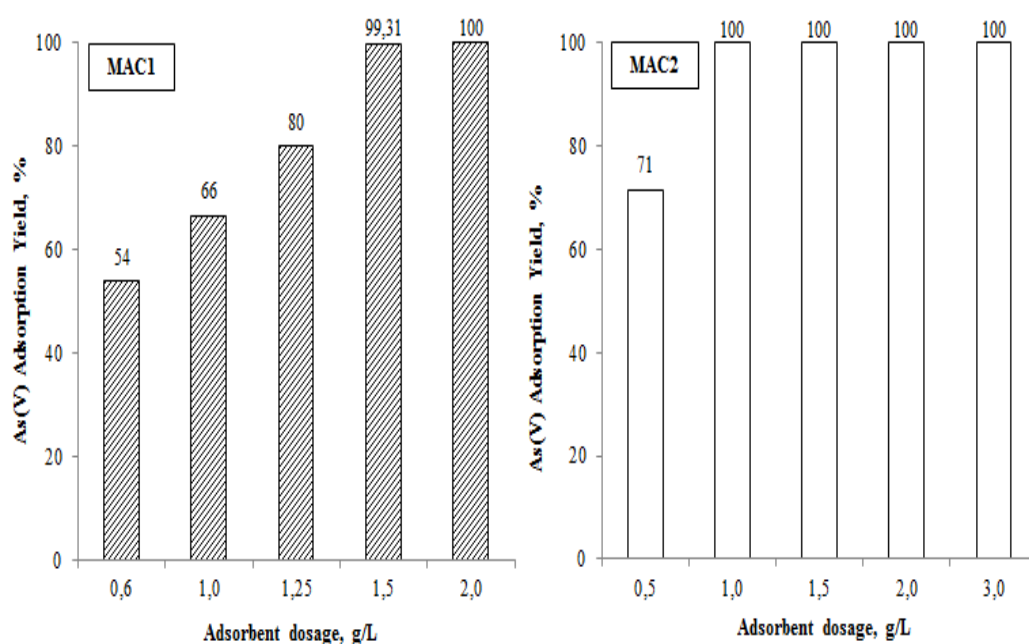
## 7.2. Adsorption Results

### 7.2.1. Effect of Adsorbent Dosage

The effect of the magnetic activated carbon dosage on the As(V) removal was studied relying on contact time through changing the adsorbent dosage in the range of 0.5-3 g/L. The results are presented in Figure 7.4. The As(V) adsorption yield increases with



the MAC1 and MAC2 dosages. But, when the both samples are compared, MAC2 appears to have higher removal efficiency with lower doses. Almost whole arsenic in the solution could be removed from the solutions in the presence of 1.5 g-MAC1/L and 1 g-MAC2/L. It can be stated that this situation is because MAC2 has a larger total pore volume and surface area than MAC1. Therefore, it can be concluded that the adsorbent dosage of 1.5 g/L and 1 g/L are the most reasonable for 10 mg-As(V)/L adsorption onto MAC1 and MAC2, respectively.

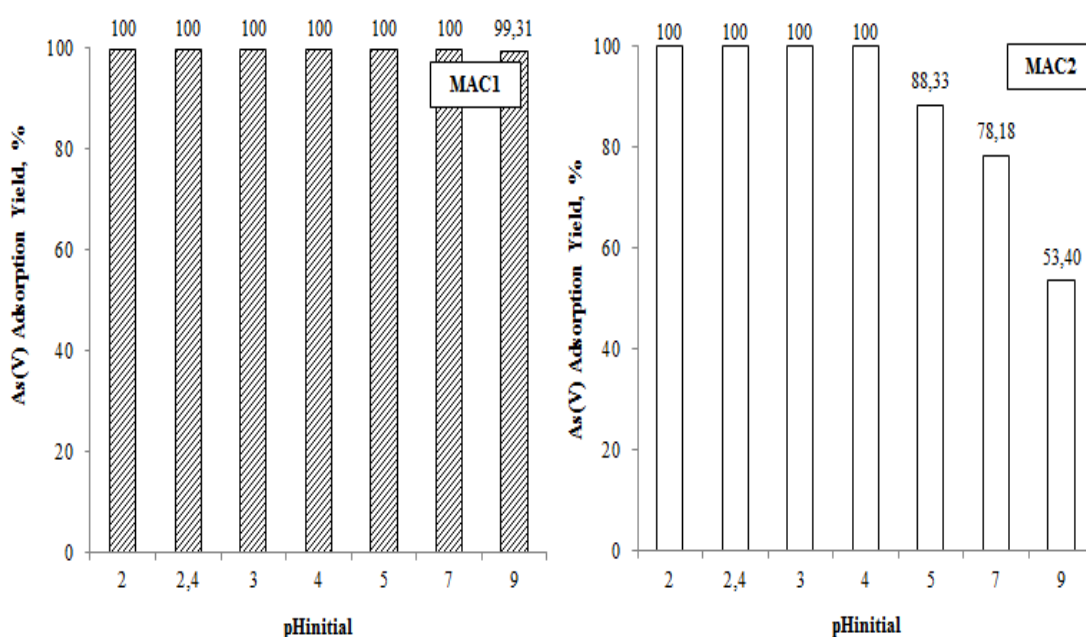


**Figure 7.4.** Effective of the adsorbent dosage on the arsenate (V) adsorption [ $\text{pH}_{\text{initial}}$ : 2.4; initial As(V) concn.: 10 mg/L; contact time: 60 min; temp.: 25°C].

### 7.2.2. Effect of pH

The pH of the solution is a significant parameter that controls the adsorption process. Therefore, the effect of pH on the As(V) adsorption through the magnetic activated carbons was investigated in the pH ranging of 2-9. Figure 7.5 shows the arsenate (V) adsorption percentage as a function of pH for both adsorbents. It has been determined that pH does not have an effect on arsenic adsorption by MAC1, but adsorption yields decrease with the increasing pH in the presence of MAC2. The  $\text{pH}_{\text{pzc}}$  value for the AC used in this study is 5.34.  $\text{pH}_{\text{pzc}}$  is the pH value at the point where net surface charge of the adsorbent is zero and it indicates the basic or acidic character of the AC surface. Net surface charge of the adsorbent under  $\text{pH}_{\text{pzc}}$  is positive, while it is negative over  $\text{pH}_{\text{pzc}}$ . The pH range studied

includes conditions where the net surface charge is negative and positive. While the adsorption efficiency was expected to decrease above the  $pH_{pzc}$  value for MAC1, the adsorption did not affected by pH. This situation is probably belong to the big surface area and active surfaces of the activated carbon depending on the iron content. Unlike, the adsorption efficiency decreased above the  $pH_{pzc}$  value for MAC2. Therefore, the most suitable pH for MAC1 and MAC2 is original pH of the initial As(V) solution having pH under the  $pH_{pzc}$  values of the samples.

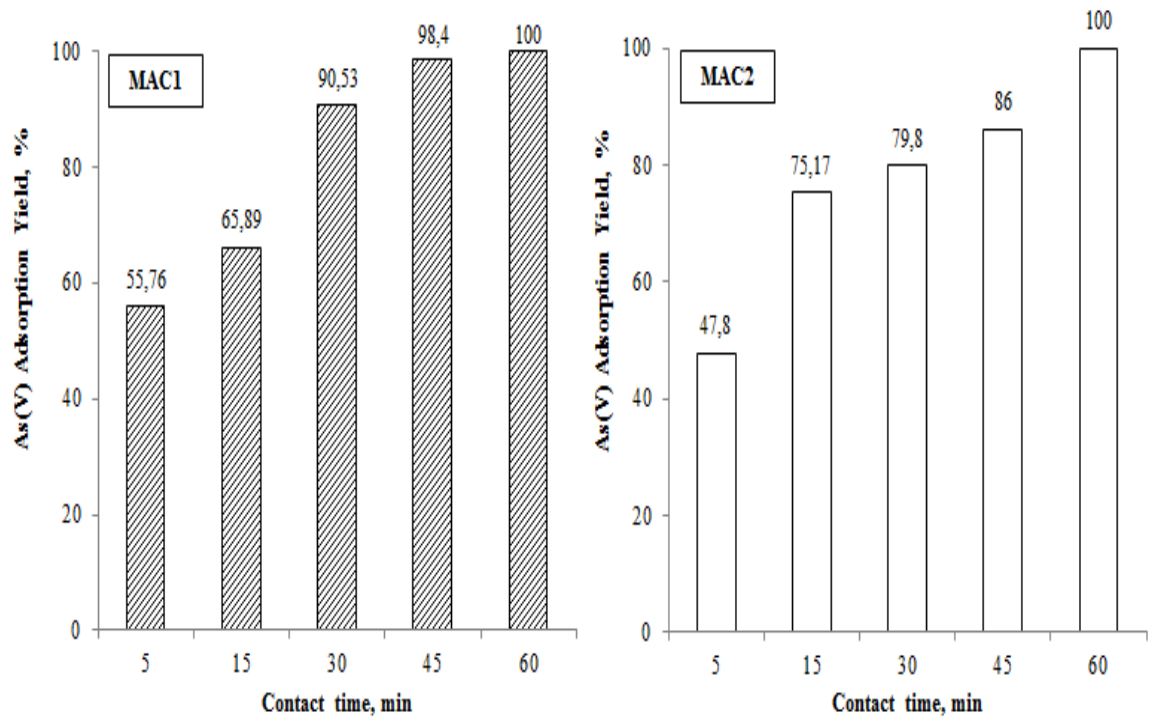


**Figure 7.5.** Effect of pH on the As(V) adsorption by magnetic activated carbons [initial As(V) concn.: 10 mg/L; MAC1 dosage: 1.5 g/L; MAC2 dosage: 1.0 g/L; contact time: 60 min; temp.: 25°C].

### 7.2.3. Effect of Contact Time

The effect of the contact time on the arsenic removal was studied in the contact time range of 5-60 min. The results are demonstrated in the Figure 7.6 The adsorption yields increased with the raising contact time and attain a greatest value at 60 min. Therefore, it can be concluded that the contact time of 60 min is a suitable for As(V) adsorption onto magnetic activated carbons prepared.



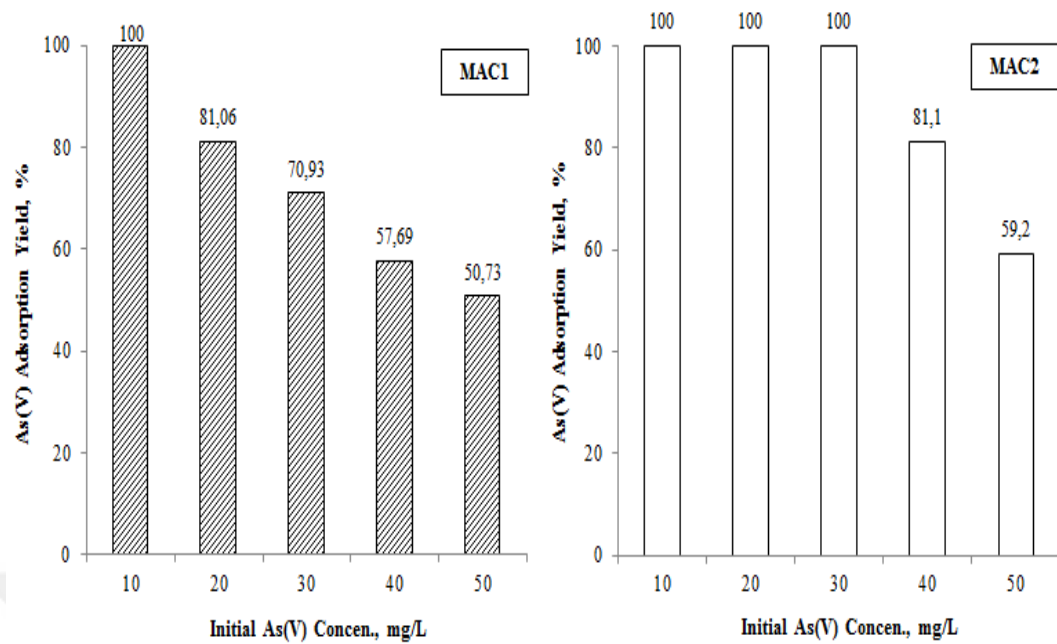


**Figure 7.6.** Effect of contact time on the As(V) adsorption by magnetic activated carbons [initial As(V) concn.: 10 mg/L; MAC1 dosage: 1.5 g/L; MAC2 dosage: 1.0 g/L; pH<sub>initial</sub>: 2.4; temp.: 25°C].

#### 7.2.4. Effect of Initial As(V) Concentration

The effect of initial As(V) concentration on the adsorption was investigated through varying the initial As(V) concentration in the ranging of 10-50 mg/L under the optimized conditions (contact time of 60 min; initial pH of 2.4; adsorbent dosages of MAC1: 1.5 g/L and MAC2: 1.0 g/L; and temperature of 25°C). The As(V) adsorption yields relying on initial As(V) concentration is demonstrated in the Figure 7.7.

The As(V) adsorption yield generally reduces with the raising initial concentration. But the decreasing in recovery efficiencies was found to be different for each magnetic activated carbon. In the presence of MAC1, when the initial As(V) concentration was raised from 10 to 20 mg/L, the adsorption percentage reduced from 100% to 81.06%. Though, it has been determined that all arsenic in the solution could be removed from the solution up to 30 mg/L concentration in the existence of MAC2. It can be stated that MAC2 has higher arsenic removal efficiency than MAC1.



**Figure 7.7.** Effect of initial As(V) concentration on the adsorption through magnetic activated carbons [MAC1 dosage: 1.5 g/L; MAC2 dosage: 1.0 g/L; contact time: 60 min;  $\text{pH}_{\text{initial}}$ : 2.4; temp.: 25°C].

## 8. CONCLUSIONS

The following results have been obtained from the study which the magnetic activated carbon production from the peach and apricot stones and almond shell mixture by  $\text{FeSO}_4$  chemical activation and usage of them for As(V) adsorption from aqueous solutions were investigated;

1. It has been determined that the effect of the impregnation ratio on the magnetic activated carbon by the chemical activation of the triple mixture directly with  $\text{FeSO}_4$  is an important parameter. The magnetic activated carbon having the higher BET-surface area and total pore volume was obtained from the triple mixture activated with  $\text{FeSO}_4$  at the impregnation ratio of 20/40. This first activated carbon (MAC1) has  $375.28 \text{ m}^2/\text{g}$  surface area,  $0.2391 \text{ cm}^3/\text{g}$  of total pore volume, 5.34  $\text{pH}_{\text{pcz}}$  and 77.57% C and 10.02% Fe content.
2. The second activated carbon (MAC2) prepared  $\text{FeSO}_4$  precipitation its surface has  $396.42 \text{ m}^2/\text{g}$  of surface area,  $0.254 \text{ cm}^3/\text{g}$  of total pore volume, 5.80  $\text{pH}_{\text{pcz}}$  and 67.43% C and 13.06% Fe content.
3. As a result of the adsorption studies using both magnetic activated carbons, the following general results were obtained. It has been determined that pH, adsorbent dosage and contact time are important parameter affecting the arsenic adsorption onto both magnetic activated carbons.
  - a. The effect of the magnetic activated carbon dosage on the As(V) removal was studied relying on contact time through changing the adsorbent dosage in the range of 0.5-3 g/L. It has been determined that the MAC2 have higher removal efficiency with lower doses than the MAC1.
  - b. From the results of the studies which effect of the pH on the adsorption was investigated, it has been observed that pH does not have an effect on arsenic adsorption by MAC1, but adsorption yields decrease with the increasing pH in the presence of MAC2.
  - c. Both activated carbons showed similar behavior depending on the contact time. The adsorption yields increased with the raising contact time and attain a greatest value at 60 min for both samples.
  - d. The As(V) adsorption yield generally reduces with the raising initial concentration. But the decreasing in recovery efficiencies was found to be

different for each magnetic activated carbon. In the presence of MAC1, when the initial As(V) concentration was raised from 10 to 20 mg/L, the adsorption percentage reduced from 100% to 81.06%. Though, it has been determined that all arsenic in the solution could be removed from the solution up to 30 mg/L concentration in the existence of MAC2. It can be stated that MAC2 has higher arsenic removal efficiency than MAC1.

- e. In order to remove arsenic ions having the concentration of 10 mg/L, the most suitable pH, adsorbent dosage and contact time have been determined as adsorbent dosage of 1.5 g /L and contact time of 60 min for MAC1, pH 4, adsorbent dosage of 1 g/L and contact time of 60 min for MAC2. Under these conditions, 99.31% and 100% of arsenic in the solution have been removed by MAC1 and MAC2, respectively.

Consequently; it can be stated that both magnetic activated carbons prepared from almond shell, apricot and peach stones mixture by  $\text{FeSO}_4$  chemical activation have high As(V) adsorption capacity. It is extremely advantageous to prepare and use these low-cost magnetic activated carbons from these types of agricultural by-products to remove As(V) from the water.

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