DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

ARSENIC REMOVAL FROM DRINKING WATER

by
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July, 2009
İZMİR

ARSENIC REMOVAL FROM DRINKING WATER

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Ph.D. THESIS EXAMINATION RESULT FROM

We have read the thesis entitled **"ARSENIC REMOVAL FROM DRINKING WATER"** completed by **MELTEM BİLİCİ BAŞKAN** under supervision of **PROF. DR. AYŞEGÜL PALA** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for degree of Doctor of Philosophy.

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ARSENIC REMOVAL FROM DRINKING WATER

ABSTRACT

Arsenate removal from drinking water was investigated using precipitation coprecipitation, lime softening, and adsorption methods. For precipitation coprecipitation method, Box-Behnken experimental design method was used to investigate the influence of major operating variables such as initial arsenic concentration, pH, and coagulant dose on arsenate removal efficiency and to find the combination of variables resulting in maximum arsenate removal efficiency. Ferric chloride, ferric sulfate, ferrous sulfate, and aluminum sulfate were used as a coagulant. Ferric chloride was found as effective and reliable coagulant considering required concentration and residual arsenate and iron concentration after sedimentation and filtration in the effluent. Although all types of polymers increased the removal efficiency of the treatment method, application of cationic polyelectrolyte was more effective than anionic and nonionic ones. Box–Behnken statistical experiment design and response surface methodology offer an efficient and feasible approach for arsenate removal and it could be employed to determine the optimum conditions for arsenate removal while minimising the number of experiments required.

Lime softening for arsenate removal was required larger amount of coagulant doses and higher operating pH than iron and aluminium salts and consequently a large volume of sludge is produced and strong acids would probably be needed to adjust the pH after treatment.

Clinoptilolite was used for arsenate removal from drinking water by adsorption. The iron modified zeolites were found as effective adsorbent for the arsenate removal from aqueous solution. According to the isotherm studies, GCFeA has larger capacities of adsorption and adsorption bond between the As(V) ion and adsorbent is the strongest. The pseudo second-order kinetic model provided a good correlation for the adsorption of arsenate by GCFeA and GCFeB in contrast to the pseudo first-order model. The GCFeA could treat approximately 3600 bed volumes of arsenate before column exhaustion.

Removal of arsenic from real groundwater in Sasalı-İzmir was investigated using obtained optimum conditions from coagulation and flocculation, lime softening, and adsorption method in order to compare arsenic treatment results of synthetic and natural arsenic contaminated water. The obtained results from natural arsenic contaminated water are consistent with the previous studies on arsenate removal from synthetic contaminated tap water.

Keywords: Arsenate removal, iron salts, aluminum sulfate, coagulation, Box-Behnken design, organic polymers, lime softening, adsorption, desorption, clinoptilolite, isotherm study, kinetic model.

İÇME SULARINDAN ARSENİK GİDERİMİ

ÖZ

İçme sularından arsenat giderimi, koagülasyon flokülasyon, kireçle yumuşatma ve adsorpsiyon yöntemleri kullanılarak araştırılmıştır. Koagülasyon ve flokülasyon yönteminde, başlangıç arsenat konsantrasyonu, pH ve koagülant dozu gibi ana işletme parametrelerini etkilerinin belirlenebilmesi ve maksimum arsenat giderme verimini sağlayan kombinasyonun bulunabilmesi amacıyla Box-Behnken istatistiksel deney tasarım yöntemi kullanılmıştır. Çalışmada koagülant olarak demir klorür, demir (II) sülfat, demir (III) sülfat ve alüminyum sülfat denenmiştir. Demir klorür, kullanılması gereken miktarı ve arıtmadan sonra suda kalan arsenat ve demir konsantrasyonu göz önünde bulundurularak en etkili kolagülant olarak belirlenmiştir. Kullanılan tüm polimerler arsenat giderme verimini arttırmasına rağmen katyonik polielektrolit uygulanması anyonik ve noniyonik polielektrolitlere göre daha iyi bir verim sağlamıştır. Box-Behnken istatistiksel denay tasarımı ve yanıt yüzey yöntemi içme sularından arsenat giderimi için etkili ve uygulanabilir bir yaklaşım getirmekte ve gerekli deney sayısını azaltarak arsenat giderimi için optimum şartların belirlenmesinde etkili olmaktadır.

Kireçle yumuşatma yöntemi ile arsenat giderimi demir tuzları ve alüminyum sülfata göre daha fazla koagülant dozu ve daha yüksek işletme pH'ı gerektirmektedir. Bu nedenle daha fazla miktarda çamur oluşumuna ve arıtmadan sonra pH ayarının yapılabilmesi için güçlü asitlere ihtiyaç duymaktadır.

Adsorpsiyon yöntemi ile içme sularından arsenat giderimi için adsorban olarak klinoptilolit kullanıldı. Demirle işlemden geçirilen zeolitlerin arsenat gideriminde oldukça etkili olduğu görüldü. İzoterm çalışmalarının sonuçlarına göre, GCFeA en yüksek adsorpsiyon kapasitesine sahip ve arsenat iyonları ile adsorban arasındaki kuvvetin en güçlü olduğu adsorban madde olarak belirlendi. Yalancı ikinci dereceden kinetik model GCFeA ve GCFeB ile arsenat adsorpsiyonunda yalancı birinci dereceden kinetik modele göre daha iyi bir korelasyon gösterdi. GCFeA kullanılarak kolon doygunluğa ulaşmadan önce yaklaşık 3600 yatak hacmi arsenat içeren su giderilebildi.

Sasalı-İzmir'deki bir yeraltı suyunda bulunan arseniğin giderilebilmesi için, koagülasyon flokülasyon, kireçle yumuşatma ve adsorpsiyon yöntemlerinden elde edilen optimum şartlar sentetik ve doğal olarak arsenikle kirlenmiş suların arıtımından elde edilen sonuçların karşılaştırılabilmesi için denenmiştir. Doğal olarak arsenikle kirlenmiş suyla yapılan deneylerden elde edilen sonuçlar sentetik olarak kirletilmiş çeşme suyundan elde edilen sonuçlar ile oldukça iyi bir uyum sağlamıştır.

Anahtar sözcükler: Arsenat giderimi, demir tuzları, alüminyum sülfat, koagülasyon, Box-Behnken, organik polimerler, kireçle yumuşatma, adsorsiyon, desorpsiyon, klinoptilolit, izoterm çalışması, kinetik model.

CONTENTS

Page

CHAPTER ONE
INTRODUCTION

1.1 The Problem Statement

Arsenic is a ubiquitous element found in the atmosphere, soils and rocks, natural waters and organisms. It is mobilised through a combination of natural processes such as weathering reactions, biological activity and volcanic emissions as well as through a range of anthropogenic activities (Smedley and Kinniburgh, 2002). As water passes through and over soil and rock formations, it dissolves many compounds and minerals including arsenic. Therefore varying amounts of soluble arsenic are present in some water sources. The presence of elevated levels of arsenic in groundwater has become a major concern especially in Bangladesh, India (Ali, 2006; Bhattacharyya et al., 2003; Halim et al., 2009; Harvey et al., 2006), and several other countries such as United States (Cory and Rahman, 2009; Farias et al., 2003; Sancha, 2006; Wang and Mulligan, 2006), China (Yuan, Luo, Hu, Ong, and Ng, 2003), Australia (Appleyard, Angeloni, and Watkins, 2006), Czech Republic (Drahota et al., 2009) and New Zealand (Gregor, 2001). According to Human Development Report Beyond Scarcity: Power, Poverty and Global Water Crisis by the United Nations Development Programme, arsenic contaminated water creates risks for million of people in some countries including Turkey in the world (Ross-Larson, Coquereaumunt, and Trott, 2006).

Unfortunately, elevated concentrations of arsenic are found in the groundwaters which are used for drinking water source in Turkey as shown in Table 1.1. Especially in Western Turkey high arsenic concentrations in groundwaters have been found related to the dissolution of some minerals in the colemanite boron formations. The observed enrichment of arsenic in groundwaters also result of both hydrothermal and evaporitic conditions, with some redistribution of both elements during diagenesis, and rock/mineral water interaction (Çolak, Gemici, and Tarcan, 2003; M. Çöl and C. Çöl, 2004; M. Doğan and A. U. Doğan, 2007; Gemici, Tarcan, Helvacı, and Somay, 2008).

Tablo 1.1 Typical arsenic concentrations in Turkey

Water Body and Location	Arsenic Concentrations (µg L^{-1})	References
Kütahya Drinking water source	5.2-9300	Çolak et al., 2003; M. Çöl and C. Çöl, 2004; M. Dogan, A. U., Dogan, Celebi and Barış, 2005; M. Dogan, A. U. Doğan, 2007; Oruç, 2004; Öztürk and Yılmaz, 2000
Bursa Drinking water source	0.051-21.423	Erdol and Ceylan, 1997
Bigadiç-Balıkesir Groundwater	33-911	Gemici et al., 2008
Van Drinking water source	5.027	Yılmaz and Ekici, 2004
Izmir Groundwater	0.7-170.1	Aksoy, Şimşek, and Gunduz, 2009
Giresun Drinking water source	50-120	N. Karakaya, M. Ç. Karakaya, Nalbantçılar, and Yavuz, 2007

The U.S. Environmental Protection Agency (USEPA) reduced the maximum contaminant level (MCL) for arsenic in drinking water from 50 µg L^{-1} to 10 µg L^{-1} (Lee et al., 2003). According to the last edition of the World Health Organization (WHO) Guidelines for Drinking-Water Quality (2006), 10 µg L^{-1} was established as a provisional guideline value for arsenic. MCL was also lowered to 10 µg L^{-1} in Turkey by Turkish Standards 266-Water Intended for Human Consumption (Turkish Standards (TS), 2005).

1.2 Background

1.2.1 Occurrence and Mobility of Arsenic

Arsenic is of increasing concern due to its high toxicity and widespread occurrence in the environment. It is widely distributed throughout the rocks and soils, and natural waters and is present in trace amounts in all-living matter (Wang and Mulligan, 2006). Figure 1.1 shows the occurrence and flow paths of arsenic in the environment. Arsenic and its compounds are mobile in the environment. Weathering of rocks converts arsenic sulfides to arsenic trioxide, which enters the arsenic cycle by dissolution in rain, rivers, or groundwater or as dust (Caniyilmaz, 2005).

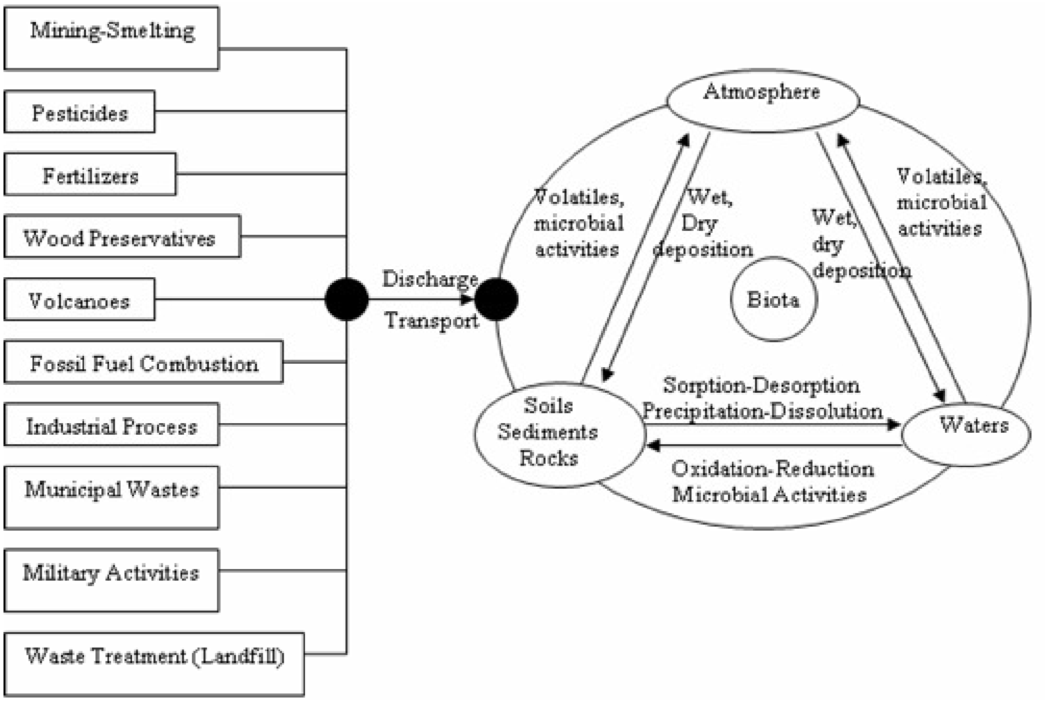


Figure 1.1 A simplified diagram of arsenic cycle (Wang and Mulligan, 2006).

Occurrence of arsenic in natural water depends on the local geology, hydrology and geochemical characteristics of the aquifer materials (Jain and Ali, 2000). In the environment arsenic is mainly associated with sulfide minerals. The most important arsenic bearing minerals are orpiment (As_2S_3), realgar (AsS), mispickel (FeAsS), loellingite ($FeAs_2$), niccolite (NiAs), cobaltite (CoAsS), tennantite ($Cu_{12}As_4S_{13}$), and enargite (Cu_3AsS_4) (Bissen and Frimmel, 2003). The distribution and mobilization of arsenic is also related to the total iron and iron oxides in the sediments (Mok and Wai, 1989).

Arsenic in the environment occurs from both natural and anthropogenic sources. It occurs naturally in soil and in many kinds of rock, especially in minerals and ores that contain lead and copper. It may enter the air, water and land from wind-blown dust and may get into water from runoff and leaching, and during the mining and smelting of these ores (Chou and Rosa, 2003). The primary natural sources of arsenic releases to the environment area: hot springs (geothermal), igneous rock (basalt), sedimentary rock (organic/inorganic clays, shale), metamorphic rock (slate), seawater, and mineral deposits (USEPA, 2003). Moreover natural activities such as volcanic action, erosion of rocks, and forest fires can release arsenic into the environment (USEPA, 2002).

M. Dogan and A. U. Dogan (2007) showed that arsenic is a naturally occurring element in minerals, including evaporitic minerals such as colemanite and gypsum, as well as alunite and chert in Tertiary deposits, in secondary epithermal gypsum in the form of realgar and orpiment along the fracture zones in the carbonates rocks, in limestone/dolomite and travertine, volcanic rocks and coal of the Tertiary age volcano sedimentary sequences, and in the thermal, ground and surface waters in the Kutahya region, western Anatolia, Turkey.

The anthropogenic sources of arsenic releases to environment are very different. Industrial products containing arsenic include wood preservatives, paints, dyes, pharmaceuticals, herbicides, semiconductors, tanneries, glass production and medical uses. The man-made sources of arsenic in the environment also include mining of copper, nickel, gold and ore smelting operations; agricultural applications; burning of fossil fuels and wastes; pulp and paper production; cement manufacturing; landfill leachate, and former agricultural uses of arsenic (USEPA, 2002).

The most important antropogenic sources, or sources associated with human activity, are the application of arsenic based insecticides and herbicides and mining (Mandal and Suzuki, 2002; Moore, 2005). The use of arsenical pesticides presents a non-point anthropogenic source of arsenic. The mainly used arsenical pesticides include lead arsenate [$Pb_3(AsO_4)_2$], calcium arsenate [$Ca_3(AsO_4)_2$], magnesium arsenate [$Mg_3(AsO_4)_2$], zinc arsenate [$Zn_3(AsO_4)_2$], zinc arsenite [$Zn(AsO_2)_2$], and Paris green [$Cu(CH_3CCOO)_2.3Cu(AsO_2)_2$] (Wang and Mulligan, 2006).

1.2.2 Arsenic Chemistry

Arsenic is the 20th most abundant element in the earth's crust, and often forms compounds by combining with oxygen, chlorine and sulfur. It is classified as a non-metal or a metalloid, but it is a grey like-metal material usually present in the environment in a crystalline form. Arsenic compounds can be also classified as inorganic and organic compounds (USEPA, 2002).

Arsenic can occur in the environment in several oxidation states but in natural waters is mostly found in inorganic form as oxyanions of trivalent arsenite [As(III)] or pentavalent arsenate [As(V)]. Organic arsenic forms may be produced by biological activity, mostly in surface waters, but are rarely quantitatively important (Smedley and Kinniburgh, 2002). Arsenate is generally the dominant form in oxic water, while arsenite dominates in sulfidic, methanic, and deeply circulating geothermal waters. Sorption, coprecipitation, and oxidation-reduction reactions of arsenic at the sorbent-water interface are important factors that affect the fate and transport of arsenic in aqueous systems (Lytle et al. 2004; Tallman and Shaikh 1980). The forms of arsenic present are dependent on the type and amounts of sorbents, pH, redox potential, and microbial activity (Wang and Mulligan, 2006).

In the aqueous environment inorganic arsenic appears commonly in the oxidation states +V and +III as arsenous acid (As(III)), arsenic acid (As(V)), and their salts (Bissen and Frimmel, 2003). The relative concentrations of each are controlled by the redox potential (Eh) and pH, as shown in Figure 1.2. Under oxidizing conditions (positive Eh) As(V) is the primary form of arsenic, while under reducing conditions (negative Eh) the primary form is As(III) (Moore, 2005). Therefore it is widely believed that arsenate is the major species in groundwater, there is increasing evidence indicating that arsenite might be more prevalent than has been previously thought since groundwater is often reducing (Shih, 2005).

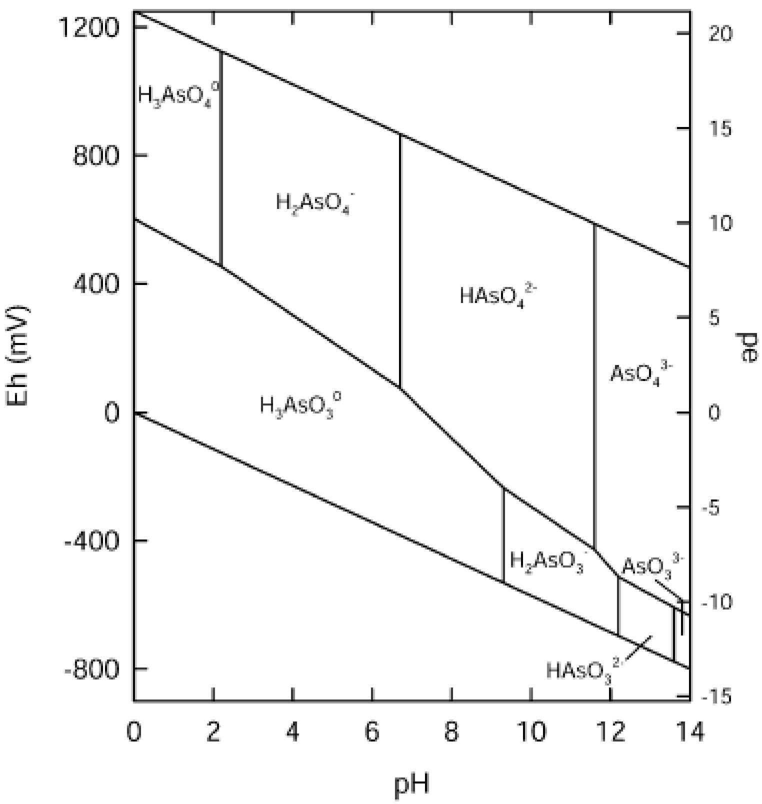


Figure 1.2 Eh-pH diagram for inorganic arsenic (Smedley and Kinniburgh, 2002).

Arsenite exists in aqueous solution in four forms: H_3AsO_3 « $H_2AsO_3^-$ « $HAsO_3^{2-}$ « AsO_3^{3-}. Similarly, arsenate exists in four forms: H_3AsO_4 « $H_2AsO_4^-$ « $HAsO_4^{2-}$ « AsO_4^{3-}. In the common groundwater pH range of 6 to 9, the predominant As(III) species is neutral (H_3AsO_3), whereas the As(V) species are monovalent ($H_2AsO_4^-$) and divalent ($HAsO_4^{2-}$) (USEPA, 2003). As shown in Figure 1.2, under oxidising conditions, $H_2AsO_4^-$ is dominant at low pH (less than about pH 6.9), whilst at higher pH, $HAsO_4^{2-}$ becomes dominant (H_3AsO_4 and AsO_4^{3-} may be present in extremely acidic and alkaline conditions respectively). Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite species H_3AsO_3 will predominate (Figure 1.2) (Yan et al., 2000). The distributions of the arsenate and arsenite species as a function of pH are given in Figure 1.3 and 1.4, respectively (Smedley and Kinniburgh, 2002).

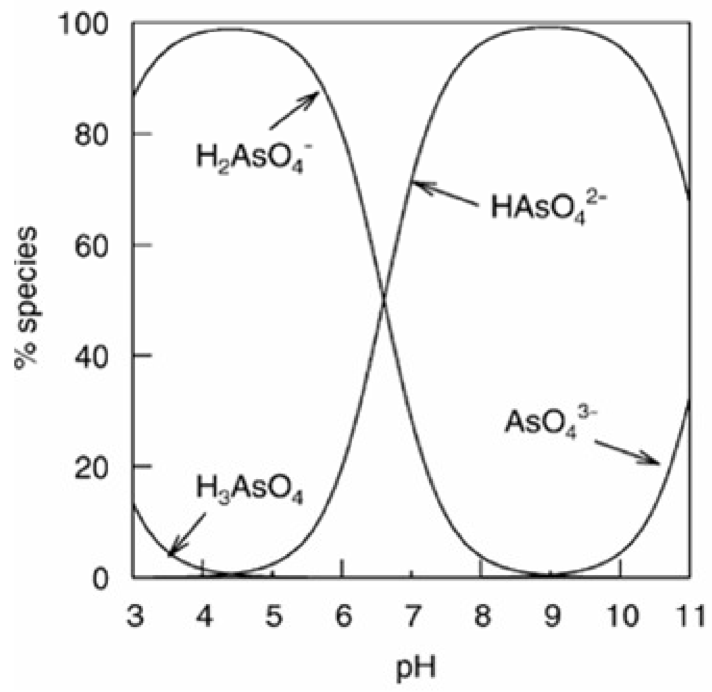


Figure 1.3 Arsenate speciation as a function of pH (Smedley and Kinniburgh, 2002).

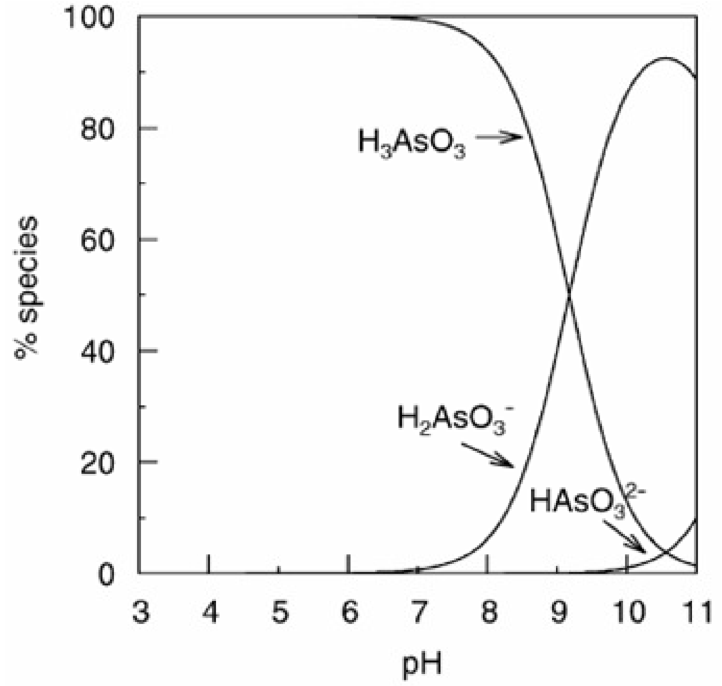


Figure 1.4 Arsenite speciation as a function of pH (Smedley and Kinniburgh, 2002)

Sadiq and Alam (1996) have investigated the arsenic chemistry in a groundwater aquifer. The most predominant arsenic species in acidic groundwater was found as $H_2AsO_4^-$, and the most abundant species in alkaline groundwater was found as $HAsO_4^{2-}$. Concentrations of H_3AsO_4 and AsO_4^{3-} were too low in this study.

Organic forms of arsenic, which result when arsenic combines with carbon and hydrogen, generally are considered less toxic than the inorganic forms (Kumaresan and Riyazuddin, 2001).

The toxicity of an arsenic-containing compound depends on its valence state (zero-valent, trivalent, or pentavalent), its form (inorganic or organic), and the physical aspects governing its absorption and elimination. In general, inorganic arsenic is more toxic than organic arsenic, and trivalent arsenite is more toxic than pentavalent and zero-valent arsenic (Ferguson and Gavis, 1972; National Academy of Sciences [NAS], 1977).

1.2.3 Toxicity and Health Effects of Arsenic

Although arsenic is useful for industrial, agricultural, medicinal and other purposes, it exerts a toxic effect in a variety of organisms, including humans (Duker, Carranza, and Hale, 2005). Inorganic arsenic has been used pharmacologically for the treatment of malaria, syphilis, leukemia, or psoriasis. Skin lesions, including dermal malignancies, were observed in the patients who were prescribed arsenical medicines (Yoshida, Yamauchi, and Sun, 2004).

The Agency for Toxic Substances and Registry (ATSDR) of the United States ranked arsenic first in its list of the twenty most hazardous substances. Its toxicity is hard to investigate because of its ability to convert between oxidation states and organometalloidal forms (Roy and Saha, 2002).

Given its ubiquitous nature in the environment, human exposure to arsenic is inevitable. Exposure can occur via all three principal routes, that is, through the inhalation of air, through the ingestion of food and water, and via dermal absorption (Smedley and Kinniburgh, 2001a). Once absorbed, arsenic is stored in the liver, kidney, heart and lung, while lower amounts are present in muscle and neural tissue. Two to four weeks after arsenic ingestion, it is incorporated into the nails, hair, and skin by binding to keratin sulfhydryl groups (Rodriguez, Jimenez-Capdeville, and Giordano, 2003).

Arsenic is a known toxin and carcinogen, but it is the magnitude of the dose (the amount and the route of administration (inhalation, ingestion, contact, etc.)) and the frequency of exposure that determines what health effects may occur (Lamm, 2001).

There are multiple end-points, with several different organ systems being affected, including the skin and the respiratory, cardiovascular, immune, genitourinary, reproductive, gastrointestinal, and nervous systems (Smedley and Kinniburgh, 2001b).

To better understand the magnitude of arsenic contamination in groundwater and its effects on human health, many studies were carried out in the world, especially in Bangladesh, West Bengal, Bihar and other states in India, China, Greece, Chilean, England, and Nepal. Effects of arsenic exposure via drinking water include various type of skin lesions such as diffuse and spotted melanosis, leucomelanosis, keratosis, hyperkeratosis, dorsal keratosis, neurological effects, hypertension, peripheral vascular disease, cardiovascular disease, respiratory disease, diabetes mellitus, non-pitting edema, gangrene, ulcers, skin and other cancers (bladder, lung, liver), spontaneous abortions, stillbirths, preterm births, low birth weights, neonatal deaths, weakness, lethargy, anemia, and the immune system (Ahamed et al., 2006; Ali and Tarafdar, 2003; Andrew et al., 2009; Caceres et al., 2005; Chakraborti, 2003; Ehrenstein, 2005; Karagas, Stukel, and Tosteson, 2002; Kelepertsis, Alexakis, and Skordas, 2006; Luu, Sthiannopkao, and Kim, 2009; Mazumder, 2003; Mukherje et al., 2003; Nguyen, Bang, Viet, and Kim, 2009; Rahman et al., 2005; Shrestha, 2003; Xia and Liu, 2004).

Elevated concentrations of arsenic in drinking water sources in Turkey also resulted in health problems. Dogan et al. (2005) have investigated arsenic-associated skin lesions and their occurrence and correspondence to the degree of arsenic exposure. A cross-sectional study was conducted and a search made for the source of arsenic known to be present in two different residential areas of the Emet region, Kutahya, in central Anatolia, Turkey. Chronic arsenic intoxication was found and adverse health effects related to skin documented from Igdekoy and Dulkadir villages in Emet as shown in Table 1.2. As it can be seen, arsenic associated scin lessions increased with increasing arsenic concentration in drinking water source.

Table 1.2 Dermatological findings in the Igdekoy and Dulkadir villages which are probably or possibly arsenic related (Dogan et al., 2005)

Symptom/findings	**Igdekoy no. (M/F)**	**Dulkadir no. (M/F)**	**Total no. (M/F)**
	As = 8.9 – 9.3 mg L^{-1}	**As = 0.3 – 0.5 mg L^{-1}**	
Palmoplantar keratoses	17 (9/8)	1 (1/0)	18 (10/8)
Basal cell carcinoma	2 (1/1)	0	2 (1/1)
Verruca plantaris	3 (3/0)	0	3 (3/0)
Verruca plantaris and palmaris	1 (0/1)	0	1 (0/1)
Plantar keratodermas	1 (0/1)	0	1 (0/1)
Plantar hyperkeratosis	1 (0/1)	0	1 (0/1)
Pigmented nodular lesion	0	1 (0/1)	1 (0/1)
Hyperhydrosis	0	1 (0/1)	1 (0/1)
Keratic papules	3 (0/3)	0	3 (0/3)
Bowenoid lesions	1 (0/1)	0	1 (0/1)
Total arsenic-related findings	30 (14/16)	3 (1/2)	33 (15/18)

1.2.4 Regulations

A comprehensive history of regulation of arsenic in drinking water is provided by WHO, beginning with the 1958 standard of 0.20 mg L^{-1}. In 1963 the standard was reevaluated and reduced to 0.05 mg L^{-1}. In 1993, 0.01 mg L^{-1} was established as a provisional guideline value for arsenic in drinking water based on analytical capability (Fujimoto, 2001; Newcombe, 2003).

The arsenic standard of 0.05 mg L^{-1} was set by USEPA in 1975 based on a Public Health Service standard set in 1942. In January 2001, the USEPA proposed lowering the amount of arsenic allowed in drinking water from 0.05 mg L^{-1} to 0.01 mg L^{-1}

based on evidence of cancer risk from high arsenic doses in Taiwan and Chile (Smedley and Kinniburgh, 2001b).

The national standard for drinking water in Turkey is 0.01 mg L^{-1} that was established by Turkish Standards 266-Water Intended for Human Consumption.

1.3 Arsenic Removal Methods

A variety of treatment processes has been developed for arsenic removal from water. The USEPA has identified seven best available technologies (BATs), which are given in Table 1.3. EPA determined these technologies to be the BATs for the removal of arsenic in drinking water based on a demonstration of efficacy under field conditions taking cost into consideration. All of these BATs are for arsenate (As(V)). Arsenate is relatively easy to remove from water, since it bears a negative charge in natural waters above pH 2.2, and is electrostatically attracted to the positive charge on metal hydroxide surfaces (Johnston, Heijnen, and Wurzel, 2001). Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite (As(III)) species will predominate (Smedley and Kinniburgh, 2002). Therefore As(III) is less efficiently removed than As(V), so pre-oxidation is necessary for better removal (Fujimoto, 2001).

Table 1.3 Best available technologies and their arsenic removal efficiencies (Johnston et al., 2001)

Treatment Technology	Maximum Removal, %
Activated alumina	95
Coagulation/Filtration	95
Ion exchange	95
Lime softening	90
Reverse osmosis	>95
Electrodialysis	85
Oxidation/filtration	80

1.3.1 Oxidation Processes

Some pretreatment processes that oxidize As(III) to As(V) include ozonation, photo oxidation, or the addition of oxidizing chemicals such as potassium permanganate, sodium hypochlorite, or hydrogen peroxide (USEPA, 2002). Moreover some solids such as manganese oxides can also oxidize arsenic. Ultraviolet radiation can catalyze the oxidization of arsenite in the presence of other oxidants, such as oxygen. Direct UV oxidation of arsenite is slow, but may be catalyzed by the presence of sulfite, ferric iron or citrate. Chlorine is a rapid and effective oxidant, but may lead to reactions with organic matter, producing toxic trihalomethanes as a by-product. Chlorine is widely available globally, though if improperly stored it can lose its potency rapidly. Oxidation alone does not remove arsenic from solution, and must be coupled with a removal process such as coagulation, adsorption or ion exchange (Johnston et al., 2001).

1.3.2 Coagulation and Flocculation

In this process chemicals transform dissolved arsenic into an insoluble solid which is precipitated. Dissolved arsenic may also be adsorbed on the surface and be co precipitated with other precipitating species. Suspended/colloidal arsenic may also be separated by coagulation and flocculation (Mondal, Majumder, and Mohanty, 2006). The most commonly used metal salts for arsenic removal are aluminum salts such as alum, and ferric salts such as ferric chloride or ferric sulfate. Ferrous sulfate has also been used, but is less effective (Johnston et al., 2001).

As with standard water treatment, to be effective the precipitative processes must be combined with a filtration process. Traditional sedimentation and filtration as well as membrane filtration (using ultrafilters or microfilters) has been shown to be effective at removing arsenic when combined with the precipitative process (Moore, 2005).

Valence state of arsenic, pH and presence of other compounds can affect precipitation/coprecipitation performance. The presence of other metals or contaminants may impact the effectiveness of precipitation/coprecipitation. For example, sulfate could decrease arsenic removal in processes using ferric chloride as a coagulant, while the presence of calcium or iron may increase the removal of arsenic in these processes (USEPA, 2002).

Coagulation aids are sometimes used to achieve optimum conditions for coagulation and flocculation. The aim is to obtain faster floc formation, produce denser and stronger flocs, decrease the coagulant dosage, broaden the effective pH band, and improve the removal of turbidity and other impurities. Synthetic organic polymers are long-chain molecules composed of small subunits or monomeric units. Polymers that contain ionizable groups such as carboxyl, amino, or sulfonic groups are called polyelectrolytes (Wang et al., 2005). Organic polymers neutralize the impurities or pollutants, and then agglomerate them into larger and heavier masses for rapid solid-water seperation by sedimentation, flotation, centrifugation, and filtration (Wang et al., 1977).

1.3.3 Lime Softening

Softening with lime is a process similar to coagulation with metallic salts. Lime $Ca(OH)_2$ is hydrolyzed and reacts with the carbonic acid to form calcium carbonate, which acts as the adsorption agent in the removal of arsenic. This process is typically used only with hard water, and shifts the pH of treated water to markedly higher values, in the range of 10–12 (Singh, 2007).

The mechanism of removal may be adsorption onto the calcium carbonate and $Mg(OH)_2$ formed (at high pH) or it may be a direct precipitation of calcium arsenates, similar to the phosphate precipitation under similar conditions (Newcombe and Dixon, 2006).

1.3.4 Adsorption

In adsorption, solutes (contaminants) concentrate at the surface of a sorbent, thereby reducing their concentration in the bulk liquid phase. The adsorption media is usually packed into a column. As contaminated water is passed through the column, contaminants are adsorbed. When adsorption sites become filled, the column must be regenerated or disposed of and replaced with new media (USEPA, 2002).

In this technique arsenic species is attached on the surface of the adsorbent by physical as well as chemical forces. (Mondal et al., 2006). Types of sorbent used in adsorption to treat arsenic are activated alumina (AA), activated carbon (AC), copper-zinc granules, granular ferric hydroxide, ferric hydroxide coated newspaper pulp, iron oxide coated sand, iron filings mixed with sand, greensand filtration ($KMnO_4$ coated glauconite), proprietary media and surfactant-modified zeolite (USEPA, 2002).

1.3.5 Ion Exchange

In this technique arsenic ions held electro statically on the surface of a strong base anion exchange resins are exchanged for ions of similar charge in the solution from the resin. Because dissolved arsenic is usually in an anionic form, and weak base resins tend to be effective over a smaller pH range, strong base resins are typically used for arsenic treatment. For ion exchange resins used to remove arsenic from water, the spent regenerating solution might contain a high concentration of arsenic and other sorbed contaminants, and could be corrosive. Spent resin is produced when the resin can no longer be regenerated. The spent resin may require treatment prior to reuse or disposal (USEPA, 2002).

Ion exchange resin can be fouled by suspended and dissolved contaminants in the feed water. If the feed water contains suspended solids the ion exchange process will need to be preceded by a pretreatment process, typically multimedia filtration. Also, source waters high in As(III) concentration may require pre-oxidation for conversion of arsenite to arsenate. Sulfate concentrations in the influent water significantly affect the capacity of the ion exchange resin with respect to the removal of arsenic (USEPA, 2000).

1.3.6 Membrane Filtration

In this technique arsenic is separated from water by passing it through a semi permeable barrier or membrane. Pressure difference is the driving force for the separation. The removal efficiency depends on the pore size in the membrane and the particle size of arsenic species. Pre oxidation step improves the removal efficiency (Mondal et al., 2006). High-pressure processes (i.e., nanofiltration (NF) and reverse osmosis (RO)) have a relatively small pore size compared to low-pressure processes (i.e., microfiltration (MF) and ultrafiltration (UF)). NF and RO primarily remove constituents through chemical diffusion. MF and UF primarily remove constituents through physical sieving (USEPA, 2000).

1.4 Experimental Design Methods

A design experiment is a test or series of tests in which purposeful changes are made to the input variables of a process or system so that we may observe and identify the reasons for changes in the output response (Montgomery, 1991). This system can be represented by the model shown in Figure 1.5.

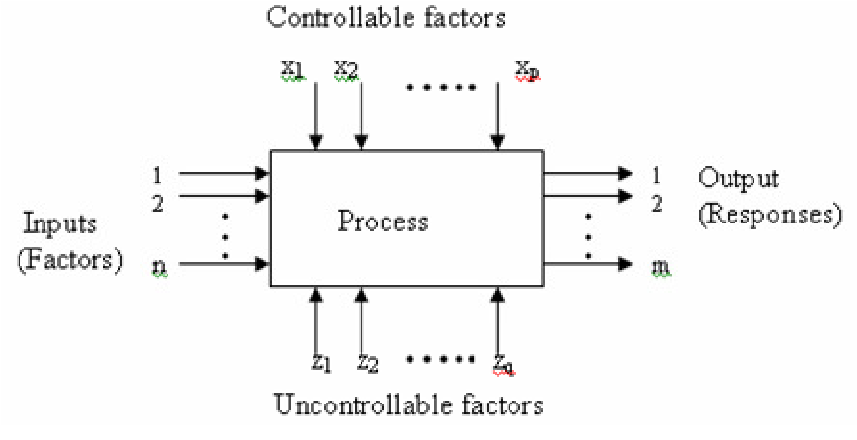


Figure 1.5 General model of a process or system (Montgomery, 1991).

The design of the experiment refers to the planning of the experiment, including the sampling process that must occur. We must know how many and what observations to take in order to answer the questions arising in the investigation. One carefully planned and executed experiment can measure the effects of the factors and the interactions as well as of several different experiments, to determine each of the factors and interactions, had been performed (Kinney, 2002).

The process of conducting an experiment requires a series of steps. These steps are identify the problem to be solved, determine the factors and levels that affect the response variable, choice of experimental design, performing the experiment and data analysis (Montgomery, 1991; Sullivan, 2004).

Experimental design methods can be investigated in four groups including comparative design, screening design, response surface method, and regression modeling. Number of factors and objectives of the experiment determine type of experimental design methods. Response surface methodology, or RSM, is a collection of mathematical and statistical techniques that are useful for the modeling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response (Montgomery, 1991). RSM does not require a large number of runs and also does not require too many levels of the independent variables (Myers and Montgomery, 2002).

Box-Behnken experimental design is a RSM used for analysis the experimental design data in order to be correlated to the independent variables. The Box-Behnken design is an independent quadratic design in that it does not contain an embedded factorial or fractional factorial design. In this design the treatment combinations are at the midpoints of edges of the process space and at the center. These designs are rotatable (or near rotatable) and require 3 levels of each factor (Kammoun, Naili, and Bejar, 2008).

1.5 Objectives and Scope of this Study

The objective of this study is to investigate removal efficiencies of arsenate from tap water by precipitation/coprecipitation, lime softening, and adsorption methods and to determine the most suitable operation method and the conditions. In precipitation/coprecipitation method, ferric chloride, ferric sulfate, ferrous sulfate, and aluminum sulfate were used as coagulant and organic polymers were used as coagulant aid. In the lime softening process, calcium hydroxide was used. Arsenate removal from tap water by adsorption was studied using natural zeolite called as clinoptilolite.

Objectives of the proposed study can be summarized as follows:

- To compare and select the most suitable coagulant type for arsenate removal by coagulation and flocculation,

- To investigate effects of important operating parameters such as initial arsenic concentrations, pH, and coagulant doses on percent removal of arsenate,

- To determine the most efficient organic polymer type (cationic, anionic, or nonionic polyelectrolyte) as coagulant aid for arsenate removal,

- To investigate residual concentration of iron and aluminum after sedimentation and filtration in coagulation-flocculation method,

- To search feasibility and reliability of response surface methodology for arsenate removal by coagulation process,

- To investigate arsenate removal by lime treatment,

- To modify the adsorption characteristics of natural zeolite using iron compounds to adsorb the arsenic anionic chemical species from water,

- To research effects of contact time, pH, clinoptilolite amount, and initial arsenate concentration on arsenate removal by adsorption, and determine the most suitable isotherm model,

- To determine the adsorption and desorption capacity of modified and unmodified clinoptilolite using batch and column experiments,

- To investigate the arsenate uptake characteristics of the natural zeolite by column studies under different flow rates,

- To analyzed the breakthrough behaviour of a column packed with natural zeolite,

- To search for the best fitted kinetic model to understand the sorption mechanism,

- To compare the arsenic removal results of synthetic and natural arsenic contaminated water.

CHAPTER TWO
LITERATURE SURVEY

Arsenic removal from drinking water using precipitation/coprecipitation have been studied in the past but limited number of studies have examined the use of cationic (Han et al., 2002; Wickramasinghe et al., 2004; Zouboulis and Katsoyiannis, 2002) and anionic (Zouboulis and Katsoyiannis, 2002) polymers for increasing removal of arsenic. No studies exist in literature concerning the removal of arsenic by coagulation using nonionic polymers as coagulant aid. Commonly used chemicals in this technique are aluminum salts such as aluminum sulfate and ferric salts such as ferric chloride or ferric sulfate because of its low cost and relative ease of handling (Mondal et al., 2006). Major studies may be summarized as follows:

Song et al. (2006) have investigated the arsenic removal from high-arsenic water by enhanced coagulation with ferric ions and coarse calcite. Coagulations are enhanced by adding appropriate coarse particles (two size fractions of 52-74 µm and 38-44 µm and they contain 99.2% and 99.0% $CaCO_3$, respectively). For this purpose, ferric sulfate ($Fe_2(SO_4)_3.5H_2O$) was used as coagulant and calcite was used as the coarse particle. The high-arsenic water sample was originally collected from channel. High arsenic water (200 ml) was mixed with 100 mg L^{-1} ferric sulfate and the suspension was filtrated through MF. In the acidic range, very high arsenic removal, about 99%, was achieved, while in the alkaline range, the arsenic removal declined sharply with the increase of pH. After that, enhanced coagulation with ferric ions and coarse calcite (pH=6) followed by filtration with filter papers (2.5 mm aperture) was tested to eliminate arsenic from the high-arsenic water. Without coarse calcite, the arsenic removal was only 85%, which was in correspondence with the cumulative oversize of arsenic-borne coagulates. As the increase of coarse calcite addition, the arsenic removal increased until it reached about 99%. The effect of pH on arsenic removal in this method is similar to that without calcite.

Wickramasinghe, Han, Zimbron, Shen, and Karim (2004) have studied on arsenic removal by coagulation and filtration. In order to investigate the efficiency of ferric ions coagulation, groundwater was obtained from in the US and from a tube well in Bangladesh. pH of groundwater is higher than 7 and arsenic concentration was higher than 50 ppb both for the US and Bangladesh water. The samples of raw US groundwater, 1.0 L in volume, pH 8.7, were dosed with ferric ions present either as ferric chloride or ferric sulfate. Two pH values were tested: 6.2 and 6.8. In addition, a cationic polyelectrolyte was added as a coagulant aid before commencing MF. As a result, the lower the initial raw water pH, the lower the residual arsenic concentration. Vacuum filtration of the Bangladesh water without the addition of ferric ions resulted in a decrease in the arsenic concentration from 138 to 64 ppb, while for US water no decrease in the arsenic concentration in the absence of ferric ion was observed. Using of polyelectrolyte as coagulant aid may lead to enhanced permeate fluxes; however, the polyelectrolyte had no effect on the residual arsenic concentration.

Pande, Deshpande, Patni, and Lutade (1997) have studied on arsenic removal by oxidation by chlorine followed by coagulation using ferric chloride. For this purpose raw water samples from some arsenic affected areas of West Bengal were used. A dose of 3 mg L^{-1} chlorine followed by a dose of 50 mg L^{-1} of ferric chloride was able to bring down the arsenic levels to permissible limit.

Sancha (2006) has investigated arsenic removal by coagulation using ferric chloride. Arsenite was oxidized to arsenate using a dose of 1 mg L^{-1} chlorine as a pre-treatment process. In this study, an arsenic concentration of surface water was 400 $\mu g\ L^{-1}$ and of groundwater was 70$\mu g\ L^{-1}$. Residual arsenic concentration of 10 $\mu g\ L^{-1}$ by this technology through adjustment of pH and control of coagulant dose was achieved.

Kang, Chen, Sato, Kamei, and Magara (2003) have also studied arsenic removal by coagulation using alum and polyaluminum chloride (PACl) and rapid sand filtration. Arsenic concentration of surface water and groundwater used for experiment was found to be 29 $\mu g\ L^{-1}$. When sufficient alum or PACl was added, 90-95% removal of arsenate was achieved with minimum soluble residual aluminum.

Yuan et al. (2003) have also investigated arsenic removal by coagulation using ferric sulfate, aluminum sulfate, mixture of ferric sulfate and aluminum sulfate (MFA), and polymeric ferric silicate sulfate (PFSiS) as coagulant and using kaoline and powder activated carbon (PAC) as coagulant aid. In this study, tap water was spiked with arsenate and arsenic concentration ranges from 0.1 to 2.5 mg L^{-1}. The results showed that the addition of kaoline and PAC did not enhance arsenic removal efficiency of ferric sulfate or aluminum sulfate. Similarly, MFA as well as PFSiS was also unable to improve the overall arsenic removal efficiency.

Lee et al. (2003) have studied arsenic removal by coagulation using ferrate (Fe(VI)) for arsenite oxidation and using Fe(III) and Fe(VI) for arsenic removal. Prepared synthetic water concentration was 517 μg L^{-1}. The pH, total alkalinity and dissolved organic carbon concentration of the river water were 7.8, 30 mg L^{-1} (as $CaCO_3$), and 4.45 mg L^{-1}, respectively. The results are showed that 2 mg of Fe(VI) L^{1} effectively removed the arsenic species, lowering the arsenic concentration from an initial 517 to below 50 μg L^{-1}. In contrast, the addition of Fe(III) even up to 8 mg L^{-1}, failed to achieve an effective reduction in the arsenic concentration below to the arsenic regulation level. So Fe(VI) not only oxidizes As(III) to As(V) but also acts as a coagulant of the arsenic. More interestingly, the effective removal of arsenic species was achieved by the combined use of very small amounts of Fe(VI) (0.5 mg L^{-1}) and Fe(III) (2 and 4 mg L^{-1}) as supplementary coagulants. When considering that Fe(VI) is not currently commercially available and is a relatively expensive chemical, arsenic removal by Fe(VI) alone is not an economical method. However, the combined use of a small amount of Fe(VI) (below 0.5 mg L^{-1}) as an oxidant for As(III) with Fe(III) as a major coagulant could be a practical method for the effective treatment of arsenic species in waters and wastewaters.

Zouboulis and Katsoyiannis (2002) have investigated arsenic removal by coagulation using alum (4-10 mg L^{-1}) or ferric chloride (2-20 mg L^{-1}) as coagulant and using cationic (0.5-3 mg L^{-1}) or anionic (0.5-5 mg L^{-1}) polyelectrolytes as coagulant aid followed by sand filtration. But in this study modified treatment method (coagulation, pipe flocculation/direct filtration) was used. Initial arsenic concentrations of synthetic water were in the range 0.1-1 mg L^{-1}. In general, both the coagulants were found to be efficient regarding arsenic removal and in both cases the use of coagulant aids increased the overall efficiency of the method.

Han, Runnells, Zimbron, and Wickramasinghe (2002) have studied on arsenic removal by coagulation using ferric chloride and ferric sulphate (0-25 mg L^{-1}) as a coagulant and using cationic polyelectrolyte as a coagulant aid followed by either microfiltration or sedimentation. Arsenic concentration of drinking water used in experiments was 60 ppb. The results obtained from this study showed that flocculation prior to microfiltration leads to significant arsenic removal in the permeate. Further, the addition of small amounts of cationic polymeric flocculants has led to significantly improved permeate fluxes during microfiltration. At the same time, microfiltration has led to more rapid and complete arsenic and turbidity removal than sedimentation.

Saha, Dikshit, and Bandyopadhyay (2001) have investigated arsenic removal by coagulation using alum (30-75 mg L^{-1}) and ferric sulfate (20-50 mg L^{-1}) followed by filtration. Concentration of arsenic in water was maintained in the range 0.1-1.0 mg L^{-1}. Chlorine was used as an oxidizing agent to convert arsenite to arsenate. 92% removal was achieved using 20 mg L^{-1} of alum in 0.1 mg L^{-1} of arsenic in water at pH 6.6 and 96% removal was achieved using 10 mg L^{-1} ferric sulphate in 0.1 mg L^{-1} of arsenic in water at neutral pH range with 6 hour retention time.

Meng and Korfiatis (2001) have also studied on arsenic removal by coagulation using ferric hydroxides (0-20 mg L^{-1}) followed by household filtration system. Concentration of arsenic in water was maintained in the range 280-600 µg L^{-1}. Hypochlorite solution was added to the water samples to oxidize As(III) and Fe(II). In general, a Fe/As ratio of greater than 40 was required to reduce arsenic concentration to less than 50 mg L^{-1}. For an arsenic concentration of 500 mg L^{-1}, approximately 20 mg L^{-1} of Fe(III) was required to treat the well water.

Gregor (2001) has investigated arsenic removal by coagulation using alum and PACl. Arsenic concentration of river water used all experiments was in the range of 16-30 μg L^{-1}. Five sampling sites were identified for each water treatment plant: source water, during the initial stages of coagulation, after flocculation/clarification, after filtration, and after final chlorination. So changing forms and concentrations of arsenic during treatment was investigated. In general, soluble As(V) is converted to particulate As(V) by adsorption during rapid mixing, and is removed along with naturally occurring particulate arsenic predominantly by clarification. Soluble As(III) tracks through the treatment processes and is converted to soluble As(V) during final chlorination. Arsenic has been removed to a concentration $\leq$ 5 μg L^{-1} during summer and winter. Better percent removals and lower concentrations in the treated water were achieved in winter (range < 1-3 μg L^{-1}) than in summer (range 3-10 μg L^{-1}).

Hering, Chen, Wilkie, and Elimelech (1997) have studied on arsenic removal by coagulation using ferric chloride (0-20 mg L^{-1}) and alum (10-40 mg L^{-1}) followed by filtration. Waters used this experiments were spiked with 20 μg L^{-1} As(V) or 9 μg L^{-1} As(III). As(V) removal by either ferric chloride or alum was relatively insensitive to variations in source water composition below pH 8. At the pH 8 and 9, the efficiency of As(V) removal by ferric chloride was decreased in the presence of natural organic matter. The pH range for As(V) removal with alum was more restricted than with ferric chloride. For source waters spiked with 20 μg L^{-1} As(V), final dissolved As(V) concentrations in the product water of less than 2 μg L^{-1} were achieved with both coagulants at neutral pH. Removal of As(III) from source waters by ferric chloride was both less efficient and more strongly influenced by source water composition than removal of As(V). The presence of sulfate (at pH 4 and 5) and natural organic matter (at pH 4 through 9) adversely affected the efficiency of As(III) removal by ferric chloride. As(III) could not be removed from source waters by coagulation with alum.

Type of coagulant, coagulant dose, pH and the range of arsenic concentrations of water used in the mentioned above studies are summarized in Table 2.1.

Table 2.1 Comparison of some studies using precipitation/coprecipitation method

As Concentration Average or Range (µg L^{-1})	**Type of Coagulant**	**Coagulant Dose (mg L^{-1})**	**Type of Coagulant Aid**	**Coagulant Aid Dose (mg L^{-1})**	**pH**	**Efficiency (%)**	**References**
70 and 400	$FeCl_3$	8-56.1	-	-	7-8.4	86–97.5	Sancha, 2006
5071	$Fe_2(SO_4)_3$	100	Coarse calcite	0-0.015	4-7	80-99	Song et al., 2006
68 and 138	$FeCl_3$, $Fe_2(SO_4)_3$	0-15	Cationic polymer	0.02-0.3	6.2; 6.8; 8.7	86->95	Wickramasinghe et al., 2004
29	Alum, PACl	0-10	-	-	4.5-8.5	90-95	Kang et al., 2003
100-2500	$Fe_2(SO_4)_3$, Alum, MFA, PFSiS	30	Kaoline PAC	0-50 0-30	6.9	48-97	Yuan et al., 2003
517	Fe(III), Fe(VI)	2->8, 0-6	-	-	6.3-6.8	>90	Lee et al., 2003
100-1000	$FeCl_3$, Alum	2-20, 4-10	Cationic, anionic polymers	0.5-3 0.5-5	6.7	80-99	Zouboulis and Katsoyiannis, 2002
60	$FeCl_3$, $Fe_2(SO_4)_3$	0-25	Cationic polymer	0.3	6.2; 6.8; 7.6; 8.7	>99	Han et al., 2002
100-1000	$Fe_2(SO_4)_3$, Alum	20-50, 30-75	-	-	7	92-96	Saha et al., 2001
280-600	Fe(III)	0-20	-	-	-	82->92	Meng and Korfiatis., 2001
300; 500; 1000	$FeCl_3$, Alum	10-30, 100-300	-	-	6	50->97	Ali et al., 2001
200	$FeCl_3$	4	-	-	7.5	88	Mamtaz and Bache., 2001
16 and 30	Alum, PACl	-	-	-	6.8-8.5	38-98	Gregor, 2001
9 and 20	$FeCl_3$, Alum	0.5-19.5, 10-40	-	-	4-9	40-98	Hering et al., 1997
490-740	$FeCl_3$	30-50	-	-	7.3-7.7	97-100	Pande et al., 1997

Besides coagulation and flocculation method, lime treatment to remove or reduce carbonate hardness (softening) is an efficient process for As(V) removal. The removal of As(V) from water (river, well and other) having a concentration of 0.1 to 20 mg L^{-1} is 40-70% for a pH range of 9-10 and removal efficiency is increased when lime softening is followed by coagulation using iron. Lime softening when the pH range is 10.6-11.4 showed a high removal of As(V), up to 95% when the initial arsenic concentration in the water was 12 mg L^{-1} (Castro de Esparza, 2006; Johnston et al. 2001).

Singh (2007) has investigated arsenic removal by lime softening using calcium oxide (lime). Different doses of lime (0.5 to 8.5 g) were added to arsenic contaminated tube-well water and allowed to stay for several hours in a container. Arsenic concentration was reduced to safe level after a period of 10 h, while no arsenic was detected after a period of 16 h.

Several papers reported the use of natural zeolite to remove a variety of environmental pollutants because of their selectivity, ion exchange capacity and low cost. However, these zeolitic materials do not remove anionic or organic pollutants and for this reason it is necessary to treat the zeolitic material to change its surface characteristics and improve the adsorption of this kind of water pollutant (Macedo-Miranda and Olguin, 2007). Naturally occurring zeolites are hydrated alumina silicate materials with high cation exchange capacities. Sorption of arsenic on natural zeolites has been studied extensively in recent years due to their low cost and availability in nature. In contrast, arsenic sorption by surfactant-modified natural zeolites has gained much less attention (Chutia, Kato, Kojima, and Satokawa, 2008).

Macedo-Miranda and Olguin (2007) have investigated arsenic sorption from aqueous solutions onto clinoptilolite-heulandite rich tuffs modified with lanthanum, hexadecyltrimethylammonium (HDTMA) or iron. In this study, the interaction between the arsenic and the Mexican natural zeolites depend on both the characteristics of the modified surface of each zeolitic material and the nature of the arsenic species present in the aqueous solution at a pH from 3 to 7. The natural

Mexican iron modified zeolite has good characteristics for potential treatment of As(III) or As(V) pollutant waters.

Chutia, Kato, Kojima, and Satokawa (2008) have proposed natural mordenite (NM), natural clinoptilolite (NC), HDTMA-modified natural mordenite (SMNM) and HDTMA-modified natural clinoptilolite (SMNC) for the removal of As(V) from aqueous solution. The As(V) sorption performance from aqueous solution by SMNM and SMNC were compared with the untreated zeolites NM and NC. The kinetics, sorption isotherms and pH effect on the removal were also studied using batch equilibrium techniques. The study shows that surfactant-modified zeolites are effective sorbent for the removal of As(V) from aqueous solution. Both SMNM and SMNC reduce As(V) concentration below WHO's earlier guideline values of 50 ppb arsenic in drinking water and SMNM further reduce the As(V) concentration below WHO's guideline values of 10 ppb.

Jimenez-Cedillo, Olguin, and Fall (2008) have also investigated arsenate adsorption from aqueous solutions onto clinoptilolite–heulandite rich tuffs modified with iron or manganese or a mixture of both iron and manganese. The results suggested that the kinetic adsorption of arsenates on the modified clinoptilolite rich tuffs depend of the metallic specie that modified the surface characteristics of the zeolitic material, the chemical nature of the metal as well as the association between different metallic chemical species in the zeolitic surface. No As(V) adsorption is obtained by manganese-modified clinoptilolite rich tuff, however the thermal treatment of the zeolitic material improves the adsorption of this metalloid.

Payne and Abdel-Fattah (2005) have conducted the batch adsorption kinetic and isotherm studies to compare and evaluate iron-treated adsorbents for arsenate and arsenite removal from aqueous media. Adsorbent materials such as activated carbon and naturally occurring zeolites (clinoptilolite and chabazite) were selected. Iron-treated activated carbon and chabazite showed the most promise as low-cost arsenic adsorbents; activated carbon removed approximately 60% of arsenate and arsenite while chabazite removed approximately 50% of arsenate and 30% of arsenite.

Arsenate removal by iron-treated activated carbon and clinoptilolite best fit the Langmuir model. Arsenate removal by iron-treated chabazite and arsenite removal by activated carbon, chabazite, and clinoptilolite best fit the Freundlich model. Applications of iron-modified activated carbon for effective arsenate removal would require pH values between 7 and 11, chabazite between 4 and 5, and clinoptilolite between 3 and 7. Arsenite removal by iron-modified activated carbon would require pH values between 7 and 11, chabazite between 7 and 10, and clinoptilolite between 4 and 11. Increasing temperature improved adsorption performance for activated carbon and the zeolites. Increasing ionic strength improved performance of iron-treated activated carbon and zeolites.

Jeon, Baek, Park, Oh, and Lee (2009) have investigated the sorption characteristics of As(V) on iron-coated zeolite (ICZ) through batch and column studies. Arsenic was completely removed within 30 min at an initial concentration of 2.0 mg L^{-1} with 100 g L^{-1} of ICZ dose. Optimum dose of ICZ was 33.3 g L^{-1} at a concentration of 20.12 mg L^{-1} and the effect of solution pH was negligible at a pH range of 3-10. Langmuir isotherm model was suitable to explain the sorption characteristics of As(V) onto ICZ. The co-presence of sulfate ions inhibited sorption of As(V) because of competitive adsorption. The adsorption capacity of ICZ for As(V)was 0.68 mg g^{-1}. The adsorption capacities in column experiments were similar to those in batch experiments.

Menhaje-Bena, Kazemian, Shahtaheri, Ghazi-Khansari, and Hosseini (2004) have investiagted the capability of Iranian natural clinoptilolites, relevant synthetic zeolites A and P and iron(II) modified of them was investigated for the uptake of arsenic anions from drinking water. Data obtained from ion-exchange using batch (static) technique showed that among the investigated zeolites, modified synthetic zeolite A was the most selective sorbent for removal of arsenic. The iron (II) modified synthetic zeolite obtained from Iranian natural clinoptilolite is suitable for removal of arsenic from drinking water. Synthesized zeolite P from Firouzkooh Clinoptilolite with 500-800 μm could be a suitable candidate for applying acontinuous sorption technique.

Siljeg et al. (2009) have investigated modified natural zeolite samples effect on arsenic removal frok aqueous solution. The pretreatment of clinoptilolite tuff by using first NaCl and later $FeCl_3$ solutions resulted in an arsenic uptake of up to 1.2 wt.%, whereas no As-uptake could be detected in the untreated zeolite. The X-ray photoelectron spectroscopy depth profile analyses of $(AsO_2)^-$ and $(HAsO_4)^{2-}$ modified samples show that arsenic concentrations decrease from the surfaces towards the subsurface region of crystallites suggesting that the arsenic atoms are mainly located at surfaces of crystallites. EXAFS (extended X-ray absorption fine structure) and XANES (X-ray absorption near edge structure) analysis revealed that arsenic cations in the samples arrange in the form of oxo-complexes attached to the iron cations on the surface of the clinoptilolite. Pretreatment of zeolite tuff with NaCl and $FeCl_3$ significantly affects the concentration of the arsenic species loaded in the zeolite. Na-Fe modified zeolite tuffs exhibit good sorption capacity for arsenites and arsenates.

Elizalde-Gonzales, Mattusch, Wennrich, and Morgenstern (2001) have studied the possible uptake of arsenite and arsenate species from aqueous solution using clinoptilolite containing rocks. Batch and isotherm studies at pH 4 in the concentration range of 0.1-4 mg L^{-1} were performed. Up to 98% of arsenite were removed from a 500 μg arsenic L^{-1} solution by three of the samples studied after a contact time of 70 days.

Li, Beachner, McManama, and Hanlie (2007) have evaluated the feasibility of using surfactant-modified zeolite and kaolinite to remove arsenic from water by batch experiments. The results showed that a significant increase in arsenate sorption capacity could be achieved as the loading level of hexadecyltrimethylammonium, a cationic surfactant, on zeolite and kaolinite surfaces exceeded monolayer coverage. At surfactant bilayer coverage, the arsenate sorption capacity reached up to 7 mmol kg^{-1} for surfactant-modified zeolite (SMZ) compared to almost none for the unmodified counterpart. Arsenite sorption on SMZ also increased although to a less degree. Similar results were observed for surfactant modified kaolinite. Solution pH had a less effect on arsenate and arsenite sorption. Solution ionic strength had a significant effect on arsenate sorption but a minimal effect on arsenite sorption. The results show that surfactant-modified zeolite and kaolinite are better sorbents for arsenate rather than arsenite removal due to differences in sorption mechanisms.

Stanic et al. (2008) have investigated the adsorption of arsenic (V) by natural zeolitic tuff modified with iron (III). Also, the iron (III) adsorption characteristic by natural zeolitic tuff was evaluated. It was determined that iron (III) adsorption by starting zeolitic tuff was best represented by the Freundlich type of isotherm, having correlation coefficient (R^2) of 0.990. Arsenic (V) adsorption by iron (III)-modified zeolitic tuff followed a nonlinear type of isotherm. The estimated maximum of arsenic (V) adsorption to iron (III)-modified zeolitic tuff was 1.55 mg g^{-1}. From kinetic experiments, it was found that adsorption of arsenic (V) on iron (III)-modified clinoptilolite was very fast and that most of the arsenic (V) was adsorbed in less than 30 min.

CHAPTER THREE
MATERIALS AND METHODS

3.1 Arsenic Removal by Coagulation and Flocculation

3.1.1 Reagents

Physical and chemical composition of the tap water used in the study is shown in Table 3.1. All the chemicals were of reagent grade or better and were used without further purification. Water samples has been provided with adding of sodium arsenate ($Na_2HAsO_4.7H_2O$) as As(V) source (purchased from Sigma). Synthetic contaminated water of 2 mg L^{-1} concentration was spiked with As(V) was prepared from tap water. In the experimental studies, this stock arsenic solution was used after diluted until desire concentration.

Table 3.1 Characterization of tap water used for experiment

Components	**Concentration**
pH	8.2
Turbidity, NTU	0.1
Chloride, mg L^{-1}	46
Nitrate, mg L^{-1}	3
Iron, mg L^{-1}	0.0343
Aluminum, mg L^{-1}	0.012
Manganese, mg L^{-1}	0.0141
Sodium, mg L^{-1}	23
Conductivity, µS cm^{-1}	463
Sulfate, mg L^{-1}	36

For the coagulation experiments all solutions were prepared with distilled water and all glassware was previously acid-washed. Ferric chloride ($FeCl_3.6H_2O$) and ferric sulfate ($Fe_2(SO_4)_3.5H_2O$) used as source of Fe(III), ferrous sulfate ($FeSO_4.7H_2O$) used as source of Fe(II), and aluminum sulfate ($Al_2(SO_4)_3.18H_2O$)

used as source of Al(III), were analytical grade and purchased from Merck or Carlo Erba. An amount of 500-5000 mg L^{-1} Fe(III) and Fe(II) stock solutions and 500-10000 mg L^{-1} aluminum sulfate solutions were prepared for further dilution to obtain a solution of desired concentrations.

The used polymers were Magnafloc LT22, Magnafloc LT27, and Magnafloc LT20 obtained from Ciba Speciality (Bradford, England). The chemical nature, molecular weight, and form of used commercial flocculants are listed in Table 3.2. Hydrochloric acid (HCl, 37%) and sodium hydroxide (NaOH) were used to adjust pH.

Table 3.2 The chemical nature, molecular weight, and form of used commercial coagulants

Flocculant	Chemical Nature	Molecular Weight	Form
Magnafloc LT22	Cationic	High	Powder
Magnafloc LT27	Anionic	High	Powder
Magnafloc LT20	Nonionic	Medium	Powder

3.1.2 Experimental Procedure

3.1.2.1 Arsenic Removal by Coagulation with Iron and Aluminum Salts

Coagulation experiments were conducted using the standard jar test apparatus. A series of jar tests was performed using the tap water has various As(V) concentrations. Coagulation was carried out with ferric chloride, ferric sulfate, ferrous sulfate, and aluminum sulfate. The coagulant was added to each 1 L jar containing the sample water with rapid mixing at 120 ± 2 rpm. After 3 minutes of rapid mix, 30 minutes of slow mixing at 45 ± 2 rpm was provided, followed by at 30 minutes of settling. Prior to addition of coagulant, the sample water pH was adjusted by adding HCl or NaOH. At the end of the settling period, water samples were taken from the supernatants, filtered by 0.45-µm pore size membrane filter, and stored for analysis by HCl addition to obtain a pH value of 2 to conserve the samples until the arsenic was detected. All the experiments were performed in duplicate to evaluate test reproducibility under identical conditions and the arithmetic average result of the two experiments was reported in this study.

3.1.2.2 Arsenic Removal by Coagulation with Iron, Aluminum Salts and Flocculants

In the second series of the experiments, arsenate contaminated water was mixed with coagulants and cationic, anionic, or nonionic polyelectrolyte in order to determine the organic polymers effect on arsenate removal. The coagulation conditions were performed in the same way as mentioned above. Each test was duplicated. The arithmetic average result of the two tests was reported in this study.

3.1.3 Analytical Methods

The determination of arsenic in the influent and effluent aqueous solutions was performed by the hydride generation procedure coupled with inductively coupled plasma-atomic emission spectrometry (HG-ICP-AES), also known as inductively coupled plasma-optical emission spectrometry (HG-ICP-OES) (Optima 2100 DV). HG-ICP-OES has been used for the trace determination of arsenic (Edwards et al., 1998). Hydride generation involves the production of volatile hydrides upon a chemical treatment with a strong reducing agent, typically sodium borohydride ($NaBH_4$) (Gong, Lu, Ma, Watt, and Le, 2002; Le, Yalcin, and Ma, 2000). Hydride generation can be coupled with various types of spectrometry: atomic absorption (HG-AAS), atomic fluorescence (HG-AFS), atomic emission (HG-AES) or mass spectrometry (HG-MS).

The sodium borohydride reduction procedure instantaneously converts As^{+3} to arsine gas; however, at room temperature, the reduction of As^{+5} to arsine occurs relatively slow. Therefore, a total arsenic determination requires a prereductant such as KI to convert all arsenic to the +3 oxidation state prior to the arsine formation step. The use of arsine gas formation provides both a way to separate the analyte from potential chemical interferences in the sample and to preconcentrate to improve analytical sensitivity. The primary advantage of this approach is the ability to simultaneously determine other hydride forming elements such as antimony, selenium, etc. The other advantage of HG techniques is that only gaseous hydrides are introduced to the detector and the remaining sample matrix is discarded. As a result, chemical interferences are eliminated. Unfortunately, the complexity of this technique can be time consuming and thus costly. (Guerin, Molenat, Astruc, and Pinel, 2000).

Water (20 ml) was first mixed with 2 ml mixture of KI (5%) and ascorbic acid (5%) and 6 ml HCl (10%) for 30 minutes at dark place to reduce As(V) to As(III). Then, 10 ml solution was taken for the analysis of As(III) concentrations. In this study, arsenic concentrations were measured at 193.7 nm wavelength and detection level was found as 1 $\mu g\ L^{-1}$.

Determination of iron and aluminum concentrations was also made by use the HG-ICP-AES. Each analysis for arsenic, iron, and aluminum concentrations was duplicated. The arithmetic average of the two analysis results was reported in this study.

3.1.4 Experimental Design and Statistical Analysis

The response surface methodology was used to investigate the influence of major operating variables on arsenic removal efficiency and to find the combination of variables resulting in maximum arsenic removal efficiency. The Box-Behnken design with three factors and three levels, including five replicates at the centre point for estimation of errors, was used to evaluate the main and interaction effects of the factors and for fitting a second-order response surface.

For precipitation/coprecipitation process, three important operating parameters such as initial arsenic concentration, coagulant dose, and pH were chosen as the independent variables and designated as X_1, X_2, and X_3, respectively. Initial arsenic concentration (X_1) was changed between 10 and 1000 $\mu g\ L^{-1}$, and pH (X_3) was ranged from 4 to 9 for all types of coagulant. However coagulant dose was (X_2) varied between 0.5 and 60 mg L^{-1} for ferric ions and varied between 0.5 and 80 mg L^{-1} for aluminum sulfate. As presented in Table 3.3, the experimental design involved three parameters (X_1, X_2 and X_3), each at three levels, coded -1, 0, and +1 for low, middle and high concentrations, respectively.

Table 3.3 Levels of each factor for Box-Behnken

Independent Factors	**Units**	**Symbol**	**Coded Levels for Iron Salts**			**Coded Levels for Aluminum Sulfate**		
			-1	**0**	**+1**	**-1**	**0**	**+1**
Initial As Conc.	µg L^{-1}	X_1	10	505	1000	10	505	1000
Coagulant Dose	mg L^{-1}	X_2	0.5	30.25	60	0.5	40.25	80
pH	-	X_3	4	6.5	9	4	6.5	9

The experimental conditions determined by Box-Behnken statistical design method for iron salts and aluminum sulfate are presented in Table 3.4 and Table 3.5, respectively. The centre point in the design was repeated five times for estimation of errors. In the correlating of the arsenic removal efficiency (Y) with other independent variables (X_1-X_3), following response surface function was utilized:

$$\begin{aligned} Y = {} & b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_{12} X_1 X_2 + b_{13} X_1 X_3 \\ & + b_{23} X_2 X_3 + b_{11} X_1^2 + b_{22} X_2^2 + b_{33} X_3^2 \end{aligned} \tag{3.1}$$

where Y is the predicted response surface function (percent As(V) removal), b_0 is the model constant, b_1-b_3 linear coefficients, b_{12}, b_{13}, and b_{23} the cross product coefficients, and b_{11}, b_{22}, and b_{33} are the quadratic coefficients. The software Design Expert (Version 7.0.0, Stat-Ease Inc., Minneapolis, USA) and Statistica 5.0 were used for experimental design, determination of the coefficients, data analysis, and graph plotting. The validity of the model was determined by comparing the experimental and predicted values. Furthermore, the predicted arsenic removal efficiencies from response function were experimentally verified in an additional study to verify the reliability of the statistical experimental strategies.

Table 3.4 Experimental data points used in Box-Behnken experimental design for iron salts

Run	**Initial As Concentration (μg L^{-1})**	**Coagulant Dose (mg L^{-1})**	**pH**
1	1000	30.25	4
2	10	60	6.5
3	505	30.25	6.5
4	1000	30.25	9
5	505	30.25	6.5
6	505	30.25	6.5
7	505	30.25	6.5
8	1000	0.5	6.5
9	505	0.5	9
10	10	30.25	9
11	505	30.25	6.5
12	10	0.5	6.5
13	505	0.5	4
14	10	30.25	4
15	505	60	9
16	505	60	4
17	1000	60	6.5

Table 3.5 Experimental data points used in Box-Behnken experimental design for aluminum sulfate

Run	Initial As Concentration (µg L^{-1})	Coagulant Dose (mg L^{-1})	pH
1	1000	40.25	4
2	10	80	6.5
3	505	40.25	6.5
4	1000	40.25	9
5	505	40.25	6.5
6	505	40.25	6.5
7	505	40.25	6.5
8	1000	0.5	6.5
9	505	0.5	9
10	10	40.25	9
11	505	40.25	6.5
12	10	0.5	6.5
13	505	0.5	4
14	10	40.25	4
15	505	80	9
16	505	80	4
17	1000	80	6.5

3.2 Arsenic Removal by Lime Softening

3.2.1 Reagents

The tap water has same physical and chemical composition with the coagulation experiments as given Table 3.1 was used for arsenic removal by lime softening. Arsenate standards were prepared from sodium arsenate ($Na_2HAsO_4.7H_2O$) and diluted with tap water until desire concentrations. In this study, arsenic removal from drinking water by lime softening using calcium hydroxide ($Ca(OH)_2$) has been performed and the hydrated lime is purchased from Merck.

3.2.2 Experimental Procedure

The coagulation conditions were performed in the same way as mentioned in part 3.1.2.1 and 3.1.2.2. Prior to addition of hydrated lime, in the mixing process and after the sedimentation, the sample water pH was measured. HCl was added to the liquid phase to obtain pH value of 2 to conserve the samples until the As was detected. All the experiments were also performed in duplicate to evaluate test reproducibility and the arithmetic average result of the two experiments was reported in this study.

3.2.3 Analytical Methods

The determination of arsenic in the influent and effluent was analyzed in the same way as explained in part 3.1.3.

3.3 Arsenic Removal by Adsorption

3.3.1 Reagents

The tap water has same physical and chemical composition with the coagulation experiments as given Table 3.1 was also used for arsenic removal by adsorption. Water samples has been provided with adding of sodium arsenate ($Na_2HAsO_4.7H_2O$) as As(V) source. The clinoptilolite from Gördes-Manisa was used in this work and it bought from Rota Mining Corporation. The particle size from 0.5 to 1 mm was chosen taking into account future column experimentation as shown in Figure 3.1. A cation exchange capacity of this clinoptilolite is 1.5-1.9 meq g^{-1}.

Figure 3.1 The photo of clinoptilolite used in this study.

3.3.2 Clinoptilolite Treatments

3.3.2.1 Treatment with NaCl solution

In order to improve the ion exchange characteristics of the zeolitic material to obtain Fe-modified clinoptilolite with different surface characteristics, 150 g of Gördes clinoptilolite (GC) were treated with 0.1 M NaCl solution under reflux for 3 hours as shown in Figure 3.2. This process was repeated once more, while changing the NaCl solution. The liquid phases were separated by centrifugation and the solid phases were washed until Cl^- was eliminated using the $AgNO_3$ test. Then, the zeolitic samples were dried at 60°C for 24 h. This sample was called GCNa.

Figure 3.2 The photo of clinoptilolite under reflux for NaCl treatment.

3.3.2.2 Treatment with $FeCl_3$ solution

Fifty grams of GCNa was treated with 500 mL of 0.1 M $FeCl_3$ solution under reflux for 5 h as shown in Figure 3.3. This process was repeated once after changing the solution. The solid phase was separated by centrifugation and was washed with distilled water and dried at 80°C for 24 h. The sample was stored in a dry atmosphere until the sample was used. This sample was named GCFeA. The procedure mentioned before was in a similar manner using 0.01 M $FeCl_3$ solutions. The resultant zeolitic materials were named as GCFeB.

Figure 3.3 The photo of clinoptilolite under reflux for $FeCl_3$ treatment.

3.3.3 Characterization Techniques

3.3.3.1 Scanning Electron Microscopy and Elemental Analysis

For scanning electron microscopy observation, the samples were mounted directly onto the sample holders and covered with gold using SC 7620 Sputter Coater to provide conductivity. The surface morphologies of clinoptilolite samples were examined by a Scanning Electron Microscope (JEOL-JSM 6060 SEM) with an Energy Dispersive X-ray spectroscopy (IXRF System EDS) system attachment. Accelerating voltage of 20 kV was used for the SEM imaging and SEM/EDX analyses. Weight percentage distributions and X-ray mapping of elements were determined by EDS.

3.3.3.2 X-ray Diffraction

X-ray diffraction (XRD) analysis was performed on the zeolitic (treated and untreated) to confirm the crystal structure and the identity of the components of the zeolitic material. XRD patterns of thin films were determined by means of multipurpose Rigaku D/Max-2200/PC Model difractometer with a Cu K_{α} radiation by using multipurpose thin film attachment. Measurements were performed by applying 40 kV voltages and 36 mA current.

3.3.3.3 Specific Surface Area

The BET specific surface areas were determined by standard multipoint techniques of nitrogen adsorption using a NOVA 2200e Surface Area & Pore Size Analyzer instrument. The untreated and modified clinoptilolite were heated at $60^{o}C$ for 12 h before specific surface areas were measured.

3.3.4 The Arsenates Uptake by Batch Tests

Five hundred milligram of GC, GCNa, GCFeA, and GCFeB were put in contact with 50 mL of 0.1 mg L^{-1} Na_2HAsO_4 solutions at pH 6.5 under agitation from 5 min to 24 h at room temperature ($20^{o}C$). The zeolitic materials were separated by centrifugation and HCl was added to the liquid phases to obtain a pH value of 2 to conserve the samples until the arsenic was detected. The amount of arsenate adsorbed was calculated from the following equation:

$$q = \frac{(C_0 - C_e)V}{m} \tag{3.2}$$

where q is the arsenate adsorbed (µg g^{-1}), C_0 is the initial concentration of arsenate (µg L^{-1}), C_e is the concentration of arsenate in solution at equilibrium time (µg L^{-1}), V is the solution volume (L), and m is the adsorbent dosage (g).

3.3.4.1 Sorption Isotherm Study

GCFeA and GCFeB were chosen in order to determine the isotherms. For this purpose samples from 25 to 600 mg of each conditioned natural zeolite were treated with 100 μg L^{-1} Na_2HAsO_4 solution for 1 h at 20°C and pH 6.5. The experimental data was fitted by the Langmuir and Freundlich adsorption models.

3.3.4.2 Kinetic Study

Kinetic studies of adsorption were also carried out at three initial arsenate concentrations as a function of time. The pseudo first-order, and pseudo second-order models were used for kinetic modelling studies.

3.3.4.3 Desorption and Regeneration Experiments

HCl (0.1 N) and NaOH (0.1 N) solutions are prepared in order to conduct desorption experiments. Following reaction to remove arsenic from solution, the zeolite (GCFeA) is separated from solution and added to 50 ml of HCl and NaOH solution. Bottles were shaken in a rotary shaker fixed at 200 rpm for 24 h at room temperature. The solids were filtered and filtrates were analyzed in order to find out desorbed As(V). The desorption efficiency was calculated as the difference between the amount of As(V) sorbed and that of desorbed. The zeolite is again treated with an arsenic solution (100 μg L^{-1}) as explained earlier to evaluate the efficiency after regeneration.

3.3.5 The Arsenate Uptake in a Packed Bed Reactor

The continuous adsorption studies were carried out in a clean and dry glass column of 1.25 cm internal diameter and a total length of 33.5 cm. The schematic diagram of the packed bed reactor is shown in Figure 3.4. A mass of 14.073 g of the GCFeA was packed in the column and the effective depth of the medium was 22 cm. The bed volume was equal to 0.027 L. Before the arsenic solution was passed through the column, the column was saturated with deionized water (pH = 7). Then, the arsenate solution (pH = 6.5) of 100 μg L^{-1} initial concentration was passed through the column in a down-flow mode at a flow rate of 2.8 mL per minute until the column reached a breakthrough concentration. The flow rate of the solution was checked regularly. The pumping was contiuned till there was no further adsorption. It was calculated that the empty bed contact time (EBCT) was 9.6 min, the surface loading rate was 2.28 mL $(cm^2.min)^{-1}$. Effluent samples were collected at different time intervals and were analyzed for arsenic.

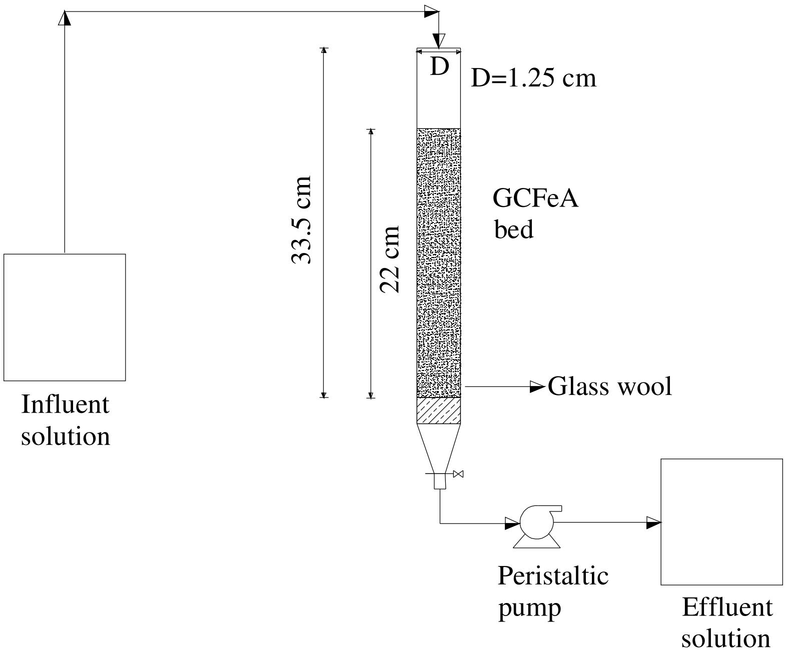


Figure 3.4 The schematic diagram of the column experiment.

In this study, the breakthrough point and numbers of bed volume (BV) were used to compare and evaluate the adsorption performance of GCFeA bed under various conditions. The breakthrough point is defined as the time interval at which the effluent concentration (*C*) from the column is about 0.1% of the influent concentration (C_0). The number of bed volume is obtained as a ratio as shown below:

$$BV = \frac{volume\ of\ the\ solution\ treated}{volume\ of\ the\ adsorbent\ bed} \qquad (3.3)$$

3.3.5.1 Desorption and Regeneration Studies of the Packed Bed Reactor

To retrieve the GCFeA adsorbent and reuse saturated column, regeneration experiments were conducted by pumping 0.1 M of NaOH as desorption solution through exhausted column. NaOH solution was passed through the packed bed reactor downward at 2.8 mL per minute using a peristaltic pump.

3.3.6 Analytical Methods

The determination of arsenic and iron in the influent and effluent was analyzed in the same way as explained in part 3.1.3.

3.4 Arsenic Removal from Real Groundwater

3.4.1 Reagents

Physical and chemical composition of the real groundwater in Sasalı used in the study is shown in Table 3.6. In the experimental studies, this arsenic contaminated groundwater was used after diluted or non-diluted until desire concentration. Sodium hypochlorite (NaOCl) was used for chlorination. Arsenic removal from drinking water by coagulation and flocculation, lime softening, and adsorption was carried out using the same chemicals as explained in part 3.1.1, 3.2.1, and 3.3.1, respectively.

Table 3.6 Characterization of Sasalı groundwater used for experiment

Components	**Concentration**
Arsenic, $\mu g\ L^{-1}$	951
pH	8.2
Turbidity, NTU	-
Nitrate, mg L^{-1}	0.005
Iron, mg L^{-1}	0.011
Aluminum, mg L^{-1}	0.001
Manganese, mg L^{-1}	0.018
Sodium, mg L^{-1}	307.1
Conductivity, $\mu S\ cm^{-1}$	1219
Sulfate, mg L^{-1}	90.34
Phosphate, mg L^{-1}	0.284
Vanadium, mg L^{-1}	0.023
Calcium, mg L^{-1}	4.405
Magnesium, mg L^{-1}	6.219
Hardness, mg$CaCO_3$ L^{-1}	5.29

3.4.2 Experimental Procedure

Groundwater was purged from well for several minutes until turbidity levels stabilized and water was collected and stored in polyethylene containers. Groundwater was chlorinated to 1 mg L^{-1} chlorine to ensure oxidation of As(III) to As(V). For this aim sodium hypoclorite was added to each 1 L jar containing the groundwater with mixing at 90 ± 2 rpm. After that the same experimental procedure as explained in part 3.1.2, 3.2.2, and 3.3.5 was applied for coagulation and flocculation, lime softening and adsorption, respectively.

3.4.3 Analytical Methods

The determination of arsenic and iron in the influent and effluent was analyzed in the same way as explained in part 3.1.3

CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Results of Arsenic Removal by Precipitation/Coprecipitation Method

4.1.1 Response Surface Experimental Design Results

Removal of arsenate (As(V)) from drinking water was investigated by precipitation/coprecipitation using different coagulants. The effects of important operating variables on percent As(V) removal was investigated by using Box-Behnken statistical experiment design. Experimental results of experimental data points used in Box-Behnken statistical design methods for iron salts and aluminum sulfate are presented in Table 4.1 and Table 4.2, respectively.

Table 4.1 Experimental results of Box-Behnken statistical design methods for iron salts

Run	**Initial As Concentration (μg L^{-1})**	**Coagulant Dose (mg L^{-1})**	**pH**	**Efficiency (%)**		
				$FeCl_3$	**$Fe_2(SO_4)_3$**	**$FeSO_4$**
1	1000	30.25	4	10.00	10.4	20.70
2	10	60	6.5	90.00	30.00	0.00
3	505	30.25	6.5	94.85	94.46	30.69
4	1000	30.25	9	84.90	93.30	85.20
5	505	30.25	6.5	95.64	96.44	30.89
6	505	30.25	6.5	95.25	95.84	26.34
7	505	30.25	6.5	92.28	96.04	28.71
8	1000	0.5	6.5	0.00	9.00	24.60
9	505	0.5	9	0.00	6.34	21.78
10	10	30.25	9	50.00	70.00	30.00
11	505	30.25	6.5	94.46	97.23	27.92
12	10	0.5	6.5	0.00	0.00	0.00
13	505	0.5	4	2.57	5.15	21.58
14	10	30.25	4	10.00	0.00	0.00
15	505	60	9	97.23	94.46	94.06
16	505	60	4	4.36	4.95	27.92
17	1000	60	6.5	98.10	98.10	30.10

Table 4.2 Experimental results of experimental data points used in Box-Behnken statistical design methods for aluminum sulfate

Run	**Initial As Concentration (μg L^{-1})**	**Coagulant Dose (mg L^{-1})**	**pH**	**Efficiency (%)**
				$Al_2(SO_4)_3$
1	1000	40.25	4	37.30
2	10	80	6.5	90.00
3	505	40.25	6.5	95.25
4	1000	40.25	9	84.40
5	505	40.25	6.5	95.45
6	505	40.25	6.5	95.64
7	505	40.25	6.5	94.65
8	1000	0.5	6.5	14.70
9	505	0.5	9	13.07
10	10	40.25	9	70.00
11	505	40.25	6.5	96.44
12	10	0.5	6.5	0.00
13	505	0.5	4	11.68
14	10	40.25	4	30.00
15	505	80	9	96.63
16	505	80	4	37.03
17	1000	80	6.5	99.10

The experimental data was used for the determination of the response function coefficients for each independent variable. The coefficients of the response function (Eq. 3.1) for arsenate removal efficiencies were obtained using experimental data and presented in Table 4.3.

Predicted values of percent As(V) removal were determined by the response functions with the obtained coefficients. Table 4.4 presents a comparison of experimental and predicted values using different coagulants for percent removal of As(V).

Table 4.3 Coefficients estimated for the quadratic model

Coefficients	**Values**			
	$FeCl_3$	**$Fe_2(SO_4)_3$**	**$FeSO_4$**	**$Al_2(SO_4)_3$**
b_0	-234.484	-205.18388	103.364	-172.377
b_1	0.032565	0.075553	0.034332	0.064209
b_2	1.107735	1.07981	-0.73751	1.512535
b_3	76.82133	63.37558	-34.6963	54.25078
b_{12}	0.000138	0.00100331	-0.00007639	-0.000071
b_{13}	0.007051	0.002600606	0.004949	0.001434
b_{23}	0.320807	0.29687	0.221647	0.14644
b_{11}	-0.00007098	-0.0000939231	-0.00003590	-0.0000585
b_{22}	-0.03398	-0.043741	-0.00445	-0.0191
b_{33}	-6.14048	-4.73016	2.618	-4.11268

Table 4.4 Observed and predicted As(V) removal efficiency

No.	**As(V) removal efficiency (%)**							
	$FeCl_3$		**$Fe_2(SO_4)_3$**		**$FeSO_4$**		**$Al_2(SO_4)_3$**	
	Observed	**Predicted**	**Observed**	**Predicted**	**Observed**	**Predicted**	**Observed**	**Predicted**
1	10.00	9.73	10.4	23.60	20.70	22.82	37.30	40.83
2	90.00	75.52	30.00	31.53	0.00	15.24	90.00	82.08
3	94.85	94.50	94.46	96.00	30.69	28.91	95.25	95.49
4	84.90	78.48	93.30	90.95	85.20	77.78	84.40	81.40
5	95.64	94.50	96.44	96.00	30.89	28.91	95.45	95.49
6	95.25	94.50	95.84	96.00	26.34	28.91	95.64	95.49
7	92.28	94.50	96.04	96.00	28.71	28.91	94.65	95.49
8	0.00	14.49	9.00	7.47	24.60	19.36	14.70	22.62
9	0.00	0.00	6.34	10.22	21.78	34.44	13.07	8.15
10	50.00	50.28	70.00	56.80	30.00	37.88	70.00	66.47
11	94.46	94.50	97.23	96.00	27.92	28.91	96.44	95.49
12	0.00	7.79	0.00	9.32	0.00	0.00	0.00	8.45
13	2.57	0.00	5.15	0.00	21.58	24.70	11.68	0.23
14	10.00	16.43	0.00	2.35	0.00	7.42	30.00	33.00
15	97.23	100.00	94.46	100	94.06	90.94	96.63	100.00
16	4.36	12.42	4.95	1.07	27.92	15.26	37.03	41.95
17	98.10	90.32	98.10	88.78	30.10	40.64	99.10	90.65

As(V) removal efficiencies varied between 0 and 98.10 for ferric chloride and ferric sulfate, 0 and 94.06 for ferrous sulfate and 0 and 99.10 for aluminum sulfate. The correlation coefficients (R^2) between the observed and predicted values were obtained as 0.96, 0.97, 0.92, and 0.97 for ferric chloride, ferric sulfate, ferrous sulfate, and aluminum sulfate, respectively. Predicted and experimental values of As(V) removal were in good agreement as shown in Table 4.4. The values of regression coefficient are closer to one indicates that the correlation is best suited in predicting values.

The statistical significance of the response function was checked by F-test, and the analysis of variance (ANOVA) for response surface quadratic models is summarized in Table 4.5, 4.6, 4.7, and 4.8 for ferric chloride, ferric sulfate, ferrous sulfate, and aluminum sulfate, respectively.

Table 4.5 ANOVA results of the response surface quadratic model for percentage arsenic removal using ferric chloride

Source	**Degree of freedom**	**Sum of squares**	**Mean squares**	**F value**	**p-value**
Model	9	30851.77	3427.97	20.61	0.0003
Residual	7	1164.25	166.32		
Lack of fit	3	1157.33	385.78	223.17	<0.0001
Pure error	4	6.91	1.73		
Corrected total	16	32016.01			

$R^2 = 0.9636$, Adjusted $R^2 = 0.9169$, R = 0.9816; Adequate precision = 12.443 (>4)

According to ANOVA results of response surface quadratic models for all types of coagulant as shown in Table 4.5-4.8, the predicted responses fit the well with those of the experimentally obtained responses. The model F values and very low probability values (0.0003 for ferric chloride, 0.0038 for ferrous sulfate, 0.0001 for ferric sulfate and aluminum sulfate) indicate that the models are statistically significant and there is only a 0.01% chance for ferric sulfate and aluminum sulfate, 0.38% chance for ferrous sulfate, and 0.03% chance for ferric chloride that a “Model

F value" this large could occur due to noise. The p-value of lack of fit implies the lack of fit is significant ($p = 0.0007$ for ferrous sulfate and $p < 0.0001$ for all types of coagulant except ferrous sulfate). High values of R^2 (0.9636 for ferric chloride, 0.9733 for ferric sulfate, 0.9228 for ferrous sulfate, and 0.9726 for aluminum sulfate) indicate that a high dependence and correlation between the observed and the predicted values of responses and equations are very reliable. As shown in Table 4.5 the quadratic regression for ferric chloride is significant at the level of 0.9816. The value of adjusted R^2 (0.9169) suggests that the total variation of about 92% for arsenate removal is attributed to the independent variables and only about 8% of the total variation can not be explained by the model. "Adequate Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Here the ratio of 12.443 indicates an adequate signal.

The quadratic regression for ferric sulfate is significant at the level of 0.9866 as shown in Table 4.6. The value of adjusted R^2 (0.9389) suggests that the total variation of about 94% for arsenate removal is attributed to the independent variables and only about 6% of the total variation can not be explained by the model. Adequate Precision ratio of 13.371 indicates an adequate signal.

Table 4.6 ANOVA results of the response surface quadratic model for percentage arsenic removal using ferric sulfate

Source	Degree of freedom	Sum of squares	Mean squares	F value	p-value
Model	9	30744.63	3416.07	28.31	0.0001
Residual	7	844.68	120.67		
Lack of fit	3	840.57	280.19	273.01	<0.0001
Pure error	4	4.11	1.03		
Corrected total	16	31589.31			

$R^2 = 0.9733$, Adjusted $R^2 = 0.9389$, $R = 0.9866$; Adequate precision = 13.371 (>4)

Similarly, as shown in Table 4.7 the quadratic regression for ferrous sulfate is significant at the level of 0.9606. The value of adjusted R^2 (0.8235) suggests that the total variation of about 82% for arsenate removal is attributed to the independent variables and about 18% of the total variation can not be explained by the model. Adequate Precision ratio of 12.775 indicates an adequate signal.

Table 4.7 ANOVA results of the response surface quadratic model for percentage arsenic removal using ferrous sulfate

Source	**Degree of freedom**	**Sum of squares**	**Mean squares**	**F value**	**p-value**
Model	9	8972.42	996.94	9.29	0.0038
Residual	7	750.93	107.28		
Lack of fit	3	736.22	245.41	66.71	0.0007
Pure error	4	14.71	3.68		
Corrected total	16	9723.36			

R^2 = 0.9228, Adjusted R^2 = 0.8235, R = 0.9606; Adequate precision = 12.775 (>4)

Finally, the quadratic regression for aluminum sulfate is significant at the level of 0.9862 as shown in Table 4.8. The value of adjusted R^2 (0.9375) suggests that the total variation of about 94% for arsenate removal is attributed to the independent variables and only about 6% of the total variation can not be explained by the model. Adequate Precision ratio of 14.899 indicates an adequate signal.

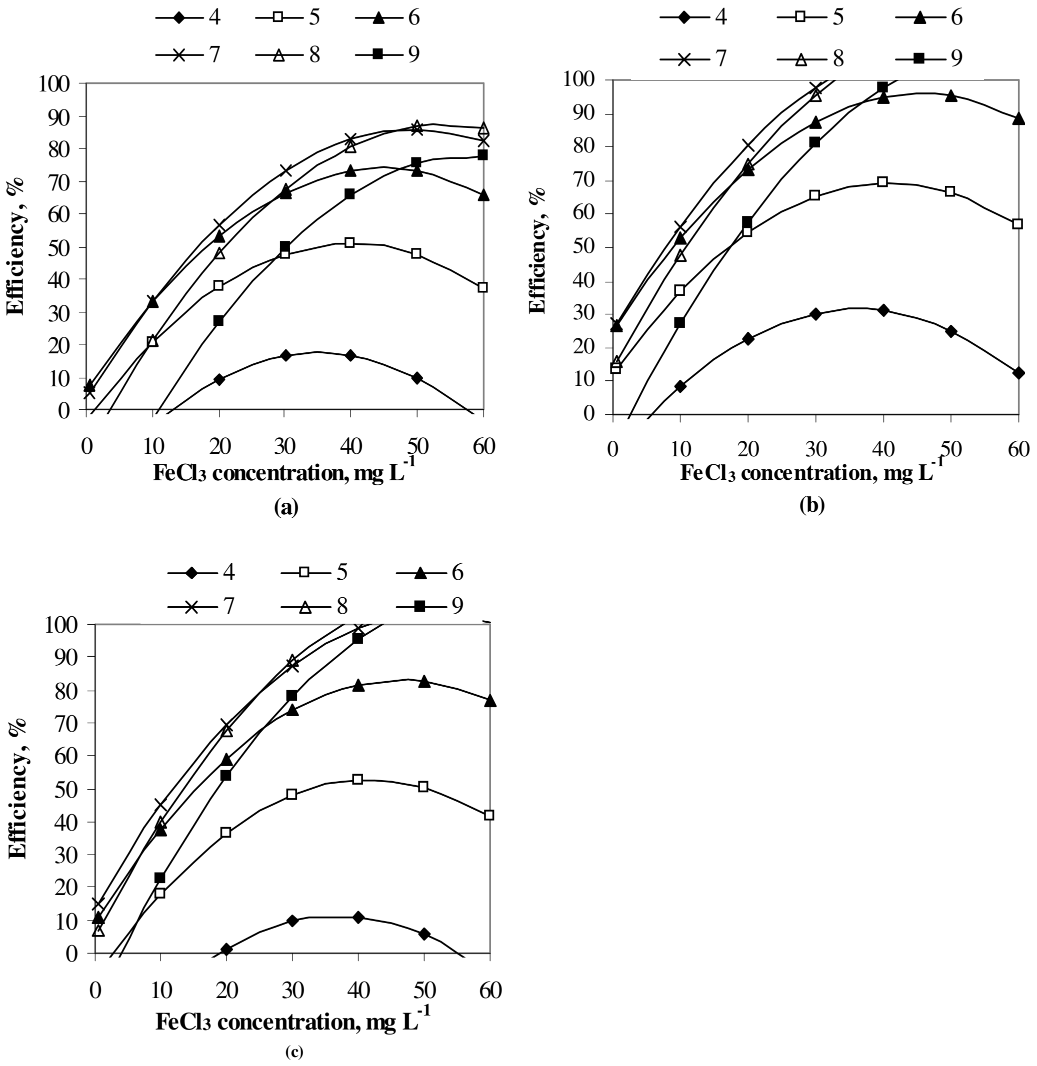
Table 4.8 ANOVA results of the response surface quadratic model for percentage arsenic removal using aluminum sulfate

Source	**Degree of freedom**	**Sum of squares**	**Mean squares**	**F value**	**p-value**
Model	9	22172.04	2463.56	27.65	0.0001
Residual	7	623.57	89.08		
Lack of fit	3	621.89	207.30	490.72	<0.0001
Pure error	4	1.69	0.42		
Corrected total	16	22795.62			

R^2 = 0.9726, Adjusted R^2 = 0.9375, R = 0.9862; Adequate precision = 14.899 (>4)

4.1.1.1 Effect of pH

In order to determine the effect of pH on arsenate removal efficiency, some experiments were executed. Figure 4.1(a-c) depicts the variation of percent arsenate removal with the ferric chloride dose at different pH and a different initial arsenate concentration of 10, 500, and 1000 μg L^{-1}. Percent arsenate removal increased with increasing pH content up to nearly 7.3, 7.5, and 7.7 for initial arsenate concentration of 10, 500, and 1000 μg L^{-1}, respectively.



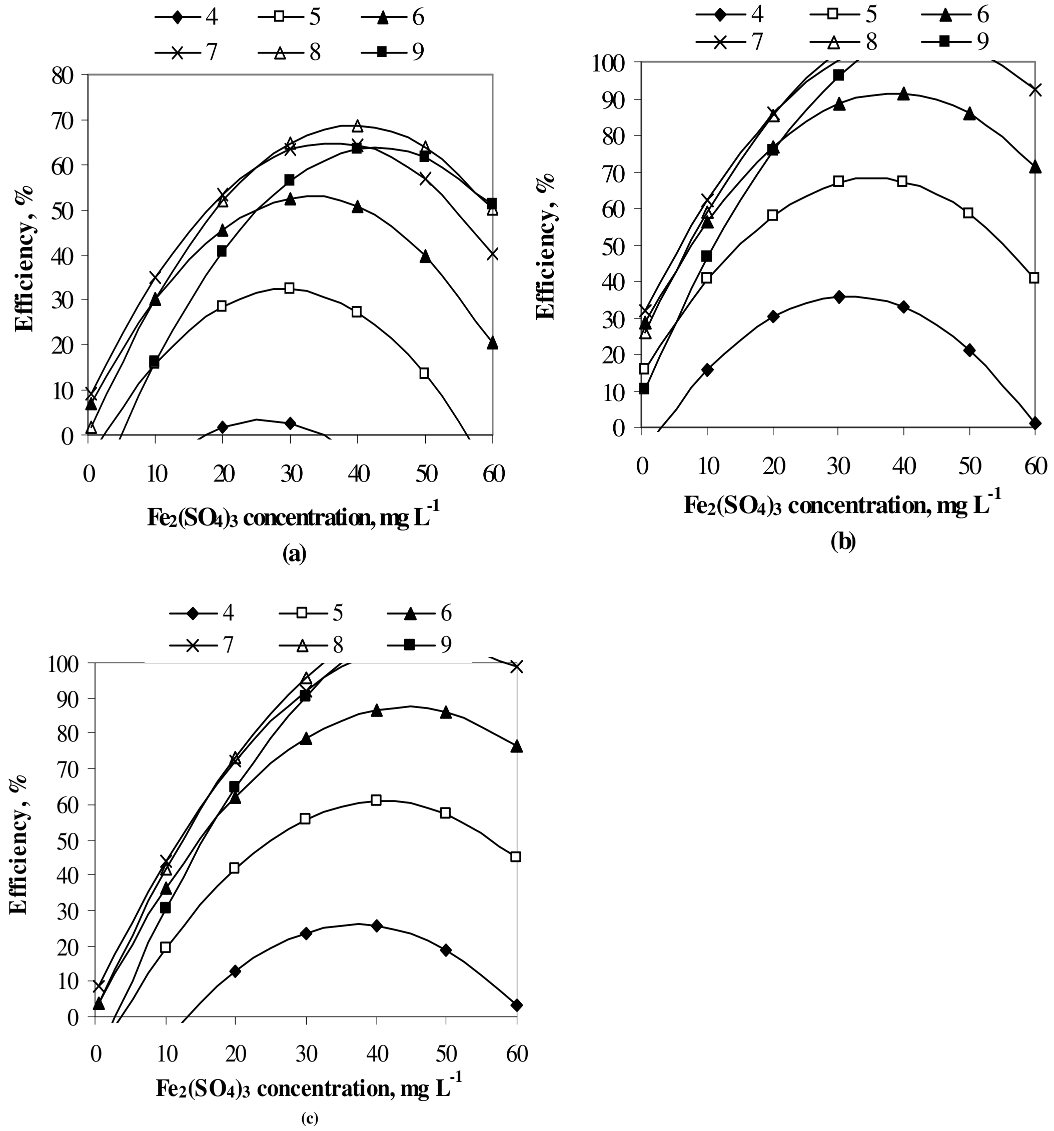
(a)

(b)

(c)

Figure 4.1 Variation of percent arsenate removal with the ferric chloride dose at different pH and constant initial arsenate concentration of a) 10 μg L^{-1}; b) 500 μg L^{-1}; c) 1000 μg L^{-1}.

Similarly, variations of percent arsenate removals with $Fe_2(SO_4)_3$, $FeSO_4$, and $Al_2(SO_4)_3$ concentration at different pH and different initial arsenate concentration of 10, 500, and 1000 μg L^{-1} are depicted in Figure 4.2(a-c), Figure 4.3(a-c), and Figure 4.4(a-c), respectively. For ferric sulfate percent arsenate removal increased with increasing pH about 8 for initial arsenate concentrations of 10 and 1000 μg L^{-1}, and 7.8 for 500 μg L^{-1}. As it can be seen in Figure 1(a-c) and 2(a-c), in the high acidic and high alkaline pH for Fe(III) caused lower efficiencies.



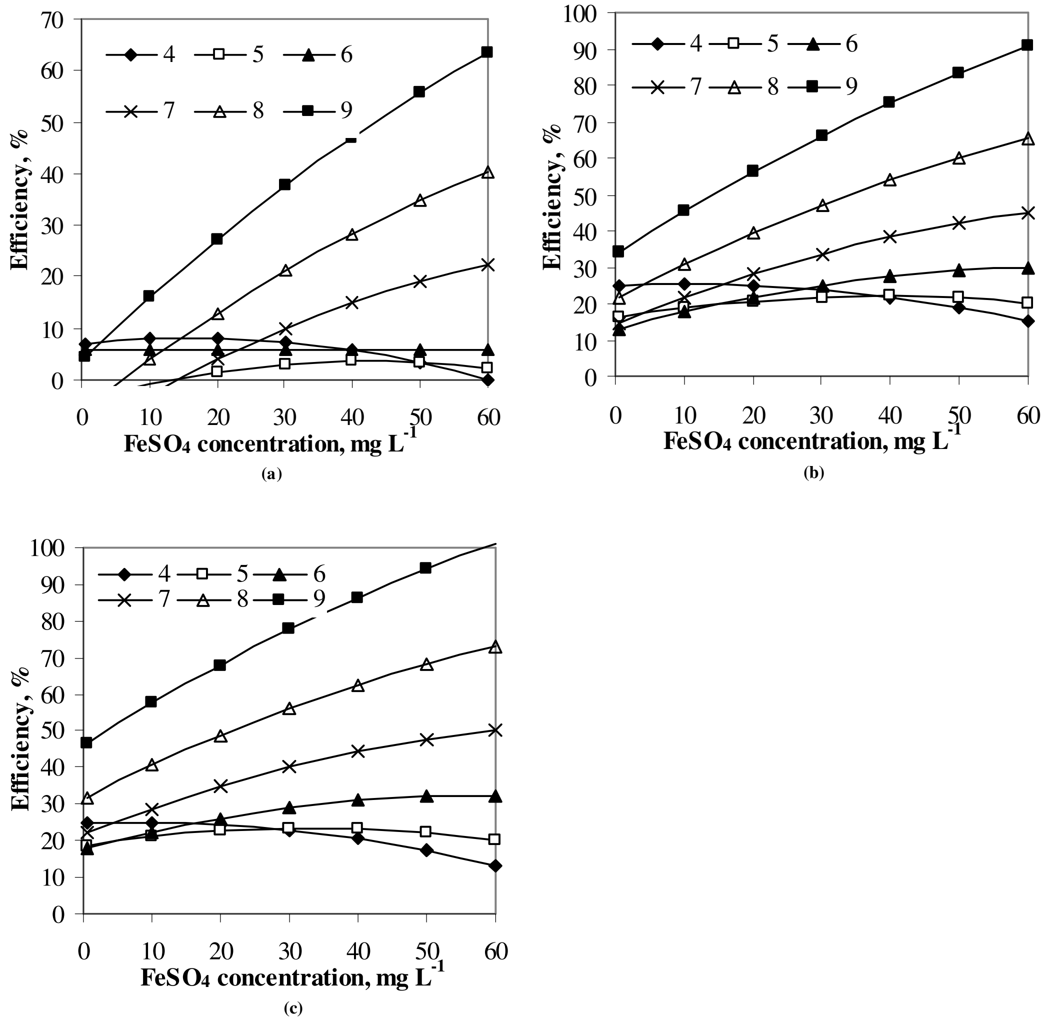
(a)

(b)

(c)

Figure 4.2 Variation of percent arsenate removal with the ferric sulfate dose at different pH and constant initial arsenate concentration of a) 10 μg L^{-1}; b) 500 μg L^{-1}; c) 1000 μg L^{-1}.

For ferrous sulfate, at the initial arsenate concentrations of 10, 500, and 1000 μg L^{-1}, maximum arsenate removal efficiency was obtained at the same pH of 9 because of the ferrous sulfate forms ferrous hydroxide in the alkaline range. The arsenate removal efficiency decreased at neutral and acidic pH values.



(a)

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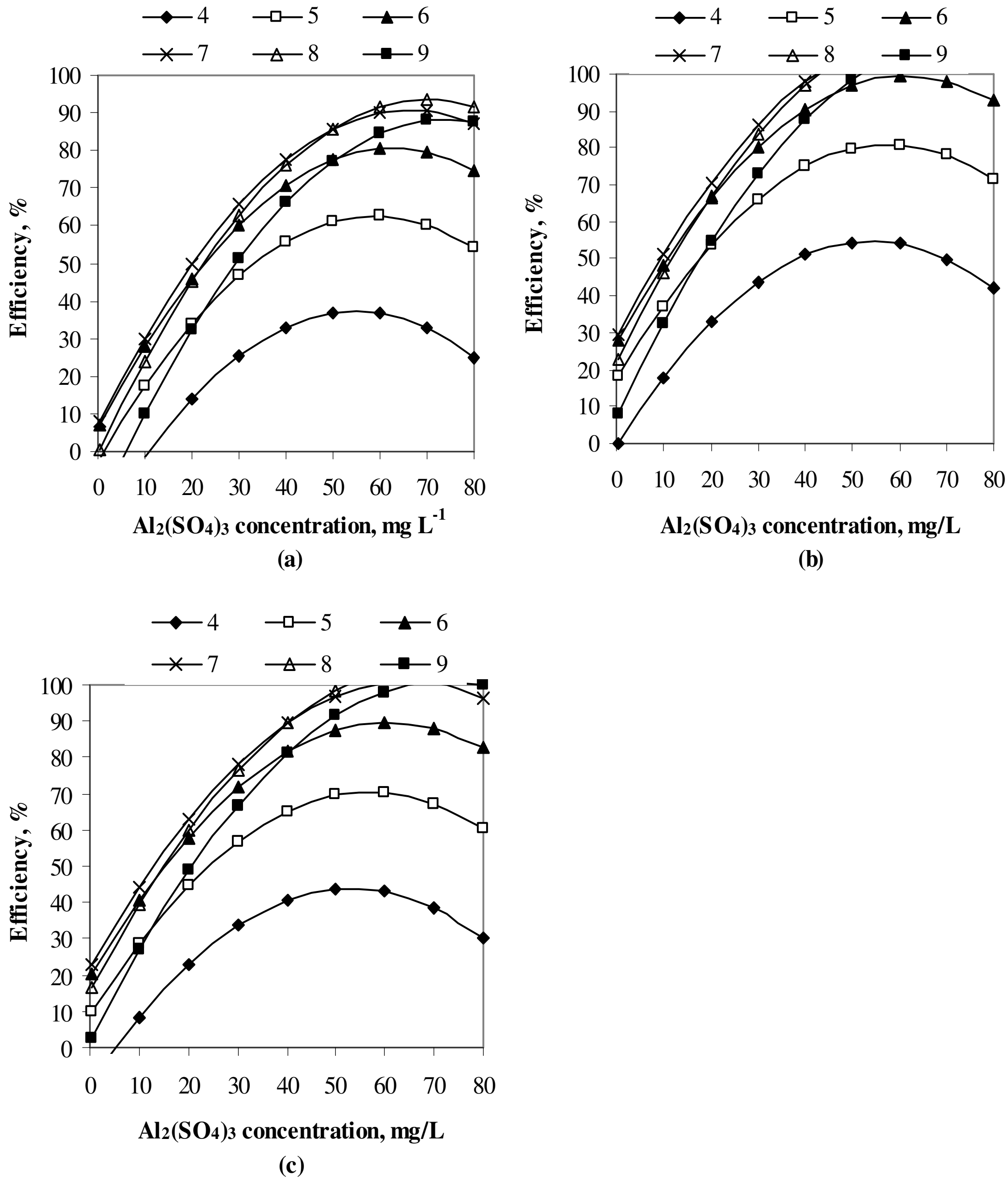
Figure 4.3 Variation of percent arsenate removal with the ferrous sulfate dose at different pH and constant initial arsenate concentration of a) 10 μg L^{-1}; b) 500 μg L^{-1}; c) 1000 μg L^{-1}.

Finally for aluminum sulfate, maximum arsenate removal efficiency was provided at nearly 7, 7.4, and 7.3 for initial arsenate concentrations of 10, 500, and 1000 μg L^{-1}, respectively. In the high acidic pH, the arsenate removal efficiency declined sharply. Similarly, high alkaline pH above 8 caused lower efficiencies.



(a) (b)

(c)

Figure 4.4 Variation of percent arsenate removal with the aluminum sulfate dose at different pH and constant initial arsenate concentration of a) 10 μg L^{-1}; b) 500 μg L^{-1}; c) 1000 μg L^{-1}.

pH value was prominently effective for arsenate removal efficiency. As it can be seen from the Figure 4.1-4.4, percent arsenate removal increased with increasing pH content up to nearly 7.5, 8, 9, and 7 for ferric chloride, ferric sulfate, ferrous sulfate, and aluminum sulfate, respectively. The obtained optimum pH values from this study are in good agreement with the values given in the literatures (Gregor, 2001; Han et al., 2002; Hering et al., 1997; Lee et al., 2003; Pande et al., 1997; Saha et al., 2001; Sancha, 2006; Song et al., 2006; Wickramasinghe et al., 2004; Zouboulis and

Katsoyiannis, 2002). The effect of the pH range on the arsenate removal efficiency is related to the solubility of the amorphous hydroxide solid of iron and aluminum. Arsenate removal efficiency increased since the amorphous hydroxide solid is stable in this pH range.

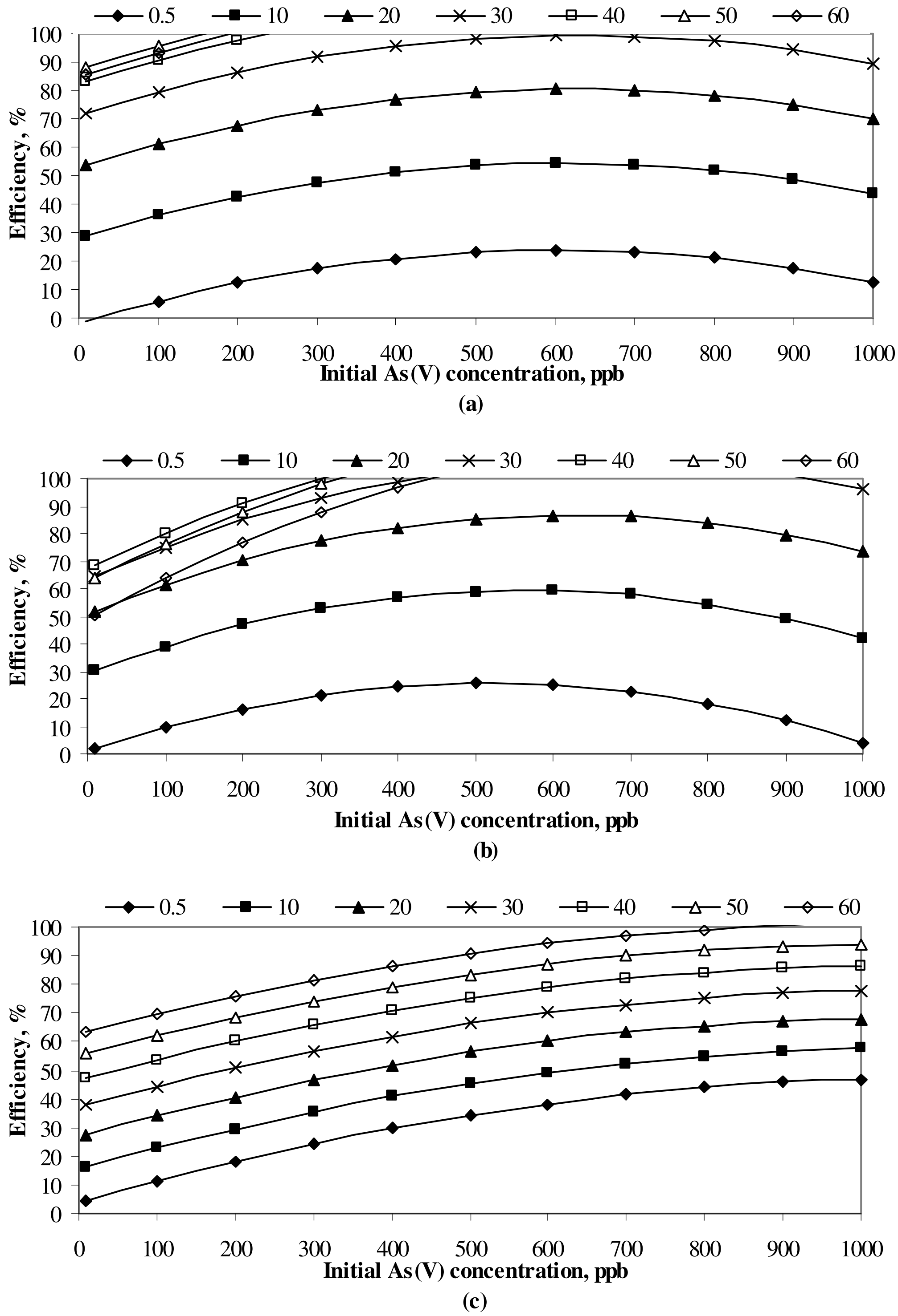
4.1.1.2 Effects of Coagulants and Initial As(V) Concentrations

According to results of Box-Behnken experimental design method for ferrous sulfate (as a source of Fe(II)), ferric chloride, ferric sulfate (as a source of Fe(III)), and aluminum sulfate, optimum pH values for maximum arsenate removal were found as 9, 7.5, 8, and 7, respectively. Figure 4.5(a-c) shows the variations of percent arsenate removals with initial arsenate concentrations at different $FeCl_3$, $Fe_2(SO_4)_3$, and $FeSO_4$, concentrations and constant pH of 7.5, 8, and 9, respectively.

Pentavalent arsenic exists in anionic form of $H_2AsO_4^-$, $HAsO_4^{2-}$ or AsO_4^{3-} above the pH of 2. Thus, addition of iron coagulants to water could facilitate the conversion of soluble arsenic species to insoluble reaction products (McNeill and Edwards, 1997). These products might form through three major steps: (i) precipitation in forms of $Fe(AsO_4)$ solid; (ii) coprecipitation where soluble arsenic species were incorporated into a growing hydroxide phase via inclusion, occlusion, or adsorption; and (iii) adsorption involving the formation of surface complexes between soluble arsenic and the solid hydroxide surface site. In terms of arsenic removal from drinking water, however, precipitation may not contribute significantly toward the overall performance. This is because thermodynamics analysis on Fe and As has suggested that $Fe(AsO_4)$ solid could be easily formed in arsenic contaminated drinking water source (Edwards, 1994; McNeill and Edwards, 1997). The possible reactions of arsenate with hydrous iron oxide are shown below where $\equiv FeOH^0$ represents oxide surface site (Ahmed, 2001; Hering, Chen, Wilkie, Elimelech, and Liang, 1996):

$$Fe(OH)_3 + H_3AsO_4 \rightarrow FeAsO_4.2H_2O + H_2O$$
$$\equiv FeOH^0 + AsO_4^{3-} + 3H^+ \rightarrow \equiv FeH_2AsO_4 + H_2O$$

$$\equiv FeOH^0 + AsO_4^{3-} + 2H^+ \rightarrow \equiv FeHAsO_4^- + H_2O$$



(a)

(b)

(c)

Figure 4.5 Variations of percent arsenate removals with initial arsenate concentrations at different a) $FeCl_3$ concentrations and constant pH of 7.5, b) $Fe_2(SO_4)_3$ concentrations and constant pH of 8, c) $FeSO_4$ concentrations and constant pH of 9.

Figure 4.6 shows the variations of percent arsenate removals with initial arsenate concentrations at different $Al_2(SO_4)_3$ concentrations and constant pH of 7. During coagulation with aluminum sulfate, arsenic is removed through three main mechanisms including precipitation, coprecipitation, and adsorption. The formation of the insoluble compounds $Al(AsO_4)$ is seen in first step. In coprecipitation, the soluble arsenic species is incorporated into a growing metal hydroxide phase via inclusion, occlusion, or adsorption. Finally, soluble arsenic is binded electrostatically to the external surfaces of the insoluble metal hydroxide. All three of these mechanisms can independently contribute towards arsenic removal. Because of the $Al(AsO_4)$ solid could not be easily formed in arsenic contaminated drinking water source, precipitation may not contribute significantly toward the overall performance. However, coprecipitation and adsorption are both active arsenic removal mechanisms (Edwards, 1994; Johston et al., 2001; McNeill and Edwards, 1997; Yuan et al., 2003). Aluminum sulfate dissociates in water and forms aluminum hydroxide, which coprecipitates with arsenic. The possible chemical equations of aluminum sulfate coagulation are as follows (Ahmed, 2001; Vu, Kaminski, and Nunez, 2003):

$Al_2(SO_4)_3.18H_2O \rightarrow 2Al^{+3} + 3SO_4^{2-} + 18H_2O$ Aluminum sulfate dissolution

$2Al^{3+} + 6H_2O \rightarrow 2Al(OH)_3 + 6H^+$ Aluminum precipitation

$H_2AsO_4^- + Al(OH)_3 \rightarrow$ Al-As complex Coprecipitation

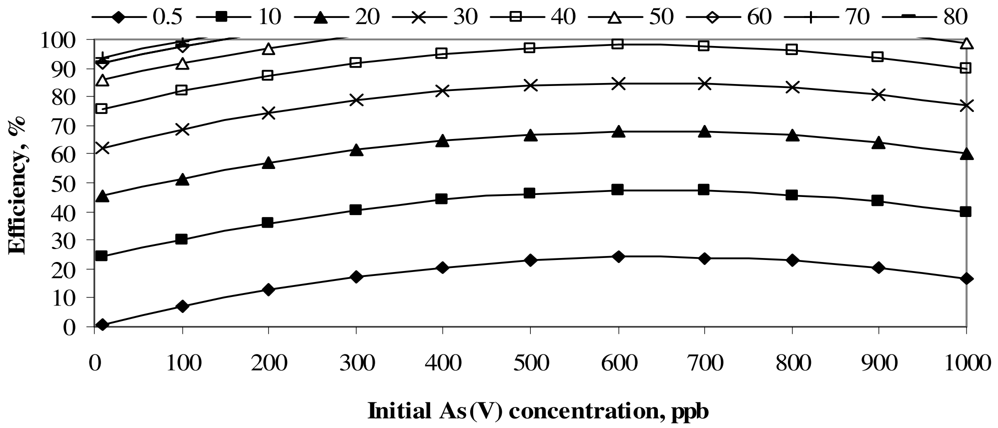


Figure 4.6 Variations of percent arsenate removals with initial arsenate concentrations at different $Al_2(SO_4)_3$ concentrations and constant pH of 7.

Coagulant concentration is important in determining the level of arsenic removal. It was found in this study that the addition of coagulant caused a substantial increase in the arsenate removal because the addition of coagulants facilitate the removal arsenate from the aqueous stream, by converting the soluble As(V) species into insoluble products. When the ferric or aluminum salts dose is increased more iron or aluminum oxide is formed, leading to a greater surface area for arsenate adsorption and a lower residual arsenic concentration (Wickramasinghe et al., 2004). But above a certain ferric chloride, ferric sulphate, and aluminum sulfate dosage, the increase in arsenate removal was not significant. $FeCl_3$ dose above 40 mg L^{-1}, $Fe_2(SO_4)_3$ dose above 30 mg L^{-1}, and $Al_2(SO_4)_3$ dose above 50 mg L^{-1} slightly increased percent arsenate removal. For ferrous sulfate, maximum arsenate removal efficiency was obtained at maximum coagulant dose. Percent arsenate removal increased with increasing coagulant concentration as a result of increasing amount of coagulant with increasing rate or kinetics of particle aggregation and floc formation.

For the initial arsenate concentration of 10, 500 and 1000 µg L^{-1}, obtained highest arsenate removal efficiencies in the optimum pH and the optimum coagulant dose are shown in Table 4.9. In the low initial arsenate concentrations, the highest arsenate removal efficiency was required high coagulant dose because of the difficulty in inducing collision between the colloids. However in the high initial arsenate concentrations, the highest arsenate removal efficiency was provided at low coagulant dose. The coagulant required was relatively small due to higher collision probabilities of the colloids in the high arsenate concentrations.

Table 4.9 Obtained highest arsenate removal efficiencies in the optimum pH and the coagulant dose

Coagulant Type	**Optimum pH**	**Initial As(V) concentrations, µg L^{-1}**					
		10		**500**		**1000**	
		Dose mg L^{-1}	**Efficiency %**	**Dose mg L^{-1}**	**Efficiency %**	**Dose mg L^{-1}**	**Efficiency %**
$FeCl_3$	7.5	50	88	31	100	37	100
$Fe_2(SO_4)_3$	8	40	70	28	100	32	100
$FeSO_4$	9	60	63	60	91	58	100
$Al_2(SO_4)_3$	7	66	91	42	100	56	100

For the determination of the most effective and economic coagulant type on arsenate removal from drinking water, obtained results for different coagulants were compared. Variations of percent arsenate removals with the coagulant concentration for each one of the coagulants as a function of optimum pH of coagulants and constant initial arsenate concentration of 500 μg L^{-1} are depicted in Figure 4.7. The addition of coagulants caused a substantial increase in the arsenate removal. As it can be seen Fe(III) ions are more effective and economic than Fe(II) ion and ferric chloride is more effective and economic than aluminum sulfate due to required lower coagulant dose and pH.

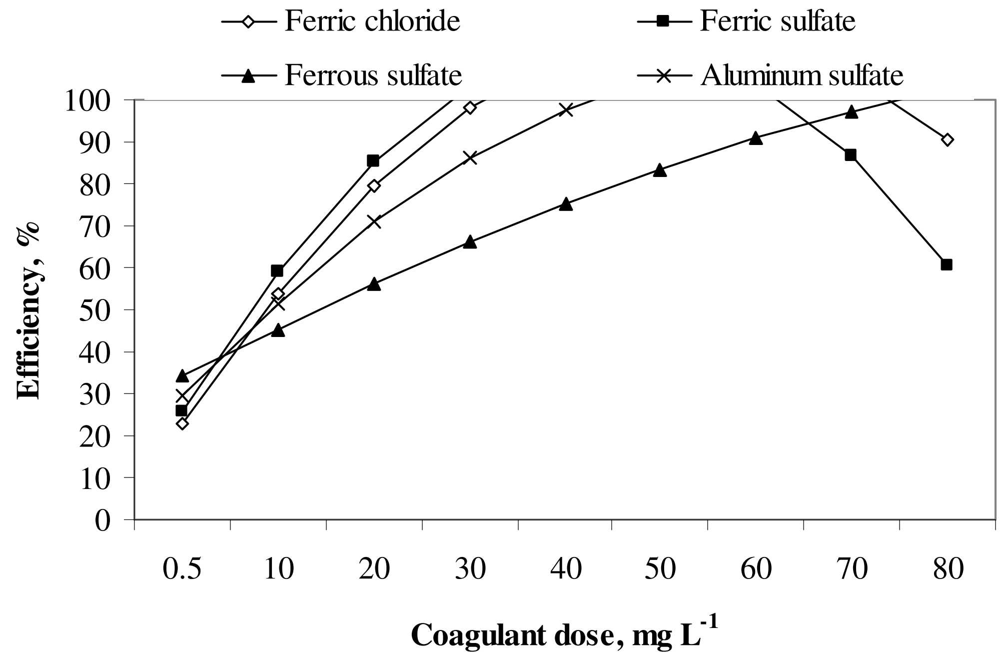


Figure 4.7 Variations of percent arsenate removals with the coagulant dose for each one of coagulants at optimum pH and constant initial arsenate concentration of 500 μg L^{-1}.

The obtained results are consistent with the previous observations on arsenate removal from drinking water using ferric salts and aluminum sulfate. The previous studies on coagulation with aluminum and ferric salts for arsenic removal showed that ferric salts have been found to be more effective than aluminum salts on a weight basis (Gregor, 2001; Han et al., 2002; Hering et al., 1997; Kammoun et al., 2008; Kang et al., 2003; Wickramasinghe et al., 2004; Yuan et al., 2003; Zoubolulis and Katsoyiannis, 2002). This difference may be attributed to incomplete precipitation of added aluminum as the amorphous hydroxide solid because iron is more soluble than aluminum in water (Zoubolulis and Katsoyiannis, 2002; Hering et al., 1997; McNeill and Edwards, 1997).

4.1.2 Model Validation and Confirmation

In order to test reliability of the response functions predictions and determine the accuracy of the predicted model, three experiments different from Box-Behnken experimental design points for all types of coagulant were carried out. The experiments points were within the range of independent variables but different from design points of Box-Behnken. In one of them, the aforementioned optimum coagulant dose and pH at the initial arsenate concentration of 500 μg L^{-1} for all types of coagulant was used.

The results of experiments and Box-Behnken response functions predictions were compared in Table 4.10. Validation experiments confirmed the suitability and the accuracy of the model. As it can be seen, response functions predictions were in good agreement with the experimental results. Therefore, Box-Behnken statistical design method was reliable and effective in determining the optimum conditions and this study provided useful information and reference conditions that Box-Behnken experimental design method may be used to optimize other chemical processes.

Table 4.10 Comparison of the experimental and predicted values for different Box-Behnken experimental design points

Coagulant type: $FeCl_3$				
As(V) concentration (µg L^{-1})	**Coagulant dose (mg L^{-1})**	**pH**	**Efficiency, %**	
			Observed	**Predicted**
50	30	7.5	80	75
500	31	7.5	98	100
100	20	7	60	64
Coagulant type: $Fe_2(SO_4)_3$				
As(V) concentration (µg L^{-1})	**Coagulant dose (mg L^{-1})**	**pH**	**Efficiency, %**	
			Observed	**Predicted**
50	40	8	80	75
500	28	8	99	100
100	15	7	59	54
Coagulant type: $FeSO_4$				
As(V) concentration (µg L^{-1})	**Coagulant dose (mg L^{-1})**	**pH**	**Efficiency, %**	
			Observed	**Predicted**
50	60	9	72	66
500	60	9	95	91
100	40	7.5	34	28
Coagulant type: $Al_2(SO_4)_3$				
As(V) concentration (µg L^{-1})	**Coagulant dose (mg L^{-1})**	**pH**	**Efficiency, %**	
			Observed	**Predicted**
50	50	7	85	88
500	42	7	99	100
100	30	8	65	69

4.1.3 Arsenic Removal Efficiency Considering Residual Iron and Aluminum

The coagulant dose has a striking influence on arsenic removal. However residual iron and aluminum concentration after sedimentation and filtration in the effluent must take into consideration because of the health effects of excess iron and aluminum in the drinking water.

Iron is an essential mineral for human health in small concentrations. Unlike lead and copper, ingesting iron from drinking water is not directly associated with adverse health effects; although, trace impurities and microorganisms that are absorbed by iron solids may pose health concerns. Aesthetic effects of iron in drinking water are undesirable tastes or odors. Iron in quantities greater than 0.3 mg L^{-1} in drinking water can cause an unpleasant metallic taste and rusty color. Physical effects of iron are damages to water equipment and reduced effectiveness of treatment for other contaminants that may present added costs to operations for water utilities. Corrosivity and staining related to corrosion not only affect the aesthetic quality of water, but may also result in distribution system problems. Among other things, corrosion of distribution system pipes can produce sediment or loose deposits that block water flow (Lytle and Schock, 2009).

The previous studies on health effects of aluminum in drinking water showed that high consumption of aluminum from drinking water may be a risk factor for Alzheimer's disease and a relationship exist between the number of diagnosed Alzheimer's disease cases and the level of aluminum present in the drinking water supply (McLachlan, Bergeron, Smith, Boomer, and Rifat, 1996; Rondeau, Jacqmin-Gadda, Commenges, Helmer, and Dartigues, 2009). The amount of aluminum present in drinking water has been recommended to be below 200 µg L^{-1} by the World Health Organization. Apparently in the initial arsenate concentration at lower concentrations, the required doses of ferric chloride, ferric sulfate, ferrous sulfate, and aluminum sulfate are high for the improve arsenate removal efficiency. Therefore residual concentration of iron and aluminum at the low initial arsenate concentration was monitored for determination the failure of the coagulation process. According to results of Box-Behnken experimental design methods, optimum pH values were found as 7.5, 8, 9, and 7 for ferric chloride, ferric sulfate, ferrous sulfate, and aluminum sulfate and the pH of the samples was adjusted as 7.5, 8, 9, and 7 for ferric chloride, ferric sulfate, ferrous sulfate, and aluminum sulfate, respectively. For initial arsenate concentration of 50 µg L^{-1} and optimum pH values of coagulants, the results of experiments and Box-Behnken response functions predictions were compared in Table 4.11. As it can be seen, response functions predictions were in good agreement with the experimental results.

Table 4.11 Comparison of the experimental and predicted percent arsenate removal for the initial arsenate concentration of 50 µg L^{-1}

Coagulant Type	**Coagulant Dose, mg L^{-1}**	**pH**	**Efficiency, %**	
			Observed	**Predicted**
$FeCl_3$	30	7.5	80	75
	35		88	82
	40		93	87
	45		96	90
$Fe_2(SO_4)_3$	30	8	68	70
	35		70	73
	40		72	74
	45		71	73
$FeSO_4$	80	9	83	79
	85		86	81
	90		89	84
	95		92	86
$Al_2(SO_4)_3$	40	7	74	80
	45		80	85
	50		85	88
	55		87	91

Effect of coagulant dosage on the arsenic removal efficiency and relationship between coagulant dose and residual iron and aluminum for initial arsenate concentration of 50 µg L^{-1} are shown in Figure 4.8(a-d). As it can be seen, after coagulation and flocculation experiments using ferric chloride, ferrous sulfate, and aluminum sulfate residual arsenate concentrations were decreased below 10 µg L^{-1} which is the maximum contaminant level of arsenic in drinking water determined by USEPA and WHO. However this efficiency was obtained for ferric chloride at concentration of 30 mg L^{-1}, while it was provided at coagulant dose of 45 mg L^{-1} for aluminum sulfate and 80 mg L^{-1} for ferrous sulfate. Maximum arsenate removal efficiency was achieved as 72% at $Fe_2(SO_4)_3$ concentration of around 40 mg L^{-1}.

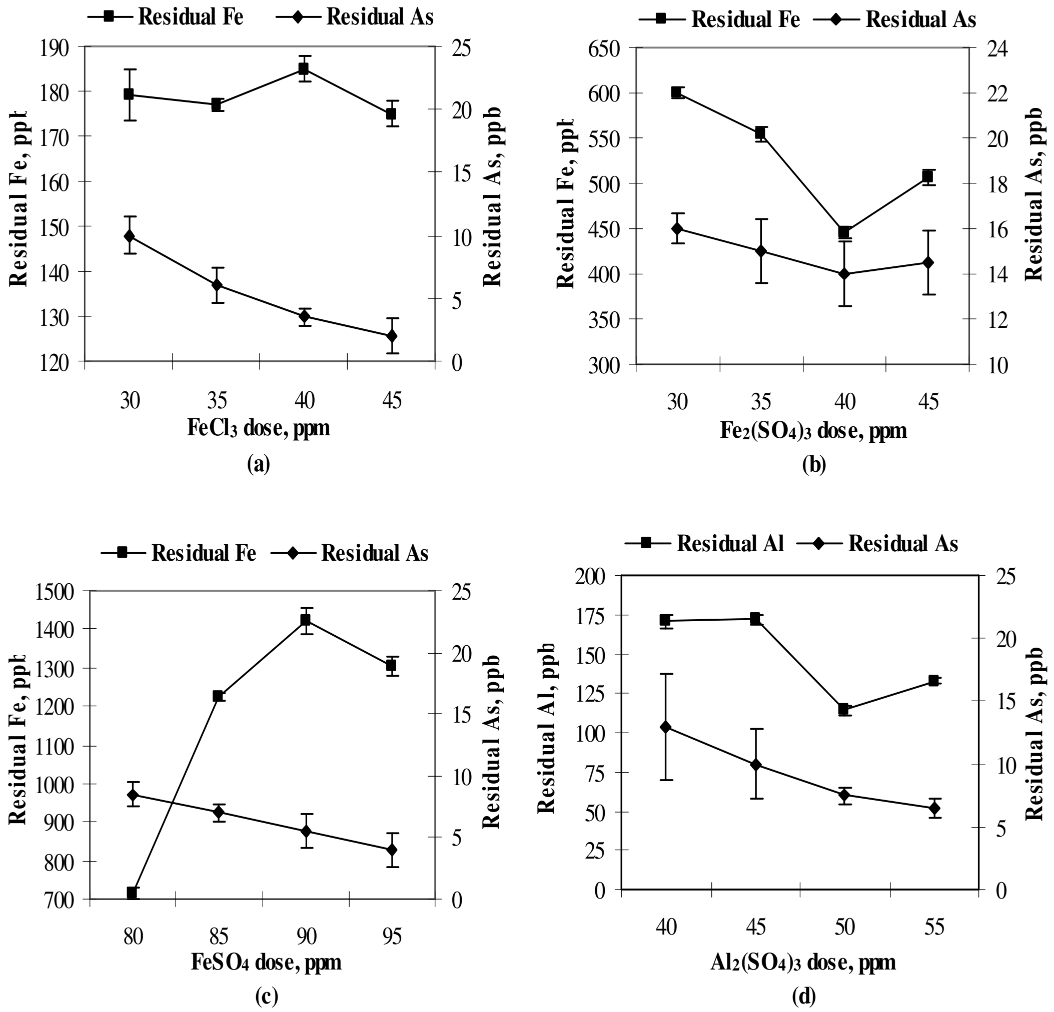


Figure 4.8(a-d) Effect of a) ferric chloride b) ferric sulfate c) ferrous sulfate d) aluminum sulfate dose on the arsenic removal efficiency and relationship between coagulant dose and residual iron or aluminum.

Effect of ferric chloride, ferric sulfate, and ferrous sulfate dosages on the iron residuals is also shown in Figure 4.8(a-c). It appears that residual iron increases with increasing ferric chloride and ferrous sulfate concentration and decreasing residual arsenic. Overdosing of ferric chloride and ferrous sulfate results in high residual iron and the highest residual iron was found at $FeCl_3$ and $FeSO_4$ concentration of 40 and

90 mg L^{-1}, respectively. Residual iron concentration is proportional to arsenate removal in the case of using ferric sulfate as a coagulant. Consequently, residual iron concentration is affected by residual arsenic concentration besides coagulant dose. Minimum residual iron was measured as about 0.175, 0.446, and 1.3 mg L^{-1} for ferric chloride, ferric sulfate, and ferrous sulfate, respectively.

Although it has been supposed that overdosing of aluminum sulfate results in high residual aluminum (Kang et al., 2003; Van Benschoten and Edzwald, 1990), relatively higher residual aluminium was found in underdose range as shown in Figure 4.8(d). Residual aluminum concentration is affected by residual arsenic concentration besides coagulant dose. Above a certain aluminum sulfate dosage (50 mg L^{-1}), the increase in arsenate removal was not significant. In the coagulant dose above 50 mg L^{-1}, residual arsenate concentration was slightly decreased but residual aluminum was increased. Kang et al. (2003) also noted that the highest soluble residual aluminum was found in the underdose aluminum-based coagulant range in sample water containing low turbidity.

Because the maximum contaminant level of iron and aluminum in drinking water is 200 $\mu g\ L^{-1}$ according to Turkish Standards (Turkish Standards 2005), aluminum sulfate is found effective and reliable coagulant considering residual aluminium but ferric chloride is found more effective and reliable coagulant than others considering required concentration and residual iron.

4.1.4 Effects of Organic Polymers on Arsenic Removal

Synthetic organic polymers are long-chain molecules composed of small subunits or monomeric units. Polymers that contain ionisable groups such as carboxyl, amino, or sulfonic groups are called polyelectrolytes. Polymers without ionizable groups are nonionic. On the other hand, polyelectrolytes may be cationic (contains positive groups), anionic (contains negative groups), or ampholytic (contains both positive and negative groups) (Wang et al., 2005). Organic polymers neutralize the impurities or pollutants, and then agglomerate them into larger and heavier masses for rapid solid-water separation by sedimentation, flotation, centrifugation, and filtration (Wang et al., 1977). While coagulant addition causes colloidal destabilization, which allows particle agglomeration and enhances subsequent particle removal, accomplished by electrical double layer compression, adsorption and charge neutralization, entrapment of particles in precipitate, and bridging between particles, flocculation is the physical process of bringing the destabilized particles in contact to form larger flocs that can be more easily removed from suspension (Semerjian and Ayoub 2003; Wang et al., 2005) accomplished by addition of organic polymers.

Organic polymers assist in the joining and enmeshing of the particles together. The use of organic polymers supply to increase the size, strength and settleability of the flocs (Vanerkar, Satyanarayan, and Dharmadhikari, 2005). In view of this, cationic, anionic, and nonionic polyelectrolytes were tried to investigate the effect on removal efficiencies of arsenate from tap water by precipitation-coprecipitation with ferric chloride, ferric sulfate, ferrous sulfate, and aluminum sulfate. Impact of polyelectrolyte types and amount for the initial arsenate concentration of 50 $\mu g\ L^{-1}$ was determined. Figure 4.9 depicts the variations of percent arsenate removal at a constant $FeCl_3$ concentration of 25 $mg\ L^{-1}$ by enhanced coagulation with cationic, anionic, or nonionic polyelectrolyte.

Using $FeCl_3$ as a coagulant without addition of polymer caused 72% arsenate removal because the addition of coagulants facilitate the removal arsenate from the aqueous stream, by converting the soluble As(V) species into insoluble products. On the other hand, arsenate removal efficiency was improved by the addition of the organic polymers. Because the addition of cationic, anionic, or nonionic polyelectrolyte enhanced the efficiency of the method, the percentage arsenate removal was found to be much higher than the removal achieved without.

Percent arsenate removal generally increased with increasing concentrations of cationic, anionic, and nonionic polyelectrolyte content up to 1.5 $mg\ L^{-1}$ for cationic and anionic and 2.5 $mg\ L^{-1}$ for nonionic polyelectrolyte. But cationic and anionic polyelectrolyte dose above 1.5 $mg\ L^{-1}$ arsenate removal efficiency did not change.

Percent arsenate removal reached a maximum level at cationic polyelectrolyte concentration of 2.5 mg L^{-1}. Increasing coagulant dose from 0.25 to 2.5 mg L^{-1} resulted in an increase in arsenate removal efficiency from 74 to 76%. Addition of anionic and nonionic polyelectrolyte provided maximum 75 and 74% arsenate removal, respectively.

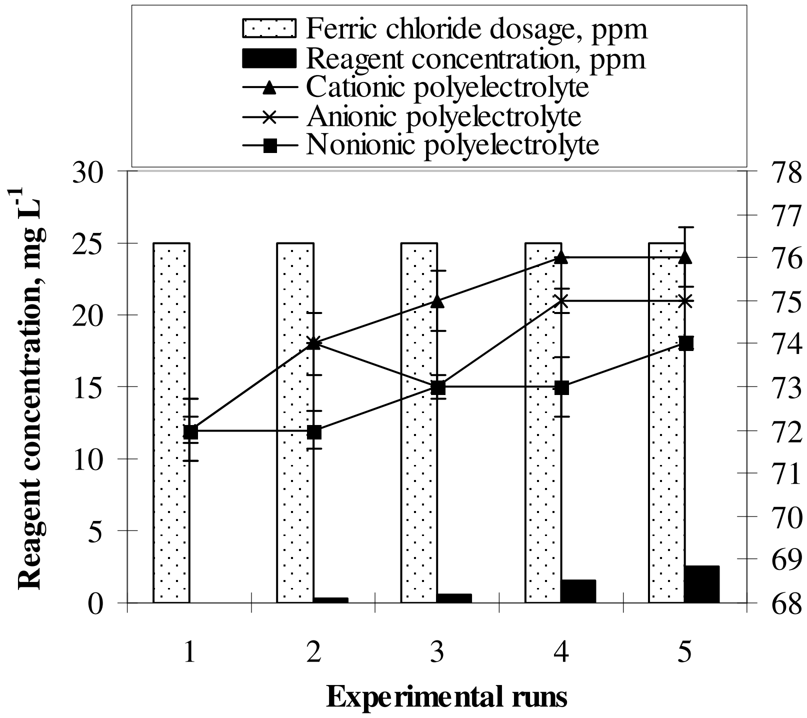


Figure 4.9 Variations of percent arsenate removal at a constant $FeCl_3$ concentration of 25 mg L^{-1} by enhanced coagulation with anionic, cationic, or nonionic polyelectrolyte.

Variations of percent arsenate removals with cationic, anionic, and nonionic polyelectrolyte dose at a constant pH of 8 and constant ferric sulfate dose of 40 mg L^{-1} are shown in Figure 4.10. Ferric sulfate concentration of 40 mg L^{-1} obtained 72% arsenate removal without addition of polymer as a result of precipitation, co-precipitation and adsorption mechanisms. Increasing cationic and anionic polyelectrolyte doses from 0.4 to 2 mg L^{-1} and increasing nonionic polyelectrolyte dose from 0.4 to 4 mg L^{-1} caused increasing of the arsenate removal efficiency. Arsenate removal efficiency did not change above 2 mg L^{-1} of both cationic and anionic polyelectrolyte dose just as is the case of ferric chloride. Percent arsenate removal reached a maximum level at cationic polyelectrolyte concentration of 2 mg L^{-1}. Increasing coagulant dose from 0.4 to 2 mg L^{-1} resulted in an increase in arsenate removal efficiency from 75 to 76%. Addition of both anionic and nonionic polyelectrolyte provided maximum 75% arsenate removal.

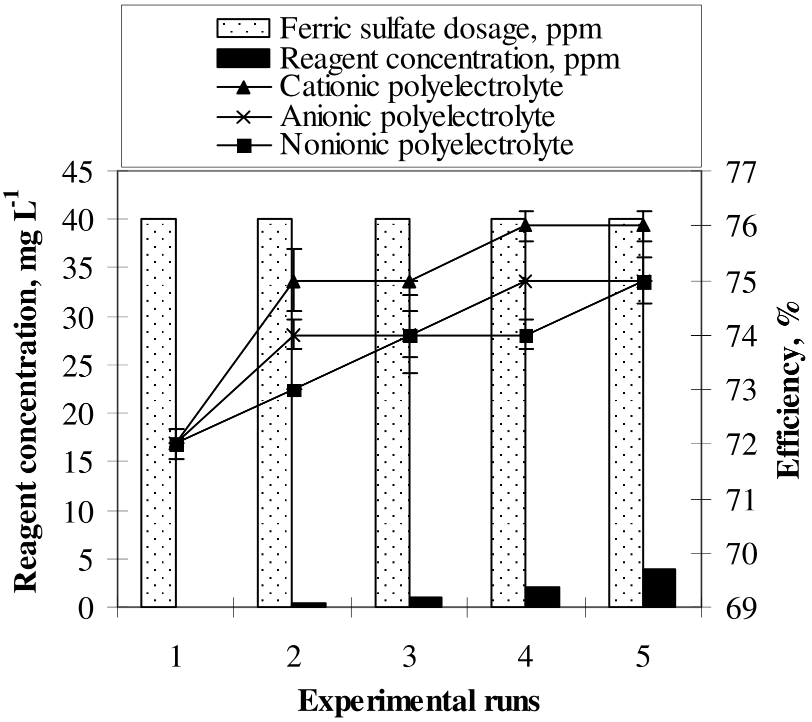


Figure 4.10 Variations of percent arsenate removal at a constant $Fe_2(SO_4)_3$ concentration of 40 mg L^{-1} by enhanced coagulation with anionic, cationic, or nonionic polyelectrolyte.

Figure 4.11 depicts the variations of percent arsenate removal at a constant pH of 9 and constant $FeSO_4$ concentration of 60 mg L^{-1} by enhanced coagulation with anionic, cationic, or nonionic polyelectrolyte. $FeSO_4$ dose of 60 mg L^{-1} without addition of polymer provided 72% arsenate removal. As is the case in ferric chloride and ferric sulfate, arsenate removal efficiency generally increased with increasing concentrations of cationic, anionic, and nonionic polyelectrolyte content up to 3 mg L^{-1} for cationic and nonionic and 6 mg L^{-1} for anionic polyelectrolyte. But cationic and nonionic polyelectrolyte dose above 3 mg L^{-1} arsenate removal efficiency did not change. Percent arsenate removal reached a maximum level at cationic polyelectrolyte concentration of 3 mg L^{-1}. Increasing coagulant dose from 0.6 to 3 mg L^{-1} resulted in an increase in arsenate removal efficiency from 75 to 76%. Addition of anionic and nonionic polyelectrolyte provided maximum 74% arsenate removal.

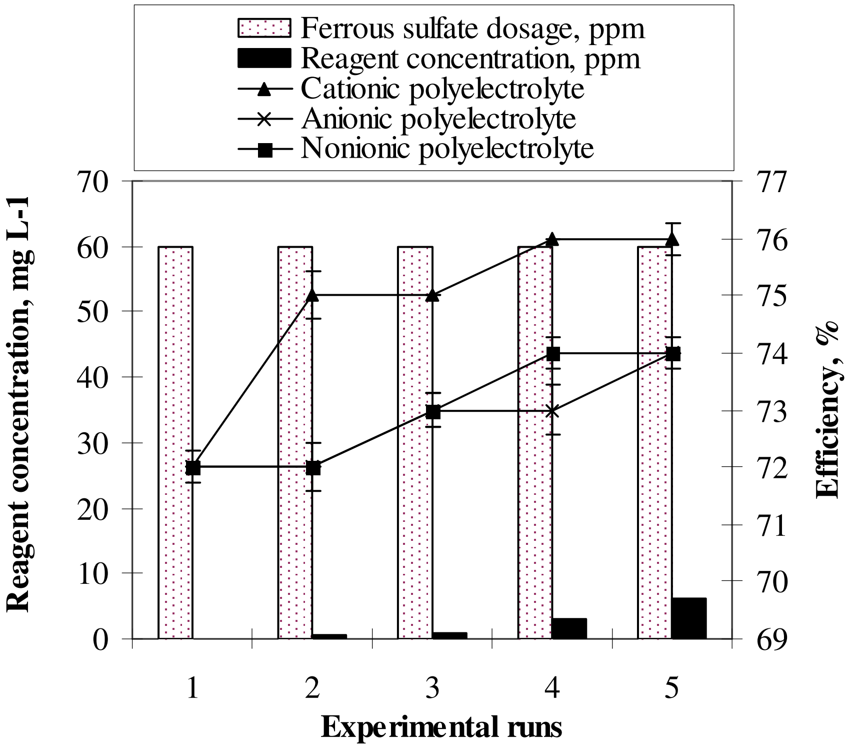


Figure 4.11 Variations of percent arsenate removal at a constant $FeSO_4$ concentration of 60 mg L^{-1} by enhanced coagulation with anionic, cationic, or nonionic polyelectrolyte.

Figure 4.12 shows the variations of percent arsenate removal at a constant $Al_2(SO_4)_3$ concentration of 40 mg L^{-1} by enhanced coagulation with cationic, anionic, or nonionic polyelectrolyte ranging within 0.35 to 3.5 mg L^{-1}. Figure 4.12 indicates that there is no appreciable removal in arsenate with respect to nonionic polyelectrolyte. Arsenate concentration was not decreased to below 10 µg L^{-1} using anionic and nonionic polyelectrolytes. Application of cationic polyelectrolyte was more effective than anionic and nonionic ones. The use of cationic polyelectrolyte dose of 2 mg L^{-1} with aluminum sulfate dose of 40 mg L^{-1} provided arsenate removal of 81% and residual arsenate concentration was reduced to below 10 µg L^{-1} while using $Al_2(SO_4)_3$ as a coagulant without addition of polymer caused 76% arsenate removal. The use of cationic polyelectrolyte has been described by previous studies and they indicated that the addition of cationic polymer as a coagulant aid has effect on the residual arsenic concentration (Han et al., 2002; Wickramasinghe et al., 2004; Zouboulis and Katsoyiannis, 2002). Zouboulis and Katsiyoannis (2002) also showed that cationic polyelectrolytes are more effective than anionic ones. No studies exist in literature concerning the removal of arsenic by coagulation using nonionic polymers as coagulant aid.

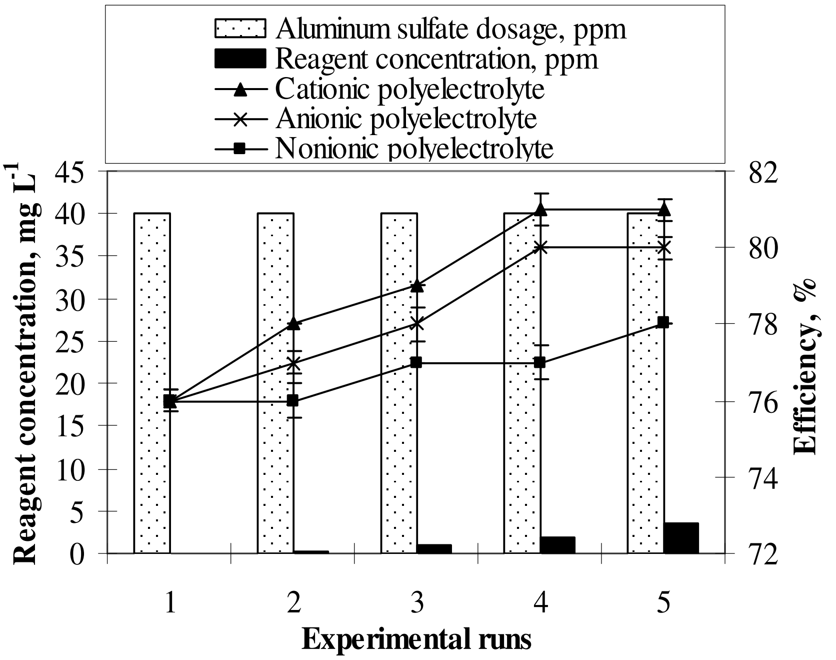


Figure 4.12 Variations of percent arsenate removal at a constant $Al_2(SO_4)_3$ concentration of 40 mg L^{-1} by enhanced coagulation with cationic, anionic, or nonionic polyelectrolyte.

The application of polyelectrolytes resulted in the formation of greater particles, faster floc formation, and produce denser and stronger flocs as shown in Figure 4.13 (Wang et al., 2005). All types of polymers increased the removal efficiency of the treatment method. But application of cationic polyelectrolytes was more effective than anionic and nonionic polyelectrolytes. This can be attributed to the fact that these polymers increase the cationic character of the inorganic coagulant, resulting in the formation of solids, which are more likely to adsorb oxyanions (arsenic) (Zouboulis and Katsoyiannis, 2002). Percent arsenate removal reached a maximum level at cationic polyelectrolyte concentration of 2.5, 2, 3, and 2 mg L^{-1} for ferric chloride, ferric sulfate, ferrous sulfate, and aluminum sulfate, respectively.

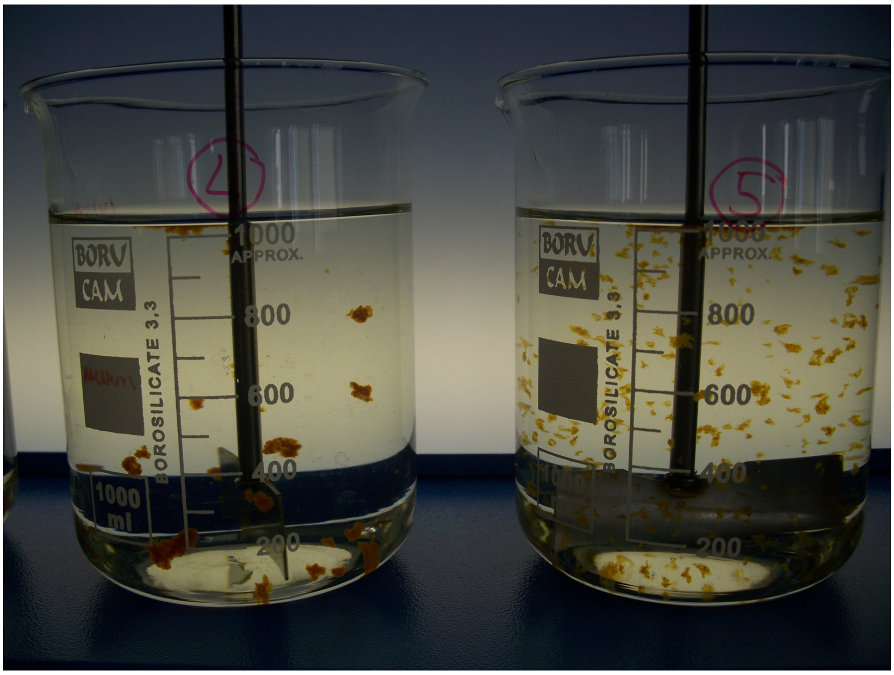


Figure 4.13 The polyelectrolyte effect on the flocs.

4.2 Results of Arsenic Removal by Lime Softening Process

Removal of arsenate from drinking water was investigated by lime softening process using calcium hydroxide. Effects of coagulant dose and variations in the pH values of arsenate contaminated water as a result of hydrated lime addition were investigated at the initial arsenate concentrations of 50, 500, and 1000 μg L^{-1}. The initial pH value of the tap water was measured as 7.45.

Figure 4.14 depicts the variation of percent arsenate removal and pH values of the water with the calcium hydroxide dose at the constant initial arsenate concentration of 50 μg L^{-1}. Percent arsenate removal increased with increasing $Ca(OH)_2$ concentration and reached a maximum level at $Ca(OH)_2$ concentration of 150 mg L^{-1}. The addition of $Ca(OH)_2$ caused a substantial increase in the pH. At the hydrated lime concentration of 110 mg L^{-1}, arsenic concentration reduced below 10 μg L^{-1} which is maximum contaminant level for arsenic in drinking water. Increasing coagulant dose from 50 to 150 mg L^{-1} resulted in an increase in arsenate removal efficiency from 66 to 94% and caused the increase in pH from 9.54 to 10.78. In the initial arsenate concentration of 50 µg L^{-1}, arsenate removal efficiency of 92% was obtained at pH of 10.24.

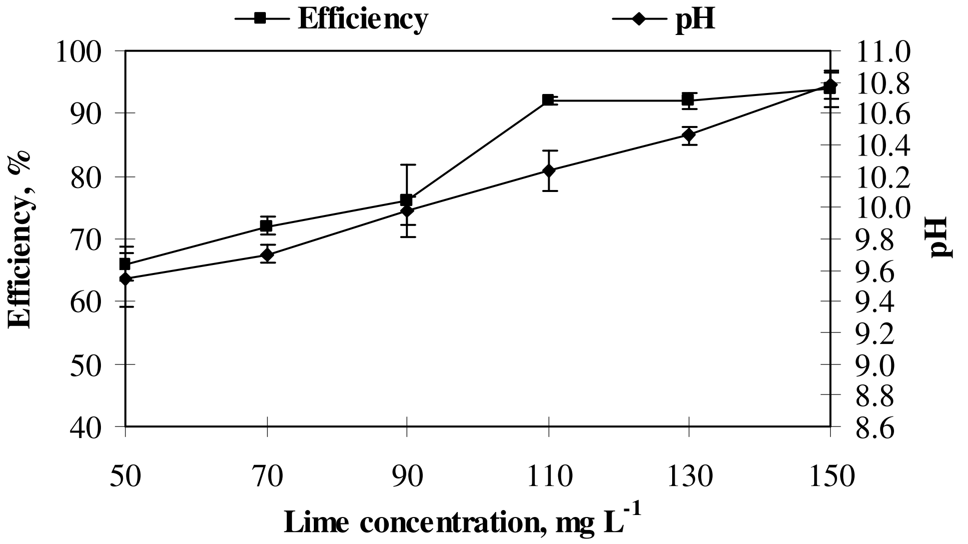


Figure 4.14 Variation of percent arsenate removal and pH values of the water with the calcium hydroxide at the constant initial arsenate concentration of 50 µg L^{-1}.

Figure 4.15 depicts the variation of percent arsenate removal and pH values of the water with the calcium hydroxide addition at the constant initial arsenate concentration of 500 µg L^{-1}. Percent arsenate removal increased with increasing $Ca(OH)_2$ concentration and reached a maximum level at $Ca(OH)_2$ concentration of 200 mg L^{-1}. The addition of $Ca(OH)_2$ caused a substantial increase in the pH. At the hydrated lime concentration of 200 mg L^{-1}, arsenic concentration reduced below 10 µg L^{-1} which is maximum contaminant level for arsenic in drinking water. Increasing coagulant dose from 50 to 200 mg L^{-1} resulted in an increase in arsenate removal efficiency from 64 to 98% and caused the increase in pH from 9.78 to 11.25.

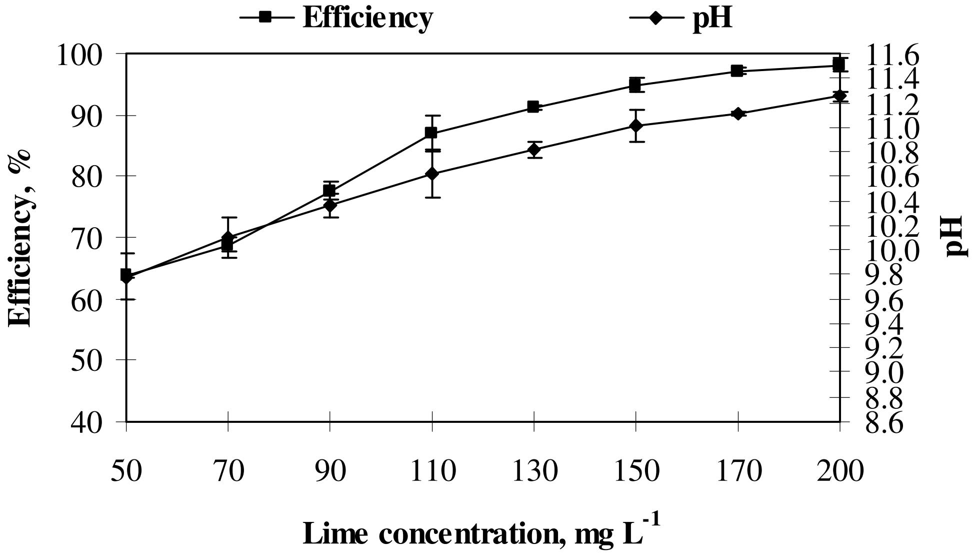


Figure 4.15 Variation of percent arsenate removal and pH values of the water with the calcium hydroxide at the constant initial arsenate concentration of 500 μg L^{-1}.

Figure 4.16 depicts the variation of percent arsenate removal and pH values of the water with the calcium hydroxide dose at the constant initial arsenate concentration of 1000 μg L^{-1}. Percent arsenate removal increased with increasing $Ca(OH)_2$ concentration and reached a maximum level at $Ca(OH)_2$ concentration of 200 mg L^{-1}. The addition of $Ca(OH)_2$ caused a substantial increase in the pH. At the hydrated lime concentration of 200 mg L^{-1}, arsenic concentration reduced below 10 μg L^{-1} which is maximum contaminant level for arsenic in drinking water. Increasing coagulant dose from 50 to 200 mg L^{-1} resulted in an increase in arsenate removal efficiency from 60 to 99% and caused the increase in pH from 9.95 to 11.35.

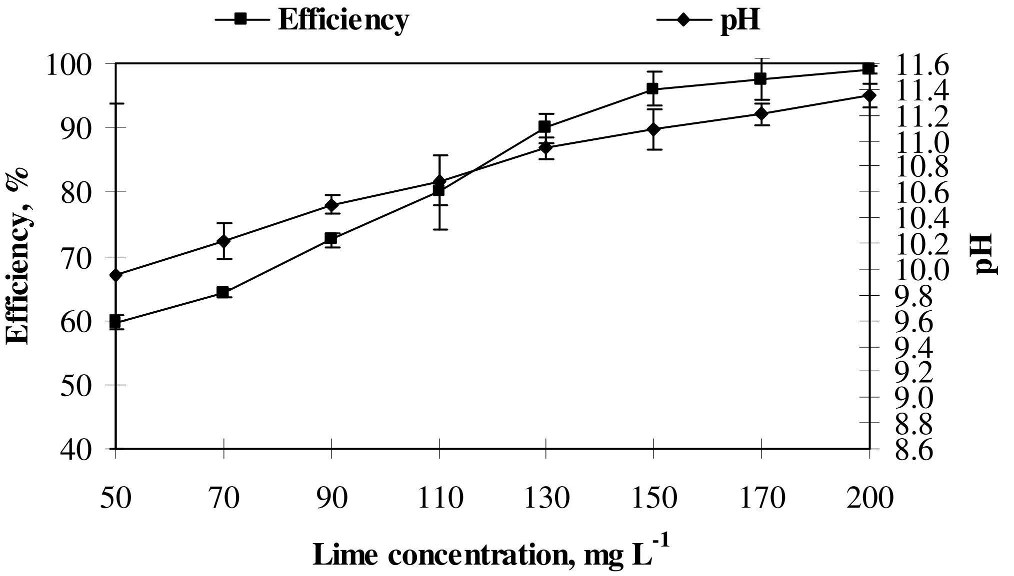


Figure 4.16 Variation of percent arsenate removal and pH values of the water with the calcium hydroxide at the constant initial arsenate concentration of 1000 μg L^{-1}.

According to results of experimental studies using calcium hydroxide, more than 90% arsenate removal was achieved if the pH is above 10.2. Figure 4.17 shows the variations of percent arsenate removals with $Ca(OH)_2$ concentrations at different initial arsenate concentrations. As it can be seen, in the initial arsenate concentration of 50 μg L^{-1}, the arsenate concentration is reduced below 10 μg L^{-1} at coagulant dose of 110 mg L^{-1}, while in the initial arsenate concentrations of 500 and 1000 μg L^{-1}, the highest arsenate removal efficiency, about 99%, was provided at coagulant dose 200 mg L^{-1}.

The mechanism of removal arsenate using calcium hydroxide may be adsorption onto the calcium carbonate and magnesium hydroxide ($Mg(OH)_2$) solids that form during softening (at high pH) or it may be a direct precipitation calcium arsenates, similar to phosphate precipitation under similar conditions (Newcombe and Dixon, 2006). Nearly 100% removal of arsenate is possible at pH 10.5 and higher using the lime-softening technique (Singh, 2007). Other studies using lime softening when the pH range is 10.6-11.4 showed a high removal of As(V), up to 95% when the initial arsenic concentration in the water was 12 mg L^{-1} (Castro de Esparza, 2006; Johnston et al., 2001).

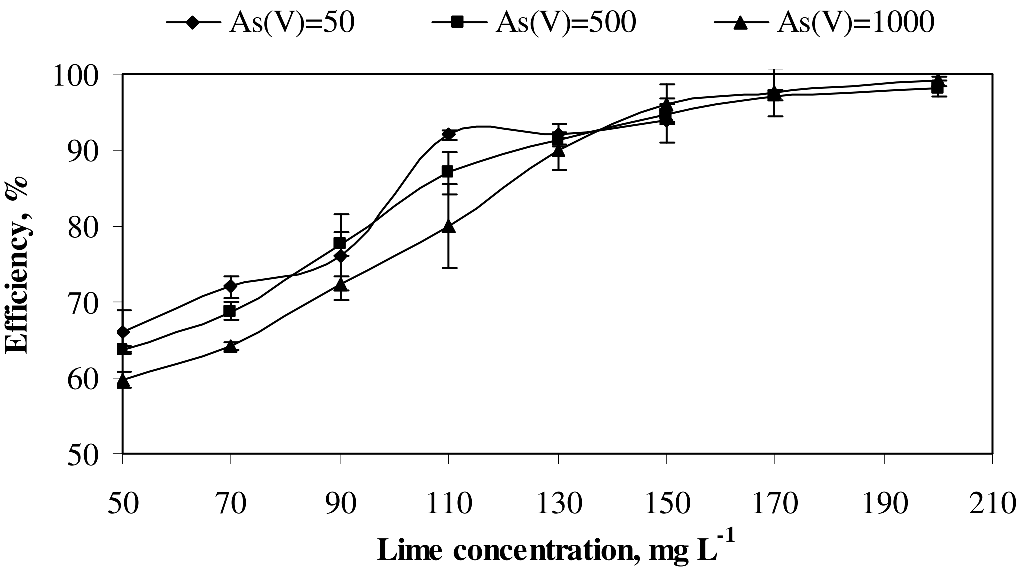


Figure 4.17 Variation of percent arsenate removal with the calcium hydroxide dose at the different initial arsenate concentrations.

Lime softening is a complex treatment process which produces a considerable amount of sludge. Disadvantages of lime-softening for arsenic removal are that large coagulant doses are required, and consequently a large volume of sludge is produced. Therefore sludge disposal might be difficult and expensive. Also the operating pH is rather extreme, and strong acids would probably be needed to adjust the pH after treatment (Singh, 2007). Lime softening is relatively inexpensive, but more expensive than coagulation with iron salts or alum because of larger doses required, and waste handling (Johnston and Heijnen, 2001). Lime softening would only be considered as a reasonable treatment alternative if the treatment goals include the removal of hardness and/or heavy metals. However, raw waters containing both high hardness and high arsenic concentrations are relatively rare (Newcombe and Dixon, 2006).

4.2.1 Effects of Organic Polymers on Arsenic Removal During Lime Softening

In order to determine the effect of organic polymers on removal efficiencies of arsenate from tap water by lime softening with calcium hydroxide, some experiments were also executed. Impacts of polyelectrolyte types (cationic, anionic, and nonionic) and dosage were determined. Figure 4.18 depicts the variations of percent arsenate removal at a constant $Ca(OH)_2$ concentration of 90 mg L^{-1} with cationic, anionic, and nonionic polyelectrolyte at the initial arsenate concentration of 50 µg L^{-1}. As it can be seen, $Ca(OH)_2$ dose of 90 mg L^{-1} without addition of polymer provided 76% arsenate removal. The addition of anionic and nonionic polyelectrolyte has not affected the arsenic removal efficiency. Percent arsenate removal reached a maximum level at cationic polyelectrolyte concentration of 5 mg L^{-1}. Increasing cationic polyelectrolyte dose from 1 to 5 mg L^{-1} resulted in an increase in arsenate removal efficiency from 76 to 80%. Before and after treatment with cationic polyelectrolyte, pH value of tap water was measured as 7.45 and 9.98, respectively.

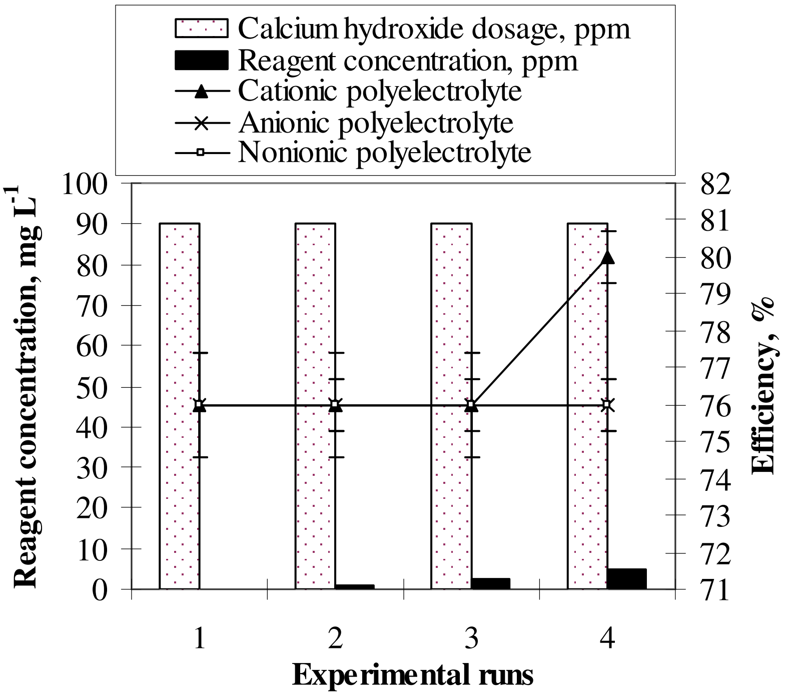


Figure 4.18 Variations of percent arsenate removal at a constant $Ca(OH)_2$ concentration of 90 mg L^{-1} with cationic, anionic, and nonionic polyelectrolyte.

4.3 Results of Arsenic Removal by Adsorption

4.3.1 Characterization

4.3.1.1 Elemental Composition

The principal components of GC are O, Na, Mg, Al, Si, K, Ca and Fe as shown in Table 4.12. It is reasonable to consider that Na, Mg, K and Ca are the extra framework cations that compensate for the deficiency of negative charge in the zeolite network (Jimenez-Cedillo et al., 2008). According to the concentration of Na, Mg, K and Ca in the GC (Table 4.12), it is considered to be a K-Ca zeolite type. The iron found in the natural zeolite GC was less than 1.6 wt.%.

Table 4.12 Elemental composition of unmodified and modified clinoptilolite

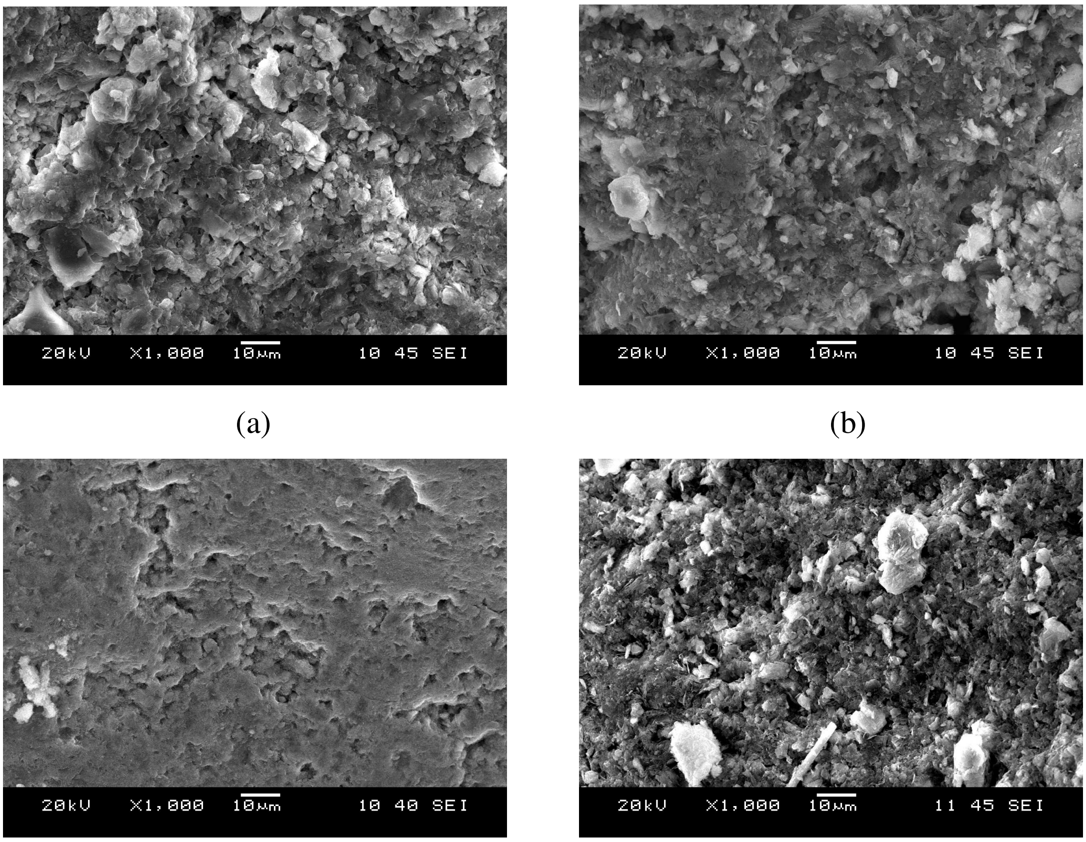
Element	**Composition (wt.%)**			
	GC	**GCNa**	**GCFeA**	**GCFeB**
O	30.489	28.307	14.28	26.002
Na	0.490	1.240	0.033	0.453
Mg	1.062	0.892	0.240	0.590
Al	9.431	9.174	3.126	8.527
Si	51.259	52.673	20.891	53.466
Cl	-	-	5.296	-
K	2.948	3.163	0.824	2.850
Ca	2.783	2.602	0.649	2.862
Fe	1.537	1.949	54.66	5.251

The treatment of the natural clinoptilolite with a NaCl solution increased the amount of sodium 2.53 times in the GC and the similar results were observed by other researchers (Jimenez-Cedillo et al, 2008; Macedo-Miranda and Olguin, 2007). In the clinoptilolite treated with $FeCl_3$ solutions, the sodium concentration diminishes, more importantly in the GCFeA relative to the GCFeB (Table 4.12), in comparison both of them to GCNa and the concentration of iron increase (54.66 and

5.251%, respectively), depending on the initial concentration of $FeCl_3$ in the solution (0.1–0.01 M). This result suggests that the iron ions are exchanged by the sodium ions from the zeolite network. However, it is important to mention that both K and Ca were also diminished. This suggests that Na^+, K^+ and Ca^{2+} play an important role in the conditioned processes of the clinoptilolite with the iron salt, probably due to an ion exchange mechanism.

4.3.1.2 Scanning Electron Microscopy

The SEM images of unmodified and modified zeolites showed morphologies characteristic of clinoptilolite revealed the presence of crystals of different sizes and morphologies. Figure 4.19(a-d) shows the surfaces of the GC, GCNa, GCFeA, and GCFeB, respectively. As shown in figure no changes were observed in the morphology of the clinoptilolite crystals of the GC after its treatment with NaCl, and $FeCl_3$ solutions, however the GCFeA have a cover in the surface probably due to the experimental conditions to obtain the iron-modified from the clinoptilolite.



(a) (b)

(c) (d)

Figure 4.19 SEM images of a) unmodified clinoptilolite, b) after the treatment with NaCl solution, c) after treatment with 0.1 M $FeCl_3$ solution, and d) after treatment with 0.01 M $FeCl_3$ solution.

4.3.1.3 X-ray Diffraction

Clinoptilolite and quartz were found in GC. A sodium-conditioned sample of natural zeolite showed no significant changes in the position of the most intense reflexions corresponding to clinoptilolite ($2\theta = 10.04^o$, 22.52^o and 22.66^o) as shown in Figure 4.20(a-b). This result suggests that sodium chloride conditioning has no effect on the structure of zeolitic material and in the position of the most intense diffraction peaks. The GCFeA, and GCFeB, X-ray diffraction patterns as shown in Figure 4.20(c-d) showed differences in the intensity of reflexions, but no changes in their position were observed relative to GCNa. These results suggest the presence of Fe in the the zeolitic network.

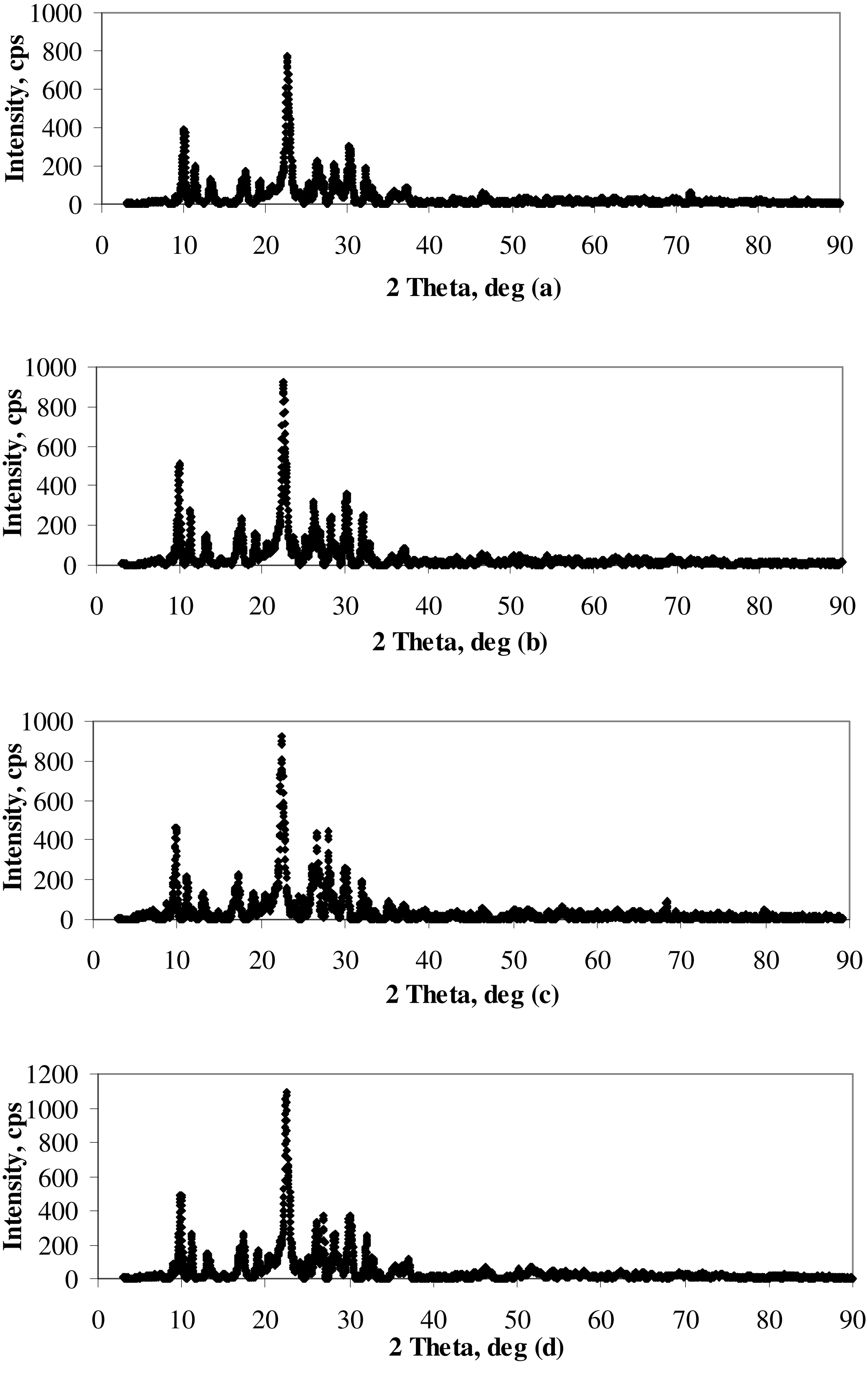


Figure 4.20 X-ray diffraction patterns of the different zeolitic materials: a) GC, b) GCNa, c) GCFeA, d) GCFeB.

4.3.1.4 Specific Surface Area

The specific surface area of the GC and GCNa is almost same. However, when the GCNa was treated with 0.1 M $FeCl_3$, the iron-modified clinoptilolite (GCFeA) increased 2.4 times its specific surface area as shown in Table 4.13. These changes could be attributed to the iron concentration in zeolites (54.66 wt.%) and the speciation of the iron in the zeolite network considering and over exchange zeolites (Jimenez-Cedillo et a., 2008). When the concentration of $FeCl_3$ in solution was diminished 10-fold, the obtained zeolitic material had a slightly specific surface area compared to GCNa, and was notably low in comparison with the values for GCFeA.

Table 4.13 Specific surface areas of unmodified and modified clinoptilolite

Materials	**Specific surface area, m^2 g^{-1}**
GC	34.118
GCNa	33.159
GCFeA	79.277
GCFeB	36.924

4.3.2 Results of Arsenic Uptake by Batch Tests

4.3.2.1 Effect of Contact Time

Figure 4.21 shows the effect of contact time on the adsorption of As(V) by the use of modified and unmodified adsorbents. GCFeA and GCFeB are very effective for removal of arsenate. It is clear from the figure that the GCFeA adsorb 7.4 µg As(V) g^{-1} in the first 5 min, reaching equilibrium after 60 min of contact time with a maximum As(V) adsorption of 9.2 µg g^{-1}. The As(V) adsorption at equilibrium is 8.4 µg g^{-1} for GCFeB and this value is 8.7% low than for GCFeA. It is clear from the figure that adsorption of As(V) on GC, GCNa, GCFeA, and GCFeB increase significantly with time and achieve saturation in 60 min for all cases. However, GC and GCNa adsorb 1.5 and 1.7 µg As(V) g^{-1} at equilibrium and they are not effective for the purpose. Compared to previous work related to As(V) sorption by iron-modified natural zeolites, where equilibrium time and removal efficiency was reported to be 180 minutes contact time with a maximum adsorption of 8 μg g^{-1} (Jimenez-Cedillo et al., 2008).

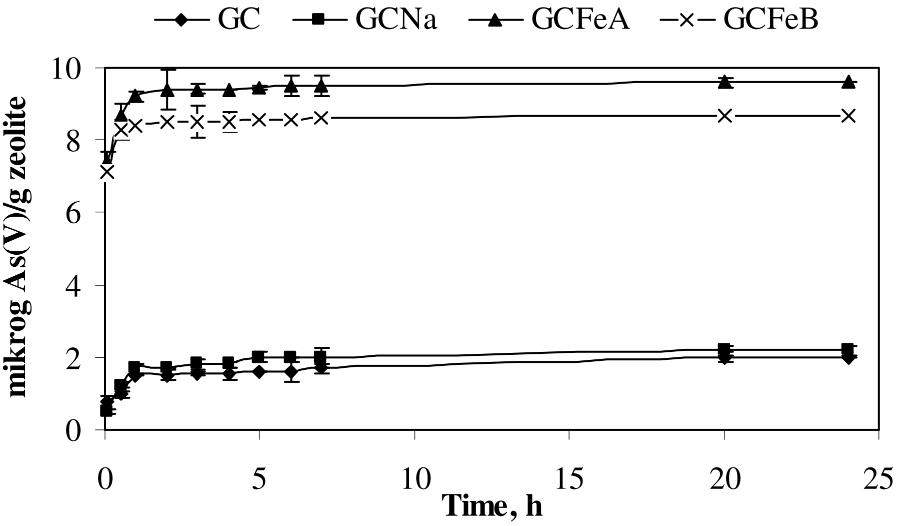


Figure 4.21 As(V) sorption uptake by modified and unmodified clinoptilolite as a function of time.

4.3.2.2 Effect of pH

The results of experiments carried out in order to evaluate the efficiency of GC, GCNa, GCFeA, and GCFeB in removing As(V) over a range of pH 4-12 are shown in Figure 4.22. The experiments were undertaken at initial As(V) concentrations of 100 μg L^{-1}. The predominant forms of arsenate in this pH range are $H_2AsO_4^-$ and $HAsO_4^{2-}$. Therefore both the GCFeA, and GCFeB removed arsenic effectively over the initial pH range 4–10. Although adsorption capacity of GC and GCNa is very low, maximum arsenate adsorption onto GC and GCNa was obtained at pH 5 and 7, respectively.

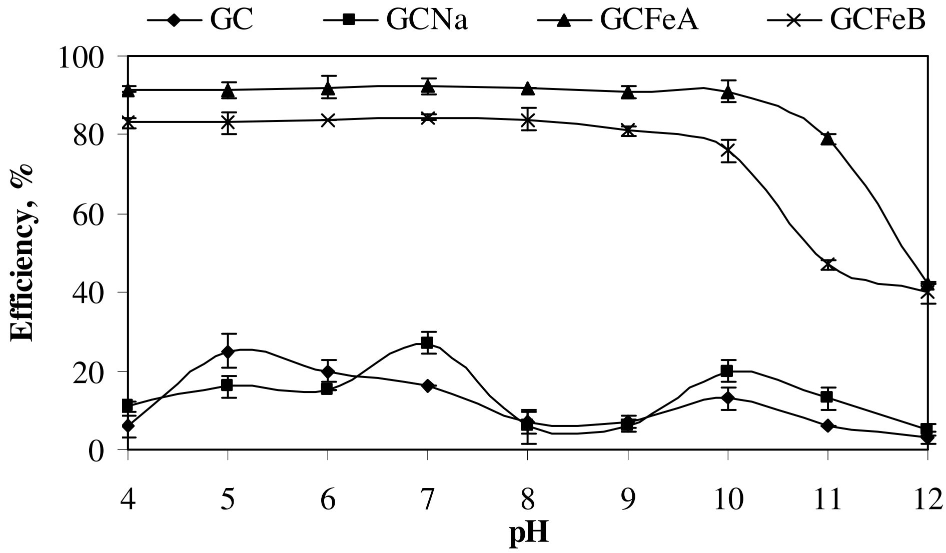


Figure 4.22 Effect of pH on the adsorption of As(V) on modified and unmodified clinoptilolite.

The surface charges of GCFeA and GCFeB are changed by deprotonation and protonation reactions of iron hydroxide coated onto zeolite. Under acidic condition, surface charge becomes more positive, because of the protonation of the GCFeA and GCFeB surface area, which provides more adsorption sites for arsenic. As a result, adsorption of As(V) highly depends on the solution pH. At the strong alkaline condition, the GCFeA and GCFeB surfaces become negatively charged and electrostatic repulsion between zeolite and As(V) resulted in a decrease of adsorption. At a strong acid condition, arsenate competed with hydrogen ions for the adsorption onto GCFeA and GCFeB. Similar results were obtained by other investigation which related to arsenate sorption by iron modified zeolite (Chutia et al., 2009; Jeon, Baek, Park, Oh, and Lee, 2009; Macedo-Miranda and Olguin, 2007).

4.3.2.3 Effect of Clinoptilolite Amount

The effect of modified and unmodified clinoptilolite amount on the As(V) adsorption is shown in Figure 4.23. The experiments were undertaken at initial As(V) concentrations of 100 μg L^{-1}, and pH value of 6.5 for both GCFeA and GCFeB, 5 and 7 for GC and GCNa, respectively. Adsorption percentage of As(V) on all types of clinoptilolite increased with the increase of amount clinoptilolite. But above a certain clinoptilolite dosage, the increase in arsenate removal was not significant. This increase may be attributed to the increase in the adsorption sites which were provided by the surface area of modified and unmodified clinoptilolite. Amount of clinoptilolite above 500 mg L^{-1} slightly increased percent arsenate removal. The removal efficiency of arsenate for GCFeA increased from 22% to 92% as the adsorbent dose increased from 25 to 500 mg L^{-1}. Jeon et al. (2009) showed that about 99% efficiency was obtained at iron-modified zeolite of 100 g L^{-1} for initial arsenate concentration of 2 mg L^{-1}. Similarly Macedo-Miranda and Olguin (2007) also showed that about 98% arsenate removal was achieved at iron-modified zeolite of 10 g L^{-1} for arsenate concentration of 100 µg L^{-1}.

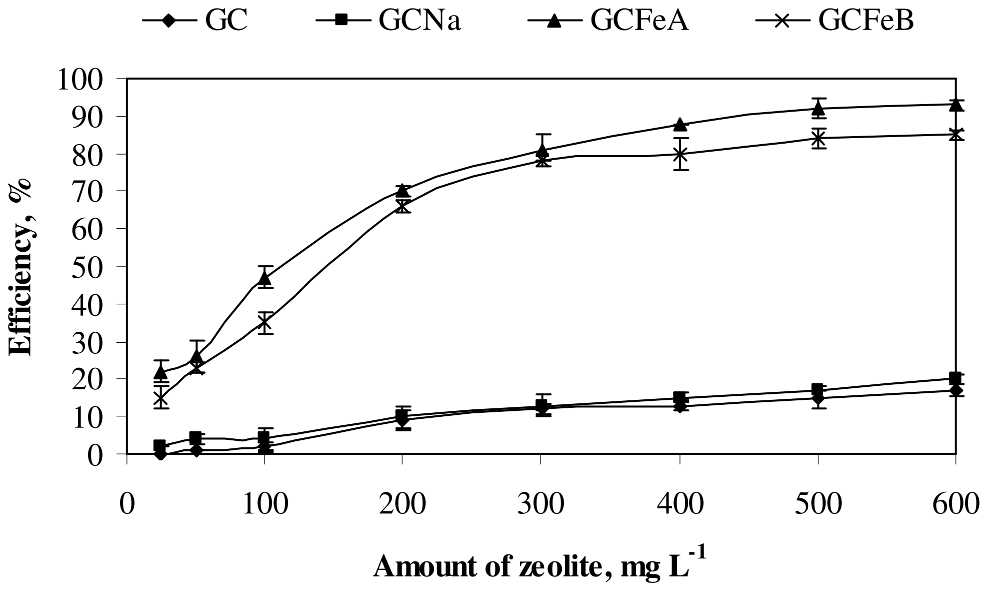


Figure 4.23 The effect of modified and unmodified clinoptilolite amount on As(V) adsorption.

Effect of iron modified zeolite amount on the arsenic removal efficiency and relationship between iron modified zeolite amount and residual iron are shown in Figure 4.24. As it can be seen, after arsenate treatment using GCFeA and GCFeB residual iron increased with increasing zeolite amount. Maximum residual iron values were measured as 0.195 and 0.556 mg L^{-1} for GCFeA and GCFeB, respectively. Because the maximum contaminant level of iron in drinking water is 200 µg L^{-1} according to Turkish Standards (Turkish Standards 2005), GCFeA is found effective and reliable iron-modified zeolite considering residual iron. Below the zeolite amount of 100 mg L^{-1}, GCFeB was also provided the maximum contaminant level for iron in drinking water but this zeolite amount was only achieved 35% arsenate removal efficiency.

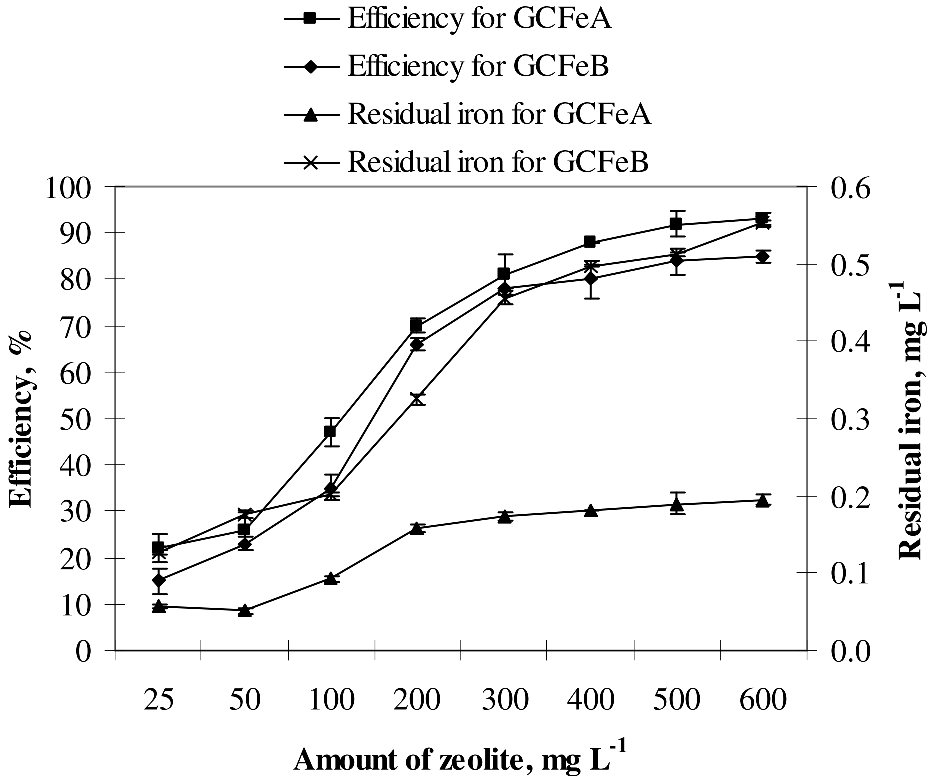


Figure 4.24 The effect of iron modified clinoptilolite amount on As(V) adsorption and relationship between iron modified clinoptilolite amount and residual iron.

4.3.2.4 Effect of Initial Arsenic Concentration

Figure 4.25 shows the effect of initial arsenate concentration on the adsorption of As(V) onto the modified and unmodified clinoptilolite. As it can be seen adsorption percentage of arsenic decreased with the increase of initial concentration of arsenic for all types of clinoptilolite. In case of arsenate adsorption onto GCFeA, the percent removal increases from 77.7% at 1000 μg L^{-1} to 92% at 100 μg L^{-1}. Similarly adsorption performance increases from 64.2% at 1000 μg L^{-1} to 82% at 250 μg L^{-1} while using GCFeB as adsorbent. At higher concentrations, some energetically less favourable sites become involved and arsenic uptake decreases with increasing arsenic concentration in the aqueous solution. At lower concentrations, most of the arsenic ions present in the solution would interact with the binding sites facilitating higher adsorption (Erdem, Karapinar, and Donat, 2004; Chutia et al., 2009).

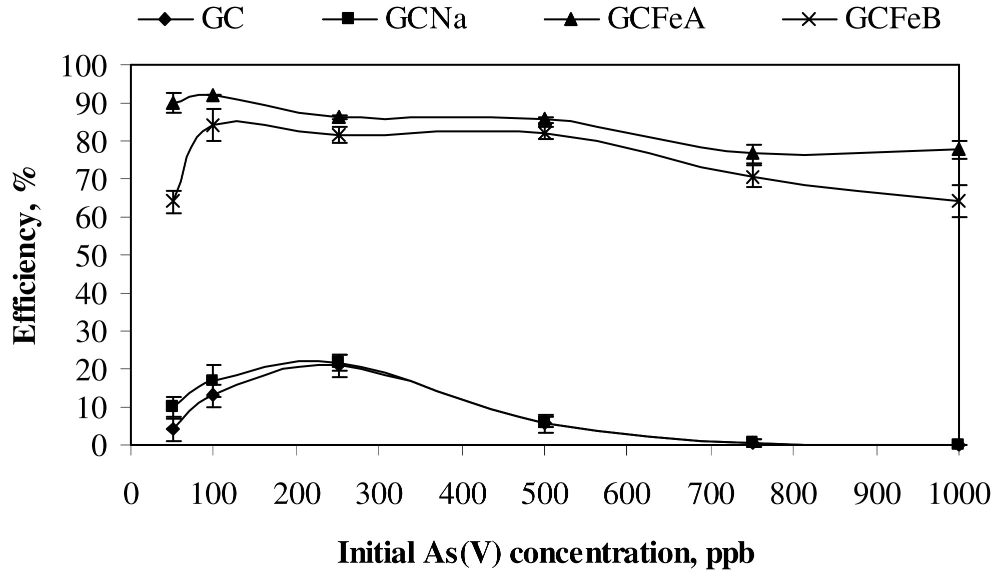


Figure 4.25 The effect of initial arsenate concentration on the adsorption of As(V) onto the modified and unmodified clinoptilolite.

4.3.3 Arsenic Adsorption Mechanism of Iron Modified Zeolites

Iron is especially important due to its known ability to form arsenic complexes such as FeH_2AsO_4 and FeH_2AsO_3. Furthermore, in aqueous solution iron oxide froms oxyhydroxides that can undergo protonation or deprotonation, yielding (depending on pH) a positive or negative surface charge (Elizalde-Gonzales et al., 2001):

$$Fe_{(s)} - OH + H^+ \Leftrightarrow Fe_{(s)} - OH_2^+$$

$$Fe_{(s)} - OH \Leftrightarrow H^+ + Fe_{(s)} - O^-$$

Hence, anions such as $H_2AsO_4^-$ can be adsorbed in the first case, through non-specific coulombic interaction according to the scheme:

$$Fe_{(s)} - OH_2^+ + H_2AsO_4^- \Leftrightarrow Fe_{(s)} - OH_2^+ \ldots{}^-O_4AsH_2$$

or they can undergo direct exchange:

$$Fe_{(s)} - OH + H_2AsO_4^- \Leftrightarrow Fe_{(s)} - H_2AsO_4$$

$$Fe_{(s)} - OH_2^+ + H_2AsO_4^- \Leftrightarrow Fe_{(s)} - H_2AsO_4 + H_2O$$

The iron (III) oxide surface has a high affinity for As(V) and is capable of forming inner-sphere bidentate, binuclear As(V)–Fe(III) complexes. In water samples treated with either ferric chloride or ferric sulphate, arsenic adsorption by iron complexes occurs via ligand exchange of the As species for OH_2 and OH^- in the coordination spheres of surface structural Fe atoms. The predominant oxidation state of arsenic depends on the pH and the potential redox.

Vaishya and Gupta (2004) proposed that the reaction of arsenate with the iron oxide surface can also be explained with the help of the surface complexation theory. In this case, the site S–Fe–OH acts as a Lewis acid and arsenate ions act as a Lewis base and cause exchange of OH^-, known as a ligand exchange mechanism.

It is proposed by Macedo-Miranda and Olguin (2007) that only iron found that the surface of natural zeolites play a role in As(V) adsorption processes via the zeolitic material. In the present work, the iron modified natural zeolites were obtained by ion exchange. When the GCFeA and GCFeB was put in contact with the arsenate solution, the following interactions are considered:

Bidentate Inner sphere complex:
Coulombic and Lewis acid-base interactions

$$2GC - FeOH_2^+ \leftarrow HAsO_4^{2-}$$

Monodentate Inner sphere complex:
Coulombic and Lewis acid-base interactions

$$GC - FeOH_2^+ \leftarrow H_2AsO_4^-$$

Ligand exchange

$$GC - Fe - OH + H_2AsO_4^- \rightarrow GC - Fe - H_2AsO_4 + OH^-$$
$$2GC - Fe - OH + HAsO_4^{2-} \rightarrow 2GC - Fe - HAsO_4 + 2OH^-$$

The adsorption of As(V) onto GCFeA and GCFeB occurred by ligand exchange reactions, and most of the hydroxide groups are involved in ligand exchange reactions. The adsorption of As(V) by iron-hydroxide resulted in the release of hydroxide. The cumulative hydroxide group release per amount of arsenic adsorbed was related with amount of arsenic adsorbed (Jain, Raven, and Loeppert, 1999).

4.3.4 Adsorption Isotherms

Isotherms of adsorption process describe a relationship determined at a constant temperature between the amount of chemical adsorbed and the amount of adsorbent used. To quantify the adsorption capacity of GCFeA and GCFeB, for removal of As(V) from water, Langmuir and Freundlich adsorption equations were used. The Freundlich equation is an empirical equation that accurately describes many adsorption data. The equation is an exponential equation of the form:

Exponential form

$$\frac{X}{M} = K_f C_e^{1/n} \tag{4.1}$$

Linear form

$$\log \frac{X}{M} = \log K_f + 1/n \times \log C_e \tag{4.2}$$

where *X/M* is micrograms of arsenic adsorbed per gram of the adsorbent, K_f is Freundlich constant, *1/n* is the Freundlich exponent provides information about surface heterogeneity and surface affinity for the solute, and C_e is arsenic concentration in final solutions. The constant K_f is related primarily to the capacity of the adsorbent to adsorb arsenic. Larger values of *K* mean larger capacities of adsorption. The constant $1/n$ is a function of the strength of adsorption. Larger values of $1/n$ mean that the adsorption bond is weak because the value of *X/M* experiences large changes for small changes in C_e. Smaller values of $1/n$ mean that the adsorption bond is strong.

The results summarized in Table 4.14 show that K_f constant for GCFeA is higher than GCFeB. Therefore GCFeA has larger capacities of adsorption. As(V) adsorption on GCFeA has the highest *1/n* constant, which means that adsorption bond between the As(V) ion and adsorbent is the strongest. Correlation coefficient (R^2) for Freundlich isotherms was found as 0.9947 and 0.9368 for GCFeA and GCFeB, respectively, representing an excellent fit of observing data. Figure 4.26 and 4.27 show the Freundlich isotherms for GCFeA and GCFeB, respectively.

Table 4.14 Freundlich and Langmuir constant for arsenic adsorption on GCFeA and GCFeB

Adsorbent	**Freundlich constants**			**Langmuir constants**		
	K_f	*1/n*	R^2	Q_{max}	*k*	R^2
GCFeA	0.608	0.5103	0.9947	6.435	0.046	0.9808
GCFeB	0.269	0.6674	0.9368	9.766	0.013	0.9718

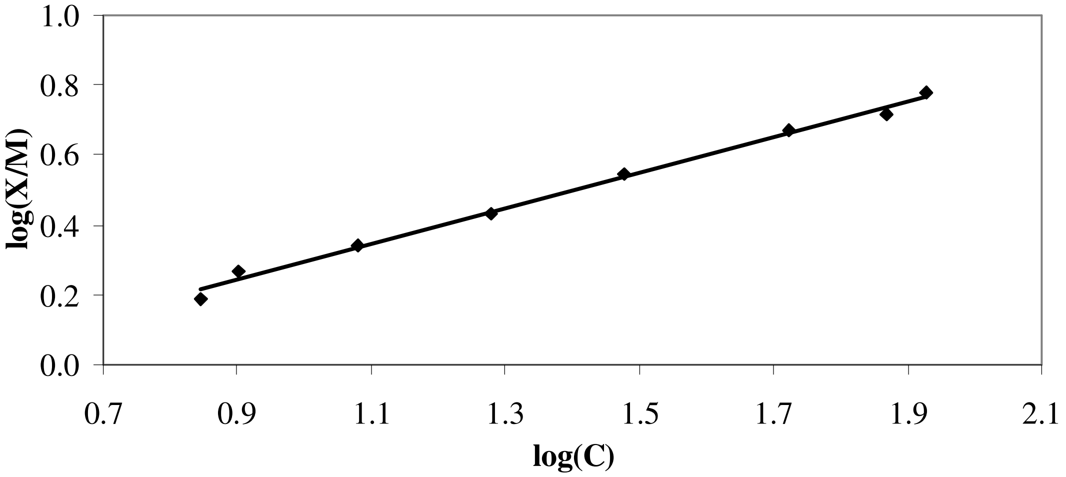


Figure 4.26 Linearized Freundlich isotherm for GCFeA.

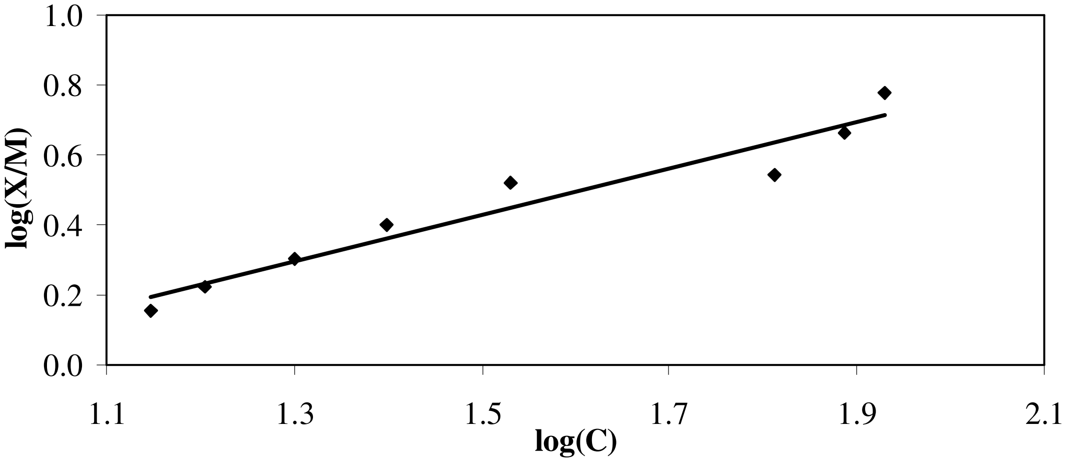


Figure 4.27 Linearized Freundlich isotherm for GCFeB.

The Langmuir isotherm is derived assuming the following: a limited area available for adsorption, arsenic is adsorbed in a monomolecular layer, adsorption is reversible and equilibrium is achieved. The equation is of the form:

Exponential form

$$\frac{X}{M}=\frac{Q_{\max}\times k\times C_e}{1+k\times C_e} \tag{4.3}$$

Linear form

$$\frac{M}{X} = \frac{1}{Q_{\max}} + \frac{1}{Q_{\max} \times k} \times \frac{1}{C_e} \tag{4.4}$$

where Q_{max} is Langmuir monolayer sorption capacity, k is Langmuir coefficient. Correlation coefficient (R^2) for Langmuir isotherms was found as 0.9808 and 0.9718 for GCFeA and GCFeB, respectively, representing an excellent fit of observing data. The results are summarized in Table 4.14. The linear plots of M/X vs. $1/Ce$ for both GCFeA and GCFeB are shown in Figure 4.28 and 4.29, respectively.

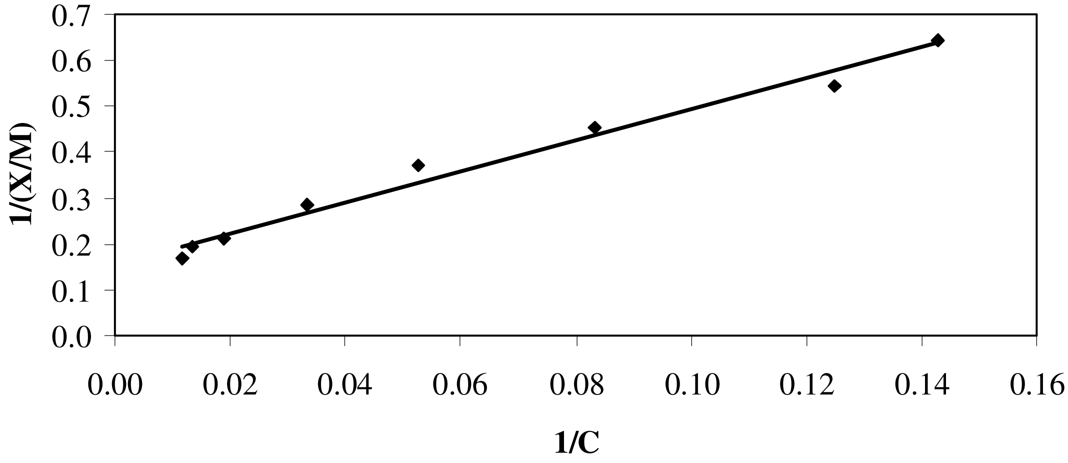


Figure 4.28 Linearized Langmuir isotherm for GCFeA.

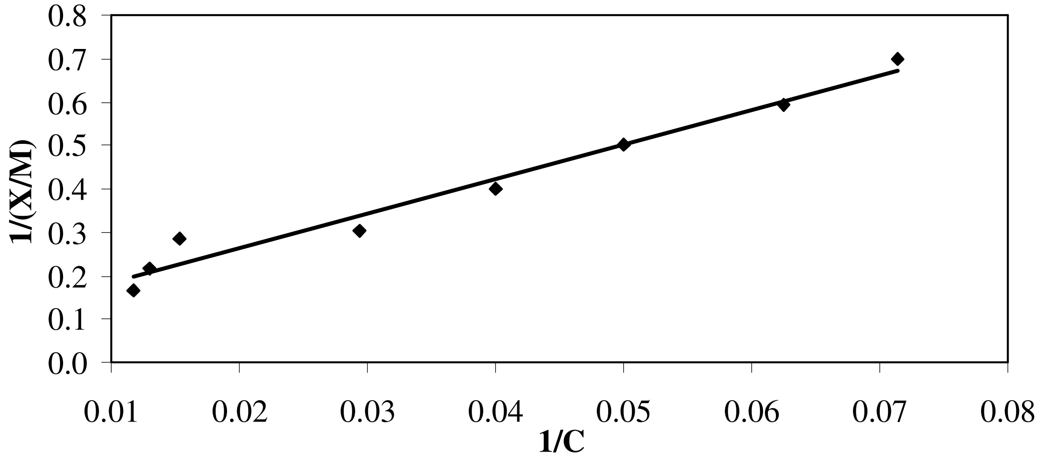


Figure 4.29 Linearized Langmuir isotherm for GCFeB.

4.3.5 Adsorption Kinetics

In the present study, two important kinetic models were applied in order to investigate the mechanism of adsorption of arsenate on GCFeA and GCFeB. In order to establish the equilibration time for maximum uptake of arsenate and to know the kinetics, adsorptions of arsenate on GCFeA and GCFeB were studied as a function of contact time and initial arsenate concentration and results are shown in Figure 4.30(a-b). It is seen from the figure that the rate of uptake of arsenate on used adsorbents is rapid in the beginning and 74% adsorption is completed in 5 min and become constant after 60 min for GCFeA, which indicates that equilibrium has been achieved. For GCFeB 71% adsorption is completed in 5 min and become constant after 60 min. Thus, equilibration time was found as 1 h.

The effect of concentration on equilibrium time was also investigated at three different initial arsenate concentrations and results are also shown in Figure 4.30(a-b). It was found that adsorption capacity at equilibrium increases from 8.56 μg g^{-1} to 9.2 μg g^{-1} with a decrease in the initial arsenate concentration from 500 to 100 μg L^{-1} for GCFeA, and adsorption capacity at equilibrium increases from 8.22 μg g^{-1} to 8.4 μg g^{-1} with a decrease in the initial arsenate concentration from 500 to 100 μg L^{-1} for GCFeB. This indicates that initial concentration plays an important role in the adsorption of arsenate on used adsorbent.

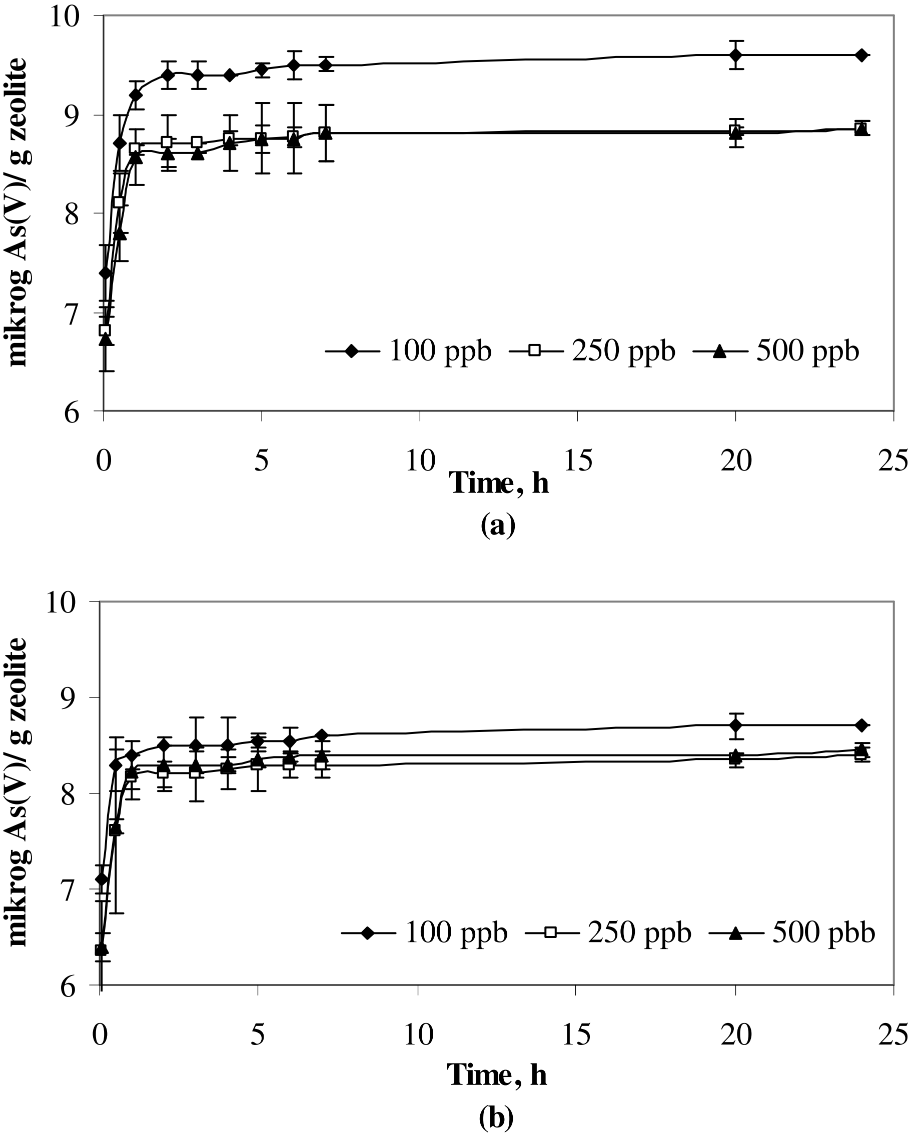


Figure 4.30 The variation of adsorption capacity with adsorption time at various initial arsenate concentrations for a) GCFeA and b) GCFeB.

Kinetics of adsorption is an important characteristics in defining the efficiency of adsorption. A number of models with varying degrees of complexicity have been developed to describe the kinetics of metal adsorption in batch systems (Bhatti, Khalid, and Hanif, 2009). The prediction of adsorption rate gives important information for designing batch adsorption systems. Information on the kinetics of pollutant uptake is required for selecting optimum operating conditions for full-scale batch process (Tuzen et al., 2009). Two simplified kinetic models namely pseudo-first-order, and pseudo-second-order models have been discussed to identify the rate and kinetics of sorption of arsenate on GCFeA and GCFeB. The pseudo-first-order rate expression of Lagergren is generally described by the following equation (Ho, 2004):

$$\frac{dq_t}{dt} = K_1(q_e - q_t)^2 \qquad (4.5)$$

where q_e and q_t are the amounts of As(V) adsorbed on the adsorbents at equilibrium and at time, t (min), respectively and K_1 is the rate constant (min^{-1}).

Integrating and applying the boundary conditions, $t = t$ and $qt = qe$ takes the form:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \qquad (4.6)$$

For the studied initial concentrations, the rate constant (K_1) and theoretical equilibrium sorption capacities, q_e (calculated), were obtained from the slope and intercept of the linear plots of the $\log(q_e - q_t)$ against t as shown in Figure 4.31(a-b) for GCFeA and GCFeB, respectively. For various initial arsenate concentrations, pseudo first-order rate constants (K_1) and the calculated amount of arsenate sorbed at equilibrium (q_e (cal)) were calculated and are listed in Table 4.15 along with the corresponding correlation coefficients.

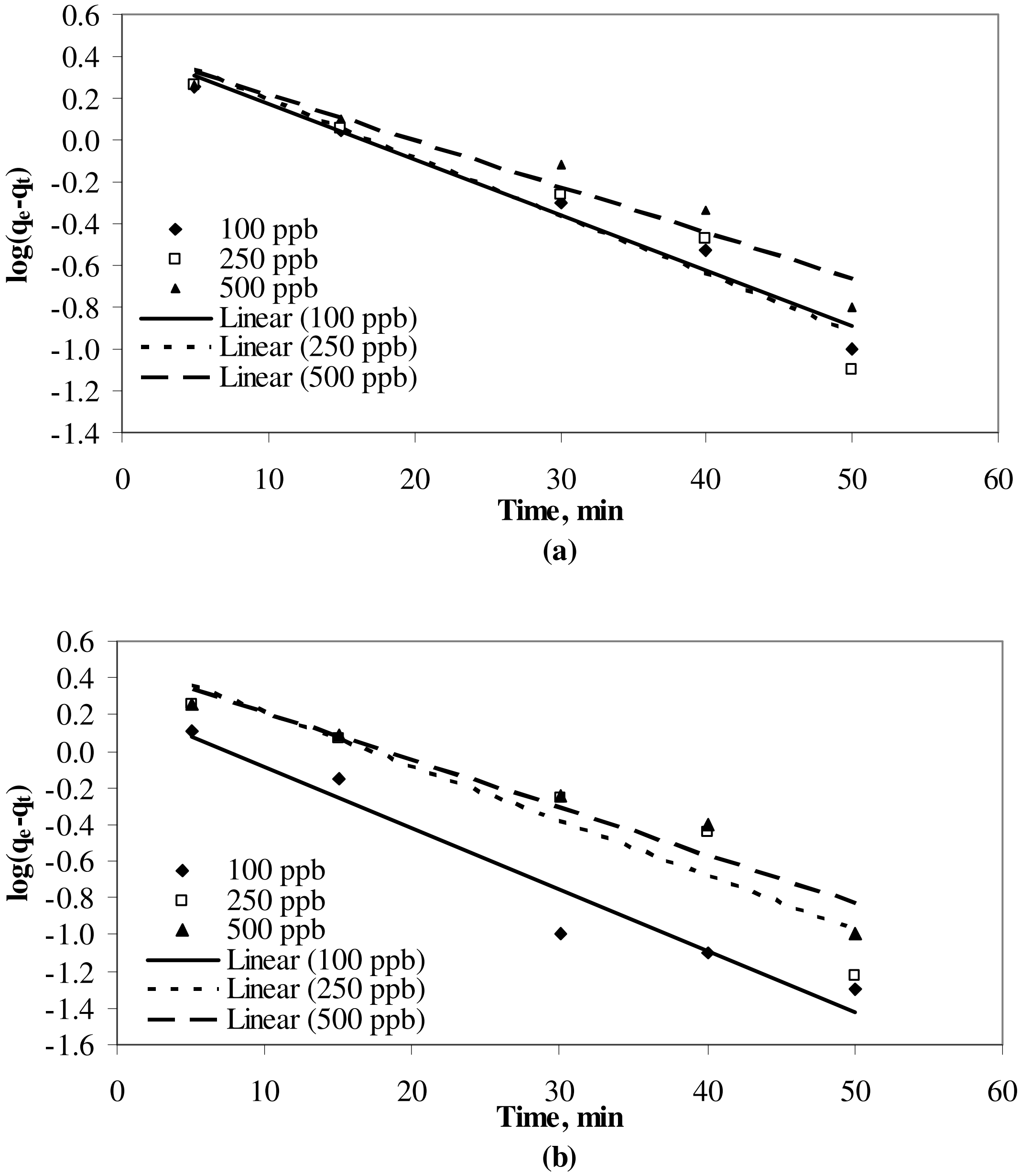


Figure 4.31 The pseudo first order model for arsenate adsorption on a) GCFeA, b) GCFeB.

The correlation coefficients (R^2) for the first-order kinetic model obtained at all the studied concentrations were low. The theoretical q_e (cal) values calculated for the pseudo first-order model did not give reasonable values with regard to the experimental uptake values, q_e (exp) (Table 4.15). This indicates that pseudo first-order equation might not be sufficient to describe the mechanism of arsenate adsorption system. As listed in Table 4.15, there is no big variation for the overall rate constant values with the change of initial arsenate concentration. Although, the correlation coefficients showed that this model was not the best fitted to the experimental data, the amounts of arsenate adsorbed at equilibrium (q_e (cal)) were the highest for GCFeA in the initial arsenate concentration of 100 µg L^{-1}, and the highest for GCFeB in the initial arsenate concentrations of 250 and 500 µg L^{-1}. This means q_e (cal) depends on the iron concentration in the clinoptilolite, but also depends on the initial arsenate concentrations. The Lagergren rate constant K_1 was highest for GCFeB for all initial arsenate concentrations. This fact shows that adsorption velocity of the arsenate on GCFeB was higher than on GCFeA.

Table 4.15 Pseudo first-order rate parameters for sorption of arsenate on GCFeA and GCFeB

		Pseudo first-order kinetic model		
C (µg L^{-1})	**q_e (exp) (µg g^{-1})**	**K_1 (min^{-1})**	**q_e (cal) (µg g^{-1})**	**R^2**
GCFeA				
100	9.20	0.081	2.738	0.9707
250	8.64	0.082	3.014	0.9326
500	8.56	0.070	2.726	0.9358
GCFeB				
100	8.40	0.103	1.765	0.9452
250	8.16	0.084	3.238	0.8904
500	8.22	0.077	2.913	0.9277

The kinetics were also described as pseudo-second-order process by the following equation (Ho and McKay, 1999):

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + K_2 t \qquad (4.7)$$

Rearranging this equation to a linear form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (4.8)$$

where, q_e and q_t have the same meaning as mentioned previously, and K_2 is the rate constant for the pseudo second-order kinetics. The plots of t/q_t versus t are shown in Figure 4.32(a-b) for GCFeA and GCFeB. The values of q_e (cal) and K_2 were determined from the slope and intercept of the plot, respectively, and are compiled in Table 4.16.

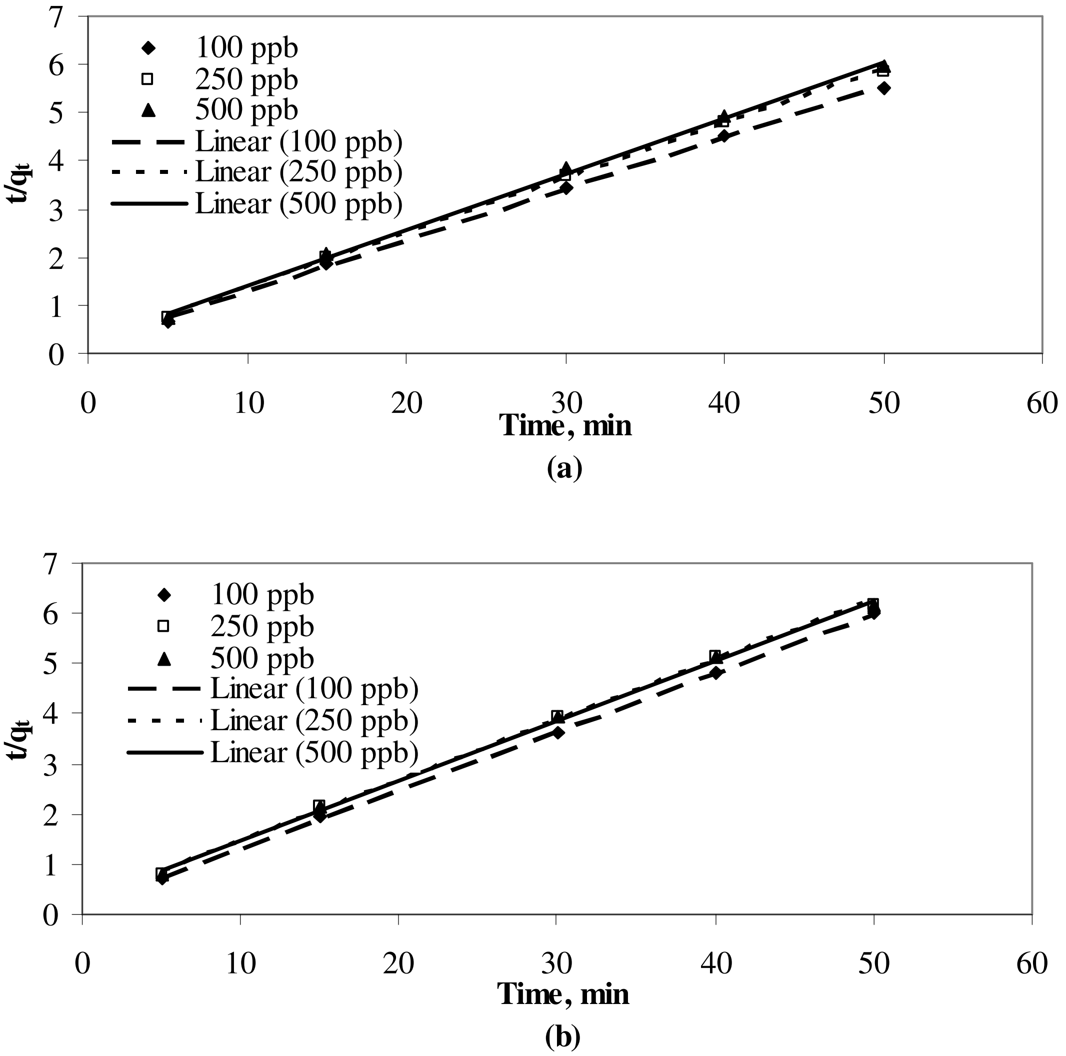


Figure 4.32 The pseudo second order model for arsenate adsorption on a) GCFeA and b) GCFeB.

The correlation coefficients (R^2) are in range of 0.9979–0.9998 and the theoretical q_e (cal) values were closer to the experimental q_e (exp) values. It can be seen from the results in Table 4.15 and 4.16 that R^2 values are higher than those obtained from the pseudo first-order kinetics. Based on these results, it can be concluded that the pseudo second-order kinetic model provided a good correlation for the adsorption of arsenate by GCFeA and GCFeB in contrast to the pseudo first-order model. According to the q_e (cal) values, GCFeA adsorbs the highest amount of arsenate from an aqueous solution. This behaviour was similar for that obtained with the first order kinetic model. The parameter K_2, which corresponds to the velocity constant of pseudo-second order, is the highest for GCFeB at the initial arsenate concentration of 100 µg L^{-1}. For the initial arsenate concentrations of 250 and 500 µg L^{-1}, rate constant values for GCFeA are the same or a bit higher than GCFeB.

Table 4.16 Pseudo second-order rate parameters for sorption of arsenate on GCFeA and GCFeB

C (µg L^{-1})	q_e (exp) (µg g^{-1})	Pseudo second-order kinetic model		
		K_2 (g µg^{-1} min^{-1})	q_e (cal) (µg g^{-1})	R^2
GCFeA				
100	9.20	0.057	9.363	0.9993
250	8.64	0.053	8.818	0.9989
500	8.56	0.051	8.628	0.9979
GCFeB				
100	8.40	0.093	8.576	0.9998
250	8.16	0.051	8.347	0.9984
500	8.22	0.051	8.375	0.9984

For other materials it was found that the pseudo second order kinetic is the best model of describing kinetic data for arsenate removal from aqueous solution by acid modified carbon black (Borah, Satokawa, Kato, and Kojima, 2009). Similar results were obtained to remove arsenate from water using agricultural residue rice polish (Ranjan, Talat, and Hasan, 2009), using a mesoporous alumina (Yu, Li, and Ahn, 2008), using Zr(IV) loaded orange waste gel (Biswas et al., 2008), using the iron modified red mud (Zhang et al., 2008).

4.3.6 Regeneration of the Adsorbent

The regeneration of sorbents is a key process in water treatment. In the present study, desorption experiments were carried out with the zeolite GCFeA considering its good performance in sorption experiments. Figure 4.22 reveals that GCFeA is more effective in acidic pH range which implies that As(V) can be desorbed by alkaline media. For convenience, desorption tests were conducted with 0.1 M NaOH and 0.1 M HCl solutions. Desorption performance of GCFeA is 54% while using NaOH solution and arsenic removal capacity of the regenerate material is almost same (83%) with the fresh material (92%). Figure 4.33 shows the variation in arsenic removal efficiency with the number of again used of regenerated GCFeA. In this experimental study, after the each arsenic treatment experiment, GCFeA is regenerated using 0.1 M NaOH and then reused for arsenic removal from the same arsenic contaminated water. As it can be seen after the GCFeA was used 6 times until arsenic removal efficiency was reduced to 19%.

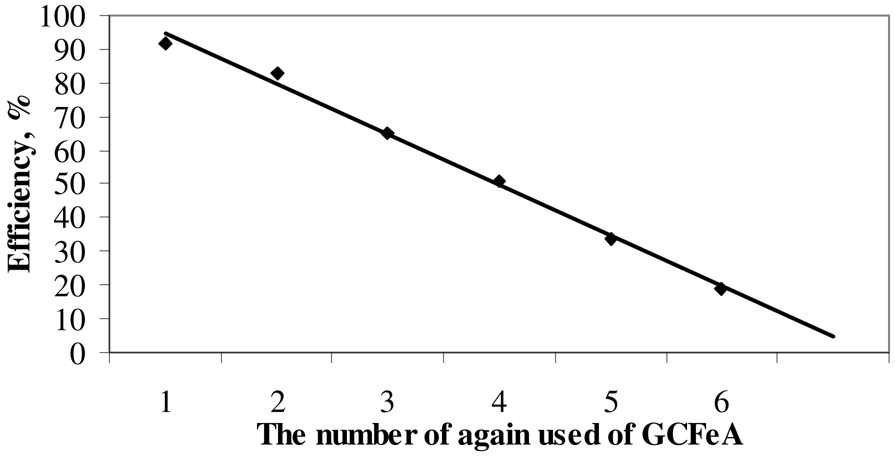


Figure 4.33 Variation of arsenic removal efficiency with the number of again used of regenerated GCFeA.

In HCl solution, desorption performances are reduced to 6%. This result indicates that desorption phenomenon is the reverse of the sorption process. The arsenic-laden zeolites have passed EPA's Toxicity Characteristics Leaching Procedure test and can be safely disposed of as non-hazardous waste (Chutia et al., 2009; Menhage-Bena, Kazemian, Ghazi-Khansari, Hosseini, and Shahtaheri, 2004).

4.3.7 Results of Arsenic Uptake in a Packed Bed Reactor

4.3.7.1 Effect of Flow Rate

Based on the batch studies, the pH of the effluent was maintained at 6.5. To find out the effect of flow rate on breakthrough curve, adsorption experiments were carried out by varying the flow rate between 2 and 3.5 mL min^{-1}. Flow rates are checked by physically collecting the discharge from column for a given time and measuring the volume collected. The effect of flow rate on breakthrough performance at the above operating conditions is shown in Figure 4.34. It can be seen from the figure that the adsorption efficiency is higher at lower flow rate. This can be explained by the fact that at lower flow rate, the residence time of the adsorbate is more and hence the adsorbent gets more time to bond with the solute efficiently. In other words, if the residence time of the solute in the GCFeA packed bed reactor is not large enough for adsorption equilibrium to be reached at the given flow rate, the As(V) solution leaves the column before equilibrium occurs. The arsenate uptake decreased with increase in flow rate. The optimum flow rate was found as 2.8 mL min^{-1} as shown in Figure 4.34.

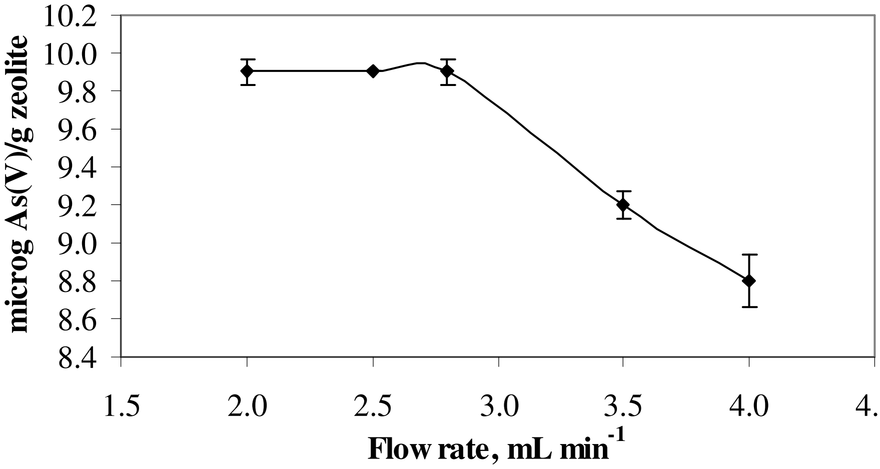


Figure 4.34 Effects of flow rate on arsenate uptake.

4.3.7.2 Arsenate Removal in the Packed Bed Reactor

The performance of GCFeA in continuous operation was studied by percolating arsenic solutions through a packed bed reactor. The C/C_0 value versus the number of bed volumes treated by GCFeA in the fixed-bed adsorption column is shown in Figure 4.35. It was found that the GCFeA was able to achieve effluent arsenate of approximately 10 $\mu g\ L^{-1}$ or below for up to 300 bed volumes in a continuous flow mode. Some of the iron was found to be detached at the beginning of the column operation while afterwards there was a negligible quantity of iron detached. The GCFeA could treat approximately 3600 bed volumes of arsenate before column exhaustion.

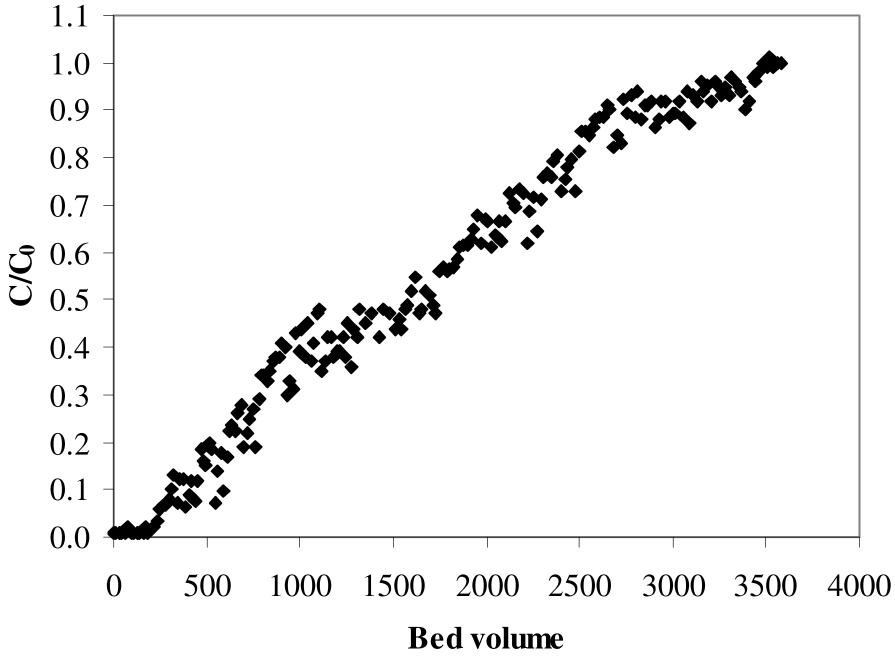


Figure 4.35 The breakthrough curve for arsenate adsorption onto GCFeA.

When the sorbent was saturated with arsenate, a simple test was carried out to see whether the GCFeA packed bed reactor could be chemically regenerated. Packed bed column regeneration study was conducted to assess the possibilities for the reuse of the adsorbent and recovery of metal ions. The exhausted packed bed reactor previously run under 2.8 mL min^{-1} was regenerated by passing 0.1 M of NaOH with a same flow rate downwards through the bed. Figure 4.36 shows an arsenate concentration profile during regeneration. The rate of arsenate desorption was reduced at the end of the packed bed reactor studies, while at the beginning of the packed bed reactor operation, desorption of arsenate was fast. As shown in Figure 4.36 the highest arsenate concentration was detected after flowing about 1.5 bed volumes of NaOH then the concentration of arsenate gradually decreased.

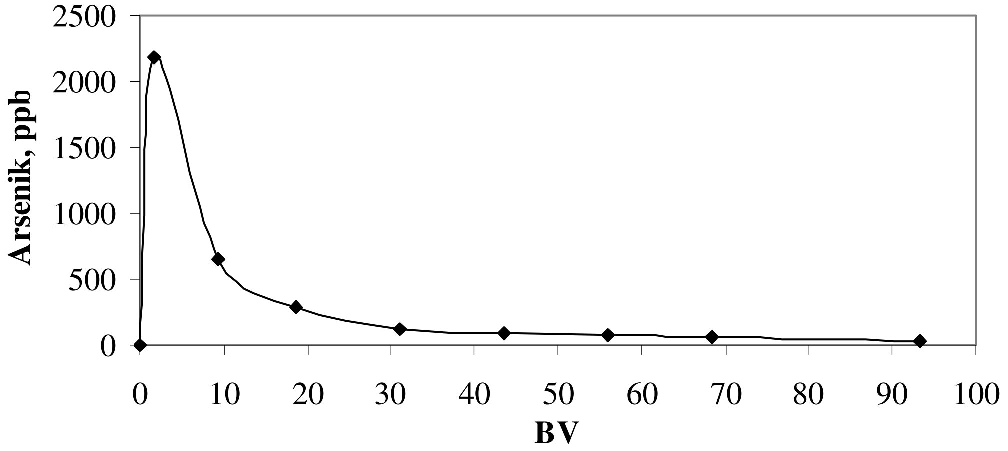


Figure 4.36 Desorption profile of arsenate from GCFeA during regeneration with 0.1 M NaOH.

4.4 The Application of Obtained Optimum Conditions from Coagulation and Flocculation, Lime Softening and Adsorption Processes to Real Groundwater

4.4.1 The Application of Obtained Optimum Conditions from Coagulation and Flocculation Process to Real Groundwater

Removal of arsenic from real groundwater in Sasalı-İzmir was investigated using obtained optimum conditions from coagulation and flocculation method in order to compare arsenic treatment results of synthetic and natural arsenic contaminated water. Sasalı groundwater has highly arsenic contamination (951 $\mu g\ L^{-1}$) as shown in Table 3.6. According to results of Box-Behnken experimental design method for ferric chloride, ferric sulfate, ferrous sulfate, and aluminum sulfate, optimum pH values for maximum arsenate removal were found as 7.5, 8, 9, and 7, respectively.

As aforementioned in part of 1.2.2, in the aqueous environment inorganic arsenic appears commonly in the oxidation states +V and +III and the relative concentrations of each are controlled by the redox potential (Eh) and pH. Under oxidizing conditions (positive Eh) As(V) is the primary form of arsenic, while under reducing conditions (negative Eh) the primary form is As(III). Arsenate is relatively easy to remove from water, since it bears a negative charge in natural waters above pH 2.2, and is electrostatically attracted to the positive charge on metal hydroxide surfaces (Johnston et al., 2001). Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite (As(III)) species will predominate (Smedley and Kinniburgh, 2002). Therefore As(III) is less efficiently removed than As(V), so preoxidation is necessary for better removal (Fujimoto, 2001). Hypochloride is commonly used oxidant because it can be rapidly oxidize trivalent arsenic to pentavalant arsenic (Ahmed, 2001):

$$H_3AsO_3 + HOCl \rightarrow HAsO_4^{2-} + Cl^- + 3H^+$$

For the demonstration of importance of oxidation process, all experiments were carried out with and without oxidation at the optimum conditions. Using Box-Behnken experimental design method, optimum coagulant doses were found for Sasalı groundwater and the calculated optimum doses were applied. The results of experiments with and without oxidation at the optimum conditions, and Box-Behnken response functions predictions were compared in Table 4.17.

Table 4.17 Comparison of the experimental and predicted values for different Box-Behnken experimental design points for Sasalı groundwater

Coagulant type	**Dose, mg L^{-1}**	**pH**	**Efficiency with oxidation, %**		**Efficiency without oxidation, %**
			Observed	**Predicted**	
$FeCl_3$	36	7.5	99	100	83
$Fe_2(SO_4)_3$	31	8	99	100	74
$FeSO_4$	59	9	98	100	68
$Al_2(SO_4)_3$	51	7	99	100	68

Figure 4.37(a-d) shows the variations of percent arsenate removals with different $FeCl_3$, $Fe_2(SO_4)_3$, $FeSO_4$, and $Al_2(SO_4)_3$ concentrations and constant pH of 7.5, 8, 9, and 7, respectively and the effect of preoxidation process. It can be seen from the Figure 4.37(a-d) that the addition of coagulant caused a increase in the arsenic removal efficiency both with and without preoxidation process. The applications of preoxidation followed by $FeCl_3$ dose of 36 mg L^{-1}, $Fe_2(SO_4)_3$ dose of 31 mg L^{-1}, $FeSO_4$ dose of 59 mg L^{-1}, and $Al_2(SO_4)_3$ dose of 51 mg L^{-1} were decreased the residual arsenic concentrations below 10 μg L^{-1} which is the maximum contaminant level of arsenic in drinking water determined by USEPA and WHO. The relationship between coagulant dose and residual iron and aluminum are also shown in Figure 4.37(a-d). It appears that residual iron and aluminum generally decreases with decreasing residual arsenic. Residual iron and aluminum concentrations are proportional to arsenic removal for all types of coagulant. At the optimum coagulant dose of $FeCl_3$, $Fe_2(SO_4)_3$, and $FeSO_4$ for coagulation flocculation process with oxidation, residual iron concentrations were measured as 0.18, 0.58, and 0.70 mg L^{-1}, respectively. At the optimum coagulant dose of $Al_2(SO_4)_3$ for coagulation flocculation process with oxidation, residual aluminum concentrations were also measured as 0.11 mg L^{-1}.

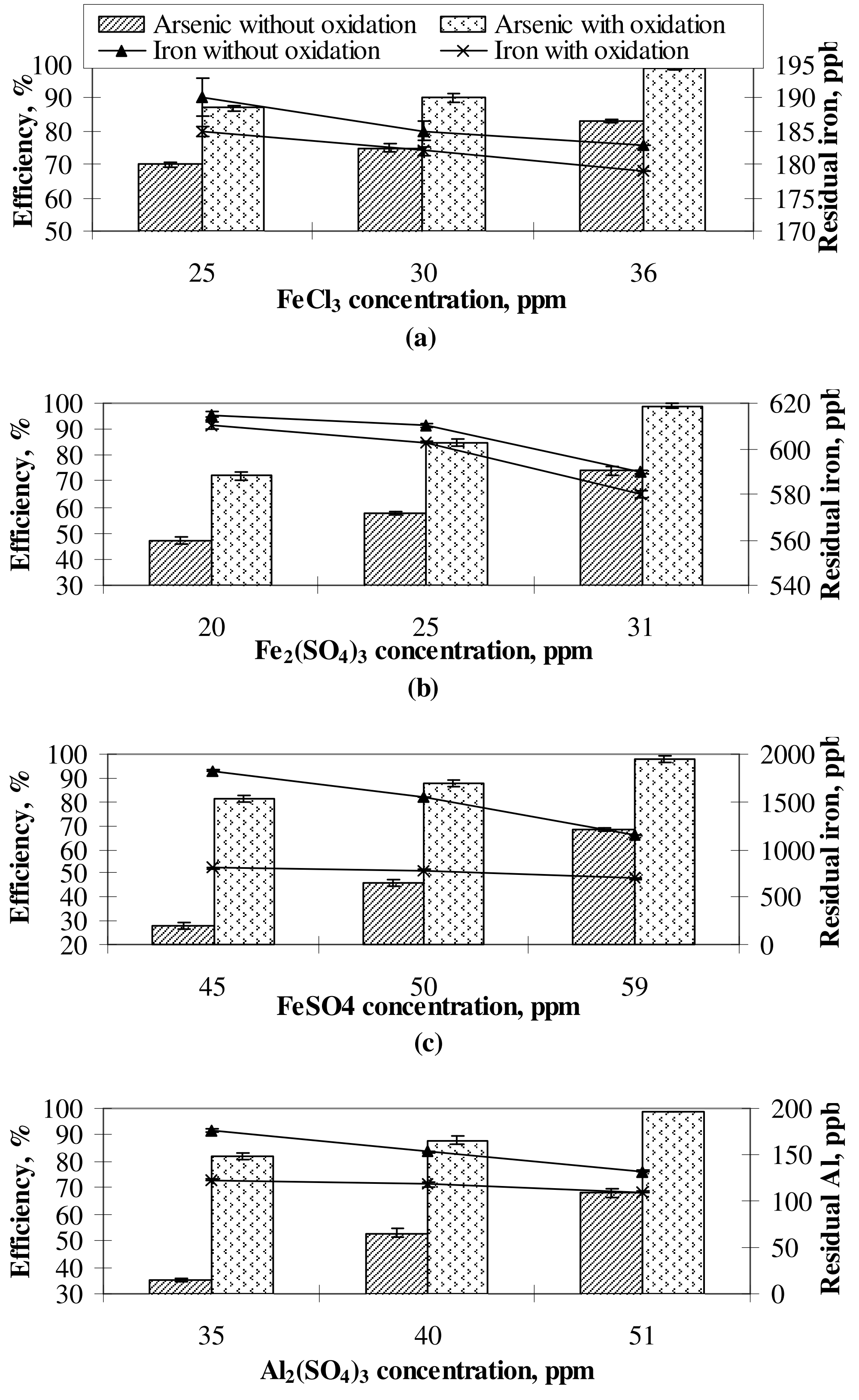


Figure 4.37 Effect of a) ferric chloride b) ferric sulfate c) ferrous sulfate d) aluminum sulfate dose on the arsenic removal efficiency of Sasalı groundwater, effect of preoxidation process, and relationship between coagulant dose and residual iron or aluminum.

The main parameter affecting the arsenic removal efficiency is the redox potential, which controls the performance of oxidation-reduction processes. Before oxidation by chlorine, the removal efficiency of arsenic was not sufficient. To improve the removal efficiency of trivalent arsenic, the redox potential was increased by sodium hypochloride from 138 to 437 mV in the Sasalı groundwater. Redox potential values of Sasalı groundwater are shown in Table 4.18 before and after treatment steps. When the redox potential was increased to values over 400 mV the removal of arsenic increased up to 98% as shown in Table 4.18 and Figure 4.36(a-d). These results indicate that the oxidation process was involved in the removal of trivalent arsenic, as an increase in the redox potential caused a significant increase in arsenic removal.

Table 4.18 Redox potentials of groundwater before and after coagulation-flocculation treatment steps

Coagulant type and dosage	**Redox potential, mV**			
	Initial	**Coagulation**	**Oxidation**	**Oxidation+Coagulation**
$FeCl_3$				
25	138	157	437	507
30	138	165	437	505
36	138	165	437	478
$Fe_2(SO_4)_3$				
20	138	150	437	444
25	138	147	437	462
31	138	151	437	470
$FeSO_4$				
45	138	127	437	441
50	138	127	437	447
59	138	135	437	453
$Al_2(SO_4)_3$				
35	138	153	437	433
40	138	162	437	434
51	138	176	437	446

Because the maximum contaminant level of iron and aluminum in drinking water is 200 μg L^{-1} according to Turkish Standards (Turkish Standards 2005), aluminum sulfate is found effective and reliable coagulant considering residual aluminum but ferric chloride is found more effective and reliable coagulant than others considering required concentration and residual iron. The obtained results from natural arsenic contaminated groundwater are consistent with the previous studies in the part of 4.1.1.1 and 4.1.1.2 on arsenate removal from synthetic contaminated tap water using ferric salts and aluminum sulfate. Therefore, Box-Behnken experimental design method was reliable and effective in determining the optimum conditions and this study provided useful information and reference conditions that Box-Behnken statistical experiment design method may be used to optimize other chemical processes.

4.4.2 The Application of Obtained Optimum Conditions from Lime Softening Process to Real Groundwater

Removal of arsenic from real groundwater in Sasalı-İzmir was investigated using obtained optimum conditions from lime softening method in order to compare arsenic treatment results of synthetic and natural arsenic contaminated water. Effects of coagulant dose and variations in the pH values of arsenate contaminated tap water as a result of hydrated lime addition were investigated at the initial arsenate concentrations of 50, 500, and 1000 μg L^{-1} in part of 4.2. Sasalı groundwater has highly arsenic contamination (951 μg L^{-1}) as shown in Table 3.6. Therefore the obtained calcium hydroxide concentrations which supply maximum arsenate removal efficiencies at the initial arsenate concentrations of 1000 μg L^{-1} were used for Sasalı groundwater treatment.

For arsenic removal from aqueous solution by lime treatment, more than 90% As(V) removal could be provided if the pH is above 10.5. As(III) could be removed to about 75% at pH values of above 11 (Newcombe and Dixon, 2006). Therefore preoxidation is necessary for better removal by lime softening like coagulation and flocculation method.

For the demonstration of importance of oxidation process, all experiments were carried out with and without oxidation at the optimum hydrated lime concentration and at the pH of 7. Figure 4.38 shows the variations of percent arsenic removals with different $Ca(OH)_2$ concentrations, effect of preoxidation process by sodium hypochloride, and the relationship between coagulant dose and pH. Percent arsenic removal increased with increasing $Ca(OH)_2$ concentration and reached a maximum level at $Ca(OH)_2$ concentration of 200 mg L^{-1} for both with and without oxidation. The addition of $Ca(OH)_2$ caused a substantial increase in the pH. At the hydrated lime concentration of 200 mg L^{-1}, arsenic concentration reduced below 10 μg L^{-1} which is maximum contaminant level for arsenic in drinking water if the preoxidation by chlorine was applied.

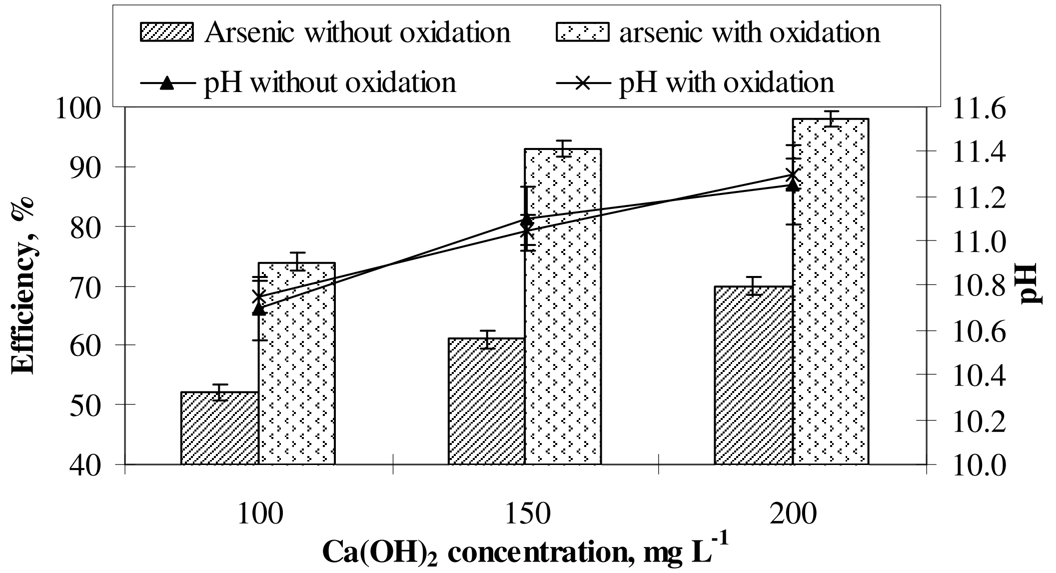


Figure 4.38 Effect of calcium hydroxide dose on the arsenic removal efficiency of Sasalı groundwater, effect of preoxidation process, and relationship between coagulant dose and pH.

It can be seen from the Figure 4.38 before oxidation by chlorine, the removal efficiency of arsenic was not sufficient. To improve the removal efficiency of trivalent arsenic, the redox potential was increased by sodium hypochloride from 138 to 437 mV in the Sasalı groundwater. Redox potential values of Sasalı groundwater are shown in Table 4.19 before and after treatment steps. When the redox potential was increased to values over 400 mV the removal of trivalent arsenic increased up to 97% as shown in Table 4.19 and Figure 4.38. These results indicate that the oxidation process was involved in the removal of trivalent arsenic, as an increase in the redox potential caused a significant increase in arsenic removal. The obtained results from natural arsenic contaminated groundwater are consistent with the previous studies in the part of 4.2 on arsenate removal from synthetic contaminated tap water using calcium hydroxide.

Table 4.19 Redox potentials of groundwater before and after lime treatment steps

$Ca(OH)_2$ dosage	**Redox potential, mV**			
	Initial	**Lime treatment**	**Oxidation**	**Oxidation+Lime treatment**
100	138	143	437	442
150	138	149	437	448
200	138	150	437	456

4.4.3 The Application of Obtained Optimum Conditions from Adsorption Process to Real Groundwater

Removal of arsenic from real groundwater in Sasalı-İzmir was also investigated using obtained optimum conditions from adsorption method in order to compare arsenic treatment results of synthetic and natural arsenic contaminated water. According to results of adsorption process, pH of the Sasalı groundwater was adjusted as 6.5. The column test was carried out at the flow rate of 2.8 mL min^{-1} which is the optimum rate. For the demonstration of importance of oxidation process, the column tests were carried out with and without oxidation. The obtained arsenic removal efficiency and residual iron results, and redox potential of the groundwater before and after adsorption treatment steps are shown in Table 4.20.

It can be seen from the Table 4.20, preoxidation by sodium hypochloride was not effected arsenic removal efficiency by adsorption method. In both cases (only adsorption and preoxidation+adsorption), arsenic removal efficiencies were almost same and very high. According the these results, GCFeA is the natural zeolite that most efficiently removes As(III) and As(V) from aqueous solution at pH 6.5.

Table 4.20 The results of adsorption process on arsenic removal efficiency and variation in the residual iron and redox potential before and after adsorption treatment steps

Parameter	Initial	Adsorption	Oxidation+Adsorption
Efficiency, %	-	99.1	99.8
Iron, mg L^{-1}	0.011	0.15	0.18
Eh, mV	138	180	537

Removal of As(III) from aqueous solutions is usually poor compared to that of As(V) by almost all of the technologies. This is because the predominant As(III) compound is neutral in charge and can undergo only Lewis acid-base interactions, while the As(V) species are negatively charged in the pH range of 4–10 and can undergo Coulombic (ion exchange) as well as Lewis acid–base interactions the As(III) species has a high affinity for the iron (III) oxide surface (Macedo-Miranda and Olguin, 2007). In the present work, when iron modified natural zeolites GCFeA was put in contact with the As(III) solution at pH 6.5, the following interactions are considered:

Monodentate inner sphere complex:
Only Lewis acid-base interaction

$$GC - FeOH \leftarrow HAsO_2$$

The obtained results are showed that preoxidation of As(III) to As(V) prior to adsorption using GCFeA was not increased the removal efficiecy because of the both As(III) was not predominant form in the Sasalı groundwater and GCFeA is capable of arsenite adsorption. At the same time the obtained results from the natural arsenic contaminated groundwater are consistent with the previous studies on arsenate removal from synthetic arsenic contaminated tap water using GCFeA as an adsorbent.

CHAPTER FIVE
CONCLUSIONS

At the beginning of the study, precipitation and coprecipitation method was used for arsenate removal from tap water. Ferric chloride and ferric sulfate were used as source of Fe(III), ferrous sulfate was used as source of Fe(II), and aluminum sulfate was used. The Box–Behnken statistical experiment design method was used to investigate the influence of major operating variables on arsenate removal efficiency and to find the combination of variables resulting in maximum arsenate removal efficiency. Initial arsenate concentration, coagulant dose and pH were considered as the independent variables while the objective functions were the arsenate removal efficiencies for four types of coagulants.

Experimental results demonstrated that the Fe(III) ions are more effective than Fe(II) ion for arsenate removal. Optimum pH values for maximum arsenate removal for ferric chloride, ferric sulfate, ferrous sulfate, and aluminum sulfate were found as 7.5, 8, 9, and 7. At the constant pH of 7.5, 8, 9, and 7, percent arsenate removal was increased with addition of coagulant as a result of floc formation and chemical destabilization of colloidal particles by neutralizing the charges that keeps them apart. Decreasing initial arsenate concentration caused increases in required coagulant dose due to collision between the colloids. At the initial arsenate concentration of 10 $\mu g\ L^{-1}$, percent arsenate removal was reached a maximum level at $FeCl_3$, $Fe_2(SO_4)_3$ and $FeSO_4$ concentrations of 50, 40 and 60 $mg\ L^{-1}$, respectively. For the initial arsenate concentration of 500 and 1000 $\mu g\ L^{-1}$, percent arsenate removal efficiencies were obtained 100% at the $FeCl_3$ concentrations of 31 and 37 $mg\ L^{-1}$, $Fe_2(SO_4)_3$ concentrations of 28 and 32 $mg\ L^{-1}$ and $FeSO_4$ concentrations of 60 and 58 $mg\ L^{-1}$. For aluminum sulfate, in the initial arsenate concentration of 10 $\mu g\ L^{-1}$, the highest arsenate removal efficiency, about 91%, was obtained at coagulant dose of 66 $mg\ L^{-1}$, while in the initial arsenate concentrations of 500 and 1000 $\mu g\ L^{-1}$, the highest arsenate removal efficiency, 100%, was provided at coagulant dose 42 and 56 $mg\ L^{-1}$, respectively.

The results suggested that A Box–Behnken statistical experiment design and response surface methodology offer an efficient and feasible approach for arsenate removal and they were effective in determining the optimum conditions for arsenate removal by coagulation and flocculationmethod using ferric chloride, ferric sulfate, ferrous sulfate, and aluminum sulfate. Therefore it could be employed to determine the optimum conditions for arsenate removal while minimising the number of experiments required and this study provided useful information and reference conditions that Box-Behnken experimental design method may be used to optimize other chemical processes.

Residual iron and aluminum concentration after sedimentation and filtration in the effluent was also investigated because of the health effects of excess iron and aluminum in the drinking water. It was found that the residual iron and aluminum concentrations are affected by residual arsenate concentration besides coagulant dose. The arsenate concentration can be reducing down to 10 $\mu g\ L^{-1}$ in the initial arsenate concentration ranging within 10 to 1000 $\mu g\ L^{-1}$ for all types of coagulants. However, ferric chloride was effective and reliable coagulant considering required concentration and residual arsenate and iron concentration after sedimentation and filtration in the effluent.

Cationic, anionic, and nonionic polyelectrolytes were also tried to investigate the effect on removal efficiencies of arsenate from tap water by precipitation-coprecipitation with ferric chloride, ferric sulfate, ferrous sulfate, and aluminum sulfate. The application of polyelectrolytes resulted in the formation of greater particles, faster floc formation, and produce denser and stronger flocs. Although all types of polymers increased the removal efficiency of the treatment method, application of cationic polyelectrolyte was more effective than anionic and nonionic ones.

Removal of arsenate from drinking water was also investigated by lime softening process using calcium hydroxide. Effects of coagulant dose and variations in the pH values of arsenate contaminated water as a result of hydrated lime addition were investigated at the initial arsenate concentrations of 50, 500, and 1000 µg L^{-1}. According to results of experimental studies using calcium hydroxide, more than 90% arsenate removal was achieved if the pH is above 10.2. In the initial arsenate concentration of 50 µg L^{-1}, the arsenate concentration is reduced below 10 µg L^{-1} at coagulant dose of 110 mg L^{-1}, while in the initial arsenate concentrations of 500 and 1000 µg L^{-1}, the highest arsenate removal efficiency, about 99%, was provided at coagulant dose 200 mg L^{-1}. Lime softening for arsenate removal was required larger amount of coagulant doses and higher operating pH than iron and aluminium salts and consequently a large volume of sludge is produced and strong acids would probably be needed to adjust the pH after treatment. Therefore lime softening would only be considered as a reasonable treatment alternative if the treatment goals include the removal of hardness and/or heavy metals.

In order to determine the effect of organic polymers on removal efficiencies of arsenate from tap water by lime softening with calcium hydroxide, some experiments were also executed. Impact of polyelectrolyte types (cationic, anionic, and nonionic) and dosage was determined. The addition of anionic and nonionic polyelectrolyte has not affected the arsenic removal efficiency.

Removal of arsenate from drinking water was also investigated by adsorption process using the GC (clinoptilolite from Gördes-Manisa). In order to improve the ion exchange characteristics of the zeolitic material to obtain Fe-modified clinoptilolite with different surface characteristics, clinoptilolite was treated with 0.1 M NaCl followed by 0.1 or 0.01 M $FeCl_3$ solutions.

According to the concentration of Na, Mg, K and Ca in the GC, it is considered to be a K-Ca zeolite type. In the clinoptilolite treated with $FeCl_3$ solutions, the iron ions are exchanged by the sodium ions from the zeolite network, and the concentration of iron increase (54.66% for GCFeA and 5.251% for GCFeB), depending on the initial concentration of $FeCl_3$ in the solution. The SEM images of unmodified and modified zeolites showed that no changes were observed in the morphology of the clinoptilolite crystals of the GC after its treatment with NaCl, and $FeCl_3$ solutions.

The X-ray diffraction analysis showed that clinoptilolite and quartz were found in GC. The results suggested that sodium chloride conditioning has no effect on the structure of zeolitic material and in the position of the most intense diffraction peaks. For GCFeA, and GCFeB, X-ray diffraction patterns showed differences in the intensity of reflexions, but no changes in their position were observed relative to GCNa. The specific surface area of the GC and GCNa is almost same. However, when the GCNa was treated with 0.1 M $FeCl_3$, the GCFeA increased 2.4 times its specific surface area.

The effects of contact time, pH, clinoptilolite amount, and initial arsenate concentrations on arsenate removal were investigated in batch experiments. The adsorption percentage of arsenate increased with increase of contact time and the equilibrium time to reach the maximum arsenate removal by the modified and unmodified clinoptilolites was found as 60 min. The As(V) adsorption capacities of GC, GCNa, GCFeA, and GCFeB at equilibrium are 1.5, 1.7, 8.4, and 9.2 $\mu g\ g^{-1}$. These results showed that iron modified zeolites are effective adsorbent for the arsenate removal from aqueous solution. GCFeA is the highest effective adsorbents and reduce arsenate concentration below the 10 $\mu g\ L^{-1}$ which is the maximum contaminant level of arsenic in drinking water determined by USEPA and WHO.

Although adsorption capacity of GC and GCNa is very low, maximum arsenate adsorption onto GC and GCNa was obtained at pH 5 and 7, respectively. Both the GCFeA, and GCFeB removed arsenic effectively over the initial pH range 4–10. Adsorption percentage of As(V) on all types of clinoptilolite increased with the increase of amount clinoptilolite. Amount of clinoptilolite above 500 mg L^{-1} slightly increased percent arsenate removal. The removal efficiency of arsenate for GC increased from 0 to 15%, for GCNa increased from 2 to 17%, for GCFeA increased from 22% to 92%, and for GCFeB increased from 15 to 84% as the adsorbent dose increased from 25 to 500 mg L^{-1}. The relationship between zeolite amount and residual iron are also investigated. The experimental results demonstrated that after arsenate treatment using GCFeA and GCFeB residual iron increased with increasing zeolite amount and maximum residual iron values were measured as 0.195 and 0.556

mg L^{-1} for GCFeA and GCFeB, respectively. Because the maximum contaminant level of iron in drinking water is 200 µg L^{-1} according to Turkish Standards (Turkish Standards 2005), GCFeA is found effective and reliable iron-modified zeolite considering residual iron. The adsorption percentage of arsenic decreased with the increase of initial concentration of arsenic for all types of clinoptilolite. In case of arsenate adsorption onto GCFeA, the percent removal increases from 77.7% at 1000 µg L^{-1} to 92% at 100 µg L^{-1}. Similarly adsorption performance increases from 64.2% at 1000 µg L^{-1} to 82% at 250 µg L^{-1} while using GCFeB as adsorbent.

To quantify the adsorption capacity of GCFeA and GCFeB, for removal of As(V) from water, Langmuir and Freundlich adsorption equations were used. GCFeA adsorption capacity was adequately described by Freundlich isotherm, whereas GCFeB adsorption capacity was described by Langmuir isotherm. According to the computed K_f constant, this is related primarily to the capacity of the adsorbent to adsorb arsenic, GCFeA has larger capacities of adsorption. As(V) adsorption on GCFeA has the highest *1/n* constant, which means that adsorption bond between the As(V) ion and adsorbent is the strongest.

Two important kinetic models namely pseudo-first-order, and pseudo-second-order models were also applied in order to investigate the mechanism of adsorption of arsenate and to identify the rate and kinetics sorption of arsenate on GCFeA and GCFeB. The correlation coefficients for the first-order kinetic model obtained at all the studied initial concentrations were low. The theoretical q_e (cal) values calculated for the pseudo first-order model did not give reasonable values with regard to the experimental uptake values, q_e (exp). This indicates that pseudo first-order equation might not be sufficient to describe the mechanism of arsenate adsorption system. The obtained results from the pseudo second order kinetic model showed that R^2 values are higher than those obtained from the pseudo first-order kinetics. Based on these results, it can be concluded that the pseudo second-order kinetic model provided a good correlation for the adsorption of arsenate by GCFeA and GCFeB in contrast to the pseudo first-order model. According to the q_e (cal) values, GCFeA adsorbs the highest amount of arsenate from an aqueous solution. The parameter K_2, which corresponds to the velocity constant of pseudo-second order, is the highest for GCFeB at the initial arsenate concentration of 100 μg L^{-1}. For the initial arsenate concentrations of 250 and 500 μg L^{-1}, rate constant values for GCFeA are the same or a bit higher than GCFeB.

The desorption experiments were also carried out with the zeolite GCFeA considering its good performance in sorption experiments. Desorption performance of GCFeA is 54% using 0.1 M NaOH solution and arsenic removal capacity of the regenerate material is almost same (83%) with the fresh material (92%). According the results of experiments the GCFeA was used 6 times until arsenic removal efficiency was reduced to 19%.

The performance of GCFeA in continuous operation was also studied by percolating arsenic solutions through a column. The optimum flow rate was found as 2.8 mL min^{-1}. The experimental results demonstrated that GCFeA was able to achieve effluent arsenate of approximately 10 μg L^{-1} or below for up to 300 bed volumes in a continuous flow mode. The GCFeA could treat approximately 3600 bed volumes of arsenate before column exhaustion. Fixed bed column regeneration study was also conducted to assess the possibilities for the reuse of the adsorbent and recovery of metal ions. The highest arsenate concentration was detected after flowing about 1.5 bed volumes of NaOH then the concentration of arsenate gradually decreased.

Removal of arsenic from real groundwater in Sasalı-İzmir was investigated using obtained optimum conditions from coagulation and flocculation, lime softening, and adsorption method in order to compare arsenic treatment results of synthetic and natural arsenic contaminated water. For the demonstration of importance of oxidation process, all experiments were carried out with and without oxidation at the optimum conditions. For coagulation-flocculation and lime softening process before oxidation by chlorine, the removal efficiency of arsenic was not sufficient. These results indicate that the oxidation process was involved in the removal of trivalent arsenic, as an increase in the redox potential caused a significant increase in arsenic removal.

The obtained results from natural contaminated groundwater are consistent with the previous studies on arsenate removal from synthetic contaminated tap water. Therefore, Box-Behnken experimental design method was reliable and effective in determining the optimum conditions and this study provided useful information and reference conditions that Box-Behnken statistical experiment design method may be used to optimize other chemical processes. The experimental studies showed that preoxidation by sodium hypochloride was not effected arsenic removal efficiency by adsorption method. In both cases (only adsorption and preoxidation+adsorption), arsenic removal efficiencies were almost same and very high. According the these results, GCFeA is the natural zeolite that most efficienctly removes As(III) and As(V) from aqueous solution at pH 6.5.

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