METHODS FOR ARSENIC REMOVAL FROM AQUEOUS SOLUTIONS

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ABSTRACT

METHODS FOR ARSENIC REMOVAL FROM AQUEOUS SOLUTIONS

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In the last few decades, one of the major environmental problems that world has been facing is limited access to clean water and depletion of water resources. Scarcity of clean water started to compel municipals to use waters which must be separated from contaminants. One of the major contaminants in water sources is arsenic which poses a challenge for separation. This study is an effort to find a feasible method for the removal of arsenic from water. Arsenic is a mineral found in rocks and soil, which can contaminate ground waters and surface waters used as public water resources. Due to adverse effect of arsenic on human health and plants allowable arsenic concentration in drinking waters was determined as10 µg/L by the World Health Organization (WHO).

In this study, arsenic removal problem was approached with two different arsenic removal methods based on the use of two different types of polymers. High porosity cationic hydrogels synthesized *via* crosslinking co-polymerization of diallyldimethylammonium-chloride (DADMAC) with N,N’-

tetraallylpiperaziniumdichloride (TAP) was used in batch and fixed colum adsorption studies; on the other hand, water soluble linear diallyldimethylammonium chloride (DADMAC) – vinyl pyridine (P(4-VP)) co-polymers were used in polymer enhanced ultrafiltration (PEUF) studies.

DADMAC hydrogels can be regarded as the most efficient hydrogels reported in literature for arsenate removal in terms of applicable pH range, arsenic removal capacity and contact time required. In this study, hydrogels synthesized showed high affinity for arsenate anions (As (V)) at a wide pH range of 6 to 10. Arsenic removal efficiency of 99 percent was obtained when arsenic solutions having concentrations of 1000 μg/L (100 mL) were treated with 0.1 g hydrogel with a contact time less than 15 minutes; regeneration and re-usability studies of hydrogels were also conducted.

Ultrafiltration experiments conducted with commercially available Polyether Sulfone (PES) membranes resulted in arsenate (As (V)) retention values around 80-85 percent in the pH range of 7 to 10, while DADMAC- P(4-VP) co-polymer addition increased this value up to 98 percent. In PEUF, polymer concentrations of 0.01 g/L were enough for successful separations without membrane fouling.

On the other hand arsenite (As(III)) removal by PEUF resulted in merely as high as 50 percent only due to the poor interaction of polymer with arsenic ions. Highest retention value obtained in ultrafiltration experiments for As(III) was also recorded as 40%.

Keywords: Arsenic Removal, Hydrogel, Polymer Enhanced Ultrafiltration (PEUF), DADMAC

ÖZ

SULU ÇÖZELTİLERDEN ARSENİK GİDERME YÖNTEMLERİ

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Geçtiğimiz birkaç onyılın en önemli çevre sorunlarından birisi tükenmekte olan su kaynakları ve temiz suya ulaşmakta yaşanan sıkıntılardır. Temiz su bulma korkusu belediyeleri sularını kirleticilerden ayırmaya ikna etmeye başlamıştır. Suda bulunan en önemli kirleticilerden birisi ayırmada da zorluklara sebep olan arsenik mineralidir. Bu çalışmada sudan arsenik arıtımı için uygulanabilir bir metod bulunmaya çalışılmıştır. Arsenik doğada kayalarda ve toprakta bulunan bir mineral olup, yer altı ve yer üstü sularına karışabilmektedir. Sağlık üzerine olan olumsuz etkileri sebebiyle içme sularında bulunabilecek arsenik miktarı Dünya Sağlık Örgütü tarafından 10 μg/L olarak belirlenmiştir.

Bu çalışmada arsenik giderim problemine iki farklı polimer kullanılarak iki farklı metotla yaklaşılmıştır. Çapraz bağlanma ko-polimerizasyonu metoduyla sentezlenen ve yüksek poroziteye sahip katyonik diallyldimetilamonyum klorür (DADMAC), N,N'-tetraallylpiperaziniumdichloride (TAP) hidrojelleri kesikli ve sabit yatak adsorpsiyon işleminde kullanılmıştır. Diğer yandan lineer suda çözülebilen diallildimetilamonyum klorür – vinil piridin ko-polimerleri ise polimer destekli ultrafiltrasyon (PDUF) işlemlerinde kullanılmıştır.

Bu çalışmada DADMAC hidrojellerin bugüne kadar literatüre sunulan hidrojellere göre çalışılabilinen pH aralığı, arsenik tutma miktarı ve temas süresi açısından daha etkili olduğu gözlemlenmiştir. Hidrojeller geniş bir pH aralığında arsenat (As (V)) anyonlarını yüksek bir verim ile tutabilmektedirler (pH 6-10). 1000 µg/L (100 mL) arsenik içeren çözeltilere 0.1 g hidrojel eklenmesiyle 15 dk. dan az bir sürede yüzde 99 arsenik giderimi elde edilmiştir. Hidrojellerin rejenerasyonu ve tekrardan kullanımıyla ilgili deneyler de bu çalışmada yer almaktadır.

Ticari olarak satılan polieter sülfon içeren membranlar ile gerçekleştirilen ultrafiltrasyon çalışmalarında pH 7-10 arasında arsenat iyonlarının (As (V)) gideriminde yüzde 80-85 civarında verim gözlemlenirken DADMAC- P(4-VP) ko-pollimerlerinin eklenmesi ile bu oranın yüzde 98'e çıkabilmiştir. Polimer destekli ultarfiltrasyon deneylerinde 0,01 g/L polimer derişimi etkili bir ayrım için yeterli bulunmuştur.

Polimer – arsenik etkileşiminin yetersiz oluşundan dolayı, sudan üç değerlikli (As (III)) arsenik anyonlarının sudan ayrılmasında en fazla yüzde 50 verim elde edilebilmiştir. Bu denemelerde ultrafiltrasyon işlemiyle elde edilen en yüksek değer ise yüzde 40 olmuştur.

Anahtar Kelimeler: Hidrojel, Arsenik arıtma, PDUF, DADMAC

To my family

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LIST OF ABBREVIATIONS

$C_{T, F}$	Concentration of targeted species in the feed
$C_{T, P}$	Concentration of targeted species in the permeate
MEUF	Micellar Enhanced Ultrafiltration
MF	Microfiltration
NF	Nanofiltration
PES	Polyethersulfone
PEUF	Polymer Enhanced Ultrafiltration
PS	Polysulfone
R	Retention
RO	Reverse Osmosis
UF	Ultrafiltration
R	Ideal gas constant (eqn 2.8)
T	Absolute temperature (eqn 2.8)
z	Valance of the solute (eqn 2.8)
F	Faraday Constant (eqn 2.8)
Ψ_d	Donnan Potential (eqn 2.8)
C_m	Solute concentration on membrane surface (eqn 2.8)
C_b	Solute concentration in bulk phase (eqn 2.8)
R_R	Real retention (eqn 2.9)
z_a	Valance of cation in the electrolyte (eqn 2.9)
z_c	Valance of anion in the electrolyte (eqn 2.9)
X	Charge density of the membrane (eqn 2.9)
S	Swelling ratio (eqn. 4.1)
S_{max}	Equilibrium swelling ratio (eqn. 4.1)
k	swelling rate constant (eqn. 4.1)
$C_{As,i}$	Initial arsenic concentration (in mol/L) (eqn. 4.2-4.3)
$C_{As,f}$	Final arsenic concentration (in mol/L) (eqn. 4.2-4.3)
C_0	Feed arsenic concentration in column experiments

C	Effluent arsenic concentrations in column experiments
m	mass of dry gel (eqn. 4.2)
v	sample volume (eqn. 4.2)
Q	binding capacity (eqn. 4.2)
c	time independent capacity (eqn. 4.4)
k_a	rate constant of the diffused mass within time (eqn. 4.4)
t	time (eqn. 4.4)
MWCO	Molecular weight cut off
t_s	Service time (eqn 4.5)
N_0	Bed capacity (eqn 4.5)
Z	Bed height (eqn 4.5)
U_0	Superficial velocity (eqn 4.5)
K_{ad}	Adsorption rate constant (eqn 4.5)
C_{br}	breakthrough arsenic concentrations (eqn 4.5)
C_{feed}	Feed arsenic concentration UF and PEUF experiments
C_p	Permeate arsenic concentration UF and PEUF experiments

CHAPTER 1

INTRODUCTION

Access to clean drinking water is still a major concern in the world. One of the pollutants that can be found in ground waters and rivers is arsenic which is considered as a very toxic chemical [1-6]; it is also reported that arsenic may cause cancer malignancies, vascular diseases and non -malignant skin [1]. Allowable arsenic concentration in drinking waters was declared by the World Health Organization (WHO) as 10 μg/L [6]**.** US environmental protection agency also decreased the allowable amount of As in drinking waters as 10 μg/L in 2001 which was 50 μg/L [2].

Methods for arsenic removal can be listed as chemical precipitation-coagulation, adsorption, ion exchange, reverse osmosis and complexation [6], although it is still a problem to remove arsenic effectively and economically. Adsorption and ion exchange are heterogeneous processes that can have additional mass transfer problems and require regeneration of the material used in the equipment. Precipitation involves chemical addition which may also be hazardous. Precipitation of metals having low concentrations is also difficult regarding the allowable limits of arsenic (10 μg/L). Lastly reverse osmosis operates at high pressures resulting in increase of the operating cost with a high retantate/permeate ratio.

Addition of polymers that can be re-generated and re-used in the treatment of water can also be used for removing arsenic. These methods are based on attraction of metals to polymers and removal of metals attracted on polymer by means of filtration of polymer or other methods. Polymers designed for this purpose can be used to reduce the arsenic amount in water to the desired levels. Polymers which are used in these processes can be re-generated and re-used; hence they may cause less solid waste when compared with traditional water treatment methods such as coagulation. Involvement of large polymer molecules in these processes also decreases the energy consumption for filtration and increases the flow rate of the product stream with respect to filtration processes like reverse osmosis. Cationic polymers with quaternary amine functional groups or other polymers with some modifications like iron addition were frequently studied in arsenic removal [1-10].

This study aims to present alternatives for arsenic treatment using methods involving polymer addition and covers research on arsenic removal from model arsenic solutions by means of polymer addition. In order to fulfill these studies two different approaches were made. Hydrogels synthesized *via* crosslinking co-polymerization of diallyldimethyl-ammonium chloride (DADMAC) with N,N'-Tetraallylpiperazinium-dichloride (TAP) were used in batch studies whereas linear and water soluble DADMAC-vinyl pyridine (P(4-VP)) co-polymers were used in PEUF studies.

Only a few sources are available in the literature on arsenic removal with hydrogels. Highly cationic DADMAC hydrogels firstly introduced by Bıçak et al. [11] were prepared according to the recipe of Korpe et al. [12] and used for removal of arsenate anions from aqueous solutions for the first time in literature.

PEUF studies including polymers with quaternary amine groups were widely studied in the literature although most of the studies were conducted by using batch filtration set-ups. Due to this fact, information on flow systems are limited for PEUF systems used in arsenic removal. This study also provides information on arsenic removal with or without polymer addition using a laboratory scale tangential flow filtration unit equipped with GE/Osmonics-PT membrane. This commercial membrane is a Polyether sulfone based ultrafiltration membrane

CHAPTER 2

BACKGROUND

2.1. Arsenic in Nature

Arsenic is a naturally occurring element in rocks, soil, air, etc. Arsenic can be found in ground and surface waters due to corrosion, dissolution and microbial action from these natural sources. Besides natural reasons arsenic can be transferred into surface and ground waters because of industrial effects. Industries like mining, petroleum refining and production of pesticides can be listed as some of the other resources for the arsenic [7].

Arsenic can be found in various forms in nature but the most abundant arsenic species are in inorganic form with valance states of As(III) and As (V). As (V) is more abundant in oxidizing environments like surface waters, rivers and lakes; on the other hand, As (III) is more abundant in reducing environments like ground waters. According to the pH and redox potential of the environment, As (III) can be found as arsenious acid (H_3AsO_3) and arsenite ions while As (V) can be found as arsenic acid (H_3AsO_4) and arsenate ions. Arsenic species according to these conditions can be represented in Figure 2.1.

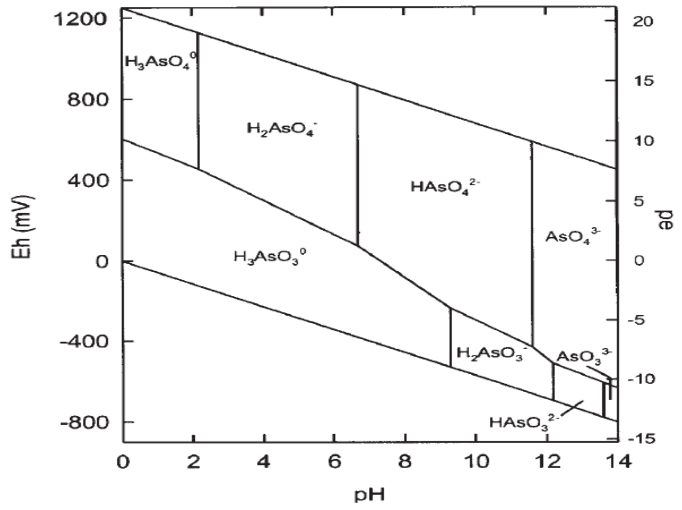

Figure 2.1. Redox potential vs. pH for arsenic species in aqueous environment. As-O_2-H_2O system 25^0C, 1 bar. Adopted from [2]

Oxidation state (As (III) or As (V)) of the arsenic species directly affects the interaction between arsenic ions and the medium which is used in treatment process. Regarding this fact, state of arsenic species can play a determining role in treatment processes. From Figure 2.1 it is obvious that arsenite ions do not exist in solutions having pH values lower than 9. On the other hand arsenate ions having -2 charge can be found in waters between pH 7 – 10 for a wide range of redox potentials. Effect of arsenic species on treatment methods will be discussed in more detail during the following chapters. During the experiments, solution pH will be the factor that could be controlled more easily; so it is also beneficial to have knowledge about abundance of arsenic ions in percentage with respect to solution pH. Abundance of ions at different pH values are given in Figures 2.2 and 2.3 for As(III) and As(V), respectively.

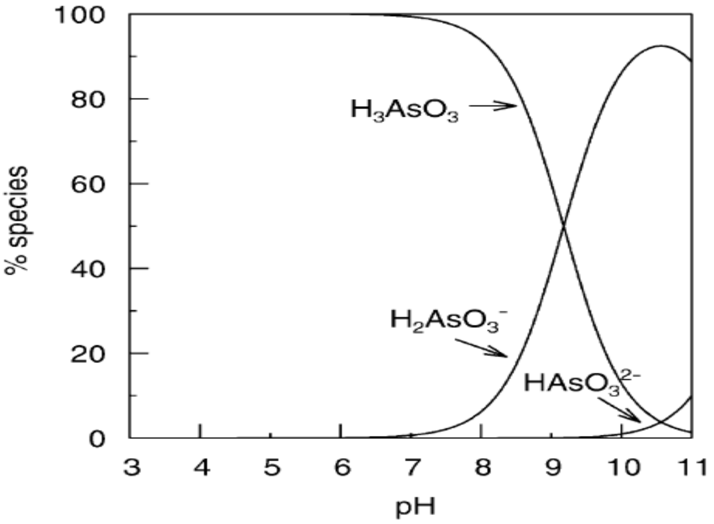

Figure 2.2. Percentage of the Arsenite species present in water versus pH.[1]

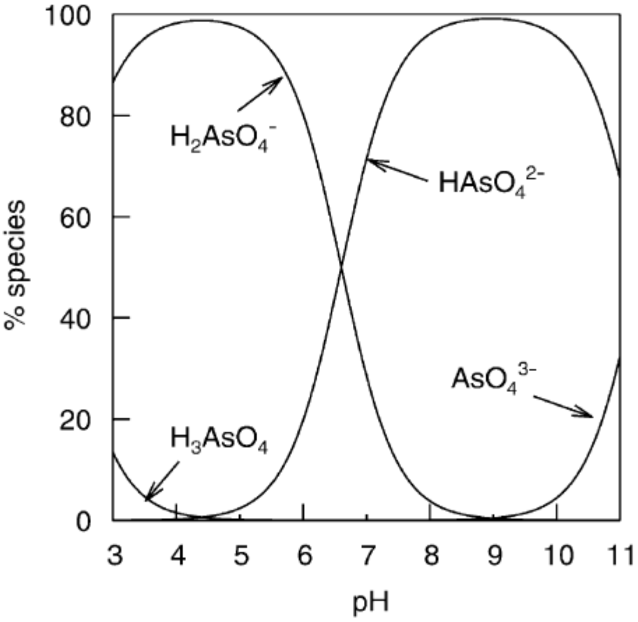

Figure 2.3. Percentage of the Arsenate species present in water versus pH.[1]

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[1] Adopted from: P.L. Smedley, D.G. Kinniburgh Applied Geochemistry 17 (2002) 517–568

The dissociation constants for the two oxidation states can be given as in the reference [2]:

Arsenous Acid/Arsenite:

$H_3AsO_3 \rightarrow H^+ + H_2AsO_3^-$ pKa = 9.23 (2.1)

$H_2AsO_3^- \rightarrow H^+ + HAsO_3^{2-}$ pKa = 12.13 (2.2)

$HAsO_3^{2-} \rightarrow H^+ + AsO_3^{3-}$ pKa =13.4 (2.3)

Arsenic acid/Arsenate

$H_3AsO_4 \rightarrow H^+ + H_2AsO_4^-$ pKa = 2.22 (2.4)

$H_2AsO_4^- \rightarrow H^+ + HAsO_4^{2-}$ pKa = 6.98 (2.5)

$HAsO_4^{2-} \rightarrow H^+ + AsO_4^{3-}$ pKa = 11.53 (2.6)

2.2. Usage of Hydrogels in Arsenic Treatment

Methods that are being used in arsenic removal can be listed as: co-precipitation, sorption and membrane-based methods such as reverse osmosis and nano-filtration [13]. Research studies are also being conducted for arsenic removal based on process including polymers. Polymers having positively charged quaternary amine groups have been investigated widely in the literature [2, 6, 14, 15].

Literature on hydrogel usage in arsenic treatment is limited. Hydrogels are insoluble cross-linked hydrophobic polymers having an ability to absorb water in great amounts [16]. Besides arsenic removal studies, hydrogel usage for treatment of other heavy metals and ions from water is also being investigated and remains as a hot research topic [17-22]. Some of the studies conducted for arsenic removal using hydrogels are also given in this section.

Barakat et al. [16] studied arsenic removal using hydrogels and a batch experimental set-up. Poly (3-acrylamidopropyl) trimethylammonium chloride (p(APTMACl)) hydrogels were synthesized and used for this purpose. Parameters such as medium pH and hydrogel amounts were studied. Feed arsenic concentration (As (V)) was recorded as 50 mg/L. Optimum conditions in terms of medium pH, duration and hydrogel amount were reported as; pH = 9, duration 360 minutes with addition of 1.5 g hydrogel. This arsenic polymer ratio corresponds to an arsenic removal potential of 1.6 mmol As/g of hydrogel. Authors also modeled the absorption process with Langmuir and Freudlich isotherms.

Şahiner et al. [23] synthesized and used Quaternized poly(4-vinyl pyridine) hydrogels in treatment of arsenate solutions. The authors studied different synthesis methods and reported 95 percent arsenic removal from arsenate solutions (10 mg/L, 1000 mL) in 15 minutes for hydrogels quaternized with HCl. Effect of medium pH, arsenic concentration, temperature and addition of other salts on arsenate removal were investigated along with re-usability studies. Suitable pH range was reported between pH 5 and 7. Decrease in arsenic removal efficiency was reported with increasing arsenic concentration (decrease in [hydrogel]/[As]). No significant changes in arsenic removals between 30-40 ^{0}C were reported. Studies conducted in the presence of sodium salts of chloride and sulfate anions (0-25 mg/L salt – 10 mg/L As) showed a slight decrease in arsenic removal where sulfate anions had more negative effect on arsenic removal. Arsenic recoveries between 97 percent and 93 percent were also reported for five consecutive arsenic removal cycles.

Santos et al. [24] studied arsenic (V) removal from aqueous solutions by means of batch and column adsorption processes. Poly(vinylalcohol)-Iron oxide xerogels with different iron loadings were synthesized for this purpose. The authors reported optimum pH range between pH 2 and 5. The maximum amount of arsenic adsorption was also reported as 1.2 mmol As/ g gel with more than 99.4 percent removal for a contact time of more than 4 h. In that study, Langmuir isotherm was reported as the most suitable model to represent the adsorption equilibrium mechanism where adsorption kinetics were investigated with first order kinetics and intra-particle diffusion model. Authors also reported that after three adsorption-desorption cycles, iron-oxide xerogels preserves adsorption capacity of 84.5 mgAs/g.

Dax et al. [25] studied the synthesis of different types of hemi-cellulose based hydrogels and conducted some batch removal experiments to test the ability of hydrogels on chromium and arsenic (V) removals. They reported maximum arsenic removal capacity of 0.9 mmol As/g gel. The authors observed the arsenic removals at pH 3, 6 and 9. Higher arsenic removal efficiencies were reported at pH 6 and 9 than the value obtained at pH 3 although the highest removal was recorded at pH 9.

2.3. Membrane Process in Water Treatment

Conventional drinking water treatment methods include coagulation, precipitation, sand filtration and chlorination [26]. Demand for high purity drinking water and descending cost of membrane raw materials made membrane filtration methods feasible alternatives of conventional treatment methods used in large scale water treatment processes [27]. Membrane filtration also has some advantages like; easy maintenance, small footprint, lower overall energy consumption, environmental friendliness (eg: no chemical addition [28]), capability to overcome the challenges presented by changes in the quality of the treated water [26]. Among these filtration methods, ultrafiltration (UF) requires a pressure difference in the range of 1-5 bar which is less than those of nanofiltration and reverse osmosis making this method less energy intensive.

Membrane separation processes are based on a semi-permeable membrane which does not allow the target element to pass through while enables the others pass through. The amount passes through the membrane is called permeate while the amount that cannot pass through is called retentate or concentrate [29]. Most important measures for the success of membrane separation can be listed as permeate flux and retention. Flux can be determined as the amount of flow per unit time per unit area of the membrane and retention can be defined as the amount or ratio of the target component that can be separated from the feed solution. Numerical representation of the retention can be given as [29]:

$$R = 1 - \frac{C_{T,P}}{C_{T,F}} \tag{2.7}$$

where;

$C_{T,P}$ = Concentration of target component in permeate

$C_{T,F}$ = Concentration of target component in feed

R = Retention

There are a lot of factors that can affect the retention like solute type, temperature, pH, membrane type, solution composition, hydrodynamics, size of the dissolved components, etc. In most of the cases solute size is the most important factor affecting the retention of the targeted component. Membrane processes are divided in mainly four groups according to the pore size of the membranes from higher pore size to the lower as: microfiltration (0.05-4 μm), ultrafiltration (0.005-0.05 μm), nanofiltration (around 1 nm) and reverse osmosis (<1 nm).

2.4. Arsenic Removal Using Ultrafiltration

Ultrafiltration can be regarded as one of the most efficient filtration methods in terms of higher permeate flux and lower energy required. Keeping these facts in mind, arsenic removal studies using ultrafiltration have drawn attention of researchers. Pore diameters available for ultrafiltration membranes do not allow retention of small anions although it was reported in the literature that membranes with negative surface charges can be used in separation of arsenic especially arsenate (As (V)) anions. Studies available in the literature on arsenic removal with ultrafiltration are given in this section.

Lohokare et al. [30] synthesized and modified surface of polyacrylonitrile based ultrafiltration membranes. They applied modification with sodium hydroxide in order to generate $-COO^-$ groups on the surface of the membrane. They tested their membrane in a flow system and reported almost 100% retention for arsenate anions in treatment of arsenate solutions having 50 μg/L feed concentration. They observed increase in arsenic retention as pH of the feed solution was increased (between pH 4 and 7) and decrease in retention as feed concentration decreased. Reported maximum arsenic retention values for feed concentrations are; <95 % for 1 mg/L and 50 mg/L, 65 % for 1000 mg/L. They explained arsenic retention behaviors by Donnan exclusion and change in arsenic retention with feed concentration by concentration polarization theories.

Yoon et al. [31] investigated removal**s** of various metals dissolved in water with different commercial membranes. They investigated and compared ultrafiltration, nanofiltration and reverse osmosis. They examined GM type of membrane from Desal / Osmonics in ultrafiltration tests. They examined surface charge of membranes and reported an increase in surface charge of the GM membrane as the solution pH increased. They also reported a maximum arsenate retention around 90% for the runs conducted with arsenate solutions treated with GM membranes. They explained the reason of the retention as electrostatic forces in between arsenate anions and membrane surface.

Brandhuber et al. [32] also investigated GM membranes in continuous ultrafiltration of arsenic solutions. They observed negative effect of other anions on retention and claimed that ultrafiltration of arsenic with GM membrane followed Donnan exclusion and concentration polarization theories. They reported maximum retention values for arsenite and arsenate anions as around 40% and 80%.

2.4.1. Donnan Exclusion Effect

Dilute ion solutions having the same charge as the molecules on the membrane surface can be retained by the membrane surface due to interaction between the co-ions. Ability to retain co-ions by the membranes was known as the Donnan exclusion and it was defined by equilibrium thermodynamics between ions on the membrane surface and in the liquid bulk [33]. This theory was based on Donnan’s study on ionic equilibrium and membrane potential which was conducted at 1911 and translated to English at 1995 [34]. Donnan's study mainly based on theories derived around a container divided into two with a membrane. Study focused on deriving thermodynamic equilibrium equations and estimating the behavior of the ions present in both sides of the membrane. One of the cases includes two different co-ions initially presenting on left and right hand side**s** of the membrane. Molecules on the left hand side cannot pass through the membrane due to size exclusion although molecules on the right hand side can pass through the membrane. Study indicated that when dilute solutions of small molecules on the right hand side brought in contact membrane, these dilute ionic molecules could be retained and retation value was related to the concentration of ions on the right hand side.

Brandhuber et al**.** [32] reported an equation showing Donnan potential between membrane surface and bulk liquid phase. Equation is given as in Equation 2.8

$$\Psi_d = \frac{RT}{z_i F} ln\left(\frac{c_m}{C_b}\right) \tag{2.8}$$

where, Ψ_d is Donnan Potential, R is ideal gas constant, T is absolute temperature, z is valance of the solute ion, F is Faraday constant, c_m is solute concentration on membrane and C_b is solute concentration in liquid bulk.

Applying series of assumptions such as no concentration polarization, low solute concentration and activity value of 1, they presented an equation which describes the concentration distribution as given in equation 2.9,

$$Log\ (1 - R_R) = \frac{z_a}{z_c}\ Log\ \left(\frac{z_c}{X} C_b\right) \tag{2.9}$$

where, R_R is the real retention which is the ratio of permeate concentration to bulk concentration, z_a and z_c are valances of cation and anion in the electrolyte and X is the charge density of the membrane.

Brandhuber et al. [32] plotted Log (1-R_R) vs. Log (C_b) by using the results which were obtained in the runs conducted with different feed concentrations. They obtained a straight line which was an expected behavior for Donnan exclusion theory; on the other hand, they could not obtain a slope of 2 which was the expected slope according to the $\frac{z_a}{z_c}$ for sodium arsenate. They explained this situation by pointing out the facts that fixed membrane surface charge assumption and method for estimation of solute concentration at the membrane surface might not be applicable for their system; besides Donnan exclusion theory was not developed for membrane systems including mass transfer through the membrane layer with a certain thickness.

2.5. Arsenic Removal using PEUF

Retention capacity of ultrafiltration method can be enhanced by the addition of water soluble materials (e.g., polymers) with high molecular weights which can form complexes with the targeted molecules. These complexes can easily be separated from the medium due to their large size; thus the targeted small molecules in those complexes can be retained. The method used with addition of polymers is referred as polymer enhanced ultrafiltration (PEUF). PEUF has been studied widely in the literature for separation of heavy metals from aqueous solutions. Examples to these metals can be given as; mercury [35, 36], Cadmium [36, 37], Nickel, Zinc [37] , Boron [38-40], etc. PEUF Processes can be described schematically as given in Figure 2.4.

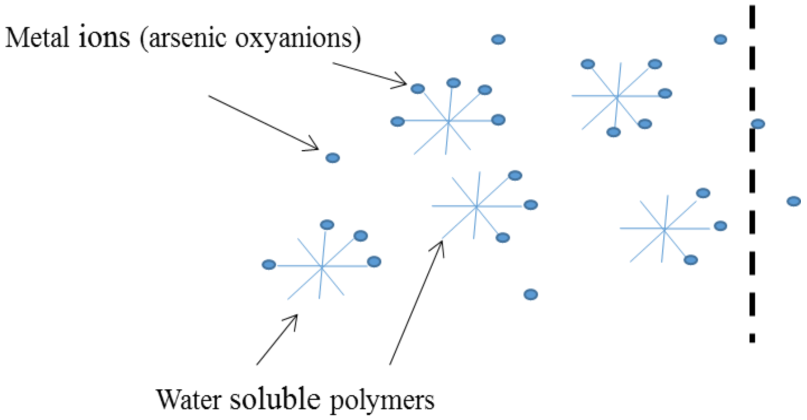


Figure 2.4. Schematic representation of PEUF.

Polymer enhanced ultrafiltration (PEUF) has gained attention in the removal of various metals because of the economical and selective treatment advantages [35-40]. Arsenic removal with PEUF was also studied by several researchers [1-8]. Since the allowable limit for arsenic level in water is 10 µg/L membrane processes mainly reverse osmosis processes are the most widely used method in treatment of this metal and other heavy metals. Although this process has high separation efficiency it is energy intensive process due to high pressures needed to achieve separation. Some of the studies on arsenic removal are given in this section.

There are various kinds of polymers available for this purpose; they can either be synthesized or they are commercially available. Some of the most important features of these polymers can be listed as high solubility in water, narrow molecular weight distribution, stability and selectivity against targeted metal(s). Generally, addition methods are used for synthesis of these polymers. They can be homo or copolymers and contain one or more coordinating and/or charged groups [41].

Water soluble polymers can be divided into two; poly-electrolytes and poly-chelatogens, the former of which have ionized groups or can be ionized easily in water, and the latter has functional groups that can make complexes with metal ions. Removal mechanism for poly-electrolytes is quite similar to those of ion exchangers; ions such as Cl^- and Br^- bound on functional groups of poly-electrolytes exchange with the metal ions in solution [3]. This mechanism may have selectivity problem since it is based on ionic bonds between metal ions and the polymer. On the other hand, coordination bonds between polymer and metal ion are formed in complex formation mechanism as in case of polychelatogen usage; in that latter case, the mechanism may be even more selective in binding the targeted molecule.

Pookrod et al. [2] used a polyelectrolyte named poly(diallydimethyl ammonium chloride) or QUAT to form complexes with arsenic species. They declared that they observed arsenic (As(V)) rejection over 99 percent between pH 6.5 and 8.5 with this commercially available polymer in treatment of arsenic solutions. They also report an increasing trend in arsenic rejection with increasing pH.

Effect of QUAT/As ratio was also studied. Increase in arsenate rejection with increasing QUAT/As ratio of 50, 100 and 150 was observed. They explained this trend as increase in the number of active sites resulted an increase in arsenic binding on polymers. They reported 99.1percent retention for the run QUAT/As =150 and 97.8 percent for the run QUAT/As = 50.

Effect of co-ion presence was also observed in this study which Na_2SiO_3, NaCl, $NaSiO_3$, $CaCl_2$, Na_2HPO_4 $MgCl_2$ and Na_2SO_4 were added to the ultrafiltration medium in order to simulate the ion matrix in real waters. They observed decrease in arsenic rejection from 100 percent up to almost no rejection as the salt concentration increases. Negative effect of salt solutions on arsenic retention was also listed in decreasing order as: $Na_2SO_4 > Na_2HPO_4 > Na_2SiO_3$, $MgCl_2$, $CaCl_2$ >NaCl > $NaHCO_3$. This order is related with the charges of the anions present; the ones with divalent negative charges can bind to the active sites of the polymer more strongly which causes a decrease in polymer's ability to make complexes with arsenate anions.

Rivas et al [3]. Synthesized cationic polymers with $(R)_4N^+X^-$ groups and pyridinium groups for removal of As(V) by free-radical polymerization. Amongst the polymers synthesized the ones with chloride group provided greatest ability to bind arsenate anions (exchange with Cl$^-$). They observed arsenic retention values of 100 percent at pH 8 for the runs conducted with the chloride exchange groups in treatment of arsenate solutions.

Authors studied pH values of 4, 6 and 8. They reported arsenic retention values of 40% for the run conducted at pH 4 while around 100 % arsenic retentions were observed for the runs conducted at pH 6 and 8 with the polymers having chloride exchange groups.

Sanchez et al.[6] synthesized polyelectrolytes by free-radical polymerization named poly[2-(acryloyloxy)ethyl]trimethylammonium chloride, P(ClAETA) and poly[2-(acryloyloxy)ethyl]trimethylammonium methyl sulfate, P(SAETA) again the one with chloride active group showed higher arsenic removal efficiency in all conditions. The results obtained in this study in terms of comparison between synthesized polymers were also supported by another study [8,3].

In another study Rivas et al. [5] observed removal of As(III) and As (V). They synthesized polychlates of poly(acrylic acid)-Sn bearing 3, 5, 10 and 20 percent of Tin (Sn) for As(III) removal while they used polyelectrolytes for removal of As (V). Using polyelectrolytes with chloride exchange groups again resulted higher retention values. On the other hand polychlates resulted a maximum retention value of 80 percent in removal of arsenite anions.

They conducted experiments for removal of arsenic (As (V)) at pH 3, 6 and 9. They reported an increasing trend in retention values as pH increases. They reported retention values of almost 100 percent for the polyelectrolytes having chloride exchange groups (X$^-$) at pH 9 while these values reduce to 50 percent for pH 6 and almost 0 percent retention at pH 3.

Authors investigated the effect of polmer/arsenic ratio on arsenic retention with polymers having chloride exchange groups; P(ClVBTA) and P(ClAETA). They observed an optimum ratio of 20:1 in the runs they conducted with the ratios of; 31:1, 20:1, 10:1, 6:1, 3:1.

CHAPTER 3

EXPERIMENTAL METHODS

Flow and batch experiments aiming to deal with arsenic contamination problem in water were conducted with arsenic solutions prepared in laboratory. Two different types of polymers were synthesized in order to be tested in two different experimental set-ups. These polymers can be listed as; DADMAC hydrogels and water soluble DADMAC- P(4-VP)polymers with different vinyl pyridine content (10 percent, 25 percent). While water in-soluble hydrogels were used in batch adsorption process for arsenic removal, water soluble polymers were used in flow experiments. Flow experiments were carried out using laboratory scale filtration set-up while batch runs were conducted using a shaker in 100 mL PTFE containers. Removal efficiencies were determined by measuring arsenic concentrations, using Atomic Absorption Spectrophotometer (AAS) coupled with a hydride generation system.

3.1. Materials

All chemicals used in this study were reagent-grade chemicals. Nitric acid (HNO_3) (Sigma Aldrich, Germany) and sodium hydroxide (NaOH) pellets (Sigma–Aldrich, Chezch Republic) were used for pH adjustment and arsenic analysis; sodium borohydride ($NaBH_4$) (Merck, Germany) and potassium iodide (KI) (Sigma– Aldrich, Germany) were used for arsenic analysis. Arsenic standard solutions (Merck, Germany) were used during calibration and $Na_2HAsO_4.7H_2O$ (Sigma, India) and $NaAsO_2$ (Sigma-Aldrich, India) were used during the preparation of arsenic solutions. Monomeric DADMAC (Aldrich, USA 65% in water), 2,20 -azo bis-(2-methyl propionamidine) dihydrochloride (Aldrich, USA), GE/Osmonics PT membranes were purchased from Sterlitech (USA).

3.2. Polymer Synthesis

DADMAC hydrogel synthesis and analysis methods are given along with DADMAC-P(4-VP) co-polymers in this section. High porosity cationic hydrogels synthesized *via* crosslinking co-polymerization of diallyldimethyl-ammonium chloride (DADMAC) with N,N’-tetraallylpiperazinium-dichloride (TAP) and the structure of the hydrogels were investigated with Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and swelling tests. On the other hand DADMAC-Vinyl pyridine (P(4-VP)) co-polymers were analyzed using FTIR analysis.

3.2.1. DADMAC Hydrogel Synthesis

The DADMAC hydrogels were synthesized via radical polymerization. The polymerization was conducted with DADMAC monomers with TAP (5 percent mole) and a radical initiator (2,2’-azo bis-(2-methyl propionamidine) dihydrochloride). The reaction occurred in a three-necked-reactor equipped with a reflux condenser at 65^{0}C. Nitrogen gas was fed into the reaction medium for 2 minutes before the reaction to remove oxygen, as described in the literature [12].

3.2.2. DADMAC- P(4-VP) Co-polymer synthesis

Linear diallyldimethylammonium chloride (DADMAC) - Vinyl Pyridine (P(4-VP)) Polymers were synthesized with different contents of vinyl pyridine (10 mole percent and 25 mole percent vinyl pyridine).

Linear co-polymers were synthesized with radical polymerization method at 70^{0}C. Amounts of monomers to be added was calculated according to the vinyl pyridine ratio and total amount of polymer aimed to be synthesized. Monomers dissolved in 50 percent (w/w) water-dimethylformamide (DMF) and 2,2 azobis methylpropionamide-dihydrochloride was used as an initiator.

3.3. Characterization of Polymers

A JEOL JSM-6610LV Scanning Electron Microscope (SEM) was used for SEM and Energy Dispersive X-ray (EDX) analyses. SEM and EDX analyses were conducted in order to understand the porous structure of the gel soaked in water and to investigate the gel composition before and after arsenic treatment. Fourier transform infrared spectroscopy (FT-IR) tests were conducted in order to understand the molecular structure of the polymer using a Shimadzu Prestige-21 equipped with an attenuated total reflectance (ATR) unit which enables measurements without the preparation of potassium bromide pellets. Swelling tests were conducted by gravimetrically measuring the water absorbed in the hydrogels at room temperature. The weight of the hydrogels placed on a 50 mL glass filter soaked with de-ionized water was measured at different time intervals. The excess water present in the medium was filtered under vacuum; only the water held by the gels was measured as a weight increase.

3.4. Separation Experiments

3.4.1. Batch Experiments

Arsenic removal experiments were conducted in 100 mL PTFE containers where arsenate solutions were continuously shaken with presence of DADMAC hydrogels for overnight. Different operating conditions were set in order to understand hydrogels' ability to remove arsenic from aqueous solutions; amount of hydrogel, effect of other anions in removal and effect of medium pH were investigated. For the runs conducted at a specific medium pH, pH of the medium was continuously monitored and adjusted with sodium hydroxide and hydrochloric acid solutions.

Different hydrogel amounts were used in the experiments in order to observe amount of arsenic that can be removed per 1g of hydrogel and obtain a relationship between arsenic removal and hydrogel concentration. Besides hydrogel concentration experiments with three different arsenic feed concentrations were conducted in order to simulate the arsenic abundance in natural surface or ground waters.

Considering the relationship between the charges of arsenate anions with pH of the medium, arsenate removal runs were also conducted at different pH values where pH of the medium was monitored with a WTW 3210 pH meter and adjusted with hydrochloric acid or sodium hydroxide addition.

Competition of arsenic with other anions present in the medium were also investigated. Chloride, carbonate, sulfate and humic acid were selected as competing anions that can be found in water in real life applications. Tests in presence of competing anions having the same concentration with arsenate anions (mass concentration mg/L) were conducted without any pH adjustments as described in the first paragraph with a constant hydrogel amount. Besides these tests, runs with changing concentrations of chlorine and sulfate were also conducted in order to further investigate the effect of these.

Contact time needed for removal is also another important parameter in real life applications which determines the space time needed for the removal process. Regarding this fact arsenic removal efficiencies which obtained at different contact times were also investigated. Treating the data obtained also helped to understand complex forming kinetics between arsenate anions and hydrogels. Intraparticle diffusion model was used to analyze kinetic data. Contact time experiments were conducted as seven identical experimental runs; without pH adjustment and with a constant value of starting arsenic and hydrogel concentrations where solutions were shaken during the time indicated and immediately filtered.

Different conditions for arsenic recovery were also tested to find an effective method for arsenic or hydrogel recovery. Arsenic recovery was achieved by soaking hydrogels that was previously used in arsenic removal in acidic solutions (HCl) or sodium chloride solutions and shaking for 3 hours.

Re-usability of the hydrogel is also another important economical parameter for arsenic removal operations. In order to test the re-usability of the hydrogel; hydrogels

(0.1 g) used in arsenic treatment were soaked in 10 g/l NaCl solutions then washed and re-used in treatment of 1 mg/L arsenate solutions.

3.4.2. Ultrafiltration Experiments

3.4.2.1. Ultrafiltration Set-up

Experiments were conducted in order to investigate the effect of polymer addition on the ultrafiltration performance. To demonstrate the effect of PEUF on arsenic removal, runs with and without DADMAC-P(4VP) co-polymers were conducted. Polyether sulfone based PT membranes produced by GE/Osmonics were used in the ultrafiltration studies.

A bench scale filtration set-up Sepa CF II was used in the ultrafiltration experiments where 2L of Arsenic/Polymer or Arsenic solution was fed to the system, permeate and retentate streams being fed back to the feed container. Ultrafiltration system is given in Figure 3.1. System is mainly composed of two stainless-steel parts (membrane cell) where membrane is placed in between. Membrane cell is then placed in a cell holder. Other components of the filtration set-up can be listed as: shim, fouling spacer and permeate carrier. More detailed pictures of the components listed above are also given in Figure 3.2 as a whole and detailed pictures of the parts are also given in Figures 3.3 - 3.9.

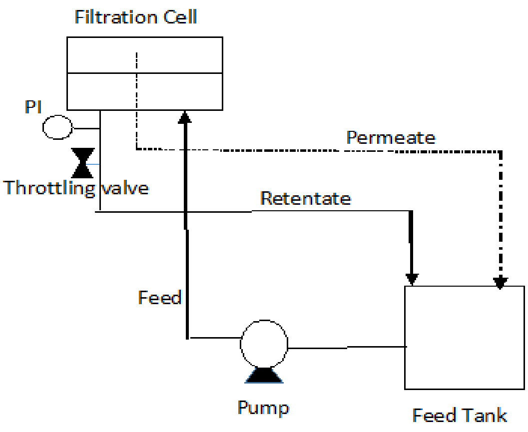


Figure 3.1. Sepa CF II Filtration Set-up

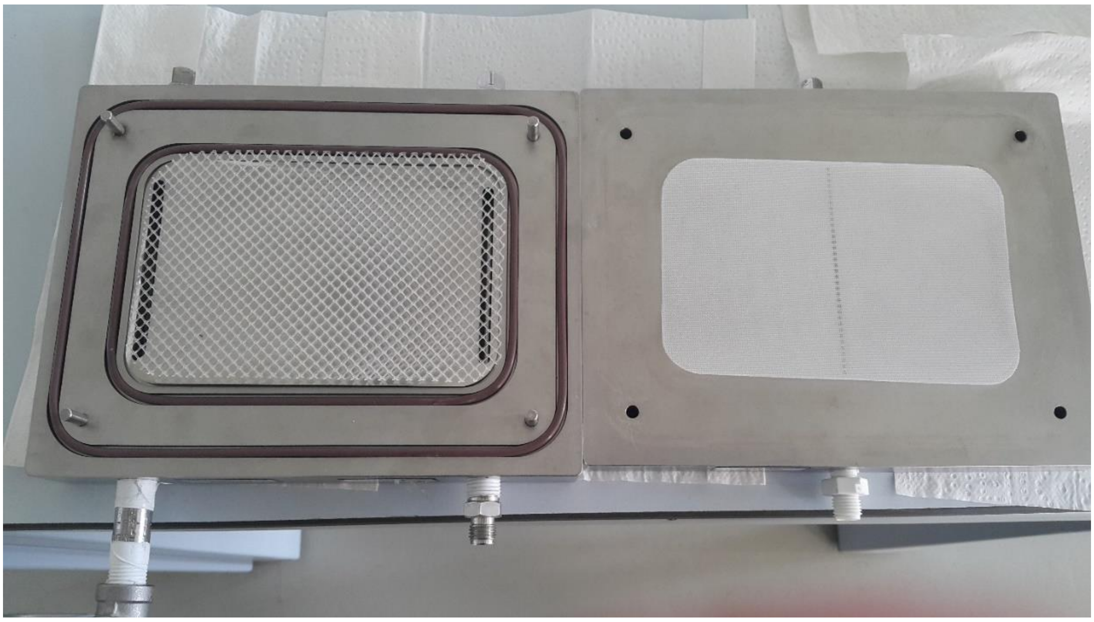


Figure 3.2. Membrane Filtration Cell with Shim, Fouling Spacer and Permeate Carrier.

Figure 3.3. Membrane Filtration Cell – Top Plate

Membrane Filtration Cell

This part can be described as two stainless steel plates. The plate which is placed at bottom contains two canals for liquid inlet and outlet. Liquid enters the cell from the canal placed at right hand side travels through the surface of the plate adjacent to the membrane placed above it then retentate leaves the bottom plate through the canal on the left. A throttling valve and a pressure indicator are placed at the outlet of the bottom plate. The valve is used to adjust the driving pressure between the two sides of the membrane. Permeate also leaves the cell through the top plate. There is a canal in the middle of the plate through which permeate stream flows.

Figure 3.4. Membrane Filtration Cell-Bottom Plate

Figure 3.5. Shim

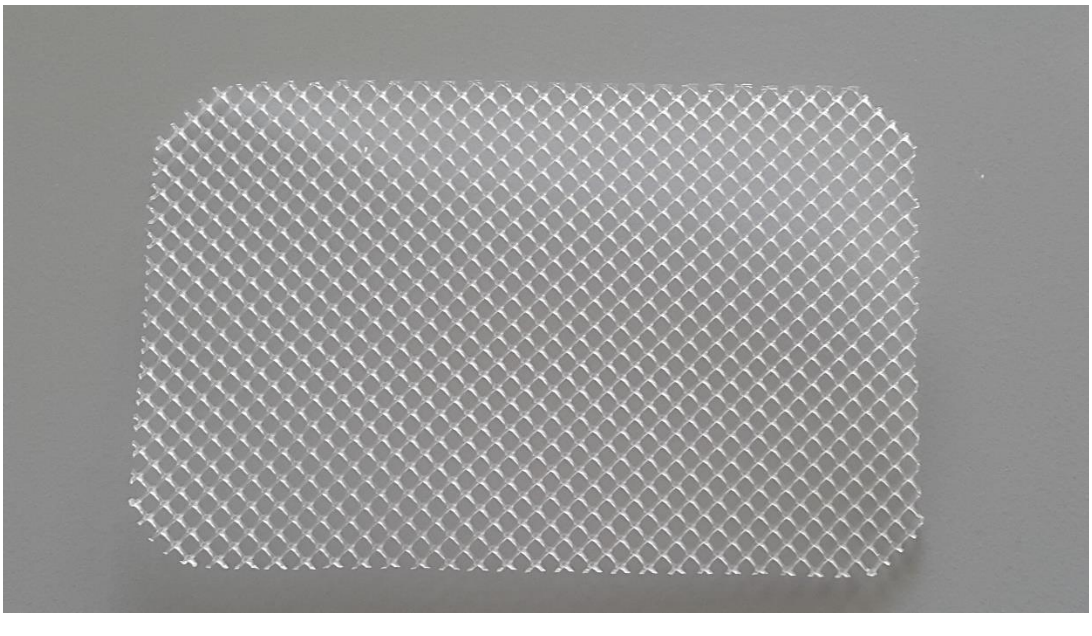


Figure 3.6. Fouling Spacer

Cell Holder

A cell holder is used to apply pressure on the cell in order to prevent leakage during the operation. It can be described as a stainless steel frame in which the cell is placed. There is a moving part at the bottom of the cell holder. This part is moved upwards by the help of a hydraulic hand pump in order to squeeze the cell inside the holder. Pressure of the oil inside the hydraulic part is measured with a pressure indicator placed at the bottom of the cell holder. Pressure applied on the cell is adjusted in a way to exceed the driving pressure applied between the two sides of the membrane (pressure of the liquid flowing through the bottom plate).

Fouling spacer

This component can be described as a thin polymeric plate with holes, which placed below the membrane. Liquid passing through the bottom plate of the cell also passes through the spacer. The purpose of placing the spacer on the membrane surface is to prevent the accumulation of molecules on the membrane surface by altering the flow hydraulics. There are different types of spacers with different thicknesses.

Permeate carrier

Permeate carrier can also be described as a flat sheet with smaller holes than those of the spacer. Permeate carrier is placed on top of the membrane. Liquid molecules passing through the membrane flow through the carrier into the canal which is placed in the middle of top plate.

Figure 3.7. Permeate Carrier

Shim

The cavity on the bottom plate of cell through which the liquid flows through should be filled with membrane, fouling spacer, shim and permeate carrier in order to achieve filtration hydraulics as desired. It was mentioned before that variety of spacers can be selected which alters the total width. A metal plate is placed on the surface of bottom plate in order to keep the width constant. Shims with different thicknesses are also available so that when a thick spacer is used a thin shim is matched with that spacer.

Figure 3.8. GE/Osmonics PT Membrane, Purchased from Sterlitech

Figure 3.9. Cell Holder and Hydraulic Hand Pump with Pump Used to Feed the Membrane Cell

Membrane

Commercial polyether sulfone membrane was used in this work. Membrane which was used in the studies was manufactured by GE/Osmonics under the code; PT. Properties of the membrane provided by the manufacturer are listed in Table 3.1

Table 3.1. Properties of PT membrane provided by the manufacturer

Feed water type	Process/Ultrapure
Area of use	Pre/Post Treatment
pH Range (25 °C)	1-11
Flux (gfd)/psi	90/50
Rejection Size	5K-Dextran
MWCO (Daltons)	5,000
Polymer	Polyethersulfone

The shim, spacer, membrane and permeate carrier set-up is also used in large scale membrane filtration systems. Using this set-up gives the advantage of simulating the real life applications.

Characterization experiments for PT membrane was also conducted and reported in the Literature by Tres et al. [42]. Authors used FTIR spectroscopy to determine the compositions of the membranes tested. According to their results PT membranes contain polyether sulfone and polyamide groups in their structure. Zeta potential analysis of the membrane also showed that the membrane’s surface is formed of negatively charged species and surface charge increases as the pH of the medium increases.

3.4.2.2. Experimental Procedure

Ultrafiltration experiments were conducted with and without the presence of linear DADMAC Vinyl pyridine co-polymers. Arsenic solutions, containing $Na_2HAsO_4.7H_2O$ (As (V) and $NaAsO_2$ (As (III)) with a concentration of 1000 μg/L were prepared by using de-ionized water and treated by using SEPA CF II bench scale membrane filtration set-up.

Polymer enhanced ultrafiltration (PEUF) studies were conducted by the addition of DADMAC-Vinyl pyridine co-polymers which were synthesized with presence of 10% and 25% (mole %) vinyl pyridine into the arsenic solutions. Stock solutions in which linear polymers were dissolved were used in the preparation of feed solutions for PEUF studies. Different amounts of polymer stock solutions were added in to approximately 700 mL of de-ionized water containing arsenic enough to obtain desired arsenic feed concentration and diluted to 1 L in order to prepare the arsenic-polymer solution. This solution is then stirred for 2 hours in order to achieve complex formation between arsenic and polymer prior to the ultrafiltration process. For the runs conducted to observe the effects of some anions on arsenic removal, the stock solutions were prepared by dissolving sodium salts of these anions also with the added polymer solution.

Ultrafiltration and PEUF processes were both operated by recycling permeate and retentate streams into the feed tank as shown in Figure 3.1 Samples from the feed tank and permeate stream were taken at certain time intervals. Samples from feed tank were taken by using a glass 20 mL pipette and samples from permeate stream were taken directly from the permeate stream. Permeate flux was determined by measuring the amount of sample collected within one minute.

Samples were analyzed by hydride generation – atomic absorption spectrophotometer (HG-AAS). Details of the method are given in Section 3.4. Some of the samples were also analyzed by governmental laboratory facilities of Turkish Republic of Northern Cyprus (TRNC) which is accredited by Turkish standards Institute (TS EN ISO/IEC 17025). Inductively coupled plasma – mass spectroscopy (ICP-MS) were used in these analyses. Results obtained from HG-AAS and ICP-MS are compared and a sample result is presented in Appendix A6. Besides HG-AAS and ICP-MS, molybdenum blue method was also used during the last period of the study. During the last six months of this thesis study HG-AAS was broken; therefore, molybdenum blue method was used as an alternative. This method was used in calculation of the results presented in Section 4.3.3. Detailed explanation of the method is given in Appendix A4.

3.4.3 Column Adsorption Experiment

Performance of DADMAC hydrogels were tested also with column adsorption experiments. For this purpose, a glass column was ordered with a glass filter placed at the bottom of the column in order to keep the material inside the column. However the column prepared for this study could not be used, because a continuous liquid flow through the column could not be achieved. As an alternative, a 50 mL burette was filled with hydrogels and used in column adsorption studies after obtaining successful results in terms of liquid flow in the preliminary tests conducted with water. Picture of burette and the column filled with water to test whether a successful flow could be obtained or not is given in Figure 3.10.

Figure 3.10. Column prepared for hydrogel adsorption and burette filled with hydrogels

3.4.3.1. Experimental Procedure

Burette was filled with hydrogels previously soaked in de-ionized water. Hydrogels were introduced in burette as suspension (in de-ionized water) while outlet of the column is closed. Hydrogels slowly settled down in column in order to form the fixed bed column. Filling the burette with dry hydrogels and introducing water caused clogging and prevented the flow of water through the column. Arsenic and salt solutions were fed from the top of the column with the help of a peristaltic pump and collected from the bottom after they contacted with hydrogels. Picture of burettes containing 1 g and 0.3 g hydrogel during operation is given in Figure 3.11.

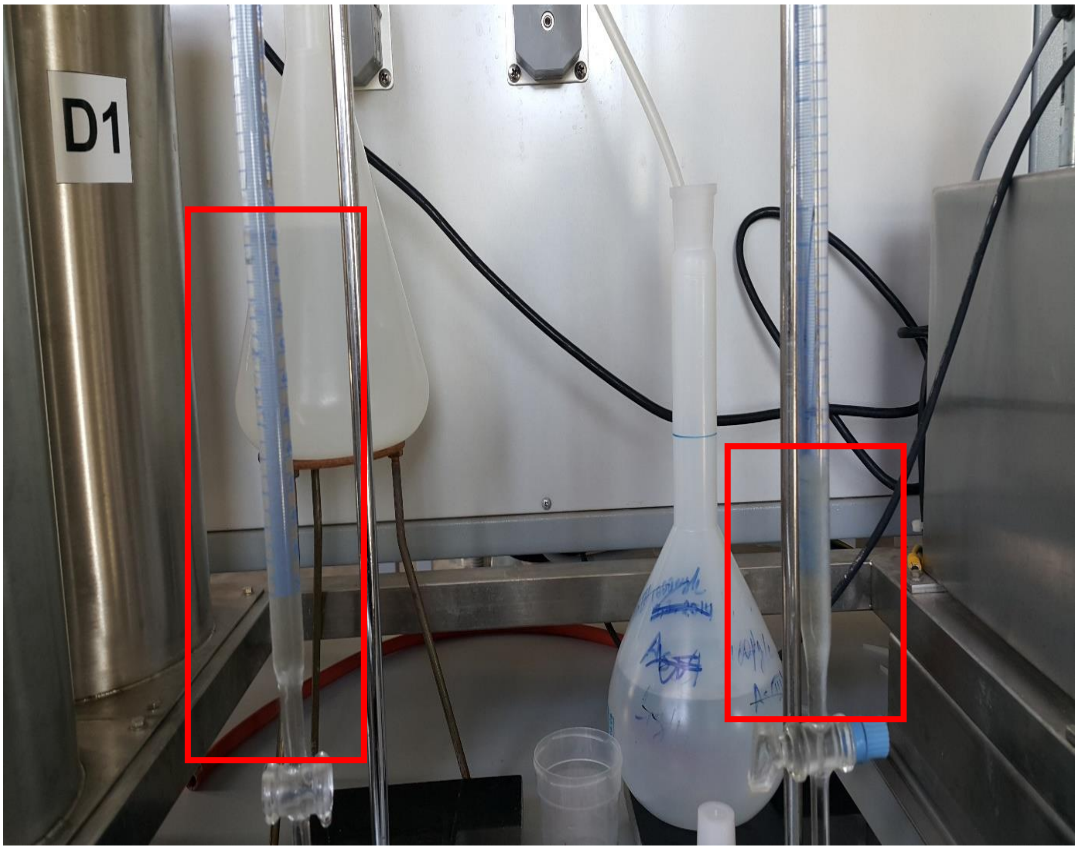


Figure 3.11. Flow study conducted simultaneously with 1 g and 0.3 g hydrogels. 1g on the left and 0.3 g on the right

These flow experiments were preliminary experiments conducted in order to understand the efficiency of hydrogels in such operations. Both arsenic and regeneration solutions were fed from top mainly due to ease of operation. Samples with different volumes were collected during the operation and effluent flow rates were determined by measuring the elapsed time during the sample collection. Samples were taken by using beakers. Sample volumes were adjusted arbitrarily by using the marks on the beakers. Concentrations of these samples measured and reported as the concentration obtained at the total volume.

Experiments with different amounts of hydrogels and regeneration-reuse experiments were conducted in column tests. Different amount of hydrogels were tested in order to observe effect of different hydrogel amounts on breakthrough capacity.

Amount of salt solution required for arsenic recovery were also tested in regeneration tests. Regeneration of DADMAC hydrogels were conducted by feeding sodium chloride (NaCl) solutions from top of the burette directly after arsenic removal studies. NaCl solutions containing 10 g and 20 g chloride were used in these runs. Column was also washed with de-ionized water after regeneration with salt solution in order to remove the salt left from regeneration process. Accumulation of chloride anions in the system decrease arsenic removal performance of hydrogels. Effluent's conductivity was measured during the washing and used to determine the time to finish the process. Two regeneration and three re-use experiments were conducted. Two different salt solutions were used for regeneration of hydrogels in these regeneration runs. Sodium chloride solution containing 10 g/L Cl^- was used in the first run while a solution containing 20 g/L Cl^- was used in the second regeneration run. Regeneration and reuse experiments were conducted with 1g DADMAC hydrogels. Sample volumes and reported volumes in some of the runs are given in Table 3.2

3.5. Arsenic Analysis

Arsenic analysis was conducted by Shimadzu AA-7000 Atomic Absorption Spectrophotometer (AAS) equipped with HVG-1 hydride generation system. Other common Arsenic measurement method is Inductively Coupled Plasma- Mass Spectroscopy (ICP-MS) was not preferred because of the interactions when chloride ions are present in the samples to be analyzed although some part of the samples were analyzed by ICP-MS for comparison. In this section hydride generation will basically be described.

Conventional test with flame AAS is not sufficient in measurement of low concentration arsenic samples. In order to obtain detectable signals arsenic is fed to the flame in gaseous phase in hydride form. Gaseous hydrides (AsH_3) are formed by the reaction between arsenic anions and sodium borohydride ($NaBH_4$).

Sample is fed to the system with sodium borohydride where they react to give arsenic hydride further carried to the tube placed on the flame. It is important to place the tube on flame in a way that it does not obstruct the light emitted from the lamp to the detector. $NaBH_4$ solutions are prepared by adding 0.5 percent NaOH and 1percent $NaBH_4$ (w/v) into de-ionized water. Samples are also prepared in 1M HCl solution. For hydride generation medium should be acidic that is why samples are prepared in 1 M HCl (although in order to have a stable solution until reaction $NaBH_4$ solutions are prepared in basic medium). As seen in Figure 3.12, both samples and $NaBH_4$ solutions are fed in to reaction coil then carried to absorption cell placed on the flame by argon gas. Another important parameter for arsenic analysis is arsenic species; As(V) species cannot directly react with sodium borohydride to form hydrides so samples containing this species should be treated with potassium iodide (KI) in order to reduce As(V) to As (III). It is also important to measure As(III) samples just after the ultrafiltration tests in order to avoid oxidation of As(III) to As (V) with the oxygen present in air. Alternatively all samples can be treated with KI to ensure reduction of all As (V) species to As(III) (treating all samples is not preferred because of economical and time consumption issues).

Table 3.2. Sample Volumes and Reported Volumes for column experiments. Data obtained from the runs conducted with 0.3 g, 0.5g and 1 g hydrogels and regeneration with 20 g/L Cl^- (NaCl) solution.

Sample Volume (ml)							
0.3 g	$V_{0.3\ g}$	0.5 g	$V_{0.5\ g}$	1 g, 2	$V_{1\ g,\ 2}$	R_{20}	V_{R20}
70	70	64	64	100	100	25	25
49	119	64	128	100	200	35	60
49	168	69	197	115	315	31	91
48	216	54	251	110	425	29	120
50	266	65	316	120	545	28	148
50	316	54	370	120	665	37	185
49	365	51	421	110	775	65	250
48	413	55	476	110	885	60	310
50	463	38	514	105	990	55	365
48	511	48	562	125	1115	69	434
49	560	49	611	62	1177	49	483
47	607	40	651	61	1238	50	533
51	658	29	680	64	1302	49	582
50	708	27	707	57	1359	51	633
		28	735	54	1413	58	691
		37	772	55	1468		
		28	800	53	1521		
		27	827	59	1580		
		31	858	55	1635		
		46	904	55	1690		
		38	942	65	1755		
		49	991	55	1810		
		25	1016				

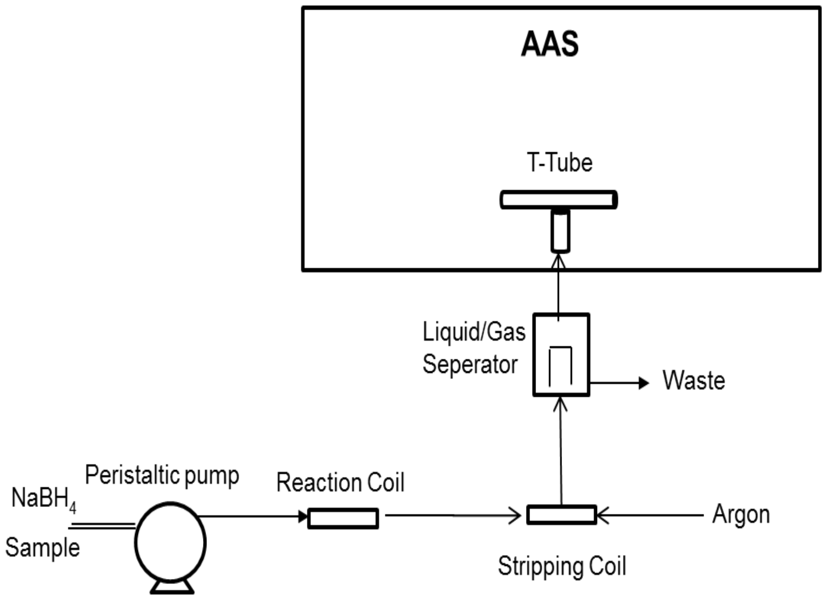


Figure 3.12. Schematic Representation of Hydride Generation System.

CHAPTER 4

RESULTS AND DISCUSSION

Arsenic removal studies conducted as batch and flow processes with two different types of polymers containing diallyldimethylammonium-chloride (DADMAC). DADMAC hydrogels which were synthesized *via* crosslinking co-polymerization of diallyldimethylammonium-chloride (DADMAC) with N,N'-Tetraallylpiperazinium-dichloride (TAP) were used in batch and column studies. Linear water soluble DADMAC–Vinylpyridine co-polymers were used in polymer enhanced ultrafiltration (PEUF) studies. Results obtained from these experiments are presented in this section.

4.1. Polymer Characterization

4.1.1. DADMAC Hydrogels

Properties of DADMAC hydrogels were investigated with Fourier Transform Infrared (FTIR) Spectroscopy, Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-ray Spectroscopy (EDX) and water sorption tests. Synthesis of DADMAC hydrogels is represented in Figure 4.1.

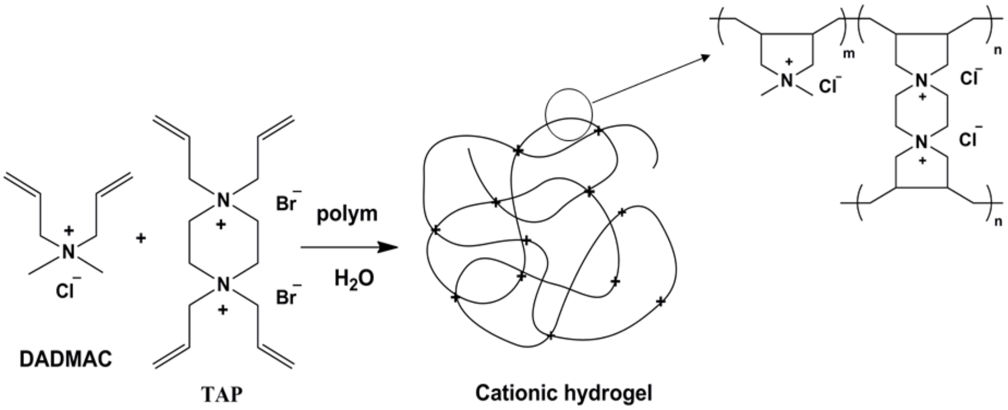


Figure 4.1. Synthesis of DADMAC Hydrogel

In order to identify the bonds forming the hydrogel, its FTIR Spectrum was obtained and presented in Figure 4.2.

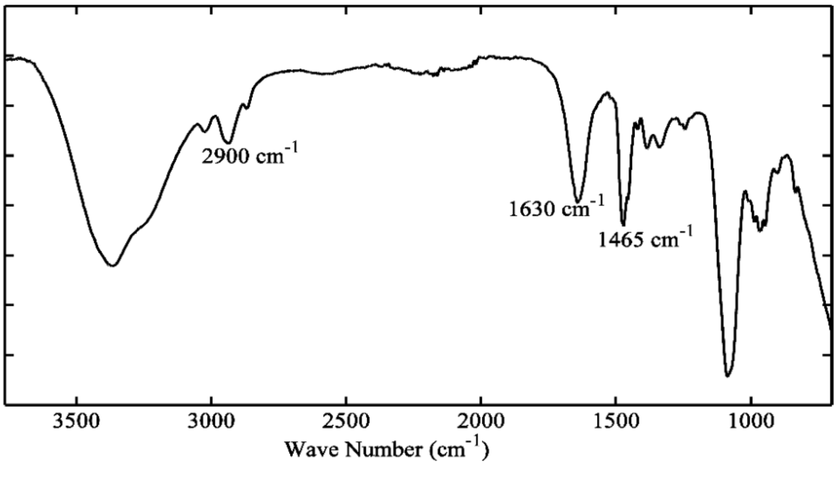


Figure 4.2. FTIR Spectrum of DADMAC Hydrogel

The FT-IR spectrum of the dry gel, shown in Figure 4.2, exhibits peaks observed at 2900 $cm^{-1}$and 1465 cm^{-1}, which are attributed to $-CH_2$ and $–CH_3$, respectively, confirming the molecular structure proposed. The band at 1630 $\mathrm{cm^{-1}}$ must be due to C=C stretching vibration of the un-reacted allyl groups of TAP.

Swelling tests were also applied in order to observe the water absorption capacity of the hydrogels. Results obtained from the swelling tests were found in accordance with the literature [12]. It was observed that most of the water sorption process took place in seconds and equilibrium was reached in around one minute. Water sorption with respect to time is given in Figure 4.3. Here water sorption was expressed in terms of swelling ratio (grams of water / grams of dry material). Swelling kinetics can be given as expressed in the literature [12]:

$$\mathrm{dS/dt} = k(S_{max} - S_t) \tag{4.1}$$

where S_t is the swelling ratio at any time t, S_{max} is equilibrium swelling ratio and k denotes swelling rate constant. Swelling kinetics was tested by plotting $ln\left(1 - \frac{S_t}{S_{max}}\right)$ vs. time (minute) for the time period of 0-1 minute. Model was found to represent the experimental data well with a regression constant (R^2) of 0.99. k value was also obtained from the linear plot as 4.25 $\mathrm{min^{-1}}$.

Synthesized DADMAC hydrogels were planned to be porous; therefore the porosity and structure of the hydrogel were tested by taking SEM images of the swollen hydrogels. SEM images are given in Figure 4.4.

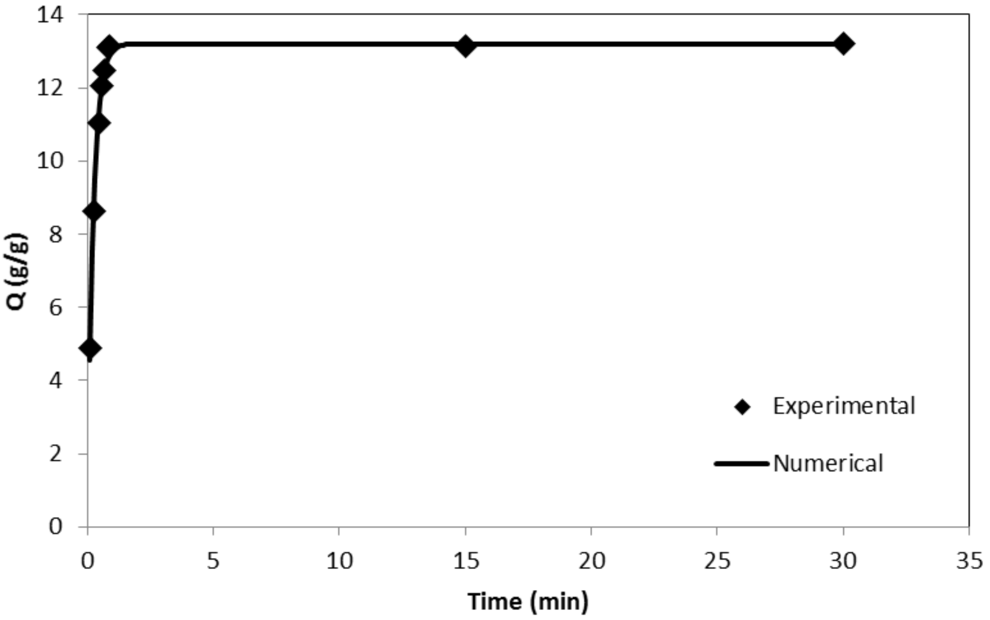


Figure 4.3. Water sorption curve. Experimental values were reported along with the values calculated from the kinetic model obtained.

SEM images of DADMAC swollen in water and in two different arsenate solutions show similar pore properties and a macro-porous structure. It can also be noted that structure of hydrogels do not change whether they are swollen in water or arsenate solutions. The polymeric porogen, Pluronics F68 was used during the synthesis of DADMAC hydrogels in order to form the porous structure. Hydrogels with macro pores were targeted during the synthesis in order to decrease mass transfer resistance inside the particles. It can also be concluded from the images that the hydrogel synthesized has an non-uniform macro-porous structure. These three tests indicate that a porous DADMAC hydrogel was synthesized according to the recipe in the literature [12].

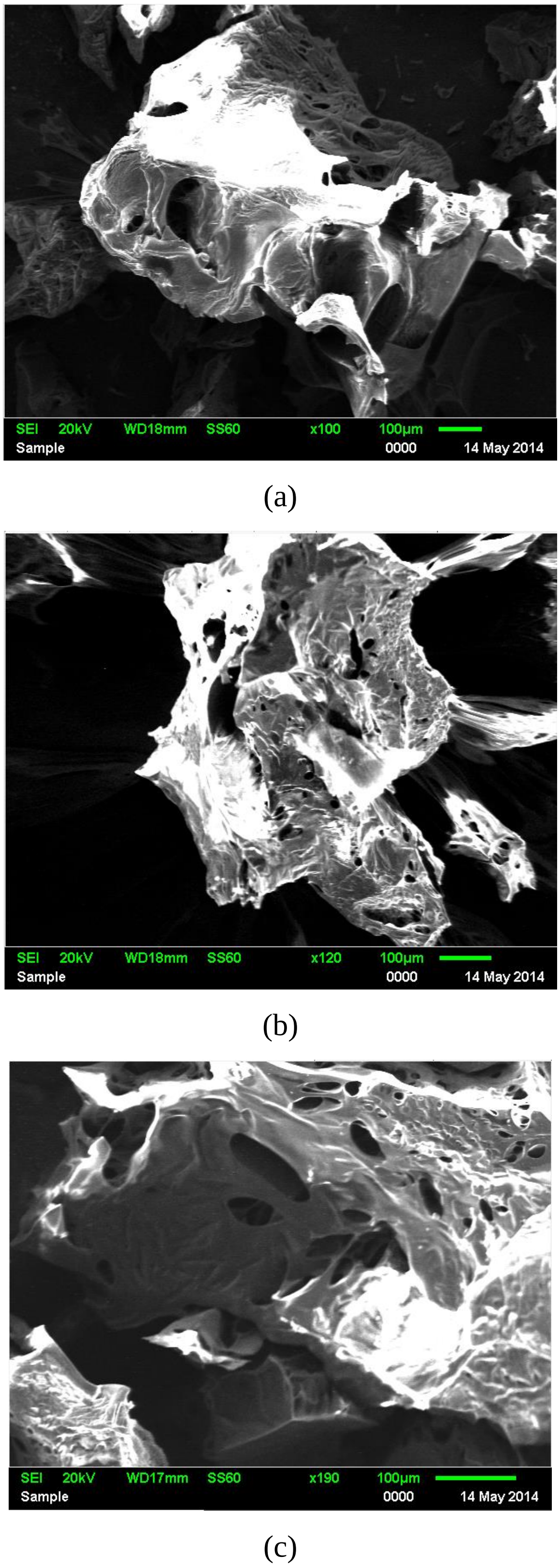


Figure 4.4. SEM images of the poly(DADMAC) gels: (a) swollen in pure water, (b) in solution with 1.0 mg/L arsenate, (c) in solution with 50.0 mg/L arsenate.

4.1.2. DADMAC-P(4-VP) Co-polymers

FTIR analyses were conducted for DADMAC-P(4-VP) Co-polymers synthesized with presence of 10 percent and 25 percent Vinyl pyridine. Results obtained from the analyses were presented in Figure 4.5. Peaks observed at 2900 cm^{-1}, 1600 cm^{-1}, 1477 cm^{-1} can be attributed to $–CH_2$, pyridine and $–C\text{-}N^+$, respectively. These molecular structures are well related with DADMAC and Vinyl pyridine structures. It can also be observed from the figures that changing the amount of vinyl pyridine addition did not affect the spectrums obtained.

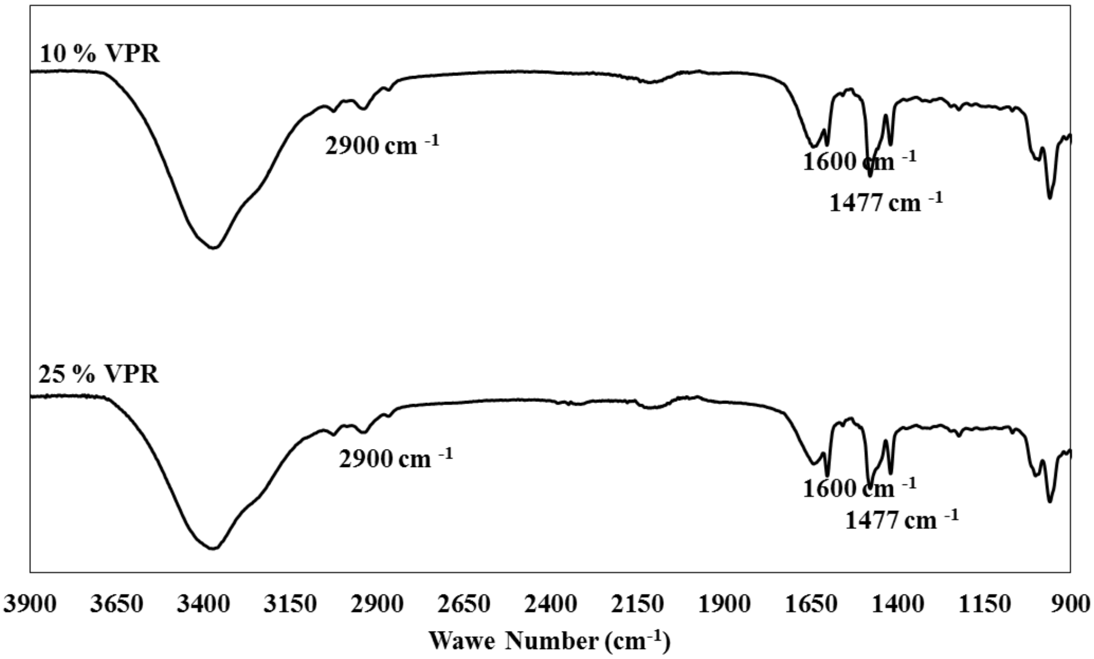


Figure 4.5. FTIR Spectrum of DADMAC- P (4-VP) Co-polymer.

4.2. Batch Separation Experiments

These sets of experiments contain detailed research on the arsenic removal capacity of DADMAC hydrogels at various conditions and on the physical characteristics of the hydrogels. Cationic DADMAC hydrogels were found to have high removal capacity and affinity towards arsenate anions in about 10 minutes of contact time. Recovery experiments also revealed that DADMAC hydrogels can be recovered and re-used in five consecutive runs.

4.2.1. Removal Experiments

Arsenic removal tests have been conducted at three different initial (starting) arsenate concentrations with various hydrogel additions. Effect of the medium pH on removal efficiency was also tested. Cationic hydrogel was not found effective on removal of arsenite (As (III)) anions in the studies carried on using arsenate (As (V)) solutions.

Arsenic removal performance was evaluated according to arsenic removal percentage and arsenic binding capacity (Q) which can be defined with the following relationships:

$$Q = \frac{(C_{As,i} - C_{As,f}).v}{m} \tag{4.2}$$

$$Arsenic\ Removal\ (percent) = \left(\frac{C_{As,i} - C_{As,f}}{C_{As,i}}\right) \times 100 \tag{4.3}$$

where $C_{As,i}$ and $C_{As,f}$ are the initial and final As (V) concentrations (in mol/L), respectively. m is mass of dry gel (g), v is sample volume (mL) and Q is binding capacity (mmol/g).

Considering the different charges that arsenate anions may have at different pH values. pH of the medium is one of the most important parameters in this study. Results obtained from the treatment of arsenate solutions having different pH values and an initial arsenate concentration of 1 mg /L are presented in Figure 4.6.

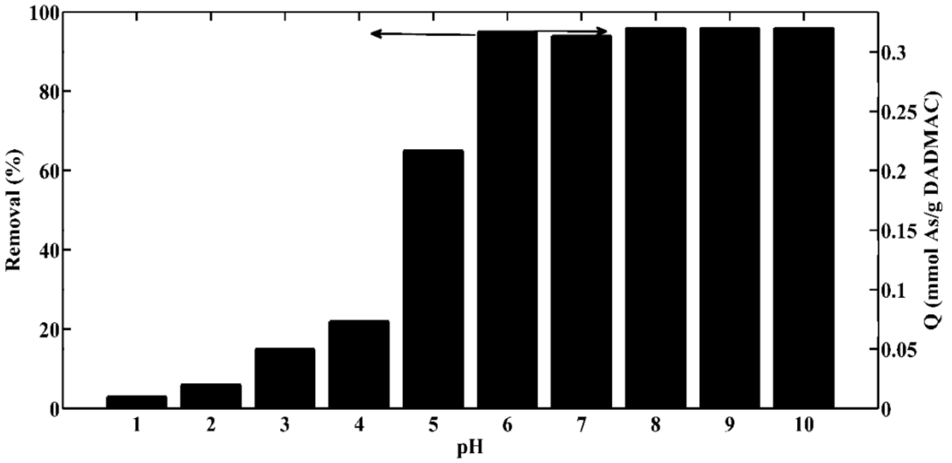


Figure 4.6. Effect of medium pH on Arsenic removal efficiency of poly(DADMAC) gel. Arsenic initial concentration: 1 mg/L, DADMAC gel amount: 0.04 g, [DADMAC]/[As]: 186, treated volume: 100 mL and shaking frequency: 200 rpm. Percent coefficient of variation (CV (%))= 1. CV (%) was calculated from a set of arsenic removal experiments conducted at pH = 7 (Appendix A2). The value was calculated in terms of arsenic removal (%).

It can be observed from the figure that removal efficiency of arsenic increase with increasing solution pH. All quaternary amine groups from DADMAC and TAP are known to be charged regardless of the solution pH; on the other hand As(V) can be found as arsenate anions only at pH values over 4. Charges of anions also increase with the increasing pH. It can be concluded from the figure that arsenic removal efficiency increases up to 95 percent at pH 6 and no considerable change was observed between pH 6 - 10. These show that DADMAC hydrogels can be used in the treatment of arsenate solutions in a very wide pH range including neutral pH. These behavior also give opportunity to design treatment processes without any pH adjustment.

Various arsenic concentrations in surface and ground waters have been reported in the literature [43]. In order to simulate low, medium and high arsenic concentrations, arsenic removal experiments with 0.1, 1 and 100 mg/L arsenate solutions were tested. Results are given in Figure 4.7.

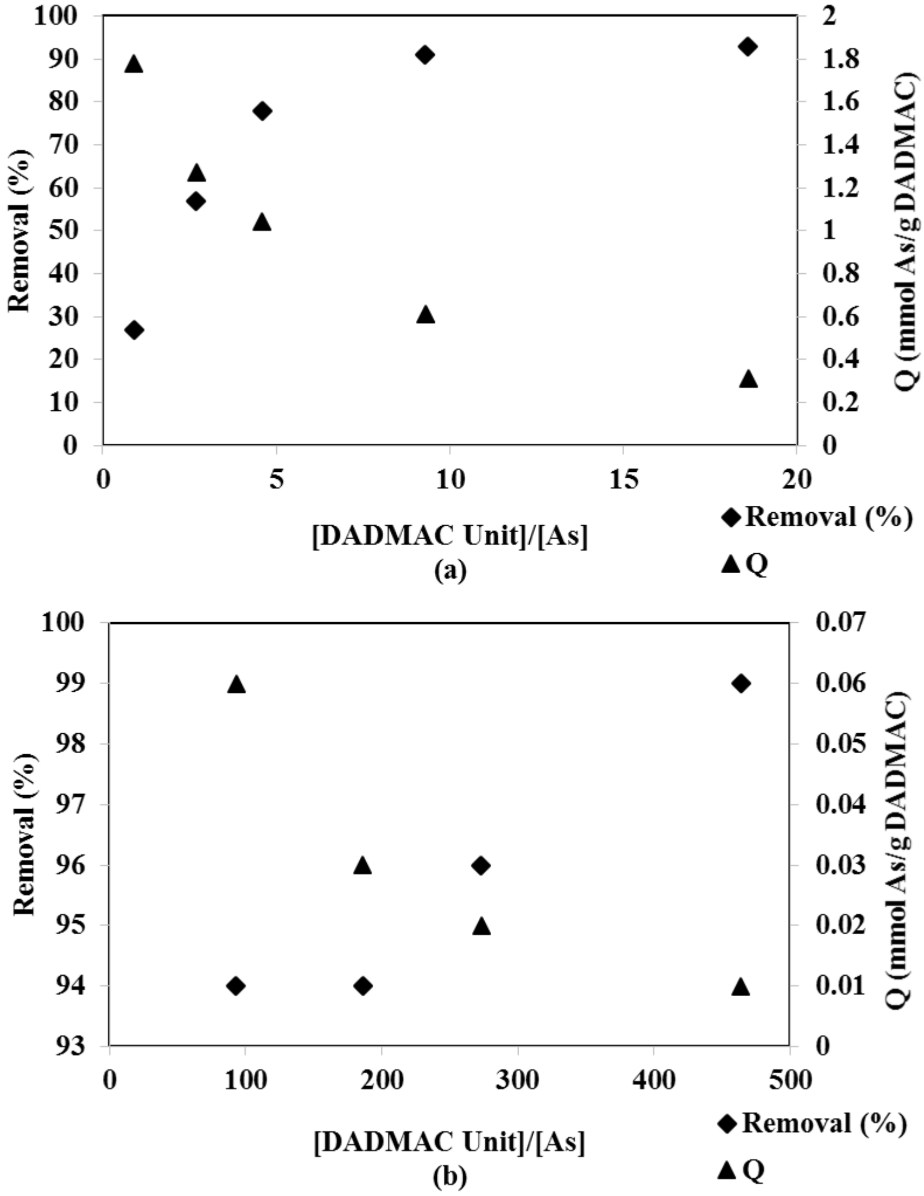


Figure 4.7. Effect of [DADMAC]/[As] molar ratio of the gel on Arsenic removal efficiency. Initial arsenic concentration: (a) 100 mg/L, (b) 1 mg/L without pH adjustment (7-6.5), treated volume: 100 mL and shaking frequency: 200 rpm. Q values represented with + and removal percent values represented with dots. CV (%) = 1 (arsenic removal)

Effect of DADMAC addition was observed for different initial arsenic concentrations. Experiments were conducted in the presence of DADMAC hydrogels in the range of 0.1 g - 0.01 g and with initial arsenic concentrations of 100, 1 and 0.1 mg/L. Arsenic concentrations well below the detection limit of 5 μg/L was recorded in the runs conducted with initial arsenic concentrations of 0.1 mg/L. Data related with those runs was not plotted due to this reason.

Experiments conducted with initial arsenic concentration of 0.1 mg/L revealed that DADMAC hydrogels (gel concentrations in the range of 1 g/L – 0.1 g/L) can be used to reduce arsenic content below the allowable limit of 10 μg/L. Experiments with moderate arsenic concentration of 1 mg/L also yielded successful runs in terms of approaching allowable limit value of arsenic concentration 10 μg/L. It was obtained after treatment of arsenic solutions with DADMAC gels, in the runs conducted with initial arsenic concentration of 1 mg/L and DADMAC gel concentration of 1 g/L achieving 99 percent arsenic removal. Experiments with high initial arsenic concentration of 100 mg/L showed that DADMAC hydrogel can also be used in pretreatment for waters with similar characteristics. Arsenic removal up to 90 percent observed in these runs showed that DADMAC hydrogels have higher binding capacity than those of other hydrogels used for arsenic removal in the literature.

4.2.2. Arsenic Removal Mechanism

Ion exchange is the proposed mechanism for the removal process. Ion exchange between chloride in the functional group of the gel and arsenic anions is proposed as the removal mechanism. Proposed mechanism is sketched as in Figure 4.8.

Figure 4.8. Proposed Arsenic Removal Pathway

This theory was tested with Energy Dispersive X-ray Spectroscopy (EDX) studies conducted with hydrogels swelled in water and in arsenate solutions. Results obtained clearly showed a change in the amount of chlorine and arsenic in the tested samples when they are soaked in arsenate solutions. Results obtained are given in Table 4.1.

Table 4.1. EDX analysis of DADMAC hydrogels soaked in water and in 50 mg/L As solution.

	Water	50 mg/L As
Element	Concentration (percent)	
C	62.4	56.4
N	7.5	7.6
O	25.7	31.6
Cl	4.2	1.5
As	0.2	2.9

EDX analyses revealed the exchange between chlorine and arsenic when the hydrogel soaked in arsenic solution. It can be observed from Table 4.1 that considerable arsenic amount was recorded for the hydrogel sample soaked in arsenate solution while a less chlorine content was recorded with respect to the sample soaked in de-ionized water. EDX results do not always yield results with high accuracy although the results clearly indicate arsenic existence in the structure of the hydrogel at the expense of chlorine.

Regeneration studies with sodium chloride also provide information on mechanism; in the regeneration studies, it was observed that arsenic anions can be replaced by chloride from sodium chloride solutions. More detailed discussion on that matter was made in the section related with regeneration.

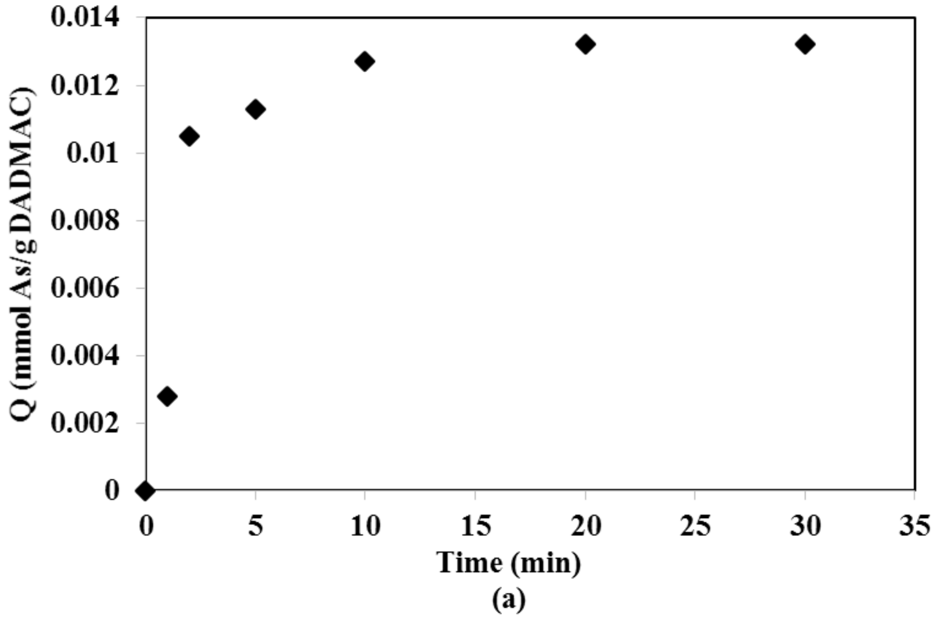
4.2.3. Arsenic Removal Kinetics and Sorption Mechanism

One of the most important design parameters for removal processes is contact time. This parameter determines the volume of the contactor. Even though this study is based on simple batch system and not focused on a specific contactor model, effect of contact time on reaching maximum arsenic removal was investigated with batch removal studies conducted with different contact times. Starting arsenic concentration was selected as 1 mg/L hydrogel concentration being 1 g/L (As/gel ratio that yielded 99 percent removal). Contact time experiments were also used for sorption mechanism analysis with intraparticle diffusion model. Intraparticle diffusion model is a widely used model in literature [44-47] in order to investigate adsorption kinetics of various species. This model is also used to obtain information about rate controlling mass transfer step during adsorption process.

Mass transfer of a molecule from liquid bulk to the solid phase includes adsorption on the surface of the solid phase, diffusion through the solid phase and adsorption on active sites. Last step is the fastest step and cannot be observed in most of the cases [47]. Analysis using intraparticle model can be used to find the rate determining step in such processes. Mass transfer rate from liquid bulk to the solid phase can be controlled by either film mass transfer or internal diffusion step or both of them. Intraparticle diffusion model is expressed with the equation below:

$$Q = k_a\sqrt{t} + c \tag{4.4}$$

where Q is the capacity in terms of mmol As per gram of gel and c is the time independent capacity. The remaining variables, k_a is a rate constant of the diffused mass within time, t. Arsenic removal with contact time and intraparticle diffusion model analysis by plotting $t^{0.5}$ vs. Q are given in Figures 4.9a and 4.9b, respectively.



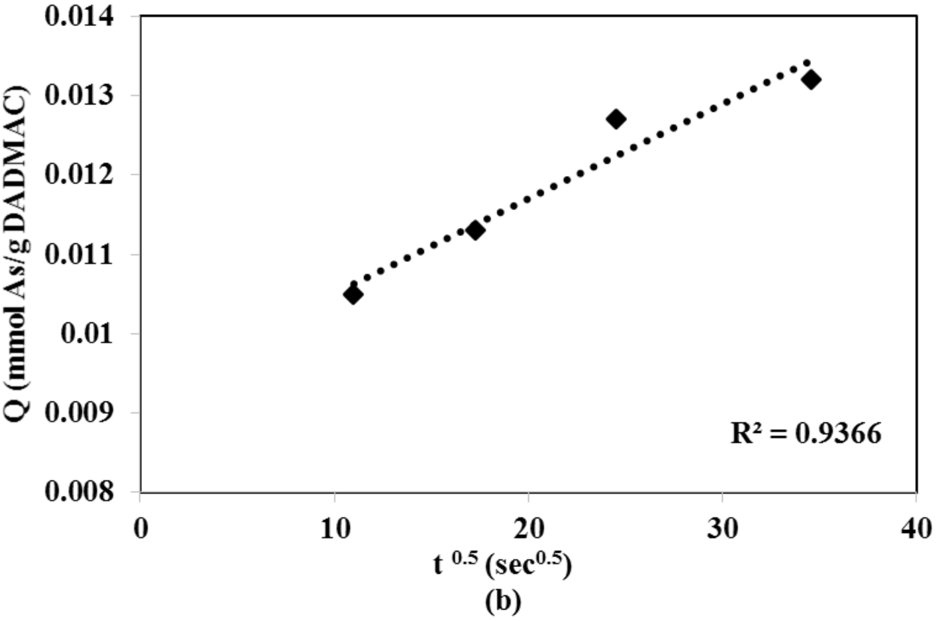


Figure 4.9. (a) Contact time for arsenic rremoval, (b) linear Q vs. √t plot indicating validity of "intraparticle diffusion model" for the arsenate sorption. Arsenic initial concentration: 1 mg/L, DADMAC gel amount: 0.1 g, [DADMAC]/[As]: 464, without pH adjustment (7-6.5), treated volume: 100 mL and shaking frequency: 200 rpm.

It can be observed from the Figure 4.9a that most of the arsenic removal takes place within around 10 minutes. Intraparticle diffusion model plot usually yields a figure having two slopes where first slope gives information about film mass transfer and the second slope gives information about the diffusion step. Despite this fact, in Figure 4.9 (b) only one slope was obtained. Considering the total time required for complete removal, first step indicating film mass transfer from liquid bulk to solid surface might take place under one minute. It was very hard to take samples below one minute with accuracy so analysis within that time interval was not conducted and film mass transfer region could not been observed.

In order to further investigate the mechanism and understand the effect of film mass transfer rate, experiments with different shaking frequencies were conducted. It is expected to observe a decrease in the effect of film mass transfer resistance with increased shaking frequency for the processes where film mass transfer rate may be important. Results obtained from these runs are also given in Table 4.2.

Arsenic removal experiments were conducted for the investigation of shaking frequency effect using arsenate solutions with an initial concentration of 1 mg/L arsenic and with a hydrogel concentration of 1 g/L. Runs were conducted for 5 minutes (below the required time for optimum removal) in order to be able to observe the effect of the shaking frequency only. It is expected to observe same removal results after a certain time for all the runs regardless of the shaking frequency. Therefore in order to avoid this, contact time was kept shorter than the required contact time for 99 percent removal at given conditions.

It can be observed from Table 4.2 that only 100 rpm shaking frequency resulted in a decrease in removal (percent); on the other hand, removal (percent) in the other runs were observed to be constant in the range of 150 – 250 rpm. This result showed that arsenic removal efficiency was not affected by the shaking frequency in the range of 150-250 rpm including the operating condition of 200 rpm. According to the results obtained, film mass transfer resistance can be considered as negligible for shaking frequencies above 150 rpm.

Table 4.2. Effect of shaking frequency on arsenic removal. t = 5 min

Rpm	Removal (percent)	Q (mmol As/g DADMAC)
100	70	0.09
150	83	0.11
200	83	0.11
250	83	0.11

Results obtained from shaking frequency experiments also support the idea of having a mass transfer mechanism controlled by internal diffusion rate only.

4.2.4. Competition of Other Anions with Arsenate Anions

Arsenate anions were removed from the liquid environment according to the ionic attraction between negatively charged arsenate and positively charged functional groups on the hydrogels. This means that other anions that can be found in the environment may also compete for the functional groups on the hydrogels.

Studies with solutions containing other anions that can be found in real water samples were also conducted in order to observe the selectivity of DADMAC hydrogels against arsenate anions. For this purpose, solutions containing equal amounts of these anions and arsenic were treated with DADMAC hydrogels. Arsenate solutions having 100 mg/L arsenic and other selected anion to be tested were prepared and treated with different amounts of DADMAC hydrogels. Results were recorded in terms of percent arsenic removal with and without these anions. Results are given in Figure 4.10

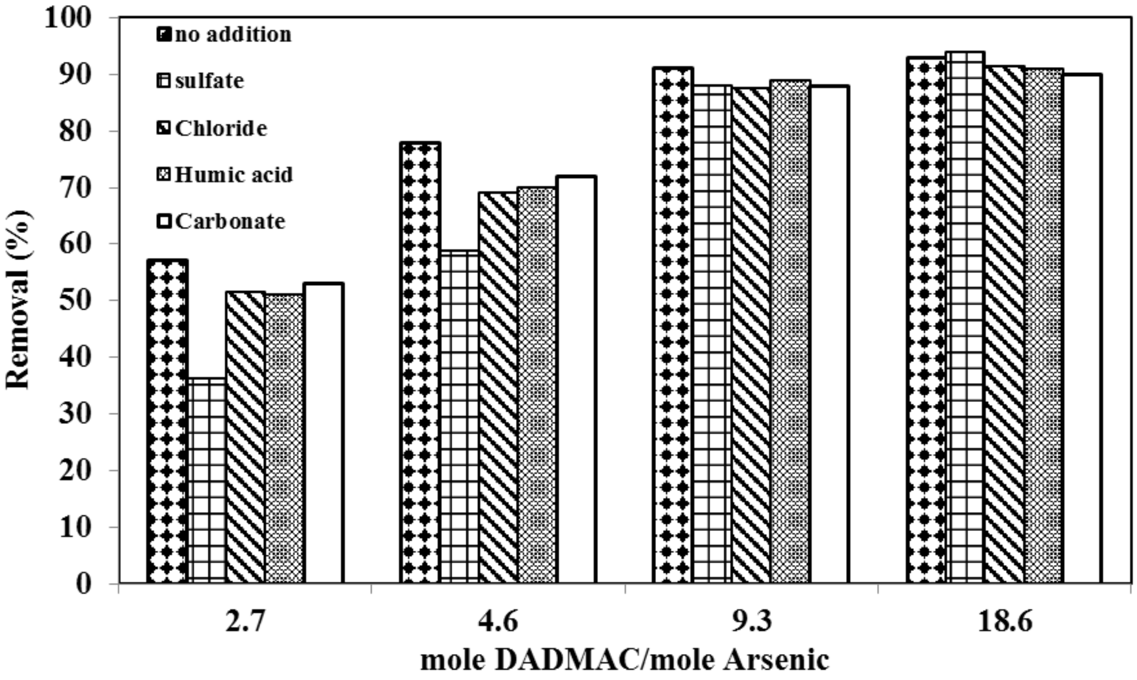


Figure 4.10. Arsenate removal in presence of other anions. Initial arsenic concentration: 100 mg/L, anion concentration: 100 mg/L, solution volume: 100 mL. solutions containing arsenic and sulfate, arsenic and chloride, arsenic and humic acid, arsenic and carbonate were prepared for these runs. CV (%) = 1 (arsenic removal)

Figure 4.10 shows that the affinity of DADMAC hydrogels is towards arsenate anions instead of other anions when they are added to the solution in the same amounts. According to the studies conducted, affinity of DADMAC hydrogels towards anions can be given as Arsenate >> sulfate > Chloride > Humic Acid ≅ Carbonate.

In real life applications, generally, arsenic concentration is lower than those of the other anions that can be found in real water samples. Runs with different chloride and sulfate concentrations were conducted in order to observe the relation between arsenic removal performance and addition of anions having higher concentrations than arsenate concentration. Results are given in Figure 4.11

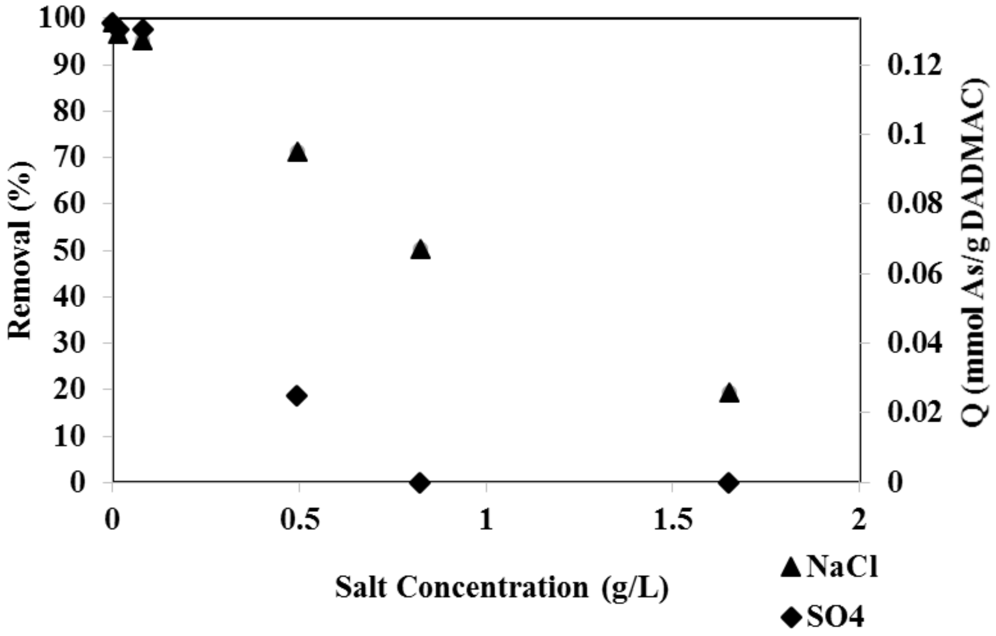


Figure 4.11. Effects of NaCl and Na_2SO_4 concentrations on the arsenic removal from 1.0 mg/L of the aqueous arsenic solutions. pH: not set (7-6.5), gel amount: 0.1 g, [DADMAC]/[As]: 464, treated volume: 100 mL and shaking frequency: 200 rpm. Please note that figure represents arsenic removal both in terms of percentage removal and in mmol/g. CV (%) = 1 (arsenic removal)

4.2.5. Regeneration of DADMAC Hydrogels

Removal processes including synthesized materials can be considered as costly processes since they involve an additional chemical synthesis step or purchasing of that additional material from a supplier. Reusability of the chemical has an economic importance and can be an important factor in the determination of feasibility of the process.

The proposed mechanism of ion-exchange for arsenic removal suggests that the arsenic molecules hold on the polymer can be recovered by a solution containing other anionic species. The ideal choice for the anion can be considered as chloride which is in the structure of the hydrogel before it was soaked in arsenate solution or decreasing the pH of the medium with hydrochloric acid. Studies with HCl and NaCl were carried out for regeneration of DADMAC hydrogels previously used in experiments. Hydrogels used in treatment of 1 mg/L arsenic solutions were soaked in sodium chloride or HCl solutions and increase in arsenic concentrations in these solutions were measured and percentage of arsenic recovery was calculated based on the arsenic amounts taken from the arsenic solutions by hydrogels. Percent recovery values for different concentrations of salt and different medium pH values are given in Figure 4.12

Arsenic recovery values of more than 95 percent were observed in the runs with HCl when the pH of the solution used for recovery was one (pH= 1). The runs with NaCl also showed that almost all arsenic was successfully recovered using NaCl solutions having concentrations above 10 g/L.

Results obtained from these runs also support the idea of ion exchange mechanism between chloride anions on functional groups of DADMAC hydrogel and arsenate anions. It is also worth to compare experiments conducted in the presence of chloride ions with recovery experiments. Arsenic removal experiments in presence of 1 g/L NaCl yielded 20 percent arsenic removal; on the other hand, recovery experiments conducted with 1 g/L NaCl solution yielded 80 percent arsenic recovery. This comparison also suggests an equilibrium between chloride and arsenate anions that can be achieved in an ion exchange process.

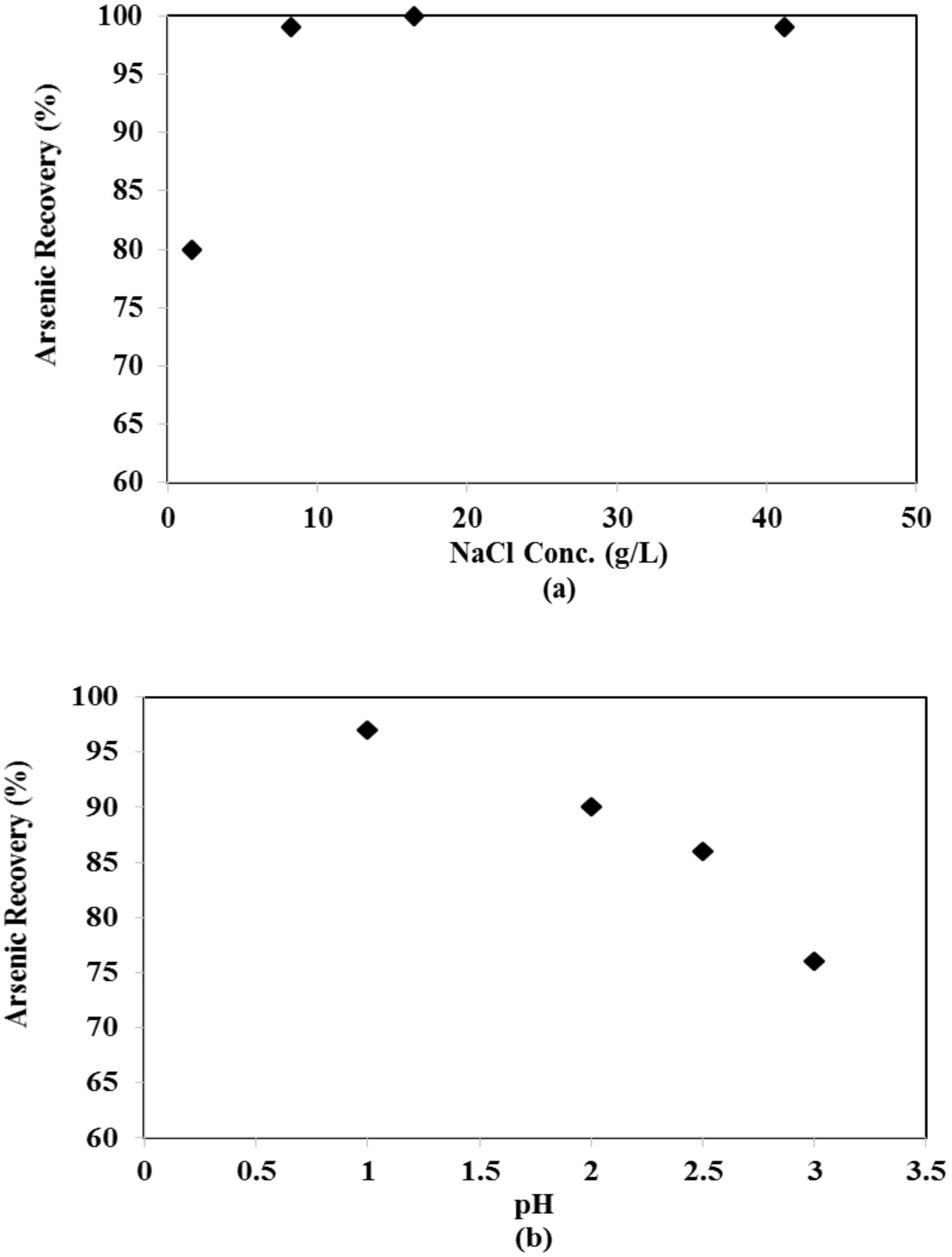


Figure 4.12. Effects of (a) NaCl concentration, and of (b) pH, on arsenic releasing from the loaded poly(DADMAC) gels. Volume: 100 mL, shaking frequency: 200 rpm and gel amount: 0.1 g used in treatment of 100 mL, 1mg/L Arsenate solution.

Efficiency of arsenic recovery for repeated runs was also investigated by conducting five consecutive recovery/removal runs. In these runs, hydrogels were used for treatment of arsenic solution then soaked in salt solutions, rinsed with water in order to remove residual sodium chloride that may affect the efficiency of removal experiment. Results for these runs are given in Table 4.3.

Table 4.3. Arsenic sorption and desorption characteristics of the regenerated of DADMAC hydrogel samples (0.1 g). The results have been derived for 5 times of repeated loading-recovery cycles.

	Removal			Recovery		
Number of Cycles	$C_{As,i}$. (μg/L)	$C_{As,f}$. (μg/L)	**Uptake[2] (μg)**	$C_{As,i}$. (ppb)	$C_{As,f}$. (ppb)	**Release[3] (μg)**
1	1050	11	**104**	0	1060	**106**
2	1050	10	**104**	0	1055	**106**
3	1050	11	**104**	0	1080	**108**
4	1050	13	**104**	0	1075	**108**
5	1050	9	**104**	0	1090	**109**

These tests proved that DADMAC hydrogels can be regenerated and reused at least in five consecutive runs. Almost 100 percent recovery was observed in these runs without a decrease in arsenic removal performance.

In conclusion, this study presents a new material for arsenate removal and improves the limited literature related with arsenic removal using hydrogels. It has been one of the most detailed studies including the effects of pH, contact time, competing anions, regeneration of the material and studies on mechanism. A comparison between this study and other available hydrogel studies on arsenic removal is given in Table 4.4.

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[2] Uptake represents the amount of arsenic removed from the arsenic solution treated

[3] Release represents the amount of arsenic released during regeneration step

DADMAC hydrogels are able to remove more arsenic than those in the other studies in shorter contact times in solutions having a wide pH range (pH = 6-10).

Table 4.4. Comparison of arsenic binding abilities of the hydrogel studies so far.

Base polymer gel	**Crosslinker**	**pH**	**Q[4] (mmol As/g gel)**	**Contact Time (min)**	**Ref.**
Poly(3-acrylamido propyl)trimethyl ammonium chloride	N,N'-methylene bisacrylamide	9	1.6 [5]	360	[22]
Quaternized poly(4-vinyl pyridine)	N,N'-methylene bisacrylamide	5,6	0.4	15	[23]
Poly(vinylalcohol)-Iron oxide xerogel	-	2-5	1.2	<240	[24]
Poly(methacryloyloxyethyl trimethylammonium chloride)	Multimethacrylate functional galactomannan	6,9[6]	0.9[4]	1440[7]	[25]
Poly(DADMAC)	Tetraallypiperazinium dichloride	6-10	1.8	<15	

---

[4] Values represent the highest removal reported and are independent of the other reported optimum conditions

[5] Values represent the estimated amount from the related figure provided in those studies

[6] pH values studied were selected as 3, 6 and 9

[7] 24 h was the only adsorption time reported; no kinetic studies were carried out.

4.3. Continuous Fixed Adsorption

In the previous section, adsorption ability of DADMAC hydrogels was tested with batch adsorption method however in real life applications continuous processes should also be considered as an alternative. Fixed bed adsorption tests were conducted in order to test the effectiveness of DADMAC hydrogels in a continuous adsorption process. Results of these preliminary experiments are given in this section. Main aim of these runs was to obtain an idea about applicability of hydrogels in column studies. It was observed during the experimental studies that swelling of the hydrogels might create some problems when column was filled with hydrogels. It was not easy to understand flow mechanics since the material was not an ordinary bead but a powder like substance which swelled by adsorbing water and formed a gel like porous structure. More rigid polymer can be synthesized by lowering the amount of cross-linker during the synthesis and can be used in future studies.

Arsenic adsorption tests were conducted by treating arsenate solutions with 100 mg/L concentration by using different hydrogel amounts. Re-usability of hydrogels were also tested where hydrogels used in arsenic removal were treated with sodium chloride solution for desorption (desorption was also conducted using fixed bed column) and washed with de-ionized water in order to remove remaining sodium chloride before the next run.

Breakthrough curves obtained from the runs conducted using different amounts of hydrogels are given in Figures 4.13-4.16. Data used to plot breakthrough curves is presented in Table 4.5. It can be observed from these figures that amount of arsenate in solution which can be treated decreases as the bed height decreases. It is expected since the adsorption capacity is directly proportional to the amount of hydrogel used [48-51]. Arsenic concentrations of the samples measured before breakthrough were also found to be different in the runs conducted with 1 g, 0.5 g and 0.3 g hydrogel additions. Arsenic concentrations of the samples were measured below the limit of quantification in the run conducted with 1 g hydrogel. On the other hand, measured concentrations were around 1 mg/L in the runs conducted with 0.3 and 0.5 g of hydrogel additions. This can be explained by the lower contact time in the runs conducted with less hydrogel. Decreasing amount of hydrogel by keeping the flow rate constant resulted in a decrease in time and contact surface available for ion exchange leading to higher effluent concentrations [48-51].

Three consecutive runs were also conducted with packed bed containing 1 g DADMAC hydrogel in order to observe continuous regeneration and re-usability of the hydrogels. Adsorption curve is presented in Figure 4.16. No significant difference in adsorption capacity was observed in these runs. Effect of sodium chloride concentration on regeneration performance was also investigated by using two different salt concentrations in regeneration part.

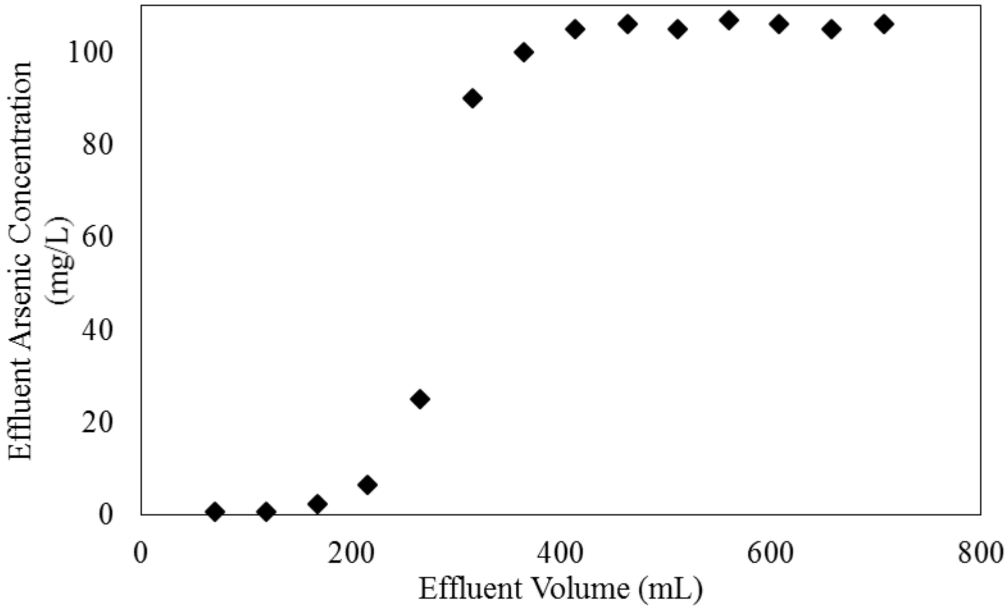

Figure 4.13. Breakthrough curve for 0.3 g DADMAC. C_0.: 100 mg/L As (V), pH: not set (6.6), amount of hydrogel in column: 0.3 g, Effluent flowrate: 0.47 ± 0.05 L/h, Coefficient of variation (CV) % = 7. CV was determined according to Table A 17

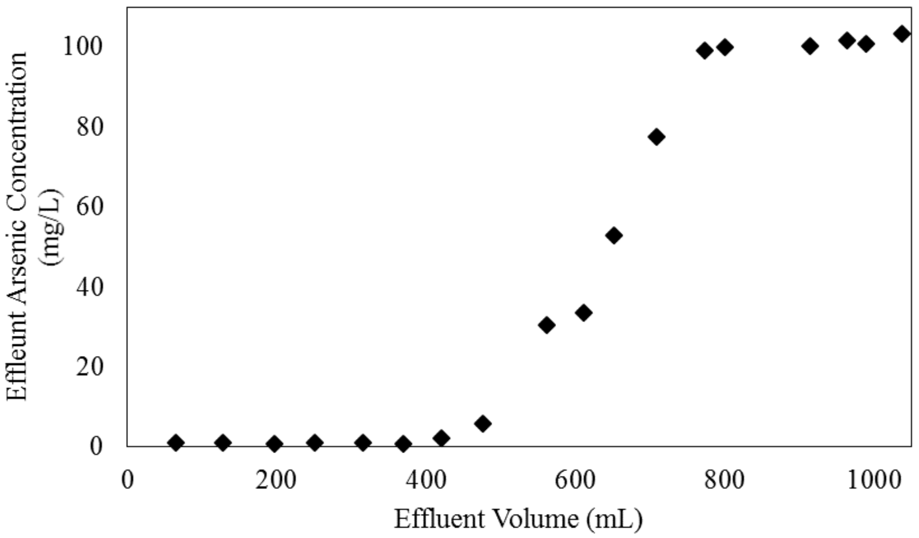

Figure 4.14. Breakthrough curve for 0.5 g DADMAC. C_0.: 100 mg/L As (V), pH: not set (6.6), amount of hydrogel in column: 0.5 g, Effluent flowrate: 0.41 ± 0.07 L/h, CV (%) = 7

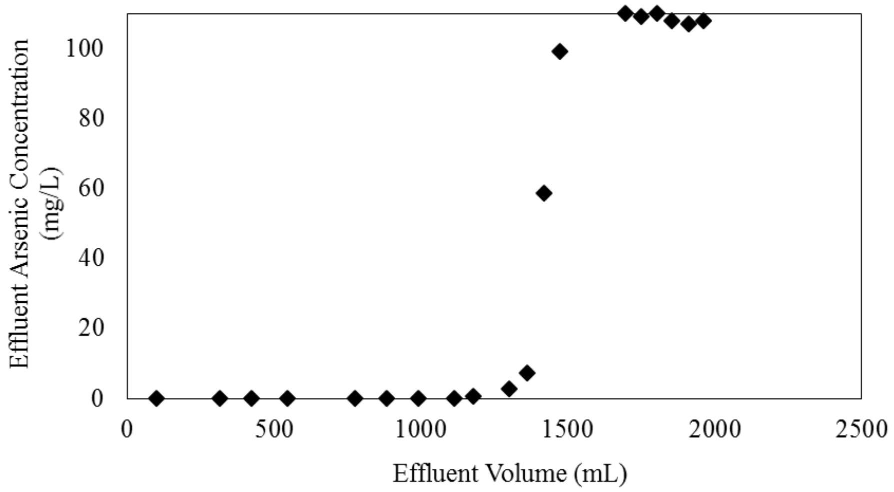

Figure 4.15. Breakthrough curve for 1 g DADMAC. C_0.: 100 mg/L As (V), pH: not set (6.6), amount of hydrogel in column: 1 g, Effluent flowrate: 0.45 ± 0.03 L/h, CV (%) = 7

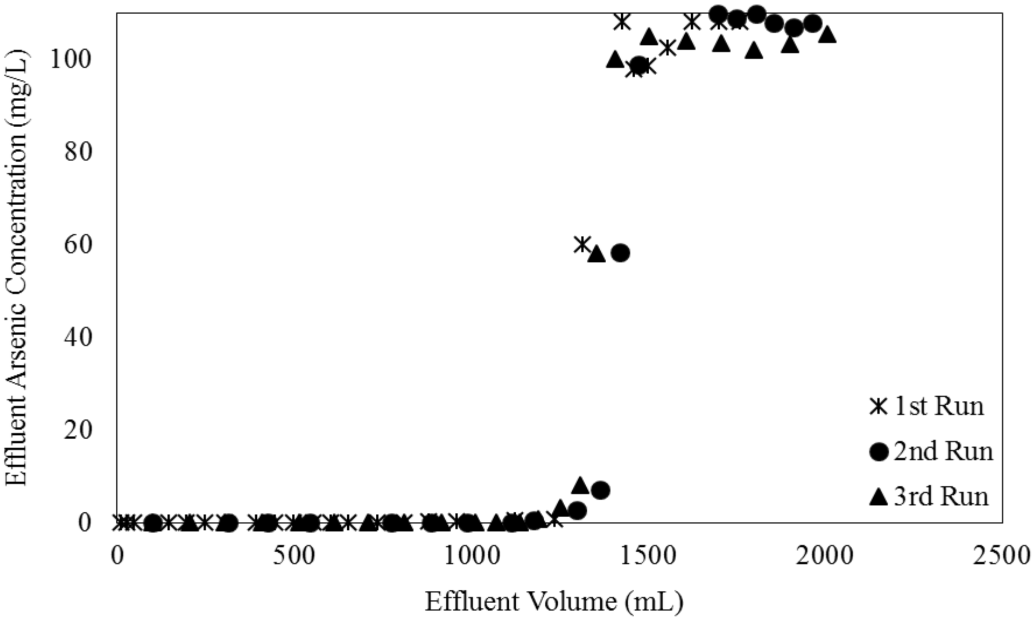

Figure 4.16. Breakthrough curves obtained in three consecutive runs. C_0.: 100 mg/L As (V), pH: not set (6.6), amount of hydrogel in column: 1 g, Effluent flowrate: 0.46 ± 0.05 L/h, CV (%) = 7

Regeneration of hydrogels were conducted by using 10 g/L and 20 g/L NaCl solutions. Regeneration performance was determined by measuring the concentration of the effluent leaving the column filled with hydrogels that was used in the previous adsorption run. Data obtained in these runs showed that important part of the regeneration process took place in the beginning (first 20 mL of the salt solutions), although complete regeneration was achieved by treating hydrogels with more than 0.5 L of the salt solutions. This amount of water can be considered as too much when it is compared with the amount of arsenic contaminated water treated in the first place.

Table 4.5. Breakthrough data obtained with different hydrogel amounts.

0.3 g DADMAC		0.5 g DADMAC		1 g DADMAC	
V_{eff} (mL)	$C_{As,e}$.(mg/L)	V_{eff}. (mL)	$C_{As,e}$ (mg/L)	V_{eff}. (mL)	$C_{As,e}$.(mg/L)
70	0.9	64	1.1	100	0.0
119	1.0	128	1.2	315	0.0
168	2.5	197	0.9	425	0.0
216	6.5	251	1.1	545	0.0
266	25.0	316	1.0	775	0.0
316	89.8	370	1.0	885	0.0
365	100.3	421	2.3	990	0.0
413	105.4	476	6.0	1115	0.0
463	105.8	562	30.5	1177	0.7
511	104.8	611	33.5	1299	2.7
560	107.3	651	52.9	1363	7.2
607	105.6	708	77.5	1420	58.5
658	104.9	773	99.0	1474	99.0
708	106.2	800	100.1	1582	111.1
		915	100.3	1696	110.2
		964	101.8	1750	108.9
		989	100.9	1805	109.7
		1037	103.4	1856	108.2
		1092	102.2	1911	106.6
		1144	99.8	1963	107.7

It can easily be observed from Table 4.6 that effluent arsenic concentrations are higher at the beginning of the operation and decrease very rapidly after first 56 mL and 25 mL of effluent in the runs conducted with 10 g/L and 20 g/L NaCl, respectively. Total amount of arsenic desorbed in these runs were calculated as 107 mg and 85 mg, respectively by numerical integration of the area under desorption curve (not shown) using trapezoidal rule. Amounts of arsenic desorbed in the first 56 ml and 25ml for these two runs were also calculated as; 103 mg As and 79 mg As which correspond to 96% and 95% of the total desorption. After this analysis, it can be concluded that instead of conducting a complete desorption (regeneration) process that will produce large amounts of arsenic contaminated water, a partially completed desorption can also be conducted which will remove almost all arsenic bound to hydrogels with much less volume of salt solution. It is also notable that there is a considerable difference between arsenic amounts desorbed. According to the data obtained, desorption process for the second run ended after first 25 mL of collected effluent, taking samples with less volumes might be helpful in increasing accuracy of the data obtained. Salt solutions used in arsenic desorption, might be treated with coagulation using a contactor having a much less volume than it would need for coagulation without adsorption. Salt solution treated by coagulation can also be re-used in regeneration of the hydrogels.

Table 4.6. Regeneration data obtained after 1st (10 g/L Cl^-) and 2nd (20 g/L Cl^-) adsorption runs. NaCl solutions were used in the regeneration runs.

10 g/L NaCl		20 g/L Cl^-	
V_{eff}. (ml)	$C_{As,e}$ (mg/L)	V_{eff} (ml)	$C_{As,e}$ (mg/L)
22	3122.07	25	4439.79
56	1483.07	60	82.56
85	244.05	120	15.84
111	11.56	148	10.24
177	2.44	185	4.43
267	1.42	250	4.48
307	0.64	310	2.83
329	0.28	365	1.33
346	0.78	434	0.45
365	0.22	483	0.32
424	0.11	582	0.75
562	0.05	691	0.09

4.3.1. Evaluation of Breakthrough Curves

Breakthrough capacities for the runs and modelling of the breakthrough curves were conducted and presented in this section. Breakthrough curve obtained in the second run conducted with 1 g hydrogel is represented in Figure 4.17 as an example for breakthrough capacity analysis. According to the literature [52] breakthrough concentration (C_B) can be defined as effluent concentration in between 1-5 % of the feed concentration (C_0)._According to this definition, breakthrough point can be selected when effluent concentration reaches breakthrough concentration (selected around two percent). Total adsorption capacity of the bed can be calculated as the total shaded area where breakthrough adsorption capacity is presented as blue area. Area shaded with red lines also show the mass transfer zone. According to the areas calculated from Figure 4.17 breakthrough capacity for the 2nd run conducted with 1 g hydrogel is 129.9 mg/1g hydrogel and total adsorption capacity is 144 mg/1g hydrogel. It is also worth to note that adsorption capacity of the hydrogels are also calculated as 135 mg/ 1g hydrogel in batch studies. Bed capacities are listed in Table 4.7

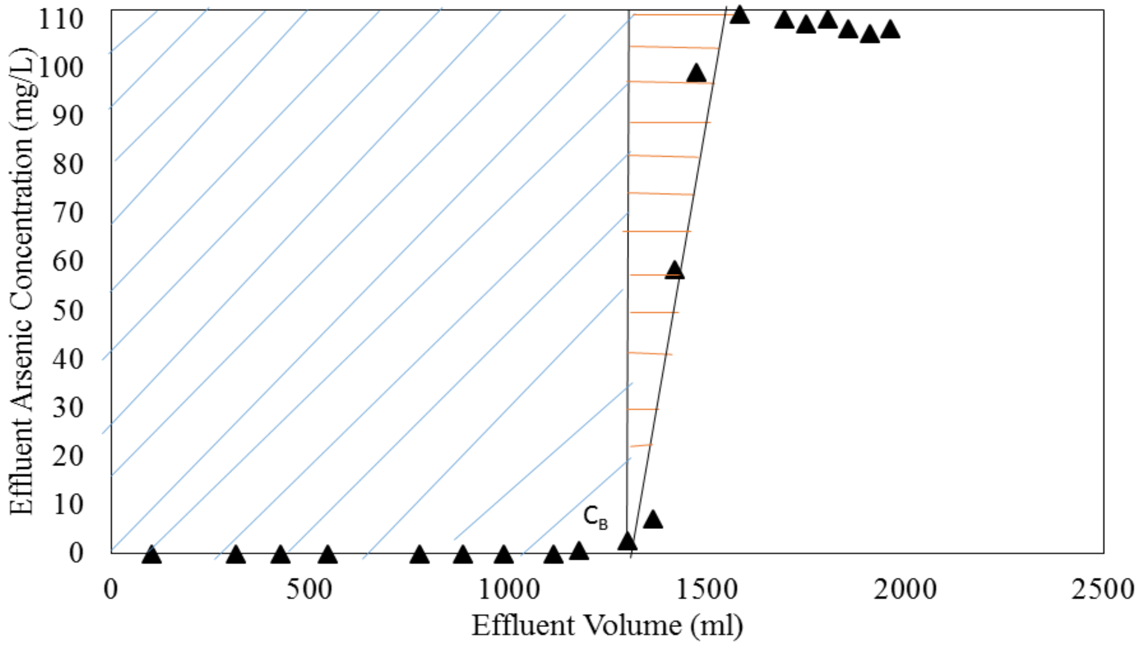

Figure 4.17. Breakthrough Analysis of 2nd Run Conducted with 1 g DADMAC Hydrogel.

Table 4.7. Breakthrough and bed capacities obtained in the experiments

Hydrogel (g)	Breakthrough Capacity (mg As / g hydrogel)	Bed Capacity (mg As / g hydrogel)
1	129	144
0.5	84	124
0.3	94	133

According to the literature [51], due to increased contact time, solute molecules have ability to diffuse inside adsorbent molecules in columns having higher bed heights. According to Table 4.7 such a trend was not observed in this study. Hydrogel amounts had an effect on effluent concentrations although total bed capacities obtained in the runs conducted were found to be similar. This may imply that mass transfer resistance of hydrogels were not important in these runs.

Slope of the mass transfer zone can also be used to obtain idea about mass transfer rate. Mass transfer rate goes to infinity as the difference in effluent volume between breakthrough and saturation concentration goes to zero [52]. When the slopes are investigated, it may be observed that “S” curves obtained in these runs look sharp which indicate high mass transfer rate. This behavior might also be explained with the sample volumes taken during these runs. Samples taken around breakthrough point were in the range of 50 mL. A sample volume of 50 mL for such a process (Figure 4.17 mass transfer zone) can be considered as too high. In order to understand the process better, samples with volumes around 10 mL should be taken.

Modelling of breakthrough curves have been studied widely in the literature and one of the common methods used during these studies is Bed Depth Service Time (BDST) model [50, 53-55]. BDST model was derived from Bohart-Adams model and modified. This model is one of the most widely used design models in metal adsorption using packed columns. BDST model neglects film and intraparticular mass transfer effects in adsorption while it only considers surface reaction between solute and particle surface [54]. BDST model is a simple model based on a linear relationship between breakthrough time and column bed height. Relationship between service time and column height is given in equation (4.5)

$$t_s = \frac{N_0 Z}{C_0 U_0} - \frac{1}{K_{ad} C_0} ln\left(\frac{C_0}{C_{br}} - 1\right) \tag{4.5}$$

Where t_s is service time (h), N_0 is bed capacity (mg/L), Z is bed height (cm), U_0 (average: 251 cm/h) is superficial velocity obtained by multiplying volumetric flow rate with column's cross-sectional area (0.000177 m^2), K_{ad} as the adsorption rate constant (L/mg.h) and C_{feed} and C_{br} are feed and breakthrough arsenic concentrations (mg/L). Service time vs. column height was plotted (Figure 4.18) to obtain N_0 from the slope and K_{ad} from the intercept of the curve. Bed heights were obtained by measuring the height of the hydrogel part in the column. Bed capacity was obtained as 5350 mg/L and K_{ad} is 0.0195 L/mg h.

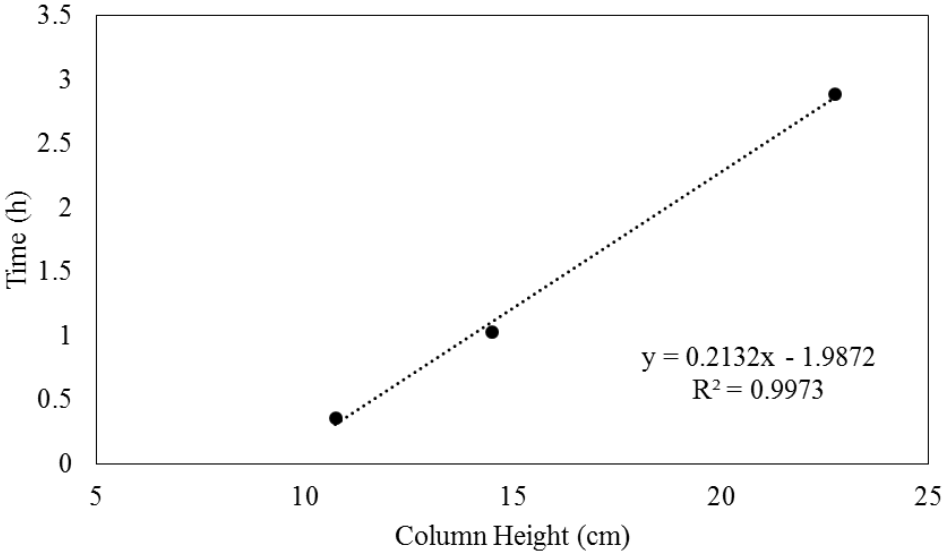

Figure 4.18. BDST model

4.4. Ultrafiltration Experiments with Linear Water Soluble DADMAC-P (4- VP) Co-Polymers

Flow experiments using a laboratory scale ultrafiltration system were conducted with and without polymer addition. Effects of medium pH, polymer concentration and presence of competing anions were tested.

4.4.1. Ultrafiltration Experiments without Polymer Addition

Main aim of the study was to investigate the effect of polymer addition on ultrafiltration with Polymer Enhanced Ultrafiltration (PEUF) process on arsenic removal. In order to observe the effect of polymer addition; performance of the selected ultrafiltration membrane on arsenic removal without polymer addition should also be tested. Arsenic removals at different pH values and arsenic feed concentrations were tested.

Experiments were evaluated with arsenic removal percent (rejection) values which can be defined as below:

$$Arsenic\ Removal\ (percent) = \frac{C_{feed} - C_p}{C_{feed}} \times 100\ \% \qquad (4.6)$$

Where C_f is concentration of arsenic in feed tank and C_p is the concentration of arsenic in permeate stream.

Experiments were conducted at different pH values and arsenic concentrations with arsenate (As (V)) and arsenite (As(III)) anions; these experiments were conducted for 90 minutes and samples were withdrawn from the feed and permeate streams for analysis during the experiments. Average of the arsenic removal results are presented in Figures 4.19 and 4.20. Arsenic concentrations measured from the samples of feed and permeate streams are also given in Appendix A3. An average arsenic rejection value of 85 percent was found in the runs conducted with arsenate anions (As (V)) at pH 10, while highest arsenic removal recorded for arsenite anions (As (III)) was 45 percent at pH 10. Arsenic concentration in the feed was 1000 µg/L in those runs which means recorded concentration in permeate stream was around 100 µg/L for As (V) removal. Considering these results UF can be used for pretreatment purposes of waters having arsenic feed concentrations of 1000 µg/L or with lower feed concentrations, permeate concentrations below 10 µg/L might be achieved. It seems that GE/Osmonics’ PT membranes tested in the ultrafiltration process have a chance to be used in treatment of As(V) containing waters even without polymer addition as a single process for treatment of low arsenic feed concentrations or in series for higher arsenic concentrations. This theory should be proved with more detailed experiments on real waters contaminated with arsenic. On the other hand treating arsenite anions with PES ultrafiltration alone was not found as effective as treating arsenate anions.

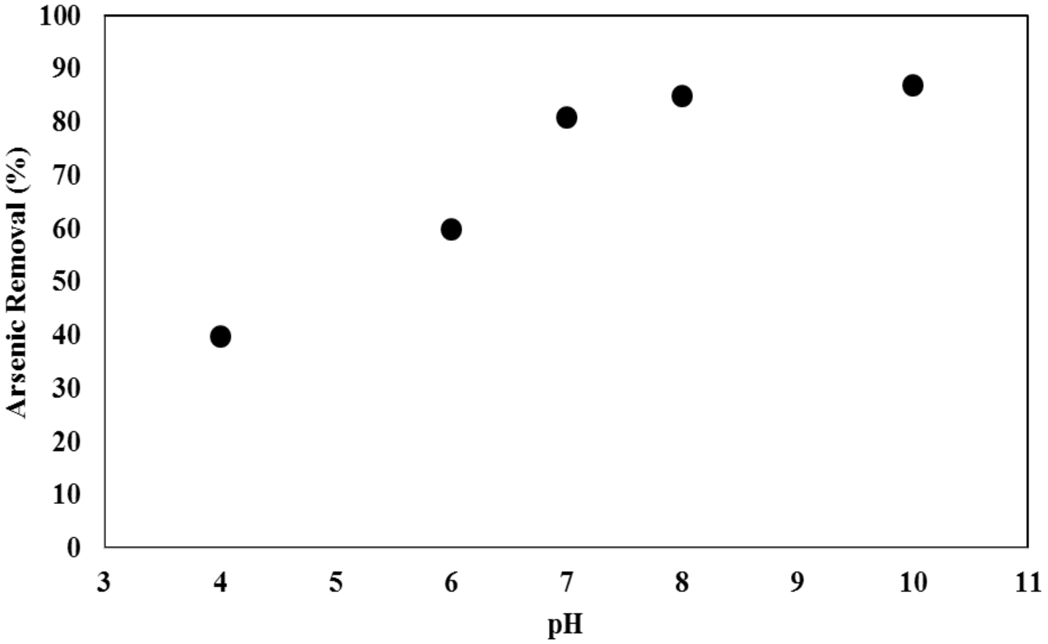

Figure 4.19. Overall As (V) removal efficiencies obtained with ultrafiltration alone. Feed concentration: 1000 µg/L, permeate flux: 83 L/m^{2}h, feed flow rate: 120 L/h, Coefficient of variation (CV) % = 5. CV values were determined according to the values presented in section A3.

Arsenic rejection in ultrafiltration processes are not expected due to the size of the anions although arsenic rejection up to some extent were also reported in literature [30-32,56,57]. This phenomenon can be explained with Donnan exclusion theory. According to Donnan exclusion theory (explained in more detail at Chapter 2), solutions containing dilute anions can be rejected by membrane surfaces having the same kind of ionic charge [32,33]. Negatively charged PT membranes were found to be effective in arsenate rejection especially at basic conditions where arsenate anions have (- 2) and (- 3) charges. It is also worth to note that surface charge of the membrane increases with increasing medium pH [42].

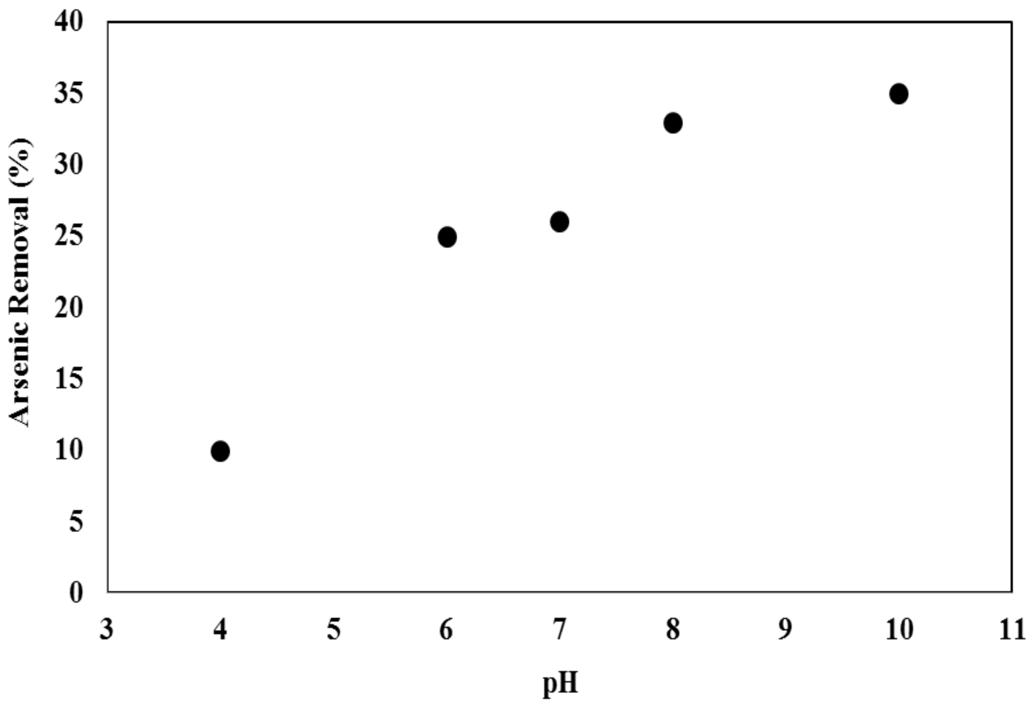

Figure 4.20. Overall As (III) removal efficiencies obtained with ultrafiltration alone. Feed concentration: 1000 µg/L, permeate flux: 83 L/m^{2}h, feed flow rate: 120 L/h, CV (%) = 5

4.4.2. Polymer Enhanced Ultrafiltration Experiments

Effect of polymer addition was tested for ultrafiltration experiments with the addition of positively charged soluble DADMAC-P(4-VP) co-polymers having quaternary amine groups to attract arsenic anions. Effects of polymer concentration and medium pH were investigated on arsenic removal. It is aimed to attract arsenate anions to polymers by the addition of polymers into the medium and conduct separation based on size exclusion instead of charge exclusion which was the case in ultrafiltration experiments.

Arsenic removal studies with addition of 1 g/L polymer for treatment of arsenic solutions containing 1000 μg/L As (III) and As (V) were conducted in order to observe the effect of polymer addition on arsenic removal efficiency. Two types of DADMAC-P(4VP) co-polymers were tested with different Vinyl pyridine contents of 10 and 25 percent (mole). Results obtained in these runs are presented in Figures 4.21 and 4.22.

It can be observed from the Figures 4.21 and 4.22 that Vinyl pyridine content of the polymer did not have any effect on arsenic removal. This fact may imply that arsenate anions were attracted by the positively charged functional groups on DADMAC polymers. One may expect a decrease in arsenic removal efficiency due to decrease in amount of active groups when amount of vinyl pyridine content increased although polymer concentration was in excess for these PEUF runs conducted. Increase in arsenic removal was also recorded with increasing pH. This was expected since arsenate anions' charge increase with increasing pH resulting in better interaction with polymers and anions (Figure 2.2).

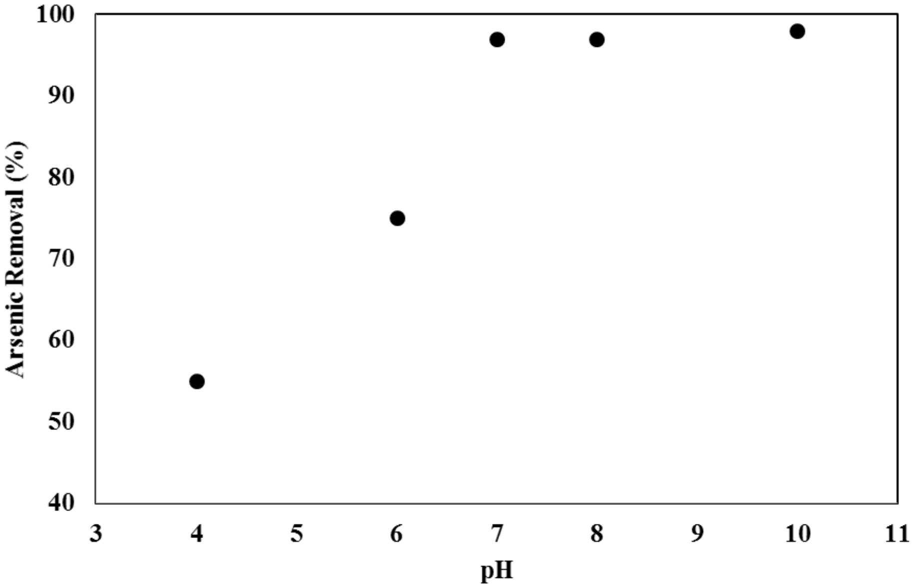

Figure 4.21. Arsenic (As (V)) removal studies with presence of DADMAC-P (4-VP) Copolymers (10 % P (4-VP)). Feed concentration: 1000 µg/L, permeate flux:40-60 L/m^2h, feed flow rate: 120 L/h, CV (%) = 5

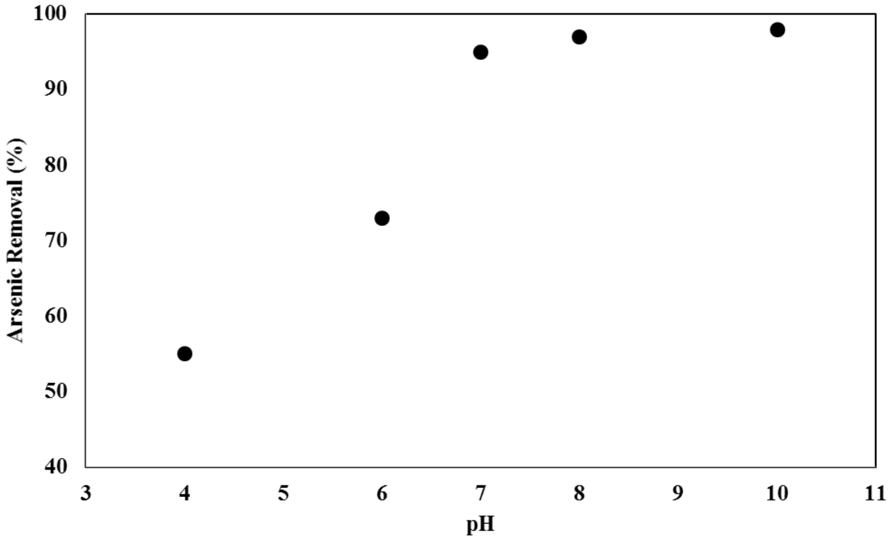

Figure 4.22. Arsenic (As (V)) removal studies with presence of DADMAC-P (4-VP) Copolymers (25 % vinyl pyridine). Feed concentration: 1000 µg/L, permeate flux:40-60 L/m^2h, feed flow rate: 120 L/h, CV (%) = 5

Runs with arsenite anions were also conducted in PEUF studies. Treatment of As(III) resulted in lower rejection in PEUF studies. Only 55 percent arsenic removal was observed at pH 10 in the runs conducted with As (III) anions with presence of 1 g/L polymer. Since polymer binding mechanism also relies on ionic interactions, presence of polymer did not show much improvement in treatment of arsenite anions except the slight increase in the run conducted at pH 10. Arsenic removal percentages which were obtained from the PEUF runs conducted with As(III) are given in Figure 4.23.

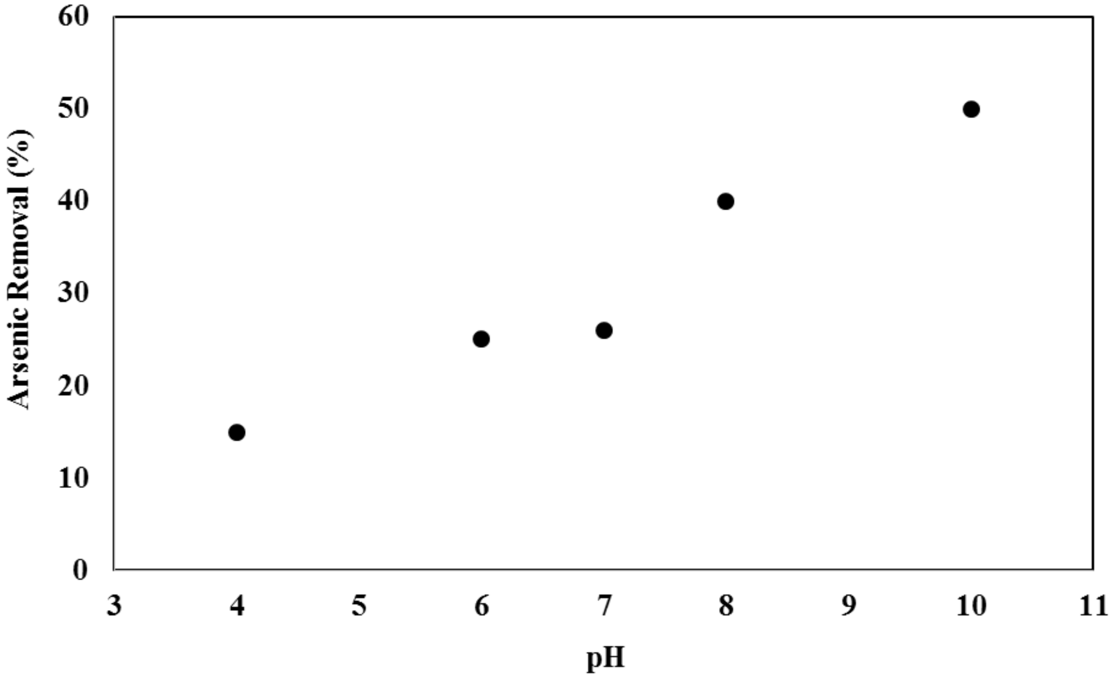

Figure 4.23. Arsenic (As (III)) removal studies with presence of DADMAC- P (4-VP) Copolymers (25 % Vinyl pyridine). Feed concentration: 1000 μg/L, permeate flux:40-60 L/m^{2}h, feed flow rate: 120 L/h, CV (%) = 5

Experiments with different polymer amounts were also conducted in order to investigate the effect of polymer addition on removal efficiency. Arsenic/Polymer mass ratio was defined as loading (L) which can be expressed with the equation below:

$$L = \frac{amount\ As\ (mass)}{Amount\ Polymer\ (mass)} \tag{4.7}$$

Results obtained with different polymer loading values for the treatment of arsenate (As (V)) solutions (feed concentration: 1000 µg/L) are given in Figure 4.24.

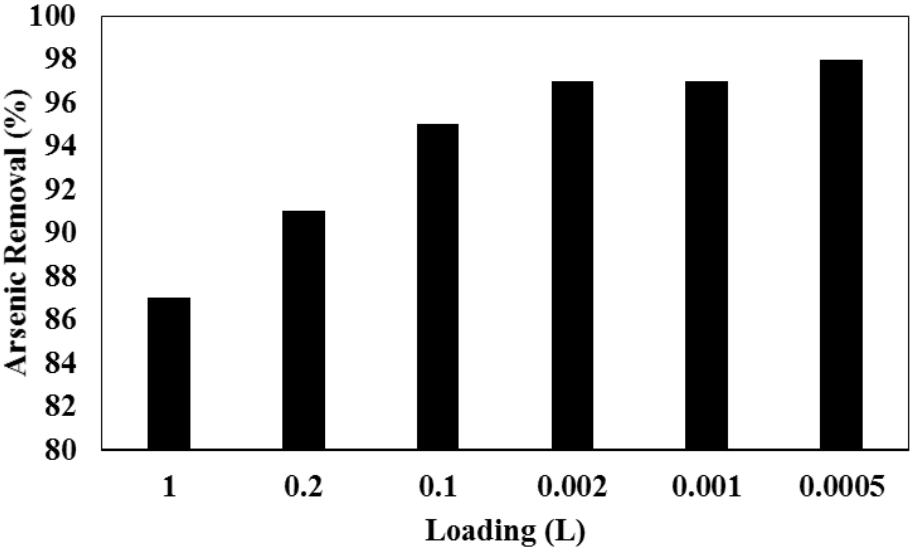

Figure 4.24. Arsenic removal efficiency with different Loading values. Feed concentration: 1000 µg/L, permeate flux: 40- 100[8] L/m^{2}h, feed flow rate: 120 L/h , pH: 8, 10% Vinyl pyridine, CV (%) = 5

According to the Figure 4.24, 95 percent arsenic removal was obtained with L = 0.1. This loading can be considered as an optimum point for this PEUF process where arsenic concentration of the feed was 1000 µg/L.

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[8] Permeate flux values are different for the runs conducted with different polymer amounts. Variations in permeate flux values were also recorded in experiments conducted with membranes which were purchased at different times

It is also informative to present polymer concentration, DADMAC amount which corresponds to that concentration and molar ratio between DADMAC and arsenic (As (V)) present in the medium. Related information is given in Table 4.8.

Table 4.8. Molar Ratio of Arsenic with respect to DADMAC

L	$C_{polymer}$ (g/L)	$M_{DADMAC10\%}$ (mM)	M_{As} (mM)	$n_{DADMAC10\%}$ / n_{As}
1	0.001	0.006	0.013	0.4
0.2	0.005	0.029	0.013	2.2
0.1	0.01	0.058	0.013	4.3
0.002	0.5	2.887	0.013	216.3
0.001	1	5.774	0.013	432.6
0.0005	2	11.549	0.013	865.2

Hypothetically it is expected to achieve complete removal at a loading value which corresponds to a molar ratio of 1 between DADMAC molecules and arsenic molecules. Removal value of 95 % was achieved at L= 0.1 meaning that around 4 moles of DADMAC was present in the medium per mole of arsenic. Deviation from the hypothetical ratio is expected because all of the functional groups which was supposed to be available for ion exchange might not be active due interactions within the polymer.

PEUF tests using polymer yielded an increase in arsenic removal efficiencies. Results are promising in terms of treating waters containing arsenate anions in the order of 1000 μg/L. 98 percent arsenic removal are found in the runs conducted at pH 8 and 10 which correspond to a arsenate concentration of 20 μg/L in the permeate stream.

These laboratory scale studies with arsenate solutions give an idea about the effectiveness of the PEUF and UF processes although studies with real water samples should be carried out in order to observe the effect of other ions. It is expected and reported in the literature [2] and in this study that the presence of anions in the medium negatively affects the removal efficiencies enhanced by the addition of DADMAC polymers. Effect of co-ion presence is also investigated in the next section.

4.4.3. Effect of Competing Anions

This work is mainly concentrated on arsenic removal by means of ultrafiltration (UF) and polymer enhanced ultrafiltration (PEUF) from model solutions at desired arsenic concentrations obtained by dissolving arsenic salts in de-ionized water. In real life applications arsenic co-exists with some other anions which may affect the removal efficiency of arsenic. Effects of sulfate and chloride as most common anions were investigated and presented in this section. Sulfate and chloride were added in solutions as sodium salts (Na_2SO_4 and NaCl) along with arsenate (As(V)).

UF runs were conducted without polymer addition with different sulfate and chloride concentrations and arsenic removal results are given in Figure 4.25 where comparison of UF and PEUF processes are also given in Figures 4.26 and 4.27.

As it can be observed from the figures, increase in anion or salt concentration caused a decrease in arsenic removal in both UF and PEUF processes.

Decrease in arsenic removal efficiency with presence of salts in ultrafiltration processes were also reported in the literature [31,32]. Decrease in removal can be explained by two factors; counter ions interact with membrane surface to neutralize the surface and increased ion concentration hinders Donnan exclusion effect. According to Donnan’s theory, dilute ion solutions are rejected from charged surfaces [31, 32].

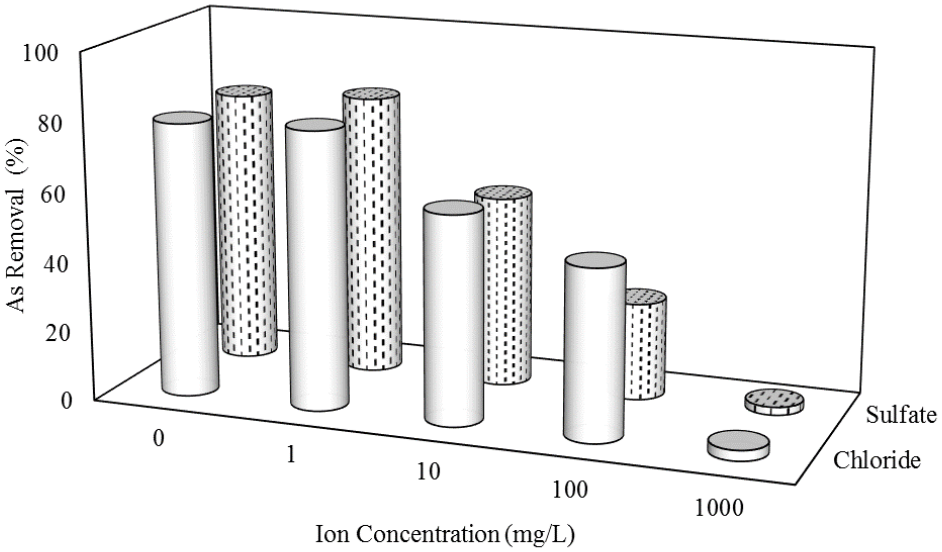

Figure 4.25. Effect of Sulfate and Chloride anions on Ultrafiltration efficiency. pH = was not set (6.7-7), L = no polymer addition, Feed concentration: 1000 µg/L (As (V)), permeate flux: 75-80 L/m^{2}h, feed flow rate: 120 L/h, CV (%) = 10

On the other hand, a decrease in the arsenic removal efficiency in PEUF can be explained by the competition between anions for the active sites on the polymer functional groups. Polymers having quaternary amine groups enhance arsenic retention by making complexes with arsenate anions via ion exchange [8,29]. Presence of anions in the medium in high concentrations prevent interaction between arsenate anions and charged groups on the polymer; as a result, arsenate anions pass through the membrane. It should also be noted that the membrane surface's ability to reject anions is also reduced or not available due to high co-ion and counter-ion presence. Keeping this fact in mind, it is worth to note that PEUF and UF studies yielded similar results in terms of arsenic retention. Such a decrease in arsenic retention for PEUF studies was also reported in literature [2, 29].

It can be concluded that it is not possible to achieve arsenic retention with ultrafiltration for waters having high conductivity. On the other hand, arsenic retention can be increased by increasing the polymer amount in the feed solution (decreasing loading (L)) which can result in a decrease in permeate flux. Results obtained in these runs are also given in more detail in Table 4.9.

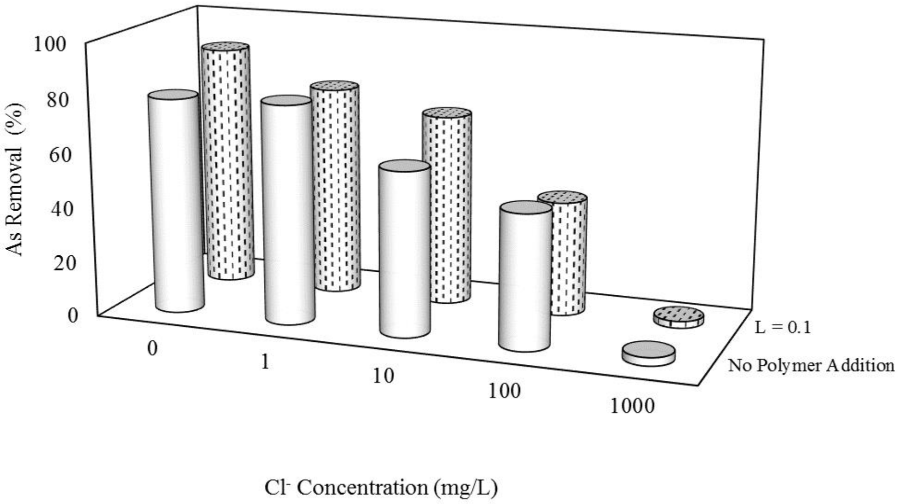

Figure 4.26. Comparison of UF and PEUF with presence of chloride anions. pH = was not set (6.7-7), Feed concentration: 1000 µg/L (As (V)), permeate flux: 75-80 L/m^{2}h, feed flow rate: 120 L/h, CV (%) = 10.

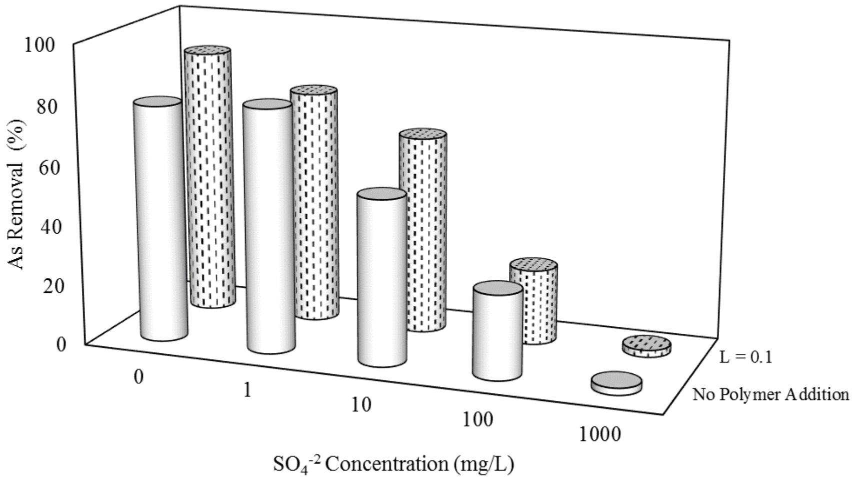

Figure 4.27. Comparison of UF and PEUF with presence of sulfate anions. pH = was not set (6.7-7), Feed concentration: 1000 µg/L (As (V)), permeate flux: 75-80 L/m^{2}h, feed flow rate: 120 L/h, CV (%) = 10

Table 4.9. Arsenic Removal Results obtained in anion tests

		Removal (%)	
ion Conc. (mg/L)	L	Cl^-	SO_4^{-2}
0	0	79	79
1	0	80	81
10	0	60	55
100	0	49	28
1000	0	3	2.3
0	0.1	89	89
1	0.1	77	78
10	0.1	70	66
100	0.1	42	25
1000	0.1	2.5	2.3

4.4.4. Mechanics of Ultrafiltration Processes

Besides arsenic removal values, operating parameters are very important for filtration processes. PEUF and UF processes were conducted under a pressure difference of 3.4 atm. Water flow rate into the filtration cell was selected as 120 L/h and average permeate flux recorded with de-ionized water was 90 L/m^2.h. Permeate flux of each sample was recorded in each run conducted. Average permeate fluxes obtained for the runs conducted with addition of different amounts of polymer in treatment of As (V) solutions with feed concentrations of 1000 µg/L are represented in Figure 4.28. Individual flux values recorded during each experiment are also reported in Appendix A8.

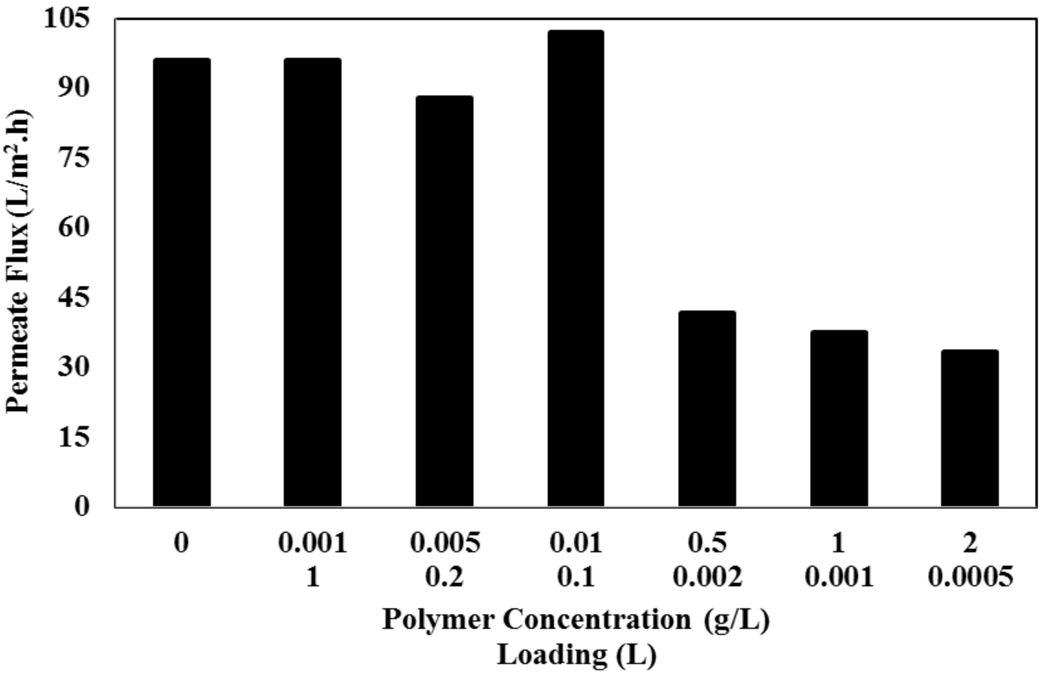

Figure 4.28. Change in permeate flux with polymer addition. Feed concentration: 1000 µg/L, feed flow rate: 120 L/h, pH: 8, CV (%) = 5

Considerable decrease in permeate flux was observed in PEUF studies in the runs conducted with presence of DADMAC- P (4-VP) co-polymers having concentrations of 0.5 g/L and higher. Comparing Figures 4.22 and 4.28 studying with loading value of 0.1 or polymer concentration of 0.01 g/L can be considered as the optimum for this study.

CHAPTER 5

CONCLUSIONS

Arsenic treatment with ultrafiltration and batch and fixed bed column adsorption were investigated in this study. Adsorption studies were conducted by using cross-linked DADMAC-TAP co-polymers (hydrogels) referred in the text as DADMAC hydrogels. This material was used in arsenic removal for the first time and provided valuable information on the usage of hydrogels for arsenic removal. Regarding the fact that the majority of the studies in literature related with polymer enhanced ultrafiltration (PEUF) studies were conducted with batch filtration set-ups, ultrafiltration results obtained in this study using bench scale tangential flow filtration cell also provided valuable information on arsenic treatment with UF and PEUF.

During batch studies DADMAC hydrogels studied showed superior arsenic (V) removal performances with respect to the limited hydrogel studies in the literature in terms of applicable pH range, arsenic removal capacity and contact time. Arsenic removal was found to be effective in the pH range of 6 to 10. Contact time required for maximum removal was measured as 15 minutes and maximum arsenic removal capacity of 1.8 mmol/g gel was experimentally determined. When these values are compared with hydrogel studies (detailed comparison was given in Table 4.4) and some of the recent arsenic adsorption studies [36-38] it can be observed that the data presented for contact time are in order of hours, some of them can only be applied at particular low pH values and arsenic removal capacities were recoreded in the range of 0.03 – 0.3 mmol As/g adsorbent for adsorption and 0.4-1.6 mmol As /g hydrogel for hydrogel studies.

In the batch experiments conducted by adding 0.1 g of DADMAC hydrogel to 100 mL of aqueous solution containing 1000 μg/L arsenic (As(V)) it was possible to reduce

As(V) content below that of the required standard limit of 10 μg/L in drinking water. Studies also revealed that the interaction between anions and hydrogels rely on ion exchange mechanism between arsenate anions and chloride anions found in the structure of the functional group of DADMAC repeating units.

DADMAC hydrogels were successfully regenerated during batch studies with sodium chloride solutions and hydrochloric acid solutions. Re-usability tests were conducted by re-using the regenerated hydrogels in arsenic removal. Five cycles of regeneration and re-using were completed without significant loss in the arsenic removal efficiency, where sodium chloride solution was used for regeneration. Separation of DADMAC hydrogels from the medium was achieved by filtration with simple filter papers. Hydrogels can also be easily settled down and separated from the medium. Hydrogels absorb water in seconds and without any shaking they rapidly settle to the bottom of the container after they are added to the solution.

Performance of DADMAC hydrogels in column adsorption studies were also tested with three different hydrogel amounts corresponding to different bed heights. Regeneration and re-usability of hydrogels in column studies were also conducted. At the studied conditions, hydrogel amounts of 0.5 g and 0.3 g did not yield effluent As (V) concentrations below 0.9 mg/L (feed concentration: 100 mg/L) while effluent concentration in the runs conducted with 1 g DADMAC hydrogels were decreased below 20 μg/L before the breakthrough. Regenerated hydrogels did not show any decrease in arsenic removal capacity. Hydrogel adsorption capacity was calculated as 144 mg As (V)/g hydrogel for the runs conducted with 1 g of hydrogel.

Arsenic (V) retention of 85 percent was observed in ultrafiltration runs without polymer addition for feed concentrations of 1000 μg/L. The retention was increased to 98 percent with the addition of DADMAC-P(4-VP) co-polymers. Arsenate retentions of around 85 percent is also worth to note since ultrafiltration alone is not regarded as an efficient treatment method for arsenic removal. Reverse osmosis method with high pressure differences and low permeate flux, and nanofiltration method with low permeate flux methods generally referred as membrane separation methods used in arsenic removal [1, 9, 35]. These quite high retention values may be attributed to the interaction between negatively charged arsenate ions and membrane surface.

Effect of anions' presence was tested by introducing sulfate and chloride anions in to the feed solution with and without the presence of polymer (DADMAC-P(4-VP). Increasing anion concentration decreased arsenic removal efficiency in the runs conducted with presence of anions having concentrations of 10 mg/L or higher in both UF and PEUF studies.

Polymer concentrations higher than 0.5 g/L was found to cause fouling and drastic decrease in permeate flow rate. On the other hand, polymer concentration of 0.01 g/L was found to yield similar retention with higher polymer concentrations without affecting the permeate flow rate.

Limited arsenite (As (III)) retention of 50 percent was recorded in PEUF studies at alkali conditions. This lower retention value may be explained as follows: non-charged As (III) species cannot be retained by the membrane due to the large pore size of ultrafiltration membrane. Addition of polymer does not help much for the separation of As (III) species, since attraction of As (III) seems to be not intense on the positively charged polymer resulting in poor arsenic removal performance.

CHAPTER 6

RECOMMENDATIONS

- Method for As (III) separation in PEUF should be improved. As (III) removal can be achieved by oxidation of As (III) to As (V) prior to treatment or developing some other material that can attract As (III) species.

- Tests should be conducted with pilot scale processes including packed bed columns or mixing settling set-ups using DADMAC hydrogels.

- Water treatment ability of the separation methods studied greatly depend on the characteristics of the waters to be treated. Keeping this fact in mind, studies with real waters having arsenic concentrations higher than the allowable arsenic concentration of 10 μg/L should be tested with the methods studied. Addition of such case studies can give us an idea about applicability of these processes.

- Different charged and non-charged membranes should also be investigated in PEUF and UF studies in order to gain more experience on arsenic retention with different types of ultrafiltration membranes.

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APPENDIX A

SUPPLEMENTARY DATA

A1. Calibration Curves

Some of the calibration curves obtained during arsenic measurements are listed below.

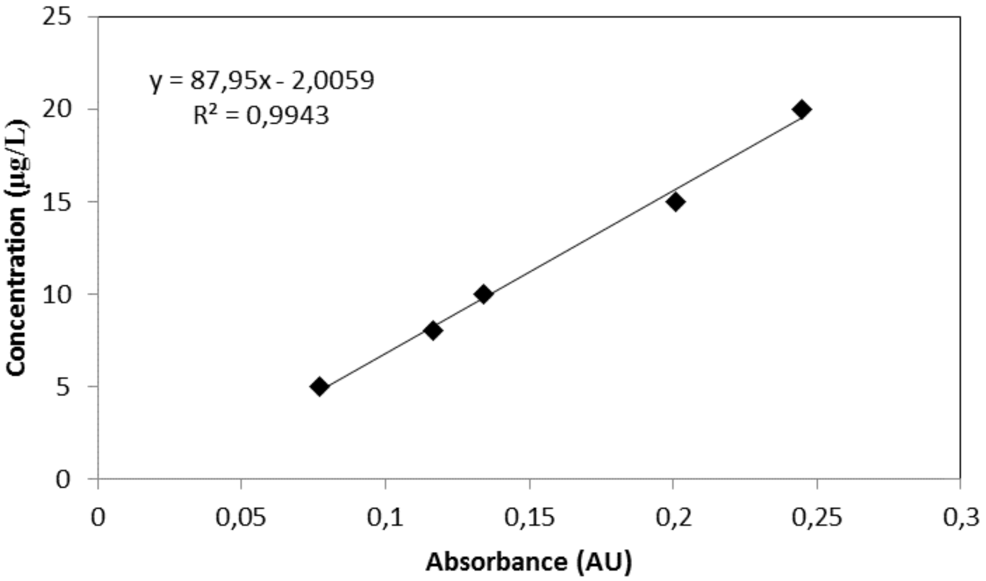

Figure A1. Calibration Curve on 15.5.2013

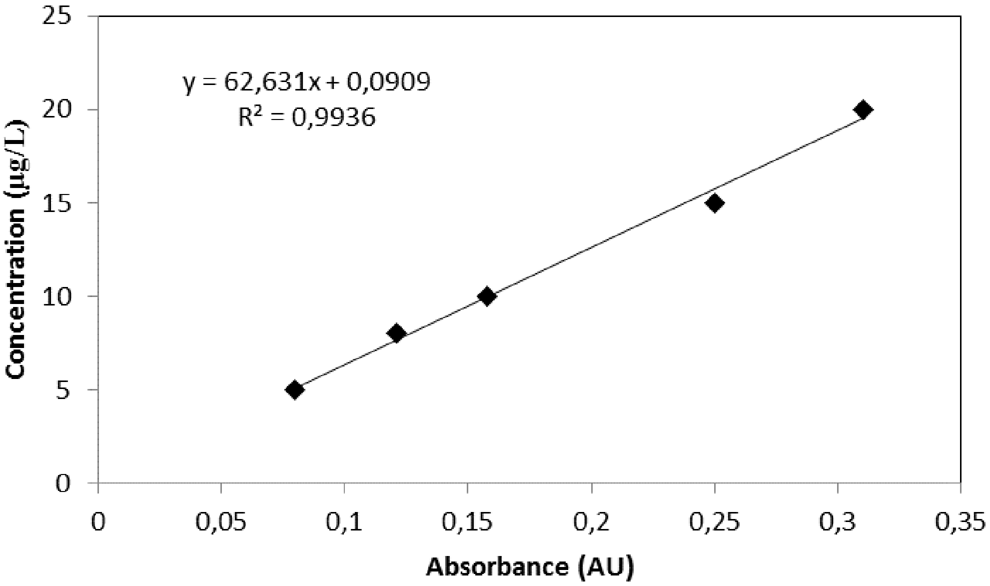

Figure A2. Calibration Curve on 8.5.2013

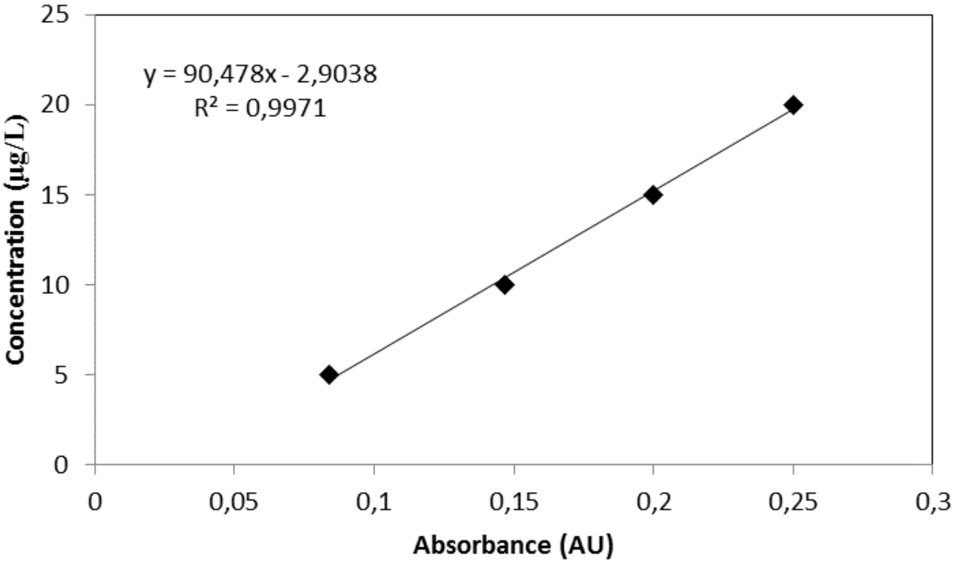

Figure A3. Calibration Curve on 2.5.2013

A2. Some Repeated Runs

In order to determine repeatability of the tests, some experiments were repeated. Results are given below.

Table A1. Repeated Batch Tests. $C_{As,i}$ = 1000 µg/L, Hydrogel addition = 0.1 g

Date	Removal (%)
May 2013	98
	99
	97
	98
	98
	99
	99
	99
21.5.2014	99
	99
	99
	99
14.5.2014	97
	98
	98
	98
6.8.2013	99
Mean	98.4
Stdev	0.7

A3. Individual Results Obtained During Ultrafiltration Experiments

Detailed individual arsenic removal values obtained through some experiments are given in this section.

Table A2. C_{feed} (As(V)): 1000 µg/L pH: 8 Polymer amount 0.005 g 10 % DADMAC-P(4-VP)

time (min)	C_{feed} (µg/L)	C_p (µg/L)	Removal (percent)
0	1042	134	87
30	1135	121	89
60	1100	125	89
90	1210	134	89
Mean	1122	129	89
Stdev	70	7	1
CV (%)	6	5	1

Table A3 C_{feed} (As(V)): 1000 µg/L pH: 8 Polymer amount 0.001 g 10% DADMAC-P(4-VP)

time (min)	C_{feed} (µg/L)	C_p (µg/L)	Removal (percent)
0	991	124	87
30	1000	140	86
60	1070	176	84
90	1080	169	84
Mean	1035	152	85
Stdev	46	24	2
CV (%)	4	16	2

Table A4. C_{feed} (As(V)): 75 µg/L pH: 8 Polymer amount: no polymer addition

time (min)	C_{feed} (µg/L)	C_p (µg/L)	Removal (percent)
0	74	24	68
30	80	27	66
60	80	21	74
90	76	23	70
Mean	78	24	69
Stdev	3	3	3
CV (%)	4	11	5

Table A5. C_{feed} (As(V)): 100 µg/L pH: 8 Polymer amount: no polymer addition

time (min)	C_{feed} (µg/L)	C_p (µg/L)	Removal (percent)
0	94	14	85
30	94	14	85
60	97	11	89
90	101	14	86
Mean	97	13	86
Stdev	3	2	2
CV (%)	3	11	2

Table A6. C_{feed} (As(V)): 100 µg/L pH: 8, Polymer amount: no polymer addition

	C_{feed} (µg/L)	C_p (µg/L)	Removal (percent)
0	1050	276.0	73.7
30	990	200.0	79.8
60	997	202.0	79.7
90	1002	212.0	78.8
Mean	1009.8	222.5	78.0
Stdev	27.3	36.1	2.9
CV (%)	2.7	16.2	3.7

Table A7. Feed and Permeate Concentrations. Process: UF, C_{feed} (As (V)): 1000 µg/L, pH: 7, anion conc: 0, L: no polymer addition

Arsenic Concentration (µg/L)			
Time (min)	C_{feed}	C_p	Removal (%)
0	1022	226	77.9
30	1200	156	87.0
60	1100	231	79.0
90	1120	246	78.0
Average	1110.5	214.8	80.5
Standard Dev.	73.1	40.1	4.4
CV (%)	6.6	18.7	5.4

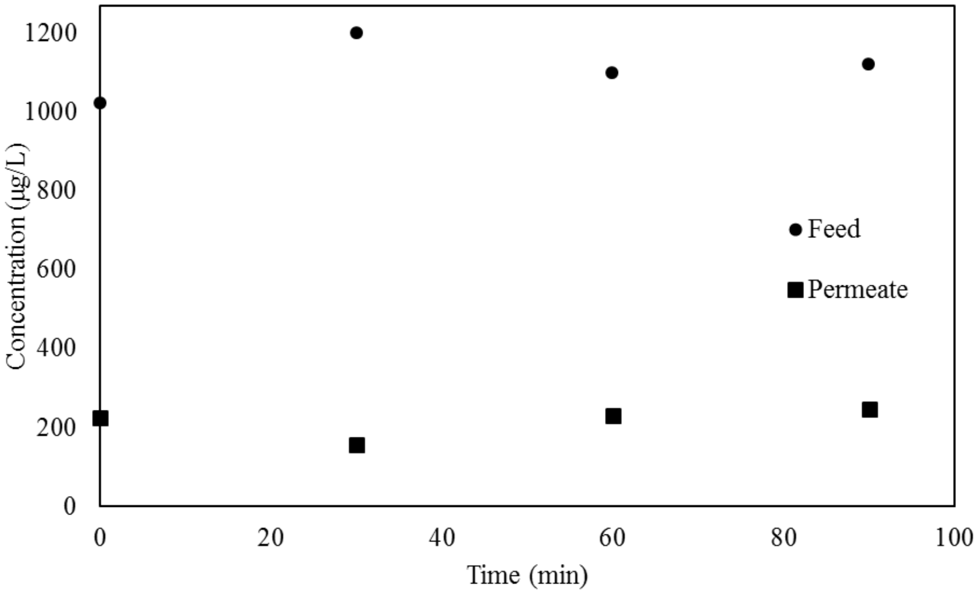

Figure A4. Feed and Permeate Concentrations. Process: UF, C_{feed} (As (V)): 1000 µg/L, pH: 7, anion conc. : 0, L: no polymer addition

Table A8. Feed and Permeate Concentrations. Process: UF, C_{feed} (As (V)).: 1000 µg/L, pH: 10, anion conc: 0, L: no polymer addition

Arsenic Concentration (µg/L)			
Time (min)	C_{feed}	C_p	Removal (%)
0	1000	122	87.8
30	1100	160	85.5
60	1050	140	86.7
90	1100	205	81.4
Average	1062.5	156.8	85.3
Standard Dev.	47.9	35.7	2.8
CV (%)	4.5	22.8	3.3

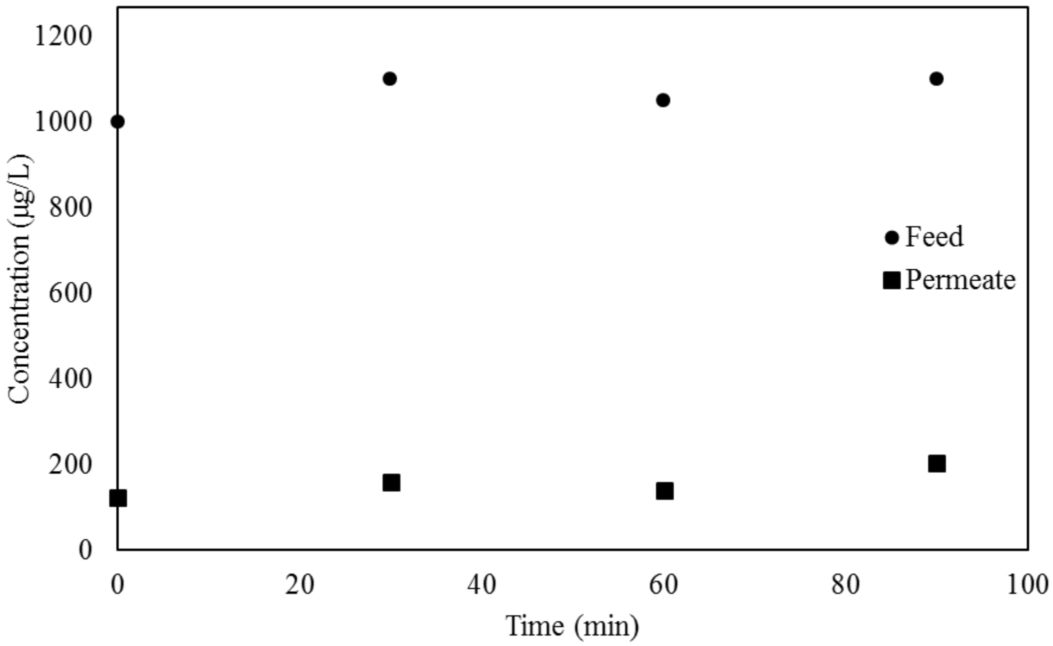

Figure A5. Feed and Permeate Concentrations. Process: UF, C_{feed} (As (V)): 1000 μg/L, pH: 10, anion conc. : 0, L: no polymer addition

Table A9. Feed and Permeate Concentrations. Process: UF, C_{feed} (As (V)): 1000 μg/L, pH: 4, anion conc: 0, L: no polymer addition

Arsenic Concentration (μg/L)			
Time (min)	C_{Feed}	C_p	Removal (%)
0	1000	621	37.9
30	1170	765	34.6
60	1050	630	40.0
90	1100	635	42.3
Average	1080.0	662.8	38.7
Standard Dev.	72.6	68.4	3.3
CV (%)	6.7	10.3	8.4

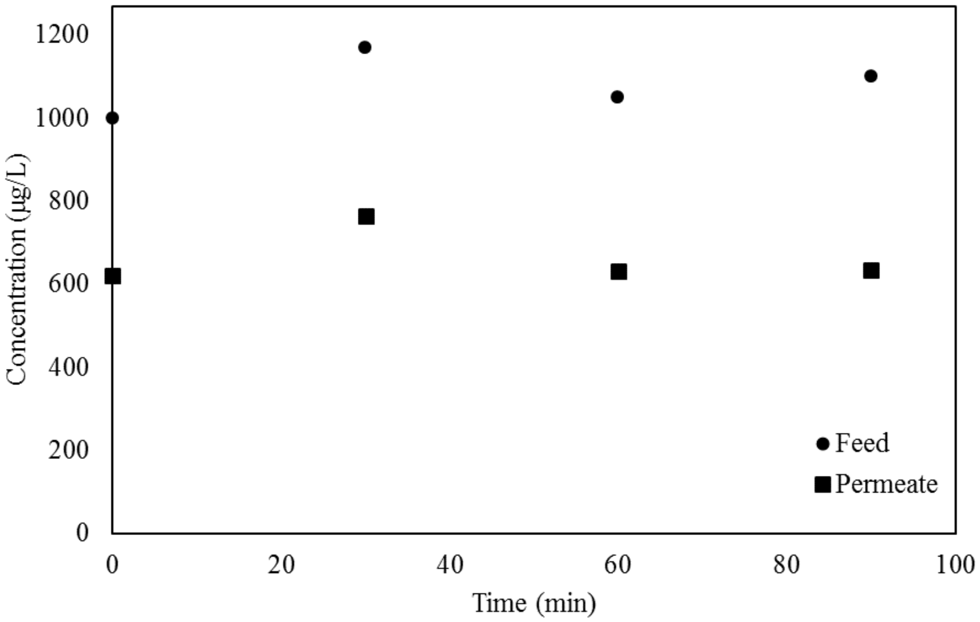

Figure A6. Feed and Permeate Concentrations. Process: UF, C_{feed} (As (V)): 1000 µg/L, pH: 4, anion conc. : 0, L: no polymer addition

Table A10. Feed and Permeate Concentrations. Process: UF, C_{feed} (As (V)): 1000 µg/L, pH: 8, anion conc: 0, L: 0.0001, 10% P(4-VP)

Arsenic Concentration (µg/L)			
Time (min)	C_{Feed}	C_p	Removal (%)
0	1150	52	95.5
30	1150	53	95.4
60	1200	50	95.8
90	1220	57	95.3
Average	1180.0	53.0	95.5
Standard Dev.	35.6	2.9	0.2
CV (%)	3.0	5.6	0.2

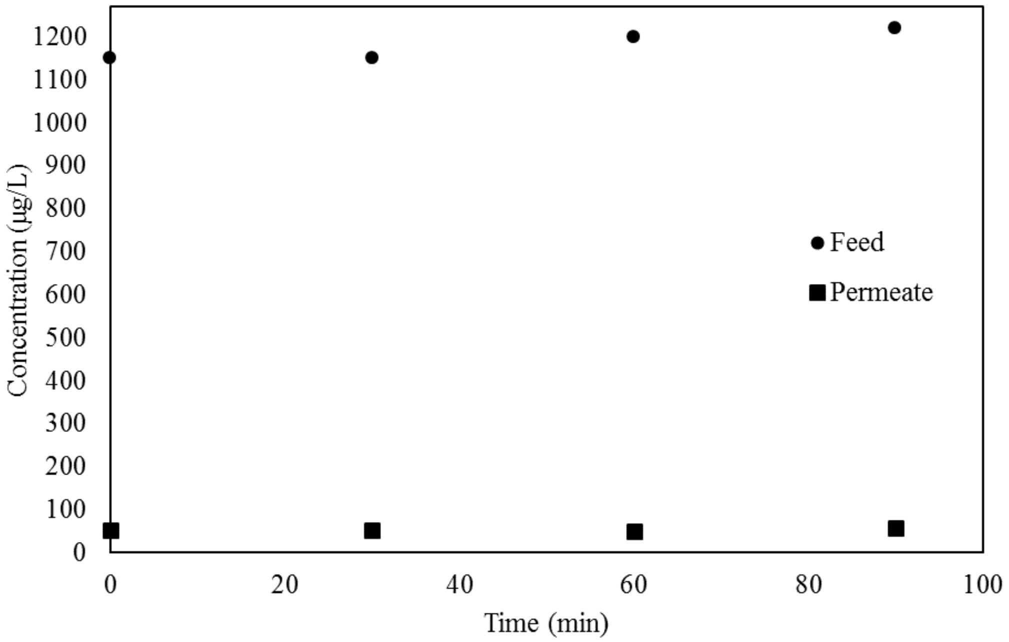

Figure A7. Feed and Permeate Concentrations. Process: UF, C_{feed} (As (V)): 1000 µg/L, pH: 8, anion conc. : 0, L: 0.0001, 10% P(4-VP)

Table A11. Feed and Permeate Concentrations. Process: UF, C_{feed} (As (V)): 1000 µg/L, pH: 4, anion conc: 0, L: 0.0001, 10% P(4-VP)

Arsenic Concentration (µg/L)			
Time (min)	C_{Feed}	C_p	Removal (%)
0	1000	452	54.8
30	980	425	56.6
60	1100	505	54.1
90	1075	505	53.0
Average	1038.8	471.8	54.6
Standard Dev.	57.8	39.9	1.5
CV (%)	5.6	8.5	2.8

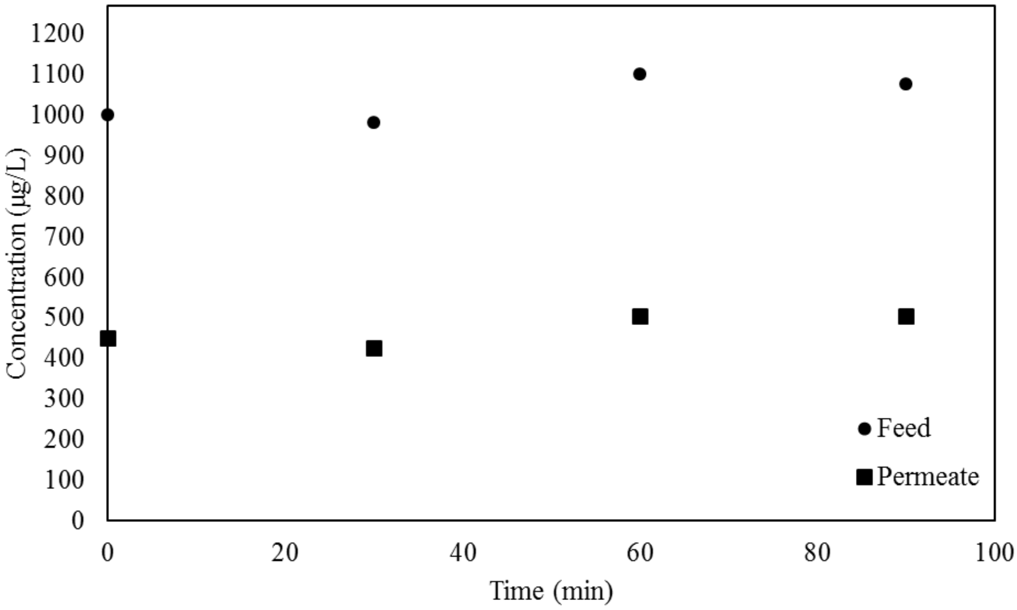

Figure A8. Feed and Permeate Concentrations. Process: UF, C_{feed} (As (V)): 1000 µg/L, pH: 4, anion conc. : 0, L: 0.0001, 10% P(4-VP)

Table A12. Feed and Permeate Concentrations. Process: UF, C_{feed} (As (V)): 1000 µg/L, pH: 6, anion conc: 0, L: 0.0001, 10 % P(4-VP)

Arsenic Concentration (µg/L)			
Time (min)	C_{Feed}	C_p	Removal (%)
0	1000	235	76.5
30	950	253	73.4
60	980	223	77.2
90	970	260	73.2
Average	975.0	242.8	75.1
Standard Dev.	20.8	16.9	2.1
CV (%)	2.1	6.9	2.8

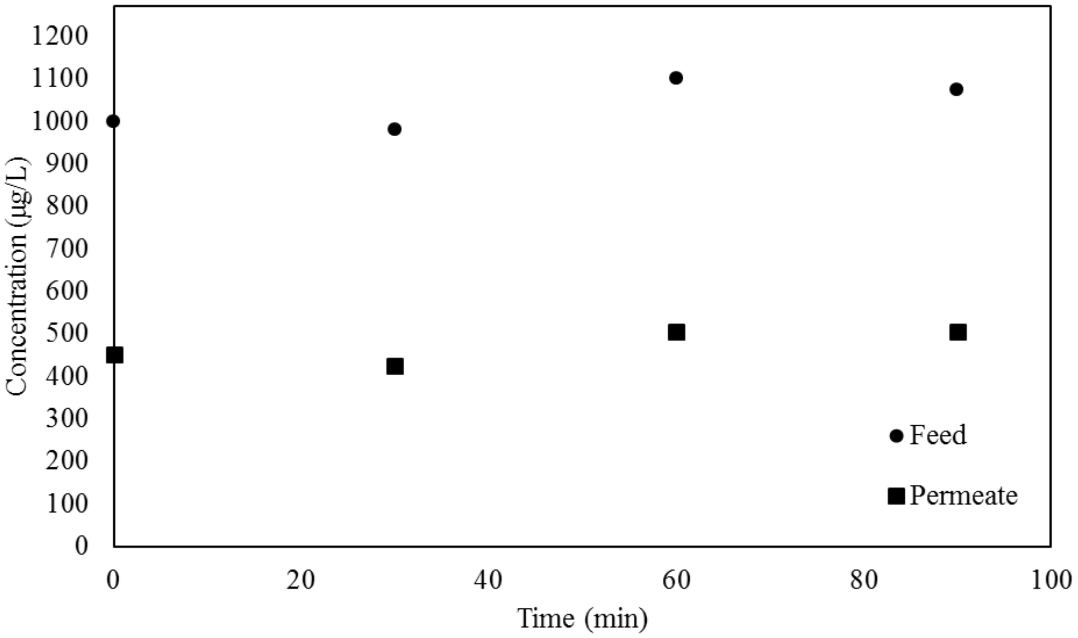

Figure A9. Feed and Permeate Concentrations. Process: UF, C_{feed} (As (V)): 1000 µg/L, pH: 6, anion conc. : 0, L: 0.0001, 10% P(4-VP)

Table A13. Feed and Permeate Concentrations. Process: UF, C_{feed} (As (V)): 1000 µg/L, pH: 8, anion conc: 0, L: 0.0001, 25% P(4-VP)

Arsenic Concentration (µg/L)			
Time (min)	C_{Feed}	C_p	Removal (%)
0	1050	55	94.8
30	1105	52	95.3
60	1208	45	96.3
90	1123	52	95.4
Average	1121.5	51.0	95.4
Standard Dev.	65.5	4.2	0.6
CV (%)	5.8	8.3	0.7

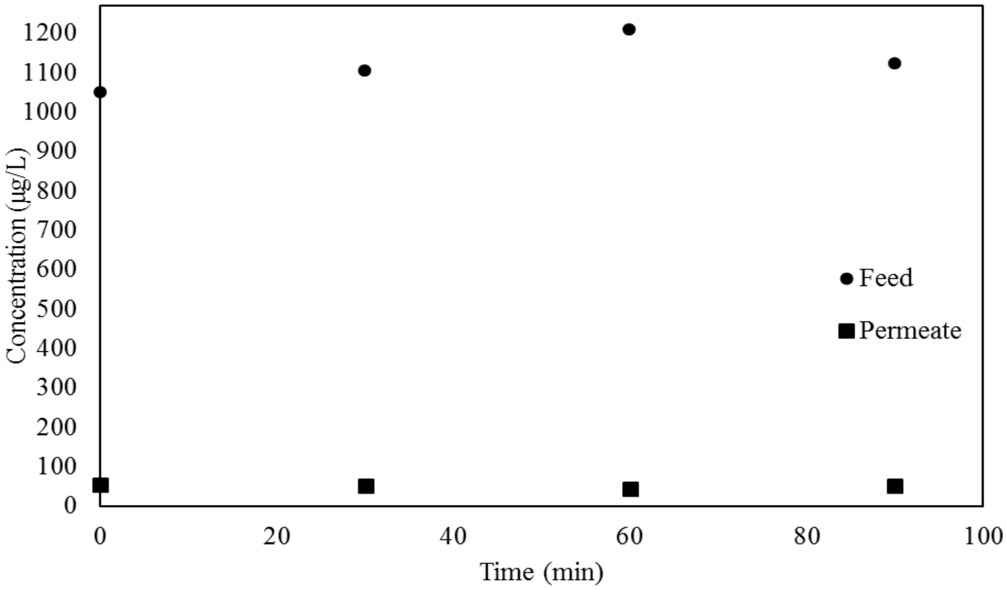

Figure A10. Feed and Permeate Concentrations. Process: UF, C_{feed} (As (V)): 1000 μg/L, pH: 8, anion conc. : 0, L: 0.0001, 25% P(4-VP)

Table A14. Feed and Permeate Concentrations. Process: UF, C_{feed} (As (V)): 1000 μg/L, pH: 6, anion conc: 0, L: 0.0001, 25% P(4-VP)

	Arsenic Concentration (μg/L)		
Time (min)	C_{Feed}	C_p	Removal (%)
0	985	245	75.1
30	980	198	79.8
60	1050	213	79.7
90	975	221	77.3
Average	997.5	219.3	78.0
Standard Dev.	35.2	19.6	2.2
CV (%)	3.5	9.0	2.9

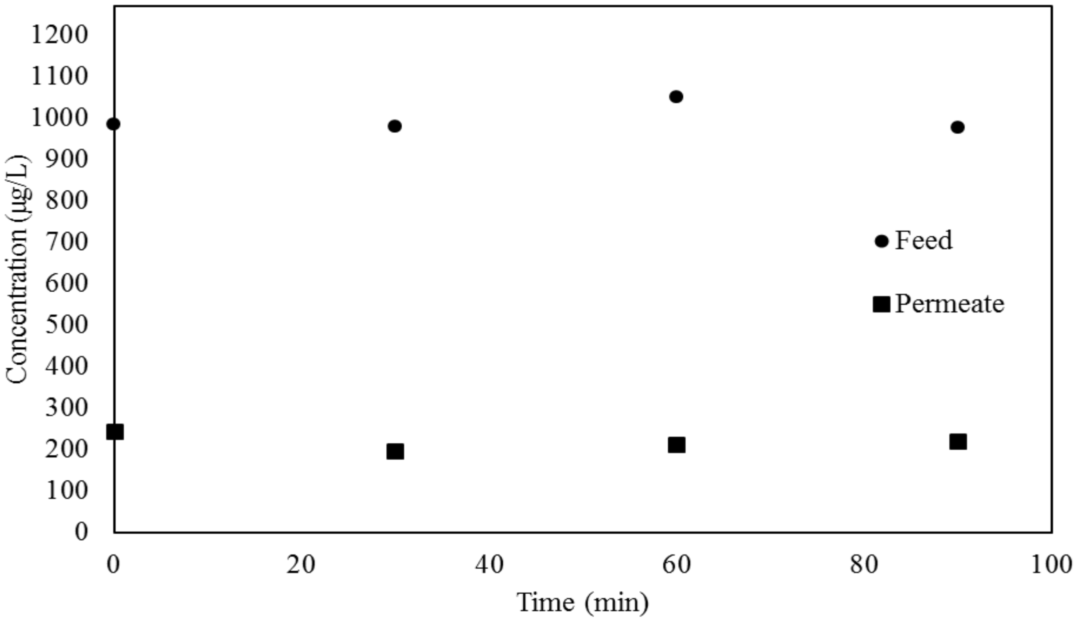

Figure A11. Feed and Permeate Concentrations. Process: UF, C_{feed} (As (V)): 1000 µg/L, pH: 6, anion conc. : 0, L: 0.0001, 25% P(4-VP)

Table A15. Feed and Permeate Concentrations. Process: UF, C_{feed} (As (V)): 1000 µg/L, pH: 4, anion conc: 0, L: 0.0001, 25% P(4-VP)

	Arsenic Concentration (µg/L)		
Time (min)	C_{Feed}	C_p	Removal (%)
0	1002	558	44.3
30	1015	572	43.6
60	1100	581	47.2
90	1085	563	48.1
Average	1050.5	568.5	45.8
Standard Dev.	49.2	10.1	2.2
CV (%)	4.7	1.8	4.7

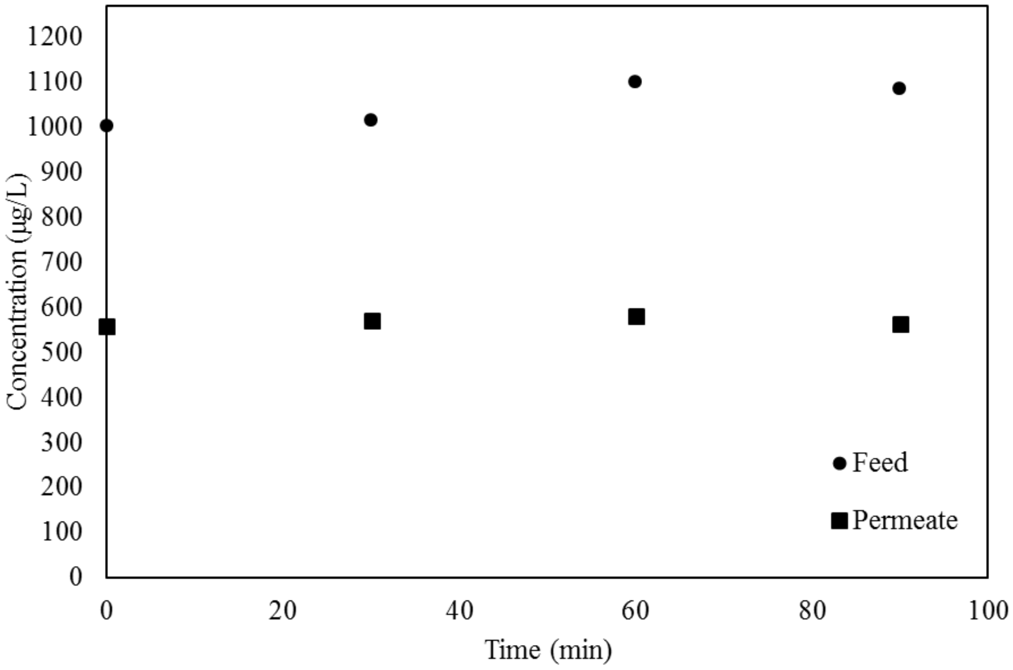

Figure A12. Feed and Permeate Concentrations. Process: UF, C_{feed} (As (V)).: 1000 µg/L, pH: 4, anion conc. : 0, L: 0.0001, 25% P(4-VP)

A4. Photometric Arsenic Determination Method

Photometric arsenic determination using ammonium molybdate has been used since 1970's [58]. Method relies on forming complexes between As(V) and reduced molybdate. This complex can absorb light at infrared region (λ = 870 nm). Major disadvantage of this method is phosphate interference. Presence of phosphate can also result in same kind of complex formation as arsenic does which influences the results obtained. This interference can be eliminated by reducing As(V) to As(III) which does not form a complex with molybdate. By this way, concentration of arsenic can be measured using the absorbance difference of the non-reduced and reduced sample [58-60]. In this study, model arsenic solutions were prepared using de-ionized water without addition of phosphate so additional pretreatment was not required.

Color development reagent reported by Dhar et al. [58] was used in this study. Samples were injected in containers (10 mL) then 1 mL of the reagent was injected. After color development concentration of samples were measured using UV-Vis Spectrophotometer at 870 nm. Color development reagent was prepared by mixing ascorbic acid (10.8 %), ammonium molybdate (AM) (3%), potassium antimony tartrate (PAT) (0.56%) and sulfuric acid (2.5 M) in the ratio of 2:2:1:5. Ascorbic acid was prepared freshly, other reagents (PAT and AM) were used for two weeks (stored at room conditions). It should be noted that absorbance values obtained decrease during this period of two weeks so daily preparation of all reagents can be considered.

Reaction time is an important factor in color development and can play an important role during the analysis of the samples, especially if the number of samples to be measured is large (duration of the analysis is long). In order to decide the optimum reaction time and investigate the relation between color development and reaction time, standard solutions with different concentrations were analyzed at different times between 15 minutes and 2 hours. Absorbance values measured at different times are given in Table A6. Calibration curves obtained from these data are also presented in Figures A4-8. Absorbance values obtained in repeated measurements after 2 hours of reaction time are also presented in Table 6. According to the standard deviation obtained in these runs and absorbance value of the blank solution limit of detection for this method was determined as 20 μg/L (As (V)). Absorbance value at limit of detection was determined as follows [40]:

$$\mathrm{Mean}_{\mathrm{blank}} + 3(\mathrm{SD}_{\mathrm{blank}}) \tag{A.1}$$

Table A16. Absorbance values obtained at different durations by using standard solutions of As(V)

Conc (μg/L)	0	10	20	50	100	500	1000
Time (min)	ABS (AU)						
15	0.017	0.019	0.022	0.030	0.040	0.159	0.297
30	0.036	0.048	0.050	0.064	0.086	0.218	0.320
60	0.091	0.100	0.116	0.120	0.162	0.318	0.485
90	0.137	0.155	0.170	0.187	0.210	0.359	0.560
120	0.179	0.200	0.210	0.237	0.283	0.430	0.556

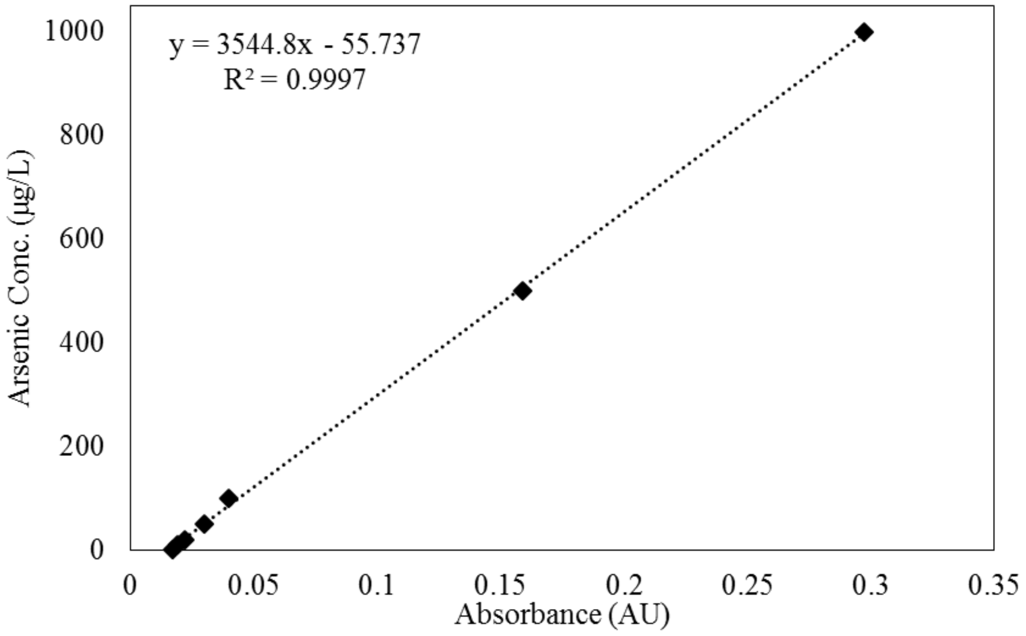

Figure A13. Calibration Curve obtained at t = 15 min.

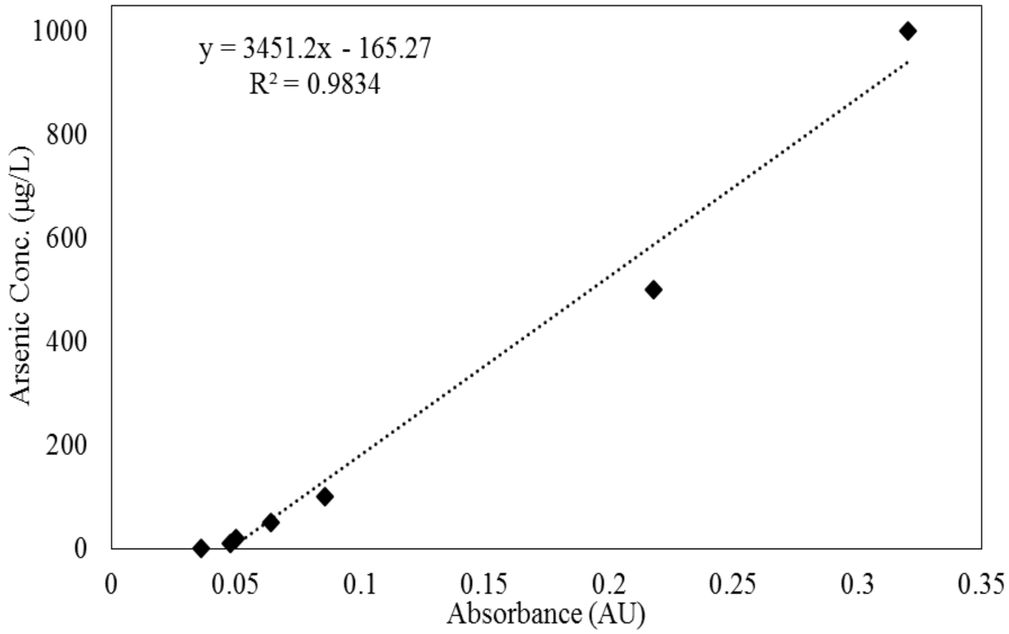

Figure A14. Calibration Curve obtained at t = 30 min.

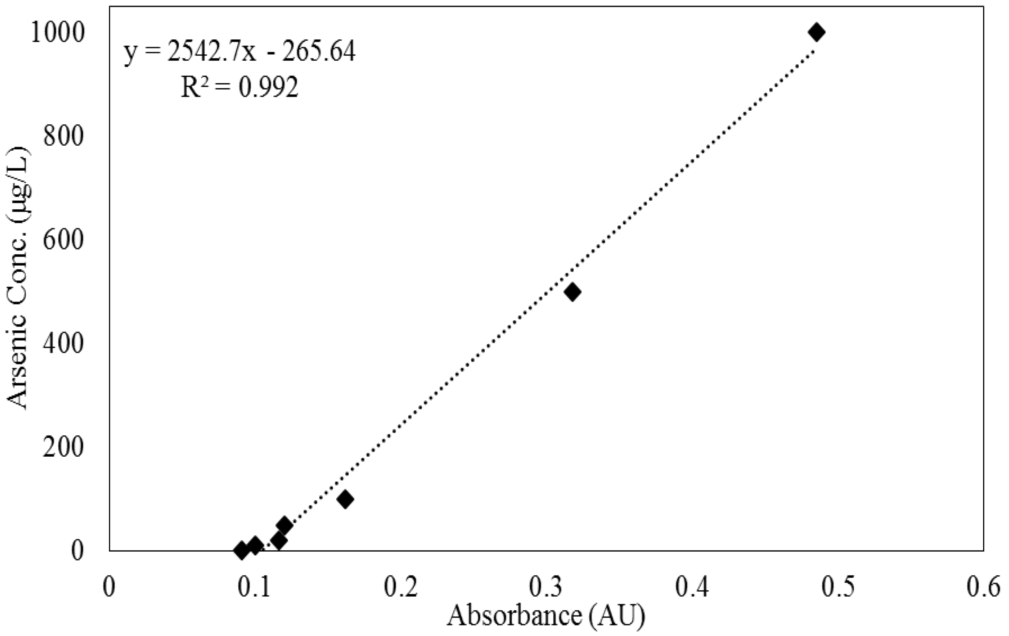

Figure A15. Calibration Curve obtained at t = 60 min.

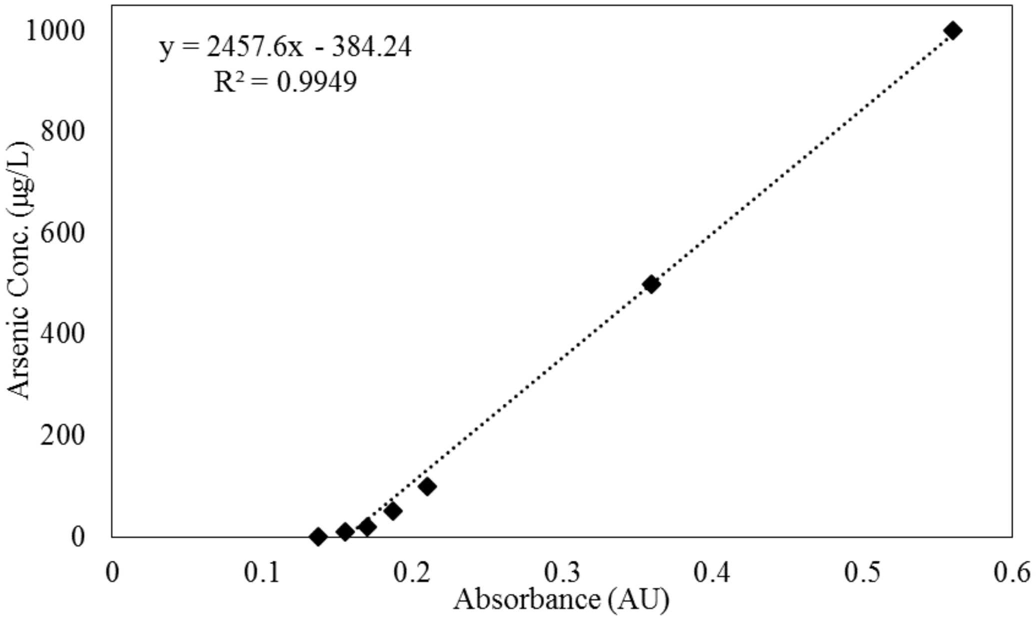

Figure A16. Calibration Curve obtained at t = 90 min

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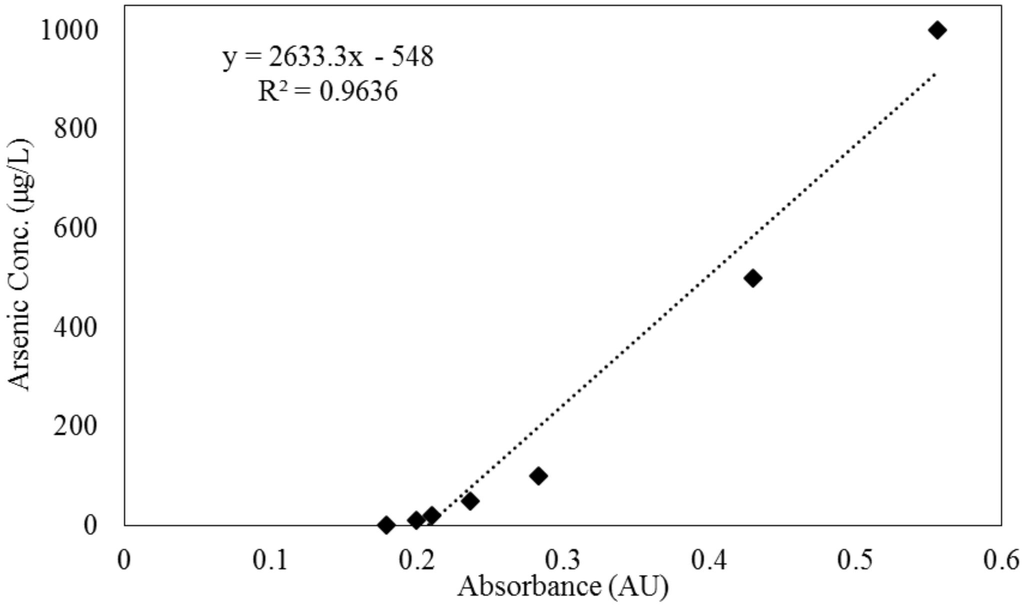

Figure A17. Calibration Curve obtained at t = 120 min.

Table A17. As (V) Standard solutions measured at t = 120 min.

	Concentration (µg/L)			
#	0	10	20	50
1	0.179	0.190	0.200	0.240
2	0.187	0.200	0.210	0.250
3	0.167	0.210	0.220	0.220
Mean	0.178	0.200	0.210	0.237
Stdev	0.010	0.010	0.010	0.015
CV (%)	5.7	5.0	4.8	6.5

According to the presented results method used to analyze arsenic concentration (As (V)) yields linear calibration curves that can be used to quantify samples and method has an acceptable precision. Limit of detection of the method was determined as 20 µg/L. regarding the value of the standard deviation calculated and absorbance value measured for blank (de-ionized water only); it can also be noticed that it is not easy to distinguish between blank and 10 µg/L and between 10 and 20 µg/L. It is also worth to note that by using this method samples having concentrations between 20 – 1000 µg/L can be analyzed without dilution. In other words, range of this method used is between 20 – 1000 µg/L.

Relationship between time and absorbance values measured was also obtained by fitting linear curves to absorbance vs. time data. Equations defining the relationship between time and absorbance were obtained for each concentration and presented with correlation coefficient (R^2) in Table A18.

Table A18. Linear curve fitting for absorbance vs time data

Conc. (μg/L)	Equation	R^2
0	Abs = 0.0016t - 0.0072	0.998
10	Abs = 0.0017t - 0.0048	0.999
20	Abs = 0.0018t - 0.0017	0.992
50	Abs = 0.0020t + 0.0027	0.998
100	Abs = 0.0022t + 0.0149	0.992
500	Abs = 0.0025t + 0.1395	0.973
1000	Abs = 0.0028t + 0.2683	0.890

According to the numerical analysis of absorbance vs. time data, it can be concluded that there is a linear dependence between reaction time and absorbance of the samples. Accuracy of the equations were also tested by recalculating the standard solutions' concentration by using the equations. Results were presented in Tables A9-15.

Table A19. Accuracy analysis at different durations. Arsenic concentration = 0

ABS	Time (min)	ABS Model	% Error
0.017	15	0.017	1
0.036	30	0.041	13
0.091	60	0.089	2
0.137	90	0.137	0
0.179	120	0.185	3

Table A20. Accuracy analysis at different durations. Arsenic concentration = 10 μg/L

ABS	Time (min)	ABS Model	% Error
0.019	15	0.024	28
0.048	30	0.050	4
0.100	60	0.101	1
0.155	90	0.152	2
0.200	120	0.203	1

Table A21. Accuracy analysis at different durations. Arsenic concentration = 20 μg/L

ABS	Time (min)	ABS Model	% Error
0.022	15	0.025	11
0.050	30	0.052	3
0.116	60	0.106	9
0.170	90	0.160	6
0.210	120	0.214	2

Table A22. Accuracy analysis at different durations. Arsenic concentration = 50 μg/L

ABS	Time (min)	ABS Model	% Error
0.030	15	0.032	7
0.064	30	0.062	3
0.120	60	0.122	2
0.187	90	0.182	3
0.237	120	0.242	2

Table A23 Accuracy analysis at different durations. Arsenic concentration = 100 μg/L

ABS	Time (min)	ABS Model	% Error
0.040	15	0.048	20
0.086	30	0.081	6
0.162	60	0.147	9
0.210	90	0.213	1
0.283	120	0.279	1

Table A24. Accuracy analysis at different durations. Arsenic concentration = 500 μg/L

ABS	Time (min)	ABS Model	% Error
0.159	15	0.181	14
0.218	30	0.218	0
0.318	60	0.293	8
0.359	90	0.368	3
0.430	120	0.443	3

Table A25. Accuracy analysis at different durations. Arsenic concentration = 1000 μg/L

ABS	Time (min)	ABS Model	% Error
0.297	15	0.305	3
0.320	30	0.347	9
0.485	60	0.431	11
0.560	90	0.515	8
0.556	120	0.599	8

Some of the calibration curves plotted during the analyses were also given in Figures A18-20.

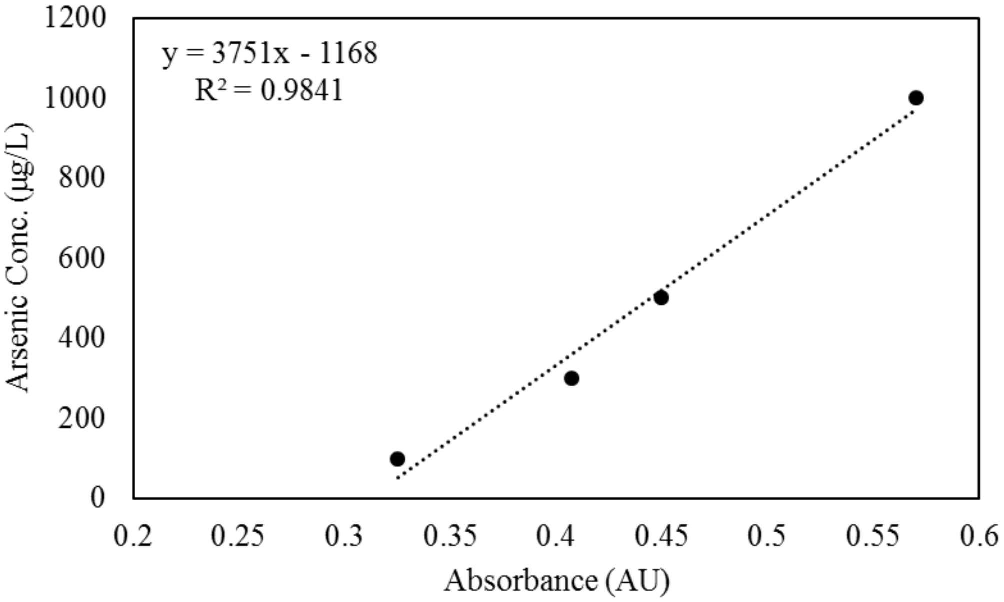

Figure A18. Calibration Curve Constructed with Molybdate Method. Standard Solutions having concentrations between 100 – 1000 µg/L As(V)

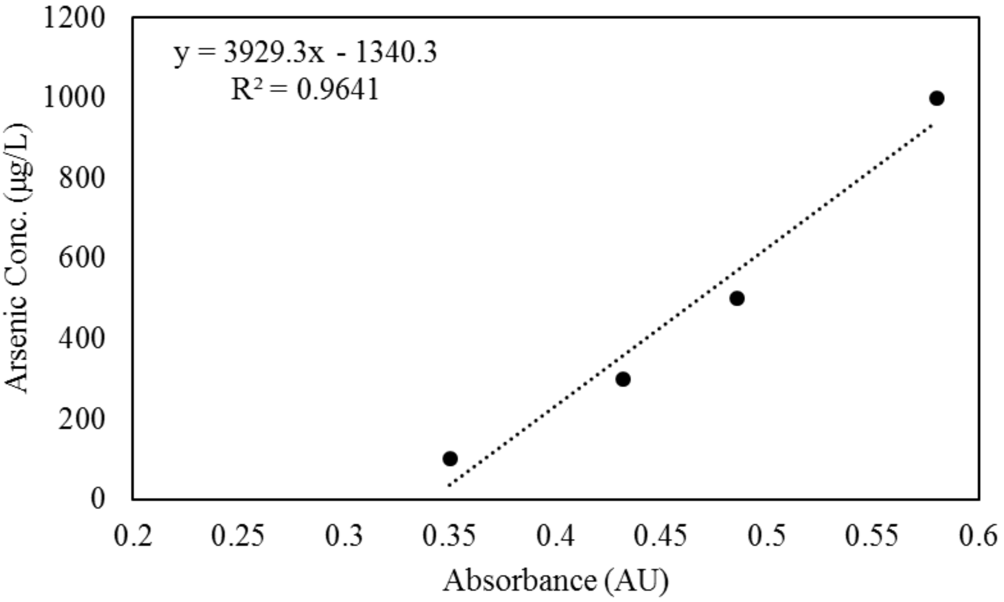

Figure A19. Calibration Curve Constructed with Molybdate Method. Standard Solutions having concentrations between 100 – 1000 µg/L As(V)

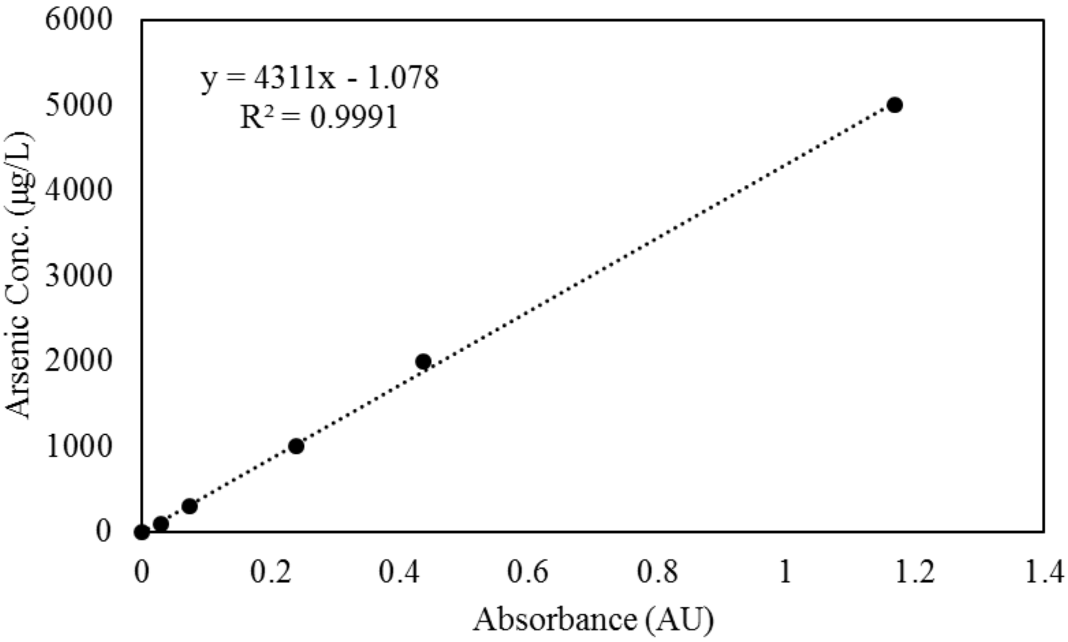

Figure A20. Calibration Curve Constructed with Molybdate Method. Standard Solutions having concentrations between 100 – 1000 μg/L As(V)

A.5. Ultrafiltration Data Obtained by Photometric Method

Data obtained from some of the runs which were conducted to observe the effect of anion presence on arsenic removal are also presented. Ultrafiltration runs were conducted for 2 hours and samples were withdrawn from feed tank and collected from permeate stream were analyzed. Results are presented in Tables A16-25 and Figures A12-21

Table A26. Feed and Permeate Concentrations. Process: UF, As (V) conc.: 1000 μg/L, pH: 6.7-7 (not set), anion conc: 0, L: no polymer addition

	Concentration (μg/L)		
Time (min)	Feed	Permeate	Removal (%)
0	1050	200	81
30	1000	190	81
60	1080	210	81
90	1030	220	79
120	1100	200	82
Average	1052	204	81
Standard Dev.	39.6	11.4	1.2
CV (%)	3.8	5.6	1.5

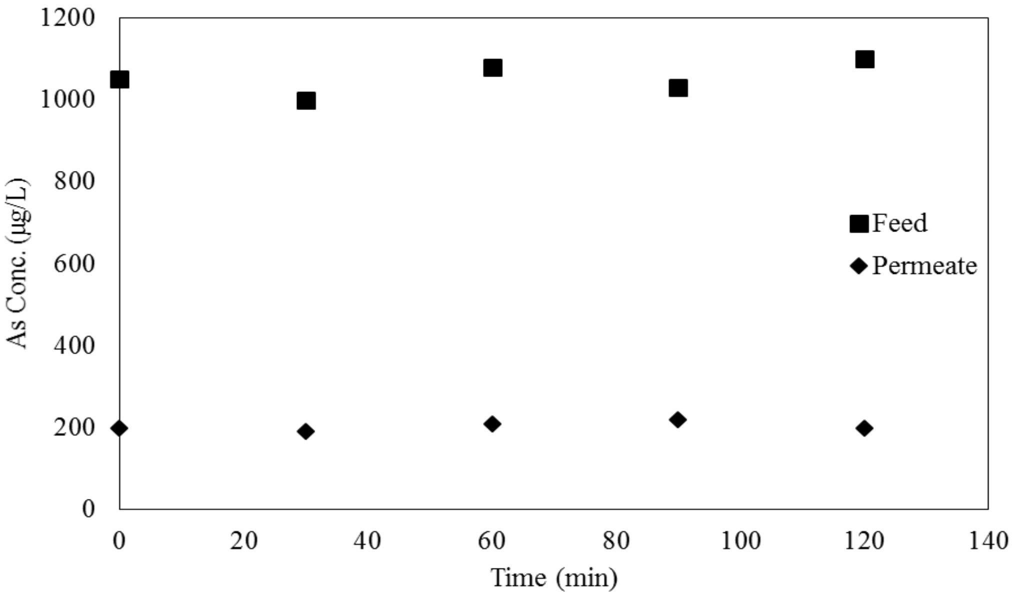

Figure A21. Feed and Permeate Concentrations. Process: UF, As (V) conc.: 1000 μg/L, pH: 6.7-7 (not set), anion conc.: 0, L: no polymer addition

Table A27. Feed and Permeate Concentrations. Process: PEUF, As (V) conc.: 1000 μg/L, pH: 6.7-7 (not set), anion conc. : 10mg/L SO_4^{-2}, L: 0.1 (DADMAC-P(4-VP) (10%))

	Concentration (μg/L)		
Time (min)	Feed	Permeate	Removal (%)
0	900	311	65
30	940	285	70
60	940	318	66
90	925	320	65
120	900	315	65
Average	921	310	66
Standard Dev.	20.1	14.3	1.9
CV (%)	2.2	4.6	2.9

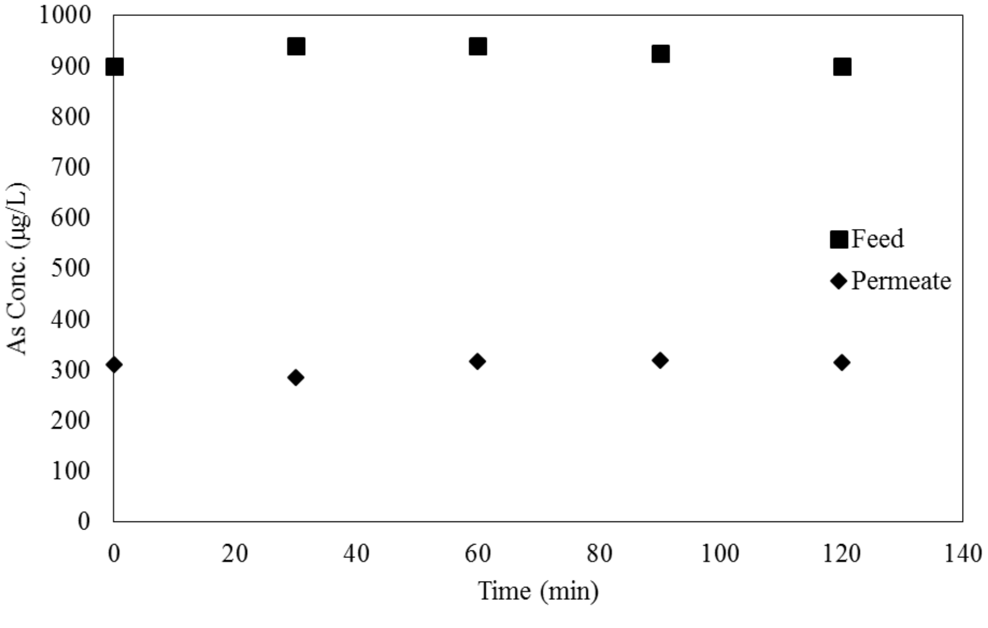

Figure A22. Feed and Permeate Concentrations. Process: PEUF, As (V) conc.: 1000 μg/L, pH: 6.7-7 (not set), anion conc. : 10 mg/L SO_4^{-2}, L: 0.1 (DADMAC- P(4-VP) (10%))

Table A28. Feed and Permeate Concentrations. Process: PEUF, As (V) conc.: 1000 µg/L, pH: 6.7-7 (not set), anion conc. : 100 mg/L SO_4^{-2}, L: 0.1 (DADMAC-P(4-VP) (10%))

	Concentration (µg/L)		
Time (min)	Feed	Permeate	Removal (%)
0	939	666	29
30	891	677	24
60	915	646	29
90	939	701	25
120	891	705	21
Average	915	679	26
Standard Dev.	24.0	24.7	3.6
CV (%)	2.6	3.6	14.0

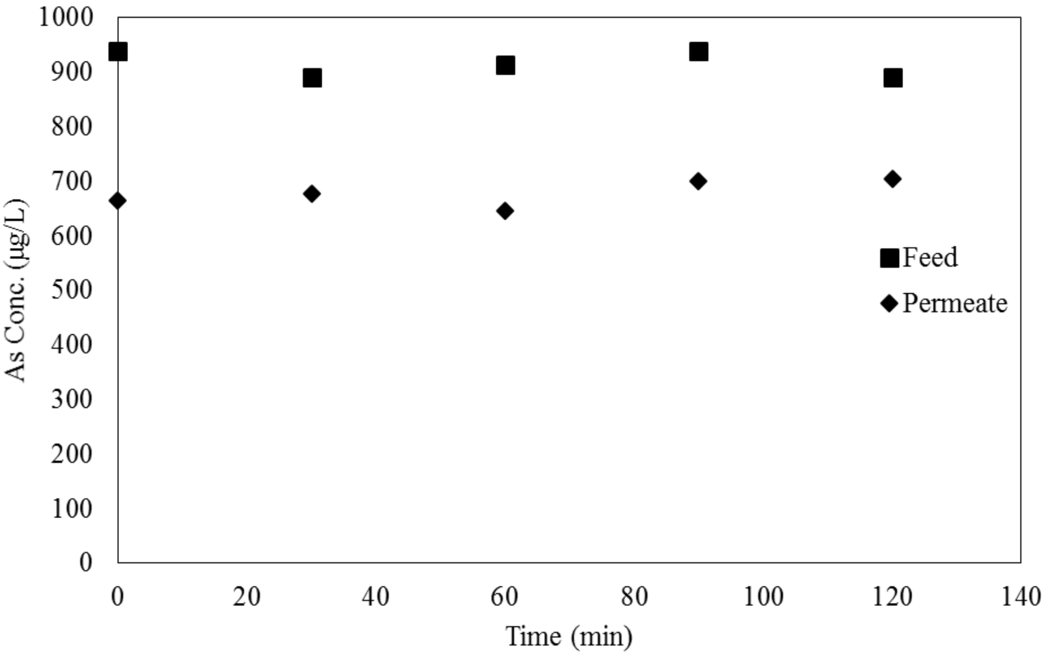

Figure A23. Feed and Permeate Concentrations. Process: PEUF, As (V) conc.: 1000 µg/L, pH: 6.7-7 (not set), anion conc. : 100 mg/L SO_4^{-2}, L: 0.1 (DADMAC- P(4-VP) (10%))

Table A29. Feed and Permeate Concentrations. Process: UF, As (V) conc.: 1000 μg/L, pH: 6.7-7 (not set), anion conc. : 1 mg/L Cl^-, L: no polymer addition

	Concentration (μg/L)		
Time (min)	Feed	Permeate	Removal (%)
0	963	208	78
30	926	160	83
60	963	193	80
90	1039	205	80
120	963	193	80
Average	971	192	80
Standard Dev.	41.1	19.3	1.6
CV (%)	4.2	10.0	2.0

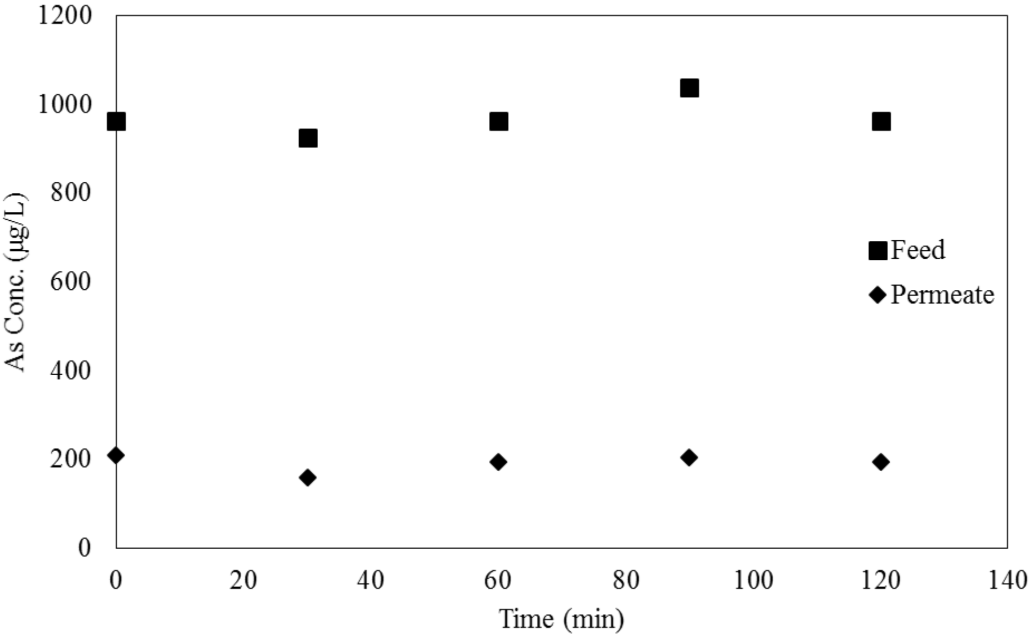

Figure A24. Feed and Permeate Concentrations. Process: UF, As (V) conc.: 1000 μg/L, pH: 6.7-7 (not set), anion conc. : 1 mg/L Cl^-, L: no polymer addition

Table A30. Feed and Permeate Concentrations. Process: UF, As (V) conc.: 1000 μg/L, pH: 6.7-7 (not set), anion conc.: 10 mg/L Cl^-, L: no polymer addition

	Concentration (μg/L)		
Time (min)	Feed	Permeate	Removal (%)
0	926	438	53
30	963	400	58
60	963	362	62
90	1001	325	68
120	980	360	63
Average	967	377	61
Standard Dev.	27.6	43.1	5.6
CV (%)	2.9	11.4	9.2

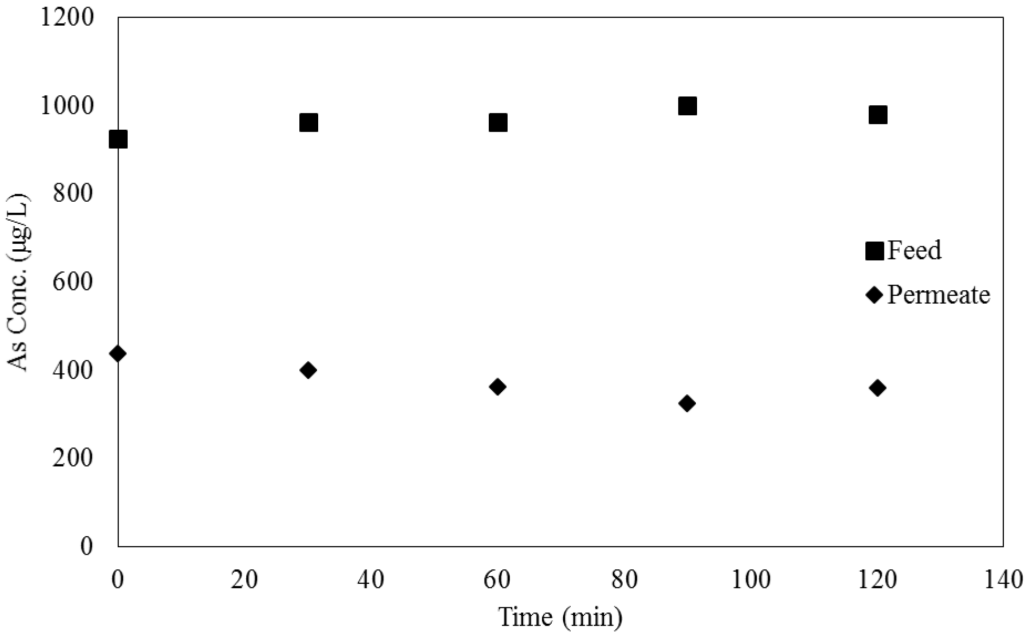

Figure A25. Feed and Permeate Concentrations. Process: UF, As (V) conc.: 1000 μg/L, pH: 6.7-7 (not set), anion conc.: 10 mg/L Cl^-, L: no polymer addition

Table A31. Feed and Permeate Concentrations. Process: UF, As (V) conc.: 1000 μg/L, pH: 6.7-7 (not set), anion conc.: 100 mg/L Cl$^-$, L: no polymer addition

	Concentration (μg/L)		
Time (min)	Feed	Permeate	Removal (%)
0	813	438	46
30	850	445	48
60	888	438	51
90	950	500	47
120	942	453	52
Average	889	455	49
Standard Dev.	58.7	26.2	2.4
CV (%)	6.6	5.8	5.0

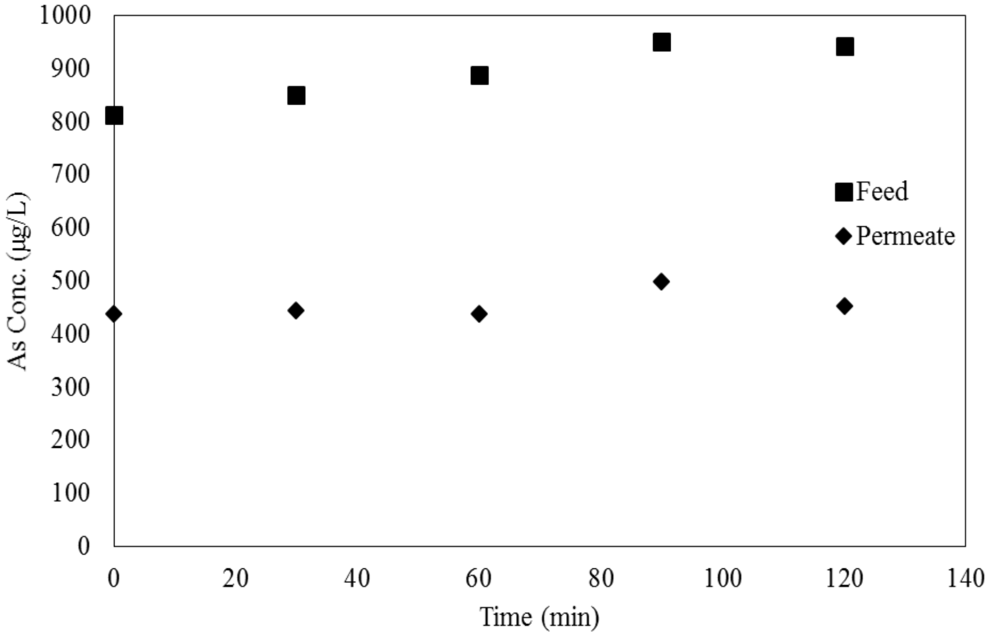

Figure A26. Feed and Permeate Concentrations. Process: UF, As (V) conc.: 1000 μg/L, pH: 6.7-7 (not set), anion conc.: 100 mg/L Cl$^-$, L: no polymer addition

Table A32. Feed and Permeate Concentrations. Process: PEUF, As (V) conc.: 1000 µg/L, pH: 6.7-7 (not set), anion conc.: 100 mg/L Cl$^-$, L: 0.1

	Concentration (µg/L)		
Time (min)	Feed	Permeate	Removal (%)
0	939	603	36
30	915	507	45
60	939	570	39
90	891	531	40
120	891	459	48
Average	915	534	42
Standard Dev.	24.0	55.6	4.9
CV (%)	2.6	10.4	11.8

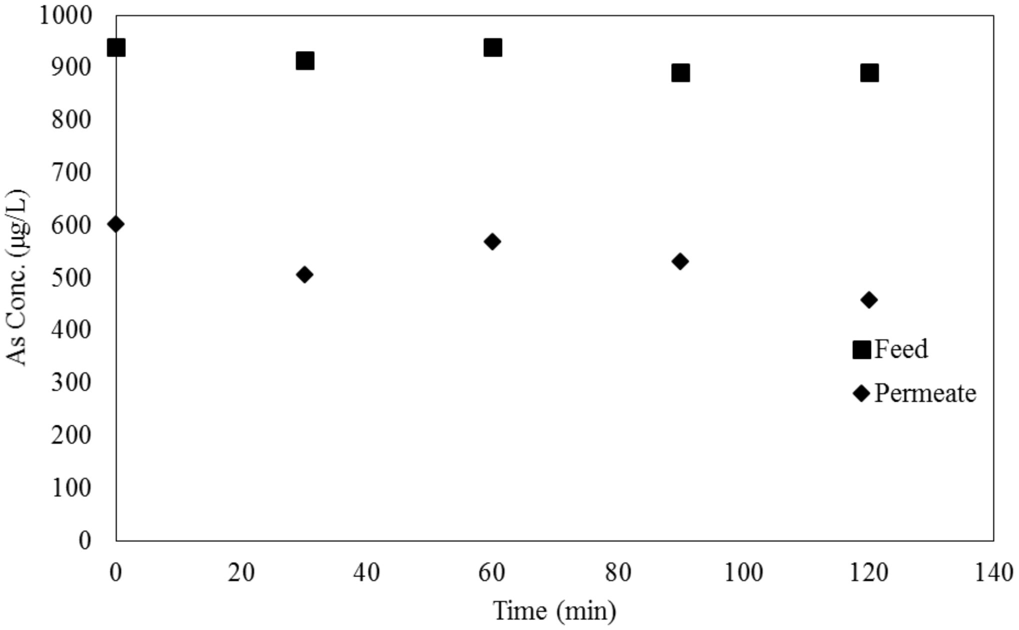

Figure A27. Feed and Permeate Concentrations. Process: PEUF, As (V) conc.: 1000 µg/L, pH: 6.7-7 (not set), anion conc.: 100 mg/L Cl$^-$, L: 0.1

Table A33. Feed and Permeate Concentrations. Process: PEUF, As (V) conc.: 1000 μg/L, pH: 6.7-7 (not set), anion conc.: 1 mg/L Cl^-, L: 0.1

	Concentration (μg/L)		
Time (min)	Feed	Permeate	Removal (%)
0	950	257	73
30	960	220	77
60	920	197	79
90	950	220	77
120	980	220	78
Average	952	223	77
Standard Dev.	21.7	21.6	2.2
CV (%)	2.3	9.7	2.8

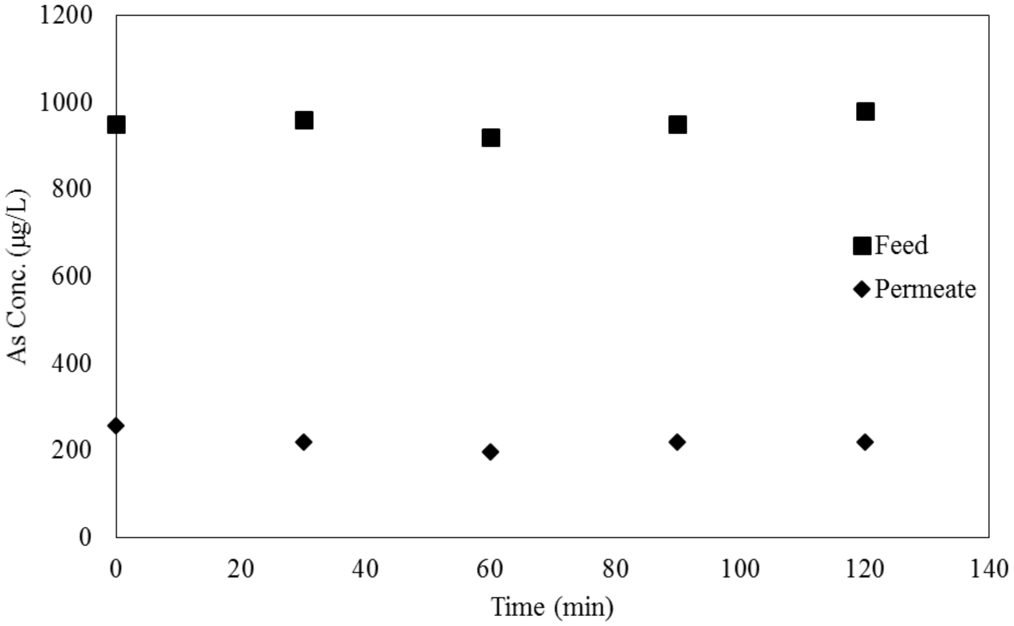

Figure A28. Feed and Permeate Concentrations. Process: PEUF, As (V) conc.: 1000 μg/L, pH: 6.7-7 (not set), anion conc.: 1 mg/L Cl^-, L: 0.1

Table A34. Feed and Permeate Concentrations. Process: PEUF, As (V) conc.: 1000 µg/L, pH: 6.7-7 (not set), anion conc.: 10 mg/L Cl-, L: 0.1

	Concentration (µg/L)		
Time (min)	Feed	Permeate	Removal (%)
0	880	257	71
30	890	295	67
60	885	257	71
90	995	257	74
120	900	295	67
Average	910	272	70
Standard Dev.	48.1	20.5	3.0
CV (%)	5.3	7.5	4.3

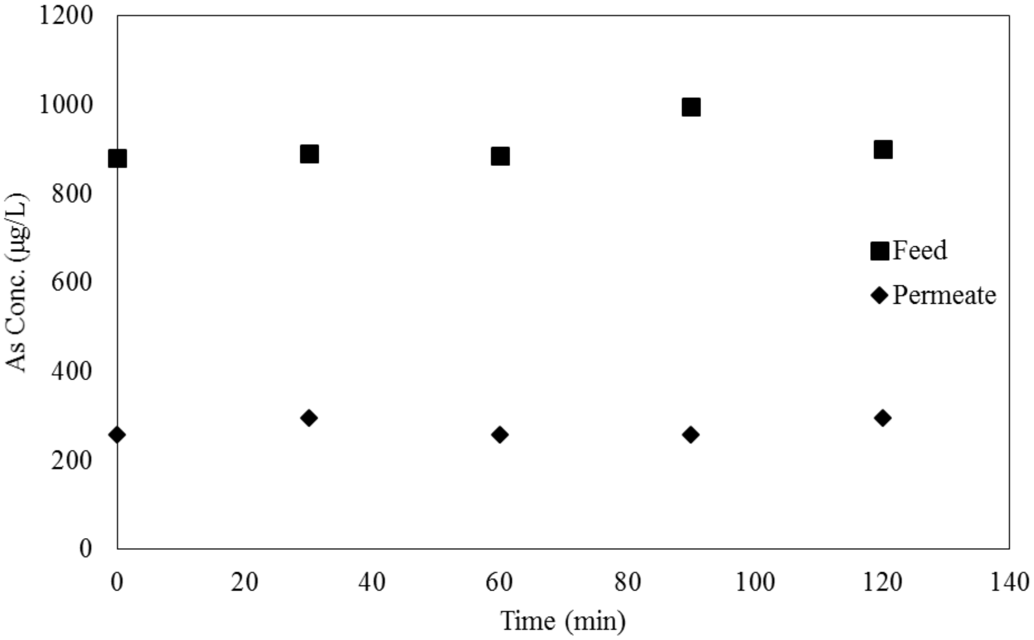

Figure A29. Feed and Permeate Concentrations. Process: PEUF, As (V) conc.: 1000 µg/L, pH: 6.7-7 (not set), anion conc.: 10 mg/L Cl$^-$, L: 0.1

Table A35. Feed and Permeate Concentrations. Process: UF, As (V) conc.: 1000 μg/L, pH: 6.7-7 (not set), anion conc.: 0, L: 0.1

	Concentration (μg/L)		
Time (min)	Feed	Permeate	Removal (%)
0	900	102	89
30	910	120	87
60	920	80	91
90	900	84	91
120	920	102	89
Average	910	98	89
Standard Dev.	10.0	16.1	1.8
CV (%)	1.1	16.5	2.0

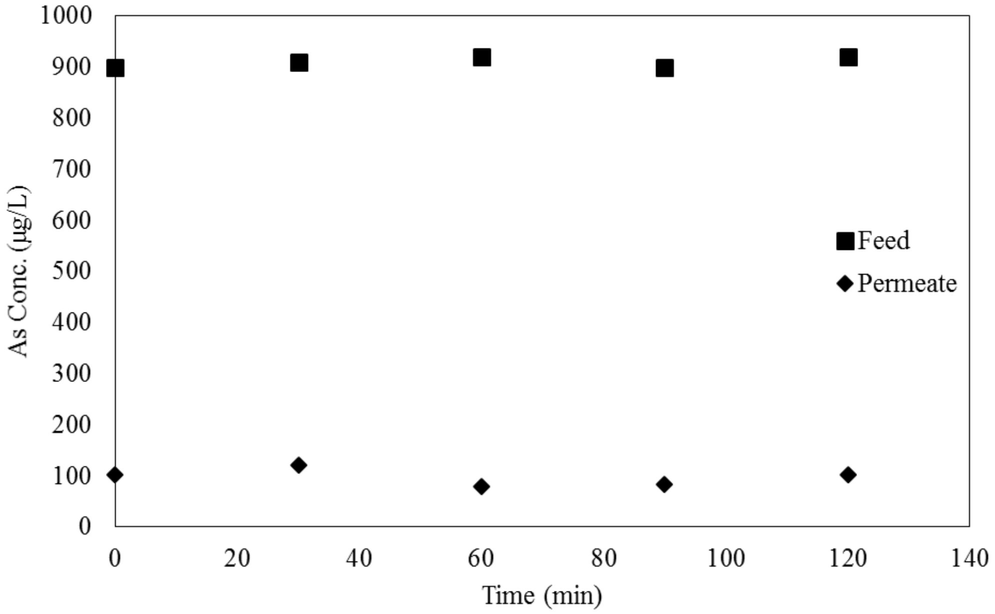

Figure A30. Feed and Permeate Concentrations. Process: UF, As (V) conc.: 1000 μg/L, pH: 6.7-7 (not set), anion conc.: 0, L: 0.1

A6. Comparison of Different Methods Used in Measurement of Samples Collected

Ultrafiltration performances were measured with different methods during different periods of this study. it can also be considered important to demonstrate the results obtained by these different analysis methods which were Atomic Absorption Spectroscopy (AAS-HG) coupled with hydride generation system (method mainly used in the study to analyze results obtained), Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) (some of the samples were sent to TRNC governmental laboratories for comparison) and Photometric analysis using ammonium molybdate (UV-vis). (Used in the analysis of samples obtained from the experiments during last period of the study due to malfunction of the AAS). Results are given in Table A36.

Table A36. Comparison of the Results Obtained by Different Methods from Different Runs.

Time (min)	Removal %		
	AAS-HG	ICP-MS	Molybdate
0	78	89	81
30	85	90	81
60	80	87	81
120	82	86	82

Standard deviation obtained from these runs by using mean removal % values was found to be 4 (in terms of % removal) while percent coefficient of variation value was 5 %.

A7. Effluent Flow Rates Measured in Column Experiments

Volumetric flow rate in column experiments were determined by measuring the time required to in taking the samples. Volumetric flow rates measured while taking randomly selected samples are given in Table A37.

Table A37 Volumetric Flow Rates Measured during some of the Column Adsorption Experiments.

	Volumetric Flow Rate (L/h)			
	1 g	0.5 g	0.3 g	20 g/L Cl^-
				0.54
				0.55
				0.53
				0.54
				0.54
	0.44	0.53		0.51
	0.41	0.41		0.49
	0.46	0.33		0.48
	0.46	0.48		0.47
	0.45	0.33	0.41	0.49
	0.43	0.50	0.53	0.46
	0.51	0.40	0.46	0.48
	0.44	0.37	0.45	0.49
	0.46	0.38	0.49	0.46
Mean	0.45	0.41	0.47	0.48
Stdev	0.03	0.07	0.05	0.02
CV (%)	5.59	17.62	9.79	3.62

A8. Flux and Volumetric Flow Rates recorded in PEUF

Permeate flux values presented in Section 4.3.4 is given in detail in Table A38

Table A38. Permeate Flux at different loading values

	Time (min)	V (mL/min)	Flux (L/m^2.h)
L =0.0005	0	9	37.5
	30	8	33.3
	60	8	33.3
	90	8	3.3
L=0.001	0	9	37.5
	30	8	33.3
	60	9	37.5
	90	9	37.5
L = 0.002	0	10	41.7
	30	9	37.5
	60	10	41.7
	90	10	41.7
L =0.1	0	24	100.0
	30	24	100.0
	60	25	104.2
	90	25	104.2
L = 0.2	0	21	87.5
	30	20	83.3
	60	21	87.5
	90	22	91.7
L = 1	0	24	100.0
	30	23	95.8
	60	22	91.7
	90	23	95.8
No Polymer	0	24	100.0
	30	24	100.0
	60	22	91.7
	90	22.5	93.8

A9. Hydrogels

Dry and wet hydrogels' photo is given in this section in order to give the reader idea on the prepared material which was used in batch and column studies. Photographs of dry and wet hydrogels are given in Figures A 31 and A 32.

Figure A31. Dry hydrogel

Figure A32. Wet hydrogel soaked with water

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PUBLICATIONS

Journal Articles

Pirgalıoğlu S., Özbelge, T. A., “Comparison of non-catalytic and catalytic ozonation processes of three different aqueous single dye solutions with respect to powder copper sulfide catalyst”, Applied Catalysis A: General, 363 (2009), 157-163.

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S.Pirgalıoğlu, Ç. D. Hacıhabiboğlu, T.A Özbelge, H.Ö. Özbelge, N. Bıçak “Arsenat iyonlarının Polimer Destekli Ultrafiltrasyon ile Sudan Ayrılması (Oral Presentation)”, Ulusal Kimya Mühendisliği Kongresi-11 Eskşehir/Türkiye (2014)