Journal of Environmental Management 152 (2015) 66–74

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

The use of superporous p(3-acrylamidopropyl)trimethyl ammonium chloride cryogels for removal of toxic arsenate anions

Nurettin Sahiner [a, b, c, *], Sahin Demirci [b, c], Mehtap Sahiner [d], Selahattin Yilmaz [a], Hamad Al-Lohedan [c]

[a] *Surfactants Research Chair, Department of Chemistry College of Science, King Saud University, P.O Box-2455, Riyadh 11451, Saudi Arabia*
[b] *Department of Chemistry, Faculty of Science & Arts, Canakkale Onsekiz Mart University, Terzioglu Campus, 17100 Canakkale, Turkey*
[c] *Nanoscience and Technology Research and Application Center (NANORAC), Canakkale Onsekiz Mart University, Terzioglu Campus, 17100 Canakkale, Turkey*
[d] *Leather Engineering Department, Faculty of Engineering, Ege University, Bornova, Izmir 35080, Turkey*

ARTICLE INFO

Article history:
Received 7 November 2014
Received in revised form
10 January 2015
Accepted 16 January 2015
Available online 21 January 2015

Keywords:
P(APTMACl) hydrogel/cryogel
Arsenate removal
Cationic magnetic-cryogel
Fast arsenic sorption
Smart cryogel composites

ABSTRACT

Poly((3-Acrylamidopropyl)trimethylammonium chloride) (p(APTMACl)) cryogels were used as a superporous polymer network for the removal of toxic arsenate anions from an aqueous medium. The fast swelling in water, in about 7 s, was shown to be very useful leading to fast arsenate adsorption by p(APTMACl) cryogels within 30 min in comparison to 12 h for bulk common p(APTMACl) hydrogels. A maximum adsorption capacity of about 120 (mg/g) arsenate was obtained for p(APTMACl) cryogels. Both the Langmuir and Freundlich adsorption isotherms were applied for adsorption of arsenate anions by p(APTMACl) cryogels, and it was observed that the adsorption of arsenate anions by p(APTMACl) cryogels are represented better via Langmuir adsorption isotherm providing the R^2 value of 0.998. Furthermore, mag-p(APTMACl) cryogels were synthesized, and shown to be very useful in the fast removal of toxic arsenate anions. The mag-p(APTMACl) cryogels including the adsorbed arsenate were removed by an externally applied magnetic field, with some reduction in the arsenate ion adsorption capacity. It was also further demonstrated that p(APTMACl) cryogels can be reused in the adsorption of arsenate 5 times from aqueous environments without significant loss of adsorption capacity, from 113.47 ± 9 to 102.67 ± 6 mg/g.

1. Introduction

Contamination in water has been a long-standing environmental problem and gains serious attention worldwide due to the scarcity of fresh water. In addition to organic contaminants, inorganic contaminants and different metals types such as arsenic, chromium, lead, mercury and so on, are the main problems for industrial effluents. Water sources can be polluted with arsenic from industrial effluents, and agriculture activities such as fertilizers and pesticides, glass and ceramics industries and medicinal activities, and discharges from chemical processing/manufacturing plants (Jain and Ali, 2000; Pan et al., 2010; Welch et al., 1988). Arsenic (As) can assume various oxidation numbers and the most commonly found forms are As(V) and As(III) (Chang et al., 2009; Sarkar et al., 2008) that are toxic and carcinogenic (Guan et al., 2009). Prolonged exposure to arsenic, can cause severe problems such as black foot, skin, bladder and even lung cancer, and there is high risk of heart attacks, anemia and anorexia (Chen et al., 2007; Sarkar et al., 2010; Smedly and Kinniburgh, 2002). Recently, the United States Environmental Protection Agency (USEPA) decreased the maximum amount of arsenic in water from 50 to 10 μg/L (USEPA, 2001). Because of the harmful effect of arsenic on the environment and living organisms, the removal of arsenic in aquatic environments has paramount significance (Zhoa et al., 2010). The most frequently used methods for removal of arsenic are complex formation, sedimentation, ion exchange, membrane filtration, adsorption and adsorption onto various porous and non porous materials (Barakat and Sahiner, 2008; Cumbal and SenGupta, 2005; Sahiner et al., 2011).

A special form of hydrogel, cryogels are prepared under

---

* Corresponding author. Nanoscience and Technology Research and Application Center (NANORAC), Canakkale Onsekiz Mart University, Terzioglu Campus, 17100 Canakkale, Turkey.
E-mail address: sahiner71@gmail.com (N. Sahiner).

http://dx.doi.org/10.1016/j.jenvman.2015.01.023
0301-4797/

cryogenic conditions with pore sizes over few tens of micrometer range and form super porous polymeric networks. Cryogels are synthesized below the freezing point of the solvent of the monomer, crosslinker and the initiator. As most of solvent for hydrogel is water, below the freezing point of water ($T < 0$ °C), the formed ice crystals are responsible for the formation of pores that the sizes ranges from few tens of micrometers to a few hundreds of micrometers. These pores are connected and provide high elasticity to the cryogels in comparison to common hydrogels (Karacan and Okay, 2013; Koshy et al., 2014; Lozinsky, 2008; Sahiner and Seven, 2014). Due to their structural flexibility, higher mechanical strength and fast responsiveness, cryogels provide many advantages in comparison to conventional hydrogels (Gulsu et al., 2010; Lozinsky, 2008; Sahiner and Seven, 2014a; Sahiner and Yildiz, 2014). The applications of cryogels include template for metal nanoparticles (Sahiner and Seven, 2014b; Sahiner and Yildiz, 2014), bioreactor (Wang et al., 2013), column (Wang et al., 2014; Yao et al., 2006) cell-scaffolds (Hwang et al., 2010), biosensor (Hedström et al., 2008; Tsai et al., 2007), and absorbents for environmental applications (Koc et al., 2011; Yamamoto et al., 2009, 2010).

Earlier the removal of arsenic with p(APTMACl) and bulk hydrogels was reported (Barakat and Sahiner, 2008; Sahiner et al., 2011). Herein, we report the use of p(APTMACl) cryogel for arsenic removal. The cationic p(APTMACl) cryogels were prepared by cryopolymerization technique and were characterized by using Fourier Transform Infrared (FT-IR) spectroscopy, Thermogravimetric Analyzer (TGA), and Scanning Electron Microscope (SEM). The synthesized p(APTMACl) cryogels are used for removal of arsenate anions from aquatic environments. Moreover, magnetic field responsive p(APTMACl) cryogel composites were also prepared by in situ reduction/preparation method from Fe(II) and Fe(III) precursors, and shown to be very useful for fast arsenate recovery and control by externally applied magnetic field. Various parameters affecting removal of arsenate anions such as the amounts of absorbent and different initial concentration of arsenate were also investigated. Also, the application of Langmuir and Freundlich isotherms on adsorption of arsenate anions was examined.

2. Experimental

2.1. Materials

The monomer, (3-Acrylamidopropyl)trimethylammonium chloride (APTMACl) (75% in H_2O, Aldrich), N,N-Methylenebisacrylamide (MBA, 99%, Sigma Aldrich) as a crosslinker, N,N,N,N-Tetramethylethylenediamine (TEMED, 99%, Merck) as an accelerator and potassium persulfate (KPS, 99%, Sigma Aldrich) as an initiator were used for synthesis of p(APTMACl) cryogels. Sodium arsenate dibasic heptahydrate ($Na_2HAsO_4.7H_2O$, 98.5%, Fluka) was used as an arsenic source. $FeCl_2.4H_2O$ (99%, Fluka) and $FeCl_3.6H_2O$ (99%, Acros) as metal ion sources, ethanol (99.5%, Sigma Aldrich), and sodium hydroxide (NaOH, 99%, Sigma Aldrich) as precipitating/agent were used for synthesis of mag-p(APTMACl) cryogels.

2.2. Preparation and characterization of p(APTMACl) cryogels

The cryogels of p(APTMACl) were synthesized by a cryopolymerization technique (Karacan and Okay, 2013; Sahiner and Seven, 2014a; Sahiner and Yildiz, 2014). For the preparation of p(APTMACl) cryogels; 0.832 g monomer (10.4 w/v %) and 0.0842 g MBA (18 mol% of APTMACl) were dissolved in 5.5 ml distilled (DI) water, and to this solution 50 μl TEMED was added and vortexed. In a separate vial 0.0083 g KPS (1 mol% of APTMACl) initiator was dissolved in 1 ml distilled water and cooled in an ice-bath at 0 ± 2 °C. The initiator was added into the monomer solution and then placed quickly into plastic straws (~8 mm in diameter). The straws were placed in -18 °C freezer for 16 h to complete cryopolymerization. Thereafter, prepared cryogels were cut to similar shapes, washed with 500 ml DI water and dried in an oven at 50 °C for further studies.

The SEM images of p(APTMACl) cryogels were acquired on freeze-dryed samples using SEM (JEOL JSM-5600) with an operating voltage of 20 kV. The images were obtained from the samples of p(APTMACl) cryogels that are placed onto carbon tape attached aluminum SEM stubs at ambient temperature after coating with gold to a few nanometer thickness under vacuum. FT-IR (Nicolet iS10, Thermo) and TGA (TG/DTA 6300, SEIKO) devices were also used for the characterization of p(APTMACl) cryogels.

2.3. Synthesis of magnetic p(APTMACl) cryogels

In situ preparation of magnetic ferrites was performed by using a previously reported method (Sahiner, 2013, 2014). Accordingly, a clean and known amount of dried cryogel (0.5 g) was placed in [$FeCl_2$] and [$FeCl_3$] solution in ethanol medium with Fe(II):Fe(III) mole ratio of 1:2 for 2 h for loading. After metal salt loading, the cryogels were washed 2 times with pure ethanol to remove unbound metal salts. Then, the metal laden p(APTMACl) cryogels were transferred into 0.75 M NaOH solution, and the reaction continued for 3 h in a beaker under constant stirring of 500 rpm at room temperature. Finally, the cryogels were washed with DI water and dried in an oven at 50 °C for adsorption studies.

2.4. Adsorption studies of arsenate from aqueous medium

Batch type adsorption experiments were performed in beakers equipped with a magnetic stirrer. To each beaker containing 400 ppm 100 ml solution of arsenate anions, 0.05 g p(APTMACl) cryogels were added. The adsorption experiments were carried out for 120 min, and 0.5 ml sample was taken from the adsorption medium at 0, 5, 15, 30, 60, and 120 min during the adsorption experiments and were diluted 10 fold before atomic adsorption measurements (AAS, Thermo ICA 3500 AA SPECTRO). Besides, pseudo-first-order, pseudo-second-order model was also applied for adsorption of arsenate anions by p(APTMACl) cryogels. Moreover, the effects of arsenate concentration and the amount of adsorbing agent, p(APTMACl) on the adsorption capacity were investigated. For the arsenate source 200, 400, 600, 800 and 1000 ppm 100 ml for arsenate solution was used while keeping the cryogel amount constant (0.05 g). Additionally, the amounts of p(APTMACl) cryogels were also varied as 0.03, 0.05, 0.1 and 0.15 g cryogel with a constant arsenate concentration of 400 ppm.

In addition to distilled water, the adsorption of arsenate anions was also studied from different arsenate aqueous solution such as seawater, and tap waters by placing 0.05 g p(APTMACl) cryogels in their corresponding 400 ppm 100 ml arsenate solutions. The adsorbed amounts of arsenates by p(APTMACl) cryogels from these two media was determined via AAS measurements as mentioned earlier.

2.5. Reusability of p(APTMACl) cryogels after removal of arsenate anions

The reuse of synthesized p(APTMACl) cryogels for arsenate anion removal was done by adopting multiple adsorption–desorption cycles. For that purpose, 0.05 g cryogel was placed in a beaker with 400 ppm 100 ml arsenate solution by mixing at 300 rpm. The adsorption experiments were carried out for 120 min, and after this time period, the arsenate anions adsorbed p(APTMACl) cryogels were washed two times with DI water, and placed into a beaker containing 100 ml 5 M HCl for the desorption of the adsorbed arsenate for another 120 min at 300 rpm stirring rate. From there, 0.5 ml samples were taken from the HCl solution and diluted 10 times with DI water, and the amount of adsorbed/desorbed arsenate anions were measured with AAS. These adsorption–desorption cycles were repeated five times by using three different sets of p(APTMACl) cryogels to present the result as mean values with standard deviations.

3. Results and discussions

3.1. Synthesis and characterization of p(APTMACl) and mag-p(APTMACl) cryogels

The p(APTMACl) cryogels were synthesized via cryopolymerization technique. The polymerization and the crosslonking of p(APTMACl) hydrogels were reported earlier (Sahiner et al., 2006) The schematic presentation of synthesis of p(APTMACl) cryogels is illustrated in Fig. 1(a). The characterization of synthesized p(APTMACl) cryogels for the illustration of the super porous structure was performed with scanning electron microscopy (SEM) (JSM-5600, JEOL) and is shown in Fig. 1(b). As can be seen, the synthesized p(APTMACl) cryogels have pore sizes ranging between 10 and 100 μm and are connected. Because of these super porous connected pores, p(APTMACl) cryogels swell much faster than common hydrogel (Barakat and Sahiner, 2008). As illustrated in the swelling digital camera images in Fig. 1(c), complete swelling of p(APTMACl) cryogels was accomplished in 7 s. This is significantly less time in comparison to bulk conventional hydrogels where swelling can take hours and days depending on the amount of crosslinker used. Even though higher amounts of crosslinker are generally used for cryogel preparation, cryogel swelling is tremendously fast because of their super porous structures that are connected. These superporous structure make cryogels very useful material for many applications e.g., fast adsorption of solutes for environmental applications or separation and purification of biological species (Koshy et al., 2014; Lozinsky, 2008; Wang et al., 2013, 2014).

The FT-IR spectrum of p(APTMACl) cryogel is illustrated in Fig. 2(a) and all the functional groups are in accordance with reported literature (Barakat and Sahiner, 2008; Sahiner et al., 2014). For example, the N–H stretching of amide groups for APTMACl was observed at 3354 and 3247 cm^{-1} respectively. The peaks for C–H stretching from $-CH_3$ at 2942 cm^{-1}, and the C=O peak for amide group at 1640 cm^{-1}, and the bending at 1540 cm^{-1} for N–H, and the ammonium ion peak at 1480 cm^{-1} are all clearly seen.

The usefulness of the magnetic ferrite or metal nanoparticles within hydrogel or cryogels were reported in many studies (Sahiner and Seven, 2014a, 2014b; Sahiner and Yildiz, 2014). The positively charged cryogels, such as p(APTMACl), can absorb metal salts from metal dissolved in ethanol solution. The mag-p(APTMACl) cryogel composites were prepared by loading [$FeCl_2$] and [$FeCl_3$] metal salt mixture in 1:2 ratio into the p(APTMACl) cryogel network, and then in situ reduction with 0.75 M NaOH shown in equation (1) (Laurent

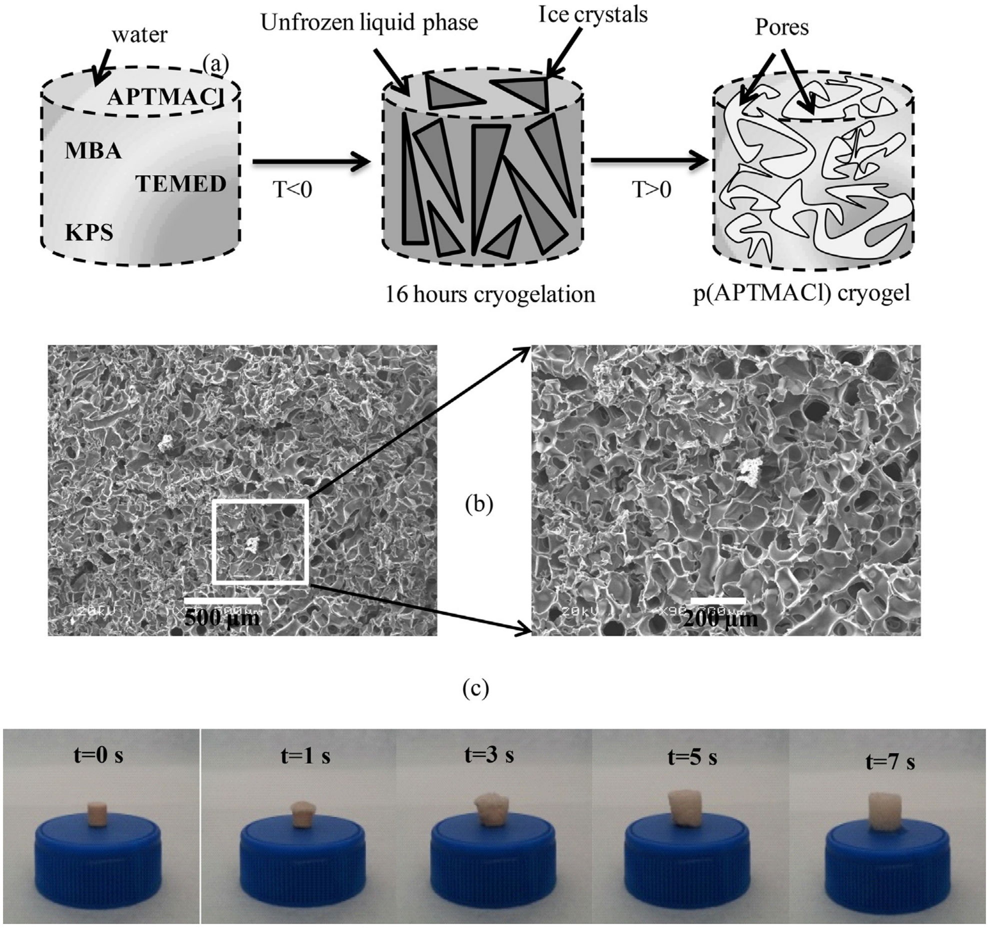

Fig. 1. (a) Schematic presentation of synthesis of p(APTMACl) cryogels, (b) SEM images of p(APTMACl) cryogels, and (c) swelling pictures of p(APTMACl) cryogels.

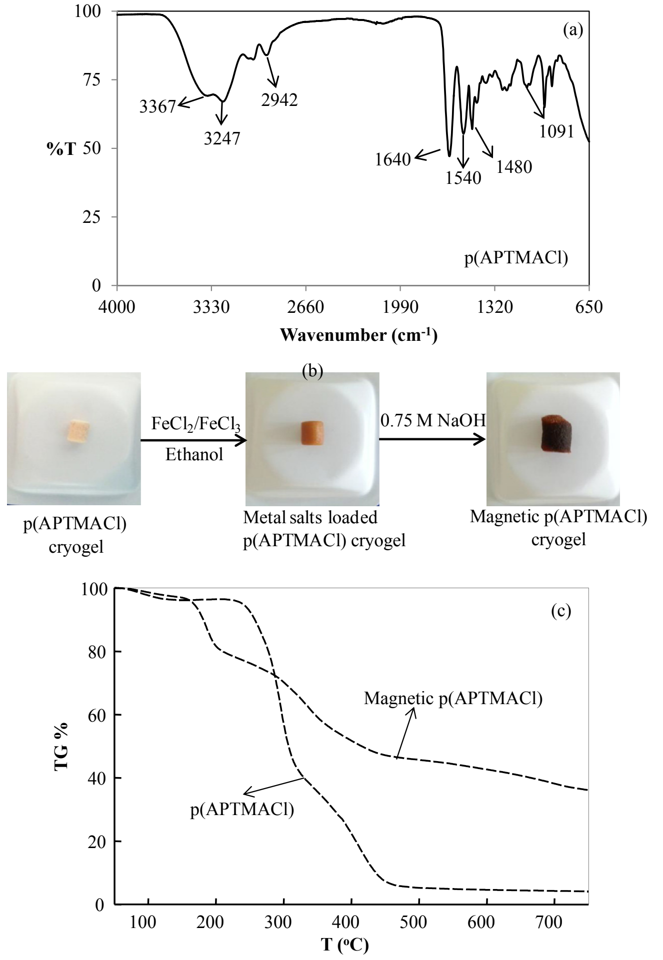

Fig. 2. (a) The FT-IR spectrum of p(APTMACl) cryogels, (b) The preparation schema for mag-p(APTMACl) cryogels, and (c) TGA thermograms of p(APTMACl), and mag-p(APTMACl) cryogel composites.

et al., 2008)

$$Fe^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow Fe_3O_4 + 4H_2O \tag{1}$$

The schematic presentation of mag-p(APTMACl) cryogels is illustrated in Fig. 2(b). Additionally, the thermal stability of p(APTMACl) and mag-p(APTMACl) cryogels were determined with thermogravimetric analyzer (TGA, SII TG/DTA 6300) by comparing thermal behavior of p(APTMACl) and mag-p(APTMACl) cryogel composites by heating up to 750 °C at 10 °C/min heating rate under N_2 flow of 20 ml/min, and the corresponding thermograms are also given in Fig. 2(c). As can be seen, the p(APTMACl) cryogels have four thermal degradation steps. Bare p(APTMACl) cryogel's first step is between 50 °C and 122 °C with 3.4% weight loss; the second step is between 230 °C and 324 °C with 58.2% weight loss; the third step is between 325 °C and 446 °C with 92.2% weight loss, and the last step is between 450 °C and 750 °C with 95.9% weight loss. On the other hand, the mag-p(APTMACl) cryogel composite again has four degradation steps. The first step of mag-p(APTMACl) cryogel composite is again between 50 °C and 162 °C with 4% weight loss; the second step is between 163 °C and 202 °C with 19% weight loss; the third step is between 210 °C and 422 °C with 50% weight loss, and fourth step is between 430 °C and 750 °C with 64% weight loss. Therefore, it is apparent that the mag-p(APTMACl) cryogel composites started to degrade earlier than bare p(APTMACl) cryogels; however, resulted in lesser amounts of total % weight loss at 750 °C in comparison to bare p(APTMACl) cryogels confirming the existence of magnetic ferrite particles.

3.2. *Removal of arsenate anions with p(APTMACl) cryogels*

The removal of arsenate (AsO_4^{3-}) anions was carried out by batch type experiments from aqueous medium at room temperature. The $Na_2HAsO_4.7H_2O$ was used as source of AsO_4^{3-} anions. For arsenate, the corresponding values of pK_a are given below (Barakat and Sahiner, 2008);

$$\begin{aligned} &H_3AsO_4 \rightarrow H^+ + H_2AsO_4^-, \quad pK_1 = 2.2, \\ &H_2AsO_4^- \rightarrow H^+ + HAsO_4^{2-}, \quad pK_2 = 7.08, \\ &HAsO_4^{2-} \rightarrow H^+ + AsO_4^{3-}, \quad pK_3 = 11.5 \end{aligned} \tag{2}$$

It is obvious that these ionization steps are affected by changes in solution pH. Here; The pH of 400 ppm 100 ml arsenate solution is 9.3, and upon addition of 0.05 g p(APTMACl) cryogel the pH was lower to 8.2 in 30 min and stayed constant during the course of the adsorption studies. As shown in Fig. 3(a), the maximum adsorption amount of AsO_4^{3-} anions of about 118 (mg/g) by p(APTMACl) cryogels was accomplished from the aqueous solution of 400 ppm 100 ml of AsO_4^{3-} using 0.05 g cryogel. During the adsorption processes, 0.5 ml sample was taken from the medium at 0, 5, 15, 30, 60, and 120 min and diluted 10 times, and then the measurements were done with AAS. The p(APTMACl) cryogels can absorb about 118.2 ± 6.5 mg/g AsO_4^{3-} anions within an hour; this adsorption

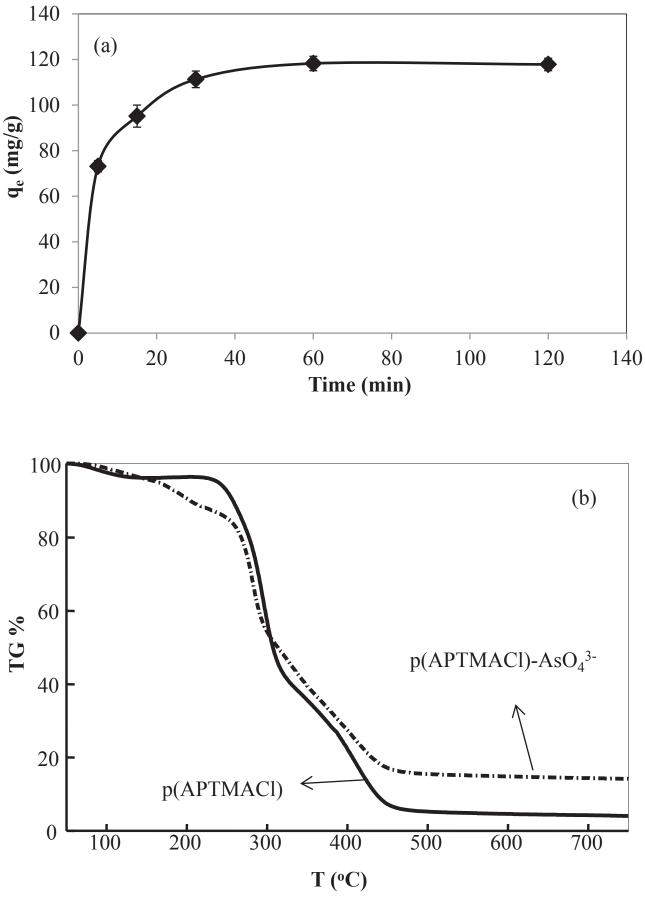

Fig. 3. (a) The adsorption graph of p(APTMACl) arsenate anions [0.05 g cryogel, 100 ml, 400 ppm arsenate] (b) TGA thermograms of p(APTMACl) and arsenate anions adsorbed in p(APTMACl) cryogels.

amount is approximately four times more than the adsorption capacity of modified p(4-VP) microgels (Sahiner et al., 2011), and it is about ten times faster than the conventional p(APTMACl) hydrogels (Barakat and Sahiner, 2008). In addition, the TGA analysis of bare p(APTMACl), and AsO_4^{3-} anions adsorbed in p(APTMACl) cryogels were done and the corresponding graph thermogram is given in Fig. 3(b). The degradation temperature ranges and the degradation amounts are given in Table 1 for p(APTMACl) and p(APTMACl)-AsO_4^{3-}. The degradation temperature ranges for p(APTMACl)-AsO_4^{3-} are 50–246 °C (14.2% wt), 250–297 °C (44.1% wt), 300–446 °C (82.5% wt) and 450–750 °C (86% wt) respectively. As can be seen due to the adsorption of AsO_4^{3-} anions, the thermal degradation of p(APTMACl) cryogel is changed and the difference between p(APTMACl) and p(APTMACl)-AsO_4^{3-} is 12% which can be attributed to adsorbed AsO_4^{3-} anions.

3.3. Adsorption kinetics studies

Different kinetic models such as pseudo-first-order model (Eq. (3)), and pseudo-second-order model (Eq. (4)) are generally used for the determination of the kinetic parameters such rate constants and their capacities (Kumar et al., 2014).

$$\log(Q_e - Q_t) = \log Q_t - (k_1/2.303)t \tag{3}$$

$$t/Q_t = 1\Big/k_2Q_e^2 + t/Q_e \tag{4}$$

where; Q_e and Q_t is the amounts of the adsorbed arsenate ion (mg/g) at equilibrium and at time t, respectively. The resultant rate constants for pseudo-first-order model is k_1 (min^{-1}), and pseudo-second-order model is k_2 ($g.mg^{-1}.min$). To determine the pseudo-first-order rate constant k_1, and the pseudo-second-order rate constant k_2, log (Q_e- Q_t) versus t, and t/Q_t versus t graphs are constructed (not shown), respectively. The determined rate constants k_1 and k_2, Qe and R^2 correlation coefficient values were given in Table 2, and these values provide a good judgment about the mechanism of adsorption. The obtained correlation coefficients (R^2) for pseudo-first-order is 0.816, and the pseudo-second-order is 0.999. So, it can be assumed that the pseudo-second-order model provide better fit for the adsorption of arsenate ion into p(APTMACl) cryogels. Moreover, both calculated Q_e values are similar to the experimental value of 118.2 ± 6.5 mg/g that are 119.34 mg/g and 121.21 mg/g for the pseudo-first-order and pseudo-second-order models, respectively. Consequently, pseudo-second-order affords superior presentation with experimental data with the better correlation coefficient.

Table 1
The thermal degradation ranges of p(APTMACl), mag-p(APTMACl), p(APTMACl)-AsO_4^{3-}, and Mag-p(APTMACl)-AsO_4^{3-} cryogels.

Materials	Thermal degredation ranges (°C), and weight loses (%)			
	I.	II.	III.	IV.
p(APTMACl)	50–122 3.4	230–324 58.2	325–446 92.2	450–750 95.9
Mag-p(APTMACl)	50–170 7.5	175–210 20	288–442 52.4	445–750 63.8
p(APTMACl) AsO_4^{3-}	50–246 14.2	250–297 44.1	300–446 82.5	450–750 86
Mag-p(APTMACl) AsO_4^{3-}	50–205 14.8	250–350 55	370–577 72.9	580–750 90.1

Table 2
Pseudo-first-order and pseudo-second-order constants and correlation coefficients for adsorption of arsenaate anions by p(APTMACl) cryogels.

Metal ion	Exp.	Pseudo-first-order-model			Pseudo-second-order-model		
AsO_4^{3-}	Q_e (mg/g)	k_1 (min^{-1})	Q_e (mg/g)	R^2	k_2 ($g\ mg^{-1}\ min$)	Q_e (mg/g)	R^2
	118.2 ± 6.5	3.1×10^{-2}	119.34	0.816	8.2×10^{-3}	121.21	0.999

3.4. Effect of the amount of adsorbent and concentration of arsenate anion

The effect of the amount of cryogel on the removal of arsenate anions was investigated and the corresponding graph is illustrated in Fig. 4(a). Different amounts of p(APTMACl) cryogels of 0.03, 0.05, 0.1, 0.15 and 0.3 g were placed in 400 ppm 100 ml solution of arsenate solution. The adsorption was observed as a function of time by removing 0.5 ml sample from the adsorption solution and diluting 10 times before AAS measurements. As is shown, the removal efficiency increased with the increase in amount of p(APTMACl) cryogels. The removal amounts were observed as 17.8%, 24.7%, 50%, 65.6%, and 95.3% for 0.03, 0.05, 0.1, 0.15 and 0.3 g

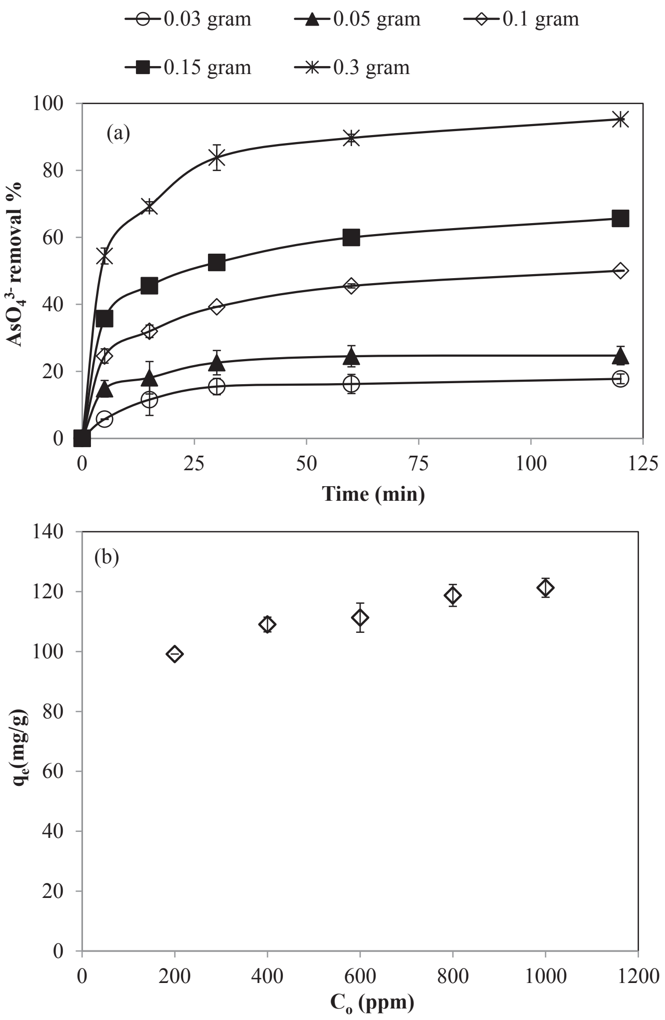

Fig. 4. (a) The effect of the amount of cryogel. [Arsenate solution: 100 ml, 400 ppm], and (b) The effect of initial arsenate ion concentration for arsenate removal [100 ml toxic arsenate anion solution, 0.05 g cryogel].

cryogels respectively in 120 min adsorption time. Although the adsorbed amount of toxic arsenate anions increased with the increase in amount of hydrogel, all the functional groups of the cryogel network which are responsible for adsorption are not completely full. This can be explained by the layer-by-layer adsorption process. Accordingly, upon cryogel swelling, initially the functional groups on the surface layer interact with toxic arsenate anions. The other functional groups within the center of cryogel become available for adsorption, and upon their interaction then the next layer of functional groups within the cryogels become available, and these processes go on until all the functional groups are filled with toxic anions. Additionally, the effect of initial arsenate ion concentration in solution was investigated using 0.05 g p(APTMACl) cryogels for different initial arsenate concentrations; 200, 400, 600, 800, and 1000 ppm aqueous solution of 100 ml each, and the results are illustrated in Fig. 4(b). As can be seen, the maximum amount of adsorbed arsenate anions slightly increases with the increase in initial amount of arsenate solution from 99 to 121 mg/g, implying that the capacity of p(APTMACl) cryogel is about 121 mg/g.

3.5. Arsenate adsorption isotherms

The adsorption of arsenate anions from their aqueous solution was carried out using five different concentrations; 200, 400, 600, 800, and 1000 ppm per 100 ml for arsenate anions. The very well known Langmuir (Eq. (3)) and Freundlich (Eq. (4)) equations were applied to determine and define the nature of adsorption of arsenate anions into p(APTMACl) cryogels:

$$C_e/q_e = (C_e/q_m) + 1/q_mK_L \tag{4}$$

where, C_e (mg/L) is the equilibrium concentration of anions in solution, q_e (mg/g) is the adsorption capacity at equilibrium, q_m (mg/g) is the maximum adsorption of anions, and K_L (L/mg) is the Langmuir adsorption equilibrium constant. The application of Langmuir adsorption isotherms on the adsorption of arsenate anions are illustrated in Fig. 5(a) and their corresponding values are given in Table 3. The q_m (mg/g), that is the maximum adsorption capacity, was approximately 126 mg/g for arsenate anions, values which are higher than those previously reported (Barakat and Sahiner, 2008). Also, to estimate the nature of arsenate anion adsorption into p(APTMACl) cryogels, the Freundlich adsorption isotherm was applied using the Freundlich equation (Eq. (4));

$$\log q_e = \log K_F + 1/n \log C_e \tag{5}$$

where, C_e is the equilibrium concentration of arsenate anions (mg/L), q_e is the amount of adsorbed anions per gram absorbent (mg/g), and K_F (g kg^{-1} (gm^{-3}))^n and n are physical constants of the Freundlich adsorption isotherm. K_F and n are indicators of adsorption capacity and adsorption intensity, respectively. Accordingly, the application of the Freundlich isotherm for adsorption of arsenate anions by p(APTMACl) cryogels is given in Fig. 5(b) and their corresponding values are given in Table 3. Linear regression analysis was used for K_F and n determination. As can be seen from the table, the Langmuir model yields a better fit than the Freundlich model with the R^2 value for the Langmuir isotherm is 0.998. From the Langmuir isotherm, the theoretical adsorption capacity (qm) is expected to be 126.58 mg/g p(APTMACl) cryogels, which is a little higher than the experimental value of 113.47 ± 9 mg/g. This could be due to the high amount of cross-linkers used for cryogel preparation that may prevent accessibility of all the functional groups to bind arsenate anions.

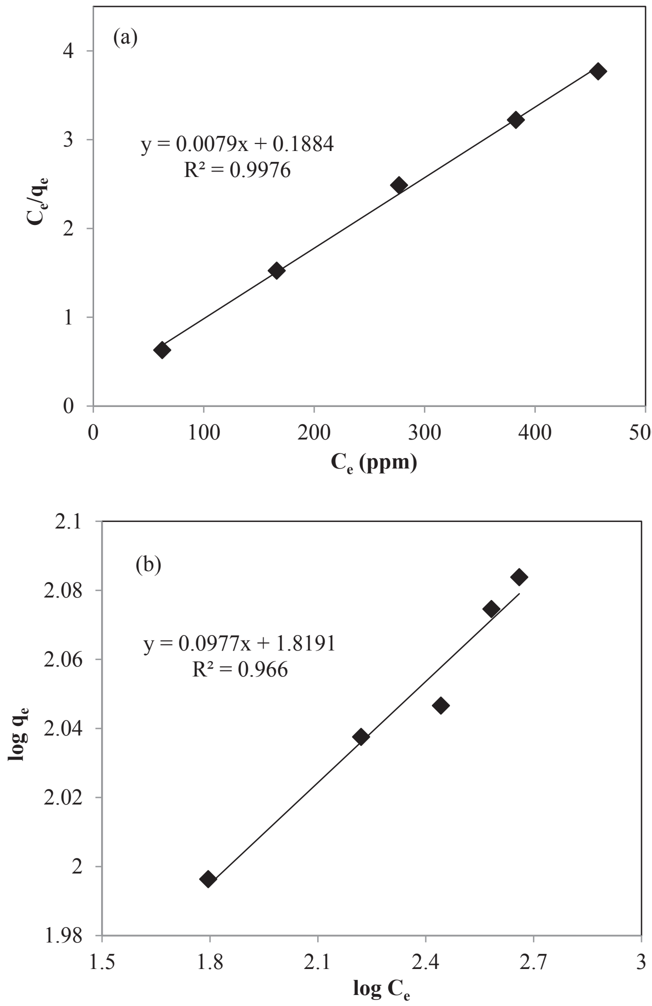

Fig. 5. (a) The application of (a) Langmuir, and (b) Freundlich isotherms on the adsorption of arsenate by p(APTMACl) cryogels.

3.6. The adsorption properties of mag-p(APTMACl) cryogel

Mag-p(APTMACl) cryogels were also used for adsorption of arsenate anions from different aqueous solutions, and their results were given in Table 4. Also, as can be seen the amount of the adsorbed arsenate anions decreased compared to bare p(APTMACl) cryogels from about 120 to 51 mg/g, shown in Fig. 6(a). Considering 36% of mag-p(APTMACl) cryogel composite is magnetic ferrite, the amounts adsorbed by mag-p(APTMACl) cryogels can be calculated as about 80 mg/g, suggesting that there is still reduction in the arsenate ion adsorption capacity of p(APTMACl) cryogels. This could be due to the interaction of some of the functional groups of p(APTMACl) cryogels with ferrite ions, as well as the repulsion of arsenate ions by the negatively charged ferrite ions. However, as shown in Fig. 6(b), the digital camera images clearly demonstrates the attraction of mag-p(APTMACl) cryogels towards a magnet.

Table 3
The AsO_4^{3-} anion adsorption parameters of p(APTMACl) cryogel with the application of the Langmuir and Freundlich isotherms.

Metal ion	Langmuir isotherm constants			Freundlich isotherm constants		
	K_L (L/mg)	q_m (mg/g)	R^2	K_F (g kg^{-1}.(gm^{-3})^n)	n	R^2
AsO_4^{3-}	0.042	126.58	0.998	65.93	10.24	0.966

Table 4
The adsorption amount of arsenate anions by mag-p(APTMACl) cryogels from different media.

Materials	DI water (mg/g)	Seawater (mg/g)	Tap water (mg/g)
Mag-p(APTMACl)	51 ± 4.9	22.5 ± 5.2	9.4 ± 0.5

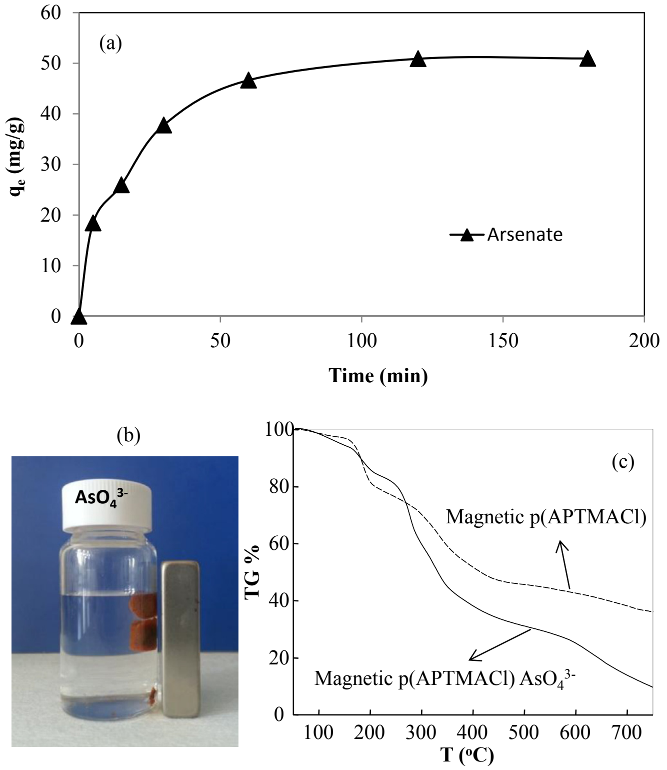

Fig. 6. (a) The adsorption graph of mag-p(APTMACl) for arsenate [0.05 g cryogel composite, 100 ml, 400 ppm arsenate], (b) digital camera image of arsenate adsorbed in mag-p(APTMACl) cryogels under externally applied magnetic field, (c) the thermograms of mag-p(APTMACl) and arsenate adsorbed in mag-p(APTMACl) cryogels.

Therefore, this mag-p(APTMACl) cryogels can be removed from the adsorption medium by an externally applied magnetic field after sorption of arsenate ions from contaminated waters. The thermal behavior of mag-p(APTMACl) cryogels with adsorbed arsenate anions changed as shown in Fig. 6(c). As can be seen, the first step of degradation of mag-p(APTMACl) cryogels with adsorbed arsenate anions started from 50 to 205 °C with 14.8% weight loss. The second step of degradation was between 250 and 350 °C, and the third one was between 370 and 577 °C with 55% and 72.9% weight losses, respectively. At the end of the thermal degradation steps, the fourth one started from 580 °C to 750 °C with 90.1% weight loss. For comparison, without arsenate ions mag-p(APTMACl) cryogels degraded at up to 750 °C with 64% wt losses. Thus proving the interaction of magnetic ferrite with arsenate ions leads to less thermal stability of the mag-p(APTMACl) cryogel composites.

3.7. The arsenate adsorption from different media

Toxic substances such as arsenate can seriously threaten environments and are dangerous to human health owing to their poisonous nature as can be encountered in many places due to natural geological disasters and human activities such as sea, lakes and even tap waters (Chen et al., 2007; Guan et al., 2009; Sarkar et al., 2010; Smedly and Kinniburgh, 2002). Consequently, the removal of arsenate from different aquatic environments has great significance, therefore; here the removal of arsenate anions in various arsenate contaminated aquatic environments such as DI water, seawater, and tap water were investigated using 0.05 g p(APTMACl) cryogels at 400 ppm 100 ml corresponding arsenate solutions, and the corresponding graph is given in Fig. 7(a). As can be seen, the adsorption capacity of p(APTMACl) cryogels for arsenate anions is much better in DI water than seawater and then tap water; they are in the order of 118.2 ± 6.5, 71.1 ± 7.5 and 47.7 ± 5.1 mg/g respectively. However, it is shown here that even harsh environments such as seawater that is contaminated with toxic arsenate can be cleaned by using p(APTMACl) cryogel with some sacrifice in the absortion capacity of p(APTMACl) in comparison to DI water environment. The higher amounts of arsenate removal in seawater in comparison to tap water could be due to the highly cationic nature of adsorbing agents that can can readly exchange chloride with arsenate anions in seawater. As the existence of the excess amounts chloride that is used for disinfectant purpose may hinder the anion exchange capability of p(APTMACl) cryogels in tap water.

3.8. Re-use of p(APTMACl) cryogels on removal of arsenate anions

In industrial applications, the most significant capabilities of the absorbents are their shelf life, reusability, durability and eco-

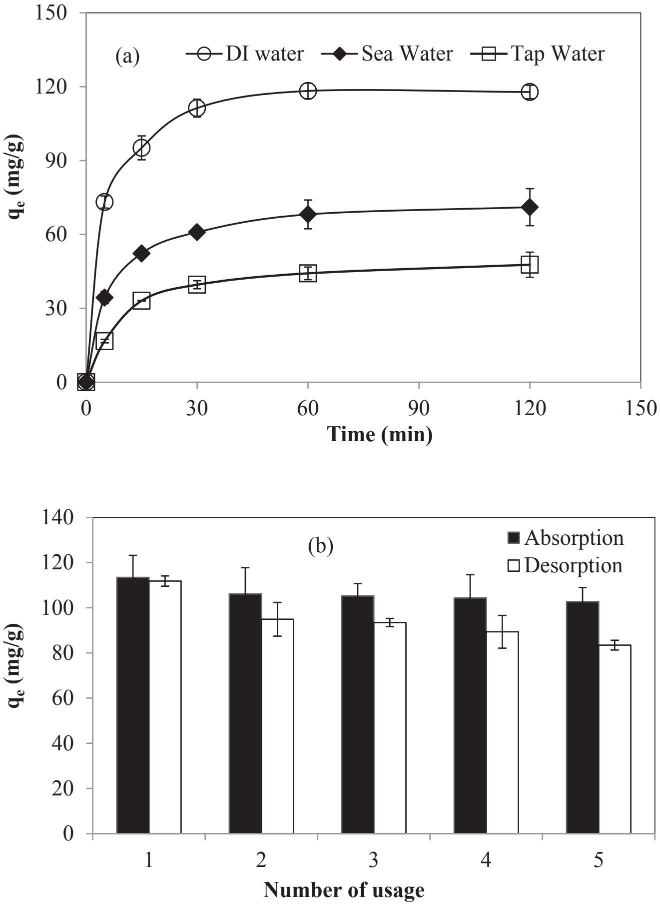

Fig. 7. (a) Arsenate anion adsorption from different aquatic environments: seawater, tap water, and DI water by p(APTMACl) cryogels, and (b) the reusability of p(APTMACl) cryogels for removal of AsO_4^{3-} with adsorption–desorption cycles, [Adsorption medium 400 ppm 100 ml arsenate solution in DI, and the release medium 100 ml 5 M HCl].

friendliness, cost and simplicity. Therefore, reusability of p(APTMACl) cryogels in the removal of arsenate anions was tested by using the same p(APTMACl) cryogel five times sequentially for adsorption/desorption cycles. As shown in Fig. 7(b) the adsorption capacity of p(APTMACl) cryogels decreased from 113.47 ± 9 to 106.13 ± 11, 105.2 ± 5, 104.3 ± 10, and 102.7 ± 6 mg/g for the 1st,2nd, 3rd, 4th, and 5th use, respectively. On the other hand the desorption amount of arsenate in 5 M HCl decreased from 111.82 ± 2 to 94.9 ± 7, 93.5 ± 2, 89.4 ± 7, and 83.5 ± 2 mg/g for 1st,2nd, 3rd, 4th, and 5th use respectively. In other words, the % release of arsenate decreased from approximately 99% to 98, 89, 86 and 81% after fifth usage. Therefore, as demonstrated here p(APTMACl) cryogels can be repeatedly used up to 5 times with less than 20% reduction in arsenate adsorption/release capacity at end of five uses.

4. Conclusion

Herein, it was demonstrated that p(APTMACl) cryogels can be used as a fast absorbent for removal of toxic arsenate anions from aqueous environments. The p(APTMACl) cryogels, which are inherently positively charged, act as an cationic exchanger for arsenate anions. The removal amount of arsenate is about 96% using 0.3 g cryogel from 400 ppm 100 ml of arsenate solution. It was demonstrated that the p(APTMACl) cryogels show faster better (about 30 min), adsorption characteristics in comparison to conventional bulk p(APTMACl) hydrogels (Barakat and Sahiner, 2008). Furthermore, the adsorption of arsenate anions by p(APTMACl) cryogels fits both the Langmuir and Freundlich isotherms, with the former being a better representation as the Langmuir isotherm for adsorption of arsenate provided a very high R^2 value (0.998) and is very close to theoretical and experimental adsorption capacities. Moreover, it was estimated from the adsorption studies that the interaction between the arsenate ion and p(APTMACl) cryogels are ion–ion in nature.

Herein, it was also shown that the p(APTMACl) cryogels can be made magnetic field responsive by loading [$FeCl_2$] and [$FeCl_3$] metal salts mixture with 1:2 mole ratio from their ethanol solution into p(APTMACl) cryogels and reducing with 0.75 M NaOH within cryogel network. These mag-p(APTMACl) cryogels were also shown to be very useful for adsorption of arsenate anions, although some reduction in the adsorption capacity of the cryogel composite was observed. However, cryogels of p(APTMACl) provided promising results for the fast removal of arsenate, as well as other oxyanions from contaminated aqueous water and can be applicable in real contaminated environmental waters. Even though there is reduction due to the existence of other metal ions, etc, still the p(APTMACl) cryogels had fast adsorption capability as well as reusability. The reusability of p(APTMACl) cryogels for removal of arsenate anions was investigated five times in a row without significant loss of adsorption and desorption capacity in the consecutive adsorption–desorption cycles.

Acknowledgments

The project was supported by King Saud University, Deanship of Scientific Research, Research Chair.

The authors are grateful for the financial support by Canakkale Onsekiz Mart University Scientific Research Commission (FBA-2014-284).

References

Barakat, M.A., Sahiner, N., 2008. Cationic hydrogels for toxic arsenate removal from aqueous environment. J. Environ. Manage 88, 955–961.

Chang, F., Qu, J., Liu, H., Liu, R., Zhao, X., 2009. Fe-Mn binary oxide incorporated into diatomite as an adsorbent for arsenite removal: preparation and evaluation. J. Coll. Inter. Sci. 338, 353–358.

Chen, W., Parette, R., Zou, J., Cannon, F.S., Dempsey, B.A., 2007. Arsenic removal by iron modified activated carbon. Water Res. 41, 1851–1858.

Cumbal, L., SenGupta, A.K., 2005. Arsenic removal using polymer-supported hydrated iron(III) oxide nanoparticles: role of donnan membrane effect. Environ. Sci. Pollut. Res. 39, 6508–6515.

Guan, X., Ma, J., Dong, H., Jiang, L., 2009. Removal of arsenic from waters: effect of calcium ions on As(III) removal in the $KMnO_4$-Fe(II) process. Water Res. 43, 5119–5128.

Gulsu, S., Evrim, B.A., Handan, Y., Adil, D., 2010. Poly(glycidyl methacrylate) beads embeded cryogels for pseudo-specific affinity depletion of albumin and immunoglobulin G. Mater. Sci. Eng. C 30, 323–329.

Hedström, M., Plieva, F., Galaev, I., Mattiasson, B., 2008. Monolithic macroporous albumin/chitosan cryogel structure: a new matrix for enzyme immobilization. Anal. Bioanal. Chem. 390, 907–912.

Hwang, Y., Zhang, C., Varghese, S., 2010. Poly(ethylene glycol) cryogels as potential cell scaffolds: effect of polymerization conditions on cryogel microstructure and properties. J. Mater. Chem. 20, 345–351.

Jain, C.K., Ali, I., 2000. Arsenic: occurrence, toxicity and speciation. Water Res. 34, 4304–4312.

Karacan, P., Okay, O., 2013. Ethidium bromide binding to DNA cryogels. React. Funct. Polym. 73, 442–450.

Koc, I., Baydemir, G., Bayram, E., Yavuz, H., Denizli, A., 2011. Selective removal of 17β-estradiol with molecularly imprinted particle-embedded cryogel systems. J. Hazard. Mater. 192, 1819–1826.

Koshy, S.T., Ferrante, T.C., Lewin, S.A., Moonwy, D.J., 2014. Injectable, porous, and cell-responsive gelatin cryogels. Biomaterials 35, 2477–2487.

Kumar, J., Mallampati, R., Adin, A., Valiyaveettil, S., 2014. Functionalized carbon spheres for extraction of nanoparticles and catalyst support in water. ACS Sustain. Chem. Eng. 2, 2675–2682.

Laurent, S., Forge, D., Port, M., Roch, A., Robic, C., Vander Elst, L., Muller, R.N., 2008. Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterization, and biological applications. Chem. Rev. 108, 2064–2110.

Lozinsky, V.I., 2008. Polymeric cryogels as a new family of macroporous and supermacroporous materials for biotechnological purposes. Russ. Chem. B+ 57, 1015–1032.

Pan, Y.F., Chiou, C.T., Lin, T.F., 2010. Adsorption of arsenic(V) by iron-oxide-coated diatomite (IOCD). Environ. Sci. Pollut. Res. 17, 1401–1410.

Sahiner, N., Singh, M., De Kee, D., Jhon, V.T., McPherson, L.G., 2006. Rheological characterization of a charged cationic hydrogel network across the gelation boundary. Polymer 47, 1124–1131.

Sahiner, N., Ozay, O., Aktas, N., Blake, D.A., Jhon, V.T., 2011. Arsenic (V) removal with modifiable bulk and nano p(4-vinylpyridine)-based hydrogels: the effect of hydrogel sizes and quarternization agents. Desalination 279, 344–352.

Sahiner, N., 2013. Soft and flexible hydrogel templates of different sizes and various functionalities for metal nanoparticle preparation and their use in catalysis. Prog. Polym. Sci. 38, 1329–1356.

Sahiner, N., 2014. Fast and high amount of uranyl ion uptake by p(Vinyl phosphonic acid) microgels prepared by UV irradiation technique. Water Air Soil Pollut. 225, 1982–1989.

Sahiner, N., Demir, S., Yildiz, S., 2014. Magnetic colloidal polymeric ionic liquid synthesis and use in hydrogen production. Colloid. Surf. A 449, 87–95.

Sahiner, N., Yildiz, S., 2014. Preparation of superporous poly(4-vinyl pyridine) cryogel and their templated metal nanoparticle composites for H_2 production via hydrolysis reactions. Fuel Process. Technol. 126, 324–331.

Sahiner, N., Seven, F., 2014a. Energy and environmental usage of superporous poly(2-acrylamido-2-methyl-1-propan sulfonic acid) cryogel support. RSC Adv. 4, 23886–23897.

Sahiner, N., Seven, F., 2014b. The use of superporous p(AAc (acrylic acid)) cryogels as support for Co and Ni nanoparticle preparation and as reactor in H_2 production from sodium borohydride hydrolysis. Energy 71, 170–179.

Sarkar, S., Blaney, L.M., Gupta, A., Ghosh, D., SenGupta, A.K., 2008. Arsenic removal from groundwater and its safe contaminant in a rural environment: validation of a sustainable approach. Environ. Sci. Technol. 42, 4268–4273.

Sarkar, P., Pal, P., Bhattacharyay, D., Banerjee, S., 2010. Removal of arsenic from drinking water by ferric hydroxide microcapsule-loaded alginate beads in packed adsorption column. J. Environ. Sci. Health A Toxic/Hazard Subs. Environ. Eng. 45, 1750–1757.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behavior, and distribution of arsenic in natural waters. Appl. Geochem. 17, 517–568.

Tsai, Y.C., Huang, J.D., Chiu, C.C., 2007. Amperometric ethanol biosensor based on poly(vinyl alcohol)-multiwalled carbon nanotube–alcohol dehydrogenase biocomposite. Biosens. Bioelectron. 22, 3051–3056.

USEPA, October 2001. Office of water. Fact Sheet: EPA to Implement10ppb Standard for Arsenic in Drinking Water. http://www.epa.gov/safewater/ars/S.

Wang, C., Dong, X.Y., Jiang, Z., Sun, Y., 2013. Enhanced adsorption capacity of cryogel bed by incorporating polymeric resin particles. J. Chromatog. A 1272, 20–25.

Wang, C., Bai, S., Tao, S.P., Sun, Y., 2014. Evaluation of steric exclusion chromatography on cryogel column for the separation of serum proteins. J. Chromatog. A 1333, 54–59.

Welch, A.H., Lico, M.S., Hughes, J.L., 1988. Arsenic in underground water of the Western United States. Ground Water 26, 333–347.

Yao, K., Yun, J., Shen, S., Wang, L., He, X., Yu, X., 2006. Characterization of a novel continuous supermacroporous monolithic cryogel embedded with nanoparticles for protein chromatography. J. Chromatog. A 1109, 103–110.

Yamamoto, T., Kim, S.I., Chaichanawong, J., Apiluck, E., Ohmori, T., 2009. Removal of aqueous organic pollutants by adsorption catalytic process using mesoporous carbon beads loaded with metal oxides. Appl. Catal. B-Environ 88, 455–461.

Yamamoto, T., Kataoka, S., Ohmori, T., 2010. Characterization of carbon cryogel microspheres as absorbent for VOC. J. Hazar. Mater. 117, 331–335.

Zhoa, X., Zhang, B., Liu, H., Qu, J., 2010. Removal of arsenite by simultaneous electro-oxidation and electro-coagulation process. J. Hazar. Mater. 184, 472–476.