

UTILIZATION OF NOVEL CATIONIC HYDROGELS FOR REMOVAL OF TOXIC ANIONS FROM WATER

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ABSTRACT

Synthesis and application of poly (3-Acrylamidopropyl)-trimethylammonium chloride (PAPTMACl) hydrogels as adsorbents for removal of toxic anions such as arsenate from water were investigated. PAPTMACl hydrogels were synthesized in the form of small cylinders, with using N, N'-methylene-bisacrylamide (MBA) as crosslinker. N,N,N',N'-tetramethylethylenediamine (TEMED) was used as an accelerator, and ammonium persulfate (APS) was used as redox initiator. Arsenic concentration was measured by Inductive Coupled Plasma (ICP) analysis. The hydrogels were regenerated and the adsorbed arsenic fractions were eluted by using 1M NaOH. Swelling and pH sensitivity were measured for hydrogels characterization. Different parameters affecting adsorption process such as metal and hydrogels concentration, retention time, pH, and equilibrium isotherm were investigated.

Results obtained revealed that the hydrogels behave as cationic exchangers and swellable gel adsorbents for As(V). The relatively bigger size of the cylinder shapes of the hydrogels solved the problem of powder separation from water after adsorption. The adsorption process was optimized by using 1.5 g/L hydrogels for 50 ppm As(V) at pH 9 for 360 minutes. The removal efficiency of As(V) was 99.7%.

Keywords: Toxic anions; Adsorption; Cationic hydrogels; Water.

INTRODUCTION

Arsenic contamination of drinking water has been an environmental issue that requires serious attention in many parts of world. Mining activities are responsible for arsenic poisoning in Thailand, while natural sources cause or have caused poisoning of populations as it has happened in Bangladesh, where nearly 30 million people were affected [1]. In January 2001, EPA published a revised MCL for arsenic in drinking water that requires public water suppliers to lower the current arsenic concentrations standard from 50 microgram per liter (part-per-billion, or ppb) to 10 ppb by 2006 [2,3]. The revised standard may affect arsenic cleanup goals for groundwater.

Most arsenic removal technologies are effective in removing the pentavalent form of arsenic. The trivalent form (arsenite) is predominantly non-charged below pH 9.2. Therefore, many treatment systems include an oxidation step to convert arsenite to arsenate. Adsorption is one of the most commonly reported techniques for removal of As(V). This process regulates the fate and mobility of As in soil, and it is mainly linked to different environmental factors such as pH, redox potential, reaction time, oxidation state of arsenic, and type of the adsorbent. Anion exchange resins (AER_s) offer an economical alternative to other As separation methods. Different AER_s have been previously tested and evaluated for pentavalent arsenic removal [4-6]. To the best of our knowledge's and after searching different previous works, no cited references were found for the adsorption of As(V) on hydrogels.

Hydrogels are three dimensional networks of hydrophilic polymers imbibing large amount of water. Due to their ability to change shape and volume in response to external stimuli, hydrogels have been studied intensively for a variety of applications ranging from biology to the environment [7-9]. Amongst hydrogel forming materials, polyelectrolytes with ionizable groups have a special significance, since they impart the network responsive properties. Many applications of polyelectrolytes are related to their ability to bind oppositely charged species to form complexes. Most of the hydrogels used for metal ion removal have or develop negative charges to form complexes with metal ions [10-12]. In this work, cationic hydrogels have been synthesized and investigated for adsorption and removal of negatively charged toxic arsenate anions {As(V)} from water.

EXPERIMENTAL WORK

1. Chemicals

(3-Acrylamidopropyl)-trimethylammonium chloride (APTMACl) (75 wt % solution in water) as monomer, N, N'-methylene-bisacrylamide (MBA) as crosslinker, N,N,N',N'-tetramethylethylenediamine (TEMED) as an accelerator, and ammonium persulfate (APS) as redox initiator were purchased from Aldrich Chemical Company, Inc. (Milwaukee, Wisconsin) as research grade chemicals and used as received. Sodium hydrogen arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$), ACS, 98.0- 102.0% (Alfa Aesar) was used as precursors of As(V). All chemical used were of technically analytical grade.

2. Hydrogel Preparation

For the bulk hydrogels synthesis in the form of cylinders, redox polymerization technique was employed. Figure 1 shows a schematic diagram of polymerization/crosslinking mechanism for the evolution of three-dimensional network formation of cationic hydrogels. Typical hydrogel synthesis is as follows: different amounts of MBA (X) dissolved in water containing APTMACl monomer with accelerator (TEMED) 10-100 μl depending on the monomer amounts. To this solution certain amount of initiator solution, typically 0.5 mole % APS (with respect to monomer

amount) in water is added. Followed by mixing homogenously all the components, the mixture was transferred to plastic straw of 0.8 cm inner diameter and let it react at least 24 h at room temperature. After this time period, the obtained hydrogels cut into ca. 5 mm length of cylindrical shapes and placed into distilled water for 2 days replacing water every 8 hours to remove the unreacted species such as monomer, crosslinker etc. The swollen hydrogels transferred onto Petri dishes and dried in oven ca. 50°C until reaches constant weight. These dried hydrogels were used for the characterization and absorption studies.

3. Hydrogel Characterization

The swelling experiment and pH sensitivity measurements for the hydrogels were evaluated in distilled water and buffer solutions with different pH values using Hydrion Chemvelope Assorted Buffers (Aldrich Chemical Company Inc.) at room temperature. The buffer solutions were prepared according to the recipe describe by the supplier and the pH values obtained between 2-11 for different buffer solutions which are checked by Corning pH meter 430 which was also calibrated by using standard buffer solutions for pH values 4, 7, and 10, the product of Fischer Company.

4. Adsorption Experiments

Batch adsorption experiments were conducted in a pyrex glass flasks, with 500 mL capacity, a magnetic rod was used for stirring. For each flask, 500 mL of a solution containing a specific amount of the hydrogels was transferred. The pH values of the solutions were adjusted from 3 to 9 with 0.5M NaOH and 0.5M HClO₄ and measured with an Orion Model 801A pH meter. The pH was kept at a specific value during experiments using a pH controller (New Brunswick Scientific, Edison, NJ). The experiments were carried out for 360 minutes. A 10-mL sample was drawn by syringe every 30 minutes during the experiments. The liquid samples were filtered for analysis through 0.45 µm syringe filters (Gelman Acrodisc syringe filter with 25 mm diameter, and Nylon membrane of 0.45 µm pore size, PN4436T, Pall Gelman Laboratory, Ann Arbor, Michigan). The adsorbed arsenic fractions were eluted from the hydrogel using 1M NaOH. Finally, the hydrogel was washed with bi-distilled water for reusing. Arsenic concentrations in solutions were analyzed by Inductive Coupled Plasma (ICP) Optical Emission Spectrometer (model Optima 5300 DV PerkinElmer).

RESULTS AND DISCUSSION

1. Hydrogel Characterization

The most common methods for hydrogels characterization are the investigation of swelling behaviors and sensitivity experiments. The swelling experiments of 1% X-ed cationic bulk hydrogels of APTMACl were performed in distilled water at room temperature, and water diffusion coefficient was calculated. The certain amount of dried gel placed in distilled water and the water intake of initially dry hydrogel was

followed in terms of weight increase with time. The hydrogel was removed from the swelling medium occasionally and, after blot drying and reweighing, it was replaced back into the same media. The percentage swelling value (%S) is calculated applying the following equation

$$\%S = \frac{w_t - w_0}{w_0} \times 100 \quad (1)$$

Where w_0 and w_t are the weights of hydrogels initially and at time t . Figure 2-A shows the swelling behavior (%S) of 1 % X-ed cationic hydrogel in water. The max % S value of around 2400 was reached after 6 hours. As soon as glassy hydrogels was contacted with water, hydrogels started to uptake water and began to swell. Diffusion involved transport of water into preexisting or dynamically formed spaces amongst polymer chains. Swelling of a hydrogel requires larger scale of segmental motion resulting in an increase in the distance of separation between chains. Due to the importance of crosslinked swellable hydrogel in many fields such as biomedical, pharmaceutical, etc. [13-15]. Diffusion of water into hydrogel is important and the equation below is used for the calculation of diffusion parameters [16].

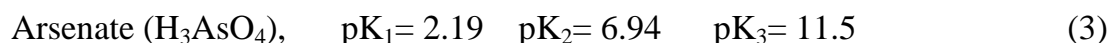
$$F = \frac{M_t}{M_\infty} = kt^n \quad (2)$$

Here, F is the fractional water uptake, M_t and M_∞ is the amount of water absorbed at time t and at infinity (at equilibrium) time in sec, respectively, and k is constant incorporating characteristic of macromolecular network and diffusing species. The n is the diffusion exponent that elucidates the transport mechanism. Equation 2 is applied at the initial 60 % of normalized solvent absorption of the swelling curve. To determine the diffusion coefficient, the plot of $\ln F$ vs $\ln t$ was constructed and shown in Figure 2-B. The two limit values for n were 0.5 and 1, which corresponds to Fickian (Case I) and non-Fickian (Case II) type of diffusions, respectively. From the slope of Figure 2-B, it was found that the value of n was between 0.5 and 1 ($n = 0.58$) indicating that the water diffusion into APTMACl hydrogel was non-Fickian or anomalous or case II in character implying slow the relaxation rate of polymer chains. To investigate the pH sensitivity of the different % X-ed cationic APTMACl hydrogel, known amount of dried bulk hydrogels immersed into 100 ml of different pH buffer solutions, and their percent swelling equilibrium (% Seq) values were calculated after 2 days. The constructed % Seq versus pH graph is shown in Figure 3-A, which is characteristic for the behavior of cationic hydrogels. In the figure the most noticeable feature is the sharp change in the % S values between pH 2 and 5, which corresponds to a transition from charged to uncharged state on the hydrogel network. Additionally, Figure 3-A shows that the pH sensitivity disappeared with the increase in the amount of crosslinker. It is conceivable by the fact that the increase in the amount of crosslinker leads to an increase in the density of the crosslinks per unit volume restraining the hydrogel from swelling. In other words, the more the number of crosslinks among the polymer chains, the less the extent of swelling. Different % X-ed

known amount of cationic hydrogels placed into 250 ml buffer solutions of pH 2 for one day and after weighing and washing with distilled water superficially, they were transfer into 250 ml of pH 11 buffer solutions and same course of action was carried out for a week (Figure 3-B). The alternating swelling and deswelling (shrinking) experiments clearly demonstrate that the pH sensitivity was attenuating with the increase in the amount of crosslinker used during the synthesis. Also, another visible feature of Figure 3-B is that the curves were not as smooth as expected for a basic or cationic hydrogels and this effect becomes more pronounced with the decrease in the amount of crosslinker. This is also perceivable because the used buffer solutions were of different kinds since it is difficult to prepare buffer solutions from same materials with the whole pH range and same ionic strength from same salts.

2. Adsorption and Removal of Arsenate

The adsorption behavior of As(V) on the PAPTMACl hydrogels as affected by solution pH at different adsorption times is shown in Figure 4. The initial As(V) and the hydrogels concentrations were 50 ppm and 0.6 g/L, respectively. The pH of the solution has a strong effect on the adsorption and removing process of As(V) from solution. At any pH value, the As(V) increased gradually with time attaining maximum values after 360 minutes. However, the removal of As(V) has not been found to be significant at low pH values but increased rapidly with increase of the pH. The maximum values of As(V) removal efficiency were 32.9, 58.4, 77.5 and 93.1 % at pH values of 3, 5, 7 and 9, respectively. The dependant of As(V) adsorption on the pH can be attributed to the following; the propensity for ionization is expressed by pK_a the constant of dissociation. For arsenate values are as follows [17]:



These ionization steps of arsenat are significantly affected by change in pH values as indicated in the redox potential (Eh)/pH relationship (Robins [18] and Welch [19]). This Eh/pH relationship is a key in understanding arsenic mobility in water and the effectiveness of arsenic water treatment systems. Figure 5 shows the effect of the hydrogels dosage on the As(V) removal. The removal efficiency increases by increasing the hydrogels concentration. The As(V) removal reached a maximum value of 98.1 % with hydrogels dosage of 1 g/L after 360 minutes. A further increase in the hydrogels dosage slightly increased the removal efficiency and facilitated the As(V) removal at a shorter time. About 99.7 % of the As(V) was removed after 360 minutes of treatment with 1.5 g/L hydrogels, and after 240 minutes with 2 g/L hydrogels. The effect of varying As(V) concentration on its removal rate is shown in Figure 6. The limitation of surface sites for the reaction may control the As(V) adsorption. By using 0.6 g/L hydrogels, the maximum removal efficiency values of 97.6, 93.1, 80.4, and 73.1 % were achieved for As(V) concentration values of 25, 50, 75, and 100 ppm, respectively. The results clearly demonstrate that the As(V) adsorption process is promising at low concentrations of the pollutant. This is also true for heterogeneous catalytic systems where the reaction occurs at the interface between two phases. The rate of the reaction was calculated by plotting C/C_0 , for As(V) concentration of

50 ppm with 0.6 g/L hydrogels at pH of 9, as a function of time, as shown in Figure 7. Here C_0 and C are the initial and remaining As(V) concentrations in the solution, respectively. The plot gave an exponential form which confirmed the strong dependence of the adsorption process on the time of the reaction. Figure 8 shows the As(V) equilibrium isotherm for the resin at the same experimental conditions of Figure 7. In the lower concentration regime, the hydrogels exhibit a higher exchange capacity, followed by a crossover at the higher residual As(V) concentration.

CONCLUSION

PAPTMACl hydrogels were synthesized and evaluated as adsorbents for removal of toxic anions such as arsenate from water. The hydrogels behave as cationic exchangers and swellable gel adsorbents for As(V). The adsorption process was optimized by using 1.5 g/L hydrogels for 50 ppm As(V) at pH 9 for 360 minutes. The removal efficiency of As(V) was 99.7%. The hydrogel cylinders were easily separated from water after adsorption. The hydrogels were regenerated and the adsorbed arsenic fractions were eluted by using 1M NaOH.

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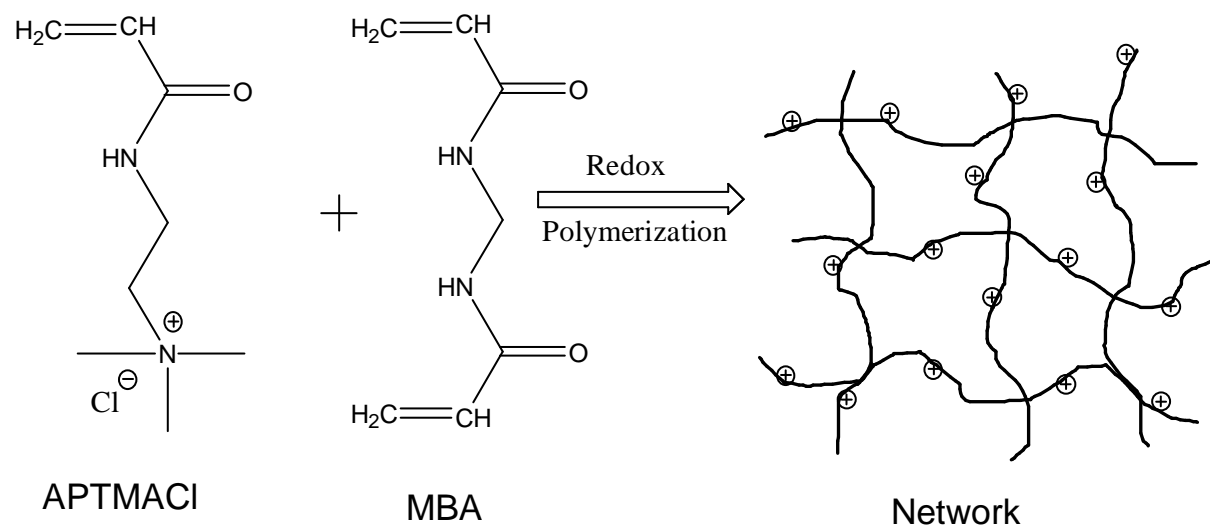


Figure 1. Schematic of polymerization/crosslinking mechanism for the Evolution of three-dimensional network formation of cationic hydrogels

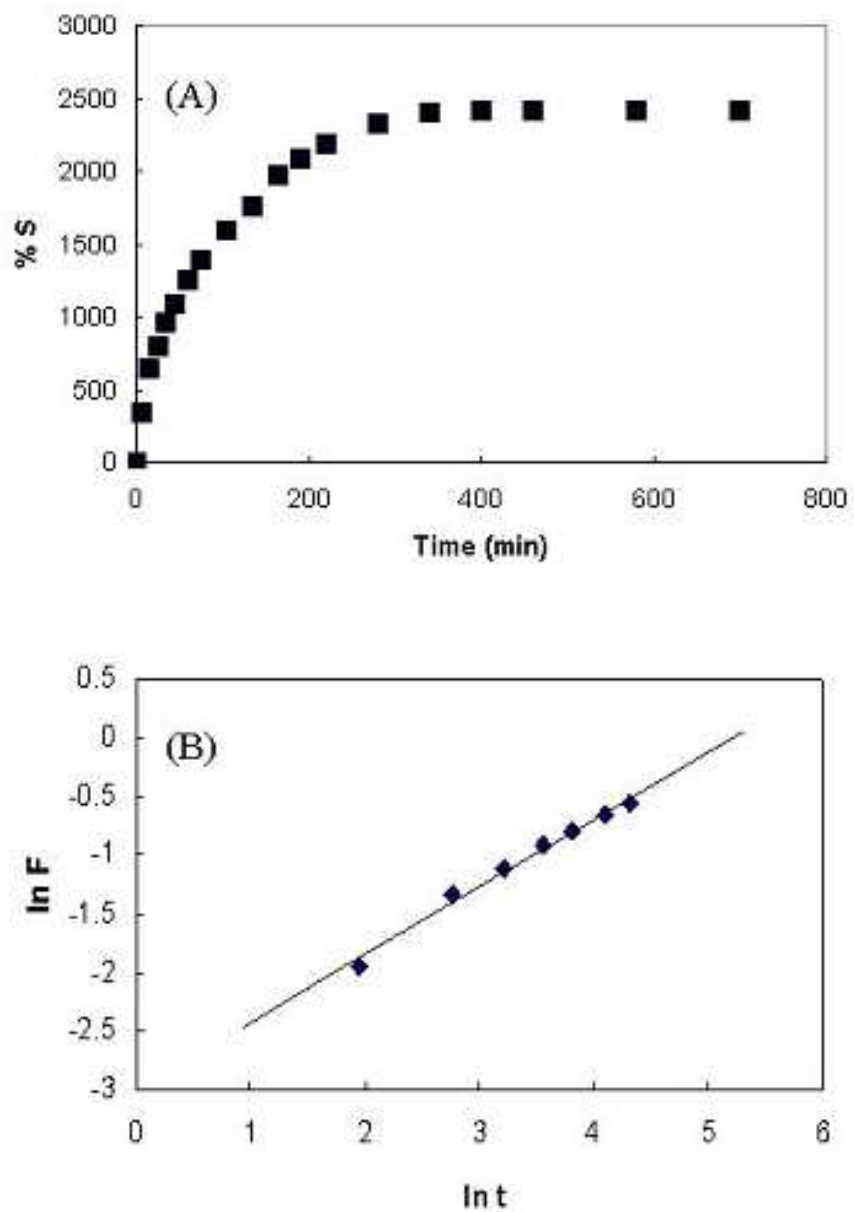


Figure 2. Swelling kinetic curves of (A) 1% crosslinked APTMACl hydrogel in water. (B) ln F vs. ln t for determination of diffusion type

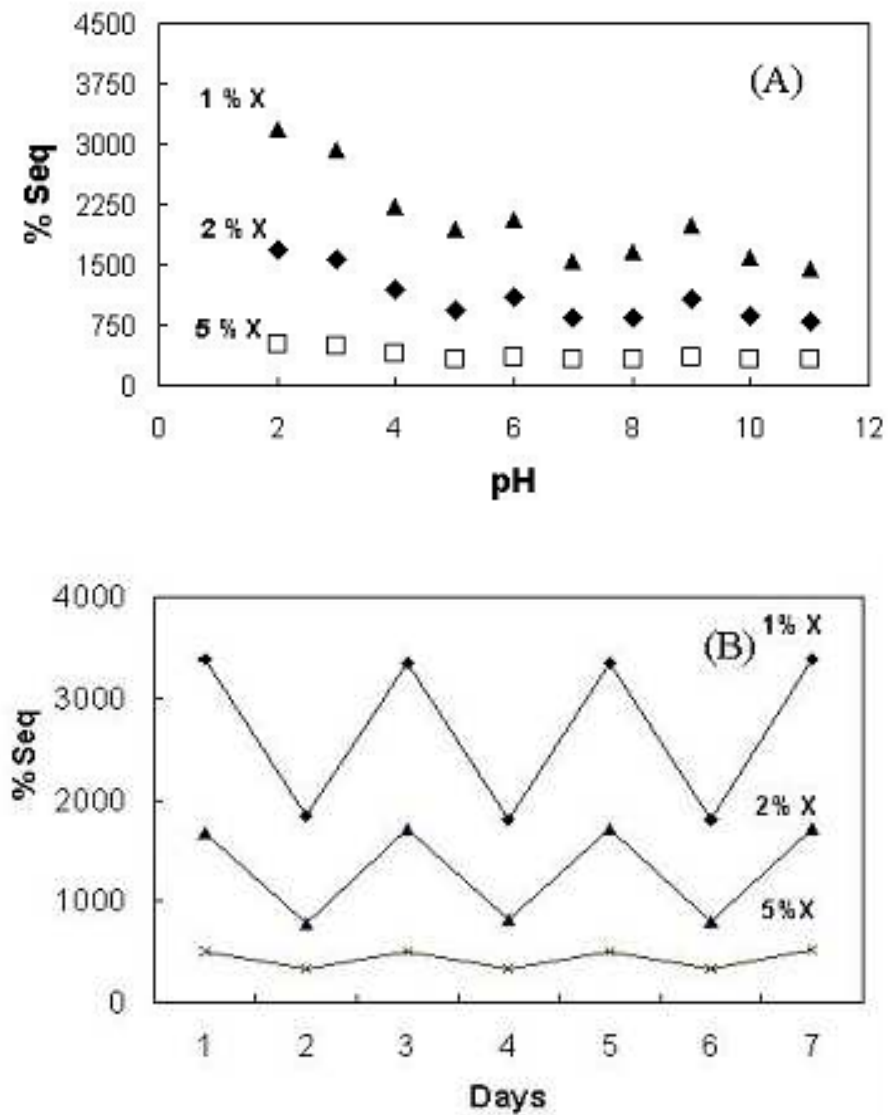


Figure 3. (A) pH sensitivity of different % crosslinked (X-ed) cationic APTMACl hydrogels in buffer solutions. (B) The reversible pH response of different % X-ed APTMACl hydrogels

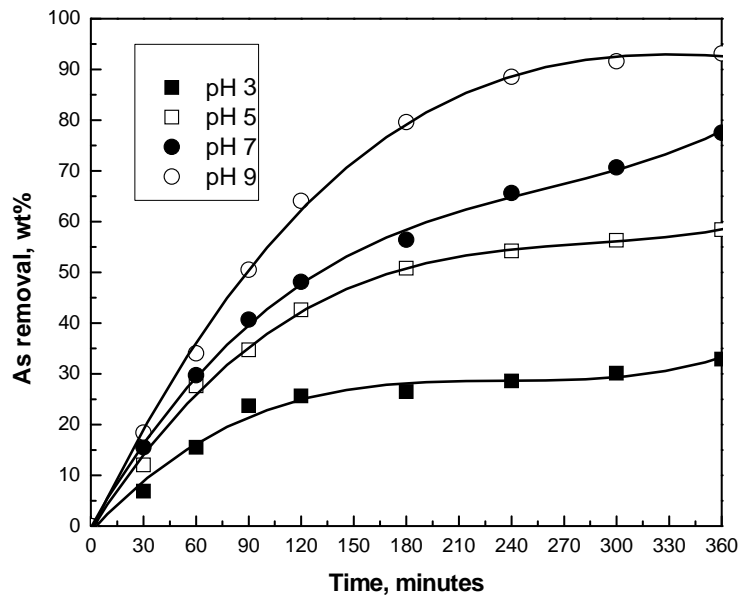


Figure 4. pH effect on the As(V) removal by the hydrogels
As(V) conc. 50 ppm, hydrogel conc. 0.6 g/L

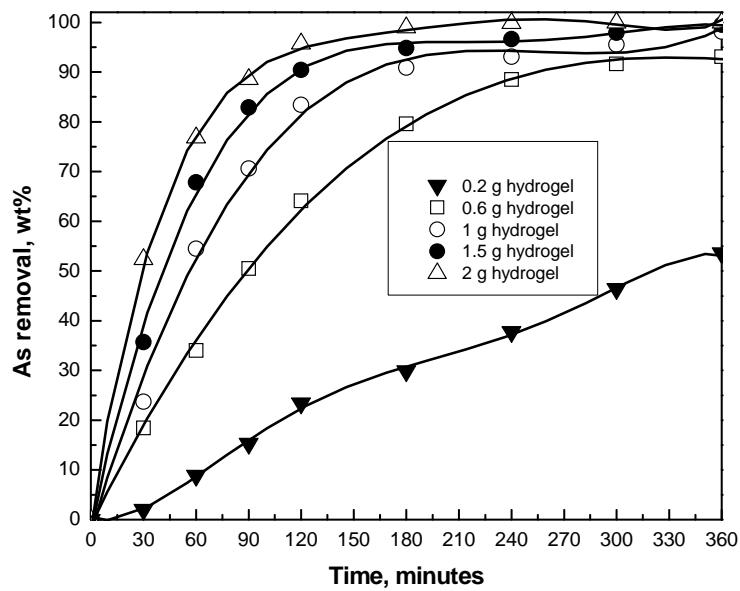


Figure 5. Effect of the hydrogel concentration on the As(V) removal
As(V) conc. 50 ppm, pH 9

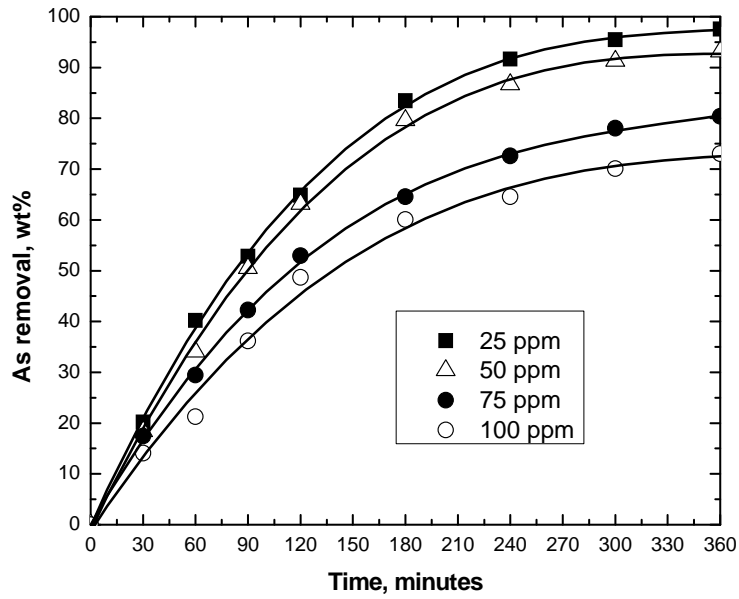


Figure 6. Effect of As(V) concentration on its removal by the hydrogels Hydrogel 0.6 g/L, pH 9

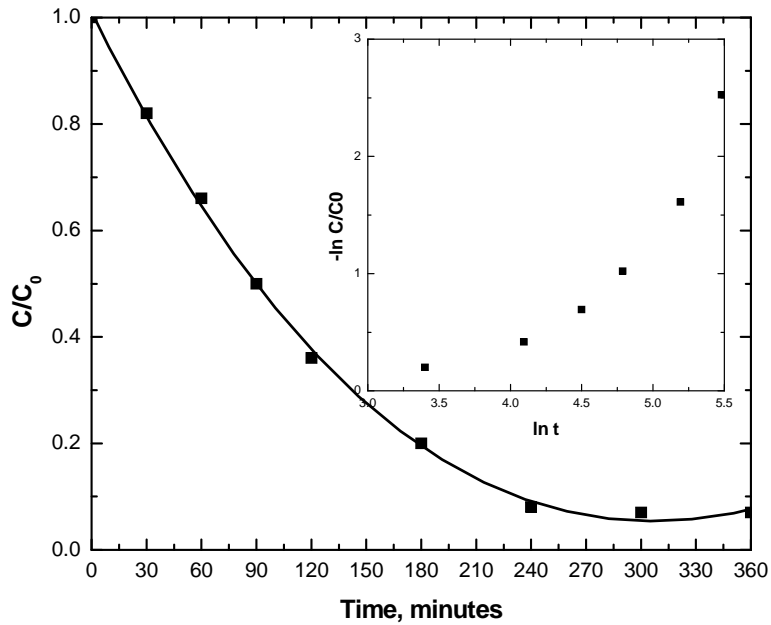
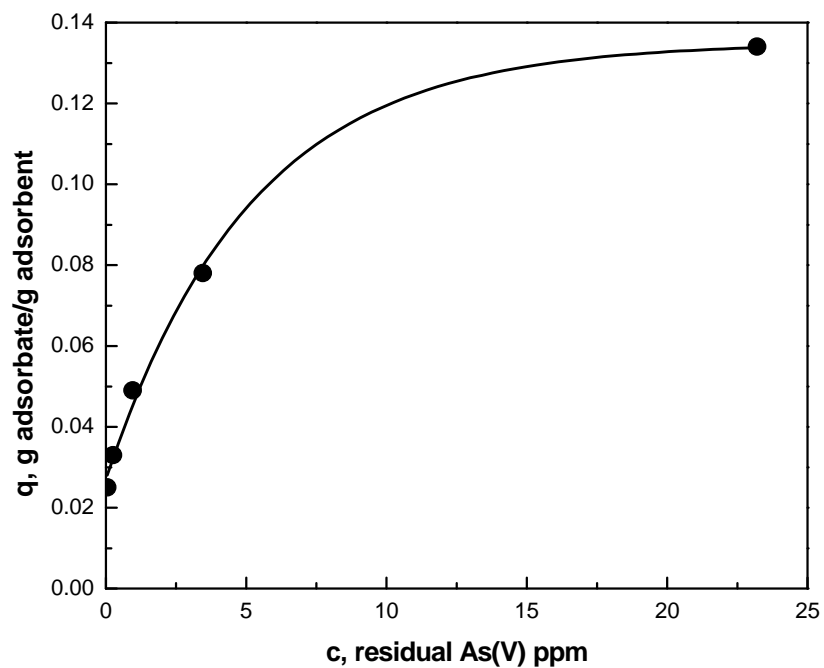


Figure 7. Rate of the adsorption reaction of As(V) onto the hydrogels As conc. 50ppm, hydrogel conc. 0.6g/L, pH 9



**Figure 8. As(V) equilibrium isotherms for the cationic hydrogel
As(V) initial conc. 50ppm, pH 9, equilibrium time 360 minutes**