Removal of arsenic from aqueous solutions using aminated poly(glycidyl methacrylate)

Hyunju Park, Duc Canh Nguyen, Choon-Ki Na, Trung Huu Bui and Kim Heung Sun

ABSTRACT

Removal of arsenic from water is significantly needed to supply safe drinking water worldwide. Here, a new and superior polymer of aminated poly(glycidyl methacrylate) (poly(GMA)-Am) adsorbents was fabricated and examined for effective removal of arsenic from water. The major result was that the arsenic adsorption of the poly(GMA)-Am adsorbents was greatly affected by the degree of amine of amination reagents. The poly(GMA)-Am-DETA fabricated by DETA reagent showed the highest arsenic adsorption efficiency, which was superior to two commercial anion exchange resins. A fast kinetic adsorption of arsenic by the poly(GMA)-Am-DETA was obtained within 1 h. The maximum adsorption capacity of the poly(GMA)-Am-DETA calculated by the Langmuir isotherm for As(V) and As(III) was found to be 78.7 and 13.5 mg/g, respectively. The Dubinin–Radushkevich model showed the arsenic adsorption on poly(GMA)-Am-DETA was governed by physical interaction, possibly due to its possessing a high density of ammonium functional groups covalent bonding to the polymer matrix. Regeneration of the poly(GMA)-Am-DETA exhibited no deterioration of the arsenic adsorption efficiency up to five cycles, where the desorption can be simply achieved with 0.1 M HCl solution. These results suggest a high potential of the reusable poly(GMA)-Am-DETA for effective removal of arsenic from drinking water.

Key words | amination, anion exchanger, arsenic removal, glycidyl methacrylate, sorption capacity

INTRODUCTION

Arsenic has become one of the most common and harmful environmental pollutants, especially in water. Arsenic is well known as a toxic and carcinogenic metalloid which can cause adverse effects on human health including skin, lung, bladder, liver, kidney, and prostate cancers (Bhowmick et al. 2018). In natural water, arsenic exists predominantly in inorganic forms of As(III) or As(V) and their formation depends on the redox potential and pH of water (Nicomel et al. 2016). The World Health Organization (WHO) has set the maximum safe concentration of arsenic in drinking water to be 0.01 mg/L (WHO 1993). Thus, the need to develop effective technology for arsenic removal has motivated extensive research.

Many techniques, such as adsorption, membrane separation, coagulation and precipitation, and lime softening have been developed for arsenic removal from water (Park et al. 2015). Among them, the adsorption process appears to be the most promising technique for removal of arsenic from water because of its simplicity, cost-effectiveness and removal-effectiveness (Bui et al. 2017). A variety of adsorbents have been developed and studied for arsenic removal, such as metal (hydr)oxides, activated carbon, and functional polymers (Nguyen et al. 2015; Lata & Samadder 2016; Fiyadh et al. 2018). Among them, functional polymers have attracted increasing interest in removal of arsenic from groundwater and drinking
water because of the simplicity of the process, easy separation, and regeneration process (Korngold et al. 2001). In addition, functional polymers with porous structures have been considered as promising hosts for the development of hybrid materials with inorganic nanoparticles for the purpose of increasing adsorption selectivity (Bui et al. 2018). Recently, there has been an interest in grafted polymers as effective adsorbents because of their selective surfaces with well-controlled characteristics and size distribution (Tatek et al. 2015; Sajid et al. 2018). Poly(glycidyl methacrylate)-based copolymers are ideal candidates for the development of base media that enable the inexpensive controllable production of spherical nanoparticle support media with different geometries, and permit the design of intraparticle properties via a number of versatile ring-opening reactions of pendant epoxy groups (Taleb et al. 2016). Furthermore, the fabrication of these base support media could be optimized to maximize porosity while maintaining high mechanical strength and uniformity of the microscopic media. Namely, these copolymers modified with suitable amines could provide high adsorption capacity toward metal ions with high chemical and mechanical stability. For example, Nastasovic et al. (2004) have reported poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) by modifying poly(glycidyl methacrylate) with ethylene diamine for removal of some heavy cation metals (Cu, Co, Ni, and Pd) through a chelating process with high capacity. Similarly, the polyGMA modified with 5-amino-tetrasole and its proton conductivity has been reported (Celik & Bozkurt 2008). However, the potential of these copolymers for arsenic removal is still limited.

To the best of our knowledge, no systematic research on poly(glycidyl methacrylate), or poly(GMA)-Am, for arsenic removal has been reported in the literature. Therefore, the aim of this study is to develop the poly(GMA)-Am adsorbents for effective removal of arsenic from water. A variety of poly(GMA)-Am adsorbents using different amination reagents were prepared and tested for arsenic adsorption. A poly(GMA)-Am adsorbent showing the highest arsenic adsorption efficiency was then selected for evaluation of the arsenic adsorption performance and reusability. This study contributes to a novel and versatile ion exchanger with a high capacity of arsenic removal from water for further consideration of material application and development.

MATERIALS AND METHODS

Materials

Glycidyl methacrylate GMA (>98%, Junsei, Japan), N,N'-methylene bis-acrylamide microbeads (MBA) (Sigma-Aldrich), potassium persulfate (K2S2O8, analytical reagent grade), and cyclohexane (Sigma-Aldrich) were used as the monomer, cross linker, initiator, and solvent, respectively. Ethylamine (EA, 97%, Sigma-Aldrich), ethylenediamine (EDA, 97%, Daejung), diethylenetriamine (DETA, 97%, Daejung Chemical Co., Korea), dimethylamine (DMA, 40% in H2O, Sigma-Aldrich), and trimethylamine (TMA, 30% in H2O, Yakuri, Japan) were used as the amination reagents. All chemicals for the arsenic study were of analytical grade and purchased from Sigma-Aldrich. The As(III) and As(V) stock solutions (1,000 ppm) were prepared by dissolving NaAsO2 and Na2HAsO4·7H2O in deionized (DI) water, respectively. These solutions were further diluted with DI water (or 0.01 M acetate buffer solution, pH 4.7) to achieve the desired concentration. Commercial anion-exchange resins, SAR10 (~N+(CH3)3Cl−, Samyang Co., Korea) and WA30 (~(CH2)nN+(CH3)2OH−, Samyang), which are strong base and weak base anion-exchange resins, respectively, were used in comparative studies.

Preparation of poly(GMA)-Am adsorbent

The poly(GMA)-Am adsorbents in this study were fabricated as follows (Figure 1). First, the poly(GMA) was synthesized by the polymerization process of GMA initiated by K2S2O8 in the presence of MBA. About 200 mL of an aqueous solution containing 0.5 g of MBA and 1.0 g of K2S2O8 was charged to a three-necked flask equipped with a reflux condenser and an overhead mechanical stirrer. A mixture of GMA (10 mL), cyclohexane (10 mL), and Tween 80 (0.5 g) was added drop-wise to the three-necked flask while stirring and heating up to 70 °C, and then, the contents were stirred vigorously for 4 h at 70 °C. After completion of the reaction, the polymerization product (poly(GMA)) was separated.
gravitationally and washed thoroughly with deionized water and methanol, to remove the physically absorbed reactants, and subsequently dried at 60 °C. The dried poly(GMA) was pulverized and then sieved into particles ranging from 0.420 mm to 0.710 mm using a 20–40 mesh sieve. Second, the obtained poly(GMA) was subjected to an amination reaction to produce a poly(GMA)-Am. To conduct the amination reaction, the poly(GMA) (5 g) was transferred to a glass bottle containing amines (20 mL), and the mixture was shaken at 150 rpm and 60–100 °C, for 4 h. The product was washed thoroughly with DI water, and dried at 60 °C, until a constant weight was obtained. Different poly(GMA)-Am adsorbents including poly(GMA)-Am-EA, poly(GMA)-Am-EDA, poly(GMA)-Am-DETA, poly(GMA)-Am-DMA, and poly(GMA)-Am-TMA were fabricated by using their related amination reagents of EA, EDA, DETA, DMA, and TMA, respectively.

Analysis

The arsenic concentration was analyzed by an inductively coupled plasma–mass spectrometer (ICP-MS, Varian 820-MS, Varian, Australia). Morphology of the poly(GMA)-Am adsorbents and the original poly(GMA) was conducted using a scanning electron microscope (SEM, S-4800, Hitachi S-4800, Japan).

Batch sorption experiments

Batch sorption experiments were carried out in 100 mL HDPE (high density polyethylene) bottles containing 100 mL working solution of known concentration of As(V) (or As(III)) and adsorbent and continuously shaken at 120 rpm and 25 °C. After shaking for a predetermined time, the solution was filtered (0.45 μm filter) and analyzed for arsenic concentration. The effect of solution pH on As(III) (or As(V)) was conducted in the pH range from 3 to 11, using HCl or NaOH solution for adjusting. For kinetic adsorption, 1.0 g/L of adsorbent added into 200 mL of either As(III) or As(V) solution (1 mg/L) was stirred for up to 24 h at 25 °C. At each predetermined time, 5 mL of solution was withdrawn, quickly filtered through a 0.45 μm filter, and stored in a regenerator (4 °C) for the arsenic analysis. An adsorption isotherm was performed by adding 0.1 g/L of poly(GMA)-Am into a varying arsenic solution having a concentration in the range of 0.5–5 mg/L at an initial pH of 4.7 and continually shaken at 25 °C for 24 h.

Regeneration study was done within five successive cycles of adsorption-desorption process. The desorption of arsenic-adsorbed poly(GMA)-Am was performed with 100 mL solution of 0.1 M HCl and shaking for 4 h. Note that the 4 h was enough for the desorption process (efficiency of 95.1 ± 3.5%, data not shown). After the desorption was complete, the adsorbent was filtered and washed with deionized water. This washed adsorbent was ready for the next adsorption cycle.

RESULTS AND DISCUSSION

Morphology study of poly(GMA)-Am

For a variety of poly(GMA)-Am materials with different amination reagents (including EA, DETA, EDA, DMA, and TMA) SEM analyses were performed and compared with the original poly(GMA). Figure 2 shows the change of morphology distribution of the poly(GMA) (including EA, DETA, EDA, DMA, and TMA) before and after the aminating process with different amination reagents using SEM analysis. It is clearly seen that the amination reaction has caused not great, but significant change of surface morphology of poly(GMA).
the poly(GMA). The surface of all poly(GMA)-Am were much rougher and more porous than that of the original poly(GMA), which could increase the number of adsorption sites of the poly(GMA)-Am for arsenic adsorption. Note that the successful amination process with the additional amine functional groups covalent bonding to the poly(GMA) was fully discussed in our recent study (Tatek et al. 2015).

**Effect of amination degree on the arsenic adsorption**

The high sorption capability of poly(GMA)-Am can be attributed to the high level of interaction of the aminated surface with the anions. Figure 3 shows the comparison of the As(V) adsorption efficiencies among different poly-(GMA)-Am adsorbents including poly(GMA)-Am-EA, poly(GMA)-Am-EDA, poly(GMA)-Am-DETA, poly(GMA)-Am-TMA, and poly(GMA)-Am-DMA. As shown in Figure 3, the choice of the reagents used for surface amination greatly affects the sorption efficiency of each adsorbent toward As(V) species. The aminated surfaces using DETA (poly-(GMA)-Am-DETA) exhibited the highest sorption efficiency (99%) which was higher than that of the EDA (poly(GMA)-Am-EDA, 97%), EA (poly(GMA)-Am-EA, 91%), DMA (poly-(GMA)-Am-DMA, 87%), and TMA (poly(GMA)-Am-TMA,
The Lagergren pseudo-first-order kinetic model is expressed as (Lagergren 1898):

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$  \hspace{1cm} (1)

where $q_e$ and $q_t$ are the adsorption capacities at equilibrium and at time $t$ (mg/g), respectively, and $k_1$ is the rate constant of the pseudo-first-order adsorption (min$^{-1}$).

The pseudo-second-order kinetic equation is given as (Ho & McKay 1999):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (2)

where $k_2$ is the rate constant of the pseudo-second-order adsorption (g/mg min).

Figure 4(a) shows the uptake of both As(III) and As(V) on the poly(GMA)-Am-DETA as a function of time. As shown, there is a fast uptake of arsenic on the poly(GMA)-Am-DETA with an equilibrium condition for both the cases of As(III) and As(V) adsorption within 1 h. The continuing increase of adsorption time (until 24 h) did not increase the adsorption efficiency (data not shown). The uptake data of As(III) and As(V) were examined by the pseudo-first-order and pseudo-second-order kinetic model and are plotted in Figure 4(b) and 4(c) while their parameters are summarized in Table 1. As shown, the pseudo-first-order kinetic model is not a reasonable representation of the adsorption process (Figure 4(b)), showing low regression coefficients $R^2$ and inconsistent $q_e$ values between the modeling and experiment (Table 1). On the other hand, Figure 4(c) shows the linear plot of the pseudo-second-order equation as a straight fitting line with high regression coefficients ($R^2 = 1$) obtained for both the cases of the As(V) and As(III) adsorption. In addition, the theoretical $q_e$ values were also very close to the experimental $q_e$ values. This indicates that the adsorption of arsenic on poly(GMA)-Am is more appropriately described by the pseudo-second-order kinetic model. The possibility of arsenic diffusion kinetics on the poly(glycidyl methacrylate) adsorbent was further examined by the Weber and Morris intraparticle diffusion equation as follows:

$$q_e = K_d t^{1/2} + C$$  \hspace{1cm} (3)

54%). In fact, this adsorption efficiency of the poly(GMA)-Am adsorbents toward arsenate was proportional to the degree of amine functional groups of the amination reagents, which was, in order: triamine (DETA) > diamine (EDA) > primary amine (EA) > secondary amine (DMA) > tertiary amine (TMA). This could be attributed to the fact that the poly(GMA)-Am adsorbent with higher amination degree contained more surface amine functional groups and enhanced the arsenate adsorption through the electrostatic interaction. Additionally, most of the poly(GMA)-Am adsorbents, except the poly(GMA)-Am-TMA, showed overall superior sorption capacities compared to the commercial strong base anion exchange (SAR10) and weak base anion exchange (WA30) resins. Therefore, the highest efficiency poly(GMA)-Am-DETA adsorbent was employed in further studies for arsenic adsorption performances.

**Adsorption kinetics**

Two types of adsorption kinetic forms were used to examine for time-dependent arsenic adsorption data of the poly(GMA)-Am-DETA. The pseudo-first-order and pseudo-second-order equations are generally used as follows.

Figure 3 | Comparison of the As(V) adsorption capacities among poly(GMA)-Am prepared using various amination reagents (EA, EDA, DETA, DMA, and TMA) and two commercial anion exchange resins (strong base SAR10 and weak base WA30). Experiment: [As(V)] = 10 mg/L, [adsorbent] = 1 g/L, pH 4.7 (10 mM acetate buffer solution), 25 °C.
where $k_d$ is the intraparticle diffusion rate constant and $C$ is the intercept of the vertical axis (Hekmatzadeh et al., 2013; Miao et al., 2014).

Figure 4(c) illustrates the intra-particle diffusion kinetics of As(V) to the poly(glycidyl methacrylate) adsorbent. As shown, the diffusion of As(V) species to the adsorbent was governed by two distinct linearity regions, showing two different kinetic mechanisms. The initial region has a much faster diffusion rate of arsenic corresponding to the external mass transfer, whereas the second state represents intra-particle diffusion as the rate controlling step. Indeed, the estimated diffusion rate for the external mass transfer (0.0696 mg/(g·min)) was more than ten times higher than that of the intra-particle diffusion (0.0054 mg/(g·min)). On the other hand, the intra-particle diffusion of As(III) is not clear, which could be due to the neutral charged form of As(III) ($\text{H}_3\text{AsO}_2$).

Table 1  First- and second-order kinetic parameters for As(III,V) adsorption of the poly(GMA)-Am-DETA

<table>
<thead>
<tr>
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<th>Pseudo-first-order kinetics</th>
<th>Pseudo-second-order kinetics</th>
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<tr>
<td></td>
<td>$k_1$ (min$^{-1}$)</td>
<td>$q_e$ (mg/g)</td>
</tr>
<tr>
<td>As(V)</td>
<td>0.0233</td>
<td>0.193</td>
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<tr>
<td>As(III)</td>
<td>0.0207</td>
<td>0.093</td>
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**Figure 4**  Kinetic of As(V) and As(III) on the poly(GMA)-Am-DETA: (a) arsenic uptake with time, (b) pseudo-first-order model, (c) pseudo-second-order model, and (d) intra-particle diffusion. Experiment: [As(V)] (or [As(III)]) = 1 mg/L, [adsorbent] = 1 g/L, pH 4.7 (10 mM acetate buffer solution), 25°C.
Adsorption isotherms

In order to conduct arsenic adsorption isotherm, the experimental data were examined with two typical isotherm models, Langmuir and Freundlich isotherms. The linear forms of the Langmuir (Langmuir 1918) and Freundlich (Freundlich 1906) isotherms are expressed as follows:

\[
\frac{1}{q_e} = \frac{1}{C_e q_m} + \frac{1}{K_L q_m}
\]

and

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]

where \(C_e\) is the equilibrium concentration (mg/L), \(q_e\) is the equilibrium adsorption capacity (mg/g), \(q_m\) is the Langmuir constant related to the maximum adsorption capacity (mg/g), and \(K_L\) is the energy term (L/mg), which varied as a function of surface coverage strictly because of variations in the heat of adsorption. \(K_f\) and \(n\) are the Freundlich constants related to the adsorption capacity of the adsorbent and the magnitude of the adsorption driving force, respectively.

Figure 5 shows the As(V) and As(III) equilibrium adsorption of poly(GMA)-Am-DETA (Figure 5(a)) and their modeling to the linear Langmuir and Freundlich isotherms (Figure 5(b) and 5(c)). As shown in Figure 5(b) and 5(c), the arsenic adsorption on poly(GMA)-Am-DETA selectively followed both the Langmuir and Freundlich isotherm models. The calculated isotherm parameters along with correlation coefficients are given in Table 2. As shown, the plots were found to be linear with high regression coefficients \((R^2 = 0.981–0.994)\) for both Langmuir and Freundlich isotherms, confirming the applicability of these models. The much higher \(K_f\) value of the As(V) adsorption than the As(III) adsorption reflects the much higher affinity of the poly(GMA)-Am toward As(V) species governed by the electrostatic interaction. The maximum adsorption capacity \((q_m)\) of the poly(GMA)-Am for As(V) and As(III) was found to be 78.7 and 13.5 mg/g, respectively.

Although the Langmuir and Freundlich models demonstrate well the isotherms of the arsenic adsorption, they did not explore the specific interaction between the poly(GMA)-Am-DETA and arsenic species. In order to determine the type of adsorption, the adsorption data were further examined by the Dubinin–Radushkevich (D-R) isotherm (Singh...
ln \( q_e \) = ln \( q_m \) – \( ke^2 \) \hspace{1cm} (6)

and

\[ E = -2k^{0.5} \] \hspace{1cm} (7)

where \( E \) is the mean free energy of adsorption, \( k \) is the constant related to the adsorption energy (mol\(^2\) kJ\(^{-2}\)), and \( \epsilon \) is the Polanyi potential, which can be expressed as: \( \epsilon = RT \ln[(1 + (1/C_0)] \). \( R \) is the universal gas constant (kJ mol\(^{-1}\) K\(^{-1}\)) and \( T \) is the temperature (K).

Figure 6 plots the D-R isotherm in linear expression of the poly(GMA)-Am-DETA for both the cases of the As(V) and As(III). The calculated isotherm parameters along with the correlation coefficients are given in Table 2. The values of \( E \) found in this study were 6.9 and 5.25 kJ mol\(^{-1}\) for As(V) and As(III), respectively, indicating the adsorption of arsenic on poly(GMA)-Am-DETA is mostly governed by physical interaction (\( E < 8 \text{ kJ mol}^{-1} \)) (Mahramanlioglu et al. 2002).

**Effect of pH on arsenic adsorption**

The pH of the solution may cause a strong influence on surface charges of the adsorbent, thus it could directly affect the uptake of arsenic species, particularly for the case of anion exchange poly(GMA)-Am-DETA. Figure 7 shows the effect of solution pH on the adsorption equilibrium of As(V) and As(III) on poly(GMA)-Am-DETA. As shown in Figure 7, the As(V) efficiency was maximum and slightly stable in the pH range of 4-7, and the efficiency decreased from pH 4 to 3 and from pH 7 onwards. For As(V) adsorption, as pH increased, the decrease of protonation of the surface amine functional groups of the polymer could result in the
reduction of As(V) adsorption. The lower adsorption at pH 3 can be explained by the low fraction of the anionic form of As(V) (pKₐ₁ = 2.3) to adsorb on the adsorbent. Since As(III) exists under a neutral form at a pH of below 9 (pKₐ₁ = 9.2), the electrostatic interaction can be neglected. Therefore, much lower As(III) adsorption was observed, and its adsorption was more favorable at low pH conditions. The amount of adsorption dropped in the high pH region (pH > 9) because of the increase in negative-charge sites on the adsorbent surfaces. Under this condition, both As(III) and As(V) were in anion form (H₂AsO₄⁻ and HAsO₄²⁻, respectively), which showed low adsorption on the surface adsorbent because of columbic repulsion between the two negative charges of the adsorbent surface and arsenic species (Cheng et al. 2005).

Regeneration efficiency

The regeneration tendency of an adsorbent surface is a basic property that is often considered in choosing the most convenient, cost-effective, and environmentally friendly adsorbent. For poly(GMA)-Am-DETA, a repetitive regeneration experiment for five cycles was conducted using 0.1 M HCl and the results are presented in Figure 8. As shown, the poly(GMA)-Am-DETA exhibited an excellent regeneration efficiency toward arsenic adsorption, which was almost no deterioration of the adsorption efficiency up to the fifth cycle of regeneration.

CONCLUSIONS

In this study, a variety of poly(GMA)-Am adsorbents were successfully synthesized and examined for their capability of arsenic removal. The poly(GMA)-Am prepared from the polymerization of GMA initiated by K₂S₂O₈ in the presence of MBA was aminated using the different amination reagents DETA, EDA, and EA, DMA, and TMA. Most of the fabricated poly(GMA)-Am showed superior sorption capacities compared to two commercial strong base and weak base anion exchange resins (SAR10 and WA30, respectively). The high adsorption capacities of the poly(GMA)-Am-DETA estimated by Langmuir isotherm model for As(V) and As(III) were 78.7 and 13.5 mg/g, respectively. The experimental sorption data were fitted to both Langmuir and Freundlich models and the D-R isotherm showed the interaction between the poly(GMA)-Am-DETA and arsenic species governed by physical interaction. Finally, the regeneration of the poly(GMA)-Am successfully maintained its arsenic adsorption efficiency up to five cycles of adsorption–desorption with a simple desorption using diluted acid (HCl) solution. These results suggest the high potential of the poly(GMA)-Am-DETA for effective removal of arsenic from aqueous solutions.

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