

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 DET A 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

Hyunju Park
Kim Heung Sun
Institute of Engineering Research,
Seoul National University,
1 Gwanak-ro, Gwanak-gu, Seoul 08826,
South Korea

Duc Canh Nguyen (corresponding author)
Sustainable Management of Natural Resources
and Environment Research Group, Faculty of
Environment and Labour Safety,
Ton Duc Thang University,
19 Nguyen Huu Tho Street, Tan Phong Ward,
District 7, Ho Chi Minh City,
Vietnam
E-mail: nguyenducanh@tdtu.edu.vn

Choon-Ki Na
Department of Environmental Engineering,
Mokpo National University,
Jeonnam 534-729,
South Korea

Trung Huu Bui
Faculty of Chemistry,
University of Science, Vietnam National University,
Ho Chi Minh City,
Vietnam

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.* 2013; 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 ($K_2S_2O_8$, 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 H_2O , Sigma-Aldrich), and trimethylamine (TMA, 30% in H_2O , 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 $NaAsO_2$ and $Na_2HAsO_4 \cdot 7H_2O$ 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 ($-N^+(CH_3)_3Cl^-$, Samyang Co., Korea) and WA30 ($(CH_2)_n N^+(CH_3)_2OH^-$, 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 $K_2S_2O_8$ in the presence of MBA. About 200 mL of an aqueous solution containing 0.5 g of MBA and 1.0 g of $K_2S_2O_8$ 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

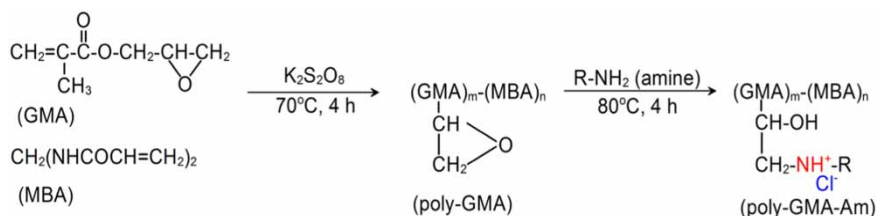


Figure 1 | Scheme of the preparation process and chemical structure of the poly(GMA)-Am-DETA.

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

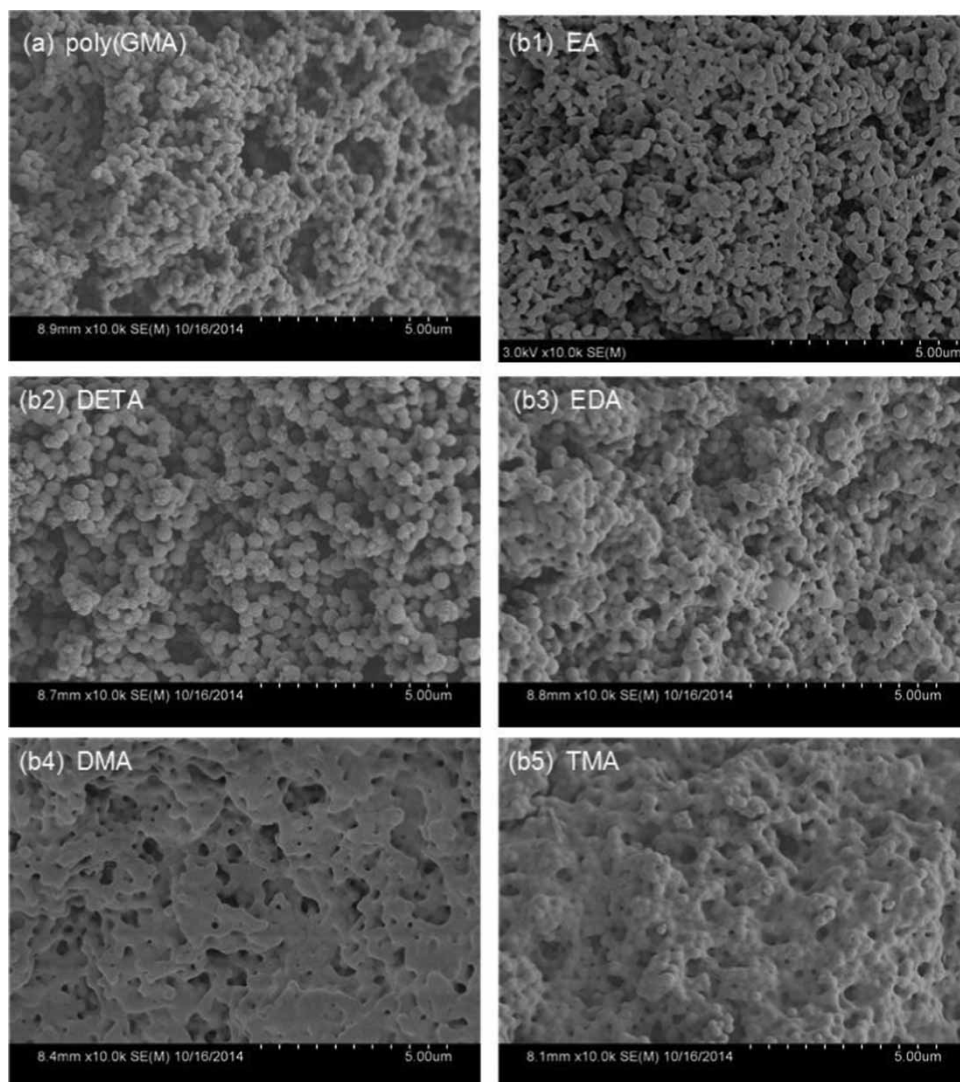


Figure 2 | SEM images of (a) the original poly(GMA) and (b) poly(GMA)-Am prepared using various amination reagents: (b1) ethylamine (EA), (b2) diethylenetriamine (DETA), (b3) ethylenediamine (EDA), (b4) dimethylamine (DMA), and (b5) trimethylamine (TMA).

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,

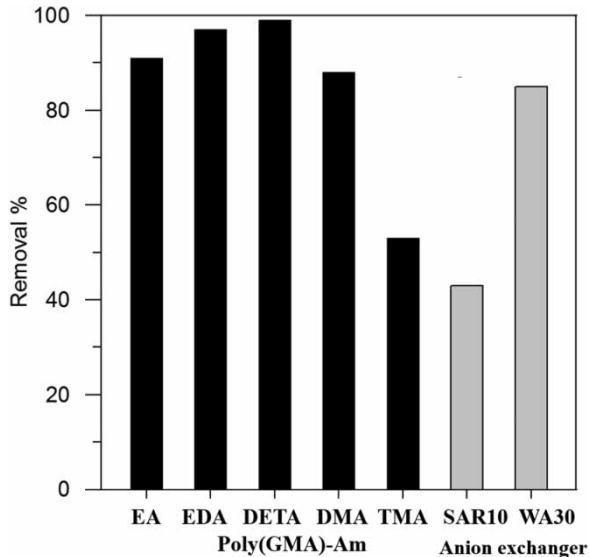


Figure 3 | Comparison of the As(V) adsorption capacities among poly(GMA)-Am prepared using various amination reagents (EA, EDA, DETA, DMA, and TMA) and two commercial anion exchange resins (strong base SAR10 and weak base WA30). Experiment: [As(V)] = 10 mg/L, [adsorbent] = 1 g/L, pH 4.7 (10 mM acetate buffer solution), 25 °C.

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.

The Lagergren pseudo-first-order kinetic model is expressed as (Lagergren 1898):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

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):

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

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:

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

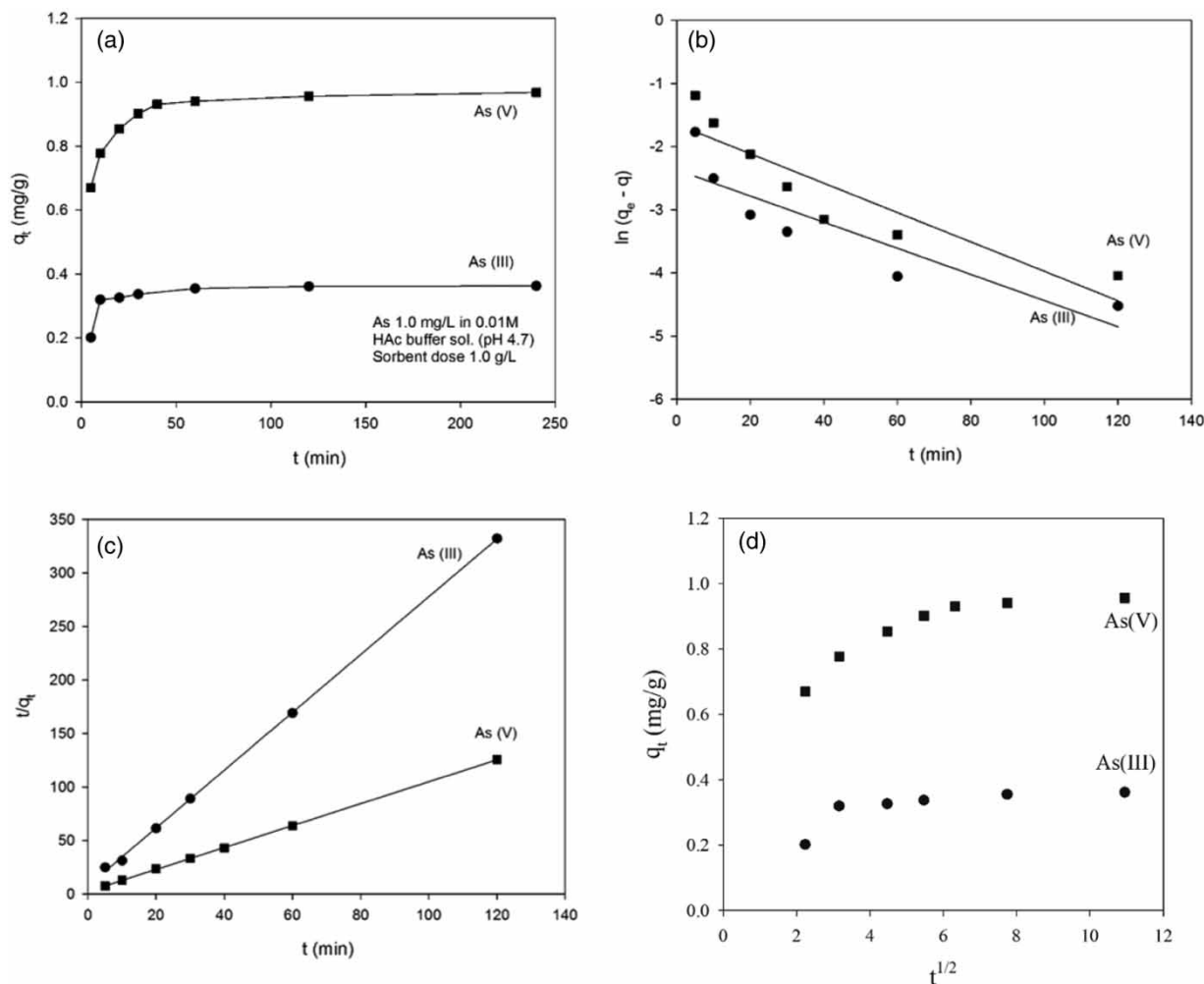


Figure 4 | Kinetic of As(V) and As(III) on the poly(GMA)-Am-DETA: (a) arsenic uptake with time, (b) pseudo-first-order model, (c) pseudo-second-order model, and (d) intra-particle diffusion. Experiment: [As(V) (or [As(III)]) = 1 mg/L, [adsorbent] = 1 g/L, pH 4.7 (10 mM acetate buffer solution), 25 °C.

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

	Pseudo-first-order kinetics			Pseudo-second-order kinetics		
	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (min^{-1})	q_e (mg/g)	R^2
As(V)	0.0233	0.193	0.824	0.488	0.977	1.00
As(III)	0.0207	0.093	0.803	0.74	0.372	0.999

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) (H_3AsO_2).

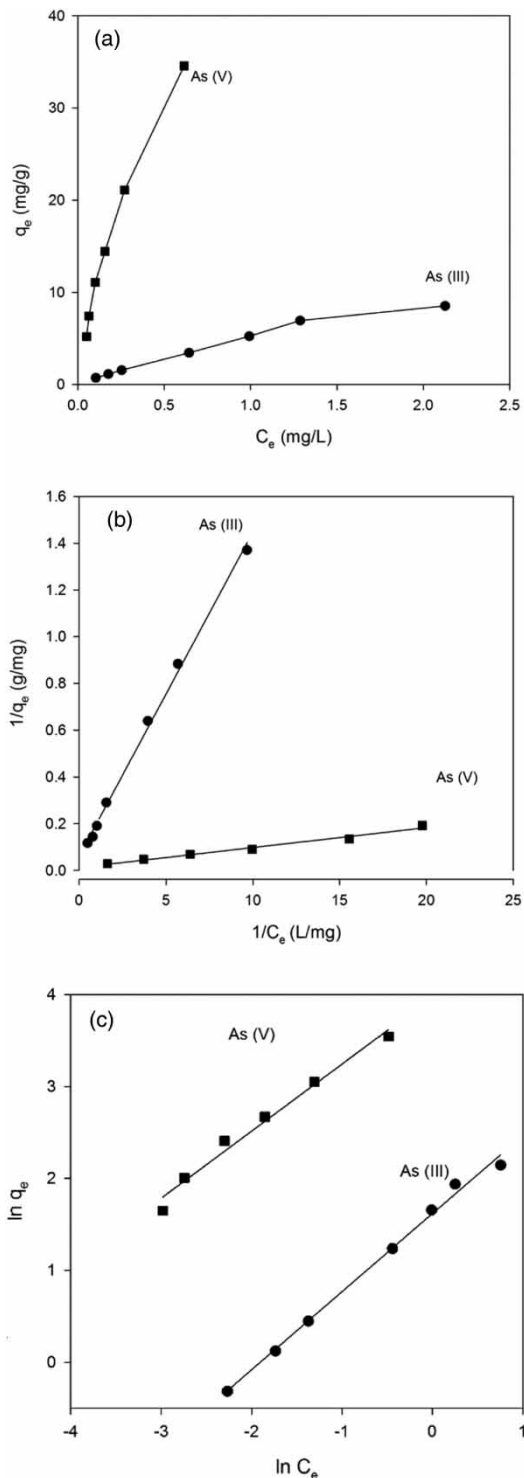


Figure 5 | Equilibrium adsorption of the As(V) and As(III) on the poly(GMA)-Am-DETA at varying initial concentrations: (a) equilibrium adsorption plot, (b) linear Langmuir isotherm regression, and (c) linear Freundlich isotherm regression. Experiment: [AsV] (or [As(III)]) = 0.2–5 mg/L, [adsorbent] = 0.1 g/L, pH 4.7 (10 mM acetate buffer solution), 25 °C, 24 h.

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:

$$\frac{1}{q_e} = \frac{1}{C_e} \cdot \frac{1}{K_L q_m} + \frac{1}{q_m} \quad (4)$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

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

Table 2 | Parameters of the Langmuir, Freundlich, and Dubinin–Radushkevich isotherms of the As(V) and As(III) adsorption on the aminated poly-GMA-DETA

	Langmuir isotherm			Freundlich isotherm			Dubinin–Radushkevich isotherm	
	q_m (mg/g)	K_L (L/mg)	R^2	K_f (mg·g ⁻¹ ·mg·L ⁻¹) ⁻ⁿ	n	R^2	E (kJ mol ⁻¹ K ⁻¹)	R^2
As(V)	78.74	1.484	0.983	53.16	1.371	0.981	7.14	0.992
As(III)	13.53	0.537	0.994	4.96	1.778	0.993	6.06	0.986

& Pant 2004; Kundu & Gupta 2006), which can be expressed as:

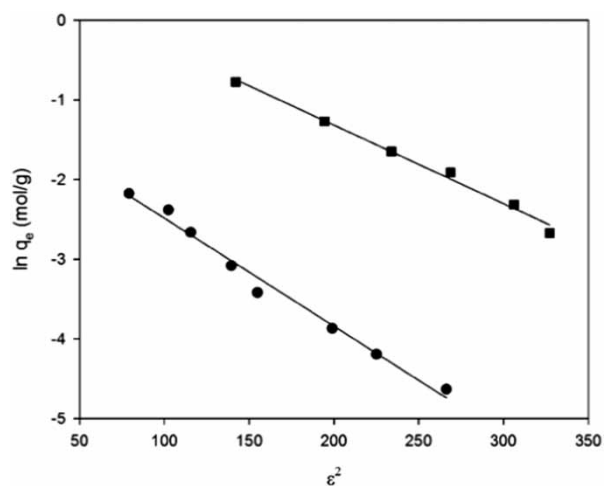
$$\ln q_e = \ln q_m - k\varepsilon^2 \quad (6)$$

and

$$E = -(2k)^{-0.5} \quad (7)$$

where E is the mean free energy of adsorption, k is the constant related to the adsorption energy (mol² kJ⁻²), and ε is the Polanyi potential, which can be expressed as: $\varepsilon = RT \ln[(1 + (1/C_e))]$. R is the universal gas constant (kJ mol⁻¹ K⁻¹) and T is the temperature (K).

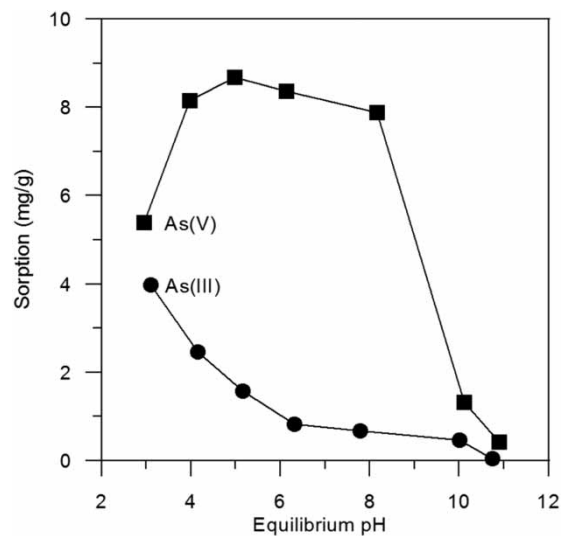
Figure 6 plots the D-R isotherm in linear expression of the poly(GMA)-Am-DETA for both the cases of the As(V) and As(III). The calculated isotherm parameters along with the correlation coefficients are given in Table 2. The values of E found in this study were 6.9 and 5.25 kJ mol⁻¹

**Figure 6** | D-R isotherm modeling for the As(V) and As(III) adsorption on the poly(GMA)-Am-DETA.

for As(V) and As(III), respectively, indicating the adsorption of arsenic on poly(GMA)-Am-DETA is mostly governed by physical interaction ($E < 8$ 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

**Figure 7** | Effect of pH on the adsorption of As(V) and As(III) on poly(GMA)-Am. Experiment: [AsV] (or [As(III)]) = 1 mg/L, [adsorbent] = 0.1 g/L, pH 4.7, 25 °C.

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) ($pK_{a1} = 2.3$) to adsorb on the adsorbent. Since As(III) exists under a neutral form at a pH of below 9 ($pK_{a1} = 9.2$), 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 ($H_2AsO_4^-$ and $HAsO_4^{2-}$, 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

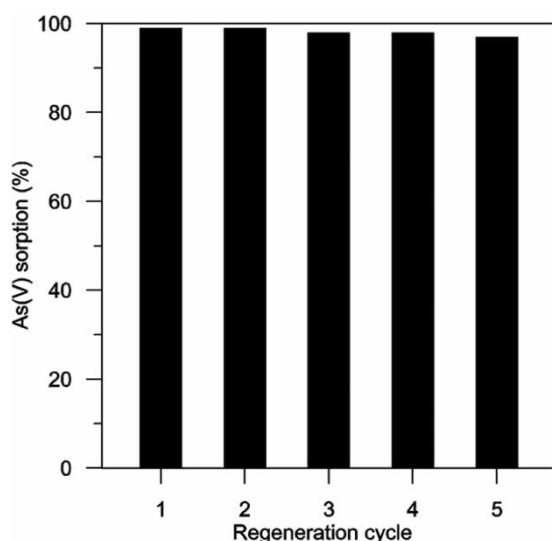


Figure 8 | Adsorption capacity of As(V) as a function of the regeneration cycle number of the poly(GMA)-Am-DETA. Adsorption conditions: $[As(V)]$ (or $[As(III)]$) = 1 mg/L, $[adsorbent]$ = 0.1 g/L, pH 4.7, 25 °C; desorption conditions: $[HCl]$ = 0.1 M, 25 °C.

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 $K_2S_2O_8$ 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.

ACKNOWLEDGEMENTS

This work was supported by Korea Environment Industry & Technology Institute (KEITI) through Public Technology Program based on Environmental Policy, funded by Korea Ministry of Environment (MOE) (2016000200007).

REFERENCES

- Bhowmick, S., Pramanik, S., Singh, P., Mondal, P., Chatterjee, D. & Nriagu, J. 2018 *Arsenic in groundwater of West Bengal, India: a review of human health risks and assessment of*

- possible intervention options. *Science of the Total Environment* **612**, 148–169.
- Bui, T. H., Kim, C., Hong, S. P. & Yoon, J. Y. 2017 Effective adsorbent for arsenic removal: core/shell structural nano zero-valent iron/manganese oxide. *Environmental Science and Pollution Research* **24** (31), 24235–24242. <https://doi.org/10.1007/s11356-017-0036-9>.
- Bui, T. H., Hong, S. P. & Yoon, J. Y. 2018 Development of nanoscale zirconium molybdate embedded anion exchange resin for selective removal of phosphate. *Water Research* **134**, 22–31.
- Celik, S. U. & Bozkurt, A. 2008 Preparation and proton conductivity of acid-doped 5-aminotetrazole functional poly(glycidyl methacrylate). *European Polymer Journal* **44**, 213–218.
- Cheng, Z., Van Geen, A., Louis, R., Nikolaidis, N. & Bailey, R. 2005 Removal of methylated arsenic in groundwater with iron filings. *Environmental Science and Technology* **39** (19), 7662–7666.
- Fiyadh, S. S., AlSaadi, M. A., AlOmar, M. K., Fayaed, S. S. & El-Shafie, A. 2018 Arsenic removal from water using N,N-diethylethanolammonium chloride based DES-functionalized CNTs: (NARX) neural network approach. *Journal of Water Supply: Research and Technology-Aqua* **67** (6), 531–542.
- Freundlich, H. M. F. 1906 Over the adsorption solution. *Journal of Physical Chemistry* **57**, 385–470.
- Hekmatzadeh, A. A., Karimi-Jashni, A., Talebbeydokhti, N. & Kløve, B. 2013 Adsorption kinetics of nitrate ions on ion exchange resin. *Desalination* **326**, 125–134.
- Ho, Y. S. & McKay, G. 1999 Pseudo-second order model for sorption processes. *Process Biochemistry* **34** (5), 451–465.
- Korngold, E., Belayev, N. & Aronov, L. 2001 Removal of arsenic from drinking water by anion exchangers. *Desalination* **141**, 81–84.
- Kundu, S. & Gupta, A. K. 2006 Adsorptive removal of As(III) from aqueous solution using iron oxide coated cement (IOCC): evaluation of kinetic, equilibrium and thermodynamic models. *Separation and Purification Technology* **51** (2), 165–172.
- Lagergren, S. 1898 About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademiens Handlingar* **24** (4), 1–39.
- Langmuir, I. 1918 The adsorption of gases on plane surfaces of glass, mica and platinum. *The Journal of the American Chemical Society* **40** (9), 1361–1403.
- Lata, S. & Samadder, S. R. 2016 Removal of arsenic from water using nano adsorbents and challenges: a review. *Journal of Environmental Management* **166**, 387–406.
- Mahramanlioglu, M., Kizilcikli, I. & Bicer, I. O. 2002 Adsorption of fluoride from aqueous solution by acid treated spent bleaching earth. *Journal of Fluorine Chemistry* **115** (1), 41–47.
- Miao, Y., Han, F., Pan, B., Niu, Y., Nie, G. & Lv, L. 2014 Antimony(V) removal from water by hydrated ferric oxides supported by calcite sand and polymeric anion exchanger. *Journal of Environmental Sciences* **26** (2), 307–314.
- Nastasovic, A., Jovanovic, S., Dordevic, D., Onjia, A., Jakovljevic, D. & Novakovic, T. 2004 Metal sorption on macroporous poly(GMA-co-EGDMA) modified with ethylene diamine. *Reactive and Functional Polymers* **58**, 139–147.
- Nguyen, D. C., Park, H. J., Dockko, S. & Han, M. Y. 2013 Arsenic removal using novel combined Fe/Mn adsorbent modified with silica. *Water Science and Technology: Water Supply* **13** (4), 1109–1115.
- Nicomel, N. R., Leus, K., Folens, K., Van Der Voort, P. & Du Laing, G. 2016 Technologies for arsenic removal from water: current status and future perspectives. *International Journal of Environmental Research and Public Health* **13** (1), 62. <http://doi.org/10.3390/ijerph13010062>.
- Park, H. J., Nguyen, D. C. & Na, C. K. 2015 Applications and limits of theoretical adsorption models for predicting the adsorption properties of adsorbents. *Water Science and Technology* **72** (8), 1364–1374.
- Sajid, M., Nazal, M. K., Ihsanullah, B. N. & Osman, A. M. 2018 Removal of heavy metals and organic pollutants from water using dendritic polymers based adsorbents: a critical review. *Separation and Purification Technology* **191**, 400–423.
- Singh, T. S. & Pant, K. K. 2004 Equilibrium, kinetics and thermodynamic studies for adsorption of As(III) on activated alumina. *Separation and Purification Technology* **36**, 139–147.
- Taleb, K., Markovski, J., Hristovski, K. D., Rajaković-Ognjanović, V. N., Onjia, A. & Marinković, A. 2016 Aminated glycidyl methacrylates as a support media for goethite nanoparticle enabled hybrid sorbents for arsenic removal: from copolymer synthesis to full-scale system modeling. *Resource-Efficient Technologies* **2** (1), 15–22.
- Tatek, T., Park, H. & Na, C. 2015 Synthesis of aminated glycidyl methacrylate grafted rice husk and investigation of its anion-adsorption properties. *Journal of Applied Polymer Science* **133** (10), 1–9.
- WHO 1993 *Guidelines for Drinking-Water Quality*. World Health Organization, Geneva, Switzerland.

First received 26 August 2018; accepted in revised form 5 March 2019. Available online 12 April 2019