Adsorption of Aluminum Ion from Water on Alginate-Modified Polyurethane

Ki-Pal KIM¹, Zubair AHMED², Kyung-Guen SONG¹, Saleh F. MAGRAM², Maged H. H. DAOUD², Kyu-Hong AHN¹ and Ki-Jung PAENG³ ¹Center for Environmental Technology Research, Energy and Environment Research Division, Korea Institute of Science and Technology, P.O. BOX 131, Cheongryang, Seoul 130-650, Korea ²Department of Civil Engineering, King Abdul Aziz University, P.O. Box 80204, Jeddah 21589, Kingdom of Saudi Arabia ³Department of Chemistry, Yonsei University, Wonju, 220-710, Korea

Keywords: Alginate-Modified Polyurethane, Aluminum Ion, Adsorption, Wastewater Reuse

A dual purpose absorbent Alginate-modified polyurethane (APU) has been prepared for the removal of residual aluminum ions by adsorption from treated wastewater. The structure of APU was confirmed by Fourier transform infrared (FT-IR) spectroscopy and proton nuclear magnetic resonance (¹H-NMR) spectroscopy. Physical characterization was preformed according to the BET method. Surface analysis using SEM/EDS revealed that an average of 0.57% aluminum by weight was adsorbed on APU. The adsorption isotherm of aluminum for APU fitted well to the Freundlich model. The analysis kinetic data suggests that adsorption of aluminum follows pseudo-first-order kinetics. The adsorption of aluminum on APU increased slightly from 25 to 35°C, indicating endothermic adsorption. The activation energy of adsorption, 8.16 kJ/mol, characterizes the dominant chemiosorption nature of this adsorption. The optimum pH for aluminum adsorption on APU (applied pH: 3–8) was found to be within the pH range of wastewater effluent. The adsorption capacity of APU for aluminum using real wastewater effluent was 3.8 mg Al/g, which demonstrates the feasibility of applying APU to the treatment of water of complex compositions.

Introduction

A potential key component of water resource conservation and environmental protection is reuse of secondary effluent, i.e. discharges from wastewater treatment plants. However, secondary effluent also contains pollutants such as suspended solids, metals, phosphorous and harmful organic compounds (George and Franklin, 1991), including residual pharmaceutical compounds and endocrine disrupting chemicals (Brain et al., 2008), which are not suitable for a water ecosystem. Particularly, the presence of dissolved phosphorus in the treated effluent from wastewater treatment plants causes eutrophication (Dueñas et al., 2003). Different physicochemical processes such as coagulation-flocculation, filtration, and combinations of both have been applied to tertiary treatment of wastewater to make it fit for reuse (Caliskaner et al., 1999; Jimenez et al., 2000). Among the various treatment technologies available for phosphorus removal, chemical precipitation is a commonly applied technique using common coagulating agents such as aluminum and iron salts (George and Franklin, 1991; Fytianos et al., 1998; Huang and Chiswell, 2000; Reali et al., 2001; de-Bashana and Bashan, 2004). However, the efficiency of the coagulation reaction depends on several factors such as the dosage of coagulants, pH of water and concentration of organic compounds. Frequently, coagulation process remains incomplete under conditions commonly occurring in wastewater treatment plants; consequently, residual coagulant appears in the treated effluent at up to 2 mg/L (Kabsch-Korbutowicz, 2005; Ki-Pal et al., 2008). The contamination caused by residual coagulant salts is a serious environmental problem as well as threat to many life forms and public health (Dueñas et al., 2003). At high concentrations there is evidence linking aluminum to effects on the nervous system, with possible connections to several diseases, such as Parkinson's, Alzheimer's, and Lou Gehrig's disease (Lione, 1983; Corain et al., 1996; WHO, 1998). To keep the residual aluminum concentration within a permissible limit of less than 0.2 mg/L, a combination of coagulation and ultrafilteration has been investigated (Kabsch-Korbutowicz, 2005). However, this combination is expected to be an expensive method in

Received on June 15, 2010; accepted on December 22, 2010 Correspondence concerning this article should be addressed to K.-P. Kim (E-mail address: ki8279@kist.re.kr).

practical applications due to the use of costly ultrafiltration membranes and fouling problems.

Polvurethane foams constitute a new class of svnthetic materials. These polymers are formed by the chemical reaction of a monomer containing at least two isocyanate functional groups with another monomer containing at least two alcoholic functional groups (Bruins, 1969). Polyurethanes are being widely used for different purposes due to their increased tensile strength and durability (Lemos et al., 2007). The surfaces are highly developed because of the high porosity; hence, polyurethane foams may be very useful for filtering wastewater (Oboznyi et al., 1976; Park et al., 2006). However, polyurethane foams cannot adsorb metal ions without prior complexation (Lemos et al., 2007). It is feasible to modify the surface chemical property of polyurethane foam, thereby increasing its affinity for adsorbate. The adsorption capacity of polyurethane foams can be improved towards highly water soluble metal ions through surface modification or functionalization by introducing functional groups chemically on the polymeric matrixes, which can provide specific interaction with the target metal ion such as aluminum (Pan et al., 2009).

Alginate possesses good adsorption capacity for coagulating agents (Gacesa, 1998; Leon et al., 2006). Therefore, it can be a good material to synthesize a new type of polyurethane with increased adsorption capacity for cationic coagulating agents by chemical binding of alginate's functional groups on the polymer. Alginate is a linear copolymer with homopolymeric blocks of (1-4)linked β -D-mannuronate and its C-5 epimer α -Lguluronate. A major property of alginate is its adsorption ability for multivalent cations by ion exchange or surface complexation mechanism due to carboxylic and alcoholic functional groups (Gacesa, 1998). Alginate has been applied as an absorbent for the removal of cationic metals, such as Pb²⁺, Zn²⁺, Cd²⁺, and Ni²⁺ from aqueous solutions (Fundueanu et al., 1999). Modified alginate beads have been used in the removal of chromium, selenium and arsenic (Min and Hering, 1998: Katsoyiannis et al., 2002; Zouboulis and Katsoyiannis, 2002; Chen et al., 2007). Alginate has also been frequently used as an absorbent for heavy metals (Wang and Chen, 2009) or as a supporting material of immobilized biomass for bio-sorption of various cationic metals (Bayramoglu and Yakup Arlca, 2009). The combined adsorption capacity of alginate and filtration ability of the polyurethane (PU) should result in enhanced removal of residual aluminum from secondary effluent.

We synthesized a new adsorbent based on alginatemodified polyurethanes (APU) and used this for removal of aluminum ion from water. APU was evaluated as a medium, which can serve in the final stage of wastewater treatment, simultaneously with a filtrating medium as well as an adsorbent. The physical characteristics of PU and APU were compared using BET method and the chemical structure was confirmed by ¹H-NMR and FT- IR analysis. A scanning electron microscope and energy dispersive X-ray spectrometer (SEM/EDS) were used to visualize the surface of APU and elemental analysis after aluminum adsorption experiments. The adsorption isotherms were fitted using Freundlich and Langmuir isotherms, and the adsorption kinetics were investigated. The adsorption capacities of APU for aluminum ion were evaluated at different temperature and pH.

1. Experimental

1.1 Chemicals and reagents

Ethylene glycol (EG), 2,4-toluene diisocyanate (2,4-TDI), and alginic acid were used for the synthesis of PU and APU. These AR grade chemicals were obtained from Sigma-Aldrich Co. and used without further purification. Dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) were obtained from Samchun Pure Chemical Co. and used as solvents for synthetic reactions. HPLC-grade methanol and Milli-Q water were used for the precipitation of PU and APU. An aluminum standard solution (AR grade) was purchased from Kanto Chemical Co., Inc. A working solution of aluminum was prepared using Milli-Q water. The pH of solutions was adjusted with a 0.1M HCl solution and 0.1M NaOH solution. All other reagents were of analytical grade.

1.2 Preparation of PU and APU

PU was synthesized using 2,4-toluene diisocyanate (2,4-TDI) and ethylene glycol (EG) according to the following procedure (Lan *et al.*, 1996). Under stirring, 0.074M of a 2,4-TDI solution (13.65 g in 50 mL) of DMF was added drop wise to a 0.074M EG solution (4.6 g in 350 mL DMF) at 80°C, with a steady flow of dry nitrogen supplied continuously over the mixture. After 3 h of reaction under constant stirring, the reaction solution was cooled down to room temperature, then deionized water was added slowly to the reaction solution in an excess amount. The formed precipitates were separated by filtration and washed with deionized water. The final product was dried in a desiccator at room temperature.

APU was synthesized using 2,4-TDI and alginate according to the following procedure (Barikani and Mohammadi, 2007; Seong-Ryul et al., 2007): excess amount of alginate (0.048M or 8.45 g/150 mL) was dissolved in anhydrous DMSO for 24 h at 80°C in a reaction vessel under constant stirring, with a steady flow of dry nitrogen supplied continuously over the mixture. Three grams of 2,4-TDI was dissolved in 50 mL of DMSO (0.016M), and this solution was added drop wise at the rate of one drop/second by a dropping funnel to the alginate solution. After complete addition, reaction was carried out for 24 h at 80°C. Residual alginate was filtered, the reaction mixture was cooled down to room temperature, and then excess methanol was added to the mixture. The precipitate was recovered by filtration. The final product was dried in a desiccator at room temperature.



Fig. 1 Synthetic scheme of (a) Polyurethanes (PU), (b) Alginate-modified polyurethane (APU)

Synthetic schemes of PU and APU are shown in **Figure 1**. Two final products were analyzed by ¹H-NMR (600 MHz, JEOL Ltd.) and FT-IR (PerkinElmer Inc.) for structure confirmation. Physical structures of the products were measured using a Sorptomatic 1990 (ThermoQuest Corp.) system according to the BET method. To confirm aluminum ion adsorption on the adsorbent, surface analysis was carried out using an electron scanning electron microscope (SEM) (FEESEM XL-30, Philips) and an energy dispersive spectrometer (EDS) (EDAX Inc.).

1.3 Adsorption experiments

Adsorption experiments were carried out in batch mode. Synthesized PU and APU were ground, using a mortar, and sieved by a standard testing sieve (mesh size 200-300 µm). Purification was carried out with distilled water. The adsorption capacities of PU and APU for aluminum ion were evaluated and compared at various conditions such as temperature, different concentration of aluminum ion, adsorption time, and pH. A fixed amount (10 mg) of adsorbents with a known concentration of aluminum ion solution were placed in a glass vials (15 mL) and shaken at 170 rpm for 5 h using a shaking incubator (Korea Instrument Co.). After mixing, the solutions were filtered through a 0.2 µm polypropylene (PP) syringe filter (Watman International Ltd.) and injected into an inductively coupled plasma-optical emission system (Optima 7100 DV, PerkinElmer Inc.) to determine the equilibrium concentration of aluminum ion. The equilibrium adsorption capacity, Q_e (mg Al/g of absorbent), was calculated according to Eq. (1).

$$Q_{\rm e} = \frac{V(C_{\rm i} - C_{\rm e})}{w} \tag{1}$$

Here, V [L] is the volume of the adsorption solution, C_i and C_e [mg/L] are the initial and equilibrium concentra-

Elmer Inc.) to deof aluminum ion. $D_e \text{ (mg Al/g of ab-}$ q. (1). (1) $D_e \text{ (mg Al/g of ab-}$ (1) $D_e \text{ (mg Al/g of a$

tions of aluminum ion, respectively, and *w* [g] is the mass of the adsorbent. To evaluate the performance of the adsorbents in real samples and to demonstrate the adsorbents ability to remove aluminum ion in the presence of other interference commonly found in wastewater of complex composition such as nitrogen and phosphorus, samples were taken from a domestic wastewater treatment plant, located at Gwachon, Republic of Korea. The treatment plant is based on a conventional activated sludge process and has a treatment capacity of 30,000 m³/d. The effluent characteristics are given as follows: turbidity, 3.25 NTU; SS, 7.8 mg/L; pH, 7.2; COD, 17.2 mg/L; TP, 0.98 mg/L; TN, 9.75 mg/L. Aluminum ion was added in the samples of treated water to make a final concentration to 10 mg/L.

2. Results and Discussions

2.1 Characterization of PU and APU

The ¹H-NMR and 2.1.1 Chemical structure of APU FT-IR spectra of APU are shown in Figure 2. The ¹H-NMR spectra revealed a peak of single proton of a urethane bond near 8 ppm and a peak of phenyl proton at 7 ppm, which confirms bonding between the carboxylic group of urethane and the phenyl group of alginate. The FT-IR analysis further confirmed the structure of synthesized APU. After alginate modification on urethane, the vibration absorption of the O-H bond appeared at 3430 cm^{-1} . The stretching vibration absorption of C=O bond appeared at $1739 \,\mathrm{cm}^{-1}$, indicating that a carboxylic functional group on alginic acid was intact and available for specific interaction with aluminum ion after reaction between alginate and urethane has occurred. These distinct peaks appearing in the ¹H-NMR and FT-IR spectra of APU are absent in the spectra of PU (Lan et al., 1996).



 Table 1
 Physical properties of PU and APU

Fig. 2 Chemical characterization of APU (a) ¹H-NMR spectra, and (b) FT-IR spectra

2.1.2 Physical properties of APU and PU Physical properties such as surface area, average pore diameter and pore volume of an absorbent are important to describe the adsorption process. In general, the adsorption capacity of an adsorbent is proportional to the available adsorption sites on the surface area of the adsorbent. The size of the pores is related to that of the molecules adsorbed in the diffusion process (Jung et al., 2001). Table 1 depicts the physical properties of PU and APU. It can be seen that the pore volume of APU is smaller than that of PU, indicating that particles of smaller size can be adsorbed on APU. According to Do et al. (2007), adsorption in large pores is very weak because of the weak solid-fluid interactions. Furthermore, aluminum ions can access adsorption sites located in pores of small diameter on APU due to its small radius of about 0.051 nm (Corwin, 2005).

2.1.3 Surface analysis To confirm the adsorption of aluminum ions on APU, surface analysis was performed before and after adsorption experiment using SEM and EDS as shown in **Figure 3**. As it can be seen in Figure 3, the surface of APU was unchanged after adsorption experiments, except for the adsorption of aluminum ions on the surface of APU. The presence of adsorbed aluminum was confirmed by surface elemental analysis as shown in Figure 3(d). After the adsorption of aluminum ions on APU, aluminum ions were detected on the surface of APU in the amount of about 0.57% (dry weight of APU). It should be noted that, due to the heterogene-

ity of APU, aluminum was measured only on the surface; however, adsorption also took place within the beads of APU.

2.2 Adsorption behavior of PU and APU for aluminum ion

2.2.1 Adsorption isotherms The aluminum isotherm plots representing the equilibrium distribution of aluminum ions on the solids (PU and APU) and liquid phase were obtained (Figure 4) at pH 7.0 by varying the initial concentration of aluminum (2.5-11.5 mg Al/L). It is evident in Figure 4 that the adsorption capacity of APU for aluminum ions ascends sharply with increasing equilibrium concentration of aluminum ions in the liquid phase. This trend clearly indicates the strong affinity of the adsorption sites for aluminum. On the other hand, the shape of the isotherm suggests a weak affinity of PU for aluminum ions. This means that presence of carboxylic and alcoholic functional groups on APU considerably enhanced the adsorption of aluminum ions. For instance, at an equilibrium concentration of 4.82 mg Al/L, the adsorption capacity of aluminum ions on APU is 0.72 mg Al/g, which is about 9.6 times greater than the adsorption capacity of aluminum ions on PU at the same applied equilibrium concentration of aluminum ions.

The adsorption data shown in Figure 4 were fitted using the well-known models, i.e. Freundlich and Langmuir models, which are given in Eqs. (2) and (3), respectively, by non-linear regression using the method of least squares (Deliyanni *et al.*, 2007).



(a) Before adsorption

(b) After adsorption

Fig. 3 Surface analysis of APU before and after Al adsorption: (a) and (b) SEM images; (c) and (d) Element analysis



Fig. 4 Adsorption isotherm of aluminum ion on PU and APU

$$Q_{\rm e} = K_{\rm F} C^{1/n} \tag{2}$$

$$Q_{\rm e} = \frac{Q_{\rm m} K_{\rm L} C_{\rm e}}{1 + K_{\rm I} C_{\rm e}} \tag{3}$$

Here $K_{\rm F}$ and 1/n are Freundlich constants; $Q_{\rm m}$ is the maximum adsorption capacity [mg Al/g]; and $K_{\rm L}$ is Langmuir constant [L/mg]. The curve fitting was performed using OriginPro 8.0 software (OriginLab Corp). The obtained values of $K_{\rm F}$, 1/n, $Q_{\rm m}$, $K_{\rm L}$ and correlation coefficients (R^2) are given in **Table 2**. Considering the values of the correlation coefficient, R^2 , the Freundlich model yielded good correlation.

The adsorption capacity constant (K_F) of the Freundlich model represents a measure of the surface area of the adsorbent and is taken as an indicator of adsorption capacity (Achife and Ibemesi, 1989). A large value of K_F reflects higher absorbent capacity. The K_F value for APU (0.42) is about 21 times higher than that for PU (0.020). This shows that APU has a larger adsorption capacity for aluminum ions due to carboxylic and alcoholic functional groups. The component 1/n is an empirical constant related to the magnitude of the adsorption driving force (Weber *et al.*, 1991), also called the heterogeneity factor. Its value ranges between 0 and 1; the more heterogeneous the surface, the closer the 1/n

Adsorbent	Freundlich equation $Q_{\rm e} = K_{\rm F} C^{1/n}$			Langmuir equation $Q_{\rm e} = Q_{\rm m} K_{\rm L} \frac{C_{\rm e}}{1 + K_{\rm L} C_{\rm e}}$		
	$K_{ m F}$	1/n	R^2	KL	\mathcal{Q}_{m}	R^2
APU PU	0.42 0.020	0.37 0.90	0.964 0.950	0.52 0.010	1.06 1.01	0.821 0.964

 Table 2
 Estimated isotherm constants for aluminum ion adsorption on PU and APU



Fig. 5 Adsorption kinetics of aluminum ion at various concentration on APU and PU

value is to zero. The values of component the 1/n were found to be 0.90 and 0.37 for PU and APU, respectively. This indicates that the surface of APU is more heterogeneous compared to surface of PU. The values of the heterogeneity factor (1/n) also imply that the interaction between APU and aluminum ions was greater than that between PU and aluminum.

2.3 Adsorption kinetics

The reaction time required for the aluminum ion adsorption reaction to reach equilibrium was determined by conducting initial kinetic experiments using the initial aluminum ions concentration of 2.8 mg/L under the following conditions: adsorbent dose of 10 mg, pH of 7.0, and temperature of 25°C. The kinetic results are shown in Figure 5. The amount of adsorbed aluminum ions on PU remained low with elapsed time. On the other hand, adsorption of aluminum ions onto APU was fast and reached to equilibrium within 2 h and a further increase in reaction time slightly improved the adsorption of aluminum ions onto APU. Similar experiments were performed with different initial concentrations of aluminum ions, i.e. 0.5-10 mg/L; however, the reaction time of the adsorption of aluminum ions on APU to reach equilibrium was found to be the same (data not shown). This result indicates that the adsorption of aluminum ions largely depends on the initial concentration of aluminum ions. The adsorption kinetics of aluminum ions on APU and PU clearly show that enhanced adsorption in the case of APU was due to the presence of func-

 Table 3
 Kinetic parameters for aluminum ion adsorption on APU and PU

	Pseudo-1st-order kinetic model k_1	R^2
- APU	1.14	0.990
PU	7.65×10^{-10}	0.948
	Pseudo-2nd-order kinetic model	
	k_2	R^2
- APU	1.54	0.980
PU	$2.60 imes 10^{-9}$	0.948
	Pseudo-3rd-order kinetic model	
	<i>k</i> ₃	R^2
- APU	1.71	0.977
PU	7.90×10^{-9}	0.948

tional groups on APU. However, the surface area and pore volume of PU were found to be larger than APU (Table 1).

Nonlinear regression analysis was performed using SigmPlot 10.0 software (Systat Software, Inc.) to fit the adsorption kinetic data with the pseudo-first-, pseudosecond-, and pseudo-third-order kinetics models. The kinetic equations utilized in nonlinear regression are given below (Deliyanni *et al.*, 2007).

$$C_{t} = C_{i} - (C_{i} - C_{e})(1 - e^{-k_{i}t})$$
(4)

$$C_{\rm t} = C_{\rm i} - (C_{\rm i} - C_{\rm e}) \left(1 - \frac{1}{1 + k_2 t} \right)$$
(5)

$$C_{t} = C_{i} - (C_{i} - C_{e}) \left(1 - \frac{1}{(1 + 2k_{3}t)^{1/2}} \right)$$
(6)

Here C_t is the aluminum ion concentration [mg Al/L] at the time t; t is the time [h]; and k_1 , k_2 and k_3 are adsorption rate constants for the pseudo-first-, pseudo-second, and pseudo-third-order models, respectively [h⁻¹]. The results of nonlinear regression analysis and relevant correlation coefficient (R^2) are summarized in **Table 3**. Considering the value of the correction coefficient, R^2 ,

JOURNAL OF CHEMICAL ENGINEERING OF JAPAN



Fig. 6 Effect of temperature on adsorption of aluminum ion on APU

the pseudo-first-order model best describes the adsorption kinetics of aluminum ions on APU. In the case of PU, however, the values of the correlation coefficient indicate that the kinetic models do not describe the adsorption of aluminum ions on PU. The lower values of adsorption rate constants for PU $(7.65 \times 10^{-10} \,\text{h}^{-1})$ as compared to APU $(1.1438 \,\text{h}^{-1})$ also clearly point out that chemical modification on urethane using alginate has imparted adsorption ability for aluminum ions to the filtering media.

2.4 Effect of temperature

The temperature dependence of aluminum ion adsorption on PU and APU were investigated at three applied temperatures, 15, 25, and 35°C. Equilibrium adsorption capacities are shown in **Figure 6**. Adsorption capacity of aluminum ion on APU increased from 0.486 to 0.567 mg Al/g, suggesting slightly endothermic adsorption from 15 to 35°C. The pseudo first order rate constant can be expressed by Arrhenius type equation given by Eq. (7).

$$k_{1} = k_{o} \exp\left(\frac{-E}{RT}\right) \tag{7}$$

Here, k_o is a temperature independent factor [g/mg min], *E* the activation energy of adsorption [J/mol], *R* the universal gas constant and *T* is the absolute temperature [K]. The calculated activation energy using Eq. (7) was found to be 18.7 kJ/mol. A magnitude of *E* within the range of 5–40 kJ/mol characterizes physiosorption nature of adsorption (El-Khaiary, 2007). However, in another report (Özcan *et al.*, 2005), a magnitude of activation energy greater than 8 KJ/mol suggested the chemical ion-exchange nature of the adsorption process. It seems that the adsorption of aluminum ions on APU is dominantly a chemical ion-exchange process due to the electrostatic force between aluminum ions and the carboxylic group of alginate.

2.5 Effect of pH

To evaluate the effect of initial pH on the aluminum ions adsorption capacity of the adsorbents, experiments



Fig. 7 Effect of pH on adsorption of aluminum ion on PU and APU

were conducted within the pH range 3-8 at 25°C. It was observed that the adsorption of aluminum ions on APU increased gradually as the initial pH of the medium increased from 3 to 7, as shown in Figure 7. The optimum pH was found to be 7 for aluminum ion adsorption on APU. Generally, the pH of many wastewater effluents ranges from 7 to 8, and within this range aluminum is employed as a coagulant (Tchobanoglous et al., 2003). Therefore, APU can comfortably be used for residual aluminum ion removal from the effluent of wastewater treatment plants. The effect of pH on the adsorption capacity may be explained on the basis of the nature of the interactions of aluminum ions with the functional groups on APU. The carboxylic groups (-COOH) on APU are responsible for the binding of positively charged aluminum ions. At a pH lower than 7 the carboxylic groups retain their protons due to the high concentration of free protons, and thus the probability of binding to positively charged aluminum ions is low. However, at neutral pH, both hydroxide and carboxylic groups remained available on APU for interaction with positively charged aluminum ions. A decline in the adsorption of aluminum ions at pH higher than 7 resulted because of the repulsion between OH⁻ on APU and negatively charged dominant species of aluminum ions $[Al(OH)_4^-]$ (Tchobanoglous *et al.*, 2003).

2.6 Removal of aluminum ions from effluent of wastewater treatment plant

In order to evaluate the performance of the adsorbents for treating real effluent, APU was applied as an adsorbent for the removal of aluminum ion from the treated effluent of a wastewater treatment plant. The effluent samples were spiked with aluminum ions at a concentration of 10 mg/L. The adsorption capacities of APU and PU under different matrices of de-ionized water with no interference and real effluent with interfering contaminants are given in **Table 4**. In the case of deionized water, the adsorption capacities of aluminum ions on PU and APU differ only due to the presence of functional carboxylic and alcoholic groups on APU. However, in the case of treated effluent, contaminants

Matrix	Adsorption Capacity (Q_e), mg Al/PUAPU	
De-ionized water	0.029	2.7
Treated wastewater	1.7	3.8

 Table 4
 Adsorption capacities of aluminum ion on PU and APU at different matrices

such as nitrogen and phosphorus can form complexes with aluminum ions, whereby enhanced adsorption capacities were observed both in the cases for PU and APU. Nevertheless, the real sample adsorption capacity of APU for aluminum ion was 3.8 mg/g, about 2.25 times higher than that of PU.

Conclusion

Alginate-modified polyurethane (APU) was synthesized using 2,4-toluene diisocyanate and alginate for the removal of aluminum ions from an aqueous medium. The structure of synthesized APU was confirmed by ¹H-NMR and FT-IR analysis. Despite having a smaller surface area compared to polyurethane (PU), APU was found to be an efficient absorbent for the removal of aluminum ions under controlled conditions such as pH and temperature. Adsorption of aluminum ions was confirmed by surface analysis of APU using SEM and EDS. The adsorption capacity of APU for aluminum ions is attributed to chemical modification of alginate on urethane, which adds carboxylic and alcoholic functional groups on PU. These negatively charged functional groups have a strong affinity for positively charged aluminum ions; therefore, adsorption of aluminum ions on APU can take place through the ion-exchange mechanism and electrostatic interactions. The adsorption isotherm of aluminum ions on APU can be adequately described by the Freundlich model. The kinetics of the adsorption of aluminum ions on APU was found to be pseudo-first order. The optimum pH for the adsorption of aluminum ions on APU match well with the pH of the effluent of wastewater plants; therefore, APU can be applied to remove residual aluminum ions without pH control. Considering the filtering ability and adsorption capacity for aluminum ions, APU can be effectively used in treatment plants both as a filtering medium as well as an adsorbent, where aluminum is employed as a coagulant. Hence, application of APU can improve the quality of wastewater effluent, making it fit for reuse purpose, and reduce possible adverse health impact associated with the reuse of treated wastewater. However, the practical potential of APU as a filtering media as well as an absorbent for the removal of aluminum ions from treated water can be fully explored by careful investigation of the adsorption mechanisms of aluminum ions on APU, effect of pH on adsorption kinetics, and impacts of other

impurities commonly found in treated water.

Literature Cited

- Achife, E. and J. Ibemesi; "Applicability of the Freundlich and Langmuir Adsorption Isotherms in the Bleaching of Rrubber and Melon Seed Oils," J. Am. Oil Chem. Soc., 66, 247–252 (1989)
- Barikani, M. and M. Mohammadi; "Synthesis and Characterization of Starch-Modified Polyurethane," *Carbohydr. Polym.*, 68, 773–780 (2007)
- Bayramoglu, G. and M. Yakup ArIca; "Construction a Hybrid Biosorbent Using Scenedesmus Quadricauda and Ca-Alginate for Biosorption of Cu(II), Zn(II) and Ni(II): Kinetics and Equilibrium Studies," *Bioresour. Technol.*, 100, 186–193 (2009)
- Brian, Q., G. François and B. Christian; "An Investigation into the Acute and Chronic Toxicity of Eleven Pharmaceuticals (and Their Solvents) Found in Wastewater Effluent on the Cnidarian *Hydra attenuate*," *Sci. Total Environ.*, **389**, 306–314 (2008)
- Bruins, P. F.; Polyurethane Technology, pp. 1–22, Interscience Publishers, New York, U.S.A. (1969)
- Caliskaner, O., G. Tchobanoglous and A. Carolan; "High-Rate Filtration with a Synthetic Compressible Media," *Water Environ. Res.*, 71, 1171–1177 (1999)
- Chen, K. L., S. E. Mylon and M. Elimelech; "Enhanced Aggregation of Alginate-Coated Iron Oxide (Hematite) Nanoparticles in the Presence of Calcium, Strontium, and Barium Cations," *Langmuir*, 23, 5920–5928 (2007)
- Corain, B., G. G. Bombi, A. Tapparo, M. Perazzolo and P. Zatta; "Aluminium Toxicity and Metal Speciation: Established Data and Open Questions," *Coord. Chem. Rev.*, **149**, 11–22 (1996)
- Corwin, C. H.; Introductory Chemistry: Concepts & Connections, pp. 140–167, Prentice Hall, Upper Saddle River, U.S.A. (2005)
- de-Bashana, L. E. and Y. Bashan; "Recent Advances in Removing Phosphorus from Wastewater and Its Future Use as Fertilizer (1997–2003)," *Water Res.*, 38, 4222–4246 (2004)
- Deliyanni, E. A., E. N. Peleka and N. K. Lazaridis; "Comparative Study of Phosphates Removal from Aqueous Solutions by Nanocrystalline Akaganéite and Hybrid Surfactant-Akaganéite," Sep. Purif. Technol., 52, 478–486 (2007)
- Do, D. D., H. D. Do and G. Birket; "A New Methodology in the Use of Super-Critical Adsorption Data to Determine the Micropore Size Distribution," Adsorption: Progress in Fundamental and Application Research, 4th Pacific Basin Conference on Adsorption Sciecne and Technology, pp. 154–173, World Scientific Publishing, Singapore (2007)
- Dueñas, J. F., J. R. Alonso, A. F. Rey and A. S. Ferrer; "Characterisation of Phosphorous Forms in Wastewater Treatment Plants," J. Hazard. Mater., B97, 193–205 (2003)
- El-Khaiary, M. I.; "Kinetics and Mechanism of Adsorption of Methylene Blue from Aqueous Solution by Nitric-Acid Treated Water-Hyacinth," J. Hazard. Mater., 147, 28–36 (2007)
- Fundueanu, G., C. Nastruzzi, A. Carpov, J. Desbrieres and M. Rinaudo; "Physicochemical Characterization of Ca-Alginate Beads Microparticles Produced with Different Methods," *Biomaterials*, **20**, 1427 (1999)
- Fytianos, K., E. Voudrias and N. Raikos; "Modellin of Phosphorus Removal from Aqueous and Wastewater Samples Using Ferric Ion," *Environ. Pollut.*, **101**, 123–130 (1998)
- Gacesa, P.; "Alginates," Carbohydr. Polym., 8, 161–182 (1998)
- George, T. and L. B. Franklin; Wastewater Engineering, Treatment, Disposal, and Reuse, pp. 1137–1193, McGraw-Hill, New York, U.S.A. (1991)
- Huang, S. H. and B. Chiswell; "Coagulation Behavior of Aluminum Salts in Eutrophic Water: Significance of Al13 Species and pH Control," *Water Sci. Technol.*, 42, 295–300 (2000)
- Jimenez, B., A. Chavez, A. Leyva and G. Tchobanoglous; "Sand and Synthetic Medium Filtration of Advanced Primary Treatment Effluent from Mexico City," *Water Res.*, 34, 473–480 (2000)
- Jung, M.-W., K.-H. Ahn, Y. Lee, K.-P. Kim, I. R. Paeng, J.-S. Rhee, J.

T. Park and K.-J. Paeng; "Evaluation on the Adsorption Capabilities of New Chemically Modified Polymeric Adsorbents with Protoporphyrin IX," *J. Chromatogr.*, **917**, 87–93 (2001)

- Kabsch-Korbutowicz, M.; "Effect of Al Coagulant Type on Natural Organic Matter Removal Efficiency in Coagulation/Ultrafiltration Process" *Desalination*, **185**, 327–333 (2005)
- Katsoyiannis, I., A. Zouboulis, H. Althoff and H. Bartel; "As(III) Removal from Groundwaters Using Fixed-Bed Upflow Bioreactors," *Chemosphere*, 47, 325–332 (2002)
- Ki-Pal, K., S. Kyung-Guen, A. Zubair, P. Ki-Jung and A. Kyu-Hong; "Enhancement of Phosphorus Removal in a Polyurethane Compressible Media Filtration System with Coagulation," *J. Chem. Eng. Japan*, **41**, 525–530 (2008)
- Lan, P. N., S. Corneillie, E. Schacht, M. Davies and A. Shard; "Synthesis and Characterization of Segmented Polyurethanes Based on Amphiphilic Polyehter Diols," *Biomaterials*, **17**, 2273–2280 (1996)
- Lemos, V. A., M. S. Santos, E. S. Santos, M. J. S. Santos, W. N. L. dos Santos, A. S. Souza, D. S. de Jesus, C. F. das Virgens, M. S. Carvalho, N. Oleszczuk, M. G. R. Vale, B. Welz and S. L. C. Ferreira; "Application of Polyurethane Foam as a Sorbent For Trace Metal Pre-Concentration—A Review," *Spectrochim. Acta Part B*, **62**, 4–12 (2007)
- Leon, F., F. Dorota and M. Marek; "Transition Metal Complexes with Alginate Biosorbent," J. Mol. Struct., 792–793, 104–109 (2006)
- Lione, A.; "The Prophylactic Reduction of Aluminium Intake," Food Chem Toxicol., 21, 103–109 (1983)
- Min, J. and J. Hering; "Arsenate Sorption by Fe(III) Doped Alginate Gels," *Water Res.*, 32, 1544–1552 (1998)
- Oboznyi, V. F., I. D. Pichakhchi and V. V. Shimkovich; "Experience in the Use of Polyurethane Foam as a Filter Material in Treating Oilcontaining Wastewaters," *Chem. Technol. Fuels Oils*, **12**, 853–856

(1976)

- Özcan, A. S., B. Erdem and A. Özcan; "Adsorption of Acid Blue 193 from Aqueous Solution onto BTMA-Bentonite," *Colloids Surf.*, A, 266, 73–81 (2005)
- Pan, B., B. Pan, W. Zhang, L. Lv, Q. Zhang and S. Zheng; "Development of Polymeric and Polymer-Based Hybrid Adsorbents for Pollutants Removal from Waters," *Chem. Eng. J.*, **151**, 19–29 (2009)
- Park, K. Y., S. K. Maeng, K. Kim, J. H. Kweon and K. H. Ahn; "A High Filtration System with Synthetic Permeable Media for Wastewater Reclamation," *Water Sci. Technol.*, **53**, 185–190 (2006)
- Reali, A. P. M., R. G. Penetra and M. E. Carvalho; "Flotation Technique With Coagulant and Polymer Application Applied to the Post-Treatment of Effluents from Anaerobic Reactor Treating Sewage," *Water Sci. Technol.*, 44, 205–212 (2001)
- Seong-Ryul, Y., K. Oh-Jin, K. Dae-Hyun and P. Jong-Shin; "Characterization of the Polyurethane Foam Using Alginic Acid as a Polyol," *Fibers Polym.*, 8, 257–262 (2007)
- Tchobanoglous, G., F. L. Burton and H. D. Stensel; Wastewater Engineering: Treatment and Reuse, 4th ed., pp. 1035–1205, McGraw-Hill, New York, U.S.A. (2003)
- Wang, J. and C. Chen; "Biosorbents for Heavy Metals Removal and Their Future," *Biotechnol. Adv.*, 27, 195–226 (2009)
- Weber, J. W. J., P. M. McGinley and L. E. Katz; "Sorption Phenomena in Subsurface Systems: Concepts, Models and Effects on Contaminant Fate and Transport," *Water Res.*, 25, 499–528 (1991)
- WHO; Guidelines for Drinking-Water Quality, Addendum to Vol. 2, Health Criteria and Other Supporting Information, World Health Organization, Geneva, Switzerland (1998)
- Zouboulis, A. I. and I. A. Katsoyiannis; "Arsenic Removal Using Iron Oxide Loaded Alginate Beads," *Ind. Eng. Chem. Res.*, 41, 6149–6155 (2002)