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Kinetic, thermodynamic, and equilibrium studies for adsorption of ammonium ion on modified polyurethane

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ABSTRACT

Modified polyurethane (APU) was used as an absorbent for removal of aqueous ammonium. The surface structure of polyurethanes were modified by covalent bonding of carboxylic functional group of alginate. Effects of various operation parameters (such as temperature and pH) on adsorption capacities of APU for ammonium ion were investigated. Langmuir and Freundlich models were fitted on experimental data. It was found that Freundlich model described best for adsorption of ammonium ion onto APU. The values of Freundlich parameter K_F was found to be 0.276, 0.367, and 0.406 $(mg/mg)/(mg/L)^{1/n}$ at temperature of 288, 298, and 308 K, respectively. Analysis of kinetic data showed that adsorption of ammonium ion follows pseudo-first-order kinetics. The value of first-order kinetic coefficient, k_1, was found to be 7.93×10^{-3}, 1.37×10^{-2}, 1.45×10^{-2} h^{-1} at 288, 298, and 308 K, respectively. The values of standard free energies at different temperatures were within −22.76 to −26.81 kJ/mol with higher value at higher applied temperature. The value of standard enthalpy was found to be −0.40 kJ/mol. The optimum pH for ammonium ion adsorption onto APU was found within pH range 5–7. Results reveal that application of APU can be beneficial for removal of aqueous ammonium; hence, it can improve the quality of water.

Keywords: Alginate-modified polyurethane; Ammonium ion; Adsorption; Wastewater reuse

1. Introduction

Ammonium ion discharge from various industries and wastewater treatment facilities into surface water is a matter of growing concern for relevant environmental protection agencies because of associated environmental and health problems. Therefore, mitigation of ammonium ion discharges from wastewater treatment has a crucial significance, particularly, when reuse of treated water is an objective. Presence of

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ammonium ion has been reported in water bodies around the world [1,2]. Numerous physical, chemical, and biological processes have been applied for removal of ammonium ion from water steams including air stripping, breakpoint chlorination, biological nitrification–denitrification, and ion exchange [3]. Among these applied treatment processes, only few biological and physicochemical processes are economically feasible for the management of ammonium ion pollution in water. Biological ion removal processes are utilized, but frequently, unacceptable high concentration of ammonium ion appears in the effluent due to high shock load [4,5] and inclusion of runoff from irrigation field during rainy season.

Polyurethane (PU) foams are being widely used for different purposes due to their increased tensile strength and durability [6]. These polymers are formed by chemical reaction of a monomer, containing at least two isocyanate functional groups, with another monomer containing at least two alcoholic functional groups [7]. Due to highly developed surfaces and high porosity, the polyurethane foams are very promising materials in the technology of wastewater for filtration [8,9]. However, without prior complexation, polyurethane foams cannot adsorb cations [6]. Adsorption capacity of polyurethane foams for cations, such as ammonium ion, can be improved through introducing functional groups chemically on the polymeric matrixes, which can provide specific interaction with the target cation [10].

Alginate contains good adsorption capacity for cations [11,12]. Alginate contains carboxylic and alcoholic functional groups which provide adsorption ability for cations by ion exchange or surface complexation mechanism [11]. It has been used for adsorption of Pb^{2+}, Zn^{2+}, Cd^{2+}, and Ni^{2+} from aqueous solutions [13]. Therefore, this biosorbent is a suitable candidate to synthesize modified polyurethane with increased adsorption capacity for cations by chemical binding of alginate's functional groups on the polymer. Modified alginate has been utilized for chromium, selenium, and arsenic adsorption [14–16]. More recently, modified polyurethane using alginate has been successfully used for removal of aluminum from water [17]. The adsorption capacity of alginate and filtration ability of the PU can be combined for removal of ammonium ion from aqueous streams including reclaimed water as well as drinking water.

The objective of current study was to investigate the potential of modified polyurethanes using alginate (APU) as an adsorbent for removal of aqueous ammonium ion. Scanning electron microscope was used to visualize the surface of APU before and after adsorption of ammonium ion. The adsorption isotherms were fitted using Freundlich and Langmuir isotherms and adsorption kinetics was investigated. The adsorption capacities of APU for ammonium ion were evaluated at different temperature, and pH. Kinetic and thermodynamic studies for adsorption of ammonium ion onto APU were also performed.

2. Experimental methods

2.1. Chemicals and reagents

Ethylene glycol (EG), 2,4-toluene diisocyanate (TDI), and alginate (Aldrich, USA) were used for synthesis of the absorbents. Dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) (Samchun Chemicals, Korea) were used as solvent for synthetic reaction. HPLC-grade methanol and Milli-Q water were used for precipitation APU. Ammonium standard solution was purchased from Kanto Chemical Co., Inc. (Japan). The solutions of pH were adjusted with 0.1 M HCl solution and 0.1 M NaOH solution. All other reagents were of analytical grade.

2.2. Preparation of APU and PU

Synthesis of APU was performed using 2,4-TDI and alginate as per reported previously [18]. In summary: alginate (0.048 M 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 continuously over the mixture. A per weighted amount of 3.0 g of 2,4-TDI was dissolved in 50 mL of DMSO (0.016 M) and mixed drop wise to the alginate solution. The reaction time was 24 h at 80˚C. Residual alginate was removed by filtration. 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 dried in a desiccator at room temperature. Synthetic schemes for the preparation of APU are given in Fig. 1. Preparation of PU was carried out according to the method described previously [17].

2.3. Adsorption experiments

The adsorption experiments were carried out in batch mode. Synthesized adsorbent was ground using a mortar and separated to 200–300 μm by standard testing sieve. Adsorption capacities of APU for ammonium ion were investigated at different adsorbent dosage, temperature, concentrations of ammonium ion, adsorption time, and pH. For comparison purpose, adsorption capacities of PU for ammonium ion were also measured

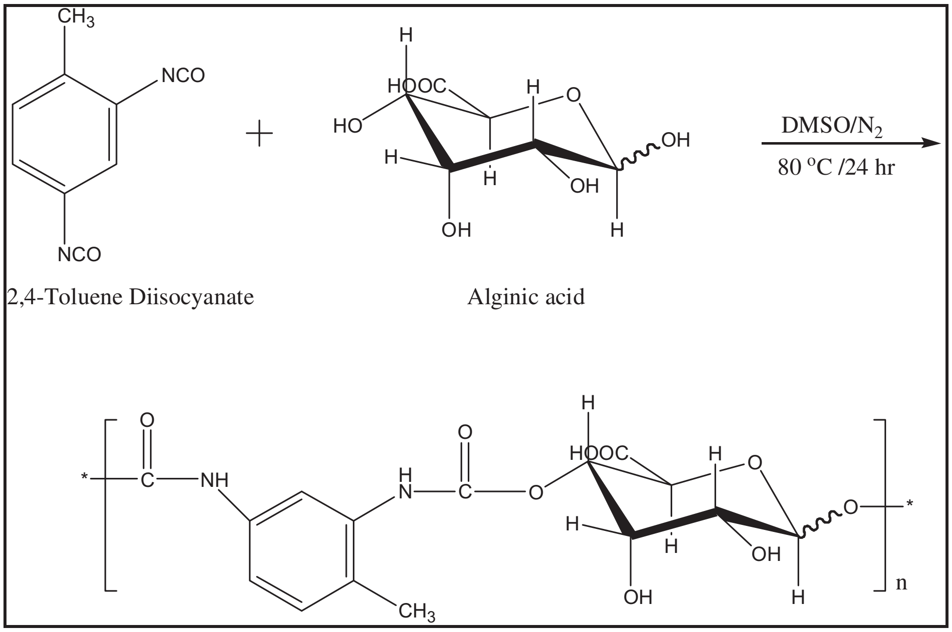


Fig. 1. Synthetic scheme for the preparation of Alginate-modified polyurethane (APU).

at different temperature and shaking time. A fixed amount of 10 mg of adsorbents and 15-ml of known concentration of ammonium ion solutions were used in 20-ml glass vials. The vials were shaken at 170 rpm for 6 h using a shaking incubator (Korea instrument Co.). After mixing, solutions were filtered through a 0.2 μm polypropylene (PP) syringe filter (Whatmann, England) and equilibrium concentration of ammonium ion was determined using HACH method no. 10205 [19]. The acidic pH was maintained by adding 0.1 M HCl solution while the basic pH was adjusted by addition of small amounts of 0.1 M NaOH solution. The equilibrium adsorbed amounts Q_e (mg NH_4/g of absorbent) were calculated according to Eq. (1).

$$Q_e = \frac{V(C_i - C_e)}{w \times 1000} \tag{1}$$

where V (ml) is the volume of the adsorption solution, C_i and C_e (mg/L) are the initial and equilibrium concentrations of ammonium ion, respectively, and w (g) is the mass of the adsorbent.

3. Results and discussions

3.1. Characterization of APU

3.1.1. Chemical structure

The ^{1}H NMR and FT-IR spectra of modified polyurethanes are shown in Fig. 2. A peak at 8 ppm of single proton of urethane bond and a peak at 7 ppm of phenyl proton can be noticed in the ^{1}H NMR spectra. These peaks indicate that bonding between carboxylic group of urethane and phenyl group of alginate were established. This bonding was further confirmed by the FT-IR. After modification on urethane using alginate, the vibration absorption of O–H bond appeared at 3,430 cm^{-1}. The stretching vibration absorption of C=O bond appeared at 1,739 cm^{-1}, which shows that carboxylic functional group on alginic acid was intact and available for specific interaction with aluminum ion after reaction between alginate and urethane.

The number of reactive carboxylic functional group on APU were determine by soaking the polymer in a solution of predetermined amount of NaOH for 24 h. The solution was titrated with 0.1 N HCl. The results confirmed that mole ratio of carboxylic functional group and monomer were 1:1.

3.1.2. Physical properties

Physical properties, such as surface area, average pore diameter, and pore volume, of an absorbent are important factors to investigate adsorption process. Adsorption capacity of an adsorbent is proportional to available adsorption sites on surface area of the adsorbent. The size of pores is related to that of the molecules adsorbed in diffusion process [20]. Physical properties of the modified polyurethanes (APU) are given in Table 1. The pore volume of APU are

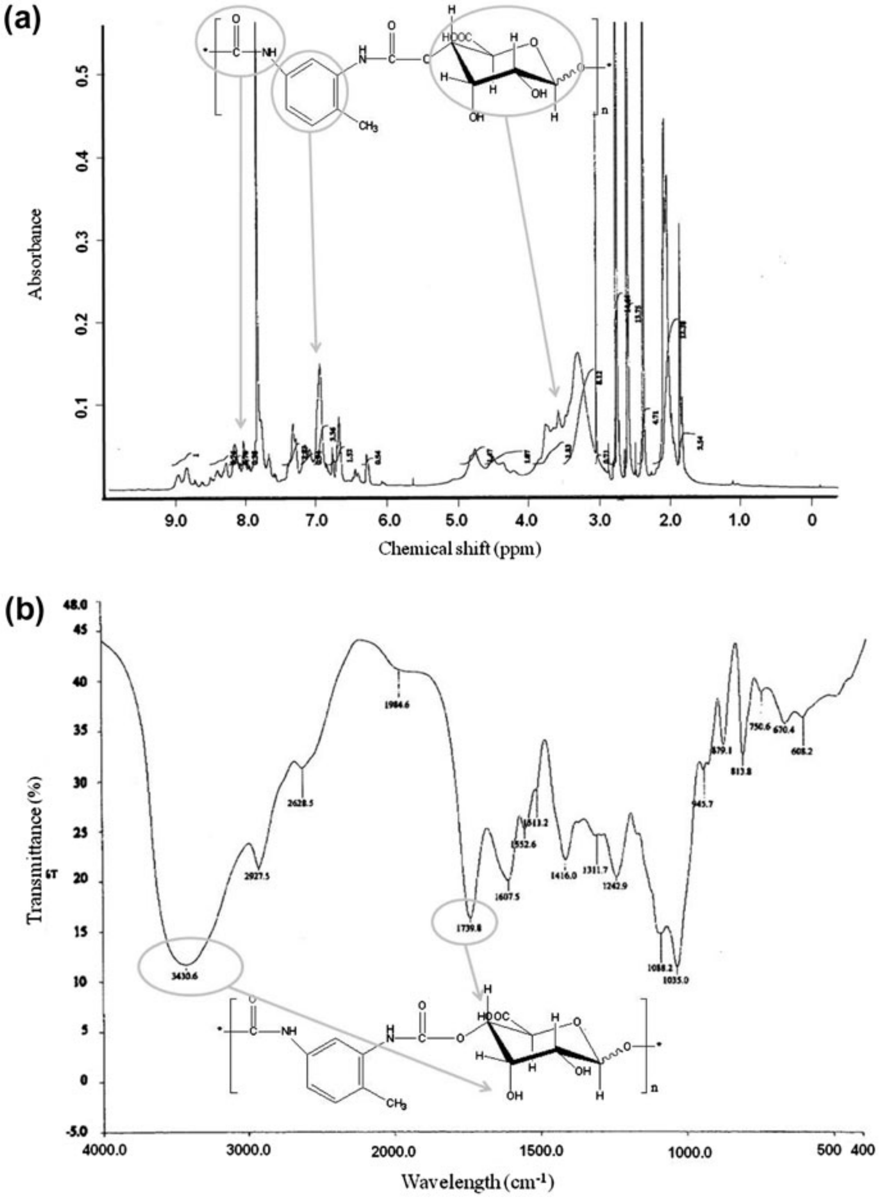


Fig. 2. (a) ^{1}H NMR spectra, and (b) FT-IR spectra of modified polyurethane (APU).

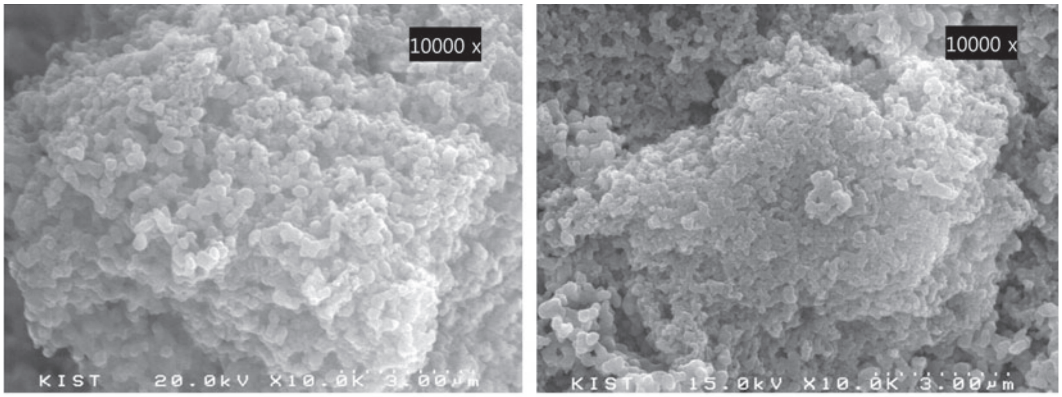
Table 1
Physical properties of APU

Adsorbent	Specific surface area (m^2/g)	Adsorption pore width (nm)	Adsorption total pore volume (cm^3/g)
APU	0.73 ± 0.12	22.9 ± 1.03	0.004 ± 0.001

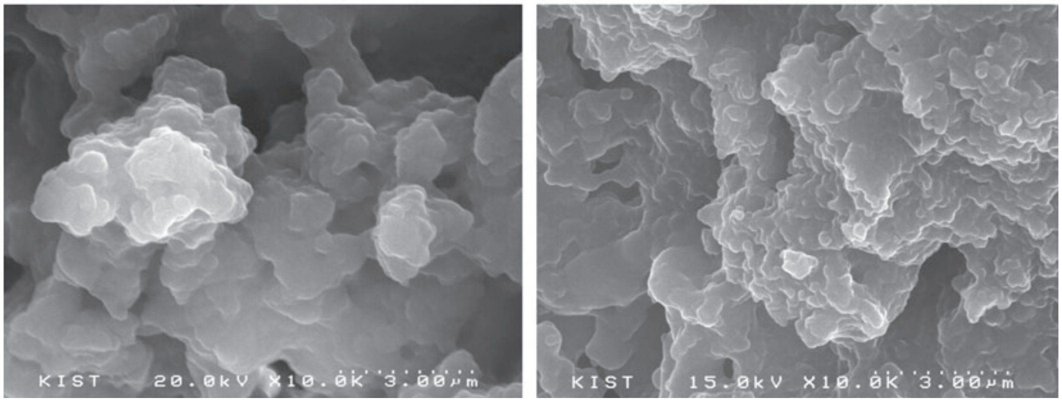
found 0.004 cm^3/g. Adsorption in large pores is considered very weak because of weak solid–fluid interactions [21,22]. Furthermore, ammonium ions can access to adsorption sites located in pores of APU (width 22.9 nm) due to its small radius about 0.143 nm.

3.2. *Surface analysis*

To confirm the adsorption of aluminum ions onto APU, surface analysis was performed before and after adsorption experiment using SEM (Fig. 3). As it can be seen in Fig. 3, the surface of APU was intact after



(a) Before adsorption (b) After adsorption



(c) PU Before adsorption (d) PU After adsorption

Fig. 3. Surface analysis of APU and PU before and after ammonium adsorption.

adsorption experiments, except for the adsorption of ammonium ions on the surface of APU. On the other hand, there was no change on the surface of PU. Moreover, a compact surface structure with narrow pores on APU can be observed as compared to surface of PU.

3.3. Kinetic studies

Adsorption of ammonium ion onto APU and PU at different shaking time was observed with initial ammonium concentration of 10 mg/L, adsorbent dosage of 10 mg/15 mL and temperature of 15, 25, and 35˚C at pH 6. The results obtained are shown in Fig. 4. The adsorption capacity of APU for ammonium ion reached to equilibrium plateau after 5 h of shaking time. Considering this time to reach equilibrium, duration of subsequent adsorption experiments was set at 5 h. For the same applied conditions, values of adsorption capacities of PU for ammonium ion remained quite low (Fig. 4(b)), which indicated that modification of polyurethanes by alginate enhanced adsorption capacities of the synthesized polymer (APU) by introduction of carboxylic functional group.

Nonlinear regression analysis was performed using OriginPro 8.0 software to fit the adsorption kinetic data for APU (Fig. 4) with the pseudo-first-, pseudo-second-, and pseudo-third-order kinetics models. The kinetic equations utilized in nonlinear regression are given below [23,24]:

$$C_t = C_\mathrm{i} - (C_\mathrm{i} - C_\mathrm{e})\left(1 - e^{-k_1 t}\right) \tag{2}$$

$$C_t = C_\mathrm{i} - (C_\mathrm{i} - C_\mathrm{e})\left(1 - \frac{1}{1 + k_2 t}\right) \tag{3}$$

$$C_t = C_\mathrm{i} - (C_\mathrm{i} - C_\mathrm{e})\left(1 - \frac{1}{(1 + 2k_3 t)^{1/2}}\right) \tag{4}$$

where C_i is the initial concentration of ammonium ion (mg ammonium/L); C_t is the ammonium ion concentration at time (mg ammonium/L); C_e is the equilibrium ammonium ion concentration (mg ammonium/L); t is the time (h); 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 2. Considering the value of correction coefficient, R^2, pseudo-first-order model best describe the adsorption kinetics of ammonium ion onto APU.

3.4. Thermodynamic studies

The effect of temperature on the adsorption of ammonium ion onto the APU was studied at 288, 298, and 308 K. The adsorption capacities at different temperatures are shown in Figs. 4 and 5. It can be seen that the adsorption capacities increased with increase in temperature. Thermodynamic behavior of adsorption of ammonium ion onto APU was investigated by the thermodynamic parameters (Fig. 5). The free energy change of adsorption (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) was calculated by variation of thermodynamic equilibrium constant, K_d as described previously by Freundlich isotherm [23] using following equations.

$$\Delta G = -RT \ln K_d \tag{5}$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{6}$$

where K_d is the equilibrium constant, R is the gas constant, and T is the temperature in Kelvin. The value of K_d was derived from Freundlich model. Despite that, Van't Hoff equation (Eq. (5)) would not fully applicable with the experimental sorption process, i.e. nonlinear shape of adsorption, it would give a reasonably good information on the adsorption mechanism [25].

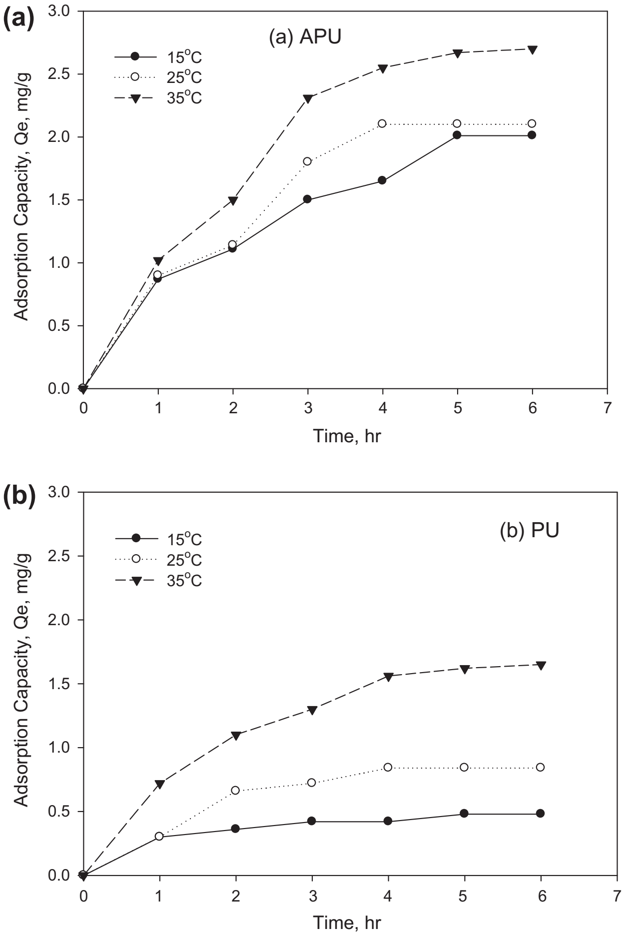


Fig. 4. Effect of shaking time on ammonium adsorption onto (a) APU and (b) PU.

The determined values of standard free energy, enthalpy, and entropy are summarized in Table 3. The standard free energy of ammonium ion adsorption onto APU was found to be in the range of −22.761 to −26.808 kJ/mole. The negative values of standard free energy indicates that the adsorption of ammonium ion onto APU was spontaneous; therefore, no energy input to the system is required. The spontaneous nature of the adsorption increased with temperature rise, indicating the adsorption of ammonium ion is inversely proportional to the temperature. The value of

Table 2
Kinetic parameters for ammonium ion adsorption onto APU

	Pseudo-first-order kinetic model		Pseudo-second-order kinetic model		Pseudo-third-order kinetic model	
Temp. (K)	k_1	R^2	k_2	R^2	k_3	R^2
288	7.93×10^{-3}	0.9852	9.76×10^{-4}	0.8565	4.88×10^{-4}	0.7565
298	1.37×10^{-2}	0.9828	8.21×10^{-3}	0.9802	4.10×10^{-3}	0.9302
308	1.45×10^{-2}	0.9643	1.89×10^{-2}	0.9477	9.43×10^{-3}	0.9547

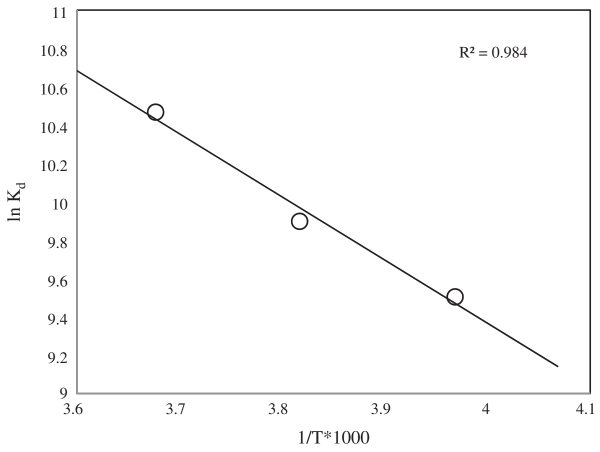


Fig. 5. Van't Hoff plot for the ammonium adsorption on APU.

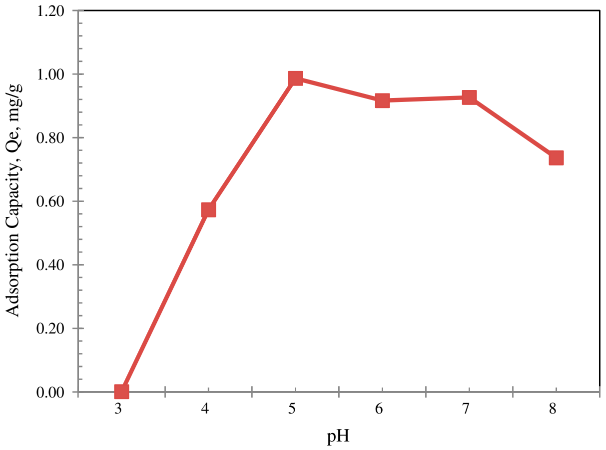


Fig. 6. Effect of pH on adsorption of ammonium ion on PU.

Table 3
Thermodynamic parameters of the ammonium adsorption onto APU and PU at different temperature

K_d	T (K)	ΔG (kJ/mol)	ΔS (J/mol K)	ΔH (kJ/mol)
13,430.2	288	−22.761	2.71	−0.40
19,913.4	298	−24.527		
35,190.0	308	−26.808		

standard enthalpy change (ΔH) was found to be negative (−0.40 kJ/mol) shows that adsorption was endothermic; therefore, rise in temperature resulted in higher adsorption of ammonium. The positive value of the standard entropy change ΔS suggests that the randomness increases the removal of ammonium ion onto APU.

3.5. Equilibrium studies

3.5.1. Effect of pH

To evaluate the initial pH on ammonium ion adsorption capacity on the adsorbents, experiments were conducted with 15 mL of 7.72 mg/L of ammonium ion solution containing 10 mg of adsorbent in the pH range 3–8 at room temperature. It was observed that adsorption of ammonium ion onto APU increased gradually as the initial pH of medium increased from 3 to 5, as shown in Fig. 6. The maximum adsorption capacity of APU was found about 1.0 mg/g for ammonium ion at pH 5. This capacity was maintained to pH 7. A further increase in pH to 8 resulted in slight decrease in adsorption capacity of APU for ammonium ion. However, this decrease was about 20% from the maximum adsorption capacity. Therefore, pH range 5–8 can be assumed effective pH range for adsorption of ammonium ion onto APU. This pH range falls within the range of many wastewater effluent ranges between 7 and 8 [3]. Therefore, APU can be used for residual ammonium ion removal from effluent of wastewater treatment plants.

3.5.2. Adsorption isotherms

The ammonium isotherm plots representing the equilibrium distribution of ammonium ions onto APU and liquid phase were obtained (Fig. 7) at pH 7.0 by varying initial concentration of ammonium (0.5–14 mg NH_4/L). It is evident in Fig. 7 that the adsorption capacity (Q_e) of APU for ammonium ion ascends

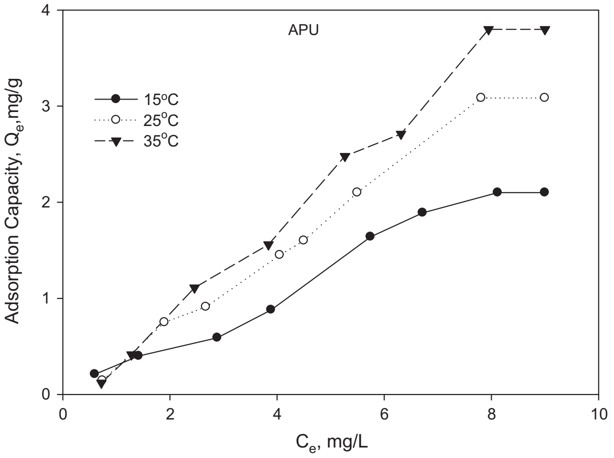


Fig. 7. Adsorption isotherm of ammonium ion onto APU.

Table 4
Estimated isotherm constants for ammonium ion adsorption onto APU

APU								
	Freundlich equation $Q_e = K_F C^{1/n}$				Langmuir equation $Q_e = Q_m K_L \frac{C_e}{1+K_L C_e}$			
Temp. (K)	K_F ((mg/g)/(mg/L)$^{1/n}$)	$1/n$	R^2	χ^2	K_L (L/mg)	Q_m (mg/g)	R^2	χ^2
288	0.2578	1.007	0.9698	0.0213	4.265	0.094	0.9094	0.0564
298	0.3670	1.002	0.9849	0.0188	6.600	0.080	0.9312	0.0937
308	0.4064	0.958	0.9856	0.0310	8.269	0.078	0.9348	0.1516

linearly with increasing equilibrium concentration of ammonium ion in liquid phase (C_e). This trend indicates moderate affinity of adsorption sites for ammonium. It means that presence of carboxylic and alcoholic functional groups on APU considerably induced capability for ammonium ion adsorption.

The adsorption data shown in Fig. 7 were fitted to Freundlich and Langmuir models which are given in Eqs. (7) and (8), respectively, by nonlinear regression using the method of least square [23].

$$Q_e = K_F C^{1/n} \tag{7}$$

$$Q_e = Q_m K_L \frac{C_e}{1 + K_L C_e} \tag{8}$$

where Q_e is the adsorption capacity (mg ammonium/g) at equilibrium; C_e is the equilibrium concentration of ammonium ion in liquid phase (mg/L); K_F and $1/n$ are Freundlich constants; Q_m is the maximum adsorption capacity (mg ammonium/g); K_L is Langmuir constant (L/mg). The curve fitting was performed using OriginPro 8.0 software. The obtained values of K_F, $1/n$, Q_m, K_L, and correlation coefficients (R^2) are given in Table 4. Considering the values of correlation coefficient, R^2, Freundlich model yield good correlation. In order to confirm the best fit, chi-square analysis was also performed. If data from model were similar to the experimental data, a small number of χ^2 would be obtained. The values of χ^2 of each model are also given in Table 2. The chi-square analysis also confirmed that Freundlich model described best adsorption of ammonium ion onto APU.

The values of Langmuir constants were comparable to the values found in other studies for removal of ammonium ion [22,24].

4. Conclusions

APU was synthesized using 2,4-toluene diisocyanate and alginate for removal of ammonium ion from aqueous medium. APU was used as an absorbent for removal of aqueous ammonium. The surface structure of polyurethanes were modified by covalent bonding of alcoholic and carboxylic functional group of alginate. Langmuir and Freundlich models were fitted on experimental data and values of parameters of respective models were determined. It was found that Freundlich model described best for adsorption of ammonium ion onto APU. The analysis kinetic data suggest that adsorption of ammonium follows pseudo-first-order kinetics. The values of standard free energies at different temperatures indicated that the adsorption was spontaneous. The value of standard enthalpy revealed endothermic nature of adsorption. The optimum pH for ammonium adsorption onto APU was found to be within pH range of wastewater effluent. Application of APU can remove residual ammonium ion from water; hence can improve the quality of water.

Acknowledgments

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