Research Article

Selective Cu(II) Adsorption from Aqueous Solutions Including Cu(II), Co(II), and Ni(II) by Modified Acrylic Acid Grafted PET Film

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Acrylic acid (AAc) grafted polyethylene terephthalate (PET) films were prepared by γ irradiation. The graft films showed little metal ion adsorption due to compact structure of the graft chains as shown by the scanning electron microscopy (SEM) images which restricted the access of metal ions to the functional groups. Therefore, the graft films were modified with KOH treatment for expansion of the graft chains to facilitate the access of metal ions to the functional groups. The modified films were used to study the selective Cu^{2+} adsorption from aqueous solution containing Cu^{2+}, Co^{2+}, and Ni^{2+}. Langmuir and Freundlich isotherm models were used for interpretation of selective equilibrium adsorption data and Langmuir model showed better fitting with experimental data. Again pseudo-first-order and pseudo-second-order equations were used for interpretation of selective kinetic adsorption data and pseudo-second-order equation showed better prediction of experimental data. The adsorbent film showed high selectivity towards Cu^{2+} in presence of Cu^{2+}, Co^{2+}, and Ni^{2+} in the pH range of 1.5 to 4.5. Desorption and reuse of the adsorbent film were also studied which indicated that the film can be used repeatedly for selective Cu^{2+} sorption from aqueous solution.

1. Introduction

In recent years, heavy metals have received much public attention as potential hazards for human life and health ignited by the well-known environmental destruction cases: Minamata disease (organic mercury poisoning) and itai-itai disease (cadmium poisoning) and the stricter environmental regulations on the discharge of heavy metals make it necessary to develop efficient and low cost technologies for their removal [1]. About heavy metal pollution it should be also realized that to prevent heavy metal poisoning, immediate detoxification of heavy-metal wastewater through appropriate treatment is essential. Because, unlike many organic pollutants, heavy metals are not decomposed by microbiological activity, rather heavy metals can be enriched by organisms and the type of bonding can be converted to more poisonous metal-organic complexes and the polluted areas can become widened by diffusion in the environment. But the conventional methods for removal of hazardous metal ions from wastewater such as precipitation, ion exchange, activated carbon adsorption, and electrolytic method have limitations like high cost, low removal rate or difficulty for regeneration, and reuse. Therefore, many researches focused on the study of alternative low-cost-effective adsorbents from sawdust [2], sporopollenin [3, 4], chitosan [5], peat [6], cellulose [7], and clay mineral [8].

One of the new developments in the field of heavy metal adsorption is the use of functional monomer grafted synthetic polymers as adsorbent. Attracting with the excellent chemical and thermal stability and mechanical properties of PET, adsorbents prepared by grafting of various monomers on PET fibers [9–17] and films [18] have been investigated

for the adsorption of hazardous heavy metal ion from water which demonstrated good potential of PET-based adsorbents in heavy metal removal. However, most of the previous studies on PET-based adsorbents focused on metal ion adsorption from single metal solution while less results appeared in the literature on metal ion adsorption from multimetal solution which is important for separation of one metal ion from wastewater containing other metal ions. Therefore, we are interested in selective metal ion adsorption from multi metal solution. In the present work, we prepared AAc grafted PET films by γ irradiation. The graft films showed little metal ion adsorption due to compact structure of the graft chains. Therefore, the graft films were modified with KOH treatment for expansion of the graft chains to increase the metal ion adsorption. The modified films were used to study the potential of selective Cu^{2+} adsorption from aqueous solution containing Cu^{2+}, Co^{2+}, and Ni^{2+} focusing with the four main objectives: (1) characterization of modified AAc grafted PET films by FTIR and SEM, (2) studying the equilibrium adsorption isotherm of selective Cu^{2+} adsorption from ternary metal solutions of Cu^{2+}, Co^{2+}, and Ni^{2+} and use of Langmuir and Freundlich isotherm models for interpretation of equilibrium adsorption data, (3) studying the kinetic of selective Cu^{2+} adsorption from ternary metal solutions of Cu^{2+}, Co^{2+}, and Ni^{2+} and use of pseudo-first-order and pseudo-second-order equations for interpretation of adsorption kinetic data, and (4) studying the desorption of metal ions from the film and reuse of the film.

2. Experimental

2.1. Materials and Reagents.
Commercial PET films (Teijin DuPont films, G2) of thickness 50 μm were kindly provided by Teijin Co., Ltd. These films were cut into small pieces (3.5 × 1.5 cm^2), washed with acetone, and dried in vacuum oven before use. AAc and FeCl$_3$ were procured from Sigma-Aldrich. KOH was supplied by Wako pure chemical industries Ltd. Cobalt(II) chloride, nickel(II) chloride, and copper(II) chloride (anhydrous, Chameleon reagent), and cobalt, nickel and copper standard solutions (Fluka) were used as a source of the adsorbate and for the calibration of metal ion concentrations, respectively.

2.2. Instrument and Apparatus.
The PET films were analyzed by a Fourier transform infrared (FTIR) spectrophotometer, Jasco FTIR 620 in the wavenumber range 400–4000 cm^{-1} to investigate the chemical and/or physical interactions. Scanning electron microscopy (SEM) image observations of the carbon coated PET films were performed using Zeiss Ultra-55 SEM operated at 7–10 keV. The metal-ion concentrations in the solutions were analyzed by an inductively coupled plasma mass spectrometer, Agilent7700 Series ICP-MS.

2.3. Grafting of AAc onto the PET Films by Gamma Radiation.
The dry PET films weighing W_{pristine} were taken into glass bottles containing different concentrations (20–40 wt%) of AAc aqueous solutions. FeCl$_3$ at a constant concentration (1 wt%) was added to the AAc solutions to minimize homopolymer formation. The contents of the glass bottles were then irradiated with different doses (20–100 kGy) of γ rays with a dose rate of 1.0 kGy/h in air (γ-ray irradiation of the PET films was carried out at the ^{60}Co γ-ray irradiation facility of Research Reactor Institute, Kyoto University). The obtained grafted films were washed in distilled water at 60°C for 24 h to remove the homopolymers. Then the films were dried in a vacuum oven at 60°C for 24 h and were weighed ($W_{\text{AAc grafted}}$). The graft yield was determined by the percent increase in the weight as follows.

Graft yield

$$\delta W_{\text{AAc grafted}} (\%) = \frac{\left(W_{\text{AAc grafted}} - W_{\text{pristine}}\right)}{W_{\text{pristine}}} \times 100. \quad (1)$$

2.4. KOH Treatment of the AAc Grafted Film.
The AAc grafted films with 40% graft yield (obtained at 40% AAc concentration and 100 kGy dose) were modified by treatment with 2.5% KOH for 2 min at 25°C.

2.5. Metal Ion Adsorption by the Modified AAc Grafted PET Film.
The modified AAc grafted films of 60 mg were soaked into the 10 mL aqueous solutions including of Cu(II), Ni(II), and Co(II) at a definite metal ion concentration and pH for 60 min at room temperature (25°C). pH of the solutions was adjusted using HCl and NaOH solution. Metal loaded films were washed and dried. The metal-ion concentrations of the solutions were analyzed by ICP-MS.

2.6. Determination of Metal Ion Uptake Capacity.
The metal ion uptake capacity of the film was calculated as follows:

$$Q = \frac{V(C_1 - C_2)}{W}, \quad (2)$$

where Q is the adsorption amount (mg/g), W the weight of the film (g), V the volume of solution (L), and C_1 and C_2 are the concentrations (mg/L) of metal ion before and after adsorption, respectively.

2.7. Desorption of Metal Ions.
The desorption of Cu(II), Ni(II), and Co(II) ions from the adsorbent films was carried out by the treatment with 2 M aqueous solution of HCl for 30 min. The percent of desorption was calculated using the following equation.

Percent desorption

$$= \frac{\text{Amount of ions (mg) desorbed}}{\text{Adsorbed amount of ions (mg) by adsorbent}} \quad (3)$$

$$\times 100.$$

3. Results and Discussion

3.1. Preparation and Characterization of the Adsorbent Film.
Grafting of AAc onto PET films was carried out by γ irradiation. AAc grafting on PET film might have followed

TABLE 1: Metal ion adsorption capacity of AAc grafted PET film and modified AAc grafted PET film compared with some other adsorbents (from single metal solution).

Adsorbent	Cu^{2+} adsorption capacity (mg/g)	Co^{2+} adsorption capacity (mg/g)	Ni^{2+} adsorption capacity (mg/g)
Pristine PET film (present study)	0	0	0
AAc graft PET film (present study)	10	7	8
Modified AAc graft PET film (present study)	100	67	85
Itaconic acid/acrylamide graft PET fiber [13]	7.73	14.81	13.79
Methacrylic acid/acrylamide graft PET fiber [12]	31.25	27.17	43.48
Cross-linked and non cross-linked chitosan [5]	>80	—	—

a free radical mechanism where at first primary free radical is formed on PET backbone initiated by γ ray which then reacts with monomer to form graft growing chain and finally the graft copolymer is formed by a termination reaction [19]. The prepared AAc grafted films (G-40%) were modified by treatment with KOH which increased the metal ion adsorption capacity of the films largely, almost 10 times than the AAc grafted films. The adsorption capacity of Cu^{2+}, Co^{2+}, and Ni^{2+} ions obtained in the present study together with that reported in previous studies are presented in Table 1. The modified AAc grafted PET film after adsorption of Cu^{2+}, Co^{2+}, and Ni^{2+} ions are shown in Figure 1.

To understand the change of the PET film after AAc grafting and KOH treatment, the IR spectra of the films were determined. IR spectrum of the PET film (Figure 2(a)) represented the peaks characteristic for poly(ethylene terephthalate) chemical structure (absorption peak for OH stretching at $3430\,cm^{-1}$, aromatic C–H stretching at $3054\,cm^{-1}$, aliphatic C–H stretching at 2969 and $2907\,cm^{-1}$, C=O stretching vibration at $1684\,cm^{-1}$, and bands associated with the aromatic ring at 1614, 1578, and $1505\,cm^{-1}$). IR spectrum of the AAc grafted PET film showed new peaks for carboxyl –OH groups around $2300–3700\,cm^{-1}$ which was absent in IR spectrum of pristine PET film (Figure 2(a)). The –OH peaks near 2580 and $2900\,cm^{-1}$ indicate the existence of strong hydrogen bonding between –COOH groups in the AAc grafted PET film [20, 21]. After KOH treatment the –OH peak near $2580\,cm^{-1}$ disappeared (Figure 2(a)) indicating the reduction of hydrogen bonding between the –COOH groups and formation of some $–COO^-K^+$ groups which is confirmed by the appearance of new peak near $1560\,cm^{-1}$ assigned for carboxylate ion (Figure 2(b)) [22]. Therefore it can be said that AAc grafted PET film can show little adsorption of metal ion due to the presence of hydrogen bonded –COOH groups, but after KOH treatment, the films showed greater metal ion adsorption due to the reduction of hydrogen bonding between –COOH groups and the presence of some ionized $–COO^-K^+$ groups. The conversion percentage of –COOH groups to $–COO^-K^+$ groups can be calculated from the IR spectra by the following equation:

$$\text{Conversion } (\%) = \left(\frac{B - C}{B - A}\right) \times 100, \qquad (4)$$
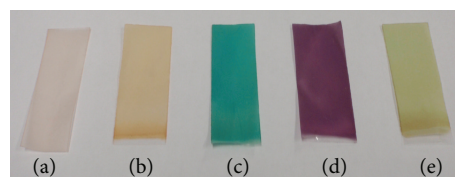

FIGURE 1: (a) AAc grafted PET film, (b) AAc grafted PET film after modification by KOH treatment (c) modified AAc grafted PET film after Cu(II) loading, (d) modified AAc grafted PET film after Co(II) loading, and (e) modified AAc grafted PET film after Ni(II) loading.

where A, B, and C represent the total area under the IR peaks from $2300–3700\,cm^{-1}$ (the region where carboxyl –OH peaks appeared) for pristine PET, AAc grafted PET, and KOH treated AAc grafted PET, respectively. The conversion percentage calculated is 28%.

The reason behind increase of metal ion adsorption after KOH treatment can be better understood from the SEM image. SEM micrographs of pristine PET film, AAc grafted PET film, and modified AAc grafted PET film are shown in Figure 3. The effect of KOH treatment is not only conversion of some extent of –COOH group to –COOK group, but rather the more significant effect is the structural change of the graft film surface after introduction of some –COOK group. Before KOH treatment, the graft chains showed a compact structure in SEM image (Figure 3(b)) which is due to the attraction between the graft chains because of hydrogen bonding (Figure 3(b1)). At this condition many of the functional groups (–COOH) were inaccessible to the metal ions. After KOH treatment, graft chains showed an expanded structure in SEM image (Figure 3(c)) which is due to the repulsion of graft chains by the electrostatic force of some ionic $–COO^-$ groups. (Figure 3(c1)). At this condition the initial functional groups (–COOH) of the graft films became easily accessible to the metal ions besides the new functional groups (–COOK). The average surface roughness (R_a) calculated from the SEM image of pristine PET, AAc grafted PET, and KOH treated AAc graft PET film is 9.6, 10.8, and 20.7 pixel, respectively (roughness is calculated by using an image processing program, imageJ). Large increase of surface roughness after KOH treatment provides further proof of the rearrangement of the graft chains from compact structure to expanded structure which facilitated the metal ion adsorption.
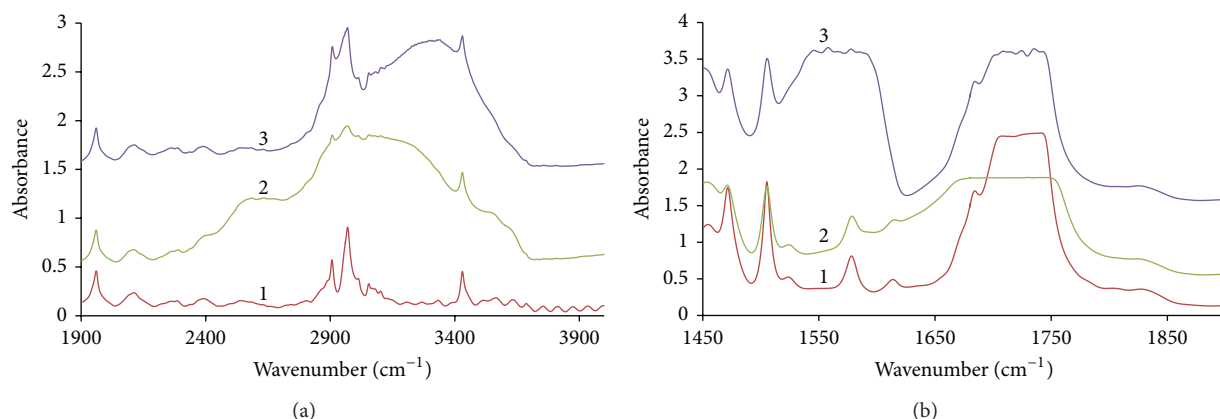
(a)

(b)

FIGURE 2: FTIR spectra of (1) ungrafted PET film, (2) AAc grafted PET film, and (3) KOH treated film AAc grafted PET film. The spectra are split into the two figures at 1900 cm^{-1}.
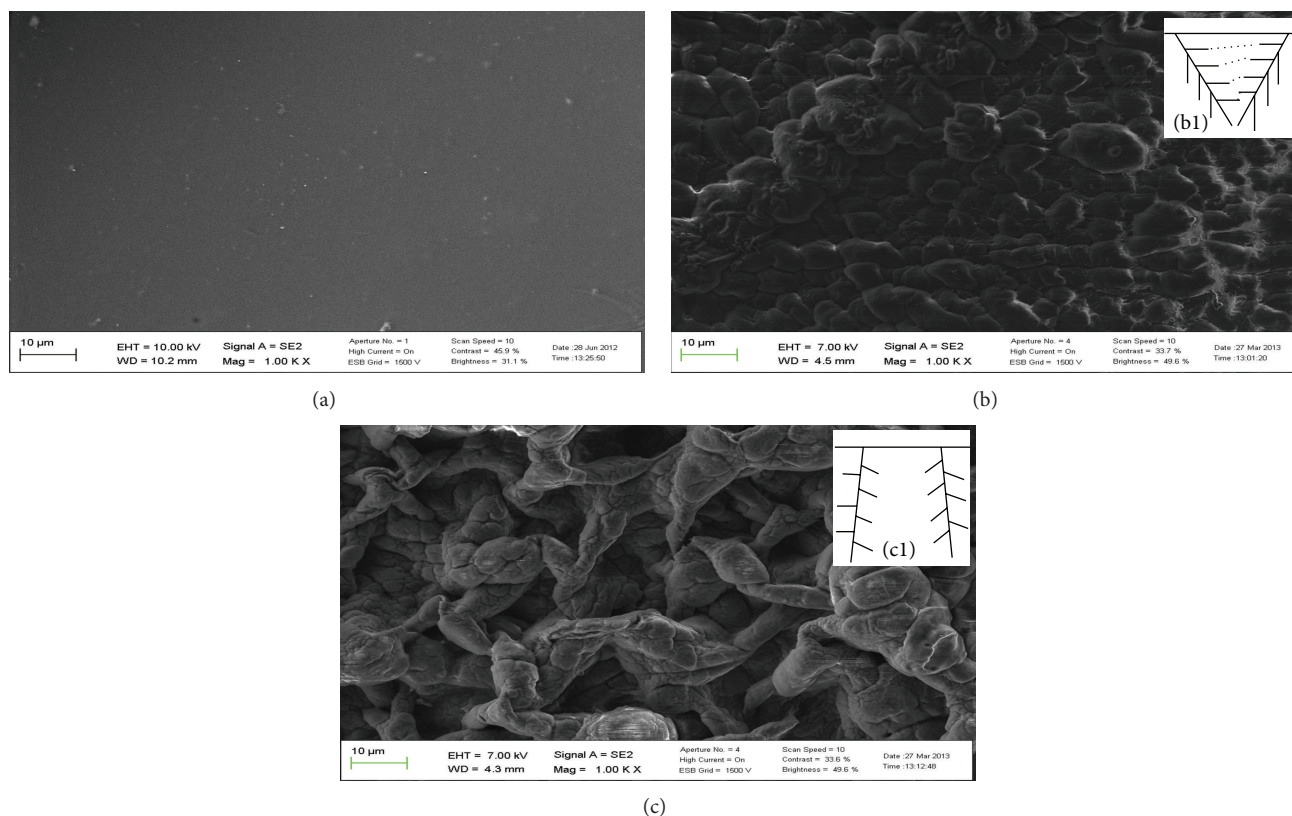

(a)

(b)

(c)

FIGURE 3: SEM micrographs of (a) ungrafted PET film, and (b) AAc grafted PET film. (b1) Graft chains are attracted by hydrogen bonding and the functional groups are inaccessible to the metal ions. (c) Modified AAc grafted PET film. (c1) Graft chains are repulsed by electrostatic force of –COO$^-$ group and the functional groups are accessible to the metal ions.

3.2. Selective Cu(II) Ion Adsorption by the Adsorbent Film.

The modified graft film adsorbed 55.6, 9.0, and 7.8 mg/g of Cu(II), Ni(II), and Co(II), respectively, from a ternary solutions of Cu(II), Ni(II), and Co(II) under the same initial concentrations of 2000 mg/L of each metal ion at pH 4. The selectivity of an adsorbent is often measured from the distribution coefficient (K_d). The term K_d refers to the affinity of an adsorbent for a particular ion in presence of interfering ions. K_d can be calculated by (5) [23] as

$$K_d = \frac{V\left(C_0 - C_f\right)}{C_f W}, \qquad (5)$$

where K_d is the distribution coefficient (mL/g), C_0 and C_f (mg mL^{-1}) are the initial and equilibrium concentrations of a metal species, respectively, V (mL) is the volume of the testing solution, and W (g) is the amount of adsorbent.

Now, the selectivity coefficient, α (dimensionless), for a specific metal ion in the presence of competitor ions can be expressed by (6) as

$$\alpha = \frac{K_d(T)}{K_d(I)}, \tag{6}$$

where $K_d(T)$ is the K_d value of the targeted metal (Cu(II) ions in this case), and $K_d(I)$ is the K_d value of the other metal in the mixed metal solutions (Ni(II) or Co(II) ions in this case). The selectivity coefficient for binding of Cu(II) over Ni(II) and Co(II) calculated (at initial concentrations of 2000 mg/L and pH 4) for modified AAc grafted PET film is $\alpha_{(Cu/Ni)} = 7$ and $\alpha_{(Cu/Co)} = 8$, respectively. The selectivity sequence for the modified graft film (Cu(II) > Ni(II) > Co(II)) followed the Irving-Williams series, which refers to the relative stabilities of complexes formed by the transition metal ions with ligands [24]. The high selectivity for Cu(II) can be explained in terms of the Pearson's concept of hard and soft acids and bases. According to the concept, the carboxylate groups can be considered as soft bases, and on the other hand Cu^{2+} can be considered as a soft acid, while Ni^{2+} and Co^{2+} are relatively hard acids [25]. Generally, hard acids coordinate better with hard bases and soft acids with soft bases. Therefore, a strong interaction between Cu^{2+} and carboxylate group bearing adsorbent films is expected.

3.3. Equilibrium Adsorption Isotherm of Selective Cu(II) Ion Adsorption. An adsorption isotherm which represents the relationship between the amount of metal ions adsorbed by the adsorbent and the metal ions concentration remaining in solution is commonly used to study the adsorption process. Adsorption isotherms for competitive adsorption of Cu(II), Ni(II), and Co(II) under the same initial concentrations are shown in Figure 4. In case of Cu(II), the adsorption capacity increased with the increase of equilibrium concentration while for Ni(II) and Co(II), the adsorption capacity reached maximum for equilibrium concentration of 167 and 172 mg/L, respectively, and thereafter decreased with increase of equilibrium concentration. This might be due to the high affinity of the adsorbent for Cu(II) than Ni(II) and Co(II) (Section 3.2), for which with increase of Cu(II) ion concentration with respect to the available adsorption sites, the adsorption of Ni(II) and Co(II) decreased.

For interpretation of the selective Cu(II) adsorption data, the Langmuir [26] and Freundlich [27] isotherm models were used. The linear form of the Langmuir isotherm is presented by

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_o} + \frac{1}{(Q_o b)}, \tag{7}$$

where C_e is the equilibrium concentration (mg L^{-1}), Q_o the monolayer saturation adsorption capacity of adsorbent (mg g^{-1}), Q_e is the equilibrium adsorption capacity, and b is
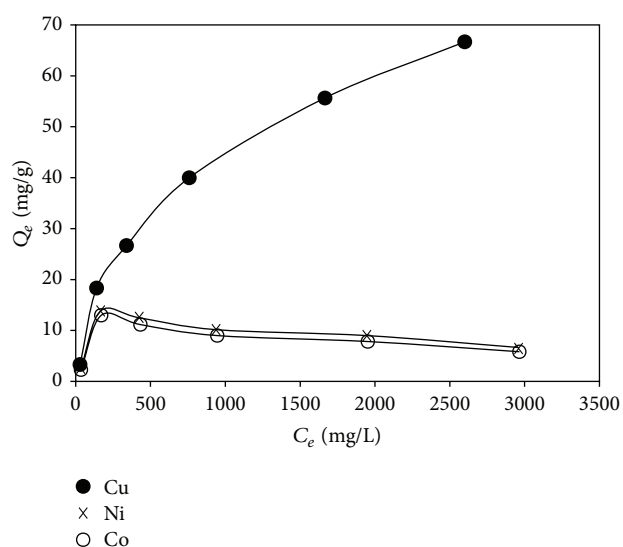

FIGURE 4: Equilibrium adsorption isotherm for competitive adsorption of Cu(II), Ni(II), and Co(II) by the modified graft films under the same initial concentrations of metal ions. (pH 4; $t = 60$ min; $G = 40\%$).
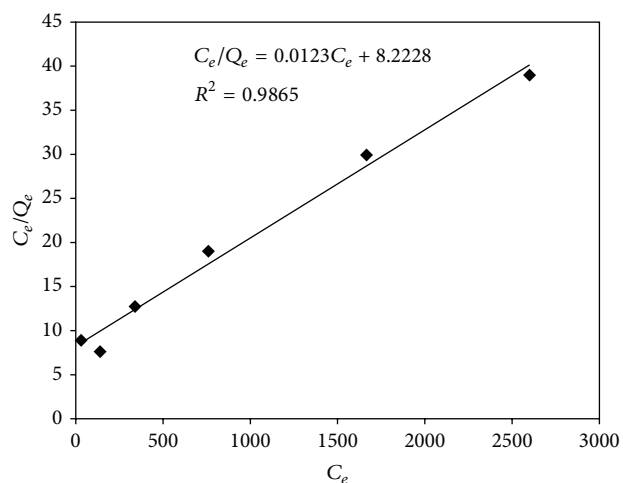

FIGURE 5: Langmuir isotherm plot for selective Cu(II) adsorption.

Langmuir adsorption constant (Lmg^{-1}). The plot of C_e/Q_e versus C_e shown in Figure 5 was drawn from the experimental data given in Figure 4. The relationship between C_e/Q_e and C_e is linear indicating that the adsorption behavior follows the Langmuir adsorption isotherm. The b, Q_o, and correlation coefficients (R^2) values are presented in Table 2.

The Freundlich isotherm is described by the following equation:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e, \tag{8}$$

where C_e is the equilibrium concentration (mg L^{-1}), Q_e is the equilibrium adsorption capacity, K_F the sorption capacity (mg g^{-1}), and n is an empirical parameter. The plot of $\log Q_e$ versus $\log C_e$ shown in Figure 6 was drawn from

TABLE 2: Langmuir and Freundlich isotherm parameters for selective Cu(II) adsorption.

	Langmuir isotherm parameters			Freundlich isotherm parameters	
Q_0 (mg/g)	b (L/mg)	R^2	K_F (mg/g)	n	R^2
81.30	0.0015	0.986	0.53	1.56	0.942

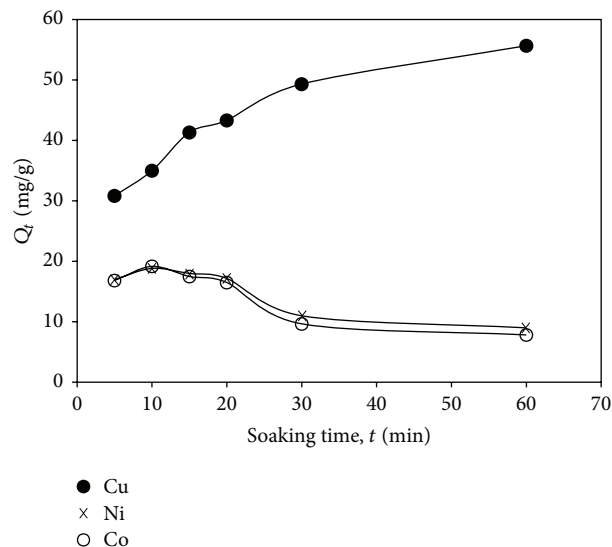FIGURE 6: Freundlich isotherm plot for selective Cu(II) adsorption.

● Cu
× Ni
○ Co

FIGURE 7: Adsorption kinetics for competitive adsorption of Cu(II), Ni(II), and Co(II) by the modified graft films under the same initial concentrations of metal ions. (pH 4; initial concentration, C_i = 2000 mg/L; G = 40%).

the experimental data given in Figure 4. The K_F, n, and correlation coefficients (R^2) values are presented in Table 2.

The linear plots show that the two studied models, the Langmuir equation and Freundlich equation, can give prediction of experimental data. The Langmuir model assumes monolayer adsorption of adsorbate on a structurally homogeneous adsorbent where all adsorption sites are identical. On the other hand, the Freundlich model is not restricted to homogeneous system or monolayer adsorption; it can also describe heterogeneous system and multilayer adsorption. Therefore, fitting of experimental data with Langmuir model suggests that a monolayer adsorption of ions on the adsorbent is appropriate to describe the selective Cu(II) adsorption on the modified AAc grafted PET. This also suggests that the adsorption was mainly chemical adsorption and the adsorption sites are identical to the metal ions; in other words surface heterogeneity of apparently heterogeneous surface of the modified AAc grafted PET is not significant in respect of adsorption phenomenon. Similar conclusion has been drawn when the adsorption of metal ions on the rough surface of meranti sawdust followed the Langmuir adsorption isotherm model [28].

3.4. Adsorption Kinetic of Selective Cu(II) Ion Adsorption. Figure 7 shows the kinetics of competitive adsorption of Cu(II), Ni(II), and Co(II) under the same initial concentrations of metal ions by modified AAc grafted PET films. It was observed that the adsorption of Cu(II) ions increased with increasing soaking time while adsorption of Ni(II) and Co(II) reached maximum after 10 min and after that decreased with increasing soaking time. This can be explained as the adsorbent Ni(II) and adsorbent Co(II) complexes are less stable than adsorbent Cu(II) complex (Section 3.2); therefore,

with increase of soaking time more stable complexes replace less stable complexes.

The pseudo-first-order and pseudo-second order kinetic models were applied to fit the selective Cu(II) adsorption by the modified AAc grafted PET films. The pseudo-first-order and pseudo-second-order equations [29, 30], are expressed as:

$$\log\left(Q_e - Q_t\right) = \log Q_e - \left(\frac{k_1}{2.303}\right)t$$

$$\frac{t}{Q_t} = \frac{1}{\left(k_2 Q_e^2\right)} + \frac{t}{Q_e},$$

(9)

where Q_t and Q_e are the amount of ions adsorbed (mg g^{-1}) at any time and equilibrium time, respectively, k_1 is the rate constant (min^{-1}) of first-order adsorption, and k_2 (g min^{-1} mg^{-1}) is the rate constant of second-order adsorption. The pseudo-first-order rate constants could be determined experimentally by plotting $\log(Q_e - Q_t)$ against t as shown in Figure 8. The experimental and theoretical Q_e value, first-order rate constant, and the correlation coefficients (R^2) are given in Table 3. It can be seen from the results that the experimental Q_e value and the Q_e value calculated from first-order kinetic model are not in agreement with each other. Pseudo-second-order rate constants could be determined experimentally by plotting t/Q_t against t as shown in Figure 9. All the second-order kinetic parameters for selective Cu(II) adsorption are

TABLE 3: The pseudo-first-order and pseudo-second-order rate constants for selective Cu(II) adsorption.

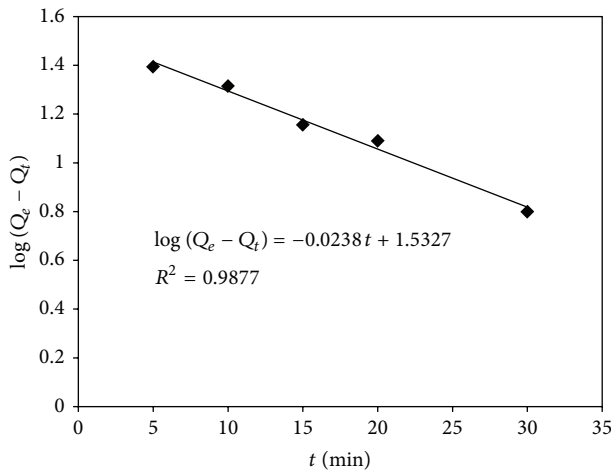| Q_e (exp.) (mg/g)	Pseudo-first-order rate constant			Pseudo-second-order rate constant		
	Q_e (theor.) (mg/g)	k_1 (min^{-1})	R^2	Q_e (theor.) (mg/g)	k_2 (g min^{-1} mg^{-1})	R^2
55.66	34.1	0.0548	0.9877	56.82	0.0034	0.9899

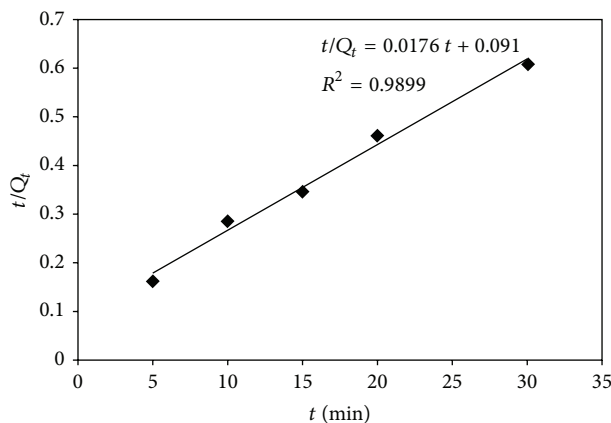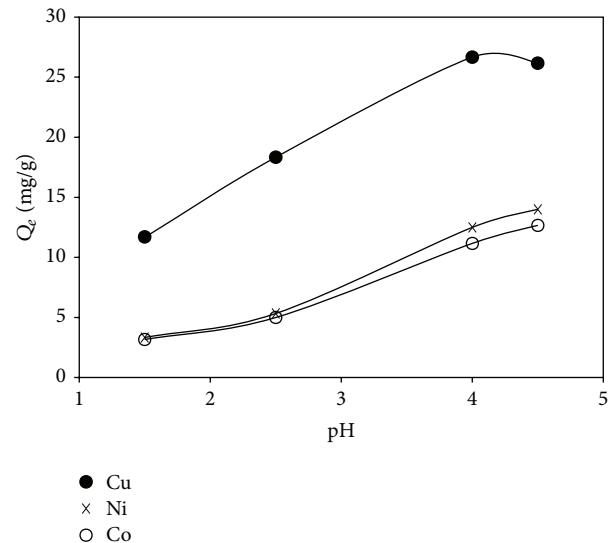FIGURE 8: Pseudo-first order plot for selective Cu(II) adsorption.

FIGURE 9: Pseudo-second order plot for selective Cu(II) adsorption.

given in Table 3. It can be seen that the experimental Q_e and the Q_e value calculated from second-order kinetic model are in accordance with each other. Therefore, the pseudo-second-order equation can be used to interpret selective Cu(II) adsorption on the modified AAc grafted PET. Pseudo-second-order model fit with the experimental kinetic data indicate that intraparticle diffusion process was the rate-limiting step of the adsorption [31] and it also proves that the chelating interaction plays the major role in the adsorption process [32].

3.5. Effect of pH on Selective Cu(II) Ion Adsorption.
Effect of pH on competitive adsorption of Cu(II), Ni(II), and Co(II) by the modified graft films at initial concentration 500 mg/L is shown in Figure 10. It can be seen that the adsorbent is highly

FIGURE 10: Effect of pH on the competitive adsorption of Cu(II), Ni(II), and Co(II) by the modified graft films under the same initial concentrations of metal ions. ($t = 60$ min; Initial concentration = 500 mg/L; $G = 40\%$).

selective towards Cu(II) in the pH range 1.5 to 4.5. At low pH, the carboxylate ions are more protonated and therefore adsorption of all metal ions was low. With increase of pH from 1.5 to 4.5, adsorption of all metal ions increased and in the pH range the adsorbent showed selectivity towards Cu(II) due to its the high affinity towards Cu(II). But increase of pH after 4.5 caused precipitation of Cu(OH)$_2$.

3.6. Desorption and Reuse of the Adsorbent.
After adsorption of metal ion on the modified AAc grafted PET, the adsorbents were regenerated using 2 M hydrochloric acid. Desorption took place rapidly and the equilibrium achieved within 10–20 min. The desorption ratio was 99%. During desorption, the hydrogen ions in the solution were exchanged with the metal ions on the sorption sites. The regenerated film (–COOH form) was treated with KOH solution (to convert to –COO$^-$K$^+$ form) before being reused in subsequent cycles. Because we found that this –COOH form showed much lower metal adsorption than –COO$^-$K$^+$ form which may be due to the formation of hydrogen bonding again. The sorption capacity of the film for Cu(II) from aqueous solution of Cu(II), Co(II) and Ni(II) in five successive cycles is shown in Figure 11. For the 2nd cycle the sorption capacity decreased which may be due to the loss of physically adsorbed homopolymer of AAc which might have washed out in acid and base solutions [33]. However, the sorption capacity
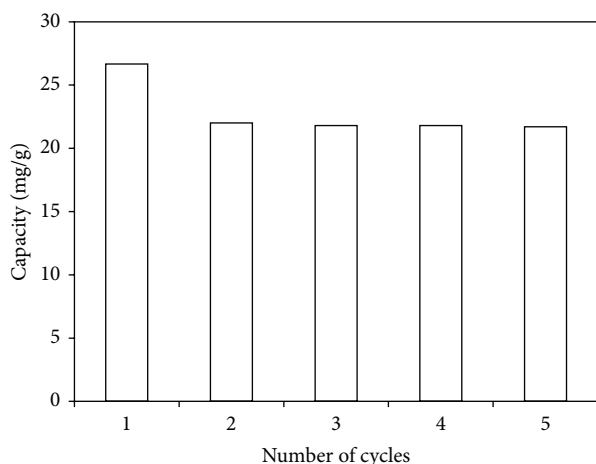
FIGURE 11: Repeated use of modified AAc grafted film for adsorption of Cu(II) from mixture of Cu(II), Co(II), and Ni(II) (pH 4; $t =$ 60 min; $C_i = 500$ ppm; $G = 40\%$).

did not change that much in subsequent cycles indicating that the film can be used repeatedly for Cu(II) adsorption.

4. Conclusion

The KOH treated AAc graft PET films containing carboxylate groups can form more stable complex with Cu^{2+} than Co^{2+} or Ni^{2+} and therefore can show selective Cu^{2+} adsorption from aqueous solution containing Cu^{2+}, Co^{2+}, and Ni^{2+} with a selectivity coefficient of 7 and 8 for binding of Cu^{2+} over Ni^{2+} and Co^{2+}, respectively, at pH 4 and initial concentration 2000 mg/L. Langmuir isotherm model and pseudo-second-order equation can be used for interpretation of selective equilibrium and kinetic adsorption data, respectively. The adsorbent film can be used repeatedly for Cu^{2+} sorption from aqueous solution of Cu^{2+}, Co^{2+}, and Ni^{2+}.

Acknowledgment

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