Use of polyethylene films photografted with 2-(dimethylamino)ethyl methacrylate as a potential adsorbent for removal of chromium (VI) from aqueous medium

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ABSTRACT: A new polymeric adsorbent material based on polyethylene (PE) was prepared by photografting of 2-(dimethylamino)ethyl methacrylate (DMAEMA) as a positively chargeable monomer to a PE film. The effects of the experimental parameters, such as the pH value, temperature, and grafted amount on adsorption of chromium(VI) (Cr(VI)) ions were investigated for the DMAEMA-grafted PE (PE-g-PDAMEMA) films. The maximum adsorption capacity was obtained at the initial pH value of 3.0 for a PE-g-PDMAEMA film with 1.8 mmol/g and the maximum adsorption capacity obtained was higher than or compatible to those of many of the other polymeric adsorbents prepared for Cr(VI) ions. The adsorption kinetics obeyed the mechanism of the pseudo-second order kinetic model and adsorption of Cr(VI) ions on PE-g-PDMAEMA films was well expressed by the Langmuir isotherm model. A high Langmuir adsorption constant suggests that the adsorption of Cr(VI) ions occurs between protonated dimethylamino groups and $HCrO_4^-$ ions mainly through the electrostatic interaction. Cr(VI) ions adsorbed were successfully desorbed from a PE-g-PDMAEMA film in solutions of NaCl, NH_4Cl, NH_4Cl containing NaOH, and NaOH and a PE-g-PDMAEMA film was regenerated and repeatedly used for adsorption of Cr(VI) ions without appreciable loss in the adsorption capacity.
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INTRODUCTION

The discharge of wastewater containing heavy metal ions, such as cadmium, zinc, mercury, chromium, lead, and so on, into surface water has exerted a negative influence on human health and environment. Their intracorporeal accumulation in a living tissue through a food chain can pose severe physiological or neurogenic damage.[1] Among them, wastewater containing chromium is one of the major sources of environmental pollution.

Chromium exists in the trivalent, Cr(III), and hexavalent, Cr(VI), oxidation states. Cr(III) is an essential element that potentiates insulin action and thus influences carbohydrate, lipid, and protein metabolism.[2,3] In addition, Cr(III) is a micro-nutrient for many living organisms. However, Cr(VI) is of high toxicity to human body tissue due to its oxidizing potential. In aqueous medium, the Cr(VI) species may exist in a variety of oxospecies, namely, dichromate ($Cr_2O_7^{2-}$), hydrochromate ($HCrO_4^-$), or chromate (CrO_4^{2-}), depending on the concentration and pH value.[4,5]

The traditionally used treatment methods for removing Cr(VI) ions from aqueous medium include chemical reduction and precipitation, ion exchange, electrodialysis, reverse osmosis, liquid–liquid extraction, and so on.[6,7] Among them, chemical reduction and precipitation is the most common, but this method has the disadvantages that a large amount of sludge is generated and a mass of reducing reagents are required. Meanwhile, the methods of ion exchange, electrodialysis, and reverse osmosis are in need of high technical equipment and operation cost.[8] However, adsorption is a superior process compared to others in terms of cost, simplicity of design and operation, availability, effectiveness, and insensitivity to toxic substances.

Different types of adsorbents, such as activated carbon,[9–11] sawdust,[12–14] chitosan and modified chitosan,[15–17] biomass materials,[18] and synthetic polymers[1,3,19–25] have been used for removal of Cr(VI) ions from aqueous medium. Unfortunately, some of these adsorbents do not have high adsorption capacities, and others have difficulty in regeneration or reuse. Of them,

adsorbent materials of amino group-containing polymers have also been attracting attention as an alternative material due to their good adsorption capacity and stability. So they have been successfully used for adsorption of Cr(VI) ions.[1,19–21,23,24] Many research groups have investigated adsorption behavior of polymeric adsorbents, such as chitosan beads and their modified products,[26–28] chemically crosslinked poly(4-vinylpyridine) (4-VP) beads, and polymer substrates grafted with 4-VP,[19,20,23,24,29,30] poly(glycidyl methacrylate) (PGMA) functionalized with 1,6-diaminohexane,[31] diethylene triamine,[25] and branched polyethyleneimine.[1,32] However, 4-VP is little photografted onto the polyethylene (PE) and polypropylene (PP) substrates by the photografting technique with ultraviolet (UV) rays. Since GMA has a functional epoxy group for the introduction of amine compounds with two or more amino groups, it is frequently used as a grafting monomer to prepare adsorbents for adsorption of Cr(VI),[1,25,31,32] However, glycidyl methacrylate (GMA) is poorly soluble in water (2.3 g/100 g H$_2$O).

It is understandable from the above articles that the use of a positively chargeable functional group is effective for removal of Cr(VI) ions. Therefore, 2-(dimethylamino)ethyl methacrylate (DMAEMA) was selected as a positively chargeable monomer in this study. DMAEMA is a water-soluble monomer and can be directly photografted to the PE and PP plates and films.[33–36] In fact, we have reported the application of DMAEMA-grafted PE (PE-g-PDMAEMA) films to various functional membranes for on-off regulation of permeation,[37] separation, and concentration of organic electrolytes by electrotransport,[34,35] adsorption, and removal of anionic dyes.[38] In addition, PE-g-PDMAEMA films possessed a practical strength in the water-swollen state.[34,37] Since one end of a grafted polymer chain is bonded covalently to the polymer substrate and the other end is not put under restraint, the grafted polymer chains possess high mobility in the grafted layer in the water-swollen state. Taking these results into consideration, we focused attention on the use of PE-g-PDMAEMA films for adsorption of Cr(VI) ions.

In this study, Cr(VI) ion adsorption behavior of PE-g-PDMAEMA films was kinetically investigated as a function of the pH value, temperature, and grafted amount. In addition, desorption of Cr(VI) ions were estimated in different eluents in repetitive use of PE-g-PDMAEMA films for adsorption and desorption.

EXPERIMENTAL

Materials
A PE film (thickness, 30 μm; density, 0.924 g/cm^3) supplied from Tamapoly Co. (Tokyo, Japan) was used as a substrate. The PE films cut into 50-mm length and 30-mm width were washed with water, methanol, and acetone, and then dried under reduced pressure. DMAEMA (Wako Pure Chemical, Tokyo, Japan) and other chemicals were used without further purification.

Photografting
The photografting of DMAEMA (CH$_2$=C(CH$_3$)COOCH$_2$CH$_2$N (CH$_3$)$_2$) onto the PE films was performed using a Riko rotary photochemical reactor, RH400-10W, equipped with a 400 W high pressure mercury lamp in the manner described in our previous articles.[39–41] The PE films were immersed in an acetone solution of benzophenone (BP) (0.50 w/v %) for 1 min, and then acetone was evaporated at room temperature to coat the PE surfaces with BP. BP will enhance the abstraction of hydrogen atoms from a PE chain, or the formation of active sites of the photografting, whereby the grafted amount can increase further. An aqueous DMAEMA solution was prepared at 1.0M. The pH value was adjusted to 8.0 with concentrated HCl to enhance the solubility of PDMAEMA homopolymers,[34,41] and then the poly-2-(dimethylamino)ethyl methacrylate (PDMAEMA) solution was degassed under reduced pressure for a few minutes.

The BP-coated PE films were immersed in a DMAEMA solution (65 cm^3) in the Pyrex glass tubes, and UV rays emitted from a 400 W high-pressure mercury lamp were irradiated at 60 °C. After the photografting, the PE-g-PDMAEMA films were thoroughly washed with water to exclude formed homopolymers and unreacted monomers, and then dried under reduced pressure. The grafted amount (G) in mmol/g was calculated from the weight increase in the PE films by photografting using eq. (1)[34,35,37,38]:

$$\text{Grafted amount (mmol/g)} = \frac{(W_g - W_0)/157.21}{W_0} \times 10^3 \quad (1)$$

where W_g is the weight of a PE-g-PDMAEMA film (g) and W_0 is the weight of the ungrafted PE film. The quantity of 157.21 (g/mol) is the molar mass of a DMAEMA monomer.

Water Absorptivity and Expansion of PE Film by Photografting
The amount of absorbed water was calculated from the weight increase of the PE-g-PDMAEMA films immersed in water at 30 °C and the length and width of the PE-g-PDMAEMA films were measured with a slide caliper. The size of the PE-g-PDMAEMA films was measured after the photografting of DMAEMA in the dry state and after subsequent immersion in water for 24 h at 30 °C, and the area ratio was calculated as the relative increase in the size in the dry and water-swollen state on the basis of the ungrafted PE film (50 × 30 mm).

Thickness of Grafted Layer
The thickness of the grafted layers formed on the PE surfaces was measured by a VH-5500 light microscope. The PE-g-PDMAEMA films cut into about 5 mm square were immersed in an aqueous indigo carmine solution at 25 mg/100 cm^3 for about 30 s to 1 min to stain the grafted layer. Then, the PE-g-PDMAEMA samples were washed in water and dried under reduced pressure. The cross section of the grafted films was photographed at 200-fold magnification, and the thickness of the grafted and ungrafted layers was measured.

Protonation of Dimethylamino Groups on Grafted PDMAEMA Chains
PE-g-PDMAEMA films of known weight (20 × 20 mm) were immersed in a 0.10 M NaOH solution so as to neutralize the protonated dimethylamino groups on the grafted PDMAEMA chains, and then washed with water several times. The PE-g-PDMAEMA films were immersed in 20 cm^3 of a 10.0 mM HCl

solution and the solutions were mildly stirred for at least 24 h under nitrogen atmosphere. The HCl solutions were titrated with a 10.0 mM NaOH solution with bromothymol blue as an indicator. The amount of effective dimethyl amino groups was calculated from the concentration difference in the HCl solution using eq. (2):

$$\text{Amount of effective dimethyamino groups (mmol/g)}$$
$$= \frac{(C_{HCl}^0 - C_{HCl}) \times 0.020}{W_{film}} \quad (2)$$

where C_{HCl}^0 and C_{HCl} are the initial concentration of HCl (10.0 mM) before immersion of the PE-g-PDMAEMA film and the equilibrium concentration after immersion. W_{film} denotes the weight of a PE-g-PDMAEMA film in the dry state. The quantity of 0.020 (dm^3) is the volume of a 10.0 mM HCl solution.

Adsorption of Cr(VI) Ions

The pH value of an aqueous $K_2Cr_2O_7$ solution at 0.20 mM was adjusted to 1.0–6.0 with HCl or NaOH. When the UV–Vis spectra of the $K_2Cr_2O_7$ solutions were measured, the isosbestic point was obtained at 338.2 nm. Therefore, a calibration curve was prepared at this wavelength. A good linear relationship was obtained between the absorbance and the Cr(VI) ion concentration with a high regression coefficient value ($r > 0.999$, for example: log $\varepsilon = 3.454$ dm^3/mol cm at pH 3.0). The Cr(VI) ion concentration determined by this technique was in good agreement with that determined from the absorbance at 540 nm obtained with 1,5-diphenylcarbazide. The volume loss of the reaction solution was prevented by this procedure.

In order to prevent the incorporation of Cr(VI) ions in the grafted layer through water absorption, PE-g-PDMAEMA films cut into about 2.0 × 1.0 cm were beforehand immersed in an HCl solution that had the same pH as that of a $K_2Cr_2O_7$ solution for 24 h at 30 °C. Then, the PE-g-PDMAEMA films were immersed in a $K_2Cr_2O_7$ solution at pH 3.0 unless otherwise noted, and the absorbance was measured at predetermined time interval. Therefore, the immersion time corresponds to the contact time for adsorption of Cr(VI) ions on the PE-g-PDMAEMA films. The aliquots were returned to the solution just after the measurement of the absorbance. The adsorption capacity was calculated from eq. (3):

$$\text{Adsorption capacity (mmol/g)} = \frac{(C_0 - C_t) \times 0.050}{W_{film}} \quad (3)$$

where C_t and C_0 are the concentration of Cr(VI) ions at time t and 0, respectively. The quantity of 0.050 (dm^3) is the volume of a $K_2Cr_2O_7$ solution.

Cr(VI) ion adsorption behavior of PE-g-PDMAEMA films was estimated from the adsorption capacity and initial adsorption rate as a function of the pH value, temperature, and grafted amount.

Desorption of Cr(VI) Ions and Repetitive Use

Solutions of NaCl, NH$_4$Cl, NH$_4$Cl containing NaOH, and NaOH were selected as an eluent for desorption of Cr(VI) ions from PE-g-PDMAEMA films by referring to articles on desorption of Cr(VI) ions from polymer materials.[1,17,26,42–45] PE-g-
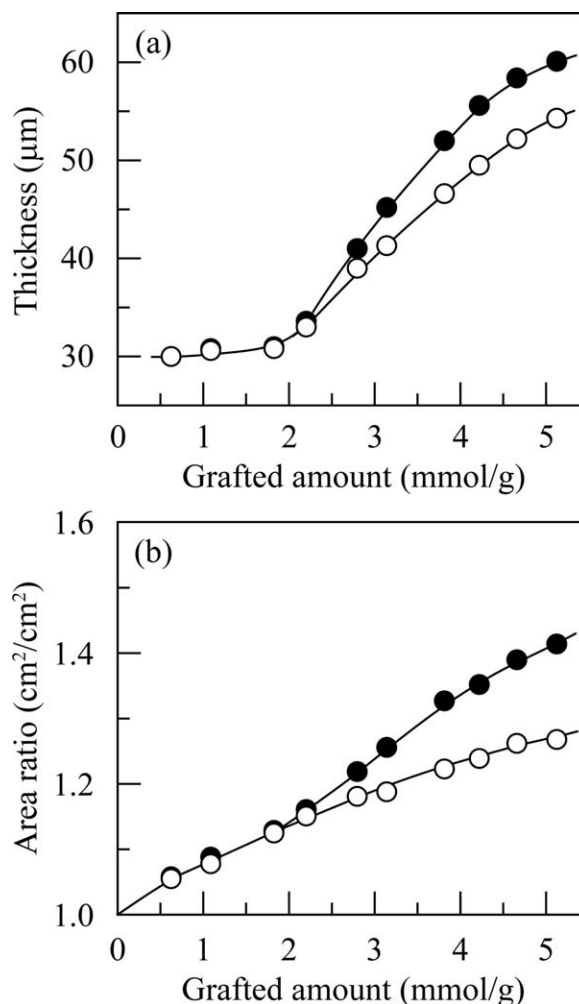

Figure 1. Changes in (a) the thickness and (b) area ratio with the grafted amount in the dry state (○) and in the water-swollen state (●).

PDMAEMA films loaded with Cr(VI) ions were immersed in the above eluents at different concentrations, and then the solutions were mildly stirred at 30 °C. The absorbance at 372.0 nm as the maximum adsorption wavelength was measured at predetermined time interval, and then the aliquots were returned to the solution. The calibration curves were formed for each eluent and the linear relationship with the regression coefficient value > 0.999 was obtained between the Cr(VI) concentration and the absorbance (log $\varepsilon = 3.429$–3.975 dm^3/mol cm). The desorption % value was calculated from the ratio of the amount of desorbed Cr(VI) ions to the amount of adsorbed Cr(VI) ions.

Alternating repetition of the cyclic process of adsorption in a $K_2Cr_2O_7$ solution at pH 3.0 and desorption in solutions of NaCl at 0.50M, NH$_4$Cl at 0.50M containing NaOH at 0.40 mM, and NaOH at 1.0 mM.

RESULTS AND DISCUSSION

Preparation of PE-g-PDMAEMA Films and Their Membrane Properties

Since PDMAEMA is a thermos-sensitive polymer with the transition point at 27 °C in a pH 10 buffer solution,[6] the pH value
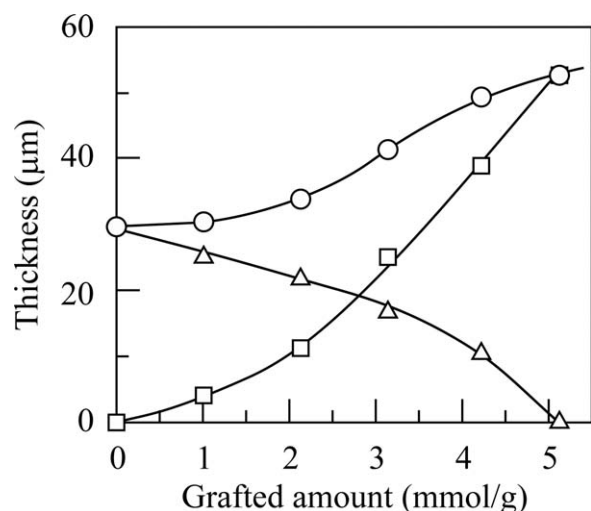
Figure 2. Changes in the thicknesses of the PE-*g*-PDMAEMA films (○) and their grafted (□) and ungrafted (△) layers with the grafted amount.

Figure 3. Change in the amount of absorbed water with the grafted amount at 30 °C.

of a DMAEMA solution was decreased to 8.0 with concentrated HCl to increase the solubility of PDMAEMA. The amount of grafted DMAEMA was varied by changing the irradiation time of UV rays at 60 °C.

Figure 1 shows the changes in the thickness and area ratio of the grafted films in the dry and water-swollen states with the grafted amount. When DMAEMA was photografted into the PE film, the PE film was expanded concomitantly with an increase in the thickness of the grafted layer though the progress of photografting into the bulk region. In addition, as shown in Figure 2, the thickness of the grafted layer increased together with a decrease in the thickness of the ungrafted layer, as the grafted amount increased. The ungrafted layer disappeared at the grafted amount of about 5 mmol/g.

Figure 3 shows the change in the water-absorptivity with the grafted amount. The amount of absorbed water increased over the grafted amount with a sharp increase at higher than about 2 mmol/g. The PE-*g*-PDMAEMA films had higher water absorptivity than that of PE films photografted with methacrylic acid, acrylic acid, and methacrylamide,[7] because DMAEMA had more affinity for PE than the above hydrophilic monomers. In addition, the PE-*g*-PDMAEMA films were further expanded and their thickness also increased by water absorption as shown in Figures 1 and 3.

The results obtained from Figures 1–3 indicate that the location of the photografting was restricted to the outer surface region and the water-absorptivity of the PE-*g*-PDMAEMA films was considerably low at <2 mmol/g. In the range of this grafted amount, the PE-*g*-PDMAEMA films were also little expanded by the subsequent water absorption. In particular, the thickness of the ungrafted layer sharply decreased and the PE film expanded by the photografting and subsequent water absorption at >2 mmol/g. Finally, the ungrafted layer disappeared at 5 mmol/g.

The protonation and deprotonation behavior of dimethylamino groups on a PDMAEMA chain is also an important characteris-
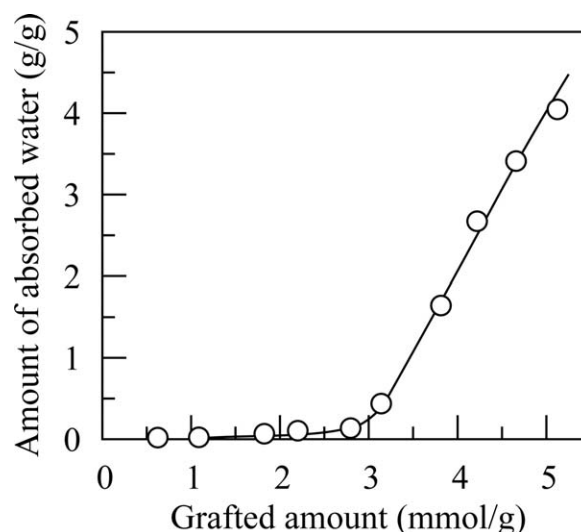
tic in adsorption and desorption of Cr(VI) ions. The degree of protonation of dimethylamino groups on a PDMAEMA homopolymer prepared was determined through the colloid titration with potassium poly(vinyl alcohol) sulfate (KPVS) in our previous article.[34] The degree of protonation of dimethylamino groups increased with a decrease in the pH value and the dimethylamino groups were fully protonated in the pH range <4. However, a PDMAEMA chain little carries positive charges in the pH range >10.[34]

Effect of the Initial pH Value for Adsorption of Cr(VI) Ions
Figure 4 shows the variations in the adsorption capacity of Cr(VI) ions and initial adsorption rate with the initial pH value for a PE-*g*-PDMAEMA film with 1.8 mmol/g. The initial adsorption rate was calculated from the slope of the linear part between the amount of adsorbed Cr(VI) ions and the immersion time in the initial state. The adsorption capacity and initial adsorption rate had the maximum values at the initial pH value of 3.0. This can be attributed to the facts that most of the hexavalent chromium species exist in $HCrO_4^-$ ion at pH 3 and that the portion of $HCrO_4^-$ ions decreased as the pH value deviates from 3.[4,5] Such pH-dependence of Cr(VI) ion adsorption was observed for other cationic polymer materials.[19,22,23,31,42,46–49]

A pH change due to adsorption of Cr(VI) ions was small at the initial pH values <3.0. That is, the pH values at equilibrium were 1.20 and 3.04 at the initial pH value of 1.0 and 3.0, respectively. It is well-known that as the pH value deviates high or low from 3, the portion of $HCrO_4^-$ ions decreases. In other words, the portion of H_2CrO_4 species increases at further decreased pH values and the portion of CrO_4^{2-} ions increases at further increased pH values. However, at the initial pH value of 4.0 and 6.0, the pH value at equilibrium reached to 4.13 and 6.45, respectively. Therefore, a decrease in the amount of adsorbed Cr(VI) ions at the initial pH values >3.0.[4,5] From the above results, the optimum pH value was determined to be 3.0.
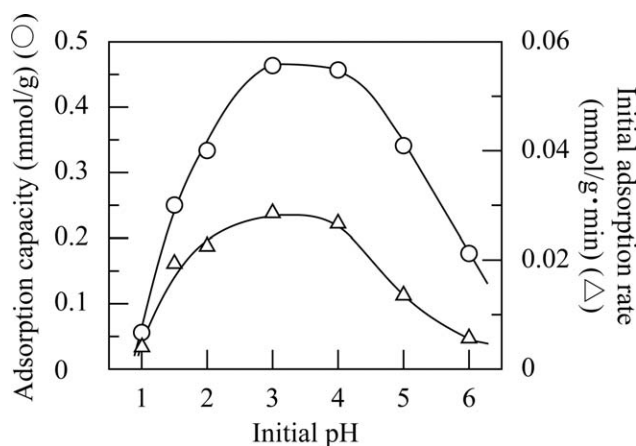
Figure 4. Changes in the Cr(VI) ion adsorption capacity ($\bigcirc$) and initial adsorption rate ($\triangle$) with the initial pH value at 30 °C in 0.20 mM $K_2Cr_2O_7$ solutions for PE-g-PDMAEMA films with 1.8 mmol/g.

Effect of the Temperature for Adsorption of Cr(VI) Ions

The effect of the temperature on adsorption of Cr(VI) ions on a PE-g-PDMAEMA film with 1.8 mmol/g was investigated at pH 3.0. Figure 5 shows the changes in the adsorption capacity and initial adsorption rate with the temperature. Although the initial adsorption rate increased over the temperature, the adsorption capacity increased with the temperature and then leveled off at >30 °C.

In addition, activation energy for the adsorption process was determined according to the Arrhenius equation:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \qquad (4)$$

where A is the frequency factor, E_a the activation energy, and R the gas constant (8.314 J/K mol).

The value of activation energy was determined to be 28.0 kJ/mol from the slope of $\ln k_2$ versus $1/T$ plot. This value was a little higher than those obtained for adsorption of Cr(VI) ions on polymeric adsorbents.[1,3]
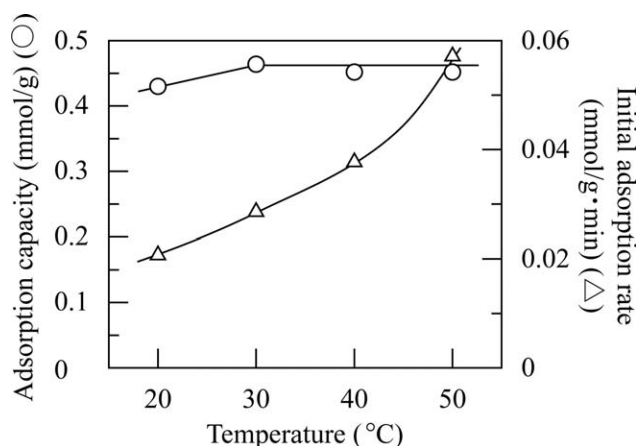

Figure 5. Variations in the Cr(VI) ion adsorption capacity ($\bigcirc$) and initial adsorption rate ($\triangle$) with the temperature in a 0.20 mM $K_2Cr_2O_7$ solution at pH 3.0 for PE-g-PDMAEMA films with 1.8 mmol/g.
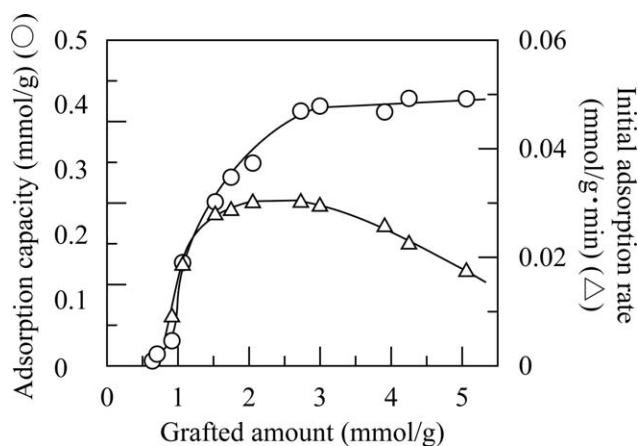

Figure 6. Variations in the Cr(VI) ion adsorption capacity ($\bigcirc$) and initial adsorption rate ($\triangle$) with the grafted amount in a 0.20 mM $K_2Cr_2O_7$ solution at 30 °C and pH 3.0 for PE-g-PDMAEMA films with 1.8 mmol/g.

Effect of the Grafted Amount for Adsorption of Cr(VI) Ions

From the above results, the effect of the grafted amount on adsorption of Cr(VI) ions was investigated at 30 °C and pH 3.0. Figure 6 shows the variations in the adsorption capacity and initial adsorption rate with the grafted amount. The adsorption capacity increased over the grafted amount with a sharp increase in the range of the grafted amount from 1 to 3 mmol/g. However, the initial adsorption rate had the maximum value at 2–3 mmol/g.

To summarize the above results, the Cr(VI) ion adsorption behavior of PE-g-PDMAEMA films was as follows: At grafted amounts <1 mmol/g, the hydrophilic property of the PE surface is poor or insufficient for adsorption of Cr(VI) ions due to a small grafted amount. When the grafted amount further increased, the PE surface became more hydrophilic and the adsorption capacity sharply increased. However, the adsorption ratio, obtained by dividing the adsorption capacity by the grated amount, also had the maximum value at 1.8 mmol/g, corresponding to 112 mg/g-grafted PDMAEMA, as shown in Figure 7. This adsorption capacity was higher than or comparable to those of other adsorbents prepared for Cr(VI) ion adsorption.[1,3,21–25,43] The low values of the adsorption ratio would be attributed to the fact that Cr(VI) ion adsorption is restricted to the easily accessible outer surface region of the grafted layer.[25] This means that some of the protonated dimethylamino groups on a grafted polymer chain present inside the grafted layer swollen is not involved in adsorption of Cr(VI) ions at higher grafted amounts.

Figure 8 shows the changes in the degree of the protonation and the degree of effective adsorption, which was determined by dividing the adsorption capacity by the amount of protonated dimethylamino groups, with the grafted amount. Most of the dimethylamino groups were protonated at grafted amounts lower than about 2 mmol/g. However, the adsorption capacity was considerably low probably due to the hydrophobicity of the PE surface at <1 mmol/g. When the grafted amount further increased, the degree of effective adsorption sharply increased followed by a constant value of 0.45. This value suggests that
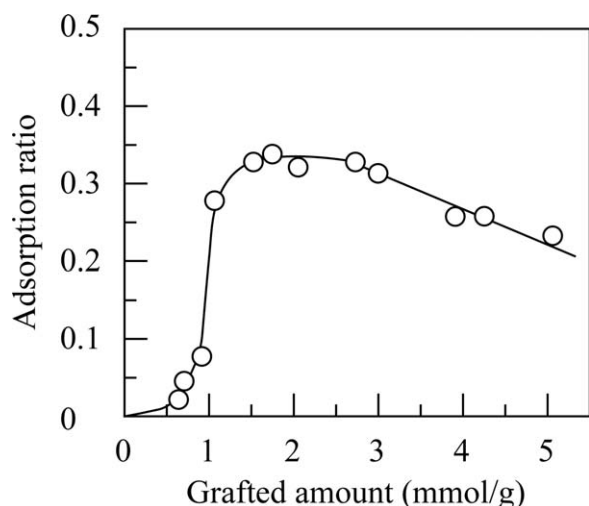
Figure 7. Variation in the adsorption ratio with the grafted amount for Cr(VI) ion adsorption at pH 3.0 and 30 °C in a 0.20 mM K$_2$Cr$_2$O$_7$ solution.

some of the protonated dimethylamino groups present in the inside of the grafted layer would not be involved in Cr(VI) ion adsorption.

Adsorption Kinetics

The experimental data obtained were analyzed with the Lagergren's pseudo-first and second-order models. The pseudo-first order rate equation is generally expressed by

$$\ln (Q_{eq} - Q_t) = \ln Q_{eq} - k_1 t \qquad (5)$$

where Q_t and Q_{eq} denote the adsorption capacity at time t and at equilibrium, respectively, and k_1 is the pseudo-first order rate constant. The pseudo-second order equation is expressed as:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_{eq}^2} + \frac{1}{Q_{eq}} t \qquad (6)$$

where k_2 is the pseudo-second order rate constant.[17,28,30,50,51]
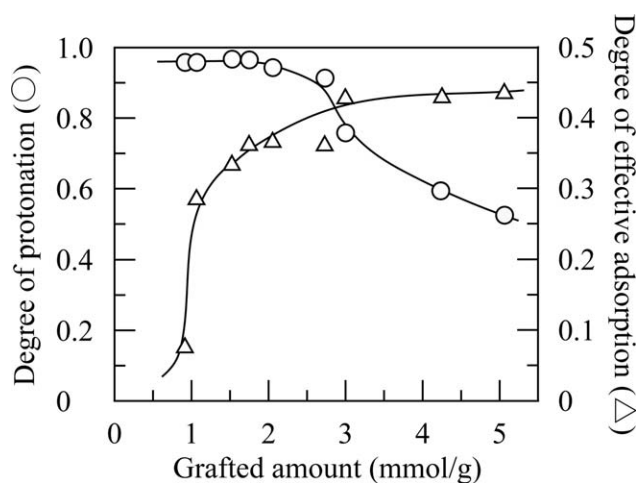

Figure 8. Changes in the amount of protonated dimethylamino groups (○) and effective adsorption efficiency (△) with the grafted amount for Cr(VI) ion adsorption at pH 3.0 and 30 °C in a 0.20 mM K$_2$Cr$_2$O$_7$ solution.

The kinetic parameters were calculated by the above two kinetic models at different temperatures for a PE-g-PDMAEMA film with 1.8 mmol/g and at different grafted amounts at 30 °C. The results at different temperatures for a PE-g-PDMAEMA film with 1.8 mmol/g were summarized in Table I. The adsorption half time, $t_{1/2}$, which was defined as the time required to reach the half of equilibrium adsorption capacity was also read from the time course of adsorption of Cr(VI) ions. The half of adsorption of Cr(VI) ions occurred within the first about 15 min of the immersion. The first-order equation did not well throughout the whole range of immersion time and was applicable over the initial 15–40 min of the adsorption process. The plotting of $\ln(Q_{eq} - Q_t)$ against the immersion time deviated considerably from the theoretical straight line after a short period for the pseudo-first order model.[49,52] However, for the pseudo-second order equation, the good linearity of t/Q_t against t was obtained for much longer immersion times as shown in Table I. It was found from these results that the experimental data in this study fit to the pseudo-second-order model much better than the pseudo-first-order model,[1,3,17,23–25,28,32,50,51] and the adsorption capacity values at calculated using eq. (6) were much close to the adsorption capacity at equilibrium. The pseudo-second order rate constant gradually increased over the temperature.[1,3] This suggests that the adsorption process is endothermic and the increased temperature is beneficial for intraparticle diffusion of Cr(VI) ions into the water-swollen grafted layer.[23,50]

The superior fit of the pseudo-second order model with experimental data supports the assumption that the adsorption process in this study is chemisorption involving the interaction of the target template with the adsorbent surface and the overall rate of the adsorption process is controlled by the rate-limiting step.[12,13,17,26,44,48] Dimethylamino groups on the grafted PDMAEMA chains are in the protonated cation form in acidic regions, depending on the pH value of the aqueous medium. This makes the outer surface region of the PE-g-PDMAEMA films positively charged as mentioned above and the electrostatic interaction occurs between the PE-g-PDMAEMA films and chromate (VI) anion species.[25,35]

Next, the kinetic parameters were calculated by the two kinetic models for PE-g-PDMAEMA films with different grafted amounts at pH 3.0 and 30 °C, and the results were summarized in Table II. The experimental data at different grafted amounts also fit to the pseudo-second-order model better than the pseudo-first-order model for much longer immersion time with a high regression coefficient values ($r^2 > 0.9983$) and calculated adsorption capacity values were much close to the experimental values.

A considerably high pseudo-second order rate constants were obtained at <1 mmol/g, because the adsorption capacity was very low as shown in Figure 6 and the adsorption equilibrium was reached for considerably shorter immersion times compared to the cases at further increased grafted amounts. In the range of the grafted amounts >1 mmol/g, the pseudo-second order rate constant value gradually decreased with an increase in the grafted amount. This suggests that adsorption of Cr(VI) ions would be involved in the diffusion in the grafted layer at higher grafted amounts. In fact, the $t_{1/2}$ value increased with the grafted amount.

Table I. Kinetic Parameters Calculated by Pseudo-First Order and Pseudo-Second Order Models for Cr(VI) Ion Adsorption on a PE-*g*-PDMAEMA Film with 1.8 mmol/g at Different Temperatures in a 0.20 mM K$_2$Cr$_2$O$_7$ Solution of pH 3.0

T (°C)	Q_{eq}^{exp} (mmol/g)	$t_{1/2}$ (min)	Pseudo-first order				Pseudo-second order			
			Q_{eq}^{cal} (mmol/g)	k_1 (1/min)	r^2	time range (min)	Q_{eq}^{cal} (mmol/g)	k_2 (g/mmol min)	r^2	time range (min)
20	0.430	12.3	0.447	0.0582	0.9937	40	0.447	0.227	0.9988	360
30	0.464	10.0	0.467	0.0787	0.9944	30	0.474	0.336	0.9990	300
40	0.452	8.5	0.460	0.0804	0.9910	50	0.450	0.503	0.9988	360
50	0.452	5.8	0.440	0.1215	0.9997	15	0.442	0.693	0.9997	360

Q_{eq}^{exp}: experimental equilibrium adsorption capacity; Q_{eq}^{cal}: calculated equilibrium adsorption capacity.

Langmuir and Freundlich Adsorption Isotherms

At pH 3.0 and 30 °C, PE-*g*-PDMAEMA films with different grafted amounts were immersed in K$_2$Cr$_2$O$_7$ solutions at the initial concentrations of 0.10–0.50 mM, and then the adsorption capacity was determined from the equilibrium concentration of Cr(VI) ions. The adsorption capacity values at equilibrium were applied to Langmuir and Freundlich isotherm models, represented by eqs. (7) and (8), respectively.

$$\frac{C_{eq}}{Q_{eq}} = \frac{1}{K_L \times Q_{max}} + \frac{C_{eq}}{Q_{max}} \tag{7}$$

where C_{eq} is the Cr(VI) ion concentration at equilibrium, Q_{max} the maximum adsorption capacity, and K_L the Langmuir adsorption constant related to the affinity of binding sites.

$$\log Q_{eq} = \log K_F + \frac{1}{n} \log C_{eq} \tag{8}$$

where K_F is the Freundlich constant related to adsorption capacity and $1/n$ the empirical parameter corresponding to adsorption intensity, depending on the heterogeneity of the adsorbent materials.

The experimental data obtained at different grafted amounts were summarized in Table III. A linear relation was obtained with a high regression coefficient value ($r^2 > 0.9948$) between the C_{eq}/Q_{eq} values and the equilibrium concentration irrespective of the grafted amount and the calculated Q_{max} values were much close to the experimentally obtained adsorption capacity values for the Langmuir adsorption model. However, even when adsorption behavior was applied to the Freundlich model, the regression coefficient values were low as shown in Table III. These results indicate that the Langmuir model was more suitable to adsorption of Cr(VI) ion on PE-*g*-PDMAEMA films than the Freundlich model.

For all of the PE-*g*-PDMAEMA films used, although the adsorption capacity was almost constant against the initial K$_2$Cr$_2$O$_7$ concentration, these values were much higher than or comparable to those of other polymeric adsorbents prepared for Cr(VI) ions.[1,3,21–25,43] The Langmuir adsorption constant obtained from the *y*-intercept ranged from 81.4 to 100 dm^3/mmol corresponding to 1.56–1.92 dm^3/mg with an average of 91.4 dm^3/mmol corresponding to 1.76 dm^3/mg. This average value was higher than the Langmuir adsorption constant values shown in other articles dealing with adsorption of Cr(VI) ions obeying the Langmuir equation.[3,16,20–22,24–26,28,32,50,51,53] These results indicate that adsorption of Cr(VI) ions occurs through the electrostatic

Table II. Kinetic Parameters Calculated by Pseudo-First Order and Pseudo-Second Order Models for Cr(VI) Ion Adsorption on a PE-*g*-PDMAEMA Film with Different Grafted Amounts at pH 3.0 and 30 °C in a 0.20 mM K$_2$Cr$_2$O$_7$ Solution

G (mmol/g)	Q_{eq}^{exp} (mmol/g)	$t_{1/2}$ (min)	Pseudo-first order				Pseudo-second order			
			Q_{eq}^{cal} (mmol/g)	k_1 (1/min)	r^2	time range (min)	Q_{eq}^{cal} (mmol/g)	k_2 (g/mmol min)	r^2	time range (min)
0.6	0.023	1.5	–	–	–	–	0.013	84.7	0.9992	360
0.7	0.029	1.0	–	–	–	–	0.029	77.8	0.9998	360
0.9	0.062	3.8	–	–	–	–	0.062	22.1	1.000	360
1.1	0.254	5.3	0.279	0.1465	0.9848	10	0.281	0.638	0.9994	360
1.5	0.403	8.5	0.401	0.0825	0.9988	30	0.411	0.379	0.9997	420
1.8	0.464	10.0	0.467	0.0787	0.9944	30	0.474	0.336	0.9990	300
2.1	0.498	12.5	0.526	0.0613	0.9987	30	0.510	0.165	0.9991	420
2.7	0.626	9.0	0.637	0.0828	0.9964	30	0.631	0.245	0.9998	480
3.0	0.638	10.3	0.658	0.0816	0.9959	40	0.655	0.213	0.9989	360
3.9	0.624	11.1	0.621	0.0633	0.9995	40	0.652	0.158	0.9992	360
4.3	0.657	19.8	0.675	0.0352	0.9987	50	0.689	0.116	0.9987	360
5.1	0.656	20.8	0.676	0.0479	0.9976	50	0.687	0.097	0.9983	420

Table III. The Langmuir and Freundlich Parameters for Cr(VI) Ion Adsorption on a PE-*g*-PDMAEMA Film with Different Grafted Amounts at pH 3.0 and 30 °C in an Aqueous $K_2Cr_2O_7$ Solutions at 0.20 mM

G (mmol/g)	Q_{eq}^{exp} (mmol/g)	Langmuir model				Freundlich model		
		Q_{eq}^{exp} (mmol/g)	Q_{eq}^{cal} (mmol/g)	K_L (dm³/mmol)	r^2	K_F (mmol/g)/(dm³/mmol)$^{1/n}$	n	r^2
1.1	0.313–0.322	0.316	0.326	95.5	0.9988	–	–	–
1.8	0.460–0.509	0.484	0.520	100	0.9990	0.556	9.25	0.796
3.0	0.617–0.638	0.630	0.680	91.1	0.9948	0.703	17.1	0.815
4.1	0.652–0.721	0.696	0.735	89.1	0.9992	0.835	8.38	0.980
5.1	0.734–0.749	0.740	0.766	81.4	0.9981	0.816	11.8	0.726

interaction between protonated dimethylamino groups on a grafted PDMAEMA chains and $HCrO_4^-$ ions and the affinity between them is rather high.

Desorption Behavior

Desorption of Cr(VI) ions from a PE-*g*-PDMAEMA film with 1.8 mmol/g, which had the maximum adsorption ratio at pH 3.0 and 30 °C, was investigated in various eluents. Solutions of NaCl, NH_4Cl, NH_4Cl containing NaOH, and NaOH were used because these solutions were used as an eluent for desorption of Cr(VI) ions from other polymeric adsorbent materials, although the concentrations differed from article to article.[1,17,26,32,42,43,45,48,51,54] Figure 9 shows the change in the desorption % value with the concentration of the eluents. The desorption % value increased with an increase in the concentration, and the maximum values of 96.1, 78.0, and 94.6% were obtained at 0.50M NaCl, 0.50M NH_4Cl, and 1.0 mM NaOH, respectively. Since the desorption % value for NH_4Cl was a little lower than those for other two eluents, an increase in the desorption % value was followed up in 0.50M NH_4Cl containing NaOH at different concentrations. As shown in Figure 10, the desorption % increased with an increase in the NaOH concentration in a 0.50M NH_4Cl solution and the maximum desorption % value was obtained at 0.40 mM. This NaOH concentration was <1.0 mM as the concentration of a single NaOH solution at which the maximum desorption % value as shown in Figure 9. Unfortunately, complete desorption was not observed perhaps due to the involvement of non-electrostatic force, for example complexation between grafted PDMAEMA chains and anionic Cr(VI) ion species.[17,42,55] A decrease in the NaOH concentration by use of a mixture of NH_4Cl and NaOH is preferable for desorption of Cr(VI) ions.

Repetitive Adsorption and Desorption Cycles

The repetitive adsorption-desorption operation and durability of PE-*g*-PDMAEMA films are of great importance in applying them to an adsorbent for Cr(VI) ion adsorption. From the above results, the adsorption/desorption operation cycles were alternately repeated for three systems, adsorption at pH 3.0 and desorption in 0.50M NaCl, 0.50M NH_4Cl containing 0.40 mM NaOH, or 1.0 mM NaOH. Figure 11 shows the results of five successive adsorption and desorption cycles for a PE-*g*-PDMAEMA film with 1.8 mmol/g. The desorption % value gradually decreased in the repeated adsorption and desorption cycles for used each eluent. Since the adsorption capacity gradu-

ally with an increase in the number of adsorption procedure in the all systems, the adsorption capacity was the sum of the amount of adsorbed Cr(VI) ions and the amount of remaining Cr(VI) ions at the last adsorption procedures. As shown in Figures 9 and 10, a small amount of Cr(VI) ions were left in the grafted layers after each adsorption procedure. The decrease in
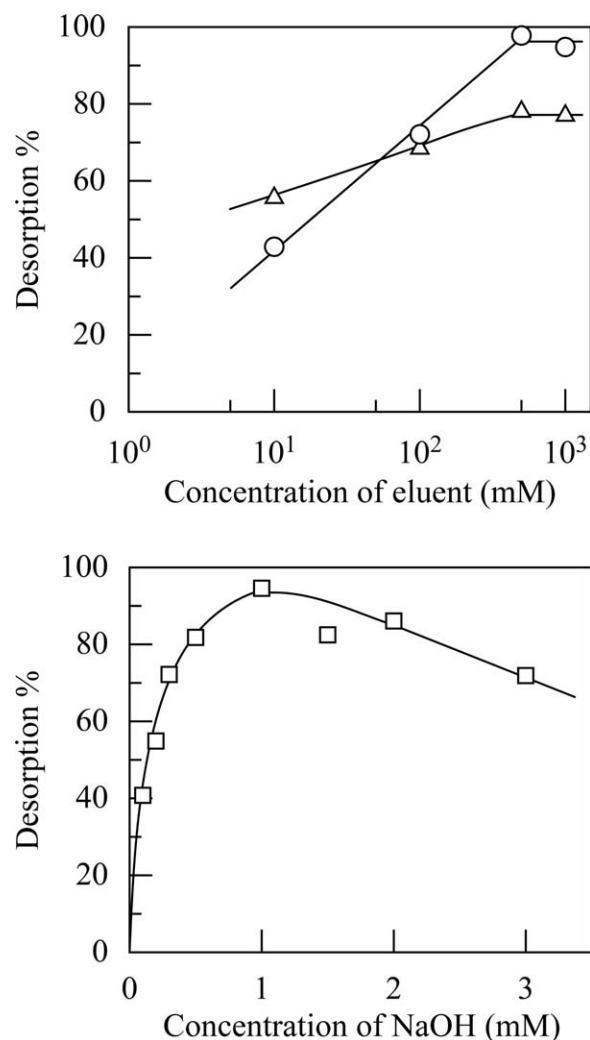
Figure 9. Desorption of Cr(VI) ions from a PE-*g*-PDMAEMA film with 1.8 mmol/g in solutions of NaCl (○), NH_4Cl (△), and NaOH (□) at different concentrations at 30 °C.
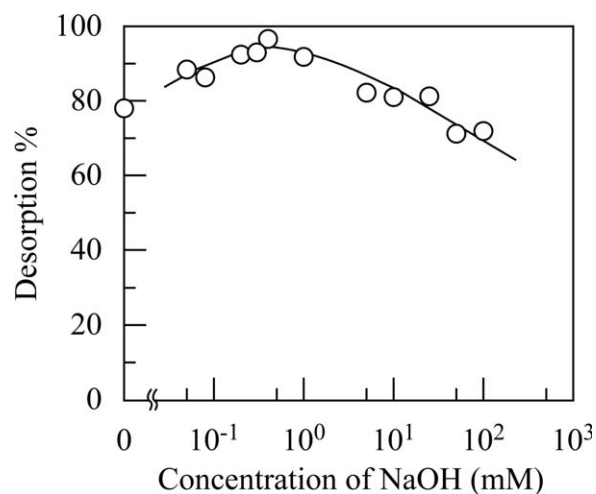
Figure 10. Desorption of Cr(VI) ions from a PE-*g*-PDMAEMA film with 1.8 mmol/g in 0.50M NH$_4$Cl solutions containing NaOH at different concentrations at 30 °C.

desorption % by the repeated cycles for NaOH was less than those for 0.50M NaOH and 0.50M NH$_4$Cl containing 0.40 mM NaOH. In addition, Compared with desorption % value at the fifth cycle, the desorption % value for NaOH was higher than the other two eluents used in this study.[17] There results indicates that a PE-*g*-PDMAEMA film can be successfully regenerated and repeatedly used for adsorption of Cr(VI) ions without appreciable loss in the adsorption capacity. In other word, the results of the adsorption-desorption cycle demonstrate that the regeneration and subsequent use of a PE-*g*-PDMAEMA film would enhance the economics of practical application for removal of Cr(VI) ions from solutions and wastewaters.

CONCLUSIONS

In this study, DMAEMA was photografted into a PE film, and Cr(VI) ion adsorption behavior of the resultant PE-*g*-
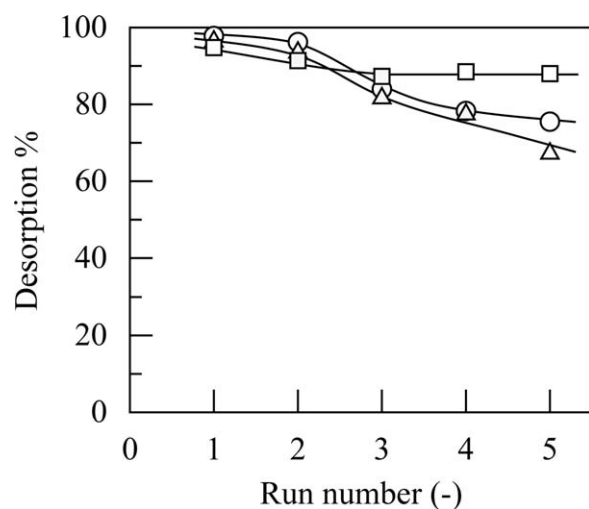
PDMAEMA films was investigated as a function of the initial pH value, temperature, and grafted amount. The kinetics and isotherms of adsorption in addition to desorption properties and repetitive usage of Cr(VI) loaded PE-*g*-PDMAEMA films were also investigated. The adsorption capacity and initial adsorption rate had the maximum values at pH 3.0.

The initial adsorption rate increased over the temperature, although the adsorption capacity remained almost constant at temperatures >30 °C. The adsorption capacity increased and the rate constant of adsorption decreased with an increase in the grafted amount at 30 °C and pH 3.0. An enhancement of hydrophilic properties of the PE surface by photografting of DMAEMA led to an increase in the amount of adsorbed Cr(VI) ions, but the initial adsorption rate gradually decreased with the grafted amount in the range of grafted amounts >1.8 mmol/g mainly due to the progression of the location of photografting in the inside of the PE film and the increase in the thickness of the grafted layer.

The Cr(VI) ion adsorption behavior of PE-*g*-PDMAEMA films obeyed the mechanism of the pseudo-second order kinetic model and was well expressed by the Langmuir isotherm model with a high Langmuir adsorption constant. This indicates that the adsorption of Cr(VI) ions occurs through the electrostatic interaction between protonated dimethylamino groups on a grafted PDMAEMA chains and HCrO$_4^-$ ions.

Cr(VI) ions were desorbed from a PE-*g*-PDMAEMA film in solutions of NaCl, NH$_4$Cl, NH$_4$Cl containing NaOH, and NaOH, and a PE-*g*-PDMAEMA film can be successfully regenerated and repeatedly used without appreciable loss in the adsorption capacity by alternating pattern between adsorption at pH 3.0 and desorption in 1.0 mM NaOH.

The results obtained in this study suggest that a PE-*g*-PDMAEMA film exhibits a significant potential as an adsorbent in removal of Cr(VI) ions from aqueous solutions and wastewaters.

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Figure 11. The repeated process of adsorption in a 0.20 mM K$_2$Cr$_2$O$_7$ solution at pH 3.0 and desorption in solutions of 0.50M NaCl (○), 0.50M NH$_4$Cl solutions containing 0.40 mM NaOH (△), and 1.0 mM NaOH (□) at 30 °C.

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