

Composites of Poly(2-chloroaniline) and Poly(*o*-toluidine) with Pumice and Their Application in the Removal of Chromium(VI) Ions from Aqueous Solutions

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ABSTRACT: Poly(2-chloroaniline) (P2ClAn)/pumice (Pmc) and poly(*o*-toluidine) (POT)/Pmc composites were synthesized via the chemical oxidative polymerization of 2-chloroaniline and *o*-toluidine in the presence of a dispersion of Pmc powders in water solvent with an $(\text{NH}_4)_2\text{S}_2\text{O}_8$ oxidant. The composites were characterized with Fourier transform infrared (FTIR) spectroscopy, thermo-gravimetric/differential thermal analysis (TG-DTA), and scanning electron microscopy devices. The presence of P2ClAn and POT in the structure of the composites was confirmed by FTIR. The results of analysis show strong interactions between the homopolymers and Pmc. The applicability of the P2ClAn/Pmc and POT/Pmc composites were investigated for the removal of Cr(VI) ions in water. Batch adsorption experiments

were carried out as a function of pH, initial concentration, time, adsorbent dosage, and temperature. The batch sorption kinetics were tested, and the applicability of the Langmuir and Freundlich adsorption isotherms for this system was tested at $20 \pm 1^\circ\text{C}$. An initial pH of 3.0 was most favorable for Cr(VI) removal by all adsorbents. The adsorption capacities obtained were 0.187 and 4.959 mmol/g of adsorbent for POT/Pmc and P2ClAn/Pmc from the Freundlich and Langmuir adsorption isotherms, respectively. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2295–2303, 2008

Key words: adsorption; composites; conducting polymers; conjugated polymers

INTRODUCTION

Polyaniline (PAN) has been one of the most intensively investigated conducting polymers during the last 15 years because of its good combination of properties, including stability, price, ease of synthesis, and treatment.¹ Various studies on the applicability of PAN have been reported in literature.^{2,3} PAN has been used for the sorption of inorganic mercury from aqueous solutions.⁴ Although PAN and its composites are the most intensively investigated conducting polymers, PAN is insoluble, infusible, and almost nonprocessable, which retards its potential applications. However, substituted PAN's, such as polytoluidine, polyanisidine, and poly(*N*-ethylaniline),^{5–7} prepared under similar conditions are more soluble than unsubstituted PAN but are less conducting because of steric constraints imposed by the substituent.

Composites of conjugated polymers are interesting because of their potential for combinations of properties that are difficult to attain separately with the individual components. *In situ* polymerization has been studied by many researchers over different hosts, such as montmorillonites, SiO_2 , Al_2O_3 , clay, and MnO_2 .^{8–12} A PAN/montmorillonite composite was

synthesized by an electrochemical method by Yang and Chen,¹³ and the structural changes and the effects of the physical properties of this composite were studied by Lee et al.¹⁴ Although composites of PAN have been made with many matrices, there are few works on the composites of substituted PAN's.^{15–17}

Al_2O_3 , red mud, montmorillonite, and metal oxides are the most used materials for the preparation of composites of conducting polymers. Among these inorganic materials, pumice (Pmc) is an interesting material because it is light, porous, igneous volcanic rock. It has a porous structure and a large surface area, and it can be processed easily.¹⁸ We used Pmc as an inorganic material to synthesize composites of poly(2-chloroaniline) (P2ClAn) and poly(*o*-toluidine) (POT). Moreover, we investigated the adsorption properties of these composites in the removal of chromium(VI) ions from aqueous solutions. As is known, chromium contamination generated from various industries, such as electroplating, leather tanning, mining, steel making, and pigments, has a significant impact on human health and on other living organisms in the environment.^{19,20} To minimize processing costs, several recent investigations have focused on the use of low-cost adsorbents, such as agricultural byproducts,²¹ waste materials,²² biosorbents,²³ slag,²⁴ polymers,²⁵ clay,²⁶ coal,²⁷ and Pmc materials.¹⁸ Adsorbents, mainly clay and Pmc minerals, are readily available inexpensive materials and offer a cost-

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effective alternative to conventional treatment of such mentioned waste streams.²⁸

Recently, we synthesized PAn/Pmc composites and investigated their adsorption properties for the removal of chromium(VI) ions from aqueous solutions.^{29,30} In this study, we selected P2ClAn and POT, which showed better solubility than PAn. P2ClAn has an electron acceptor group ($-\text{Cl}$), whereas POT has an electron donor group ($-\text{CH}_3$). We compared the effect of substituted group in the PAn ring on the structural and adsorption properties of the P2ClAn/Pmc and POT/Pmc composites, also just to compare them with those of the parent PAn. Additionally, the modification of the sorption properties of Pmc given in literature³⁰ was tried. The chemical synthesis of the P2ClAn/Pmc and POT/Pmc composites and their applicability for the removal of chromium(VI) ions from aqueous solutions were investigated and compared to each other, to the best of our knowledge, for the first time. The P2ClAn/Pmc and POT/Pmc composites were synthesized *in situ* with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as an oxidant in aqueous media. The structural characteristics and properties of the P2ClAn/Pmc and POT/Pmc composites were investigated with different techniques.

EXPERIMENTAL

Materials

The monomers *o*-toluidine and 2-chloroaniline (2-ClAn; Aldrich) were purified by distillation *in vacuo* and kept at 5°C before use. Ammonium peroxydisulfate (APS; Merck) was used as an oxidant without further purification. Pmc (powder) was obtained from the Middle Anatolia region (Nevşehir) of Turkey, and its chemical composition and some properties are given Table I. Analytical-grade $\text{K}_2\text{Cr}_2\text{O}_7$ (Merck) was used without further purification. All of the experiments used distilled water.

Synthesis of the P2ClAn and POT homopolymers and the P2ClAn/Pmc and POT/Pmc composites

P2ClAn and POT were chemically synthesized with APS as an oxidant. A solution of APS (mol ratio of oxidant to monomer ($n_{\text{oxidant}}/n_{\text{monomer}}$) = 1) dissolved in 200 mL of water was added to the monomer solution (3.3 and 4.0 mL for 2-ClAn and *o*-toluidine, respectively) dropwise; this solution was stirred for 24 h at 25°C. The precipitate was collected by filtration,

washed with the corresponding acid solution until the filtrate became colorless and then with distilled water several times, and finally dried at 50°C for 24 h. The yield of P2ClAn and POT were calculated as 65 and 53%, respectively.

Known weighed amounts of Pmc powder and monomer (3.3 and 4.0 mL for 2-ClAn and *o*-toluidine, respectively) were placed in a conical flask containing 200 mL of water and stirred magnetically for 1 h. Thereafter, a particular amount of APS was added this solution at room temperature. The polymerization of the monomer was found to be initiated immediately after addition. After the mixture was stirred for 24 h, the P2ClAn/Pmc and POT/Pmc composites were collected by filtration, washed with distilled water several times until the filtrate became colorless, and finally dried at 50°C for 24 h. The P2ClAn and POT percentages in the P2ClAn/Pmc and POT/Pmc composites were determined as 67 and 61% (m/m), respectively.

Instruments

Fourier transform infrared (FTIR) spectra were recorded between 400 and 4000 cm^{-1} with a 4- cm^{-1} resolution from KBr pellets on a PerkinElmer Spectrum BX FTIR system (Beaconsfield, Buckinghamshire, England). For scanning electron microscopy (SEM) analysis, samples were sputter-coated with gold layers, and photographs were taken on a scanning electron microscope (model Jeol 5600-LV, Tokyo, Japan). The thermal stabilities of P2ClAn/Pmc and POT/Pmc were investigated with a PerkinElmer model thermal parametric analyzer with nitrogen a pure gas at a flow rate of 35 mL/min. A PerkinElmer model AA800 atomic absorption spectrometer (Bodenseewerk, Germany) operating with an air-acetylene flame was used to measure residual Cr(VI) ion concentrations. The pH of the solution was measured with a Crison (Crison SA, Alella, Barcelona, Spain) Basic20 model pH meter with a glass electrode. A mechanical shaker model Memmert WB 29 thermostatic shaker was used to shake the adsorption batches and in the temperature experiments.

Chromium adsorption

Batch adsorption experiments were conducted in 100-mL flasks, each of which contained 30 mL of chromium solution prepared with $\text{K}_2\text{Cr}_2\text{O}_7$. A 100-mg amount of POT/Pmc and P2ClAn/Pmc was added to a water bath with a thermostatic shaker at $20 \pm 1^\circ\text{C}$ for 2 h. Samples were then filtered, diluted, and finally submitted to analysis of chromium by a flame atomic absorption spectrometer at 357.9 nm. The amount of adsorption was calculated on the basis of the difference of Cr(VI) concentration in aqueous solution before and after adsorption. Sorption experiments were performed by equilibration of the composites

TABLE I
Chemical Composition of Pmc

| SiO_2 (%) | Al_2O_3 (%) | Na_2O (%) | K_2O (%) | CaO (%) |
|--------------------|-----------------------------|---------------------------|--------------------------|---------|
| 72.11 | 14.07 | 3.8 | 3.9 | 1.35 |

Particle dimensions of Pmc, < 63 μm , density (d) = 0.7 g/cm^3 , acidic Pmc, dirty white color, traces of TiO_2 and SO_3 .

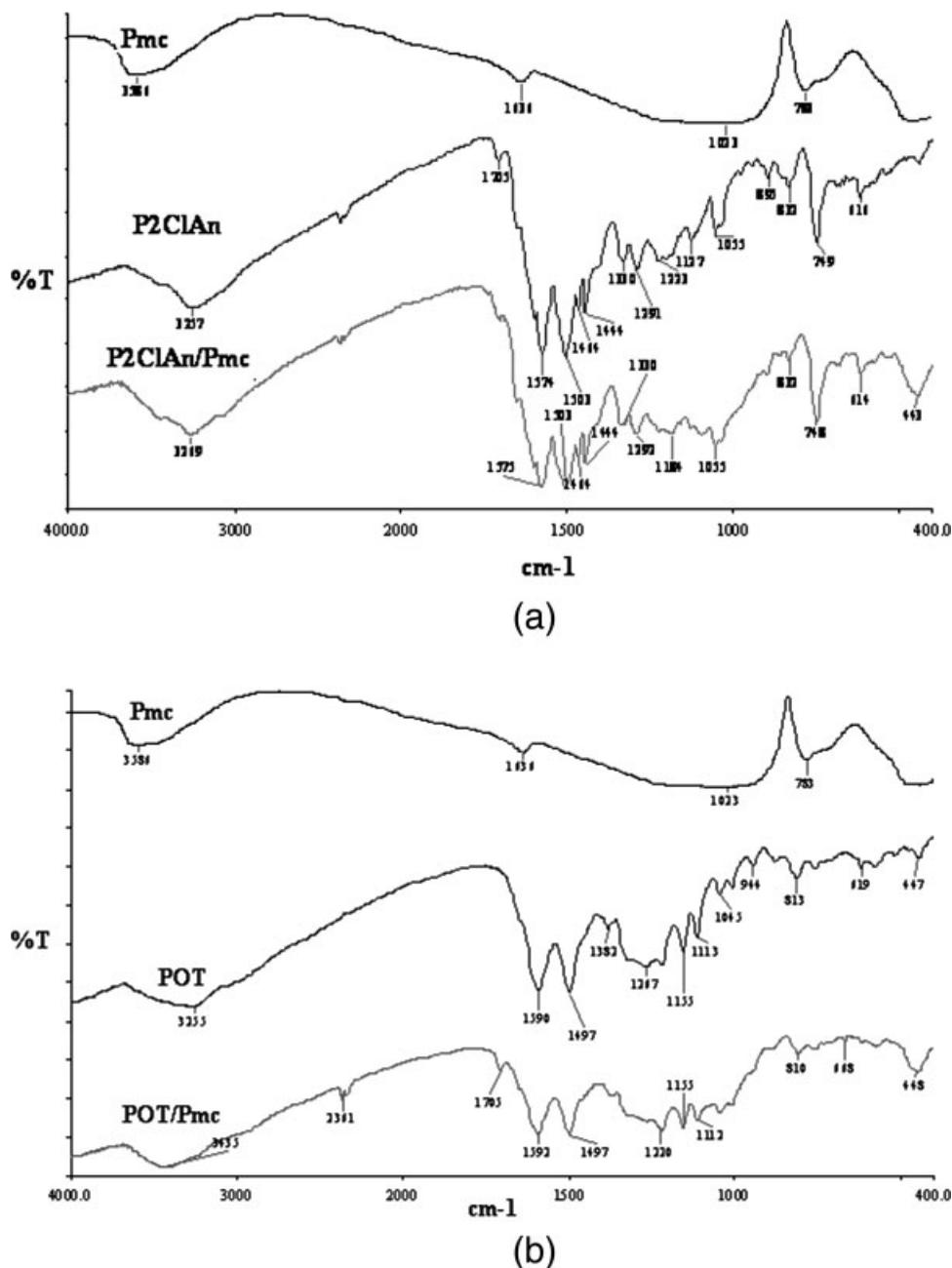


Figure 1 FTIR spectra of (a) P2ClAn/Pmc and (b) POT/Pmc.

with Cr(VI) solutions at various concentrations. The working solutions (1×10^{-4} to 1×10^{-3} mol/L chromium) were prepared by appropriate dilution of the stock solutions immediately before their use.

The investigation for the effect of solution pH values on chromium adsorption was conducted at an initial chromium concentration of 1×10^{-3} mol/L, but the solution pH values were changed from 3 to 7. The pH of the chromium solution was adjusted with 0.1M HCl or 0.1M NaOH.

The amounts of the POT/Pmc and P2ClAn/Pmc composites in the batch vessel were varied from 25 to 150 mg for the adsorption studies. Contact time

adsorption experiments were conducted at $20 \pm 1^\circ\text{C}$ in a well-mixed Pyrex glass vessel with a cover. The sorption of Cr(VI) on the composites at different temperatures ranging from 20 to 65°C was investigated.

RESULTS AND DISCUSSION

Characterization

Figure 1(a,b) shows the FTIR spectra of the P2ClAn/Pmc and POT/Pmc composites, Pmc, and their homopolymers, respectively. For Pmc, the characteristic IR peak observed at 1023 cm^{-1} may have been due to the

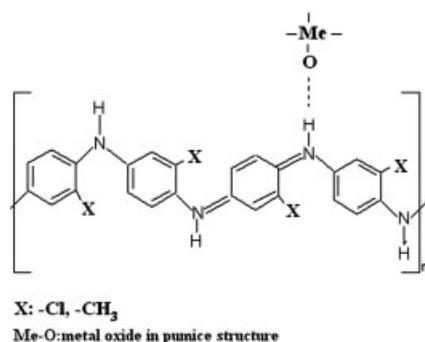


Figure 2 Structure showing hydrogen-bonding interactions between Pmc and the polymer.

presence of silica. This peak confirmed the highest percentage of silica in the Pmc, which was confirmed by chemical analysis. The broadening of the peak may have been due to the merging IR peaks corresponding to the other metal oxides present in the Pmc. POT and P2ClAn exhibited —NH— vibration peaks at 3255 and 3257 cm^{-1} .³¹ The FTIR spectra of the POT and POT/Pmc composite showed bands at 1590 and 1497 cm^{-1} , which corresponded to the C—C ring stretching vibration of the quinoid and benzenoid forms [Fig. 1(b)]. The absorption at 1267 cm^{-1} was ascribed to C—N stretching, and the absorption at 1255 cm^{-1} corresponded to the in-plane C—H bending mode.³² Similar bands were observed for P2ClAn and its composite. As evident in Figure 1(a,b), the FTIR spectra of the P2ClAn/Pmc and POT/Pmc composites contained contributions from both Pmc and the homopolymers. Also, by comparing the FTIR spectra of all of the samples, we observed that some P2ClAn and POT peaks were shifted because of interactions with Pmc. This was probably because of hydrogen bonding between the electronegative edge belonging to metal oxide in Pmc and the N—H group in the POT and P2ClAn (Fig. 2). It is well known that in composites systems with PAn, strong guest–host interactions, such as hydrogen bonding, occur in the form of $\text{NH} \cdots \text{O}=\text{Metal}$.³³

Figure 3(a–e) shows the results of the thermal analyses of P2ClAn, P2ClAn/Pmc, POT, and POT/Pmc. As shown in Figure 3(a), pure Pmc was thermally stable and only gave a small weight loss (8%) in the range of low temperature, which was presumably the water content of the Pmc substrate. Pmc is a hydrophilic material, and absorbed water and the presence of water could also be seen in its FTIR spectrum (O—H vibration bands at 3586 and 1636 cm^{-1}). Moreover, the differential thermal analysis (DTA) curve of Pmc exhibited endothermic peaks belonging to the removal of adsorbed moisture. P2ClAn, POT, and their composites exhibited decomposition in one step. This weight loss was possibly due to a large thermal degradation of the PAn chain.³⁴ Endothermic peaks in the DTA curve of the samples supported decompositions belonging to the thermogravimetric (TG) results. When

the initial decomposition temperatures of the samples were compared to each other, we observed that P2ClAn and POT had higher decomposition temperatures than the P2ClAn/Pmc and POT/Pmc composites, respectively. However, Pmc also had weight loss (8%) at 171 °C. This weight loss could have been the cause of the lower decomposition temperature in the composites. However, the residue amounts of the P2ClAn/Pmc and POT/Pmc composites were higher than those of homopolymers. The increasing residue amounts in the composites exhibited the incorporation of Pmc in the polymer structure and interactions between the polymer and Pmc.

SEM micrographs of P2ClAn, POT, P2ClAn/Pmc, and POT/Pmc are given in Figure 4(a–d). P2ClAn exhibited a big globular structure unlike P2ClAn synthesized in the presence of HCl.³⁴ However, POT had smaller particles than P2ClAn [Fig. 4(a,b)]. P2ClAn and the P2ClAn/Pmc composite had bigger particles than POT and the POT/Pmc composite. As seen in the surface morphologies of the P2ClAn/Pmc and POT/Pmc composites, P2ClAn and POT exhibited homogeneous mixtures with Pmc. The Pmc particles were present not only in the composite particle surfaces but were also distributed through their interior, a situation quite similar to that reported elsewhere.³⁵

Adsorption properties of the composites

Effect of pH

The initial pH of the adsorption medium is related to the adsorption mechanisms onto the adsorbent surface from water and reflects the nature of the physicochemical interactions of the species in solution and the adsorptive sites of adsorbents.^{36,37}

The amounts of adsorption for Cr(VI) as a function of the solution pH values are shown in Figure 5. The results clearly show that the adsorption of Cr(VI) decreased with increasing solution pH values from 3 to 7. The results in Figure 5 also suggest that the POT/Pmc and P2ClAn/Pmc composites could be very good adsorbents for Cr(VI).

The Cr(VI) species in the solution were in the form of HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, or CrO_4^{2-} . For Cr(VI), the hydrochromate (HCrO_4^-) species has been known to be predominant at pH values around 4, whereas chromium (CrO_4^{2-}) became the main species in solution at pH values of 7 and above.^{37–40} The surface interactions between the Cr(VI) species and the composites were electrically attractive at $\text{pH} < 8$ but became repulsive at $\text{pH} > 8$.³⁷ This could probably explain the decreased adsorption of the Cr(VI) species on POT/Pmc and P2ClAn/Pmc for pH values from 3 to 7, as shown in Figure 5. We also concluded that the active form of Cr(VI) that could be adsorbed by POT/Pmc and P2ClAn/Pmc was HCrO_4^- . The lower the solution pH was, the more Cr(VI) was adsorbed on the POT/P

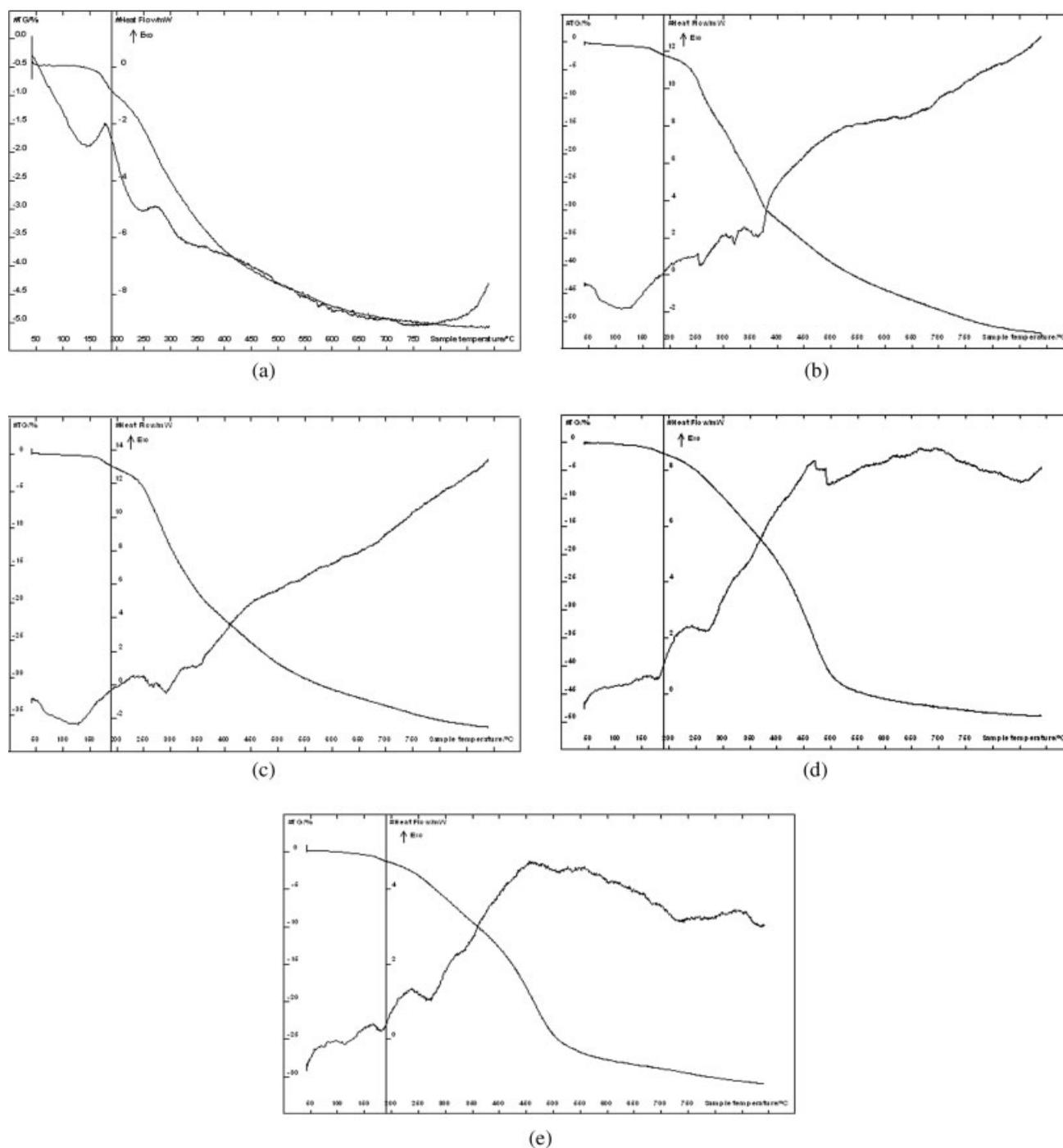


Figure 3 Thermo-gravimetric/differential thermal analysis (TG-DTA) curves of (a) Pmc, (b) P2ClAn, (c) P2ClAn/Pmc, (d) POT, and (e) POT/Pmc.

Pmc and P2ClAn/Pmc composites, which was attributed to the stronger electrostatic attraction.^{39,41,42} Another explanation could have been that at very low pH values, the surface of the sorbent was also surrounded by the hydronium ions, which enhanced Cr(VI) interaction with the binding sites of the sorbent by greater attractive forces. As the pH increased, however, the overall surface charge on the sorbents became negative and sorption decreased.^{36,40,25}

The percentage removal of Cr(VI) decreased from 83 to 57 and from 56 to 28 for POT/Pmc and P2ClAn/Pmc, respectively, with increasing pH. The maximum percentage of removal of Cr(VI) was at pH 3.

Adsorption kinetics

The adsorption process is generally known to be controlled by the transport of chromium to be adsorbed

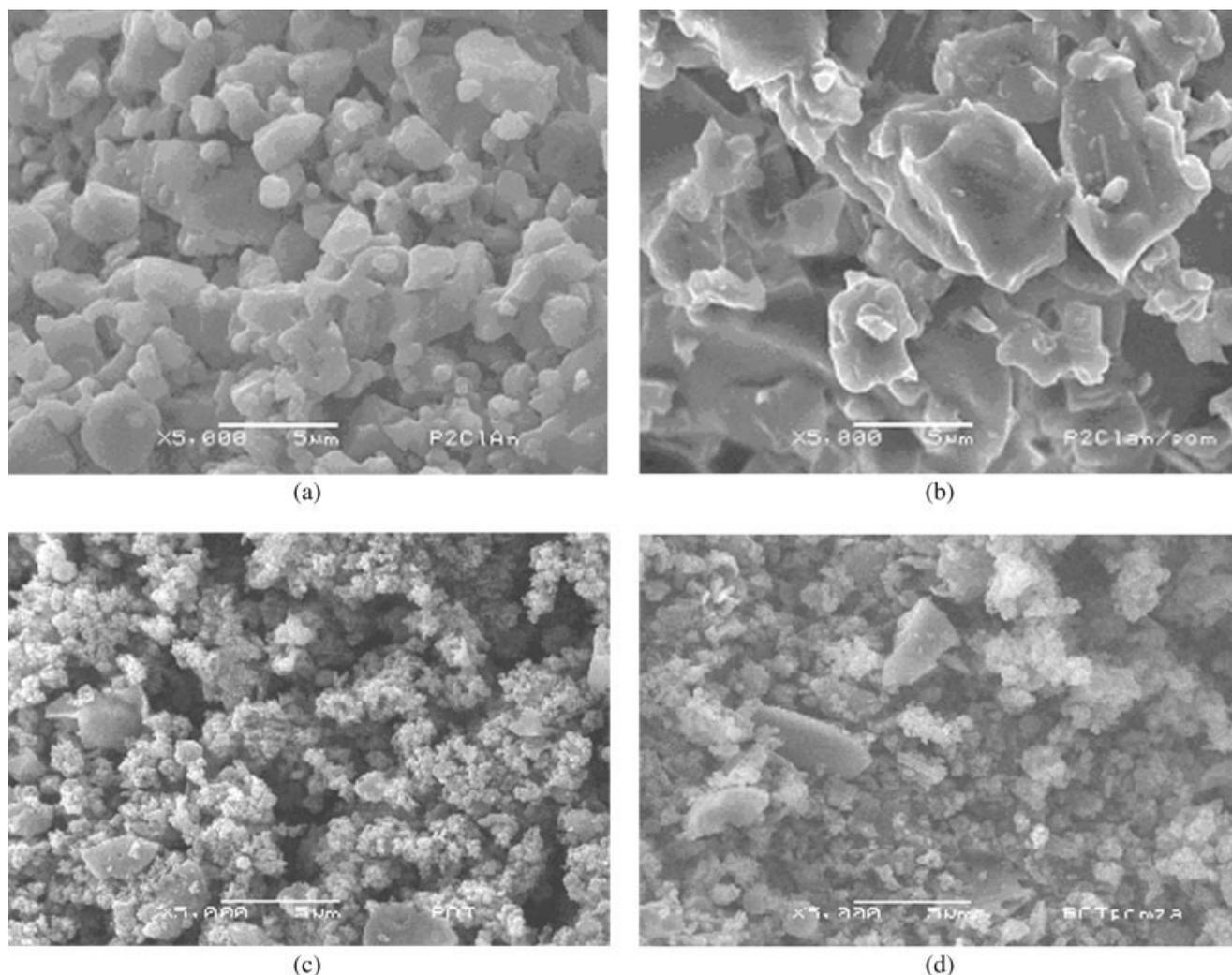


Figure 4 SEM micrographs of (a) P2ClAn, (b) P2ClAn/Pmc, (c) POT, and (d) POT/Pmc.

from the bulk solution to the surface of the adsorbent and then the attachment of the transported chromium on the surface of the adsorbent.³⁷

Figure 6 shows typical results of the sorption of Cr(VI) on the composites versus adsorption times at a 1×10^{-3} mol/L. The adsorption equilibriums were reached very fast for Cr(VI) and took only 20 and 30 min for POT/Pmc and P2ClAn/Pmc, respectively. At equilibrium, for example, at 1500 min, the maximum sorption values of POT/Pmc and P2ClAn/Pmc were 87 and 62%, respectively. However, Pmc exhibited a lower sorption value (50%) for the same adsorption time.³⁰ The rapid adsorption equilibrium for Cr(VI) was an indication that the surfaces of the composites were readily available for adsorption.³⁷ In this study, the agitation period varied from 10 to 2880 min. The adsorption of Cr(VI) increased with agitation period and, thereafter, rose slowly before a saturation value was attained. The removal versus time curves were single, smooth, and continuous, which led to saturation and suggested the possibility of monolayer cover-

age of Cr(VI) on the outer surface of the sorbent.²⁵ These observations were in agreement with the study reported earlier with other metal ion adsorbent systems.^{37,40,43}

Effect of the amount of adsorbent dosage

The data in Figure 7 establish that weights of POT/Pmc and P2ClAn/Pmc higher than 25 mg were enough to eliminate almost all Cr(VI) from 1×10^{-3} mol/L solutions at $20 \pm 1^\circ\text{C}$ temperature. This condition is useful in studies. Additionally, the sorption values were better than those given in the literature for Pmc.³⁰

Effect of initial concentration

The adsorption of Cr(VI) was measured at 2 h for six different initial Cr(VI) concentrations. Initial concentrations of Cr(VI) used in this investigation were kept

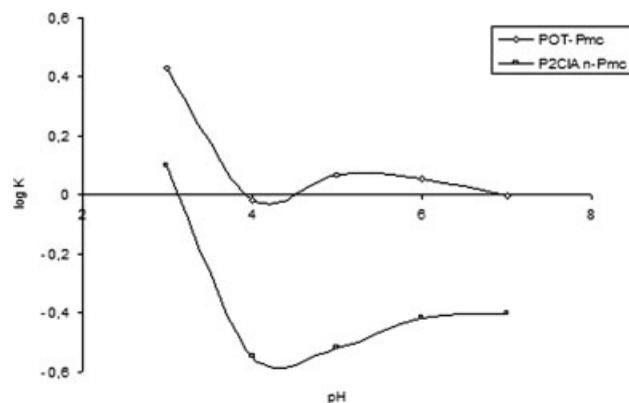


Figure 5 Distribution coefficients of Cr(VI) metal on the adsorbents as a function of pH [adsorption conditions: initial concentration of Cr(VI), $1 \times 10^{-3} M$; amount of adsorbent, 100 mg; volume of adsorption medium, 30 mL; adsorption time, 120 min; temperature, $20 \pm 1^\circ C$].

at concentrations of 1×10^{-4} , 2×10^{-4} , 4×10^{-4} , 6×10^{-4} , 8×10^{-4} , and 1×10^{-3} mol/L. The effect of initial Cr(VI) concentration on the rate of adsorption is shown in Figure 8. First, the plot reveals that the rate of percentage chromium removal was higher at the beginning. That was probably due to the larger surface area of the adsorbents being available at beginning for the adsorption of Cr(VI). As the surface adsorption sites became exhausted, the uptake rate was controlled by the rate at which the adsorbate was transported from the exterior to the interior sites of the adsorbent particles.⁴³

Values at low concentrations are useful when the objective is to remove chromium from aqueous solutions. The adsorption of Cr(VI) in low concentrations were in the range of Henry's linear isotherm and are confirmed in Figure 8. A parameter to determine favorable condition of Langmuir isotherm and its tendency as an irreversible process is used in adsorp-

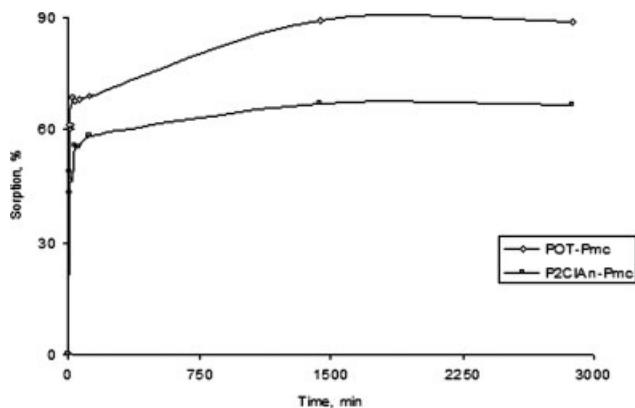


Figure 6 Effect of contact time on the sorption of Cr(VI) by the adsorbents [adsorption conditions: initial concentration of Cr(VI), $1 \times 10^{-3} M$; adsorption time, 5–2880 min; amount of adsorbent, 100 mg; volume of adsorption medium, 30 mL; temperature, $20 \pm 1^\circ C$].

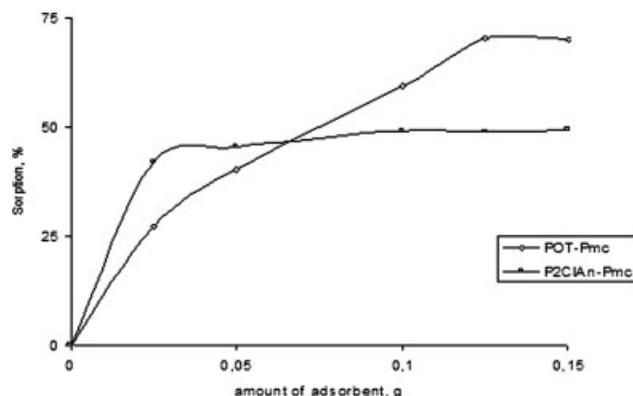


Figure 7 Effects of the amount of adsorbents for Cr(VI) from aqueous solutions [adsorption conditions: initial concentrations of Cr(VI), $1 \times 10^{-3} M$; amount of adsorbent, 25–150 mg; volume of adsorption medium, 30 mL; adsorption time, 120 min; temperature, $20 \pm 1^\circ C$].

tion studies. This considers the shape of the isotherm. The equilibrium parameter, or Langmuir parameter (R_L),⁴⁰ is evaluated in accordance with eq. (1). If $R_L < 1$, the process is favorable; if $R_L = 1$, the process is linear; and if $R_L > 1$, the process is unfavorable. R_L depends on the equilibrium concentration (C_e) and the affinity constant of Langmuir (b); the higher b is, the more favorable the process is. Values of R_L were less than 0.98 at 1×10^{-3} mol/L of initial concentration. This means that the adsorption of Cr(VI) with the POT/Pmc and P2ClAn/Pmc composites was a favorable and useful process for chromium removal:

$$R_L = 1/(1 + bC_e) \quad (1)$$

The Langmuir equation is as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0 b} \quad (2)$$

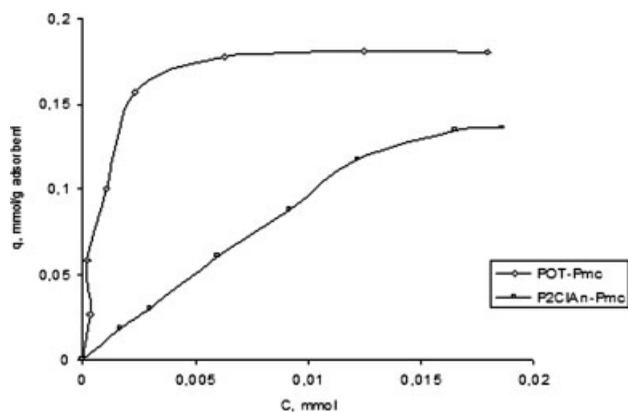


Figure 8 Sorption isotherms of Cr(VI) ion on POT/Pmc and P2ClAn/Pmc [adsorption conditions: initial concentration of Cr(VI), 1×10^{-4} to $1 \times 10^{-3} M$; amount of adsorbent, 100 mg; volume of adsorption medium, 30 mL; adsorption time, 120 min; temperature, $20 \pm 1^\circ C$].

TABLE II
Freundlich and Langmuir Adsorption Isotherm Parameters of POT/Pmc and P2ClAn/Pmc

| Adsorbent | Freundlich isotherm | | | Langmuir isotherm | | | |
|-----------------------|-----------------------------|-------|-------|-----------------------------|----------|-------|-------|
| | K_f (mmol/g of adsorbent) | n | R^2 | Q_0 (mmol/g of adsorbent) | b | R^2 | R_L |
| POT/Pmc | 0.584 | 3.920 | 0.903 | 0.187 | 1911.899 | 0.999 | 0.343 |
| P2ClAn/Pmc | 4.959 | 1.146 | 0.990 | 0.449 | 25.559 | 0.847 | 0.975 |
| PAn/Pmc ³⁰ | 0.768 | 2.770 | 0.870 | 0.184 | 517 | 0.979 | 0.659 |
| Pmc ³⁰ | 0.412 | 1.327 | 0.990 | 0.054 | 34 | 0.860 | 0.967 |

where C_e is the equilibrium concentration (mg/L), q_e is the amount of adsorbed material at equilibrium (mg/g), b is the affinity parameter or Langmuir constant (L/mg), and Q_0 is the capacity parameter (mg/g).

The Freundlich equation indicated the adsorptive capacity on the POT/Pmc and P2ClAn/Pmc composites. The empirical Freundlich equation based on sorption on a heterogeneous surface is given below:³⁴

$$q = K_f C^{1/n} \quad (3)$$

The Freundlich equation is expressed linearly as

$$\log q = \log K_f + 1/n(\log C) \quad (4)$$

The K_f , the sorption capacity and n values, the sorption intensity, as calculated from Figure 8 for POT/Pmc were found to be 0.584 mmol/g and 3.920, respectively (Table II). The P2ClAn/Pmc composite had K_f and n values of 4.959 mmol/g and 1.146, respectively. A value of n higher than 1 indicated that the adsorption on composites was favorable, and the capacity was only slightly reduced at lower C_e 's.^{39,25,44,45} These values were comparable with several published literature reports for various sorbents.⁴³ R_L and n values for Pmc and PAn/Pmc were 0.9667 (R_L) and 1327 (n) and 0.6591 (R_L) and 2.77 (n), respectively.

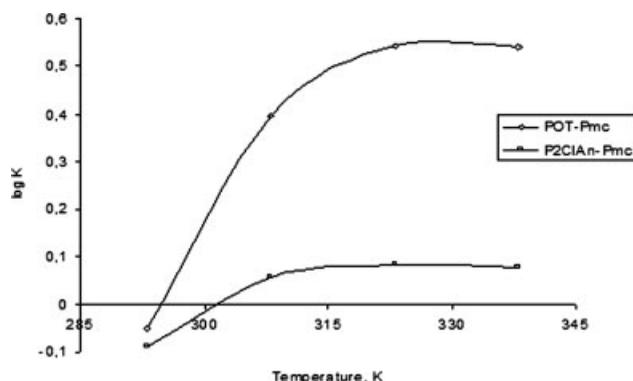


Figure 9 K 's of Cr(VI) on the adsorbents as a function of temperature [adsorption conditions: initial concentration of Cr(VI), $1 \times 10^{-3}M$; amount of adsorbent, 100 mg; volume of adsorption medium, 30 mL; adsorption time, 120 min; temperature, $20 \pm 1^\circ C$].

According to the R_L and n values, Pmc exhibited lower adsorption properties than the POT/Pmc and P2ClAn/Pmc composites. The sorption capacity of Pmc was increased in the presence of POT and P2ClAn, as with PAn.³⁰ As compared with the literature, the sorption order for adsorbents can be written as PAn/Pmc > POT/Pmc > P2ClAn/Pmc > Pmc.

The isotherms of the adsorption process with Cr(VI) depicted in Figure 8 show that the experimental data fit both the Freundlich correlation coefficient (R^2) = 0.903 and Langmuir R^2 = 0.999 models for POT/Pmc and the Freundlich R^2 = 0.990 and Langmuir R^2 = 0.847 models for P2ClAn/Pmc. This hinted that the adsorption tended to be monolayer.^{38,39} According to these results, we concluded that the equilibrium adsorption data for POT/Pmc fit the Langmuir adsorption isotherm, whereas P2ClAn/Pmc obeyed the Freundlich isotherm.

Effect of temperature

Figure 9 shows increasing equilibrium constant (K) values with changing temperature. The Gibbs free energy (ΔG) for the adsorption process for each effluent was obtained with K values and the following formula:

$$\Delta G = -RT \ln K \quad (5)$$

where R is ideal gas coefficient and T is Kelvin temperature. Values of ΔG , ΔH , and ΔS , for the composites are shown in Table III. ΔG indicates the spontaneity of the adsorption process, where higher negative values reflect a more energetically favorable adsorption process. The negative ΔG values obtained for the POT/Pmc and P2ClAn/Pmc composites in this study confirmed the feasibility of the adsorbent and the spontaneity of adsorption.³⁹

CONCLUSIONS

POT/Pmc and P2ClAn composites were synthesized by the *in situ* polymerization of *o*-toluidine and 2-ClAn in the presence of Pmc. The composites were characterized in terms of microscopic morphology, FTIR spectroscopy, and thermal analysis. POT/Pmc and P2ClAn/Pmc composites were used as adsorb-

TABLE III
Thermodynamic Parameters of POT/Pmc and P2ClAn

| Adsorbent type | ΔH° (J/mol) | ΔS° (J K ⁻¹ mol ⁻¹) | ΔG° (J/mol) | | | |
|----------------|--------------------------|---|--------------------------|----------------|----------------|----------------|
| | | | $T = 298.15$ K | $T = 308.15$ K | $T = 323.15$ K | $T = 338.15$ K |
| POT/Pmc | 24761.084 | 85.513 | -307.081 | -1589.778 | -2872.474 | -4155.171 |
| P2ClAn/Pmc | 6914.607 | 22.578 | 295.779 | -42.896 | -381.570 | -720.245 |

ΔG^* , free energy change; ΔH^* , enthalpy change; ΔS^* , entropy change.

ents and were found to be effective in the adsorption of Cr(VI) from aqueous solutions. All adsorption parameters confirmed that POT/Pmc had a higher adsorption capacity for the removal of Cr(VI) than P2ClAn/Pmc. The composites are considered to have potential applications in water and wastewater treatment for the removal of heavy-metal ions such as Cr(VI). The adsorption equilibrium was reached within about 2 h. The maximum adsorption capacities observed for the POT/Pmc and P2ClAn/Pmc composites were 0.187 and 4.959 mmol/g, respectively. An increase in the dose of adsorbent, initial concentration of Cr(VI), and contact time up to 2 h were favorable for increasing the adsorption of Cr(VI). ΔG , ΔH , and ΔS values were obtained for each system. The adsorption data of composites were satisfactorily explained by the Freundlich and Langmuir isotherms.

References

- Andreu, Y.; Marcos, S. de; Castillo, J. R.; Galb'an, J. *Talanta* 2005, 65, 1045.
- Syed, A. A.; Dinesan, M. *Analyst* 1992, 117, 61.
- Balarama Krishna, M. V.; Karunasagar, D.; Rao, S. V.; Arunachalam, J. *Talanta* 2005, 68, 329.
- Balarama Krishna, M. V.; Arunachalam, J.; Prabhu, D. R.; Manchanda, V. K.; Kumar, S. *Sep Sci Technol* 2005, 40, 1313.
- Liao, Y. H.; Angelopoulos, M.; Levon, K. *J Polym Sci Part A: Polym Chem* 1995, 33, 2725.
- Gupta, M. C.; Umare, S. S.; Huque, M. M.; Visvanath, S. G. *Ind J Chem B* 1997, 36, 703.
- Wawere, U. S.; Umare, S. S. *React Funct Polym* 2005, 65, 343.
- Lee, D.; Lee, S. H.; Char, K.; Kim, J. *Macromol Rapid Commun* 2000, 21, 1136.
- Ballav, N.; Biswas, M. *Synth Met* 2004, 142, 309.
- Jia, W.; Segal, E.; Kornemandel, D.; Lamhot, Y.; Narkis, M.; Siegmann, A. *Synth Met* 2002, 128, 115.
- Biswas, M.; Ray, S. S.; Liu, Y. P. *Synth Met* 1999, 105, 99.
- Su, S. J.; Kuramoto, N. *Synth Met* 2000, 114, 147.
- Yang, S. M.; Chen, K. H. *Synth Met* 2003, 135, 151.
- Lee, D.; Char, K.; Lee, S. W.; Park, Y. W. *J Mater Chem* 2003, 13, 2942.
- Frish, H. L.; Mark, J. E. *Chem Mater* 1996, 81, 735.
- Gök, A.; Sarı, B.; Talu, M. *Synth Met* 2004, 142, 41.
- Gök, A.; Sarı, B. *J Appl Polym Sci* 2002, 84, 1993.
- Akbal, F.; Akdemir, N.; Onar, A. N. *Talanta* 2000, 53, 131.
- Afkhami, A.; Convey, B. E. *J Colloid Interface Sci* 2002, 251, 248.
- Cimino, G.; Passerini, A.; Toscano, G. *Water Res* 2000, 34, 2955.
- Samantaroy, S.; Mohanty, A. K.; Misra, M. *J Appl Polym Sci* 1997, 66, 1485.
- Namasivayam, C.; Yamuna, R. T. *Chemosphere* 1995, 30, 561.
- Ülkü, Y.; Haluk, Ç. *Water SA* 2001, 27, 15.
- Curkovic, L.; Cerjan-Stefanovic, S.; Rastovean-Mioe, A. *Water Resour* 2001, 35, 3436.
- Raji, C.; Anirudhan, T. S. *Water Res* 1998, 32, 3772.
- Harvey, N. W.; Chantawong, V. *J Univ Inf Sci* 2001, 5, 79.
- Göde, F.; Pehlivan, E. *Energy Sources A* 2006, 28, 447.
- Akbal, F. *J Colloid Interface Sci* 2005, 286, 455.
- Gök, A.; Göde, F.; Esencan Turkaslan, B. *Mater Sci Eng B* 2006, 133, 20.
- Gök, A.; Göde, F.; Esencan Turkaslan, B. *Asian J Chem* 2007, 19, 3023.
- Li, X. G.; Huang, M. R.; Wang, L. X.; Zhu, M. F.; Menner, A.; Springer, J. *Synth Met* 2001, 123, 435.
- Waware, U. S.; Umare, S. S. *React Funct Polym* 2005, 65, 343.
- Li, N.; Li, X. T.; Geng, W. C.; Zhang, T.; Zuo, Y.; Qui, S. L. *J Appl Polym Sci* 2004, 93, 1597.
- Gök, A.; Oğuz, İ. *J Appl Poly Sci* 2006, 99, 2101.
- Gemeay, A. H.; Mansour, I. A.; El-Sharkawy, R. G.; Zaki, A. B. *Eur Polym J* 2005, 41, 2575.
- Gök, A.; Omastova, M.; Prokes, J. *Eur Polym J* 2007, 43, 2471.
- Baran, A.; Bıçak, E.; Hamarat Baysal, Ş.; Önal, Ş. *Bioresour Technol* 2007, 98, 661.
- Deng, S.; Bai, R. *Water Res* 2004, 38, 2424.
- Rojas, G.; Silva, J.; Flores, J. A.; Rodriguez, A.; Ly, M.; Maldonado, H. *Sep Purif Technol* 2005, 44, 31.
- Sarin, V.; Pant, K. K. *Bioresour Technol* 2006, 97, 15.
- Sankaramakrishnan, N.; Dixit, A.; Iyengar, L.; Sanghi, R. *Bioresour Technol* 2006, 97, 2377.
- Korngold, E.; Belayev, N.; Aronov, L. *Sep Purif Technol* 2003, 33, 179.
- Bayat, B. *J Hazard Mater B* 2002, 95, 275.
- Acar, F. N.; Malkoc, E. *Bioresour Technol* 2004, 94, 13.
- Gezici, O.; Kara, H.; Ersöz, M.; Abali, Y. *J Colloid Interface Sci* 2005, 298, 381.