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Adsorption of Cr(VI) from aqueous solution onto short-chain polyaniline/palygorskite composites

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ABSTRACT

Hexavalent chromium in aqueous environment may result in severe environmental and public health problems. In this study, short-chain polyaniline/palygorskite composites (PANI/PA) were prepared and developed to remove aqueous Cr(VI). Characterized results showed that short-chain polyaniline was successfully incorporated on the surface of PA. The maximum Cr(VI) adsorption amount was found to be 11.54, 14.34, and 16.22 mg/g at 15, 25, and 35˚C, respectively, and polyaniline on the adsorbent surface may account for the enhanced Cr(VI) adsorption. Cr(VI) adsorption was highly dependent on both solution pH and ionic strength, which indicates that electrostatic force and anion exchange may account for the increased Cr(VI) adsorption onto PANI/PA. Cr(VI) saturated PANI/PA can be easily desorbed in alkaline solution and regenerated adsorbents still possess high adsorption amount for aqueous Cr(VI). The current study shows that PANI/PA can be used as an effective and recyclable adsorbent for the removal of Cr(VI) in water and wastewater treatment.

Keywords: Hexavalent chromium; Short-chain polyaniline/palygorskite composites; Adsorption; Regeneration

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1. Introduction

Removal of heavy metals such as chromium, lead, nickel, and copper from aqueous environment has received great attention in recent years because they may result in severe environmental and public health problems. As a priority metal pollutant, chromium is frequently identified in natural waters discharged from various industrial wastewaters such as electroplating, leather tanning, textile, and metal finishing industries. Chromium exists in natural water mainly in two states: trivalent Cr(III) and hexavalent Cr(VI). Cr(VI) salt is considered more toxic to human health than Cr(III) because it is quite soluble in aqueous phase and mobile in the natural environment [1]. Excessive exposure to Cr(VI) may cause epigastric pain, nausea, vomiting, severe diarrhea, corrosion of skin, respiratory tract, and lungs carcinoma, due to its mutagenic and carcinogenic properties [2–4]. Hence, minimization and

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removal of Cr(VI) from water is of practical importance and interest.

A variety of treatment techniques have been developed to remove Cr(VI) from water, including chemical precipitation, electrodialysis, adsorption, ion exchange process, and membrane filtration [4–9]. Among these techniques, adsorption has been considered as one of the most effective removal processes for the low concentrations of Cr(VI) due to its feasibility in various fields. Many adsorbents, such as activated carbon and resin, have been reported to be efficient adsorbents for the removal of Cr(VI) from aqueous solution, but they are too expensive. An increasing attention has been paid to develop the low-cost and easily-available adsorbents for the removal of Cr(VI).

Clay minerals are widely applied to eliminate the pollutants due to their high removal efficiency, low cost and simple operation. As natural clay, palygorskite (PA) is a hydrated magnesium silicate mineral with a fibrous morphology, which is abundant in China. Because of its large surface area, porous structure, moderate cation exchange, and negatively charged surface, PA has been intensively investigated as adsorbents for the removal of heavy metal cations, such as Cu(II), Pb(II), Ni(II), Cd(II), and so on [10–15]. However, a few studies have been made for the removal of Cr(VI) from aqueous solution because Cr(VI) is primarily present in the form of anion.

As a conductive polymer with large amount of imine and amine groups, polyaniline (PANI) and its composites have been widely used as effective sorbents for the removal of organic and inorganic pollutants from aqueous solution [16–24]. It has been revealed from the literature that PANI adsorbents, such as PANI coated on sawdust [16,20] and PANI synthesized on jute fiber [22], exhibited high adsorption capacity for Cr(VI) in aqueous solution. Therefore, incorporating PANI on the surface of PA may improve adsorption capacity of Cr(VI) on PA adsorbent. To our best knowledge, no attempts have been made to remove aqueous Cr(VI) using short-chain PANI-modified PA adsorbent. In this study, short-chain polyaniline/palygorskite (PANI/PA) composite was prepared by grafting of PANI onto the surface of PA, and the physicochemical and structural properties of the adsorbent were characterized by Fourier transform infrared (FTIR), powder X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and zeta analyzer. Adsorption and desorption behaviors of aqueous Cr(VI) onto the adsorbent were investigated by batch experiments and adsorption kinetic tests. Effects of different water chemistry conditions such as solution pH and coexisted ions were also studied.

2. Experimental

2.1. Materials

PA clay with the average diameter of 300 mesh was provided by Jiangsu Huda Co. Ltd., Jiangsu, China. Sodium hydroxide (NaOH) and ammonium persulfate (APS), aniline, potassium dichroromate, and p-phenylenediamine were analytical grade reagents received from Tianjin Chemical Co., Tianjin, China.

2.2. Preparation of PANI/PA

PANI/PA was prepared by oxidation of aniline in presence of p-phenylenediamine, a chain terminator in acidic aqueous medium in the presence of an oxidant, APS. Firstly, 10 g of PA particles were dispersed into 100 mL 1 mol/L HCl and the mixture was sonicated for 30 min and stirred for next 5 h at room temperature. Then, the PA was rinsed with deionized water to eliminate the chlorine and dried at 80°C in vacuum.

Secondly, aniline (2.17 g) and p-phenylenediamine (0.36 g) were dissolved in 62 mL of 1 M HCl. The mixture was cooled in iced bath followed by addition of 5 g PA and stirred for 30 min. The solution of APS (1.63 g dissolved in 16 mL 1 mol/L HCl) pre-cooled at ice bath was dropwisely added to the above mixture. The reaction mixture was stirred at ice bath for 60 min and then kept overnight at room temperature. The resulting solids were filtered and washed with deionized water for several times until the filtrate was found to be at neutral pH value, followed by drying at 40°C in vacuum for 24 h.

2.3. Characterization of PANI/PA

The FTIR spectra of the adsorbents were recorded on a Vector-22 FTIR spectrometer (Bruker, Germany) with the KBr pellet technique. The TGA curves were performed on a Perkin-Elmer Pyris 1 TGA instrument (Perkin-Elmer, USA) at heating rate of 10°C/min from room temperature to 700°C. XRD patterns were collected in a range of 3–60° from a Shimadzu XRD-6000 powder diffraction-meter using Cu Kα radiation. TEM images of the adsorbents were collected on a JEM-3010 transmission electron microscope (JEOL, Japan). SEM observations of the adsorbents were collected on a S4800 scanning electron microscope (Hitachi, Japan). Carbon, hydrogen, and nitrogen contents were determined with a Heraeus CHN–O-Rapid elemental analyzer (Heraeus, Germany). Zeta potentials of PANI/PA were measured using a zeta potential analyzer (Zeta PALS, Brookhaven Instruments Co., USA). Detailly, 0.04 g of PANI/PA was dispensed in 400 mL of 1 mmol/L NaCl solution and sonicated for 10 min.

The pH of mixture was adjusted with 0.1 mol/L HCl or NaOH to the desired pH. The dispersion was then settled for 24 h and the supernatant was used for zeta-potential tests.

2.4. Adsorption tests

The batch experiments were carried out to evaluate adsorption isotherms of Cr(VI) on PANI/PA. Briefly, 20 mg of PANI/PA was added to 60-mL flask receiving 40 mL of Cr(VI) solution with initial concentration from 2.5 to 35 mg/L at pH 5.5–5.97. The flasks were shaken in an incubator at 25℃ for 24 h. After reaching adsorption equilibrium, the adsorbents were filtrated by 0.45 μm membrane filter and the residual concentrations of Cr(VI) in the aliquot were determined using a UV–Vis spectrometer with detecting wavelength at 540 nm [25]. The equilibrium adsorption amounts of Cr(VI) were calculated according to Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{1}$$

where q_e (mg/g) is the amount of Cr(VI) adsorbed at equilibrium, C_0 (mg/L) is the initial Cr(VI) concentration, C_e (mg/L) is the equilibrium Cr(VI) concentration, V (L) is the volume of Cr(VI) solution, and M (g) is the adsorbent mass.

The effect of solution pH on Cr(VI) adsorption onto PANI/PA was investigated in a pH range from 1.5 to 8.0. A series of flasks containing 20 mg of PANI/PA and 40 mL of 10 mg/L Cr(VI) solution with different pH pre-adjusted with HCl and NaOH solution was shaken at 25℃ for 24 h. The residual Cr(VI) concentrations were determined spectrophotometrically and adsorption amount of Cr(VI) were calculated according to Eq. (1).

For adsorption kinetics at 25℃, 200 mg of PANI/PA was introduced into a 500-mL three-neck flask containing 400 mL of Cr(VI) solution with an initial Cr(VI) concentration of 2.5, 5, 10, or 30 mg/L, respectively, under magnetic stirring. Four milliliter of solution was withdrawn at different time intervals. After separation of the adsorbent particles, the residual Cr(VI) concentration was determined spectrophotometrically.

Effect of coexisted anions on Cr(VI) adsorption were studied by dispersing 20 mg of adsorbents in 40 mL NaCl, $NaNO_3$, or Na_2SO_4 solution (2.5–20 mg/L), containing 10 mg/L Cr(VI) at about pH 5.8.

2.5. Desorption and regeneration

The regeneration was explored by batch adsorption–desorption experiments. Briefly, 50 mg PANI/PA was dispensed in 40-mL flask containing 20 mg/L Cr(VI) and shaken in an incubator for 20 h at solution pH of 5.8. The mixture was centrifuged and the filtrate was measured for residual Cr(VI) concentration. The Cr(VI)-loaded PANI/PA was desorbed in 2 M NaOH and shaken for 10 min and the regenerated adsorbent was centrifuged and washed for three times with deionized water for next adsorption–regeneration cycles.

3. Results and discussion

3.1. Characterization of PANI/PA

The FTIR spectra of PA and PANI/PA are illustrated in Fig. 1. Compared with the spectrum of PA, the main characteristic peaks of PANI/PA at 3,360 cm^{-1} is attributed to N–H stretching mode, and the bands at 1,598 and 1,512 cm^{-1} are assigned to C=N and C=C stretching mode for the quinonid and benzenoid units, and the band at 1,330 cm^{-1} is ascribed to C–N stretching mode for benzenoid unit, indicating of the oxidation state of PANI (Emeraldine Salt) [26,27]. The band at 1,030 cm^{-1} corresponded to the overlap peaks of the Si–O–Si, and the band at 829 cm^{-1} corresponded to the overlap peaks of Si–O and C–H stretching mode are also observed. The FTIR analysis confirmed that PANI was successfully grafted on the surface of PA. The results of element analysis show that the C, N, and H content of the PANI/PA are 6.13, 1.94, and 1.46%, respectively.

The TGA curve of PANI/PA is shown in Fig. 2. From the result, the weight loss below 120℃ is about 4.14%, which is attributed to the departure of moisture

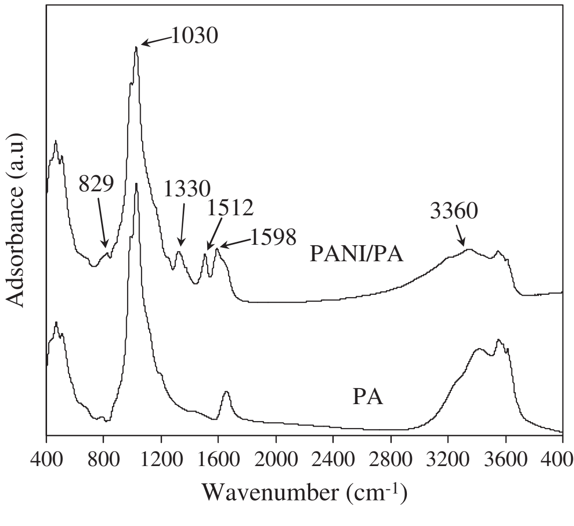

Fig. 1. The FTIR spectra of PA and PANI/PA.

and HCl doped [28]. The weight loss (10.81%) between 120 and 700℃ is mainly corresponded to the decomposition of PANI coverage on the PA. The content of PANI (9.53%) is higher than that calculated from the result of element analysis, which may be caused by the breakout of the structure water in PA crystallines [29].

The crystal structures of bare PA and PANI/PA were characterized by XRD and the corresponding results are illustrated in Fig. 3. The characteristic peaks of PA at $2\theta = 8.32$, 19.84, 27.49, 34.96, and 42.7 are in correspondence to the crystal structure of PA. The similar peaks are also found in PANI/PA, whereas the peak intensity is weakened, which reflected that the crystal structure of clay mineral was not destroyed after PANI incorporation. The broad peaks at $2\theta = 20\text{–}30^{\circ}$ are ascribed to the structure of polyaniline, indicating successful coverage of PANI onto PA surface by the polymerization reaction. The morphology and size of PA and PANI/PA are characterized by TEM and SEM observations (Fig. 4). Fig. 4(a1) and (b1) are the TEM images of PA and PANI/PA. It can be seen that PA was a type of fibrillar clay mineral. From Fig. 4(b1), it is obvious that the surface of PANI/PA was incorporated on the surface of PA. From the SEM observations of the natural PA (Fig. 4(a1)) and PANI/PA (Fig. 4(b2)), it is obvious that PA is laminated structure with many pore canals in the layer and the surface is uneven. After PANI coating, the surface of PANI/PA becomes smooth and very different from the bare PA, indicating the successful polymerization of aniline on the surface of PA.

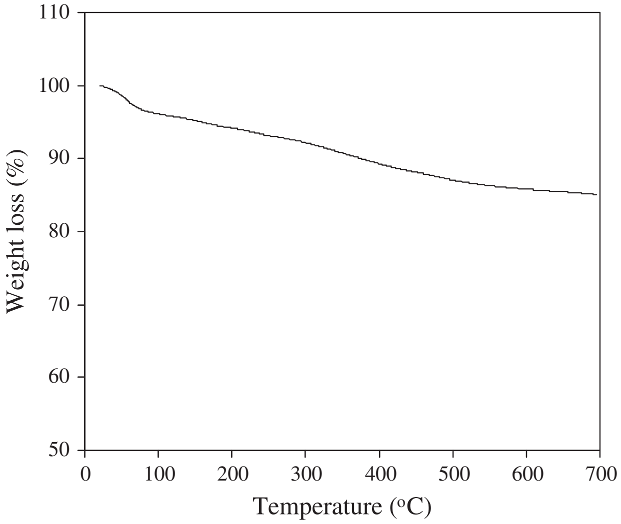

Fig. 2. The TGA curve of PANI/PA.

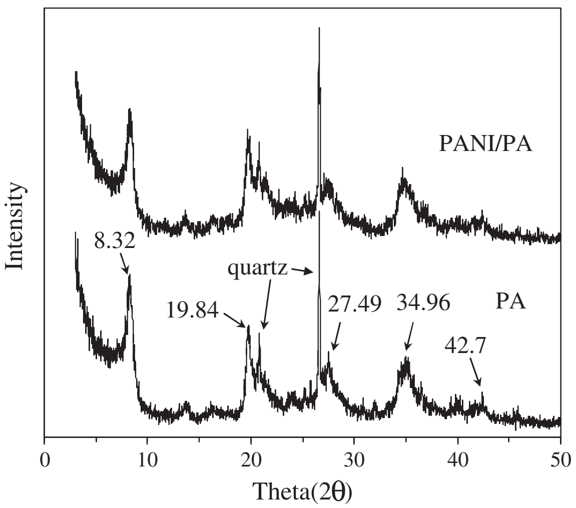

Fig. 3. The XRD patterns of PA and PANI/PA.

3.2. Adsorption isotherms

Langmuir, Freundlich, and Sips models were frequently used to follow the adsorption process of organic and inorganic pollutions on adsorbents.

Langmuir model is expressed as follows:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{2}$$

Freundlich is given as follows:

$$q_e = K_f C_e^{\frac{1}{n}} \tag{3}$$

$$q_e = \frac{q_m K_s C_e^{1/n}}{1 + K_s C_e^{1/n}} \tag{4}$$

where q_e (mg/g) is the equilibrium adsorption amount, C_e (mg/L) is the equilibrium concentration of Cr(VI), q_m (mg/g) is the theoretical adsorption capacity of adsorbent for Cr(VI), b (L/mg) is the affinity coefficient, K_f ($\text{mg}^{1-1/n}\text{L}^{1/n}$/g) is Freundlich constant and $1/n$ is the heterogeneity factor, K_S $(\text{L/mg})^{1/n}$ is the Sips equilibrium constant, and $1/n$ is the Sips model exponent.

Adsorption isotherms of aqueous Cr(VI) on PA and PANI/PA are shown in Fig. 5. Simulated parameters based on Langmuir, Freundlich, and Sips equations are tabulated in Table 1. For Freundlich equations, the correlation coefficients (R^2) were lower than 0.95, which indicated that Freundlich equation cannot follow the Cr(VI) adsorption on PANI/PA. But for Langmuir equation, the correlation coefficients

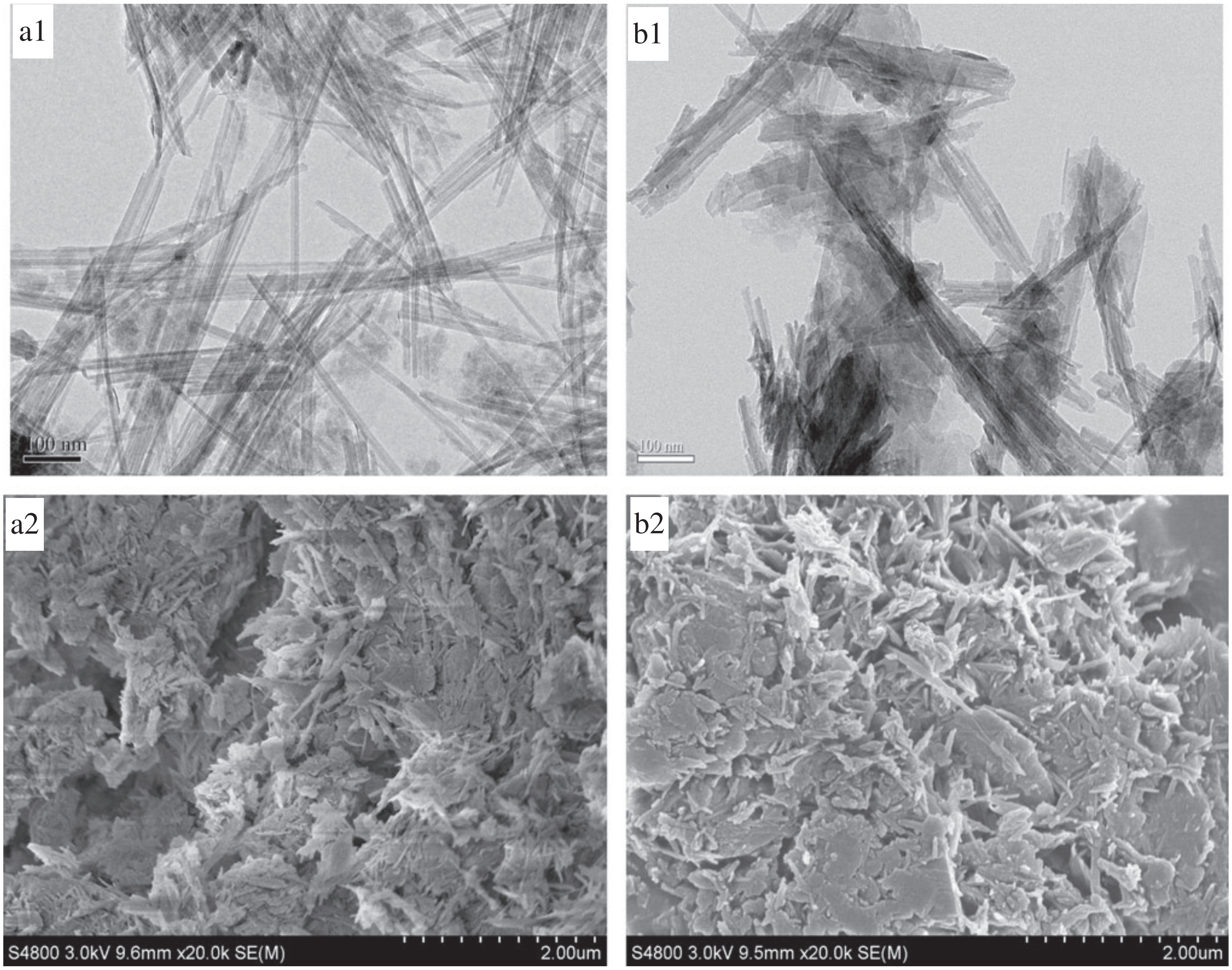

Fig. 4. The TEM images of PA (a1) and PANI/PA (b1), SEM image of PA (a2) and PANI/PA (b2).

were higher than 0.99, which is higher than Sips equation, and the calculated adsorption amounts were in good agreement with the experiment data, suggesting that Cr(VI) adsorption on PANI/PA could be better described by the Langmuir model than by Sips model. The maximum adsorption amounts based on Langmuir model were found to be 11.54, 14.34, and 16.22 mg/g at 15, 25, and 35℃, respectively, while untreated PA was almost no adsorption for Cr(VI) in aqueous solution, indicating that PANI on the surface of PANI/PA may account for the enhanced Cr(VI) adsorption. Cr(VI) adsorption onto PANI/PA increased with increasing temperature, suggesting that Cr(VI) adsorption process onto PANI/PA was endothermic. The separation factor, R_L, is the essential characteristic of Langmuir model, which can be expressed as [30,31]:

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

where C_0 (mg/g) is the initial Cr(VI) concentration. The value of R_L indicates the nature of adsorption process to be either unfavorable ($R_L > 1$), linear ($R_L = 1$) or favorable ($0 < R_L < 1$). The calculated values of R_L are between 0.016 and 0.185 at 25℃ with initial concentration from 2.5 to 35 mg/g, which indicates that Cr(VI) adsorption onto PANI/PA is favorable.

3.3. Adsorption kinetics

Adsorption kinetics of Cr(VI) onto PANI/PA at initial concentrations of 2.5, 5, 10, and 30 mg/L are

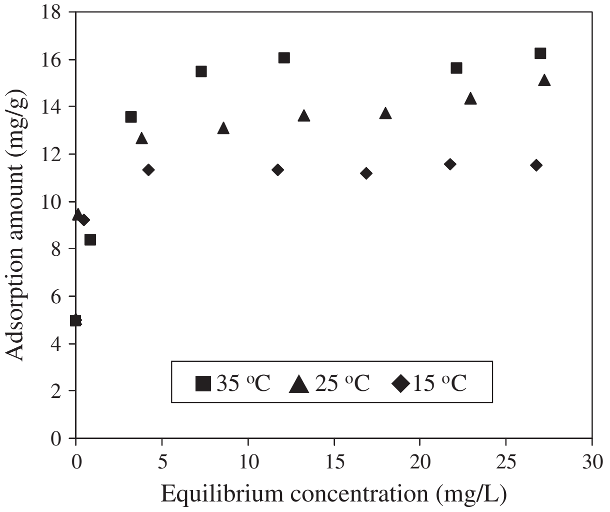

Fig. 5. Adsorption isotherms of Cr(VI) onto PANI/PA at 15, 25, and 35°C, respectively.

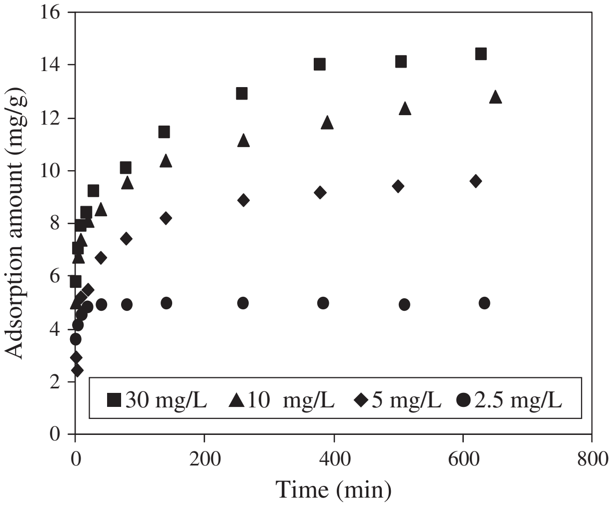

Fig. 6. Adsorption kinetics of Cr(VI) onto PANI/PA at initial Cr(VI) concentration of 2.5, 5, 10, and 30 mg/L, respectively.

illustrated in Fig. 6. Based on the plots, Cr(VI) adsorption amount on adsorbents increased with increasing initial Cr(VI) concentration and adsorption equilibrium was achieved within 400 min, indicating a rapid Cr(VI) adsorption process. To further describe the adsorption mechanism, pseudo-first-order and pseudo-second-order model were used to follow the Cr(VI) adsorption onto PANI/PA. For pseudo-fist-order kinetic, the adsorption process can be described by Lagergren's rate equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{6}$$

where q_e (mg/g) is the adsorption amount at equilibrium, q_t (mg/g) is the adsorption amount at time t (min), and k_1 (1/min) is the pseudo-first-order rate constant.

The pseudo-second-order kinetic based on adsorption capacity can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e}t \tag{7}$$

where q_e (mg/g) is the adsorption amount at equilibrium, q_t (mg/g) is the adsorption amount at time t (min), and k_2 (g/mg min) is the pseudo-second-order rate constant.

Fitting parameters of Cr(VI) adsorption onto PANI/PA based on the pseudo-first-order kinetic and pseudo-second-order kinetic are shown in Table 2. As shown in the Table 2, the correlation coefficient (R^2) obtained from the pseudo-first-order kinetic is lower than 0.98, and the calculated adsorption amounts are not in accordance with experimental results, suggesting that pseudo-first-order kinetic model could not simulate Cr(VI) adsorption process onto PANI/PA. However, for pseudo-second-order kinetics model, the correlation coefficient R^2 is higher than 0.99, and Cr(VI) adsorption capacities obtained from experimental data are approximately identical to those calculated from fitting results, indicating that Cr(VI) adsorption process onto PANI/PA obeys pseudo-second-order kinetics. These results show that the pseudo-second-order mechanism is predominant and adsorption behavior is in agreement with chemical adsorption, which is the rate-limiting step. The adsorption rate

Table 1
Langmuir and Freundlich model parameters for Cr(VI) adsorption on PANI/PA at 15, 25 and 35°C

	Langmuir model parameters			Freundlich model parameters				Sips model parameters		
Temperature (°C)	q_m (mg/g)	b (L/mg)	R^2	n	K_f	R^2	q_m (mg/g)	Ks (L/mg)$^{1/n}$	n	R^2
15	11.52	8.35	0.999	9.78	8.79	0.922	12.20	4.71	2.41	0.989
25	14.79	1.77	0.996	8.22	10.14	0.945	16.27	2.39	2.96	0.976
35	16.45	1.54	0.999	6.33	10.17	0.950	16.35	1.25	0.81	0.986

Table 2
Fitting parameters of Cr(VI) adsorption onto PANI/PA using pseudo-first order and pseudo-second order kinetic models at initial Cr(VI) concentration of 2.5, 5, 10, and 30 mg/L

		First order kinetic			Second order kinetic		
C_0 (mg/L)	q_{exp} (mg/g)	k_1 (1/min)	q_{cal} (mg/g)	R^2	k_2 (g/(mg min)	q_{cal} (mg/g)	R^2
2.5	4.94	4.95×10^{-2}	0.74	0.852	3.1×10^{-1}	4.94	0.999
5	9.76	8.29×10^{-3}	5.06	0.974	5.73×10^{-3}	9.83	0.999
10	12.34	5.53×10^{-3}	5.65	0.975	5.27×10^{-3}	12.61	0.998
30	14.37	7.14×10^{-3}	15.60	0.979	3.88×10^{-3}	14.62	0.998

constants (k_2) based on pseudo-second-order model with initial Cr(VI) concentrations of 2.5, 5, 10, and 30 mg/L are 3.1×10^{-1}, 5.73×10^{-3}, 5.27×10^{-3}, and 3.88×10^{-3} g/(mg min), respectively, indicating a rapid adsorption at low initial Cr(VI) concentration.

3.4. Influence of solution pH and ionic strength

Solution pH is one of the most important parameters during Cr(VI) adsorption. Adsorption amounts of Cr(VI) onto PANI/PA at various solution pH are shown in Fig. 7. As illustrated in Fig. 7, Cr(VI) adsorption amounts decrease monotonously with increasing solution pH, which may be attributed to the impaction of pH on the speciation of the chromium and the surface charge of the adsorbent. Cr(VI) exists in different ionic forms in aqueous solution depending on the solution pH. At low pH values, $HCrO_4^-$ is the predominant Cr(VI) species [32–34]. While the isoelectric point of PANI/PA is at pH 4.2 (in Fig. 8), and PANI/PA is positively charged at pH below 4.2 due to the protonation of amine and imine groups of PANI [27]. Hence, the strong electrostatic forces were awoken between the anions of Cr(VI) and deprotonated PANI/PA, which accounted for the enhanced Cr(VI) when the pH is lower than 4.2. In addition to adsorption under acidic condition, the reduction reactions also occurred, which was another reason for high Cr(VI) adsorption at low pH. At pH above 4.2, PANI/PA composite was charged negatively, which may weaken the electrostatic force of attraction between adsorbent and Cr(VI), leading to the decreased Cr(VI) adsorption. With increase in solution pH, the concentration of OH^- was increased, which would be competed with Cr(VI) or exchanged with Cr(VI) adsorbed on the surface of the adsorbent [22], leading to the suppressed Cr(VI) adsorption onto PANI/PA.

Ionic strength is also an important factor to influence the equilibrium adsorption capacity. The effect of anions (Cl^-, NO_3^-, and SO_4^{2-}) on Cr(VI) adsorption are illustrated in Fig. 9. From the results, Cr(VI) adsorption amount onto PANI/PA decreased with increasing concentrations of Cl^- and NO_3^- at ionic concentration of anions lower than 10 mmol/L, and no significant decrease was observed at ionic concentration higher than 10 mmol/L. For the effect of SO_4^{2-}, Cr(VI) adsorption decreased continuously with increasing concentration of SO_4^{2-}. Furthermore, the decrease in the presence of SO_4^{2-} is more significant than that of Cl^- and NO_3^-. This may be because that the electrostatic repulsion between Cr(VI) and added ions as well as with the active sites of the adsorbents may be enhanced, and resulted in decreased Cr(VI) adsorption. Another possible impact is that anions in solution will compete with Cr(VI) sorbed on the active sites of the adsorbent by anion-exchange process [22,35], which also lead to the suppressed Cr(VI) adsorption. Results indicate that electrostatic interaction and anion exchange may be the main mechanism for Cr(VI) adsorption onto PANI/PA.

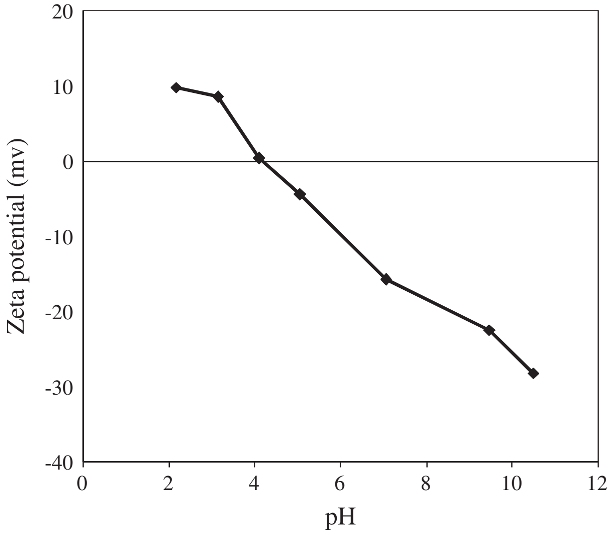

Fig. 7. Effect of solution pH on Cr(VI) adsorption onto PANI/PA.

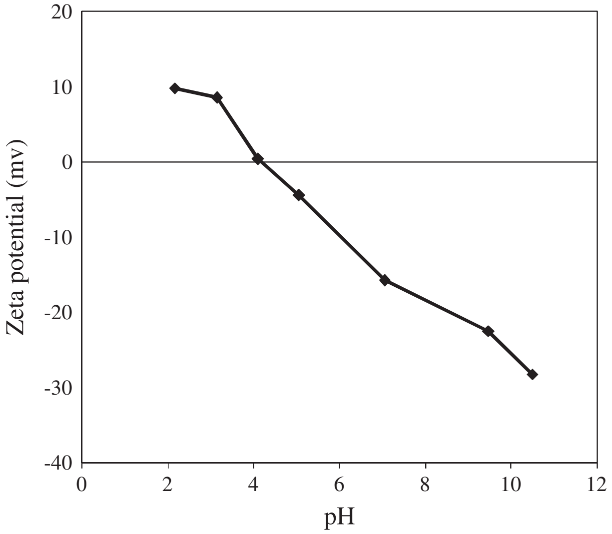

Fig. 8. Zeta potential of PANI/PA as a function of solution pH.

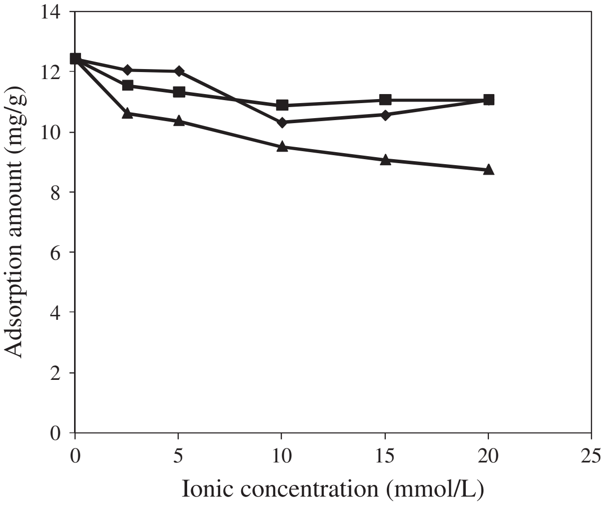

Fig. 9. Effect of ionic concentration in aqueous solution on Cr(VI) adsorption onto PANI/PA.

3.5. Desorption and regeneration of PANI/PA

Repeated availability is an important factor for an advanced adsorbent because it will reduce the overall cost of the applied adsorbent. The suppressed Cr(VI) adsorption onto PANI/PA at higher pH indicates that Cr(VI) saturated adsorbent can be desorbed in alkaline solution. In this study, NaOH was used as a desorbing agent. The adsorption capacities of Cr(VI) onto the adsorbent and regenerated adsorbent are shown in Fig. 10. It is clear that adsorption amount of Cr(VI) was decreased from 11.19 to 6.46 mg/g in first adsorption–regeneration cycle, and no significant reduction of Cr(VI) adsorption amount was observed in next three adsorption–regeneration cycles. Results show that PANI/PA is an available substitute for the removal and recovery of Cr(VI) from aqueous solution.

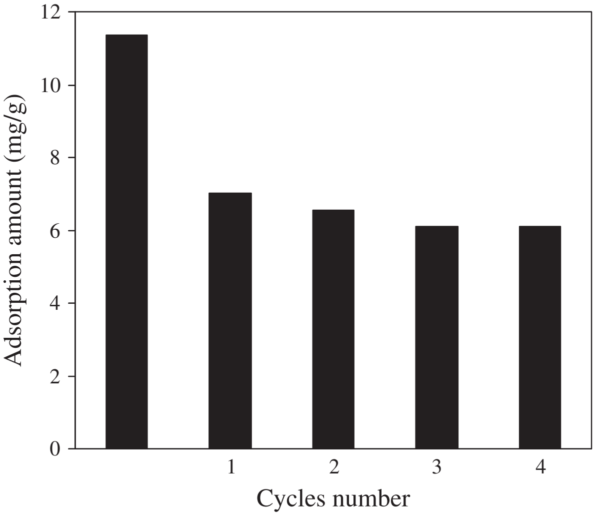

Fig. 10. Adsorption amount of Cr(VI) onto virgin PANI/PA and regenerated PANI/PA.

4. Conclusions

In this study, short-chain PANI/PA were synthesized and characterized by FTIR, XRD, TEM, SEM, and elemental analysis. As-synthesized adsorbent was used as a novel adsorbent for the removal of Cr(VI) from aqueous solution. PANI/PA exhibits high adsorption capacity for Cr(VI) in aqueous solution and adsorption amount increase with increasing temperature, indicating an endothermic process. Cr(VI) adsorption onto adsorbents can be well described by pseudo-second-order kinetic and adsorption rates decreased with increasing initial Cr(VI) adsorption. Moreover, the enhanced Cr(VI) adsorption at lower pH was observed and Cr(VI) adsorption amount decreased with increasing ionic strength in solution, which indicated that electrostatic forces and anion exchange may account for Cr(VI) adsorption onto PANI/PA.

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