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Removal of Chromium(VI) Ions from Aqueous Solutions with Protonated Crosslinked Chitosan

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ABSTRACT: This articles provided information on Cr(VI) adsorption onto protonated crosslinked chitosan particles (PCPs) as an adsorbent. Batch experiments were performed to investigate the effects of the adsorbent dosage, pH, contact time, initial Cr(VI) concentration, and coexisting ions on the adsorption capacity and the regeneration ability of the adsorbent. The equilibrium data fit well with the Freundlich and Redlich–Peterson isotherm models. The presence of other anions weakened Cr(VI) adsorption, especially high-valence anion such as sulfate. PCP could be regenerated well by a 0.1*N* sodium hydroxide solution. Electrostatic attraction was the main driving force for Cr(VI) adsorption. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

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INTRODUCTION

Cr(VI) ion is a kind of toxic inorganic pollutant that often exists in the effluents of the electroplating, tanning, mining, and fertilizer industries, and so on.[1] If the Cr effluents cannot be treated properly, they will pose a serious problem to ecosystems. China has fixed an enforceable maximum contamination level for Cr(VI) in drinking water of 0.05 mg/L for their public water system. The removal of Cr(VI) from these effluents is deemed necessary not only for the protection of aquatic environments but also for compliance with the stringent discharge limits.

Among the viable technologies that have been developed for the removal of Cr(VI) from industrial wastewater, conventionally, chemical reduction followed by precipitation is the most common method used for the compliance with regulation limits. However, this approach is not used broadly because of these drawbacks, which include the consumption of chemical agents and the generation of a large amount of sludge. Other methods, such as ion exchange, reverse osmosis, electrodialysis, and membrane separation, are not economically viable because of their high operational costs. Adsorption would be an alternative technology for the removal of heavy metals from wastewater.[2] With the selection of a proper adsorbent, the adsorption process could be a promising and effective technique for the removal of certain types of contaminants because of its advantages, which include a low cost and convenient operation. Activated carbon, as one of the most effective adsorbents, has broadly been applied for wastewater treatment to remove a variety of contaminants. However, activated carbon shows the following disadvantages: a high adsorbent cost, a loss of adsorption capacity after regeneration, and difficulty in its separation from the solution after adsorption. Thus, many researchers have focused on seeking low-cost adsorbents as alternatives to activated carbon.

Recently, great attention has been paid to natural biosorbents such as chitosan. Chitosan is a kind of biopolymer with a linear polysaccharide of β-1,4-*O*-glycosyl-linked glucosamine residue; it is derived from the deacetylation of chitin, which is a major component of crustacean shells and fungal biomass. Chitosan is well known as an excellent biosorbent for metal cation removal in near-neutral solutions because of the large number of NH_2 groups. Also, the protonation of amine groups leads to the adsorption of anions by ion exchange because of its cationic behavior in acidic media.[3–6] However, few reports have focused on the adsorption of metal anions such as Cr(VI).

Several methods have been used to modify natural chitosan either physically or chemically to improve its adsorption capacity. Chitosan naturally occurs in the form of flakes or powder; these forms have limited utility because of swelling, low mechanical strength, difficulty in its separation from solution after adsorption, and so on. At present, many researchers have paid much attention to the formation of chitosan beads to overcome these drawbacks.[7]

In this study, we attempted to develop protonated crosslinked chitosan particles (PCPs) that were stable and could be regenerated. The free —NH_2 groups in chitosan were protonated and became —NH_3^+ groups, which should have showed a greater tendency to adsorb Cr(VI) existing in the form of $Cr_2O_7^{2-}$ or $HCrO_4^-$ anions. Here, chitosan was molded into membranes, and the membranes were crosslinked and then protonated. The membranes were ground to obtain particles 200 mesh in size. The PCPs could remove Cr(VI) from aqueous solution because of their large specific surface area and many positive charges. Also, the PCPs had good subsidence and could be separated from solution rapidly after adsorption, so the PCPs were employed to remove Cr(VI) from aqueous solution in this work. The characteristics of the PCPs were also investigated. Batch experiments were conducted to evaluate their adsorption capacity and determine the regeneration feasibility of the adsorbent.

EXPERIMENTAL

Materials

Chitosan with a deacetylation degree of 90% was purchased from the Sinopharm Group Chemical Reagent Limited Co. (Shanghai, China). A stock solution of Cr(VI) (1000 mg/L) was prepared by the dissolution of an appropriate quantity of the analytical reagent $K_2Cr_2O_7$ in 1000 mL of deionized water. The stock solution was further diluted with deionized water to the desired concentrations. All of the adsorption experiments were carried out at room temperature (20 ± 1 °C). The initial pH was adjusted with 0.1*N* HCl or 0.1*N* NaOH. Sodium hydroxide, glacial acetic acid, glutaraldehyde, chlorhydric acid, and all of the other reagents were analytical grade.

Adsorbent Preparation

Preparation of the Crosslinked Chitosan Membrane. To prepare the chitosan membranes, 3.6 g of chitosan powder was dissolved in 120 mL of a 2 wt % acetic acid solution. The solution was dissolved completely and debubbled after a 1-h standing reaction. The homogeneous solution (10 mL) was coated in a Petri dish with a diameter of 35 cm and then dried at 60 °C. Subsequently, a 0.1*N* NaOH solution was poured onto the surface of the dry membranes, and thus, these membranes were separated from the Petri dish. The wet chitosan membranes were washed extensively with deionized water to remove any NaOH.

The membranes were crosslinked with 2.5 wt % glutaraldehyde solution, and the ratio of glutaraldehyde to chitosan membranes was approximately 25 mL/g of dry membranes. The crosslinking reaction occurred for 23 h at 60 °C, and then, the crosslinked membranes were washed with deionized water to remove residual glutaraldehyde and dried at 60 °C for 2 h.

Preparation of the PCPs. The PCPs were prepared to effectively use the amino groups of the crosslinked chitosan membranes for Cr(VI) adsorption. After the crosslinked chitosan membranes were treated with concentrated HCl for 90 min at room temperature to protonate the membranes, they were washed with deionized water to neutral pH, dried at 60 °C, and ground to obtain particles 200 mesh in size; these particles were used for the adsorption studies. These particles were referred to as PCPs.

Adsorbent Characterization

The surface morphology of the absorbent was visualized with a scanning electronic microscope (JEOL-2100 F, Japan). The scanning electron microscopy (SEM) enabled us to directly observation of the changes in the surface microstructures of the absorbent. A Fourier transform infrared (FTIR) spectrometer (Avatar-360, Nicolet) was used to investigate the changes in the functional groups present in chitosan during the modification process and after Cr(VI) adsorption.

Adsorption Experiments

The adsorptions were carried out by batch experiments. A specific amount of PCPs (the adsorbent) was added to 50 mL of Cr(VI) solution, and the mixture was shaken in a shaker at a speed of 200 rpm and at room temperature. Afterward, the resulting solution was filtered with filter paper. The Cr(VI) concentration was measured with an ultraviolet–visible spectrophotometer. We investigated the removal of Cr(VI) toward Cr(VI) under various conditions, including different adsorbent dosages, pHs of the medium, and initial Cr(VI) concentrations, and the effect of coexisting ions on Cr(VI) removal. Additionally, the experiments were conducted at various concentrations (between 58 and 174 mg/L), different contact times (from 0 to 100 min), a constant adsorbent amount (0.1 g), and optimized pH. Samples were taken at predetermined time intervals for the analysis of the Cr(VI) concentration in solution until the adsorption equilibrium was reached. Subsequently, we determined the equilibrium isotherm by keeping the adsorbent amount and optimized pH constant and varying the Cr(VI) concentrations.

Desorption Study

Desorption was conducted to investigate the regeneration and reusability of PCP. After 10 g of saturated PCPs with Cr(VI) were treated with 100 mL of a 0.1 *N* NaOH solution for 3 h, the PCPs were separated from the solution, washed with deionized to neutral pH, and dried at 60 °C for 2 h. Desorption experiments were performed with different initial concentrations of Cr(VI) from 67 to 670 mg/L by maintenance of the adsorbent amount at 0.1 g and with an initial pH value of 5 at room temperature.

RESULTS AND DISCUSSION

Characterization of the Adsorbents

SEM Analysis. Figure 1 shows the SEM micrographs of the chitosan and PCPs. It can be seen from Figure 1(a) that the raw chitosan particles were mostly irregular in shape and had loose surfaces. After they were crosslinked and protonated, the PCPs [Figure 1(b)] become regular in shape and had dense surfaces. Also, the PCPs became rigid relative to raw chitosan. The rigidness endowed the PCPs with good settling ability, which made the PCPs prone to being separated from the solution. During the adsorption experiments, we truly observed that the PCPs could subside rapidly.

FTIR Analysis. The specific surface area of PCP was found to be 4.37 m^2/g. The FTIR spectra in Figure 2 were obtained to

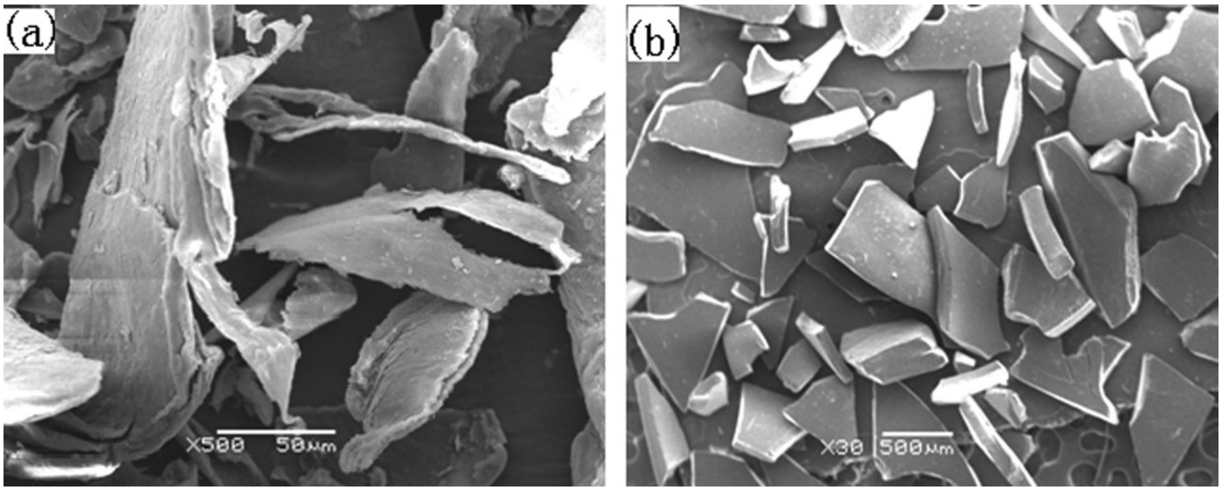

Figure 1. SEM micrographs of the (a) raw chitosan and (b) PCPs.

observe in detail the transmutation of the functional groups in the chitosan molecules during the modification and adsorption process. The FTIR spectrum of chitosan particles is shown in Figure 2(a). A broad peak appeared in the range 3500–3200 cm^{-1} and was attributed to O—H and N—H stretching vibrations, whereas the other major bands for chitosan were assigned as follows: 3442 cm^{-1} (—OH and $—NH_2$ stretching vibrations), 2920 cm^{-1} (—CH stretching vibrations in —CH and $—CH_2$), 1599 cm^{-1} (the $—NH_2$ of glucosamine residues), 1376 cm^{-1} (—CH symmetric bending vibrations in —CHOH—), and 1067 cm^{-1}.[8–10] The FTIR spectrum of the crosslinked chitosan is presented in Figure 2(b). After chitosan was crosslinked, an important peak in this region appeared near 1663 cm^{-1}; it was attributed to the —CN— (Schiff alkali) band. Meanwhile, the band of free amine functions at 1599 cm^{-1} almost disappeared because of a high level of consumption during the crosslinking reaction. Also, an important band of $—NH_3^+$ appeared at 1516 cm^{-1}. The transformation of the functional groups indicated that the $—NH_2$ group in chitosan was protonated and became $—NH_3^+$ in the acidic medium, which was favorable for anion adsorption. Figure 2(c) illustrates the profile of the PCPs loaded with Cr(VI). Compared with that in Figure 2(b), the band of $—NH_3^+$ at 1516 cm^{-1} almost disappeared; this resulted from a strong electrostatic attraction between the positively charged chitosan surfaces and negatively charged Cr(VI) ions. Therefore, the previous observations show that the adsorption process of Cr(VI) onto PCP was achieved through electrostatic attraction, which was attributed to physical adsorption.

Optimization of the Adsorbent Dosage.. To obtain the optimal adsorbent dosage, Cr(VI) removals with different adsorbent dosages ranging from 1.5 to 8.5 g/L were investigated. The results [Figure 3(a)] show that the removal of Cr(VI) significantly increased with increasing adsorbent dosage; this was obviously due to the increases in the surface area and available adsorption sites.[11] The removal gradually reached a maximum and remained almost constant with further increases in adsorbent dosage when the dosage was more than 0.1 g. However, the drop in the adsorption capacity was basically due to the sites remaining unsaturated during the adsorption process. For the adsorbent amount of 5 g/L, the optimum values of Cr(VI) removal and the adsorption capacity were found to be 99.2% and 28.7 mg/g, respectively. Therefore, the 5 g/L adsorbent dosage was fixed as the optimum dosage for all of the subsequent experiments.

Influence of pH

The pH is one of the most important parameters for the adsorption process as it controls the adsorption capacity because of its influence on the adsorbent surface properties and ionic forms of metal ions in the solution. In acid media, when the pH ranges from 2 to 6, $HCrO_4^-$ and $Cr_2O_7^{2-}$ are predominantly in equilibrium; in basic solutions, chromium exists in the form of CrO_4^{2-}.[12] The effect of pH on the adsorption was studied at six different initial pH levels, 2, 3, 5, 7, 9, and 11, with all of the other parameters kept constant, as shown in Figure 3(b). The PCPs had a relatively high removal toward Cr(VI) when the pH was less than 7. The results suggest that the electrostatic interactions between the negatively charged Cr(VI) and positively charged amine groups of chitosan played

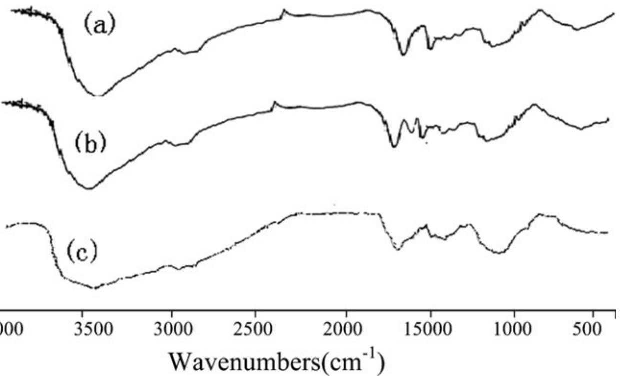

Figure 2. FTIR spectra of the (a) raw chitosan particles, (b) crosslinked chitosan particles, and (c) PCP loaded with Cr(VI).

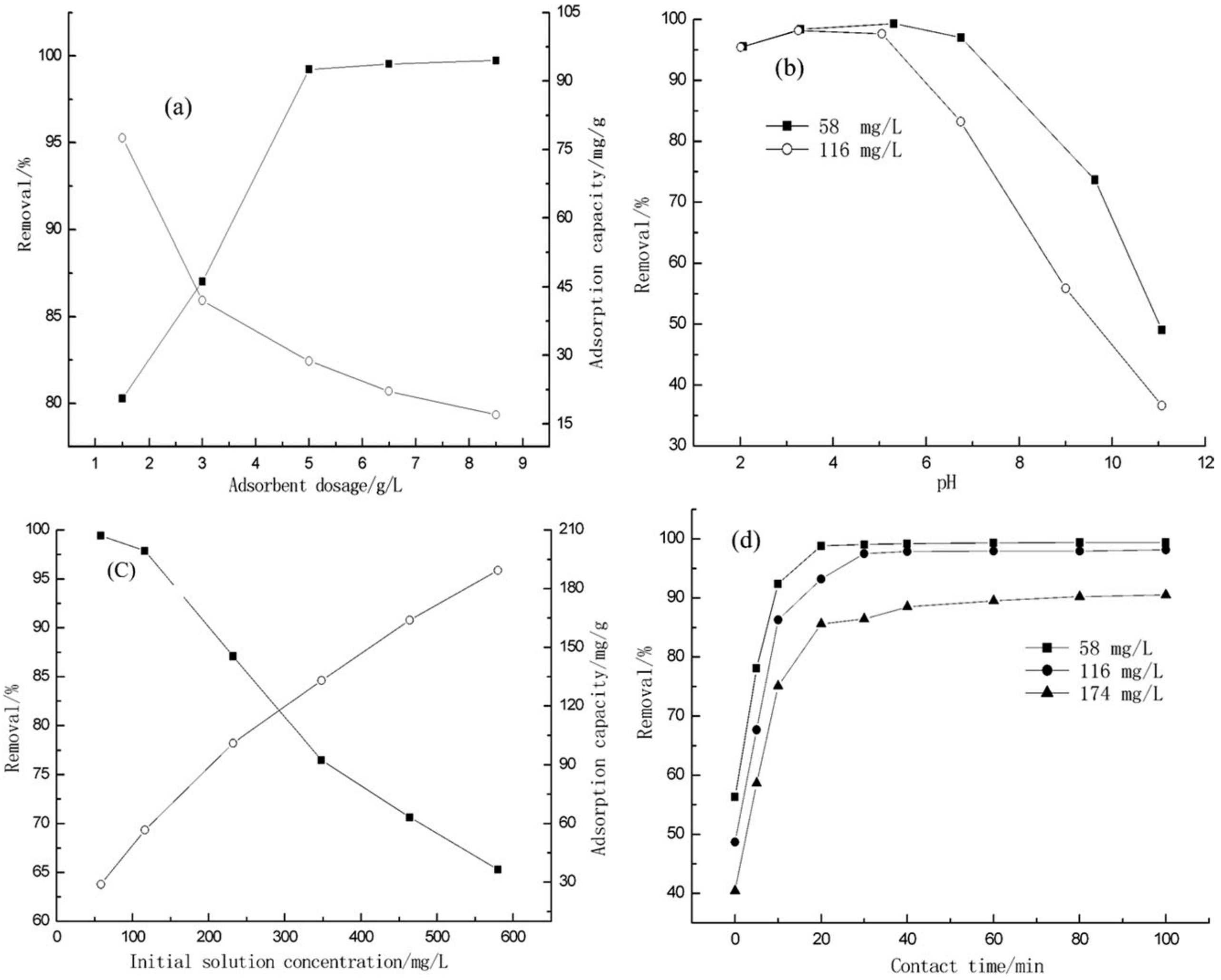

Figure 3. Results of Cr(VI) removal with different (a) adsorbent dosages ranging from 1.5 to 8.5 g/L, (b) pHs, (c) initial solution concentrations, and (d) contact times.

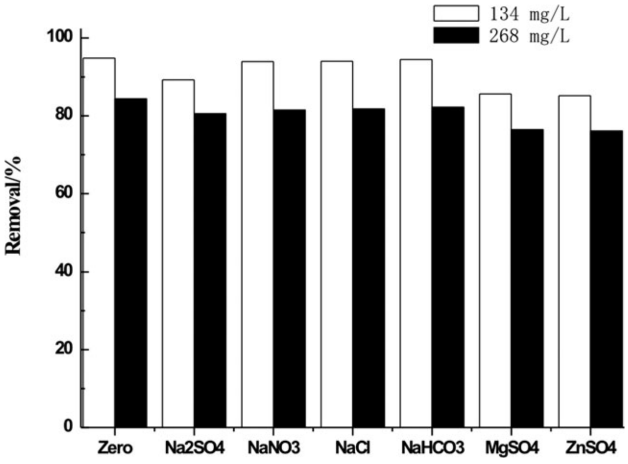

Figure 4. Adsorption of Cr(VI) on PCP in the presence of co-anions with a concentration of 1000 mg/L and initial Cr(VI) concentrations of 134 and 268 mg/L.

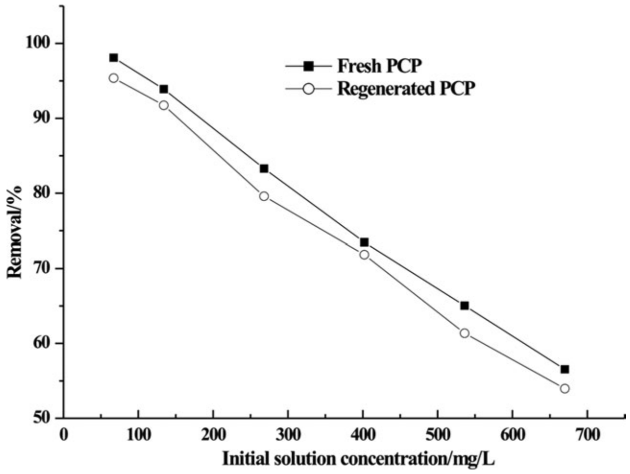

Figure 5. Cr(VI) removal with fresh and regenerated PCP at different initial solution concentrations.

Table I. Nonlinear and Linear Isotherm Equations

Isotherm	Nonlinear equation	Linear equation
Langmuir I		$\frac{c_e}{q_e}=\frac{c_e}{q_m}+\frac{1}{bq_m}$
Langmuir II	$q_e=\frac{q_m bc_e}{1+bc_e}$	$\frac{1}{q_e}=\frac{1}{q_m}+(\frac{1}{bq_m})\frac{1}{c_e}$
Langmuir III		$q_e=q_m-(\frac{1}{b})\frac{q_e}{c_e}$
Langmuir IV		$\frac{q_e}{c_e}=bq_m-bq_e$
Freundlich	$q_e=K_F c_e^{1/n_F}$	$\log(q_e)=\log(K_F)+\frac{1}{n_F}\log \mathrm{c_e}$
Redlish-Peterson	$q_e=\frac{K_{RP}c_e}{1+a_{RP}c_e^{\beta}}$	$\ln(K_{RP}\frac{c_e}{q_e}-1)=\beta\ln(c_e)+\ln(a_{RP})$

C_e is the concentration of Cr(VI) (mg/L) at equilibrium.

an important role in the adsorption of Cr(VI) onto the PCPs. With a further increase in pH, a reduction in removal occurred. As mentioned previously, chromium exists in the form $CrO_4{}^{2-}$ in basic solutions. Therefore, there may have been competition between OH^- and chromate ions ($CrO_4{}^{2-}$), with the former being the dominant species at higher pH values. The net positive surface potential of PCP decreased; this resulted in weakening in electrostatic attractions between the Cr(VI) ions and PCP, which ultimately led to the decrease in the adsorption capacity. Similar results were also observed with Turkish montmorillonite clay used for Cr(VI) removal.[13] When the pH increased up to 11.1, the adsorption amount was very weak, so it greatly facilitated the regeneration of the PCPs. Therefore, pH 5 was recognized as the optimal value, and the pH of solution was controlled at 5 for later experiments.

Influence of the Initial Cr(VI) Concentration

The adsorption experiments were performed to study the influence of the initial Cr(VI) concentration, which ranged from 58 to 580 mg/L, at an initial pH value of 5; a PCP amount of 0.1 g was maintained, and the obtained results are presented in Figure 3(c). The results show that Cr(VI) adsorption was significantly influenced by the initial Cr(VI) concentration in the solutions. With increasing Cr(VI) concentration from 58 to 580 mg/L, the removal decreased from 99.4 to 65.3%, and the adsorption capacity increased from 28.83 to 189.33 mg/g. The decrease in Cr(VI) removal could be explained by the fact that all of the adsorbents had a limited number of active sites, which became saturated above a certain concentration. The increase in the adsorption capacity with increasing Cr(VI) concentration may have been due to the higher adsorption rate and the utilization of all of the active sites available for adsorption at higher concentrations. For an initial Cr(VI) concentration of 116 mg/L, the values of Cr(VI) removal and adsorption capacity were found to be 97.8% and 56.76 mg/g, respectively.

Influence of the Contact Time

The influence of the contact time on the Cr(VI) adsorption was investigated to study the rate of Cr(VI) removal. Figure 3(d) shows the removal variation of Cr(VI) with the contact time for different initial Cr(VI) concentrations ranging from 58 to 174 mg/L at pH 5. The rate of Cr(VI) removal increased rapidly with increasing contact times of 30, 40, and 60 min for 58, 116, and 174 mg/L initial Cr(VI) concentrations, respectively. A further increase in the contact time had a negligible effect on the rate of Cr(VI) adsorption. The nature of the adsorbent and the available adsorption sites affected the rate of Cr(VI) adsorption. The mechanism of solute transfer to the solid included diffusion through the fluid film around the adsorbent particles and diffusion through the pores to the internal adsorption sites. In the initial stages of Cr(VI) adsorption, the concentration gradient between the film and the available pore sites was large, and hence, the rate of Cr(VI) adsorption was faster. The decrease in the rate of adsorption in the later stages of Cr(VI) adsorption was probably due to the slow pore diffusion of the solute ions into the bulk of the adsorbent. Hence, 60 min was adopted as the equilibrium time for Cr(VI) adsorption onto the PCPs to ensure equilibrium. This short equilibrium time suggested an excellent affinity of Cr(VI) ions for the PCPs.

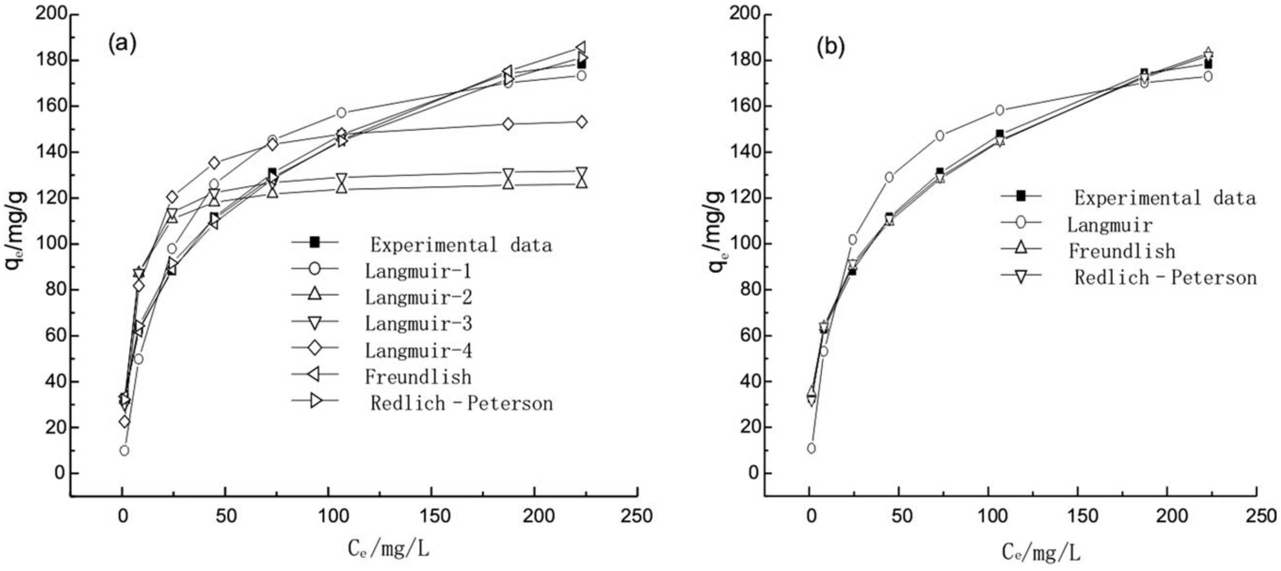

Figure 6. Experimental data fitted to the Langmuir, Freundlich, and Redlich–Peterson isotherm equations.

Influence of the Coexisting Ions

In many cases, various kinds of ions, including chloride, sulfate, bicarbonate, magnesium, and zinc ions, exist in industrial wastewater, surface water, and underground water. The adsorption of Cr(VI) onto the PCPs was investigated in the presence of co-anions with a concentration of 1000 mg/L with 134 and 268 mg/L as the initial Cr(VI) concentrations. The results are given in Figure 4. There was a slightly decrease in Cr(VI) removal in the presence of other anions, such as chloride, nitrate, and bicarbonate anions, compared with that in the absence of coexisting ions. However, the presence of high valence anions such as sulfate reduced Cr(VI) removal onto the PCPs considerably. These results show that there was competition among the ions for the adsorption sites on the adsorbent surface, and this resulted in less Cr(VI) adsorption.

Regeneration Studies

The saturated adsorbent, which contains Cr(VI), is not safe for disposal because of stringent environmental constraints. It is important and appropriate to propose a method for the regeneration and reuse of the adsorbent to reduce the load on the environment in terms of the disposal of polluted adsorbents. In this study, after the PCPs were regenerated with a 0.1 *N* NaOH solution, it was used for Cr(VI) removal at different initial Cr(VI) concentrations ranging from 67 to 670 mg/L. Figure 5 shows that the removal of Cr(VI) obtained was found to decrease from 98.1 to 56.5% as compared to the corresponding values for fresh PCP, which ranged from 95.4 to 54.0%. These results with the regenerated PCPs exhibited a higher desorption efficiency by more than 95% of that of fresh PCPs for Cr(VI) removal. Hence, Cr(VI) desorption was accomplished by an increase in the solution pH, as indicated by the results obtained in this study. Therefore, the regenerated PCPs were considered reusable.

Adsorption Equilibrium Isotherms

Adsorption isotherms are helpful for understanding how adsorbates interact with adsorbents. The Langmuir and Freundlich isotherm models were applied for Cr(VI) adsorption on the PCPs at 20 °C. The Langmuir isotherm is described as a homogeneous one with the assumption that all of the adsorption sites have equal adsorbate affinities and that the adsorption at one site does not affect the adsorption at an adjacent site. The Freundlich isotherm is an empirical equation used to describe heterogeneous systems. The Redlich–Peterson isotherm model combines elements from both the Langmuir and Freundlich equations, where the mechanism of adsorption is a hybrid one and does not follow ideal monolayer adsorption.[14] The Redlich–Peterson equation is widely used as a compromise between the Langmuir and Freundlich systems. The Redlich–Peterson isotherm incorporates three parameters and can be applied either in homogeneous or heterogeneous systems. The Freundlich, Langmuir, and Redlich–Peterson isotherms, and their linearized forms are given in Table I. The correlation coefficient (r^2) values were used to predict the best fit linear equation. However, it did not describe the equilibrium data adequately on the basis of the r^2 values. χ^2 (Chi-Square) and average percentage errors (APEs) are often adopted to further determine the proper isotherm model. χ^2 and APEs were calculated with eqs. (1) and (2), respectively, and this indicated the fit between the experimental and calculated values of adsorption capacity:

$$\chi^2 = \sum \frac{\left(q_{e,\mathrm{exp}} - q_{e,\mathrm{cal}}\right)^2}{q_{e,\mathrm{exp}}} \tag{1}$$

$$APE = \frac{\sum_{1}^{N} \left| q_{e,\,\mathrm{exp}} - q_{e,cal} \right| \Big/ q_{e,exp}}{N} \tag{2}$$

where $q_{e,m}$ is equilibrium capacity obtained by calculating from the model (*mg/g*) and q_e is experimental data on the equilibrium capacity (*mg/g*). *N* is the group number of experiments.

The experimental data fitted to the Langmuir, Freundlich, and Redlich–Peterson isotherm equation are shown in Figure 6. These parameters (q_m, b, K_F, $1/n$, k_{RP}, a_{RP}, and β), obtained from nonlinear and linear isotherms together q_m is the maximum adsorption capacity (*mg/g*) and b is the constant related to the free energy of adsorption (*L/mg*). K_F is a constant, it indicates the relative adsorption capacity of the adsorbent ($(mg^{1-(1/n)}\ L^{1/n})/g)$) and ($1/n$) is a constant, heterogeneity factor ($1/n$). K_{RP} (L/g) and α_{RP} $(L/mg)\beta$ are Redlich-Peterson isotherm constants and β is the exponent which lies between 1 and 0, with r^2, χ^2, and APE, are listed in Tables II. From Table II, it can be inferred that the Langmuir I equation showed a higher correlation coefficient ($r^2 = 0.9929$) than the other three linearized equations (Langmuir II–IV), as shown in Table II. However, their APE values (including Langmuir I) were more than 15%, and the χ^2 values were also high (this indicated that the difference between the experimental values and calculated values was very high), which indicated that the models were not able to describe the equilibrium data. For the Freundlich models, the values of K_F and $1/n$ obtained from both the linearized and nonlinearized isotherms were found to be close to each other (shown in Tables II); this was unlike the variation in the Langmuir linearized and nonlinearized models. Also the correlation coefficients for both the linearized and nonlinearized isotherms were found to be high, as shown in Tables II. Also, for the Redlich–Peterson isotherms, we observed, as shown in Tables II, that the correlation coefficient values were high and the APE and χ^2 values were very low for the nonlinear and linear equations. Thus, this indicated that the Redlich–Peterson model was able to describe equilibrium data perfectly. Therefore, we concluded that the adsorption of Cr(VI) followed the Freundlich and Redlich–Peterson models and was attributed to a heterogeneous system.

A wide range of adsorption capacities for Cr(VI) ions by different adsorbents based on chitosan have been reported (Table III). In our study, the adsorption capacity of modified chitosan was moderate.

Kinetics of Adsorption

The kinetics of adsorption were evaluated to determine the mechanism of adsorption with pseudo-second-order kinetics. The equation for the pseudo-second-order kinetic model can be written as follows:[22]

Table II. Nonlinear and Linear Isotherm Parameters for Cr(VI) Adsorption onto the PCPs

Isotherm model	Value
Linear isotherm	
Langmuir I	
q_m	191.4
b	0.04309
r^2	0.9929
χ^2	24.03
APE	17.11
Langmuir II	
q_m	128.2
b	0.2622
r^2	0.9601
χ^2	49.16
APE	19.14
Langmuir III	
q_m	143.4
b	0.2278
r^2	0.8028
χ^2	45.85
APE	19.45
Langmuir IV	
q_m	158.5
b	0.1307
r^2	0.8028
χ^2	33.25
APE	19.44
Freundlich	
K_F	30.92
$1/n$	0.3316
r^2	0.9993
χ^2	0.4826
APE	1.836
Redlish-Peterson	
K_{RP}	144.76
a_{RP}	3.9785
β	0.702
r^2	0.9987
χ^2	0.3330
APE	1.847
Nonlinear isotherm	
Langmuir	
q_m	189.3
b	0.0478
r^2	0.9960
χ^2	24.03
APE	17.27
Freundlich	
K_F	32.72
$1/n_F$	0.3185
r^2	0.9994
χ^2	0.5175
APE	2.527
Redlish-Peterson	
K_{RP}	145.56
a_{RP}	4.055
β	0.6987
r^2	0.9997
χ^2	0.3148
APE	1.835

$$\frac{t}{qt} = \frac{1}{k_2 q_{2e}^2} + \frac{1}{q_{2e}} t \qquad (3)$$

where q_{2e} and q_t are the amounts of the dye adsorbed at equilibrium and at time t (mg/g), respectively, and k_2 is the equilibrium rate constant of the pseudo-second-order model for the adsorption process (g mg^{-1} min^{-1}). The straight-line plots of t/q_t versus t for the pseudo-second-order (Figure 7) process of the adsorption of Cr(VI) onto the PCPs were examined to obtain these parameters. The kinetic data of phenol at different concentrations were calculated from these plots and are listed in Table IV. The adsorption of phenol conformed to pseudo-second-order kinetics, with a high correlation coefficient (>0.999). However, this adsorption process disagreed with both the pseudo-first-order and intraparticle diffusion models; accordingly, these are not mentioned in detail. In addition, the

Table III. Comparisons of Adsorbents Based on Chitosan

Adsorbent	Adsorption capacity	Reference
Chitosan-coated fly ash composite	33.27 mg/g	15
Improved synthesized crosslinked chitosan resin	84.19 mg/g	16
Alkyl-substituted polyaniline/chitosan composites	88.25 mg/g	17
Fe-crosslinked chitosan complex	295 mg/g	18
Silicate-chitosan-silicate-chitosan-silicate	0.89 mmol/g	19
Chitosan derivative	935 mg/g	20
Protonated crosslinked chitosan beads	250 mg/g	21
Protonated crosslinked chitosan	189.3 mg/g	This study

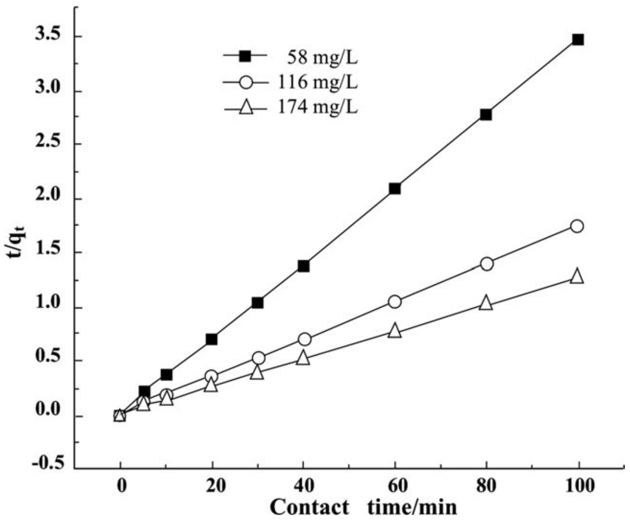

Figure 7. Straight-line plots of t/q_t versus t for the pseudo-second-order process of the adsorption of Cr(VI) onto PCP.

k_2 value decreased from 0.0631 to 0.0076 g mg^{-1} min^{-1} with an increase in the initial Cr(VI) concentration. The equilibrium adsorption capacity was found to be close to the value of the experimental adsorption capacity.

CONCLUSIONS

The PCPs were an effective adsorbent for Cr(VI) removal from aqueous solution. SEM analysis showed that the PCPs allowed good settlement. The FTIR results showed that protonated amino groups were favorable for Cr(VI) adsorption. Batch experiments were conducted to investigate the adsorption capacity and the regeneration feasibility of the adsorbent. The equilibrium data fit well with Langmuir and Freundlich isotherm models, and the maximum monolayer adsorption capacity was 198.0 mg/g. PCP was prone to be regenerated with a 0.1 *N* sodium hydroxide solution. Electrostatic attraction was the main driving force for Cr(VI) adsorption. The results indicate that the bioadsorbent of protonated and crosslinked chitosan has potential for Cr(VI) removal from contaminated water.

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Table IV. Pseudo-Second-Order Kinetic Parameters for Cr(VI) Adsorption onto the PCPs

C_0 (mg/L)	q_{2e} (mg/g) from the fitted data	q_{2e} (mg/g) from the experimental data	R^2	g mg^{-1} min^{-1}
58	29.0	28.7	0.9999	0.0631
116	57.7	57.0	0.9998	0.0159
174	80.0	78.9	0.9998	0.0076

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