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Evaluation of a novel chitosan polymer-based adsorbent for the removal of chromium (III) in aqueous solutions

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ABSTRACT

Novel poly(vinyl alcohol)/citric acid/chitosan (PVA/CA/CHT, PCC) beads were prepared as an adsorbent for the removal of trivalent chromium (Cr^{3+}) in aqueous solutions. PCC beads with different mass ratios (I, II, III, IV, V, ad VI) between PVA/CA/CHT were evaluated for the removal of Cr^{3+} ions to find an optimal stoichiometry of PCC beads, which indicated that the PCC bead (II) with the PVA/CA/CHT mass ratio of 1/5/1 showed the highest adsorption for Cr^{3+} ions. The surface characteristics of PCC beads (II) were determined by scanning electron microscopy using a field emission scanning electron microscope (FESEM) and Fourier transform infrared spectroscopy (FTIR). The results obtained in this study implied that PCC bead (II) had an obviously rough and folded structure, and its spectrum manifested significant changes compared to those of PVA, CA and CHT. The sorption experiments were conducted to evaluate the performance of PCC beads (II) to adsorb Cr^{3+} ions in aqueous solutions. Results indicated that the Cr^{3+} ion sorption onto PCC beads (II) was highly pH-dependent with the maximum uptake at pH 6.0. The sorption kinetics data were well fitted by the pseudo-second-order equation with high regression coefficients. Sorption isotherm of PCC beads (II) was well described by Langmuir equation, with a maximum sorption at 41.5 mg Cr/g PCC beads (II). Desorption studies were also carried out by the repeated sorption/desorption experiments. The high efficiency and reusability of PCC beads (II) make them an attractive sorbent for the removal of Cr^{3+} and possibly other metals in aqueous solutions.

1. Introduction

Heavy metals such as copper (Cu), chromium (Cr) and cadmium (Cd) are not degradable and therefore persist in the environment. Environmental exposure to heavy metals is of concern as they are toxic, but their toxicity varies between the chemical forms in which they exist. For example, Cr^{3+} and Cr^{6+} are the two stable oxidation states of Cr, but Cr^{6+} is more toxic than Cr^{3+}. However, Cr^{3+} could be oxidized to Cr^{6+} in the presence of strong oxidants such as MnO_2 (Tadesse, Isoaho, Green, & Puhakka, 2006). In view of this chemical conversion of Cr^{3+} to Cr^{6+} under favorable environmental conditions, Cr^{3+} ions are considered to be potentially hazardous to aquatic environmental systems. The main sources of Cr^{3+} include mining, cement ceramics, electroplating, tanneries and dyeing plants (Gupta, Agarwal, & Saleh, 2011).

Adsorption is one of the commonly used treatment methods for the removal of heavy metals in the contaminated water bodies. A number of natural and synthetic adsorbents have been used for the removal of Cr, for example, feldspar (Singh, Rupainwar, & Prasad, 1992), black locust leaves (Aoyama et al., 2000), pyrophyllite and pyrophyllite-Al (Talidi et al., 2005), sawdust (Vinodhini & Das, 2010), carbon nanotube (Gupta et al., 2011), and cobalt-coated bamboo charcoal (Wang et al., 2012). However, most of these adsorbents are not effective in sequestering Cr from contaminated waters due to low adsorption capacity, slow kinetics and/or high cost. Thus, there is a strong need to develop low cost, easily available, efficient and reusable adsorbents for the control of heavy metal pollution in various aquatic environments.

Poly(vinyl alcohol) (PVA) is a water-soluble material with a large number of hydroxyl groups in it. Recently, increasing attention has been paid to PVA, due to its various practical advantages such as low cost, easy preparation, high durability and chemical stability (Kao, Wu, Chang, & Chang, 2009). On the other hand, chitosan (CHT) comprises a large number of amino and hydroxyl functional groups which could potentially be blended with hydroxyl groups in PVA by the formation of hydrogen bonds (Chen, Wang, Mao, & Yang, 2007). Some new adsorbents prepared by blending PVA with CHT have been used for the removal of heavy metal ions from aqueous samples (Fajardo, Lopes, Rubira, & Muniz, 2011; Li, Li, & Ye, 2011). Although these adsorbents were effective for the removal of heavy metals, the adsorption kinetics i.e. the rate of removal of metals by adsorbents was rather slow. It is therefore important to select and

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maintain optimum operational conditions for efficient heavy metal removal processes in industry (Kurniawan et al., 2011).

In this study, citric acid (CA) was blended with PVA and CHT to prepare a new adsorbent (PCC–PVA–CA–CHT) to overcome the limitations of the PVA–CHT adsorbent. CA was selected for preparing this adsorbent as it contains carboxyl functional groups. After the cross-linking with PVA and CHT, the redundant carboxyl groups in CA could potentially improve the uptake of heavy metals and thus improve the rate of removal of metals and also the adsorption capacity. The influence of pH on adsorption kinetics was studied. The surface characteristics of the new adsorbent were examined by both the field emission scanning electron microscopy (FESEM) and Fourier transform infrared spectroscopy (FTIR).

2. Materials and methods

2.1. Reagents

The main chemicals were purchased from Sigma–Aldrich Company (Singapore), including poly(vinyl alcohol) (87–90% hydrolyzed, average molecular weight 30,000-70,000), sodium hypophosphite (SHP) ($NaPH_2O_2$, molecular weight 87.98), citric acid (purity 99%) and chitosan (75% deacetylation). All other chemicals used were in high purity. The deionized (DI) water was used to prepare all the aqueous solutions. The stock solution of Cr^{3+} was prepared from chromium nitrate nonahydrate ($Cr(NO_3)_3{\cdot}9H_2O$, 99%).

2.2. Preparation of PCC bead adsorbents

CA (5 g) and SHP (1 g) were dissolved in 50 mL DI water in a 150 mL breaker, and then a known quantity of PVA was added into the above mixture. The resultant solution was placed in a hotplate to dehydrate at 90 °C for 1 h with magnetic stirring for the formation of alkyd resin. Subsequently, a known quantity of CHT was added into the solution and heated at 90 °C for 2 h with magnetic stirring. The solution was then kept at room temperature for 2 days to ensure the completion of the chemical reaction among PVA, CA and CHT. Then, the solution was slowly added to sodium hydroxide solution with a concentration of 3 M to form small PCC beads. The PCC beads were then washed using DI water to remove residual reagents. Finally, these beads were kept at room temperature to dry for 4 days. The mass ratios among PVA, CA and CHT were 0/5/1, 1/5/1, 3/10/2, 5/5/1, 2/10/3 and 1/5/0 and these beads were designated as adsorbent I, II, III, IV, V, and VI in this study, respectively. The esterification of PVA with CA can be found in S1 with a sequence of reactions. A schematic of the cross linking of alkyd resin with CHT is shown in S2.

2.3. Metal sorption experiments

Batch sorption experiments were conducted as a function of pH, sorbent dosage and contact time using 250 mL Erlenmeyer flasks as reaction vessels. A known quantity of PCC beads was added into 50 mL metal solutions consisting of 10 mg/L Cr^{3+} ions. The pH of metal solutions was adjusted to desired values at the range of 1-8 using 0.1 M HCl and 0.1 M NaOH. The reaction vessels were placed on a rotary shaker at 200 rpm. All experiments were conducted at 25 °C. The aqueous samples were taken at different time intervals. After completion, the reaction mixture was filtered through a 0.45 μm PTFE membrane filter. Inductively coupled plasma - optical emission spectrometer (ICP-OES) (Perkin-Elmer Optima, 2000, USA) was used to determinate the total concentration of chromium (the sum of the concentration of Cr^{6+} and Cr^{3+}) in solutions, due to the possible transformation of Cr^{3+} into Cr^{6+} during the course of the experiments. The concentration of Cr^{6+} was then determined, according to the Standard Methods (SM) 3500B for Cr (American Public Health Association, 1998). Finally, the Cr^{3+} concentration was determined from the difference between total chromium and Cr^{6+} concentrations.

The amount of metals adsorbed by a sorbent was calculated using the following equation:

$$Q = \frac{V(C_0 - C_f)}{M} \quad (1)$$

where Q is the metal uptake (mg/g); C_0 and C_f are the initial and equilibrium metal concentrations in the solution (mg/L), respectively; V is the solution volume (L); M is the mass of sorbent (g). All experiments were done in triplicate, and then the mean values of three replicate experiments were calculated and used for data interpretation.

2.4. Desorption experiments

The sorption/desorption experiments were repeatedly carried out for the investigation of the reusability of the adsorbent. 0.5 mol/L H_2SO_4 was used as an elution reagent. PCC (1 g) was contacted with 200 mL Cr^{3+} solution (0.2 mmol/L) at pH 7.0 for 24 h. The chromium loaded PCC beads were then filtered, washed by DI water, and finally kept at room temperature to dry for 4 days. Subsequently, the dried PCC beads were immersed into 0.5 mol/L H_2SO_4 (100 mL) at a 250 mL Erlenmeyer flasks with magnetic stirring at 200 rpm for 2 days. Cr^{3+} ions could be potentially replaced by the hydrogen ions during the process of desorption. 0.1 mol/L NaOH was used for the regeneration of PCC beads. The regenerated PCC beads were repeatedly used, based on the above mentioned experiments. Moreover, the weight loss of PCC beads in each sorption/desorption cycle was measured.

2.5. PCC beads surface morphology observation

The surface morphologies of PCC beads before and after the Cr^{3+} ion uptake were characterized by FESEM (JEOL JSM-6700F). The PCC beads were dried in a dryer until constant weight. The dried PCC beads were incorporated into a JEOL JFC-1300 Auto Fine Coater fitted with Pt target before the observation.

2.6. FTIR

The initial PVA, CA, CHT, and PCC beads were analyzed with a Nicolet 5700 FTIR spectrophotometer to examine the characteristics of the sorbents before and after the adsorption experiments. Before the FTIR analysis, the samples were air-dried. Each dried sample was first mixed with KBr at an approximate ratio of 1/100 (sorbent/KBr), and then placed on an agate mortar. The resulting mixture was pressed at 10 tons for 5 min to form the pellet. Finally, the pellets were analyzed using the reflection mode in the wave number range of 400-4000 cm^{-1}. The background signal obtained from the scan of pure KBr was automatically subtracted from the signal of samples in the same wave number range. All the spectra were recorded and plotted on the same scale for comparison of their absorbance.

3. Results and discussion

3.1. The optimal ratio among the used chemical reagents

In this study, six beads comprising CA, PVA and CHT in different proportions (mass ratios) were prepared and used to adsorb Cr^{3+} under the same experimental conditions, in order to evaluate their relative performance and select the best PCC bead. Fig. 1 shows the removal of Cr^{3+} by different PCC beads.

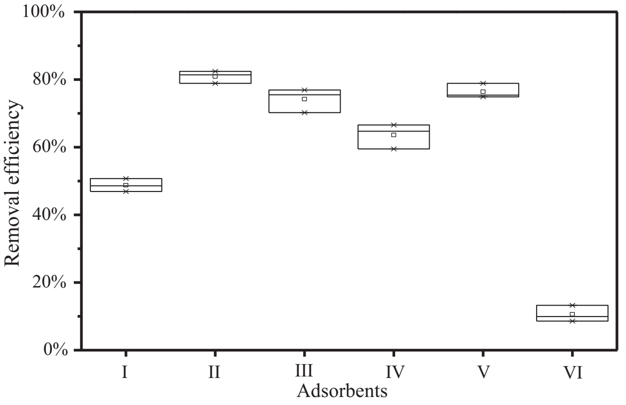

Fig. 1. Effect of different mass ratios of PVA/CA/CHT on the removal efficiency of Cr^{3+} ions (solution pH = 7.0; adsorbent dosage = 3 g/L; contact time = 24 h; temperature = 25 °C; agitation rate = 200 rpm).

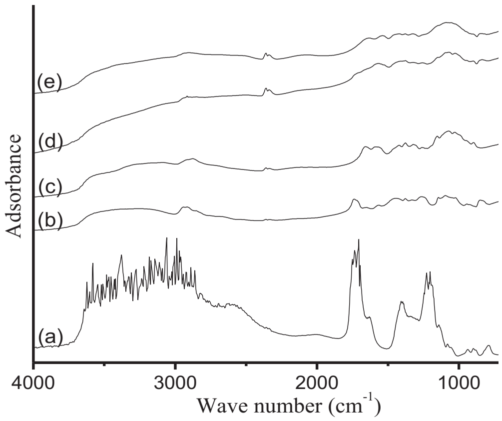

Fig. 3. FTIR spectra of (a) critic acid, (b) poly(vinyl alcohol), (c) chitosan, (d) PCC beads, and (e) PCC beads with chromium.

The removal of Cr^{3+} is low by the adsorbents (I and VI) where there is no PVA or CHT, while the Cr^{3+} uptake by the PCC beads (II, III, IV and V) is significant (Fig. 1). The improved performance of the latter adsorbents may be due to the increase of the PCC surface area and the presence of specific surface functional groups after the reactions among PVA, CA and CHT, which is consistent with similar observations made in an earlier study reported in the literature by Li et al. (2011). On the other hand, PCC beads with PVA/CA/CHT in different mass ratios displayed different uptakes for Cr^{3+}, which could be related to the type and completion of chemical reactions determining the performance of the adsorbents. PCC beads (II) show the highest adsorption (% removal efficiency) for Cr^{3+} (Fig. 1). Thus, the PCC bead with PVA/CA/CHT mass ratio of 1/5/1 was the optimal choice for the adsorptive removal of Cr^{3+} from aqueous solutions. The same bead was used for further adsorption experiments in this study.

3.2. Characteristics of the used adsorbent

The surface morphology of PCC beads characterized by FESEM indicated a significantly rough and folded structure (Fig. 2). Moreover, the shape of beads was not completely spherical with the size of beads ranging from 1.0 to 1.5 mm.

Results from Fig. 3a indicated that there were numerous and multifarious functional groups on the surface of critic acid. The broad and strong band ranging from 3200 to 3600 cm^{-1} should be due to the O—H stretching in the spectrum, while the peaks at 1739.8, 1712.8, 1226.7 and 1203.6 cm^{-1} were assigned to C═O stretching. These features of the FTIR spectra are in line with the nature of critic acid. The broad and strong band ranging from 3200 to 3600 cm^{-1} may be due to the O—H stretching in the spectrum of PVA (Fig. 3b). Moreover, the peaks at 2916.4 and 1377.2 cm^{-1} could also be assigned to O—H stretching, and the peaks at 1265.3 and 1095.6 cm^{-1} were attributed to C—O stretching. There was the broader and weaker band ranging from 3200 to 3600 cm^{-1} in the spectrum of CHT than that of critic acid and PVA (Fig. 3c). The peaks at 2877.8, 2337.7, 1658.8 1589.3 cm^{-1} should be attributed to N—H stretching, while the peaks at 1076.3, 1030 and 898.8 cm^{-1} may be due to the C—O stretching. The peaks at 1319.3 and 1153.4 cm^{-1} were assigned to C—H stretching (Shriner, Hermann, Morrill, Curtin, & Fuson, 2004).

After the formation of the adsorbent, the spectrum of PCC beads shows significant changes in functional groups (Fig. 3d). The absorbance of peaks ranging from 3200 to 3600 cm^{-1} for PCC beads is obviously stronger than that for PVA and CHT, while significantly weaker than that for critic acid. This difference could be related to the changes between O—H stretching and N—H stretching in the reaction process confirmed by S1 and S2. However, peaks at 2916.4 cm^{-1} and 1377.2 cm^{-1} assigned to O—H stretching were the same as those in the spectrum of PVA. It indicated that —OH groups from 3200 to 3600 cm^{-1} for PVA played a crucial role in the cross linking reaction. The peaks at 1562.3 cm^{-1} were assigned to C = O stretching, which implied that —COOH groups in critic acids obviously underwent changes in the reaction process. Similarly, the peak at 2360.9 cm^{-1} attributed to N—H stretching indicated that a significant change took place for —NH_2 groups in CHT. In addition,

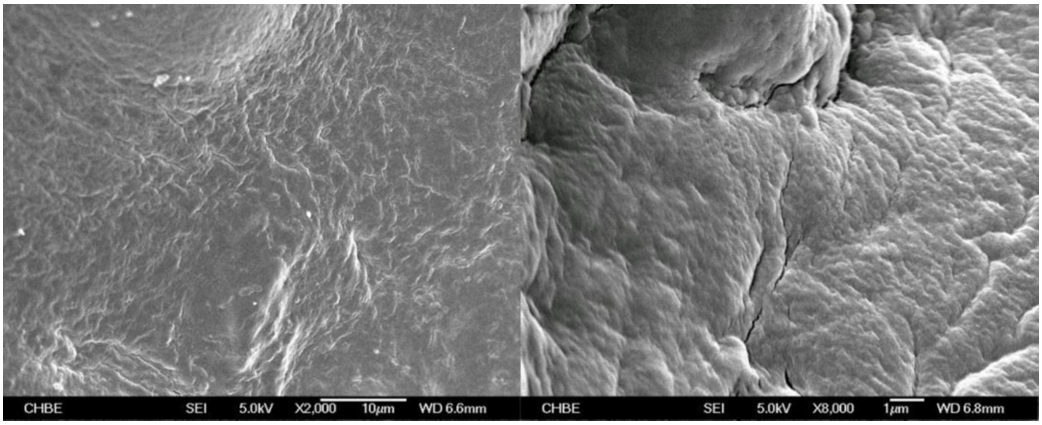

Fig. 2. Scanning electron microscopic images of PCC beads.

Table 1
Removal of Cr^{3+} ions by PCC beads under different pH values in aqueous solution (%).

pH values	Average removal
1	1.5 ± 0.8
2	3.6 ± 0.5
3	6.2 ± 0.4
4	44.2 ± 1.0
5	61.4 ± 0.7
6	80.2 ± 1.5
7	79.8 ± 1.2
8	79.5 ± 1.6

Note: Adsorbent dosage, 3 g/L; temperature, 25 °C; agitation rate, 200 rpm; contact time, 24 h.

the peak at 1068.6 cm^{-1} attributed to C—O stretching may be from the corresponding groups in CHT.

Fig. 3e shows the changes in the spectrum of PCC beads after the uptake of Cr^{3+} ions. The peak at 2916.4 cm^{-1} attributed to O—H bending shifts to the lower peak at 2900.9 cm^{-1} after the sorption. Similarly, the peak at 1562.3 cm^{-1} assigned to C=O stretching changes into the lower peak at 1543.0 cm^{-1}, which reflected that carboxyl groups from critic acid in PCC beads took part in adsorbing metal ions. The broad overlapping region for N—H and O—H stretching in the range of 3200-3600 cm^{-1} has also shown changes. Moreover, it is clear that —OH group results in the shift based on the constitution of PCC beads as shown in S2. The peak at 1068.6 cm^{-1} attributed to C—O stretching changed into the lower peak at 1053.1 cm^{-1}, which may be caused by the sorption reaction between —OH group and metal ions. Therefore, the adsorption of metal ions was determined by the hydroxyl and carboxyl groups on the PCC bead surface, which also verified that the cross linking reaction between the two functional groups was effective in this study.

3.3. *Effect of pH values*

The removal efficiencies for Cr^{3+} by PCC beads under different solution pH values are shown in Table 1.

Results from Table 1 indicated that the adsorption behavior of PCC beads toward Cr^{3+} was significantly affected by pH values in aqueous solutions. The removal of Cr^{3+} by PCC beads reached the peak value at pH close to 6.0, and then there was no significant increase with the increase of pH values. Cr^{3+} ions mainly existed as free Cr^{3+} and $[CrOH]^{2+}$ at pH values between 3.0 and 4.0, and as $Cr(OH)_3$ (aq) at pH values from 7.0 to 10.0 (Cao, Guo, Mao, & Lan, 2011). Meanwhile, the sorption sites on PCC beads for metal uptakes were protonated at a low pH. It implied that the removal of Cr^{3+} ions depended on negatively charged species on the surface of PCC beads at the low pH values. However, the sorption sites on PCC bead surface were rarely protonated at pH > 7.0. Therefore, the impact of pH values on metal uptakes in aqueous solutions was related to both the metal speciation and the surface characteristic of the adsorbent. The pH value of 6.0 was selected for further studies.

3.4. *Influence of adsorbent dosage*

In this study, the adsorbent dosage was changed from 0.1 to 10 g/L to explore the influence of adsorbent dosage on Cr^{3+} ion removal (Fig. 4).

Results from Fig. 4 indicated that removal efficiency for Cr^{3+} ions increased with the increase of adsorbent dosage, which should be related to the increase for both total surface area and the number of binding sites (Esposito, Pagnanelli, Lodi, Solisio, & Vegliò, 2001). On the other hand, the increasing interaction between surface binding sites could cause more reduction of metal uptakes with the increase of adsorbent dosage (Gadd, White, & DeRome, 1988). In addition, the removal efficiency and uptake capacity of metals are two important parameters determining the sorption performance of adsorbents. The removal of Cr^{3+} ions reached the maximum at the PCC bead dosage of more than 5 g/L, while its uptake capacities gradually appeared to be constant at the used adsorbent dosage above 5 g/L. Thus, the sorbent dosage of 5 g/L was selected for further studies.

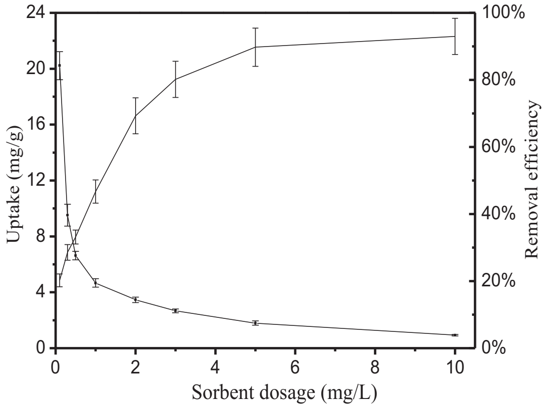

Fig. 4. Effect of adsorbent dosage on Cr^{3+} ion uptakes in aqueous solutions by PCC beads (II) (solution pH = 6.0; temperature = 25 °C; agitation rate = 200 rpm; contact time = 24 h).

3.5. *Adsorption kinetics*

Adsorption kinetics could significantly impact the pathway and mechanism of sorption reactions (Febrianto et al., 2009). In order to investigate the mechanism of controlling the sorption process and potential rate-controlling steps, the empirical equations were used to interpret the experimental data (at the initial concentration of 10 mg/L, temperature of 25 °C, pH 6.0), including the pseudo-first-order (Lagergren, 1898), Pseudo-second-order (Ho & McKay, 2000) and Elovich equations (Elovich & Larinov, 1962). The Lagergren pseudo-first-order equation (2) is represented in the form:

$$\ln(C_f - C_t) = \ln C_f - K_1 t \tag{2}$$

where K_1 (min^{-1}) is the rate constant of pseudo-first-order sorption; C_f (mg/g) and C_t (mg/g) denote the amount of sorption on the used sorbents at equilibrium and at any time, t (min), respectively. The plots of $\ln(C_f - C_t)$ versus t give values of K_1 and C_f. The pseudo-second-order Eq. (3) expressed by:

$$\frac{t}{C_t} = \frac{1}{K_2 C_f^2} + \frac{t}{C_f} \tag{3}$$

where K_2 (g/(mg min)) is sorption rate constant of pseudo-second-order model. The constant K_2 and C_f can be obtained from a linear regression plot of t/C_t versus t. Elovich Eq. (4) is one of the most useful models for describing chemisorption, which is generally expressed as follows:

$$C_t = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \left(\frac{1}{\beta}\right)\ln(t) \tag{4}$$

where α (mg/(g min)) is the initial sorption rate, and β (g/mg) is the parameter related to the extent of surface coverage and activation energy for chemisorption.

The kinetic curves of Cr^{3+} uptake by PCC beads (Fig. 5) indicated that there was the rapid sorption process during the first 120 min. The sorption equilibrium appeared around 360 min for Cr^{3+} ions on the used adsorbent. Meanwhile, the concentration of Cr^{3+} ions gradually became lower, as the increasing binding sites

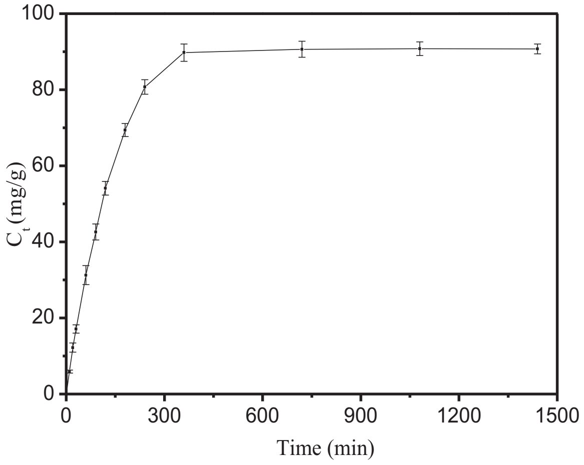

Fig. 5. Pseudo-second-order kinetic model of Cr^{3+} by PCC beads ($[Cr^{3+}] = 10$ mg/L; temperature = 25 °C; solution pH = 6.0; sorbent dosage = 5 g/L; stirring rate = 200 rpm).

were taken up. This caused the slow adsorption rate at the later stage of sorption process.

The pseudo-second-order equation could describe the sorption kinetics of Cr^{3+} ions by PCC beads better than other kinetic equations, with the high correlation coefficients above 0.990 and low % error (see S3). Moreover, the C_f values of the pseudo-second-order equation were in good agreement with the experimental ones. Thus, as an indication of a chemisorption mechanism, the pseudo-second-order equation was dominant for adsorption kinetics of Cr^{3+} ions by PCC beads.

3.6. Adsorption isotherm

Langmuir (5) and Freundlich isotherms (6) were employed to model the sorption behavior of Cr^{3+} ions by PCC beads in this study.

$$\text{Langmuir equation :} \quad Q = \frac{Q_{\max} b_L C_f}{1 + b_L C_f} \tag{5}$$

$$\text{Freundlich equation :} \; Q = K_F C_f^{1/n} \tag{6}$$

where $Q_{\max}$ is the maximum metal uptake (mg/g), b_L the Langmuir equilibrium constant (L/mg), K_F and n are the Freundlich constant.

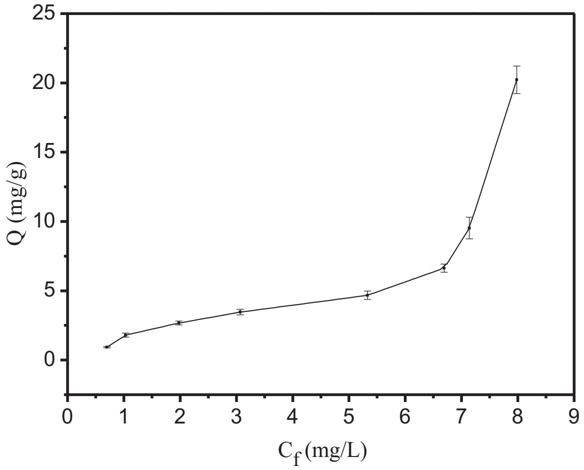

Fig. 6. Sorption isotherms of Cr^{3+} ions on PCC bead surface (0.5 g adsorbent in 100 mL metal solutions with initial pH 6.0).

Table 2
Correlation coefficients and sorption isotherm constants for Cr^{3+} ion adsorption by PCC beads.

Langmuir	
$Q_{\max}$ (mg/g)	41.5
b_L (L/mg)	0.035
R^2	0.957
Freundlich	
K_F (L/g)	1.376
n	1.024
R^2	0.882

The relationship of the metal uptake (Q) with the metal equilibrium concentrations (C_f) is given in Fig. 6. Results from Fig. 6 indicated that the uptake of Cr^{3+} ions by the used adsorbent increased with the increase of metal equilibrium concentration. The sorption data were fitted by the Langmuir equation and Freundlich equation, and the correlation coefficients (R^2) are provided in Table 2. Based on the correlation coefficients (R^2) in Table 2, adsorption isotherms of the used adsorbent for removal of Cr^{3+} ions could be better described by the Langmuir equation than by the Freundlich equation. The maximum amount of Cr^{3+} adsorbed ($Q_{\max}$) was 41.5 mg/g of PCC beads, which indicated that the used adsorbent could perform well for the sorption of Cr^{3+} in this study. However, it was found that the Freundlich adsorption isotherm could not fit the sorption data of Cr^{3+} satisfactorily by the used adsorbent. The agreement between the experimental data and the Langmuir model suggests that there was a monolayer adsorption of Cr^{3+} onto the PCC beads with constant adsorption energy. Emara, Tawab, El-ghamry, and Elsabee (2011) reported a sorption capacity of 14.89 mg Cr^{3+}/g Chitosan. Aravindhan, Aafreen Fathima, Selvamurugan, Rao, and Balachandran (2012) and Sepehr, Nasseri, Zarrabi, Samarghandi, and Amrane (2012) used biosorbents for their study and reported that the sorption capacities were 23.9 mg Cr^{3+}/g bacillus subtilis biomass and 96.0 mg Cr^{3+}/g aspergillus niger (with addition of nutrients), respectively. Zhang et al. (2012) observed a sorption capacity of 77 mg Cr^{3+}/g Fe_3O_4–SiO_2–poly(1,2-diaminobenzene) core–shell sub-micron particles. It is thus clear that the PCC beads in this study have a great potential for the treatment of Cr^{3+} from contaminated waters.

3.7. Desorption and reuse

The recovery of adsorbents for the continued reuse is highly important for the treatment of wastewater. After sorption experiments, Cr^{3+} from the PCC bead surface was desorbed using acid (0.5 M H_2SO_4) in this study. The parameters of adsorption/desorption experiments can be found in S4, including the sorption capacity, desorption efficiency and weight loss of PCC beads after 3 cycles of adsorption/desorption experiments. The results indicate that PCC beads are promising adsorbents for the effective removal of Cr^{3+} from aqueous solutions.

4. Conclusion

Novel poly(vinyl alcohol)/citric acid/chitosan (PVA/CA/CHT, PCC) beads were prepared as an adsorbent for the removal of trivalent Cr (Cr^{3+}) in aqueous solutions in this study. The PCC bead (II) with PVA/CA/CHT mass ratio of 1/5/1 showed the highest removal efficiency for Cr^{3+}. Further FESEM results implied that PCC bead (II) had an obviously rough and folded structure, and its spectrum manifested significant changes compared to those of PVA, CA and CHT. The sorption experiments indicated that the Cr^{3+} sorption onto PCC beads (II) was highly pH-dependent with the maximum uptake at pH 6.0. The sorption kinetics data were well fitted by the pseudo-second-order equation with high regression coefficients. The sorption isotherm of PCC beads (II) was well described by the Langmuir equation, with a maximum sorption capacity of 41.5 mg

Cr^{3+}/g PCC beads (II). The high efficiency of removal of Cr^{3+} and reusability of PCC beads (II) make this adsorbent very attractive for the treatment of Cr^{3+} and possibly other metals in aqueous solutions.

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