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Adsorption of Cr(VI) from aqueous solutions using chitosan-coated fly ash composite as biosorbent

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ABSTRACT

The structure characteristics of chitosan/fly ash composite and equilibrium adsorption of Cr(VI) from aqueous solutions on this novel biosorbent were investigated. Adsorption experiments were carried out as a function of contact time, types of adsorbent, ratio, pH, temperature and coexisting ions. It was found that the adsorption of Cr(VI) reached equilibrium within 50 min. Adsorption capacity of Cr(VI) on composite adsorbent was higher than that on chitosan and fly ash, respectively. Composite adsorbent had the highest adsorption efficiency when the ratio was 30 wt%. The composite adsorbent was particularly effective for the Cr(VI) removal at pH 5.0 with the mechanism of electrostatic adsorption coupled reduction. Evaluation of adsorption process from 288 K to 328 K identified its exothermic nature. The maximum adsorption capacity of Cr(VI) was 33.27 mg/g at 288 K. Equilibrium data of Cr(VI) onto this composite adsorbent was well described by Langmuir isotherm model which indicated a physical adsorption process. Recovery studies showed that an effective desorption can be achieved by adding NaOH at pH 10.0, while it decreased as the adsorption-desorption cycles.

adsorbents.

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1. Introduction

Chromium ion, which exists in both trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)), usually presents in the effluents of electroplating, tanning, mining and fertilizer industries [1,2]. Chromium is on the top-priority list of toxic pollutants defined by the US Environmental Protection Agency (EPA) [3]. Cr(III) is relatively immobile and innocuous. Cr(VI) is a suspected carcinogen and can pose risks to human health such as skin ulceration, liver damage, and pulmonary congestion [4]. As for the pollution hazards caused by Cr(VI), several methods of removal have been reported including chemical precipitation, reverse osmosis, ion exchange, electrolysis and adsorption [3-5]. Among all the mentioned methods, adsorption is an economically feasible alternative due to easy operation and development of various cheap adsorbents. Therefore, the aim of this research is to study the removal of Cr(VI) from aqueous solution using an adsorption technique.

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Recently, considerable attention has been paid to the adsorption of Cr(VI) using natural polymeric materials as adsorbents in wastewater treatment. Chitosan (CHS), the deacetylated derivative of chitin, is the most abundant biopolymer found on the earth next to cellulose [6–8]. It has demonstrated to be one of the most promising adsorbents for the removal of heavy metals due to its special structure, biocompatibility and biodegradation [9]. Nevertheless, CHS is regarded as a relative expensive material, which restricts its practical operation and should be improved. Therefore, several attempts have been made to develop cheaper and effective

Fly ash, which has physical characteristics such as small particle size and large surface area, can be used as an alternative low-cost adsorbent for the removal of heavy metal ions [10]. Fytianos et al. [11] investigated the removal of Cr(VI) from tannery wastewater using fly ash. Sharma et al. [12] reported that fly ash is a good adsorbent and can be recommended for treatment of Cr(VI) in particular. These suggest that fly ash is a potential adsorbent for Cr(VI)

Copello et al. [13] prepared silicate/chitosan composite biosorbent and studied its capability in the removal of Cr(VI) from aqueous solution. Gandhi et al. [14] discovered that the synthesized alumina/chitosan (AlCs) composite possesses an enhanced chromium sorption capacity compared with the original alumina and chitosan flakes, respectively. These indicate that chitosan composites are attracting considerable attention in the removal of Cr(VI). However, there were few reports on Cr(VI) removal using

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Table 1Total content of some elements in the fly ash.

Elements	SiO ₂	Al_2O_3	Fe ₂ O ₃	CaO	K ₂ O	Others
Content %	54.5	28.5	2.2	5.9	0.4	8.5

chitosan/fly ash composite. So the objective of this paper was to synthesize this novel biosorbent and analyze its characteristics using FTIR, XPS and SEM with EDS. Also, the capacity of the composite adsorbent was evaluated using batch adsorption process. Working parameters such as contact time, composite adsorbent ratio (the weight of chitosan divided by the weight of composite adsorbent), pH and temperature were considered. Two isotherm models were used to evaluate this adsorbent.

2. Materials and methods

2.1. Chemicals

Chitosan derived from deacetylated lobster shell wastes was supplied by Jinan Haidebei Marine Bioengineering Co. Ltd., China. The degree of deacetylation and molar mass of chitosan were measured to be 86% and 1.6×10^6 , respectively. Acetic acid, diphenyl carbazide, sulfuric acid, phosphoric acid, and other reagents were of analytic grade. Fly ash was taken from the boiler room in our school and contents of the major elements of fly ash were showed in Table 1.

2.2. Preparation of composite adsorbent

Chitosan powder $(0.3\,g)$ was dissolved in 2 wt% of acetic acid solution $(30\,\text{mL})$ using a glass-rod. Fly ash was screened with a sieve of 100 mesh in order to remove impurities. Then, twenty grams of screened fly ash were activated with $100\,\text{mL}$ of $5\,\text{M}$ H $_2\text{SO}_4$ at $30\,^\circ\text{C}$ for 12 h in a flask. The suspension was filtered off and then washed several times with double-distilled water and dried in an oven at $60\,^\circ\text{C}$ for $8\,\text{h}$ prior to use. The activated fly ash $(2.70, 1.20, 0.70\,\text{and}\,0.45\,\text{g})$ was added to the chitosan solution to obtain composite with various ratios of $10, 20, 30\,\text{and}\,40\,\text{wt}\%$, respectively. They were agitated for $45\,\text{min}$ at room temperature $(298\pm1\,\text{K})$, and washed with distilled water until the supernatant turned into neutral pH, got dried in $323-333\,\text{K}$ vacuum oven and was screened with a sieve of $100\,\text{mesh}$.

2.3. Characterization of the adsorbent

The Fourier transform infrared (FTIR) spectra of fly ash, chitosan, and composite were measured with a Nicolet 5700 with KBr disks. XPS can be used to measure the composition and valence state of the adsorbed chromium ions. XPS experiments were carried out on a RBD upgraded PHI-5000 C ESCA system (Perkin Elmer) with Al K α radiation ($h\nu$ = 1486.6 eV). Curve fitting of the chromium peak was achieved by fitting to Gaussian curves using RBD AugerScan 3.21 software. Scanning electron microscope (Philips, XL30) and energy dispersive spectrometer (Link 300) were used to observe the surface morphology and analyze elements distribution on the surface of the composite. The specific surface area, average pore diameter and total pore volume of activated fly ash were respectively measured to be 26.95 m²/g, 6.203 nm and 0.00418 cm³/g via an Autosorb iQ analyzer (Quantachrome, USA) by nitrogen adsorption at 77 K using the Brunauer–Emmett–Teller (BET) method.

2.4. Effect of contact time and initial concentration of Cr(VI) on adsorption capacity

Chitosan/Fly ash composite adsorbent (0.1 g, ratio 30 wt%) was placed in a 150 mL conical flask, followed by the addition of distilled water to Cr(VI) stock solution (1000 mg/L) to obtain different initial concentrations of Cr(VI) solutions (40, 50, 60, 70, 80, 90 and 100 mg/L). The pH of the solution was adjusted to 5.0 by adding 0.1 M HCl solutions. Each sample was shaken with contact time varied from 10 min to 50 min at (298 \pm 1 K).

2.5. Effect of types of adsorbent and initial concentration of Cr(VI) on equilibrium adsorption capacity

Fly ash, chitosan and chitosan-coated fly ash composite adsorbent (0.1 g, ratio 30 wt%) were placed in 150 mL conical flasks including Cr(VI) solutions with chromium concentrations of 40, 50, 60, 70, 80, 90 and 100 mg/L, respectively. Each sample was shaken for 50 min until the adsorption reached equilibrium at (298 \pm 1 K, pH 5.0).

2.6. Adsorption equilibrium experiments

Chitosan-coated fly ash composite adsorbents with different weight ratio of chitosan to composite (0.1 g, ratios at 10, 20, 30 and 40 wt%) were placed in a 150 mL conical flask including Cr(VI) solutions with chromium concentrations of 40, 50, 60, 70, 80, 90 and 100 mg/L, respectively. Each sample was shaken for 50 min until the adsorption reached equilibrium at (298 \pm 1 K, pH 5.0). The effect of pH on adsorption of Cr(VI) using composite (weight ratio of 30 wt%) as adsorbent was determined by adjusting the pH to 2.0, 5.0 and 8.0, followed by shaking for 50 min until the adsorption reached equilibrium at 298 ± 1 K. The effect of temperature on Cr(VI) equilibrium adsorption capacity was evaluated by shaking for 50 min at different temperatures (288, 298, 308, 318, and 328 K) and for weight ratio 30 wt% and pH 5.0. Finally, the effect of coexisting ions $(HCO_3^-, Cl^-, SO_4^{2-}, Ca^{2+})$ and Mg^{2+} on Cr(VI) adsorption was investigated with a fixed initial ion concentration of 2 mM at 298 K and pH 5.0.

2.7. Recovery studies

To examine the desorption behavior of Cr(VI) from composite adsorbent, three adsorption–desorption cycles were performed in this study. Adsorption experiments were first conducted by placing the adsorbent (0.1 g, ratio 30 wt%) in Cr(VI) solutions (50 mL of 50 mg/L and a solution pH value of 5.0). The adsorbents adsorbed with Cr(VI) were desorbed in solutions at pH 10.0 using NaOH. This sample was shaken for 50 min at 298 K, and the Cr(VI) concentration was analyzed. The adsorbents were finally collected from the wastewater by filtration, washed with distilled water, and then reused in the next cycle of adsorption experiments.

The residual chromium concentrations were determined by a UNICO-2100 UV/visible spectrometer at wavelength λ_{max} = 540 nm, according to the 1,5-diphenyl-carbazide method [15]

The adsorption amount q was computed according to Eqs. (1) and (2) [16]:

$$q_t = \frac{V(C_0 - C_t)}{M} \tag{1}$$

$$q_e = \frac{V(C_0 - C_e)}{M} \tag{2}$$

where C_0 and C_e are the initial and equilibrium concentrations of Cr(VI) (mg/L), respectively; V is the volume of aqueous solutions (mL); M is the weight of adsorbent (g); q_e is equilibrium adsorption

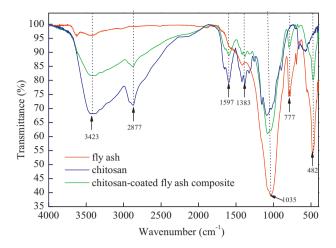


Fig. 1. FTIR spectra of fly ash, chitosan and chitosan-coated fly ash.

capacity of Cr(VI); q_t is adsorption capacity of Cr(VI) at time t. All the batch adsorption experiments were carried out in triplicate to confirm reproducibility of the experimental results.

3. Results and discussion

3.1. Structure characterization

Structures of the sorbents were characterized by FTIR, SEM and EDS analysis. FTIR spectra of fly ash, chitosan, and composite (30% chitosan) are shown in Fig. 1. The major bands for the chitosan can be assigned as follows: $3423\,\mathrm{cm^{-1}}$ (–OH and –NH₂ stretching vibrations), $2877\,\mathrm{cm^{-1}}$ (–CH stretching vibration in –CH and –CH₂), 1655, $1597\,\mathrm{cm^{-1}}$ (–NH₂ bending vibration), 1421, $1325\,\mathrm{cm^{-1}}$ (stretching vibration of C–O), $1383\,\mathrm{cm^{-1}}$ (stretching vibration of C–O). The bands of fly ash at 1035, 777 and $482\,\mathrm{cm^{-1}}$ indicated

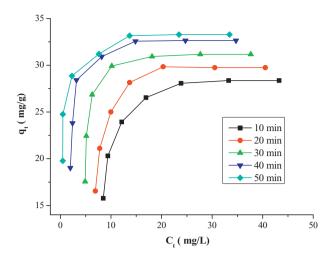


Fig. 3. q_t – C_t adsorption isotherm of Cr(VI) at different contact time.

the presence of asymmetric Si–O–Si bond stretching, symmetric Si–O–Si bond stretching and vibration of aluminium oxide, respectively [13,14]. Fig. 1 revealed that most of the functional groups for Cr adsorption (Si–OH, –NH $_3$ ⁺ and Al 3 +) originally present on chitosan and fly ash were also present after the coating. According to the previous literatures [13,17], both the physical and chemical interactions between silicon matrix (in fly ash) and polysaccharide (in chitosan) could form an interpenetrating network, supporting the immobilization of chitosan on fly ash.

Fig. 2 showed the SEM images of fly ash (a), chitosan (b) and chitosan–fly ash composite (c). Fig. 2c clearly illustrated the disordered intercalated and exfoliated structure in chitosan–fly ash composite, thereby increasing the contact area, which facilitates the metal ions adsorption onto composite [18]. The EDS spectra of chromium sorbed chitosan–fly ash composite indicated that aluminum and silicon were the two major metal constituents of the

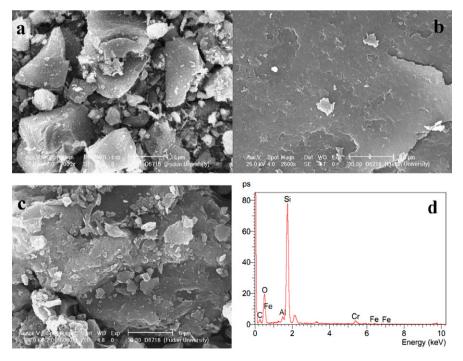


Fig. 2. SEM images of (a) fly ash, (b) chitosan, (c) chitosan-coated fly ash, EDS spectra of (d) chromium treated chitosan-coated fly ash.

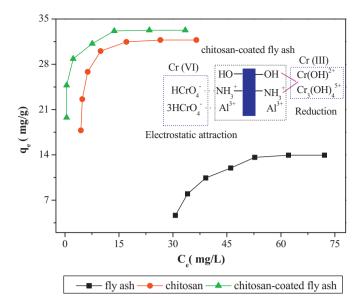


Fig. 4. Equilibrium adsorption isotherm of Cr(VI) on different adsorbents and the mechanism of chromium sorption by chitosan-coated fly ash composite.

composite. The presence of chromium peaks in Fig. 2d confirmed that the chromium sorption had occurred onto the composite.

3.2. Effect of contact time and Cr(VI) concentration on adsorption capacity

The effect of contact time on adsorption capacity of Cr(VI) is shown in Fig. 3. Adsorption amount of Cr(VI) increased with the contact time at any initial concentration of Cr(VI). Adsorption capacity of Cr(VI) on composite adsorbent was fast for the first 30 min at different initial concentrations, which indicated instantaneous adsorption of Cr(VI) within the early contact time. It may be attributed to the boundary layer diffusion effects [19,20]. With further increase of time, the adsorption started slowing down which showed a gradual equilibrium before reaching the equilibrium state. It was due to the utilisation of all active sites on the adsorbent surface and related to the intraparticle diffusion effects [19,20]. The adsorption equilibrium was achieved within 50 min. Consider C_0 = 100 mg/L, for example, C_t decreased from 43.26 to 33.45 mg/L and q_e increased rapidly from 28.37 to 33.28 mg/g with the rise in time from 10 to 50 min. For the sake of the combined experiments, all further studies were carried out for 50 min.

3.3. Effect of types of adsorbent and Cr(VI) concentration on equilibrium adsorption capacity

It can be seen from Fig. 4, the adsorption amount of Cr(VI) from aqueous solutions on chitosan-coated fly ash had been improved compared with chitosan and fly ash, especially that the adsorption amount on composite adsorbent was much higher than that on fly ash at any initial Cr(VI) concentration. This may be attributed to the fact that it was more difficult for HCrO₄-, Cr₂O₇²⁻ groups got into the small cavity of fly ash which resulting in less efficiency for Cr(VI) removal [21]. The functional NH₂ groups in chitosan molecules can be protonated to NH₃⁺ in acidic solution, thereby increasing the electrostatic attractions between HCrO₄⁻, Cr₂O₇²⁻ and -NH3+ groups and enhancing the adsorption amount. However it is not economical due to its high cost of Cr(VI) removal. The surface acidic functional groups (silanol groups Si-OH, Al3+, and protonated amino groups NH3+) of the chitosan-coated fly ash could play multi-component adsorption performance which is more effective for the adsorption of Cr(VI). Moreover, coating

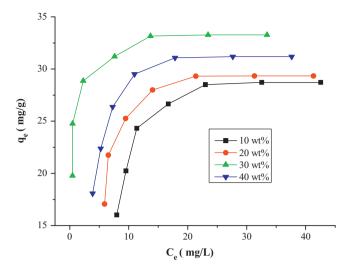


Fig. 5. Equilibrium adsorption isotherm of Cr(VI) on composite adsorbent at different ratios.

chitosan over fly ash could form an exfoliated structure (seen in Fig. 2c), resulting in the good performance of chromium adsorption [13]. The possible mechanism of chromium removal by composite was shown in Fig. 4. For the sake of the combined experiments, later studies used chitosan-coated fly ash for the adsorption of Cr(VI).

3.4. Effect of composite adsorbent ratio on Cr(VI) equilibrium adsorption capacity

The effect of weight ratio of chitosan to composite on the removal of Cr(VI) ions from aqueous solutions was shown in Fig. 5. The adsorption amount of Cr(VI) increased with the rising initial concentration of Cr(VI) ions at different adsorbent ratios. As the composite adsorbent ratio increased from 10 wt% to 40 wt%, the adsorption amount increased firstly, and decreased afterwards, reaching its maximum equilibrium adsorption capacity when the ratio was 30 wt%. After the critical ratio 30 wt%, the adsorption capacity of Cr(VI) decreased with further increasing the ratio. It was attributed to that the amount of intercalated chitosan was saturated which reduced the adsorption capability of Cr(VI) [22]. This also showed that the composite adsorbent has an optimal ratio and a small quantity of chitosan coats over fly ash can significantly improve adsorption capacity. Compared with various low-cost adsorbents, the adsorption capacities of the chitosancoated fly ash (30 wt%) in this study were higher than those which ranging from 19.6 to 26.3 mg/g [23]. For the sake of the combined experiments, later studies were carried out for 30 wt% ratio.

3.5. Effect of pH on Cr(VI) equilibrium adsorption capacity

The pH value is an important parameter that strongly influences the adsorption of Cr(VI) onto the solid–liquid interface. Batch adsorption experiments were carried out by varying the initial pH from acidity to alkaline to identify its effect on Cr(VI) adsorption. The results are shown in Fig. 6. At this pH range, the maximum adsorption on composite was 33.27 mg/g at pH 5.0, and it dropped to 29.73 and 26.86 mg/g at pH of 2.0 and 8.0, respectively. The pH-dependent metal adsorption can be mainly related to functional groups of adsorbent and also to the metal chemistry [24]. Cr(VI) has various forms such as CrO_4^{2-} , $HCrO_4^{-}$, $Cr_2O_7^{2-}$ in wastewater, which is relevant to pH of the wastewater [25]. In neutral and alkaline conditions, Cr(VI) is mainly in the form of CrO_4^{2-} . Furthermore, the anions such as OH^- increase with the increasing pH, resulting in a competitive adsorption with CrO_4^{2-} . Therefore, the activity

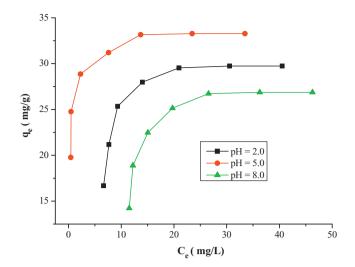


Fig. 6. Equilibrium adsorption isotherm of Cr(VI) at different pH.

of Cr(VI) existence in oxygen radical on composite adsorbent surface has been weakened and adsorption capacity of $\text{CrO}_4{}^{2-}$ has decreased under alkaline conditions. A balance between $\text{HCrO}_4{}^-$ and $\text{Cr}_2\text{O}_7{}^{2-}$ at pH ranging from 1.0 to 6.0 was established previously [26]. According to the Cr(VI) balance, the surface acidic functional groups (silanol groups Si–OH, Al $^{3+}$ and protonated amino groups $\text{NH}_3{}^+$) found on the chitosan/fly ash composite surface might be considered the active sites for adsorption of Cr(VI). However, acid-soluble chitosan in solution and decreased adsorption efficiency were also observed under the severe acidity environments [27], favoring our idea of adsorption capacity being optimal under subacid environment. For the sake of the combined experiments, later studies were carried out at pH 5.0.

Fig. 7 showed the XPS spectra of chitosan-coated fly ash that had adsorbed Cr(VI) at pH 5.0. The binding energies of 572–581 eV and 582–592 eV correspond to Cr $2p_{3/2}$ and Cr $2p_{1/2}$ orbitals, respectively. The bands at 576.9 eV and 579.0 eV can be attributed to Cr(III) and Cr(VI) binding energies for $2p_{3/2}$ orbitals, respectively [28]. Thus, as shown in the spectra, Cr(VI) was partially reduced to Cr(III) under acidic conditions (pH 5.0). Furthermore, the peak area ratio of Cr(III)/Cr(VI) on the composite was 2.7, suggesting that the mechanism of chromium removal by chitosan-coated fly ash was dominated by both the electrostatic adsorption and reduction under acidic conditions. The reduction of toxic Cr(VI) to less toxic

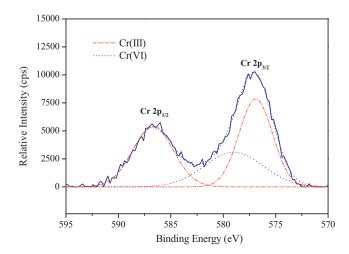


Fig. 7. XPS Cr 2p spectra of chitosan-coated fly ash after adsorption of Cr (VI).

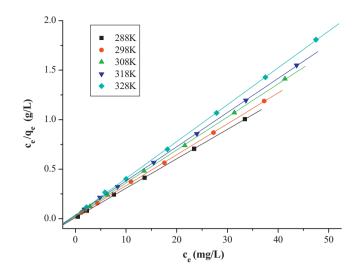


Fig. 8. Langmuir isotherm plot for adsorption of Cr(VI) at different temperatures.

Cr(III) was likely due to the reactive –OH and –NH₂ electron donor present in the chitosan-coated fly ash [14].

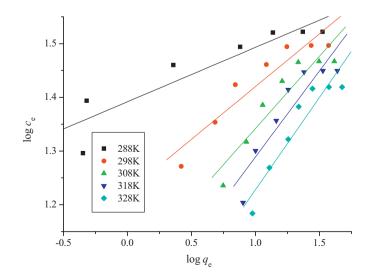
3.6. Adsorption isotherm models

The adsorption equilibrium study of interaction between Cr(VI) ions and adsorbent can be well described by two commonly used isotherm models, namely Langmuir and Freundlich [29,30]. Langmuir isotherm is applicable to monomolecular layer adsorption, while Freundlich isotherm is an empirical equation applicable to adsorption onto heterogeneous surface [25]. The experimental data conformed to the linear forms of Langmuir and Freundlich models expressed as the following equations [29,30]:

$$\frac{C_e}{q_e} = \frac{C_e}{q^0} + \frac{1}{bq^0}$$

$$\log q_e = \frac{1}{n} \log C_e + \log K$$

where C_e is the equilibrium concentration of Cr(VI) (mg/L), q_e is equilibrium adsorption capacity of Cr(VI), q^0 is the theoretical maximum monolayer adsorption capacity of the adsorbent (mg/g), b is the Langmuir isotherm constant related to the adsorption energy



 $\textbf{Fig. 9.} \ \ \textbf{Freundlich} \ \ \textbf{isotherm} \ \ \textbf{plot} \ \ \textbf{for adsorption of Cr(VI)} \ \textbf{at different temperatures.}$

Table 2Langmuir and Freundlich isotherm parameters obtained from the adsorption of Cr(VI) in aqueous solution at different temperatures.

T/K	Langmuir			Freundli	Freundlich		
	b (L/mg)	q ⁰ (mg/g)	R^2	n	K	R ²	
288	3.0808	33.6306	0.99988	9.8648	24.6496	0.84294	
298	1.4203	32.0616	0.99986	7.9936	21.1973	0.84898	
308	1.2743	29.9760	0.99994	8.4027	19.9196	0.85788	
318	0.9686	28.9519	0.99986	8.1103	18.6406	0.91073	
328	1.1018	26.8528	0.99984	9.4206	18.2608	0.87651	

(L/mg). K is the Freundlich adsorption constant related to the adsorption capacity of adsorbent, 1/n is the adsorption intensity, which gives an indication of the favorability of adsorption. The values of q^0 and b were calculated from the slope and intercept of the plot of C_e/q_e versus C_e , respectively, as shown in Fig. 8. The values of K and 1/n were calculated from the intercept and slope of the plot of $\log q_e$ versus $\log C_e$, respectively, as shown in Fig. 9. The parameters and correlation coefficients obtained from the two isotherm models were summarized in Table 2.

As shown in Table 2, adsorption isotherms modeling showed good agreement with the experimental data. Values of q^0 derived from the Langmuir theory decreased with the increase in temperature, indicating the exothermic nature of Cr(VI) sorption [12]. The constant K, which is derived from the Freundlich theory, decreased with the rise in temperature, thereby confirming a favorable adsorption process at lower temperature. Furthermore, all the conditions were found to be favorable for Cr(VI) adsorption as the values of 1/n lying between 0 and 1 and the values of n greater than 1. On the basis of the correlation coefficients (R^2), the Langmuir model gives higher R^2 at all the five temperatures investigated, indicating the suitability of Langmuir isotherm than the Freundlich isotherm.

3.7. Effect of coexisting ions on Cr(VI) equilibrium adsorption capacity

Fig. 10 showed that SO_4^{2-} have the most interference on the Cr(VI) adsorption, followed by the CI^- and HCO_3^- , and Ca^{2+} and Mg^{2+} do not have significant effect on Cr(VI) adsorption. This is because of the fact that the sorbent (chitosan-coated fly ash) has positive charge due to the protonation of amino groups $(-NH_3^+)$ in acid solution, causing the electrostatic attractions between anion and sorbent. Therefore, the anions such as SO_4^{2-} , CI^- , HCO_3^- in

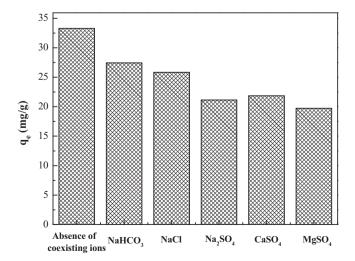


Fig. 10. Effect of coexisting ions on the adsorption capacity of chitosan-coated fly ash at $298\,\mathrm{K}$ and pH 5.0.

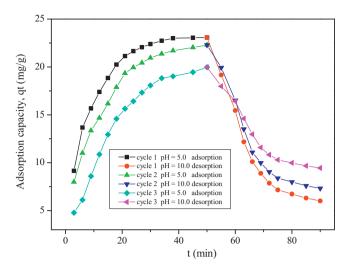


Fig. 11. Adsorption and desorption kinetics of Cr(VI) on chitosan/fly ash composite adsorbent.

the solution could result in a competitive adsorption with Cr(VI) (mainly in form of $Cr_2O_7^{2-}$ and $HCrO_4^-$) on the sorbent. In contrast, the electrostatic repulsion could occur between cation (Ca^{2+} and Mg^{2+}) and the adsorbent, leaving the adsorption site of adsorbent still available for Cr(VI).

3.8. Reuse of chitosan/fly ash composite adsorbent

The desorption studies are very important since the economic success of the adsorption process depends on the regeneration of adsorbent. In this study, the adsorption conditions were carried out at pH 5.0, 298 K with initial Cr(VI) concentration of 50 mg/L, and the desorption conditions were carried out at pH 10.0, 298 K. NaOH was used as a solvent of desorption due to its ability of deprotonation of $-NH_3^+$ and $Si-OH_2^+$ on the chitosan-coated fly ash. The effects of adsorption–desorption cycles on adsorption and desorption capacities were given in Fig. 11.

Fig. 11 showed that the first adsorption step took 45 min at equilibrium and the adsorption capacity reached 23.07 mg/g. The desorption step took 40 min and the desorption capacity was 17.06 mg/g. The adsorbed Cr(VI) in the first cycle of adsorption can be removed by NaOH and the removal percentage is about 74% at pH 10.0. The second cycle of adsorption and desorption capacities were 22.30 mg/g and 14.97 mg/g, respectively. Compared with the first cycle, the adsorption capacity (19.97 mg/g) and desorption capacity (10.52 mg/g) of the third cycle dropped 13.44% and 38.34%, respectively. Therefore, we think the influence of adsorption—desorption cycles on the adsorption/desorption capacity of chitosan—coated fly ash is significant especially the desorption capacities, while nearly half of the adsorbed Cr(VI) can still be desorbed after the third cycle.

4. Conclusions

The adsorption capacity of Cr(VI) from aqueous solutions on chitosan-coated fly ash was higher than that on CHS and fly ash at different initial Cr(VI) concentrations. Adsorption equilibrium experiments were carried out as a function of contact time, ratio, pH, temperature and coexisting ions. The equilibrium time of Cr(VI) adsorption was found to be 50 min. Composite adsorbent had the highest adsorption efficiency when the ratio was 30 wt%. The maximum adsorption capacity of Cr(VI) took place at the initial pH 5.0. The percentage removal of Cr(VI) decreased with the rise in temperature from 288 to 328 K which identified its exothermic nature. The maximum adsorption capacity of Cr(VI) was 33.27 mg/g at 288 K.

Equilibrium data of Cr(VI) were found to be well represented by Langmuir isotherm model which indicated a physical adsorption process. An effective desorption can be achieved by adding NaOH at pH 10.0, while it decreased as the adsorption–desorption cycles.

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