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Fast and effective removal of cadmium ion from water using chitosan encapsulated magnetic Fe_3O_4 nanoparticles

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ABSTRACT

A novel CS_2-modified chitosan encapsulated magnetic Fe_3O_4 nanoparticles (CMCS@Fe_3O_4) was prepared for the removal of Cd(II) from aqueous solution. The adsorption behavior of the CMCS@Fe_3O_4 toward Cd(II) was studied using batch method. The CMCS@Fe_3O_4 showed a rapid process and a superior adsorption capacity for Cd(II). The adsorption kinetics followed the pseudo-second-order and the equilibrium data were well described by the Langmuir isotherm for the CMCS@Fe_3O_4. The maximum adsorption capacity of CMCS@Fe_3O_4 for Cd(II) was 200 mg g^{-1} from the Langmuir isotherm. Based on Fourier transform infrared spectroscopy analysis, the $–NH_2$ and –SH groups on the CMCS@Fe_3O_4 mainly participated in the Cd(II) adsorption process. In addition, the common coexisting ions had a negligible impact on Cd(II) adsorption on the CMCS@Fe_3O_4. Overall, the results reported herein indicated that the CMCS@Fe_3O_4 is very attractive and implies a potential of practical application for the removal of toxic heavy metals.

Keywords: Cd(II); Adsorption; Magnetic chitosan; Modification

1. Introduction

Toxic heavy metal pollution is one of the most serious environment problems. The heavy metals are of particular concern because they are non-degradable and tend to accumulate in living organisms, causing various diseases and disorders [1]. Cadmium (Cd) is one such metal known to be carcinogenic and teratogenic by impacting lungs, kidneys, liver, and reproductive organs [2]. The World Health Organization has set a maximum guideline concentration of 0.003 mg L^{-1} for Cd in drinking water [3]. Given pervasive cadmium contamination and the low drinking water guideline, there is considerable interest in the development of new alternative techniques to remove Cd from contaminated waters before they are discharged into natural waters.

Currently various methods are available for removing the heavy metals such as ion-exchange [4],

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chemical precipitation [5], reduction [6], membrane filtration [7], evaporation [8], flotation [9], reverse osmosis [10], liquid extraction [11], and adsorption [12]. However, most of these methods have their own drawbacks like high capital, high operational cost, and problems in disposal of residual metal sludge. Due to the advantages of economical feasibility and environmental friendly behavior, adsorption is considered as a promising technique for removing contaminants [13–15]. Several common adsorbents of different origin, primarily including activated carbons, clays, zeolites, biomass, and polymeric materials, have been used for the removal of heavy metal from the industrial wastewater [16–20]. However, many adsorbents suffer from low adsorption capacities and separation inconveniences. Therefore, there is an urgent need to explore new adsorbents and systems.

Chitosan, which is a deacetylated product of chitin (found in abundance in nature), had currently earned a reputation for its economic, biodegradable, and easy modification properties, and therefore sparked great interests in many fields such as pharmaceutical, cosmetics, health care, and water treatment. [21–24]. Recently, chitosan and modified chitosan have been used as adsorbents to remove heavy metal ions from ground water and industrial effluents [25,26]. The metal binding capacity of chitosan is mainly due to the presence of chemically reactive amine and hydroxyl groups on chitosan chain. However, chitosan is soluble in acidic-to-neutral solution. Consequently, it is necessary to reinforce its chemical stability using cross-linking agents like glutaraldehyde [27], epichlorohydrin [28], tripolyphosphate [29], ethyleneglycol diglycidyl ether [30], etc. Glutaraldehyde has been frequently used to cross-link chitosan and to stabilize it in acidic solutions whereby the reaction occurs through Schiff's base reaction between aldehyde groups of glutaraldehyde and some amine groups of chitosan. Due to cross-linking may reduce the adsorption capacity, chemical modification to introduce a variety of functional groups can enhance the sorption performances [31]. For example, grafting of sulfur compounds can create new chelating groups on chitosan backbone.

In this study, a novel CS_2-modified chitosan encapsulated magnetic Fe_3O_4 nanoparticles (CMCS@Fe_3O_4) has been prepared for the removal of Cd(II) from aqueous solution. The adsorption behavior of the CMCS@Fe_3O_4 toward Cd(II) was studied using batch method. Magnetic separation provides a very convenient approach for removing and recycling magnetic particles after batch experiments. The influences of the solution pH and common coexisting ions on the Cd(II) uptake were tested. The regeneration of the loaded adsorbent was also studied.

2. Materials and methods

2.1. Materials and reagents

Chitosan was purchased from Zhejiang Golden-Shell Biochemical, Zhejiang, China (deacetylation degree = 91.2%). $Cd(NO_3)_2$, $FeCl_3·6H_2O$, Glutaraldehyde, and ethanol were obtained from National Medicines, China. The high-purity water used in this study was produced using a UPK/UPT ultrapure water system. Other chemical reagents were of analytical grade and used without further purification.

2.2. Preparation of chitosan encapsulated magnetic Fe_3O_4 nanoparticles

The chitosan encapsulated magnetic Fe_3O_4 nanoparticles (CS@Fe_3O_4) was prepared by water-in-oil emulsification. Chitosan powder (2.0 g) was dissolved in 2% (v/v) acetic acid solution (100 mL) with stirring at room temperature for 12 h. Subsequently, the Fe_3O_4 nanoparticles were added into the mixture and dispersed sufficiently. The oil phase, composed of 20 mL of Span-80 dissolved in 120 mL of OP-10 emulsor, was mixed with the chitosan solution and sonicated for 40 min to ensure homogeneous dispersion of the colloidal solution. Then, it was placed in 2 mL of 25% glutaraldehyde solution, which was kept in a water bath at 40℃ for 1 h. Next, the reaction was terminated using 50 mL of 1 mol L^{-1} NaOH to adjust the pH of the reaction system to 9–10. Finally, the product was filtered, washed for several times with ethanol, and double distilled water, respectively, and then dried under atmospheric conditions at 60℃. Furthermore, the CS@Fe_3O_4 was modified by CS_2 under 100 mL of 14 wt.% NaOH solution.

2.3. Characterization of chitosan encapsulated magnetic Fe_3O_4 nanoparticles

The morphologies and the sizes of the CMCS@Fe_3O_4 were examined using transmission electron microscopy (TEM) with a JEM-1230 (JEOL, Japan) transmission electron microscope at an accelerating voltage of 200 kV. Magnetic studies were made using vibrating sample magnetometer (Cryogenic Mini, J3426, UK). The Fourier transform infrared spectroscopy (FTIR) of the CMCS@Fe_3O_4 samples was recorded by an AVATAR 370-FTIR spectrometer (Thermo Nicolet, UAS) using KBr powder containing ca.1% (w/w) of sample.

2.4. The adsorption experiments of Cd(II) from aqueous solution

The kinetic study was performed in 500 mL flasks with 250 mL of Cd(II) at concentrations of

100–200 mg L^{-1} at 25˚C. The dosage of the CMCS@Fe_3O_4 was 0.25 g, and the flasks were agitated in a thermostatic shaker at 130 rpm. At predetermined time internals, the CMCS@Fe_3O_4 containing the adsorbed Cd(II) was easily separated using a magnet, and a spot of sample solution was withdrawn. The concentrations of Cd(II) were analyzed by a cadmium specific ion electrode (PXJ-1C, 307). The amount of the adsorbed Cd(II), q_t, was calculated by Eq. (1):

$$q_{\mathrm{t}} = \frac{(C_0 - C_{\mathrm{t}})V}{M} \tag{1}$$

where q_t is the Cd(II) capacity in the adsorbent at different intervals (mg g^{-1}), C_0 is the initial concentration of Cd(II) (mg L^{-1}), C_t is the liquid-phase Cd(II) concentration at different intervals (mg L^{-1}), V is the volume of solution (L), and M is the mass of adsorbent used (g).

In the pH and coexisting anions study, the experiments were executed at 25˚C for 1 h. The dosage of the adsorbent was 1,000 mg L^{-1}. The pH was adjusted by 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} NaOH solutions.

For the equilibrium study, the flasks, containing 0.01 g of the CMCS@Fe_3O_4 and 10 mL of the Cd(II) solution, were agitated in a thermostatic shaker at 25˚C until equilibrium was approached. The amount of the adsorbed Cd(II), q_t, was calculated by Eq. (1).

For the CMCS@Fe_3O_4 desorption experiments, the used adsorbent (0.05 g) was resuspended in 10 mL of different eluents at 25˚C for 30 min, 150 rpm, and separated by a magnetic field. Then the adsorbent was thoroughly washed with distilled water several times, and dried at 80˚C for 2 h. Finally, the CMCS@Fe_3O_4 was used in the next cycle of adsorption process.

3. Results and discussion

3.1. Characterization of the CMCS@Fe_3O_4

The morphologies and sizes of the magnetic Fe_3O_4 and CMCS@Fe_3O_4 were examined by TEM. Fig. 1(a) and (b) show typical TEM images of the resulting Fe_3O_4 nanoparticles with regular spherical morphology and smooth surfaces. Theses spheres have uniform size of about 500 nm and disperse well. The CMCS@Fe_3O_4 core–shell structures were synthesized

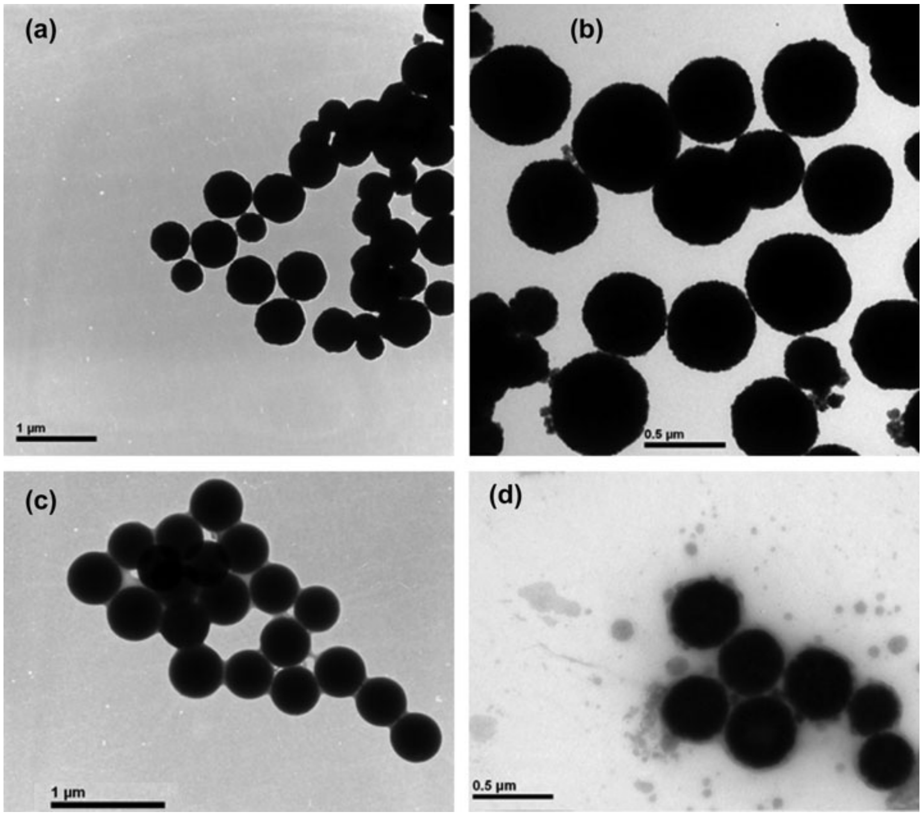

Fig. 1. ((a) and (b)) TEM images of the magnetic Fe_3O_4 at low and high magnification. ((c) and (d)) TEM images of the CMCS@Fe_3O_4 at low and high magnification.

by coating a chitosan shell on the magnetic Fe_3O_4 spheres by water-in-oil emulsification. As shown in Fig. 1(c) and (d), the two representative TEM images of the CMCS@Fe_3O_4 core–shell spheres possess good dispersibility, and they are composed of roughly 450 nm core of Fe_3O_4 and 50 nm shell of cross-linked-chitosan, with about 500 nm overall outer diameter. Furthermore, the magnetic hysteresis loop of CMCS@Fe_3O_4 at room temperature is given in Fig. 2. The high coercive field (H_c) of 100 Oe, remanent magnetization (M_r) of 5 emu/g, and shape of the loop indicate the ferromagnetic nature. Magnetization value (M_s) of 29 emu/g is obtained at a maximum applied field of 5,000 Oe. Separation test by a magnet (inset of Fig. 2) confirmed that CMCS@Fe_3O_4 can be easily separated in spite of its low M_s.

Additionally, FTIR spectroscopy was used to investigate the surface functional groups of the CS@Fe_3O_4 before and after modified by CS_2 (Fig. 3). The peaks at 3,418 cm^{-1} (O–H stretching vibration), 2,920 cm^{-1} (C–H stretching vibration), 1,609 cm^{-1} (assigned to the –NH gruoup in amine), 1,246 cm^{-1} (C–N stretching vibration), 1,066 cm^{-1} (asymmetric stretching of the C–O–C bridge), were similar to previously reported spectra of chitosan [32,33]. However, peaks around 880 and 666 cm^{-1}, which are related to –SH and C–S groups, respectively, appeared to be sharper after the CS_2 modification. The results confirm the success of modification.

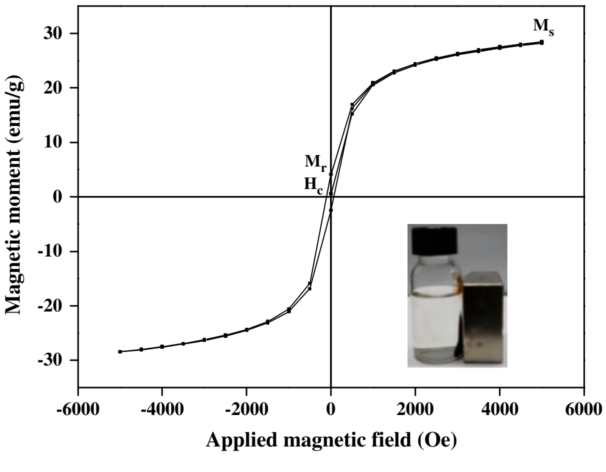

Fig. 2. Room temperature magnetization loop of CMCS@Fe_3O_4 and optical photo (inset) of CMCS@Fe_3O_4 in the water solution separated by a magnet.

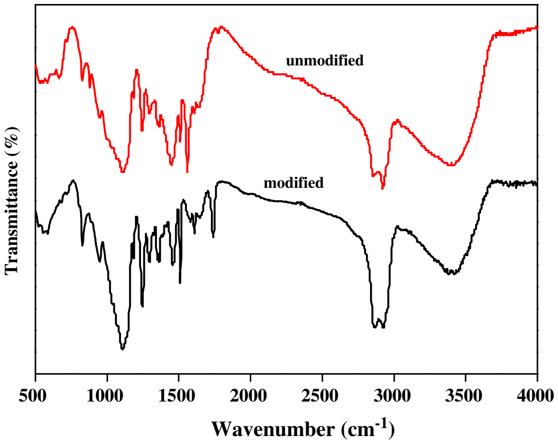

Fig. 3. FTIR spectra of the CS@Fe_3O_4 before and after modified by CS_2.

3.2. Adsorption kinetics

The kinetics behavior of the adsorption process was studied at different initial concentrations. The results from the kinetics experiments on the Cd(II) adsorption (Fig. 4(a)) shows that Cd(II) uptake on the CMCS@Fe_3O_4 was a rapid process. The amount of adsorption increased dramatically in the first 2.5 min for various initial concentrations and then increased slowly and reached the adsorption equilibrium gradually at 5, 15, and 35 min, corresponding to the initial concentrations of 100, 150, and 200 mg L^{-1}, respectively. This type of adsorption was typical because the high adsorption rate might be dependent upon the number of available adsorption sites on the surface of the adsorbent. As these sites became progressively occupied, the rate of adsorption might decrease. The increased amount of time to reach the adsorption equilibrium with an increase in the initial concentration of Cd(II) was because the competition for the active adsorption sites increased. However, the total amount of the Cd(II) that was adsorbed increased with the increasing initial concentrations. As shown in Fig. 4(a), the amount of the Cd(II) that was adsorbed onto the CMCS@Fe_3O_4 at equilibrium increased from 97.2 to 146.3 mg g^{-1} as the initial concentration of Cd(II) increased from 100 to 200 mg L^{-1}.

To understand the adsorption process, the most common kinetics models, including pseudo-first-order and pseudo-second-order, were applied for the batch adsorption experiment to study the adsorption type and mechanism. Their equations are expressed as follows:

$$q_t = q_e[1 - \exp(-k_1 t)] \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_e} \tag{3}$$

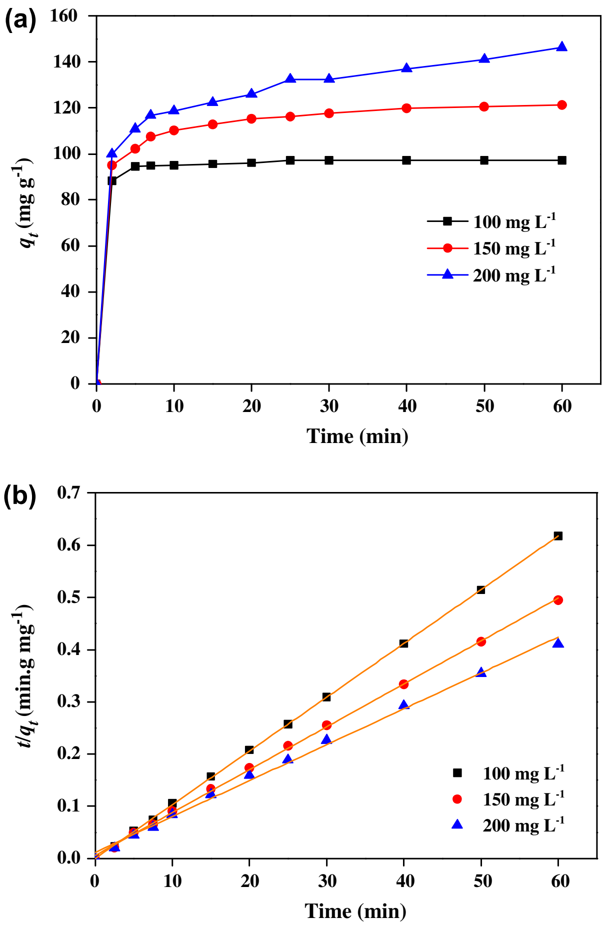

Fig. 4. Adsorption kinetics (volume 250 mL, $T = 25$℃, adsorbent dosage 0.25 g). (a) Time profile of the CMCS@Fe_3O_4 (initial concentration ranging from 100 to 200 mg L^{-1}) and (b) fitting curve of the pseudo-second-order model for the CMCS@Fe_3O_4.

where q_t (mg g^{-1}) and q_e (mg g^{-1}) are the amount of Cd(II) absorbed on the adsorbent at time t and at equilibrium; k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the rate constants of the pseudo-first-order and pseudo-second-order model, respectively.

The kinetic parameters for adsorption of Cd(II) by the CMCS@Fe_3O_4 are given in Table 1. The correlation coefficient (R^2) of the pseudo-first-order model is less than that for the pseudo-second-order model for various initial concentrations. However, the pseudo-second-order rate constant correspondingly decreases with the initial Cd(II) concentrations from 100 to 200 mg L^{-1}. Moreover, the theoretical equilibrium adsorption capacities (q_e) was in better agreement with the experimental value of the pseudo-second-order model. The plot of t/q_t against t using the different initial concentrations of Cd(II) yielded straight lines (Fig. 4(b)) and showed excellent fitness. Therefore, the adsorption system of Cd(II) onto the CMCS@Fe_3O_4 followed the pseudo-second-order kinetics, suggesting chemical sorption as the rate-limiting step of the adsorption mechanism.

3.3. Adsorption isotherms

To optimize the design of the adsorption processes, it is important to establish the most appropriate correlation for the equilibrium curves. The adsorption isotherms describe the relationship between the equilibrium adsorption capacity of adsorbate adsorbed onto adsorbent at a constant temperature.

The adsorption equilibrium isotherm of Cd(II) onto the CMCS@Fe_3O_4 at 25℃ is presented in Fig. 5(a). It was shown that the adsorption capacity increased with the equilibrium concentration of Cd(II) in solution, progressively saturating the adsorbent for the CMCS@Fe_3O_4. The adsorption capacity of the CMCS@Fe_3O_4 for Cd(II) was about 197.8 mg g^{-1}. Additionally, the adsorption capacities $q_{\max}$ (mg g^{-1}) of other materials for heavy metals adsorption are presented in Table 2 [34–44]. It was found that either chitosan modified adsorbent or modified chtiosan adsorbent has great potential for Cd(II) or Hg(II) adsorption, as well as the CMCS@Fe_3O_4 prepared in the present study.

In this study, the data were analyzed with the linearized Langmuir and Freundlich isotherm models. The Langmuir model describes the monolayer adsorption on a structurally homogeneous adsorbent, and is based on the assumption that all the active sites are

Table 1
Parameters of the kinetics study of Cd(II) adsorption onto the CMCS@Fe_3O_4

	Pseudo-first-order equation			Pseudo-second-order equation		
Initial concentration (mg L^{-1})	q_e (mg g^{-1})	k_1 (min^{-1})	R^2	q_e (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
100	96.23	1.2416	0.9986	97.56	0.057	0.9999
150	114.78	0.8159	0.9727	121.92	0.010	0.9996
200	129.69	0.6306	0.9323	145.56	0.004	0.9968

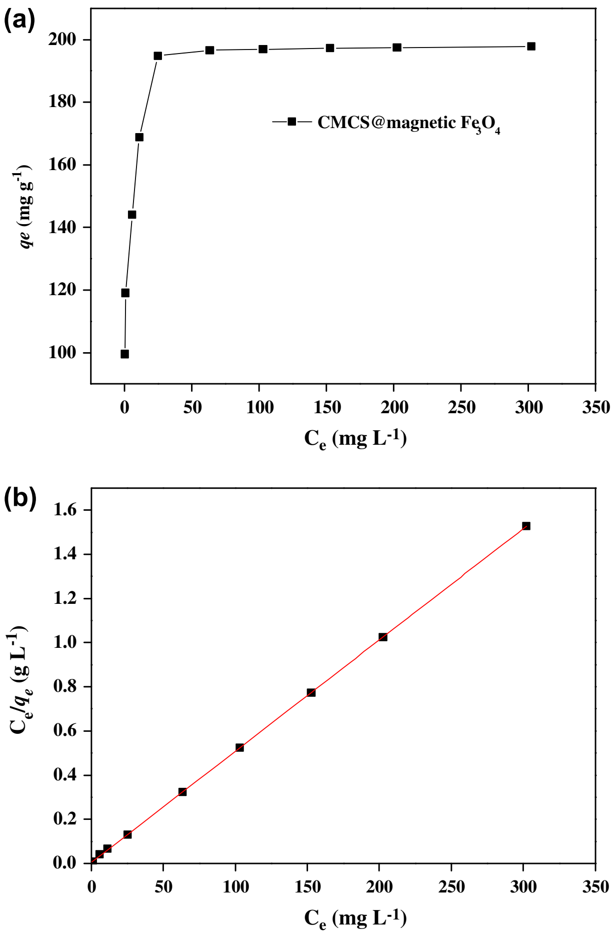

Fig. 5. (a) Equilibrium adsorption isotherm of Cd(II) by the CMCS@Fe_3O_4 and (b) fitting curve of the Langmuir isotherm model for the adsorption of Cd(II) on the CMCS@Fe_3O_4.

energetically equivalent and independent [45]. The linearized Langmuir equation is expressed as:

$$\frac{C_e}{q_e}=\frac{C_e}{q_m}+\frac{1}{bq_m} \tag{4}$$

where b and q_m (mg g^{-1}) are constants related to the capacity and energy of adsorption process. The Freundlich isotherm models is assumed that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation [46]. The isotherm model is expressed as:

$$\log q_e=\log K_f+\frac{1}{n}\log C_e \tag{5}$$

where K_f (mg g^{-1}) (L mg$^{-1})^{1/n}$ is a measure of adsorption capacity and n stands for the heterogeneity. The results showed that the Langmuir isotherm fitted the data better with high correlation coefficients ($R^2 = 0.9999$) than the Freundlich isotherm ($R^2 = 0.8812$). Fig. 5(b) illustrated that the experimental data of Cd(II) were in good agreement with the Langmuir mode, suggesting a monolayer adsorption.

Table 2
Adsorption capacities q_{max} (mg g^{-1}) of heavy metals by other adsorbents

Adsorbents	q_{max} (mg g^{-1})	Heavy metals	References
Blast furnace sludge	10.2	Cd(II)	[34]
Coir pith carbon	93.2	Cd(II)	[35]
Cassava waste	18.1	Cd(II)	[36]
Olive cake	10.6	Cd(II)	[37]
Wheat bran	0.7	Cd(II)	[38]
Rice husk	8.6	Cd(II)	[39]
Mixed magnetite–maghemite	2.7	Cd(II)	[40]
Bamboo charcoal	12.1	Cd(II)	[41]
Mungbean husk	35.4	Cd(II)	[42]
Graphite oxide–magnetic chitosan	397	Hg(II)	[43]
Chitosan–epichlorohydrin	331	Cd(II)	[44]
CMCS@Fe_3O_4	197.8	Cd(II)	Present study

3.4. Influence of pH

The pH factor is very important in the adsorption process for metal ion removal, which can affect the adsorbent surface charge and the degree of ionization. The influence of pH on adsorption of Cd(II) was studied by varying the pH from 2 to 6. Initial pH range was chosen in order to avoid metal solid hydroxide precipitation. From Fig. 6, it is clearly indicated that the adsorption capacity of Cd(II) on the CMCS@Fe_3O_4 increased with increasing pH. When the initial solution pH of Cd(II) was increased from 2 to 6, the adsorption capacity gradually increased from 75 mg g^{-1} to 95 mg g^{-1}. The functional groups namely –NH_2 and –SH of the CMCS@Fe_3O_4 are the potential binding sites for chemisorption of Cd(II) ions [47]. The chemisorption of Cd(II) ions and complex formation through –SH group of the adsorbent occur throughout the pH range from 2 to 6. However, at low pH values, the –NH_2 and –SH groups are to some extent in the protonated form, which lead to the unavailability of the functional groups for complexation with Cd(II), and H_3O^+ ions compete with Cd(II) ions to same binding sites on the adsorbent. As a result, the adsorption

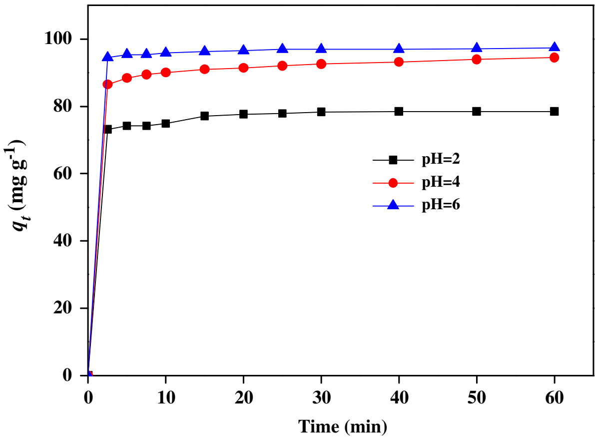

Fig. 6. Effect of the solution pH on Cd(II) adsorption by the CMCS@Fe_3O_4.

capacity of CMCS@Fe_3O_4 for Cd(II) ions is the lowest at pH 2. As pH increased, the extent of protonation form decreased gradually. Consequently, the degree of formation of coordination complex between Cd(II) ions and the adsorbent through $-NH_2$ and –SH groups increases. Thus, the adsorption capacity increases with increase in pH and reaches a maximum at pH 6.

3.5. Effect of the coexisting ions

The effect of the ionic strength is important in the study of Cd(II) adsorption onto adsorbents. The common cations, such as Na^+, K^+, Mg^{2+}, and Ca^{2+}, and the common anions, such as Cl^-, NO_3^-, and SO_4^{2-}, were used in the coexisting ions investigation. The influences of the coexisting ions on the Cd(II) adsorption capacity of the CMCS@Fe_3O_4 are shown in Fig. 7. As shown in Fig. 7(a) and (b), the common ions exerted no evident change in the Cd(II) adsorption capacity, even with the concentrations of the cations and anions varying from 50 to 200 mg L^{-1}, showing that the presence of the coexisting ions had no significant effect on the Cd(II) removal by the CMCS@Fe_3O_4. Therefore, there is no competitive effect between Cd(II) ions and the common ions for the available sites for the adsorption process. This result demonstrates the practicality for the application of the CMCS@Fe_3O_4.

3.6. Desorption and reuse of the CMCS@Fe_3O_4

Desorption studies help to elucidate the mechanism of adsorption and to regenerate the adsorbent, as to well as recover Cd(II) from the spent adsorbent. In this study, NaOH, HCl, EDTA, $NaHCO_3$, Na_2CO_3, and $Na_2S_2O_3$ were used as eluents to desorb the Cd(II) from the CMCS@Fe_3O_4. Regeneration of the CMCS@Fe_3O_4 saturated with Cd(II) was performed at 25℃ by using 0.1 mol L^{-1} above mentioned eluents and the regeneration efficiency for Cd(II) was below 50% (Fig. 8), which suggested that the adsorbed Cd(II) remained almost stable on the CMCS@Fe_3O_4 and chemisorption might be the major mode of Cd(II) removal by the adsorbent.

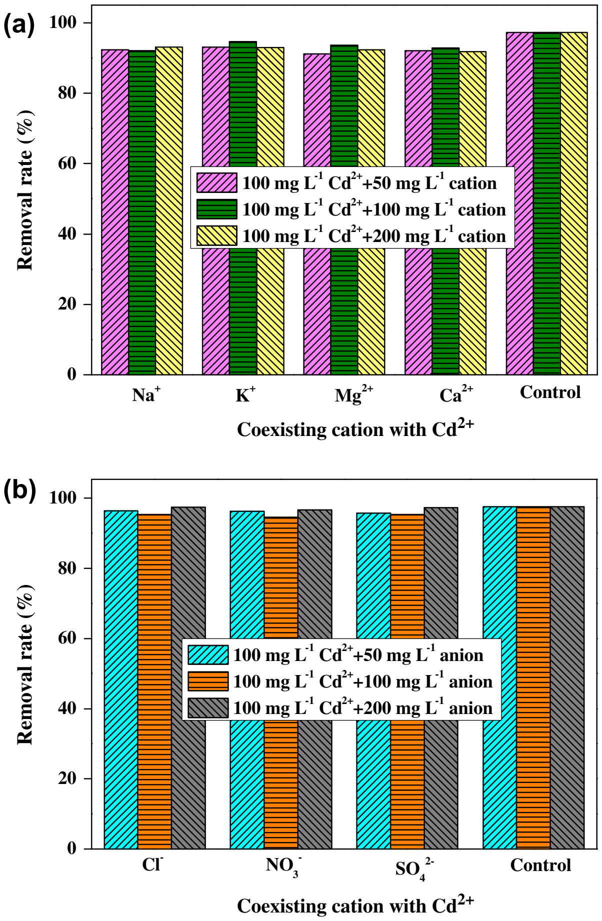

Fig. 7. Effect of the common ions (50 and 200 mg L^{-1}) on the removal ratio of Cd(II) by the CMCS@Fe_3O_4. (a) The common cations; (b) the common anions.

3.7. Mechanism of adsorption

The elucidation of the underlying adsorption mechanism is important for process design and control of the adsorption system. The kinetics models reveal that Cd(II) adsorption on the CMCS@Fe_3O_4 follows the second-order-rate model, suggesting that the overall process was controlled by chemisorption. In addition, through the analysis of FTIR spectra and effect of pH above, it can be concluded that the adsorption sites for Cd(II) are the nitrogen atoms of the amino group in

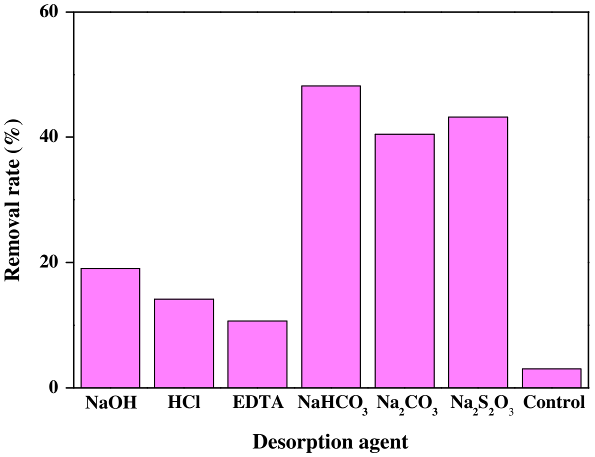

Fig. 8. Reuse of the CMCS@Fe_3O_4 regenerated by different eluents.

chitosan and the sulphur atoms of attached mercapto group. This conclusion was consistent with the studies by Chauhan and Sankararamakrishnan [48]. They concluded that thiol and amino group participate in the Pb adsorption process.

4. Conclusions

A novel CS_2-modified chitosan encapsulated magnetic Fe_3O_4 nanoparticles was prepared and characterized. CMCS@Fe_3O_4 showed a rapid process and a very high adsorption capacity for Cd(II) from aqueous medium. The adsorption kinetics followed the pseudo-second-order and the adsorption process obeyed both the Langmuir isotherms. The maximum adsorption capacity of CMCS@Fe_3O_4 for Cd(II) was 200 mg g^{-1} from the Langmuir isotherm. FTIR analysis showed that $-NH_2$ and –SH groups participated in the Cd(II) adsorption process by CMCS@magnetic Fe_3O_4. Moreover, the common coexisting ions had little effect on the adsorption of the Cd(II) onto the CMCS@Fe_3O_4. Considering that CMCS@Fe_3O_4 had superior adsorption capacity, along with its cost-effectiveness, it may be an excellent substitute for expensive adsorbents in removal of heavy metal from the industrial wastewater.

Acknowledgments

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