Preparation and characterization of iron oxide nanoparticles coated with chitosan for removal of Cd(II) and Cr(VI) from aqueous solution

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ABSTRACT

This study investigated the applicability of magnetite Fe_3O_4 nanoparticles coated with chitosan (CMNs) for the removal of some toxic heavy metals from simulated wastewater. Magnetic nanomaterials were synthesized using the co-precipitation method and characterized by transmission electron microscope, scanning electron microscope, X-ray diffraction, and Fourier transformer infrared spectroscopy. The magnetic properties of the prepared magnetic nanoparticles were determined by a vibrating-sample magnetometer. Batch experiments were carried out to determine the adsorption kinetics of Cr(VI) and Cd(II) by magnetic nanoparticles. It is noteworthy that CMNs show a highly efficient adsorption capacity for low concentration Cr(VI) and Cd(II) ions solution, which can reach 98% within 10 min.

Key words | adsorption, adsorption kinetics, chitosan, co-precipitation, heavy metals, magnetic nanoparticles

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INTRODUCTION

Heavy metal pollution of wastewater has steadily increased over recent years as a result of overpopulation and expansion of industrial activities. Metal pollution has a harmful effect on biological systems and does not undergo biodegradation (Jang *et al.* 2008). Cr(VI) is recognized as a human genotoxic carcinogen that can be easily absorbed into the body through the digestive system, respiratory tract and skin contact. Cadmium in waste effluents is generated by several anthropogenic sources. It is one of the trace elements that is considered to be an essential nutrient required by the human body. However, investigation has revealed that high dosages can lead to health problems such as lesions in the central nervous system, and liver and kidney damage, or Wilson's disease. It is therefore important to remove excess cadmium in industrial effluents before discharging it into surface water and groundwater, for the protection of human health and the environment (Wang *et al.* 2012).

Adsorption has proved to be the most effective method for removal of heavy metal, especially for effluents with moderate and low concentrations (Manohar *et al.* 2006). The efficiency of adsorption depends on many factors, including the surface area, pore size distribution, polarity, and functional groups of the adsorbent (Ewecharoena *et al.* 2009). Metal oxide particles enjoy a unique position having a significant amount of surfaces, thus, attracting much interest as potential adsorbents because of their exclusive properties and potential application (Imtiaz & Rafique 2011). Compared to the traditional adsorbents, magnetic nanoparticles not only can be manipulated or recovered rapidly by an external magnetic field but also possess quite good performance owing to highly efficient specific surface area and the absence of internal diffusion resistance (Xu & Zhao 2007).

Iron oxide nanoparticles tend to aggregate into micron-sized or larger particles because of direct inter-particle interactions such as van der Waals forces and magnetic interactions. Aggregation reduces the specific surface area and the interfacial free energy, thereby decreasing particle reactivity and losing the unique property of nanoparticles (Palanisamy *et al.* 2013). To prevent agglomeration of nanoparticles, various stabilizers have been found effective for stabilizing nanoparticles, including carboxylic acids (Kataby *et al.* 1999), and polymers (Ditsch *et al.* 2005; Fu *et al.* 2011). Chitosan with presence of amino groups can be used for functionalization. It is a suitable kind of polymer

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to be used to modify the magnetic nanoparticles (MNPs) (Wang *et al.* 2008).

The chitosan magnetic nanocomposites (CMNs) not only have strong metal chelating tendency due to presence of chitosan but also possess additional features of nanomaterials such as large surface area, dispersed nature and rigid membranes. In addition, due to the magnetic nature of CMNs, they can easily be separated from the sorption system by using a magnetic field of appropriate strength (Namdeo & Bajpai 2008). The wide usefulness of CMNs is essentially a result of their high specific surface area, high chemical and mechanical stabilities, and a variety of surface and structural properties (Zhou *et al.* 2006).

The present study is designed with the objective to synthesize the Fe_3O_4 nanoparticles coated with chitosan (CMNs) followed by their application as potential adsorbent for the removal of some toxic heavy metals such as Cd(II) and Cr(VI) from aqueous solutions. Batch adsorption is applied as the decontamination method for industrial pollutants. The effect of influent concentration, contact time, and the pH of the aqueous solutions was studied.

MATERIALS AND METHODS

Chemicals and reagents

$FeCl_3.6H_2O$, $FeCl_2.4H_2O$ ($>99\%$), and chitosan with deacetylation $\geq 85\%$ were obtained from Sigma Aldrich Co., Germany. Sodium hydroxide (NaOH) bullets and acetic acid (96%) are chemical grade. K_2CrO_7 and $CdSO_4$ are analytical grade.

Preparation and characterization of adsorbent

Preparation of CMNs

Firstly, iron oxide nanoparticles were synthesized using co-precipitation according to the method of Amin *et al.* (2010). $FeCl_2.4H_2O$ and $FeCl_3.6H_2O$ [Fe^{2+}:$Fe^{3+} = 1{:}2$] were dissolved in about 50 mL deionized water, and the solution was thoroughly stirred for 10–15 min while heating the solution to 80 °C. Then, the pH of the solution was increased slowly to 11 by adding 1.0 M NaOH solution until the appearance of black precipitate. To ensure the complete growth of the nanoparticle crystals, the reaction was carried out for 30 min at 80 °C under constant stirring and bubbling of N_2 gas. The chemical reaction of Fe_3O_4 precipitation is expected as follows:

$$FeCl_2.4H_2O + 2FeCl_3.6H_2O + 8NaOH \rightarrow Fe_3O_4 + 8NaCl + 20H_2O \quad (1)$$

Black Fe_3O_4 particles were decanted by a permanent magnet and cleaned by deionized water several times.

For preparation of CMNs, the magnetic nanoparticles solution (containing 0.2 g) was added very slowly to a 5% chitosan solution prepared using a 2% aqueous acetic acid solution. During this process chitosan molecules were adsorbed on the surface of the nanoparticles and a homogeneous dark brown suspension was obtained. To obtain the pure and neutral products, synthesized materials were washed with ultrapure water several times and then in ethanol. The particles were finally dried in a vacuum oven at 70 °C.

Characterization of CMNs

The size and morphology of CMNs were determined by transmission electron microscopy (TEM, JEOL-100 CX). Elemental information and structure were investigated using an X-ray diffractometer (Shimaduz, XRD-7000, Maxima, Japan) operated at a voltage of 30 kV and a current of 30 mA with CuKα radiation (=1.54 Å) and analysed between 5 and 100° (2θ).The Fourier transformer infrared spectroscopy (FTIR) spectra of CMNs were recorded on a FTIR spectrophotometer (Shimazdu IR Prestige-21) with a diffuse reflectance mode (DRS-8000) attachment. All measurements were carried out in the range of 400–4,000 cm^{-1} at a resolution of 4 cm^{-1}.The degree of magnetism of the MNPs and CMNs was evaluated using a vibrating-sample magnetometer (VSM-9600-1DSM-LDG-USA).

Batch adsorption experiments

A time-dependent batch experiment was conducted for the study of adsorption of Cr(VI) and Cd(II) using CMNs. For adsorption kinetic studies, the experiment was carried out in pH 2.5 and 6.5 solution using CMNs as adsorbent for adsorption of Cr(VI) and Cd(II), respectively. For Cr(VI) and Cd(II) adsorption, the experiment was carried out in a 50 mL batch reactor at four different initial concentrations (10, 20, 40 and 80 mg/L). The adsorbent mass was fixed at 0.1 g. The reactor was stirred with a magnetic stirrer operated at 400 rpm at 22 °C. At predetermined time intervals, 5 mL samples were taken from the reactor for metal measurements, CMNs were magnetically separated from the aqueous solution, and the residual concentrations of metal ions in the aliquot were determined using an atomic absorption spectrophotometer (Thermo Scientific ICE 3500).The adsorption capacity (q_e, mg/g) was calculated based on the change of Cd(II) and Cr(VI) concentration in aqueous solutions before and after adsorption, the volume of aqueous solution and the weight of magnetic nanoparticles according to Equation (2):

$$q_e = \frac{C_i - C_e}{W}.V \tag{2}$$

where q_e is the adsorption capacity (mg/g), C_i and C_e are the initial and equilibrium concentrations (mg/L), W is the mass of the adsorbent (g), and V is the volume of solution (L). The removal efficiency (%) can be calculated from Equation (3):

$$\%\ \text{removal} = \frac{C_i - C_e}{C_i} \times 100 \tag{3}$$

RESULTS AND DISCUSSION

Characterization of magnetic nanoparticles

The TEM image of CMNs (Figure 1(a)) showed that the structure of chitosan-coated magnetite nanoparticles was loose; without agglomeration, the average diameter of such a structure was 13 nm. The surface and textural morphology of CMNs was studied using a scanning electron microscope as shown in Figure 1(b). The result showed that the synthesized magnetic nanoparticles were spherical in shape and were aggregated, which resulted in a rough surface and porous structure.

The structure identity and purity of the prepared nanoparticles were verified by X-ray diffraction (XRD). The XRD analysis of CMNs is shown in Figure 2. The diffraction peaks at 2θ values of 30.10°, 35.45°, 37.01°, 43.09°, 53.46°, 56.98°, 62.75° and 65.79° can be ascribed to the reflection of the (220), (311), (222), (400), (422), (511), (440) and (533) planes of the cubic Fe_3O_4, respectively. The strong and sharp peaks indicate that MNPs are well crystallized. It is clear that only the phase of Fe_3O_4 is detectable. It could also been learned that particle size is quite small from the relatively wide half-peak breadth. The average particle size was calculated to be 11.68 nm using Sherrer's equation ($D = K\lambda/\beta\cos\theta$), which agrees with that obtained by TEM.

FTIR analysis was also performed to reveal the surface nature of CMNs as shown in Figure 3. The spectra display a broad band at 580 cm^{-1}, which is believed to be associated with the stretching vibrations of the tetrahedral groups (Fe^{3+}–O^{2-}) for Fe_3O_4.The presence of magnetite nanoparticles can be seen by absorption bands at 578.371, 690.989 and 726.075 cm^{-1}. The bands at 3,849, 3,440, 2,917 and 2,057 cm^{-1} indicated the presence of stretching O—H vibrations. Other peaks at 1,627, 1,440 and 1,020 cm^{-1} were due to C = O, $(CH_2)_n$ and C—O, respectively. Therefore, the composition of CMNs was magnetite.

The magnetic properties of magnetic absorbents directly influence the call back efficiency. The hysteresis loop of Fe_3O_4 nanoparticles and CMNs at room temperature is shown in Figure 4. As can be seen, no remanence or coercivity was observed in the magnetic loop. This phenomenon proved that magnetic nanoparticles made from this study are superparamagnetic. The saturated magnetization of pure MNPs was 60.3 emu/g while that for CMNs was 27 emu/g. This superparamagnetic property of the magnetic

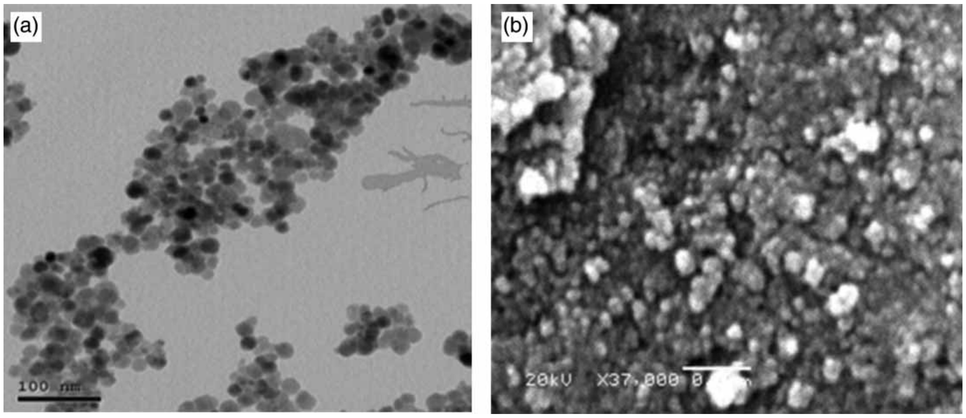

Figure 1 | (a) TEM micrographs and (b) scanning electron microscope image for CMNs.

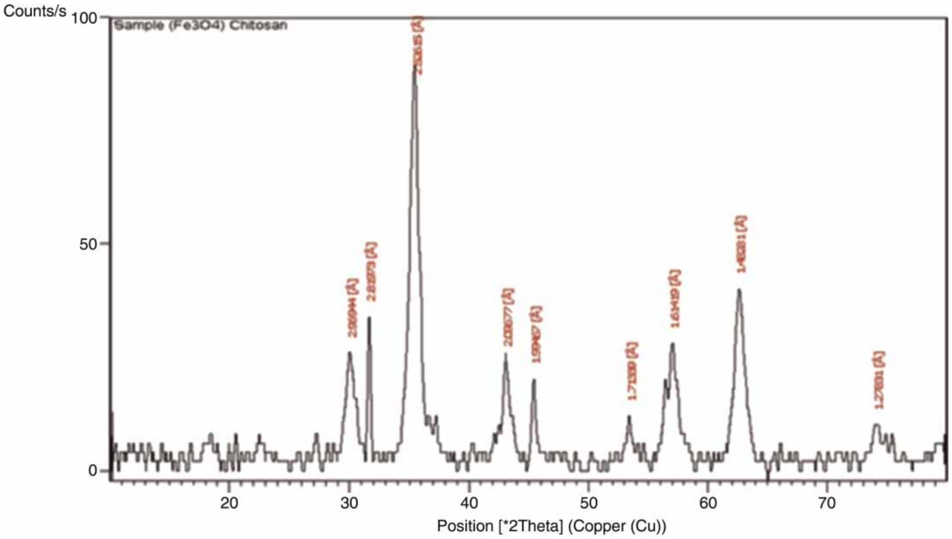

Figure 2 | XRD pattern for CMNs.

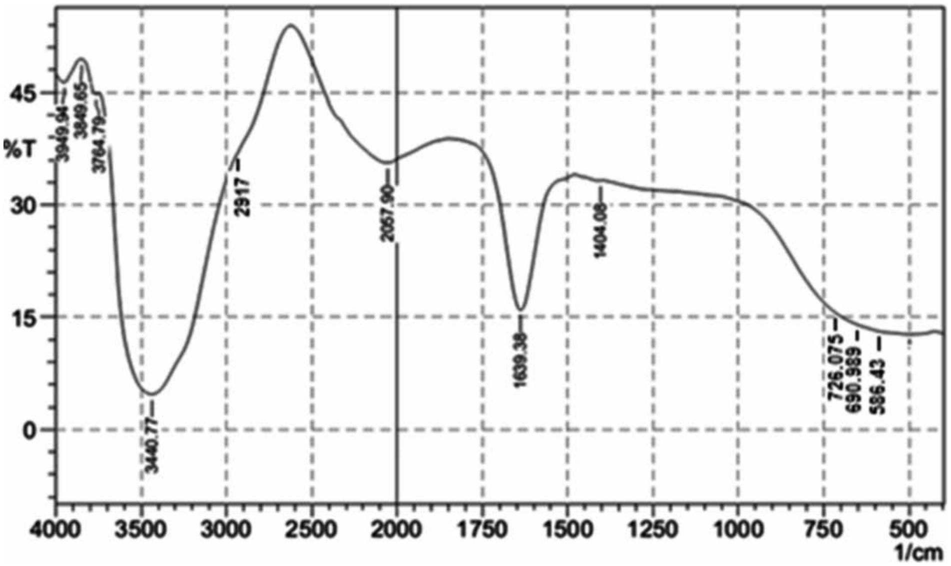

Figure 3 | FTIR for CMNs.

nanoparticles makes them very susceptible to magnetic fields, and therefore the nanoparticles separate easily from solution.

Removal of heavy metals from aqueous solution using magnetic nanoparticles

Effect of pH

The adsorption of Cr(VI) and Cd(II) was carried out at pH 2.5 and 6.5, respectively using CMNs as adsorbent. The dependence of metal removal on the pH can be explained from the perspective of surface chemistry in an aqueous phase; the surfaces of metal oxides are generally covered with hydroxyl groups that vary in form at different pH levels. The surface charge is neutral at the point of zero charge, pHpzc, which is 5.8 for magnetite (Hu *et al*. 2004). Below the pHpzc, the adsorbent surface is positively charged, and anion adsorption occurs by simple electrostatic attraction. Above the pHpzc, the adsorbent surface is negatively charged, and cation adsorption occurs. With an increase in pH, the uptake of Cr(VI) ions decreases,

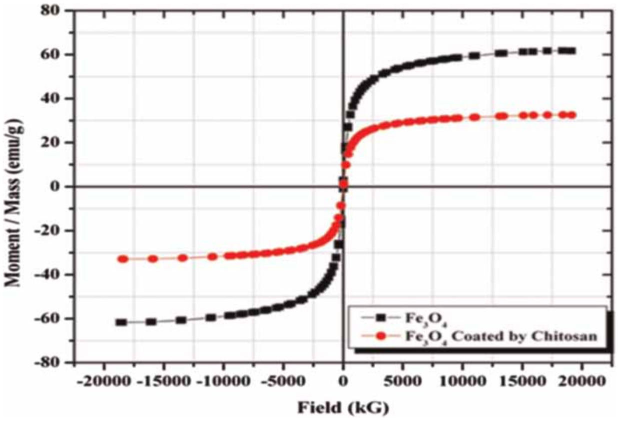

Figure 4 | Magnetic moments of CMNs with applied magnetic field.

which is apparently due to the higher concentration of OH^- ions present in the mixture, which compete with Cr(VI) species (CrO_4^{2-}) for adsorption sites. On the other hand, as the adsorption surface is negatively charged (pH < pHpzc), increasing electrostatic repulsion between negatively charged Cr(VI) species and negatively charged nanoparticles would also result in a release of the adsorbed $HCrO_4^-$ and CrO_4^{2-}. As far as Cd(II) is concerned, the increase in metal removal with pH is due to a decline in competition between proton and metal species for surface sites, thereby decreasing in positive surface charge and resulting in a lower Coulombic repulsion of the adsorbed metal. It was found that the optimal pH for Cd^{2+} ions removal was 6.5. At lower pH, competition between H^+ and Cd^{2+} ions could thus explain the weak adsorption in acid medium. At pH 6.5, cadmium adsorption was increased because of OH^- enhancement, which suggested that ion exchange between Cd^{2+} and H^+ may play a role during this pH range (Vik *et al.* 1984).

Removal of Cr(VI)

Adsorption kinetics of CMNs

Since pH 2.5 and 6.5 are the optimal conditions for Cr(VI) and Cd(II) adsorption, respectively, adsorption kinetics for Cr(VI) and Cd(II) were obtained at their optimal pH. The adsorption of the Cr(VI) metal ions onto CMNs as a function of contact time and initial concentration is shown in Figure 5. It was observed that the adsorption increased with increasing contact time. The adsorption increased rapidly during the first 10 min, and thereafter the adsorption remained constant. An exciting experimental result was obtained in that the removal efficiency of CMNs for Cr(VI) ions nearly reached 98%.This may have been due to the fact that the presence of chitosan reduces the particle aggregation and so increases the adsorption surface; in addition the presence of chitosan increases the functional groups (NH_2) which are responsible for metal adsorption. This result shows that the CMNs can treat wastewater with high concentrations of heavy metal ions.

Isotherm adsorption study

Langmuir model. The Langmuir isotherm is expressed as

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{K_L q_{max}} \frac{1}{C_e} \qquad (4)$$

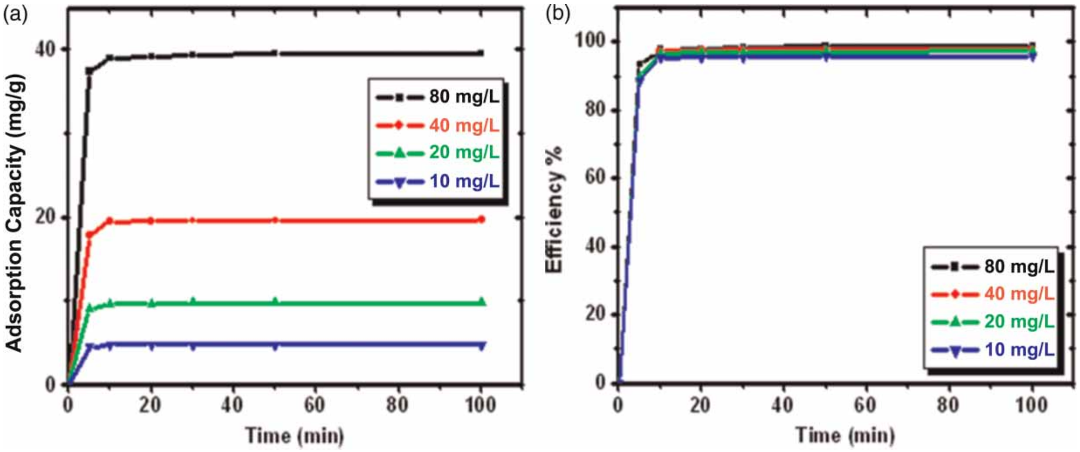

Figure 5 | (a) Adsorption capacities (mg/g) and (b) the removal efficiency (%) of CMNs for different concentrations (10, 20, 40 and 80 mg/L) of Cr(VI) at pH 2.5.

Table 1 | Adsorption isothermal constants for adsorption of Cr(VI) calculated from Langmuir model and Freundlich model at pH 2.5

	Langmuir model				Freundlich model		
Adsorbent	q_{max}	K_L	R_L	R^2	K_F	$1/n$	R^2
CMNs	39.5	0.013	0.0998	0.999	1.99	1.018	0.954

where q_{max} is the maximum amount of adsorption with complete monolayer coverage on the adsorbent surface (mg/g), and K_L is the Langmuir constant related to the energy of adsorption (L/mg). The Langmuir constants K_L and q_{max} can be determined from the linear plot of $1/C_e$ versus $1/q_e$. The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the equilibrium parameter R_L that is defined by the following equation:

$$R_L = \frac{1}{(1 + K_L C_0)} \tag{5}$$

where C_0 is the initial concentration. The value of R_L is calculated from the above expression. The nature of the adsorption process is either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

Freundlich adsorption isotherm. The Freundlich adsorption isotherm can be expressed as

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{6}$$

where K_F and n are the Freundlich adsorption isotherm constants, being indicative of the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively. Table 1 shows the calculated values of the Freundlich and Langmuir models' parameters. The comparison of correlation coefficients (R^2) of the linearized form of both equations indicates that the Langmuir model yields a better fit for the experimental equilibrium adsorption data than the Freundlich model. This suggests monolayer coverage of the surface of CMNs by Cr(VI).

Cd(II) removal

Adsorption kinetics of CMNs at pH 6.5

The removal of Cd(II) from aqueous solution using CMNs as a function of contact time was investigated. The time to reach equilibrium was 10 min with different concentrations of Cd(II) ions. Figure 6 shows the adsorption capacity (mg/g) and the removal efficiency (%) of CMNs for different concentrations of Cd(II) at pH 6.5. The removal efficiency of Cd(II) reached 99% at pH 6.5; thus, the selective removal of Cd(II) using CMNs can be verified by controlling the pH of the solution. This result shows that the CMNs can treat wastewater with high concentrations of heavy metal ions.

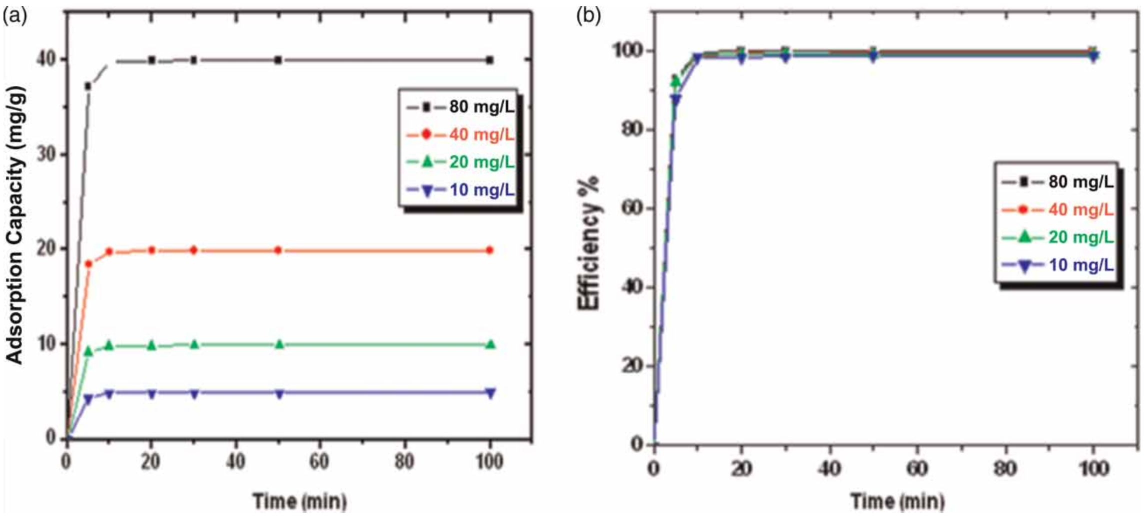

Figure 6 | Adsorption capacities (mg/g) (a) and the removal efficiency (%) (b) of CMNs for different concentrations (10, 20, 40 and 80 mg/L) of Cd(II) at pH 6.5.

Table 2 | Adsorption isothermal constants for adsorption of Cd(II) calculated from the Langmuir and Freundlich models at pH 6.5

	Langmuir model				Freundlich model		
Adsorbent	q_{max}	K_L	R_L	R^2	K_F	1/*n*	R^2
CMNs	39.6	0.012	0.0998	0.999	2	1.003	0.984

Isotherm adsorption study

The Langmuir and Freundlich models were applied for isothermal adsorption study of Cd(II)at pH 6.5. Table 2 shows the calculated values of the Freundlich and Langmuir models' parameters.

All the R_L values for the adsorption of Cr(VI) and Cd(II) onto CMNs, as listed in Tables 1 and 2, are in the range of 0–1, indicating that the adsorption process is favourable. All the $1/n$ values are >1, indicating that the isotherm is concave and that the presence of more adsorbate in the adsorbent enhances the free energy of adsorption (Wang *et al*. 2012).

CONCLUSION

Magnetic nanomaterials as sorbents are useful tools for heavy metal removal, due to their unique structure and surface characteristics. These materials are capable of removing heavy metal ions at low concentration, with high selectivity and adsorption capacity. Batch removal of toxic hexavalent chromium and divalent cadmium from aqueous solution using CMNs was investigated. The Cr(VI) and Cd(II) uptake was dependent on the equilibrium pH and their concentrations, with pH 2.5 and 6.5 being the optimum pH for Cr(VI) and Cd(II) removal, respectively. The maximum efficiencies of Cr(VI) and Cd(II) removal were 98 and 99%, respectively. The experimental adsorption data observed agreed with Langmuir and Freundlich isotherm models. A study on the removal of heavy metals using MNPs can provide a practical solution for wastewater treatment, to reduce waste discharges, recover useful materials, and reduce pollution.

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