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Fe_3O_4/cyclodextrin polymer nanocomposites for selective heavy metals removal from industrial wastewater

Abu Zayed M. Badruddoza[a,*], Zayed Bin Zakir Shawon[a], Tay Wei Jin Daniel[a], Kus Hidajat[a], Mohammad Shahab Uddin[b]

[a] Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117576, Singapore
[b] Department of Biotechnology Engineering, Faculty of Engineering, International Islamic University Malaysia, P. O. Box 10, 50728 Kuala Lumpur, Malaysia

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ABSTRACT

In this work, carboxymethyl-β-cyclodextrin (CM-β-CD) polymer modified Fe_3O_4 nanoparticles (CDpoly-MNPs) was synthesized for selective removal of Pb^{2+}, Cd^{2+}, Ni^{2+} ions from water. This magnetic adsorbent was characterized by TEM, FTIR, XPS and VSM. The adsorption of all studied metal ions onto CDpoly-MNPs was found to be dependent on pH, ionic strength, and temperature. Batch adsorption equilibrium was reached in 45 min and maximum uptakes for Pb^{2+}, Cd^{2+} and Ni^{2+} in non-competitive adsorption mode were 64.5, 27.7 and 13.2 mg g^{-1}, respectively at 25 °C. Adsorption data were fitted well to Langmuir isotherm and pseudo-second-order models for kinetic study. The polymer grafted on MNPs enhanced the adsorption capacity because of the complexing abilities of the multiple hydroxyl and carboxyl groups in polymer backbone with metal ions. In competitive adsorption experiments, CDpoly-MNPs could preferentially adsorb Pb^{2+} ions with an affinity order of $Pb^{2+} \gg Cd^{2+} > Ni^{2+}$ which can be explained by hard and soft acids and bases (HASB) theory. Furthermore, we explored the recyclability of CDpoly-MNPs.

1. Introduction

Water contamination due to toxic heavy metals has attracted significant attention because of their detrimental effects on the environment and human health. Heavy metal ions such as lead (Pb^{2+}), cadmium (Cd^{2+}), and nickel (Ni^{2+}) are toxic and carcinogenic at even relatively low concentrations. Heavy metals are non-biodegradable and they can accumulate in living organisms. They are generally discharged to the environment from various industrial activities such as smelting, electroplating, painting, mining, leather tanning, alloy and battery manufacturing, etc., posing a significant threat to the environment and public health (Ozay, Ekici, Baran, Aktas, & Sahiner, 2009). Therefore, reliable methods are necessary for the removal of heavy metals from aquatic environment.

A great deal of effort has been devoted to the effective removal of heavy metal ions from environmental matrices. Various treatment techniques available for the removal of toxic metals are adsorption, chemical precipitation, ion exchange, coagulation, reverse osmosis, electrolysis and membrane process, etc. (Gupta & Suhas, 2009; Gupta, Rastogi, Saini, & Jain, 2006; Heidari, Younesi, & Mehraban, 2009; Xu et al., 2011). However, among all these methods, adsorption is considered an effective, efficient and economic method for the removal of pollutants from wastewater (Ali & Gupta, 2007; Feng et al., 2010; Gupta & Nayak, 2012; Gupta & Rastogi, 2009; Gupta, Mittal, Kurup, & Mittal, 2006; Gupta, Jain, Mittal, Mathur, & Sikarwar, 2007; Gupta, Ali, & Saini, 2007a; Gupta, Jain, & Varshney, 2007; Gupta, Rastogi, & Nayak, 2010a; Gupta, Rastogi, & Nayak, 2010b; Gupta, Gupta, Rastogi, Agarwal, & Nayak, 2011; Mittal, Gupta, Malviya, & Mittal, 2008). This technique can be applied frequently on large scale, as it can handle fairly large flow rates, producing a high quality of water without producing notorious sludge, residual contaminants, etc. (Gupta, Ali, & Saini, 2007b; Gupta, Jain, et al., 2011). Moreover, adsorption is universal and fast in nature and applicable for the removal of organic and inorganic pollutants even at low concentration. Recent research focused on adsorbents such as activated carbons, zeolites, clays, biomass and polymeric materials for the removal of heavy metals (Crini, 2005). In wastewater treatment, especially in the removal of heavy metals, natural polymers, mainly polysaccharides such as chitosan, starch and its derivatives, cyclodextrins, have attracted particular attentions, due to their physico-chemical characteristics, low cost, availability and the presence of various reactive groups on the backbone chain (Crini, 2005). Natural polymers present, however some disadvantages that limit their use in practical wastewater treatment applications, such as their low surface area and difficult separation from the liquid phase. Magnetic sorbents on the other hand, have a relatively high surface area and are easy to separate and manipulate in complex multiphase systems with an external magnetic field. Their advantages prevail over the difficulties normally associated

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[*] Corresponding author. Tel.: +65 6516 2099; fax: +65 6779 1934.
E-mail address: cheazmb@nus.edu.sg (A.Z.M. Badruddoza).

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with other polymeric powdered adsorbents. A step further in developing adsorbents with superior properties would be the inclusion of magnetic particles into natural polymers, thus combining the advantages of both materials. It was reported that magnetic nanomaterials functionalized with biopolymers such as chitosan (Chang & Chen, 2005; Tran, Tran, & Nguyen, 2010; Zhou, Nie, Branford-White, He, & Zhu, 2009), alginate (Bée, Talbot, Abramson, & Dupuis, 2011; Lim, Zheng, Zou, & Chen, 2009), gum arabic (Banerjee & Chen, 2007), cellulose (Zhu et al., 2011), etc. have been used for the removal of toxic metals from aqueous solution. Recently, we have synthesized carboxymethylated β-cyclodextrin modified magnetic nanoparticles which could remove Cu^{2+} ions effectively from water based on complexation reactions between metal ions and carboxyl groups (Badruddoza, Tay, Tan, Hidajat, & Uddin, 2011). Cyclodextrins (CDs) are cyclic oligosaccharides consisting of 6 (α), 7 (β), 8 (γ) glucopyranose units linked together via α (1–4) linkages. They form a torus-shaped ring structure which contains an apolar cavity with primary hydroxyl groups lying on the outside and secondary hydroxyl groups inside (Szejtli, 1998). This renewable and biodegradable compound has the ability to complex various metal ions and this complexation ability can be improved by modifying CDs with suitable functional groups through esterification, oxidation reactions and cross-linking of hydroxyls outside the interior cavity (Norkus, 2009). Though β-CD/metal complexation has been used in water decontamination technique, particularly in the removal of heavy metals (Crini & Peindy, 2006; Mahlambi, Malefetse, Mamba, & Krause, 2010), very little attention has been paid to the adsorption selectivity of heavy metal ions on these cyclodextrin based adsorbents.

In this work, with an effort to improve the metal complexing ability and selectivity of cyclodextrin, carboxymethyl-β-cyclodextrin (CM-β-CD) polymer was synthesized and used to graft on the Fe_3O_4 nanoparticles surface (Scheme 1). The ligands on the crosslinked β-CD polymers were predominantly carboxyl groups, along with hydroxyl groups. This polymer grafted magnetic nanoparticles (CDpoly-MNPs) were used as easily separable, recyclable and highly selective nanoadsorbent for the effective removal of metal ions, i.e., Pb^{2+}, Cd^{2+} and Ni^{2+} ions from contaminated water. The adsorption characteristics of CDpoly-MNPs for the removal of heavy metal ions from aqueous solution were studied in non-competitive and competitive adsorption modes. Efforts were devoted to elucidate adsorption selectivity and mechanism and to explore the recyclability of these nanoadsorbents.

2. Materials and methods

2.1. Chemicals

Iron (II) chloride tetrahydrate (99%), iron (III) chloride hexahydrate (98%), chloroacetic acid (99%) was purchased from Alfa Aesar (MA, USA). Ammonium hydroxide (25%), lead(II) nitrate, cadmium(II) nitrate and nickel(II) nitrate were purchased from Merck (MA, USA). β-Cyclodextrin (99%) was obtained from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. All other chemicals were of analytical grade and used as received without further purification. The water in this work was Milli-Q ultrapure water.

2.2. Synthesis of CM-β-CD polymer

CM-β-CD polymer was prepared following the procedure of literature (Fernández et al., 2004), with the detailed description as follows: β-cyclodextrin (5 g) was dissolved in 50 mL of 10% (w/v) NaOH and 10 mL of epichlorohydrin was added. The system was vigorously stirred for 8 h before another 5 mL of epichlorohydrin was added with stirring and the mixture kept overnight at room temperature. The solution was concentrated to about 15 mL and precipitated by addition of cold ethanol (500 mL). The gummy precipitate was crushed several times with ethanol in a mortar until a fine precipitate was obtained. The precipitate was then washed again with ethanol and acetone and dried under high vacuum overnight. The yield of β-CD/epichlorohydrin co-polymer was 80%. Two grams of the above polymer was further dissolved in 50 mL 5% (w/v) NaOH and 2 g of monochloroacetic acid was added. The system was vigorously stirred for 24 h, neutralized with 2 M HCl, concentrated to about 15 mL and cooled to 4 °C. The precipitated NaCl was filtered off and the supernatant was precipitated by addition of cold ethanol (500 mL). The gummy precipitate was crushed several times with ethanol in a mortar until a fine precipitate was obtained. The precipitate was then washed two more times with ethanol and acetone and dried under high vacuum overnight. The yield of CM-β-CD polymer was 60%. The molecular weight of this polymer (Mp = 10,500, Mw = 12,700 and Mn = 12,450) was determined by gel permeation chromatography on Fractogel EMD BioSEC (S) (1.6 cm × 100 cm) calibrated with dextran standards as previously described (Fernández et al., 2004). The degree of carboxymethylation of CM-β-CD polymer determined by potentiometric titration was estimated as 40% (D-glucose, mol/mol).

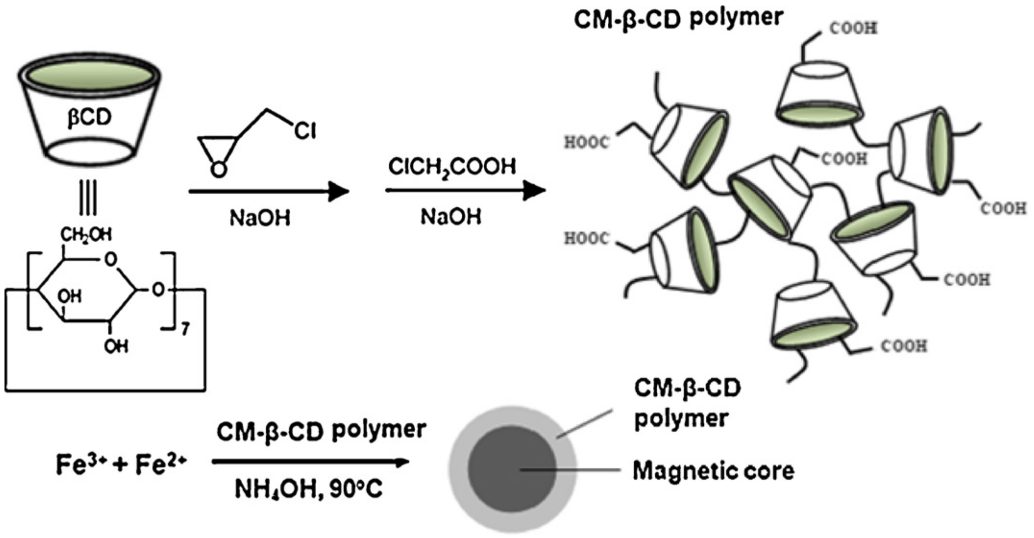
2.3. Synthesis of CM-β-CD polymer coated magnetic nanoparticles (CDpoly-MNPs)

CDpoly-MNPs were fabricated by one step co-precipitation method. Briefly, 0.86 g of $FeCl_2{\cdot}4H_2O$, 2.36 g $FeCl_3{\cdot}6H_2O$ and 1.5 g CM-β-CD polymer were dissolved in 40 mL of de-aerated Milli-Q water with vigorous stirring at a speed of 1200 rpm. 5 mL of NH_4OH (25%) was added after the solution was heated to 90 °C. The reaction was continued for 1 h at 90 °C under constant stirring and nitrogen environment. The resulting nanoparticles were then washed with Milli-Q water five to six times to remove any unreacted chemicals and dried in a vacuum oven.

2.4. Adsorption and desorption of heavy metal ions

Pb^{2+}, Cd^{2+} and Ni^{2+} ions adsorption experiments were carried out using batch equilibrium technique in aqueous solutions at different pH range and at 25–55 °C. In general, an average of 120 mg of wet magnetic nanoadsorbents (20% dry particle content) was added to 10 mL of Pb^{2+}, Cd^{2+} and Ni^{2+} solution of various concentrations (from 50 mg L^{-1} to 400 mg L^{-1}) and shaken in a thermostatic water-bath shaker operated at 230 rpm. After equilibrium was reached, magnetic nanoadsorbents were removed using a permanent Nd–Fe–B magnet and the supernatant was collected after reaching equilibrium. The concentrations of Pb^{2+}, Cd^{2+} and Ni^{2+} ions were measured using Inductive Couple Plasma Mass Spectrometry (Agilent ICP-MS 7700 series). The solution pH was adjusted by NaOH or HCl. For the kinetic experiments, the initial Pb^{2+}, Cd^{2+} and Ni^{2+} ion concentrations used were 300 mg L^{-1} and the pH used was 5.5. At various time intervals, samples were collected after magnetic decantation and the concentrations of studied pollutants were determined. In the binary and ternary adsorption experiments, either 2 or 3 species of the studied metal ions were added in equal mass concentration (each 100 mg L^{-1}) to a 10 mL solution contained in the vial. The vials were shaken for 2 h to ensure equilibrium before the magnetic nanoparticles were removed and the concentrations of remaining metal ions were measured as mentioned previously. The amount of metal ions adsorbed onto CDpoly-MNPs was calculated by a mass balance relationship,

$$Q_e = (C_i - C_e)\frac{V}{w} \tag{1}$$



Scheme 1. Schematic presentation of CM-β-CD polymer grafting on Fe_3O_4 nanoparticles.

where V (L) is the volume, C_i and C_e (mg L^{-1}) are the initial and final solution concentration of metal ions respectively, and w (g) is the dry mass of the solid.

Desorption study was conducted using different desorption eluents such as 0.01 M nitric acid, 0.1 M Na_2EDTA and 0.02 M phosphoric acid. Adsorption was first conducted using 120 mg of wet CDpoly-MNPs in 10 mL of 300 mg L^{-1} Pb^{2+}, Cd^{2+} and Ni^{2+} solution at pH 5.5 and shaken for 2 h. Desorption was then examined by adding 10 mL of either desorption eluent to the metal-sorbed CDpoly-MNPs. After shaking at 230 rpm for 3 h, the solid phase CDpoly-MNPs were collected by magnetic decantation and the concentration of each pollutant in the supernatant was measured. The reusability was checked by following the above adsorption–desorption process for four cycles for Pb^{2+} ions.

2.5. Characterization of the materials

A Field Emission Transmission Electron Microscopy (JEOL 2011F) was used to determine the size and morphology of magnetic particles. The sample was prepared by coating a thin layer of diluted magnetic particle suspension on a copper grid (200 mesh and cover with formvar/carbon). The copper film was then dried at room temperature for 24 h before the measurement. The functionalization of CM-β-CD polymer onto the surface of Fe_3O_4 nanoparticle was detected by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). FTIR measurements were performed using a Shimadzu infrared spectrometer (Model 400) with KBr as background over the range of 4000–400 cm^{-1}. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an Axis Ultra DLD (Kratos) spectrometer with Al mono Kα X-ray source (1486.71 eV photons) to determine the elements. All binding energies (BEs) were referenced to the C 1s neutral carbon peak at 284.6 eV. The zeta potentials of as-synthesized nanoparticles were measured at different pH using a Malvern ZEN 3600 Zetasizer Nano ZS.

3. Results and discussion

3.1. Synthesis and characterization of magnetic nanoparticles

CDpoly-MNPs were synthesized by simple co-precipitation where iron precursors (Fe^{2+} and Fe^{3+}) and CM-β-CD polymer were mixed together in the reaction medium. The step-by-step reaction procedures to synthesize CM-β-CD polymer modified magnetic nanoparticles are shown in Scheme 1.

The functionalization of CM-β-CD polymer on magnetic nanoparticles was confirmed by FTIR spectroscopy. Fig. 1(A) shows the FTIR spectra of CM-β-CD polymer, bare and polymer coated Fe_3O_4 nanoparticles in the 4000–400 cm^{-1} wavenumber range. The spectrum of CM-β-CD polymer shows the characteristic peaks at 1028, 1155 and 1710 cm^{-1}. The peaks at 1028 and 1155 cm^{-1} correspond to the antisymmetric glycosidic ν_a(C—O—C) vibrations and coupled ν(C—C/C—O) stretch vibration. The peak at 1710 cm^{-1} corresponds to carbonyl group (=CO) stretching which confirms the incorporation of the carboxymethyl group ($-COOCH_3$) into CM-β-CD polymer. The characteristic absorption band of magnetic nanoparticles is 586 cm^{-1} which is due to Fe—O bonds in the tetrahedral sites. All the significant peaks of CM-β-CD polymer in the range of 900–1200 cm^{-1} are present in the spectrum of CDpoly-MNPs with a small shift. Moreover, as shown in Fig. 1(A), two main characteristic peaks appeared at 1628 and 1400 cm^{-1} due to bands of COOM (M represents metal ions) groups, which indicates that the COOH groups of CM-β-CD polymer reacted with the surface OH groups of Fe_3O_4 particles resulting in the formation of the iron carboxylate (Badruddoza et al., 2011).

XPS analysis was applied to find the chemical binding in the as-synthesized CDpoly-MNPs. The C 1s deconvoluted spectrum is shown in Fig. 1(B). The C 1s spectrum can be curve-fitted into four peak components with binding energy of about 284.6, 286.1, 287.9 and 288.7 eV, attributable to the carbon atoms in the forms of C—C (aromatic), C—O (alcoholic hydroxyl and ether), C=O (carbonyl) and COO^- (carboxyl and ester) species, respectively (Zheng et al., 2009). The C—O/C—O—C and C=O peaks are the characteristic peaks of CM-β-CD polymer. Moreover, the presence of COO^- peak at 288.7 eV indicates that the COOH functional groups on CM-β-CD polymer reacted with surface OH groups to form metal carboxylate (COOM). Typical TEM image of CDpoly-MNPs are shown in Fig. 1(C). It shows that Fe_3O_4 nanocomposites bonded with CM-β-CD polymer are spherical particles with size range from 8 to 15 nm (size distribution is shown in Fig. S1). The magnetic hysteresis loop (Fig. S2) of the samples indicates no remanence and no coercivity and reveals their superparamagnetic nature, which is beneficial to their dispersibility and redispersibility in the solution.

Zeta potential plays an important role not only to find the isoelectric point but also the pH where maximum adsorption can

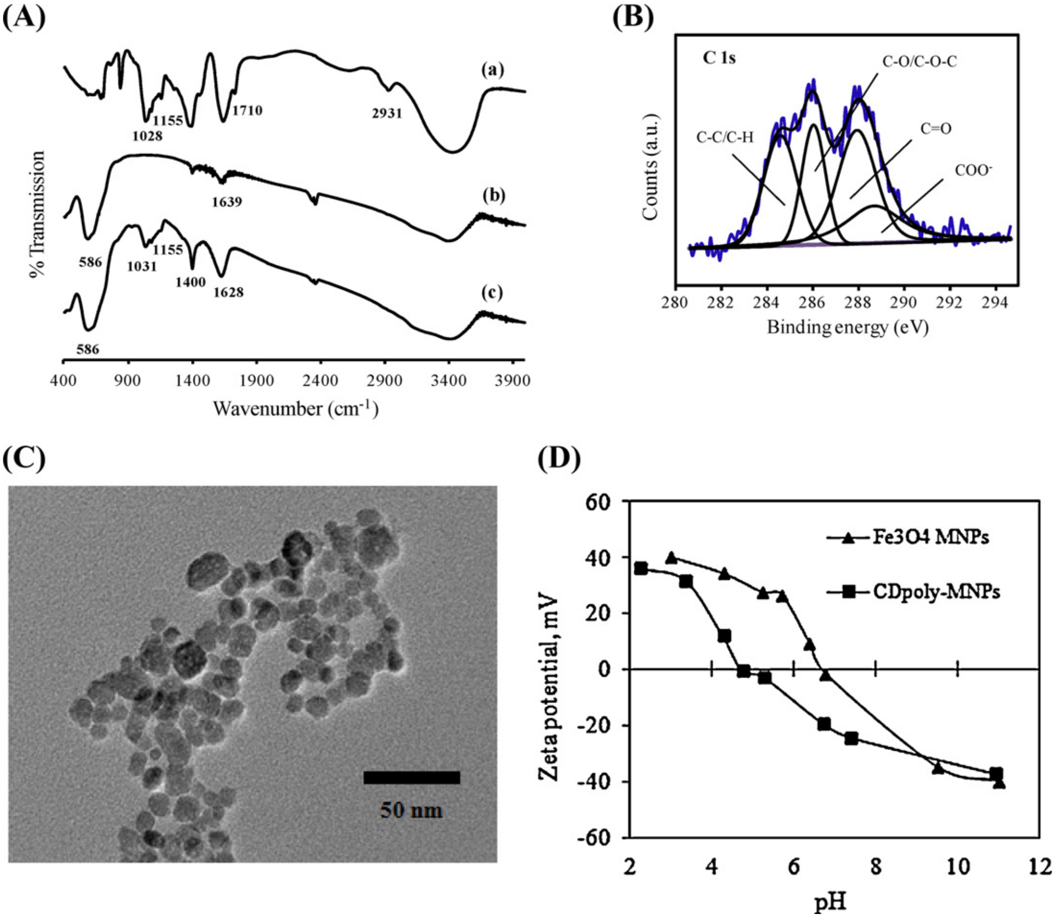


Fig. 1. (A) FTIR spectra of (a) CM-β-CD polymer, (b) uncoated MNPs and (c) CDpoly-MNPs, (B) XPS C 1s spectrum of CDpoly-MNPs, (C) TEM image of CDpoly-MNPs, and (D) zeta potentials of bare MNPs and CDpoly-MNPs at different pH.

occur, as it gives a prediction of the nature of the charge of the grafting material. Zeta potentials of uncoated and CM-β-CD polymer coated magnetic nanoparticles (0.1 mg L^{-1}) were measured in 10^{-3} M NaCl aqueous solution at different pH. The solution pH was adjusted by NaOH or HCl. As shown in Fig. 1(D) the pH_{ZPC} values of unmodified and CM-β-CD polymer modified MNPs were determined to be 6.8 and 4.4, respectively. Upon surface modification with CM-β-CD polymer containing multiple carboxyl groups, the pH_{ZPC} shifts to a lower pH value because of the introduction of acidic surface groups.

3.2. Adsorption of Pb^{2+}, Cd^{2+} and Ni^{2+} ions

3.2.1. Effects of pH

The solution pH plays an important role in the adsorption process and particularly on the adsorption efficiency of affinity. The effect of initial solution pH on Pb^{2+}, Cd^{2+} and Ni^{2+} adsorption onto CDpoly-MNPs was investigated at pH 2–6, 25 °C, and an initial M^{2+} ion concentration of 300 mg L^{-1}. Experiments were not conducted at initial pH above 6 as the precipitation of metal hydroxide, $M(OH)_2$, is likely to occur (Naiya, Bhattacharya, & Das, 2009), introducing uncertainty into the results. From Fig. 2(a), it is observed that the metal uptake capacity increases with an increase in pH from 2 to 6. All studied metal ions exhibit maximum adsorption capacity at pH 5.5–6. Below pH 6, the dominant species of all metals are M^{2+} and $M(OH)^+$ (Naiya et al., 2009; Nassar, 2011). The variation in metal uptake capacity with pH can be explained by considering the zero point of charge (ZPC) of CDpoly-MNPs (pH_{ZPC} = 4.4). At pH above the zero point charge, the negatively charged carboxylate ions (COO^-) have strong coordinative affinity towards positively charged metal ions. The electrostatic forces of attraction allow the carboxylate ions to capture the M^{2+} through surface complexation, forming chelate complexes (Singh, Barick, & Bahadur, 2011). The degree of surface complexation increases with increasing pH. Hence, maximum adsorption capacity occurs at pH 5.5–6.

At pH below the zero point charge, there is a net positive charge on the CDpoly-MNPs. This enhances the repulsion forces that exist between the positively charged metal ions and the sorbent adsorption sites, therefore decreasing the adsorption. In addition, the presence of a large amount of H^+ ions at low pH causes the H^+ ions to compete effectively with M^{2+} ions for CDpoly-MNPs' adsorption sites through ion exchange mechanism, decreasing the metal uptake capacity (Singh et al., 2011). This suppressed adsorption of metal ions by CDpoly-MNPs at low pH suggests that treatment with acid would enable the regeneration of the CDpoly-MNPs.

3.2.2. Effects of ionic strength

To evaluate the effect of ionic strength on the adsorption of metal ions, adsorption experiments were carried out by adding $NaNO_3$ at different concentrations (from 0 mol/L to 0.2 mol/L). In the experiment, the initial metal concentration was 300 mg L^{-1} and the pH was 5.5. The results are illustrated in Fig. 2(b), which show that increasing the ionic strength leads to a decrease in adsorption of metal ions on the CDpoly-MNPs. The presence of inorganic salt in the solution may have two opposite effects. On the one hand, since the salt screens the electrostatic interaction of the opposite charges on the adsorbent surface and metal ions, the adsorption capacity

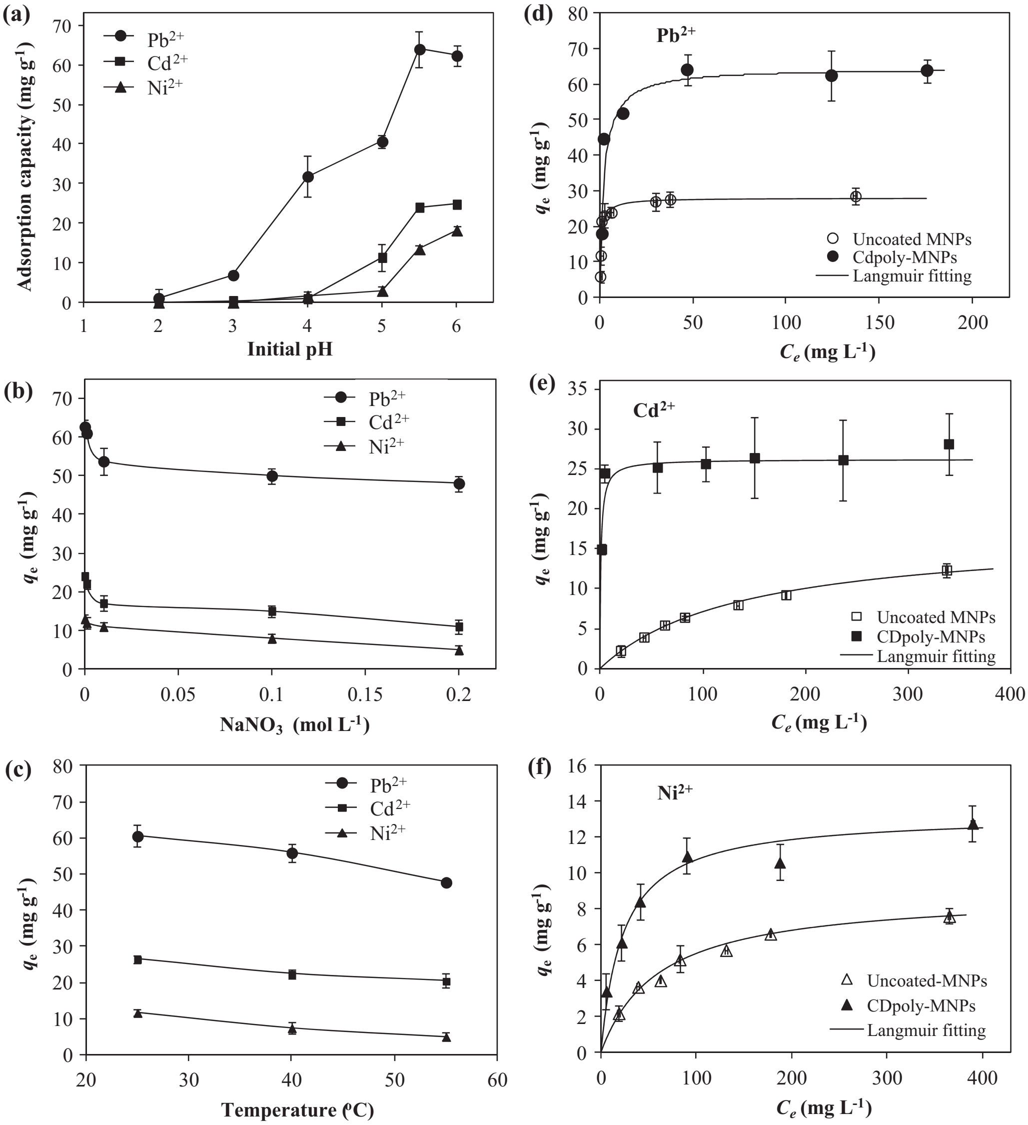


Fig. 2. (a)–(c) Effect of pH, ionic strength and temperature on the adsorption of Pb^{2+}, Cd^{2+} and Ni^{2+} ions onto CDpoly-MNPs, (d)–(f) the adsorption isotherm of Pb^{2+}, Cd^{2+} and Ni^{2+} ions in single-component system onto uncoated MNPs and CDpoly-MNPs at pH 5.5 and 25 °C.

should decrease with the increase of inorganic salt concentration. On the other hand, the salt promotes the dissociation of the functional groups like carboxyl groups on the adsorbent, and then the adsorbed amount increases (Liu, Wang, & Wang, 2010). At the lower $NaNO_3$ concentration (<0.02 mol/L), the former effect seemed to be dominant during the adsorption process. However, at higher $NaNO_3$ concentration (>0.02 mol/L), both effects were comparable to each other, so the effect of $NaNO_3$ concentration on adsorption was not significant.

3.2.3. Effects of temperature

The effects of temperature on the adsorption of metal ions by CDpoly-MNPs were investigated at pH 5.5, 25–55 °C and an initial concentration of each metal ion of 300 mg L^{-1}. As shown in Fig. 2(c), the adsorption capacities for CDpoly-MNPs decreased with the increase in temperature for all metal ions, indicating that the adsorption process was exothermic in nature. Similar observations have been reported in our previous study for the adsorption of Cu^{2+} onto CMCD modified Fe_3O_4 nanoadsorbents (Badruddoza et al., 2011). The decrease in adsorption with temperature may be attributed to either decrease in the number of active surface sites available for adsorption on the adsorbent or the decrease in the attractive forces responsible for the adsorption.

3.2.4. Equilibrium studies in single-component system

The equilibrium isotherms for the adsorption of metal ions in single-solute system by uncoated MNPs and CDpoly-MNPs at 25 °C are presented in Fig. 2(d)–(f). It can be seen that the increase in adsorption capacity with increase in equilibrium metal ion concentration for different metal ions is in the order $Pb^{2+} > Cd^{2+} > Ni^{2+}$. The equilibrium data are fitted by Langmuir and Freundlich adsorption isotherm models. Langmuir and Freundlich adsorption isotherms which can be expressed in Eqs. (2) and (3), respectively are widely used to describe the relationship between the amount of adsorbate adsorbed on adsorbent and its equilibrium concentration in aqueous solution (Langmuir, 1918; Freundlich, 1906).

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \qquad (2)$$

$$\ln q_e = \left(\frac{1}{n}\right) \ln C_e + \ln K_F \qquad (3)$$

where q_e is the amount of adsorbate adsorbed per mass of adsorbent at equilibrium ($\mathrm{mg\,g^{-1}}$), C_e is the equilibrium concentration of adsorbate in aqueous solution ($\mathrm{mg\,L^{-1}}$), q_m is the monolayer adsorption capacity at equilibrium ($\mathrm{mg\,g^{-1}}$), K_L is the Langmuir equilibrium constant, K_F is a Freundlich constant (index of adsorption capacity), n is Freundlich constant (index of adsorption intensity or surface heterogeneity). To determine whether the adsorption is favorable, a dimensionless constant separation factor or equilibrium parameter R_L is defined based on the following equation (Weber & Chakravorti, 1974):

$$R_L = \frac{1}{1 + K_L C_i} \tag{4}$$

where K_L ($\mathrm{L\,mg^{-1}}$) is the Langmuir isotherm constant, and C_i ($\mathrm{mg\,L^{-1}}$) is the initial metal concentration. The R_L value indicates whether the type of the isotherm is favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$).

The values of q_m and K_L are determined from the slope and intercept of the linear plots of C_e/q_e versus C_e and the values of K_F and $1/n$ are determined from the slope and intercept of the linear plot of $\ln q_e$ versus $\ln C_e$ (figures are not shown). The isotherm parameters and related correlation coefficients (R^2) are shown in Table 1. The adsorption isotherm data of all metal ions on this adsorbent are better fitted to Langmuir isotherm model ($R^2 > 0.99$) compared to Freundlich model. Based on Langmuir isotherms, the maximum uptake for Pb^{2+}, Cd^{2+} and Ni^{2+} ions using uncoated magnetic particles were 28.01, 17.01 and 8.83 $\mathrm{mg\,g^{-1}}$, respectively which are in agreement with the results obtained by Nassar (2010, 2011). The maximum adsorption capacities (q_m) of CDpoly-MNPs toward Pb^{2+}, Cd^{2+} and Ni^{2+} were 64.50, 27.70 and 13.20 $\mathrm{mg\,g^{-1}}$ respectively at 25 °C which are higher than those using uncoated magnetic nanoparticles. These results indicate that the modification of magnetite surface by CM-β-CD polymer could enhance the adsorption capabilities of CDpoly-MNPs. The multiple oxygen containing groups (mainly carboxyl and hydroxyl groups) present in CM-β-CD polymer can form complexes with Pb^{2+}, Cd^{2+} and Ni^{2+} ions on the surface of CDpoly-MNPs. It is also reported that carboxymethyl-β-cyclodextrin (CMCD) has the ability to complex heavy metals such as cadmium, nickel, strontium and mercury in the presence of various organic contaminants (Brusseau, Wang, & Wang, 1997; Wang & Brusseau, 1995). Furthermore, the values of R_L for the Langmuir isotherm were between 0 and 1, and all the Freundlich adsorption intensity variables (n values) were >2, which supports the favorable adsorption of metal ions with this adsorbent. However, the significant difference among the values of q_m should be attributed to the different complexation capacity of the oxygen containing groups on surface with the metal ions. K_L values of Pb^{2+}, Cd^{2+} and Ni^{2+} by CDpoly-MNPs are in decreasing order (0.417, 0.214, 0.043 $\mathrm{L\,mg^{-1}}$, respectively), showing the order of metal affinity is the same as that obtained from the kinetic studies. Table 2 summarizes the comparison of different adsorbents for Pb^{2+}, Cd^{2+} and Ni^{2+} metal ions in single-solute system. Though the performance of this adsorbent is comparable with that of other adsorbents, cost comparisons are difficult to make due to scarcity of consistent cost information in the literature data. It is noteworthy that commercially available adsorbents such as, activated carbons are costly, time-consuming and its regeneration and recovery is the most expensive which accounts for about 75% of the total operating and maintenance costs (Nassar, 2010). β-CD molecules are available commercially at a low-cost. Both soluble and insoluble CD-based materials are also straightforward to prepare with relatively inexpensive chemical reagents and are available in a variety of structures with a variety of properties (Crini & Morcellet, 2002). Anchoring the β-CD derivatives on the surfaces of Fe_3O_4 nanoparticles in one step precipitation method is also a simple and inexpensive method. The nanoadsorbents synthesized in this way, show higher adsorption capacities and faster kinetics and they could be regenerated and recycled using simple magnetic separation technology which is obviously a great advantage. Moreover, these nanoadsorbents can potentially be used for the removal of organic pollutants from wastewater as β-CD has the inclusion capabilities with a wide variety of organic molecules.

3.2.5. *Effects of contact time and adsorption kinetics*

Fig. S3 illustrates the adsorption of Pb^{2+}, Cd^{2+} and Ni^{2+} ions on CDpoly-MNPs from aqueous solution as a function of contact time. It can be noted that the adsorption of all the metals on the adsorbent increased with contact time. The adsorption rate was fast and the maximum adsorption was achieved almost within 45 min for all three metal ions. The contact time required for the metal adsorption using this adsorbent is very short compared to other adsorbents reported such as activated carbon (Shekinah, Kadirvelu, Kanmani, Senthilkumar, & Subburam, 2002) and clay minerals (Ozdes, Duran, & Senturk, 2011). The short time required to reach equilibrium shows that mainly external adsorption occurs in the nonporous Fe_3O_4 nanoadsorbent (Nassar, 2010). The contact time is one of the important parameters for economical wastewater treatment application. Short adsorption equilibrium contact time favors the application of the adsorption process.

The adsorption kinetics of Pb^{2+}, Cd^{2+} and Ni^{2+} ions onto CDpoly-MNPs is investigated with pseudo-second-order model which is expressed by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

where q_e and q_t represent the amount of contaminant adsorbed on adsorbent ($\mathrm{mg\,g^{-1}}$) at equilibrium and at any time, t (min), respectively, k_2 are the rate constant of pseudo second-order adsorption ($\mathrm{g\,mg^{-1}\,min^{-1}}$).

The initial adsorption rate, v_0 ($\mathrm{mg\,g^{-1}\,min^{-1}}$) of these metal ions was also calculated from the pseudo-second-order model using Eq. (6):

$$v_0 = k_2 q_e^2 \tag{6}$$

The slope and intercept of the plot of t/q_t versus t are used to calculate k_2 and $q_{e,cal}$ (Fig. S3). The corresponding kinetic parameters from this model are listed in Table 3. It is found that the correlation coefficient (R^2) for the pseudo-second-order adsorption model has high value (>99%), and the q_e values ($q_{e,cal}$) calculated from pseudo-second-order model are more consistent with the experimental q_e values ($q_{e,exp}$). These suggest that the adsorption data is well represented by the pseudo-second-order kinetic model. This kinetic model was based on the assumption that the rate controlling step of chemisorptions involved valence forces through sharing or exchange of electrons between adsorbent and adsorbate (Heidari et al., 2009; Pang et al., 2011; Reddad, Gerente, Andres, & Le Cloirec, 2002). Furthermore, the initial sorption rate for all the metals is in the order $Pb^{2+} > Cd^{2+} > Ni^{2+}$. The pseudo-second-order adsorption has also been reported for some heavy metals on many adsorbents such as functionalized magnetic mesoporous silica (Li, Zhao, Liu, & Jiang, 2011), magnetic hydroxyapatite nanoparticles (Feng et al., 2010) and polyethylenimine grafted magnetic porous adsorbent (Pang et al., 2011).

3.2.6. *Multi-component adsorption*

To examine the competitive effects the metals exert on each other in multi-metal solutions, the removal efficiencies of CDpoly-MNPs for each metal in single, binary and ternary solutions were compared and are shown in Fig. 3(a). It can be seen that the percentage removal of Pb^{2+}, Cd^{2+} and Ni^{2+} ions in single-metal system (non-competitive) were 99.5%, 55.9% and 24.3%, respectively. In binary metal solution (Pb^{2+}–Cd^{2+} and Pb^{2+}–Ni^{2+}), Pb^{2+} adsorption

Table 1
Adsorption isotherm parameters for Pb^{2+}, Cd^{2+} and Ni^{2+} ions onto bare MNPs and CDpoly-MNPs at 25 °C in single-component system.

Isotherm models	Parameters	Pb^{2+}		Cd^{2+}		Ni^{2+}	
		Bare MNPs	Coated MNPs	Bare MNPs	Coated MNPs	Bare MNPs	Coated MNPs
Langmuir	q_m (mg g^{-1})	28.01	64.50	17.01	27.70	8.83	13.20
	K_L (L mg^{-1})	1.253	0.417	0.007	0.214	0.016	0.043
	R^2	0.999	0.999	0.991	0.998	0.996	0.994
	R_L	0.002–0.016	0.006–0.046	0.263–0.851	0.012–0.156	0.135–0.714	0.055–0.701
Freundlich	n	4.010	4.98	1.69	12.24	2.43	3.32
	K_F (L g^{-1})	13.44	25.82	0.426	17.64	0.755	2.39
	R^2	0.7312	0.656	0.981	0.724	0.952	0.923

Table 2
Comparison of maximum adsorption capacity of CDpoly-MNPs with those of some other adsorbents reported in literature for Pb^{2+}, Cd^{2+} and Ni^{2+} adsorption.

Adsorbent	Maximum adsorbed amount, q_m (mg g^{-1})			Conditions	Reference
	Pb^{2+}	Cd^{2+}	Ni^{2+}		
Iron oxide nanoparticles	29.0	18.59	11.34	pH 5.5, 25 °C	Nassar (2010, 2011)
Sugar beet pulp	73.76	24.30	11.86	pH 5.5, 25 °C	Reddad et al. (2002)
Powdered activated carbon	26.9	3.37	–	pH 5.0, 30 °C	Reddad et al. (2002)
Multiwalled carbon nanotubes	97.08	10.86	–	pH 5.0, 25 °C	Li et al. (2003)
Alginate beads magnetic nanoparticles	99.5	–	–	pH 4.7, 25 °C	Bée et al. (2011)
Magnetic Fe_3O_4 baker's yeast biomass	89.2	41.0	–	pH 5.5, 25 °C	Xu et al. (2011)
Silica-supported dithiocarbamate	70.4	40.3	–	pH 5.0 (Pb), pH 7.0 (Cd), 25 °C	Bai et al. (2011)
Chitosan/magnetite nanocomposite	63.33	–	52.55	pH 6.0, r.t.	Tran et al. (2010)
Chitosan immobilized on bentonite	26.38	–	15.82	pH 4.0, 25 °C	Futalan et al. (2011)
Activated alumina	83.33	35.07	–	pH 5.0, 30 °C	Naiya et al. (2009)
Hydroxyapatite/chitosan composite	12.04	–	8.54	30 °C	Gupta, Kushwaha, and Chattopadhyaya (2012)
CDpoly-MNPs	64.50	27.70	13.20	pH 5.5, 25 °C	This study

was slightly reduced (to 95.6% and 96.4% respectively) by the presence of Cd^{2+} or Ni^{2+}. However, the percentage removal of Cd^{2+} and Ni^{2+} were reduced significantly to 12.7% and 9.4% respectively in the same binary mixtures. This indicates that Pb^{2+} ions were preferentially adsorbed on the surface of CDpoly-MNPs as compared to Cd^{2+} or Ni^{2+} ions. In the binary Cd^{2+}–Ni^{2+} mixture, the removal of Cd^{2+} and Ni^{2+} also decreased to 30.1% and 14.4% respectively, showing the competitiveness of the two metals. In the ternary system, the percentage removal of Pb^{2+} was slightly reduced (94.9%), whereas the percentage removal of Cd^{2+} and Ni^{2+} were lower than that of single or binary metal mixtures (10.3% and 7.3% respectively).

The decrease in sorption capacity of same adsorbent in multi-metal solution than that of single metal ion may be ascribed to the less availability of binding sites. In case of multi-metal solution, when metals compete for the same adsorption sites of an adsorbent, metals with a greater affinity could displace others with weaker affinity (Qin et al., 2006). The results from the binary and ternary metal mixtures show that the presence of Cd^{2+} and/or Ni^{2+} has little influence on the adsorption of Pb^{2+} onto the CDpoly-MNPs, whereas the adsorption of Cd^{2+} and Ni^{2+} are significantly reduced when in a competitive metal ion environment. Hence, the order of removal efficiencies for the three metal ions was $Pb^{2+} \gg Cd^{2+} > Ni^{2+}$, implying the stronger affinity of the adsorbent for Pb^{2+} than Cd^{2+} and Ni^{2+}. This tendency of higher adsorption of Pb^{2+} on different adsorbents containing —COOH and —OH functional groups in multi-metal solutions was reported in other studies (Ducoroy, Bacquet, Martel, & Morcellet, 2008; Qin et al., 2006).

The extent to which a metal ion will bind to a ligand depends strongly on the chemistry of the metal ion and its preference to form covalent or ionic bonding (Wang & Chen, 2006). Metal ions act as Lewis acids by accepting electron pairs from ligands. Pearson divided metal ions into class A 'hard' ions, class B 'soft' ions and borderline ions. The theory was further refined by Nieboer and Richardson (1980), and Nieboer and McBryde (1973) who described class A metal ions as nonpolarizable hard metals that prefer to bind to nonpolarizable hard bases by bonds that are principally ionic, and class B metal ions as polarizable soft metals that prefer to bind to polarizable soft bases by bonds that are mainly covalent. Pb^{2+} is classified as a class B ion, while Cd^{2+} and Ni^{2+} are classified as borderline ions (intermediate between class A and B, but with properties nearer that of class B metal ions). It was argued by Tsezos, Remoudaki, and Angelatou (1995, 1996) that the competition between ions was more for metals belonging to the same class, and adsorption of borderline ions were affected by the presence of soft ions, but not the other way around. Based on this, the competition effects observed in our study could be explained. Due to Pb^{2+} belonging to a different class (borderline class) as Cd^{2+} and Ni^{2+} (soft ions), these two cations did not have much effect on Pb^{2+}

Table 3
Adsorption kinetic parameters of Pb^{2+}, Cd^{2+} and Ni^{2+} onto CDpoly-MNPs at 25 °C and pH 5.5.

Metals	Initial conc., C_o (mg mL^{-1})	Pseudo-second order				
		q_e [a], mg g^{-1}	k_2, g mg^{-1} min^{-1}	ν_o, mg g^{-1} min^{-1}	q_e [b], mg g^{-1}	R^2
Pb^{2+}	300	67.25	0.003	11.98	66.67	0.996
Cd^{2+}	300	25.02	0.016	10.00	25.19	0.999
Ni^{2+}	300	13.54	0.033	6.18	13.68	0.999

[a] Experimental.
[b] Calculated.

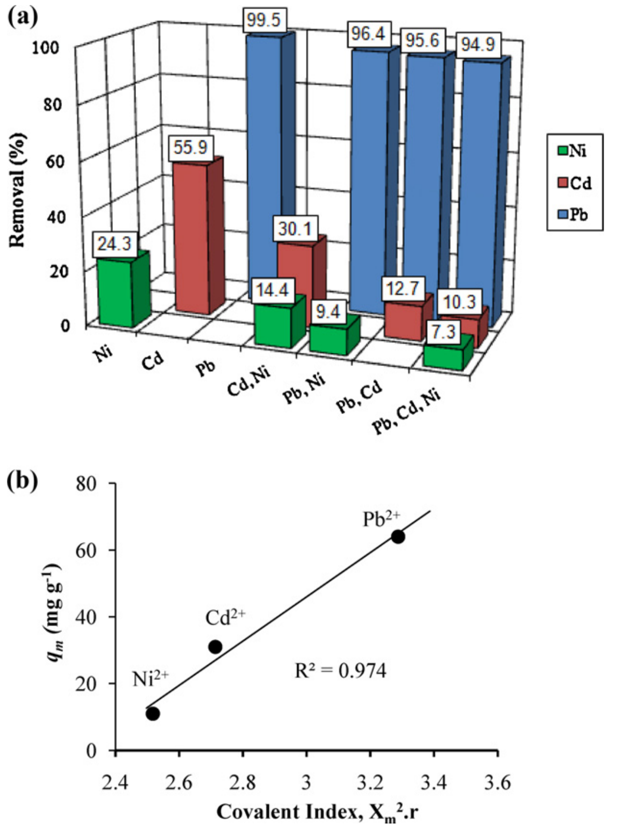


Fig. 3. (a) Percentage removal of Ni^{2+}, Cd^{2+} and Pb^{2+} from single, binary and ternary mixtures (each metal concentration: 100 mg L^{-1}, adsorbents: 120 mg, temperature: 25 °C, pH: 5.5 and contact time: 2 h). (b) Plot of the adsorption capacities versus the covalent indexes.

adsorption onto CDpoly-MNPs. On the other hand, the soft Pb^{2+} ions have a suppressive effect on the adsorption of Cd^{2+} and Ni^{2+}. This can be explained by the metals' chemical coordination, stereochemical and redox characteristics (Tsezos et al., 1995, 1996). Even in the absence of Pb^{2+}, Cd^{2+} and Ni^{2+} removal by CDpoly-MNPs is greatly reduced in the binary Cd^{2+}–Ni^{2+} mixture as compared to single metal solutions, an indication of their competitive effect against each other because they belonged to the same class, viz. borderline class (Puranik & Paknikar, 1999). The competitive effect Cd^{2+} and Ni^{2+} ions have on each other is consistent with that found in other studies (Petrangeli Papini, Saurini, Bianchi, Majone, & Beccari, 2004).

To evaluate the performance of our developed nanoadsorbent in real wastewater treatment, urban wastewater from Tuas area in Singapore was collected and spiked with cadmium nitrate, nickel nitrate, copper nitrate and cadmium nitrate to obtain wastewater which simulated paint industry effluent. These metal ions are particularly common heavy metals found in paint industries's wastewater (Malakootian, Nouri, & Hossaini, 2009). Despite the presence of competitive effect of Cd^{2+} and Ni^{2+} metal ions, about 99.9% and 85% reduction in Pb^{2+} concentrations was achieved at pH 7 and 4, respectively as a result of treatment with the developed magnetic nanoadsorbent. These results are presented in Table 4 which clearly indicate that the adsorbent has potential applications for the removal of Pb^{2+} from industrial wastewater.

3.2.7. Adsorption mechanism

To elucidate the reaction mechanisms occurring on the adsorbents, FTIR spectra of the CDpoly-MNPs before and after metal adsorption are shown in Fig. S4. Before adsorption, the carboxylate ions give rise to two bands at 1628 and 1400 cm^{-1} which correspond to strong asymmetrical and symmetrical stretching bands respectively. The peak at 1628 cm^{-1} turned to a shoulder after Pb^{2+} adsorption, and this may indicate a strong Pb^{2+} interaction with C=O groups. Moreover, bands at 1628 and 1400 cm^{-1} also exhibit shifts to different extents after contact with Cd^{2+} and Ni^{2+} solutions. This suggests that the deprotonated carboxyl forms (carboxylate anions) on CDpoly-MNPs interacted with metal ions. The peak at 1340 cm^{-1} which is assigned to C—O stretch of COO—M groups indicates the presence of metal–carboxylate complex (Kurniawan et al., 2011). In addition, the coordination type of metal–carboxylate complexes can also be determined by examining the vibrational modes of ν_{asym} (COO^-) and ν_{sym} (COO^-) in the wavenumber region of 1300–1750 cm^{-1}. The difference ($\Delta\nu$) between ν_{asym} (COO^-) and ν_{sym} (COO^-) is larger than 200 cm^{-1} in our study, suggesting the formation of metal–carboxylate complex through unidentate chelating coordination (Kurniawan et al., 2011).

The C—O stretching of alcoholic/ether groups at 1033 cm^{-1} were shifted in the range 9–11 cm^{-1} after metal adsorption. The broad peak at 3423 cm^{-1} was shifted to higher wavenumber 3431 cm^{-1}. A band at 1385 cm^{-1} appeared after M^{2+} adsorption, which could be attributed to the bending mode of C—O—H that would occur in an alcoholic group or a protonated alcoholic group or a protonated ether group (Chen, Hong, Wu, & Wang, 2002). This result indicates that hydroxyl groups may also be involved in metal binding. Indeed, complexation of metals with neutral or anionic polysaccharides in solution involving hydroxyl groups has already been reported (Dronnet, Renard, Axelos, & Tbibault, 1997).

The nature of bonding and the difference in affinities for the binding sites of the metal ions affects the adsorption capability onto the same adsorbent. It is difficult to attribute this adsorption capability by a single factor such as atomic number, ionic potential or ionic radius (Jing et al., 2009). Therefore, the concept of covalent index was devised by Nieboer and McBryde (1973). The values of this covalent index can be expressed by:

$$\text{Covalent Index} = X_m^2 \times r \tag{7}$$

where X_m is electronegativity of the metal ion and r is the cationic crystal radius. The covalent index could reflect the importance of chelating interactions with ligands relative to ionic interactions (degree of class B behavior). The metal adsorption capacity has been found positively correlated to the covalent index (Jing et al., 2009). The plot of adsorption capacity (mg g^{-1}) against covalent index is shown in Fig. 3(b). The linear fitted plot has a relatively good R^2 value of 0.975, an indication that the chelating interaction did have an important role to play during the adsorption process. However, deviation from total linearity probably indicates that the sorption of one or more of these metals was not totally governed by covalent binding. Other types of ionic interactions might be involved (Puranik & Paknikar, 1999). This is further supported by the desorption studies (Section 3.2.8), which showed that 0.1 M EDTA was able to recover 94.2% of adsorbed Pb^{2+}, but only 61.3% and 60.2% of Cd^{2+} and Ni^{2+} respectively, suggesting that Pb^{2+} is more likely to be affected by complexation interactions. In other research, Reddad et al. (2002) found that the adsorption mechanism of cadmium and nickel by sugar beet pulp consists of a significantly higher percentage ionic interaction than complexation as compared to lead. Therefore, our study allows us to conclude that complexation reactions played an important role in the adsorption of Pb^{2+}, Cd^{2+} and Ni^{2+} by CDpoly-MNPs, but the effect of ionic interaction should not be excluded as well.

3.2.8. Desorption and reusability

To evaluate the possibility of regeneration and reusability of the CDpoly-MNPs as an adsorbent, batch desorption experiments were

Table 4
Quality of urban wastewater simulating a typical paint industry effluent.

	pH	Pb^{2+} (mg L^{-1})	Cd^{2+} (mg L^{-1})	Ni^{2+} (mg L^{-1})	Cu^{2+} (mg L^{-1})
Sample 1:					
Quality of wastewater before treatment	7.35	16.90	6.19	13.90	1.23
Quality of wastewater after treatment	5.80	0.010	3.29	9.78	0.45
Sample 2:					
Quality of wastewater before treatment	3.98	7.34	14.14	13.45	1.70
Quality of wastewater after treatment	3.82	1.10	11.48	13.28	0.36

conducted. Desorption of Pb^{2+}, Cd^{2+} and Ni^{2+} from CDpoly-MNPs was demonstrated using three different buffers, namely 0.01 M nitric acid, 0.1 M Na_2EDTA and 0.02 M phosphoric acid. The results of the desorption of Pb^{2+}, Cd^{2+} and Ni^{2+} using the three buffers are summarized in Fig. 4(a). HNO_3 and Na_2EDTA solutions show excellent desorption efficiency for Pb^{2+} (96.0% and 94.2% recovery), whereas H_3PO_4 is a better eluent for Cd^{2+} and Ni^{2+} desorption, with a recovery of 61.8% and 82.7% respectively. The bonding between the active sites of magnetic nanoadsorbent and metal ion is not sufficiently strong to be held in acidic conditions (Nassar, 2010). Under acidic conditions, H^+ ions protonate the adsorbent surface, i.e. the carboxyl group (—COOH) regeneration is more favorable, thereby reflecting the metal ions from the adsorbent surface leading to the desorption of positively charged metal ions. Moreover, Na_2EDTA solution could desorb Pb^{2+} ions more efficiently from the surface than Cd^{2+} or Ni^{2+} ions. When Na_2EDTA solution was added to the metal adsorbed-CDpoly-MNPs, stronger coordination ligands in the Na_2EDTA would have formed a stronger bonding with Pb^{2+} ions, making the metal ions more easily desorb from the CDpoly-MNPs (Yu et al., 2011).

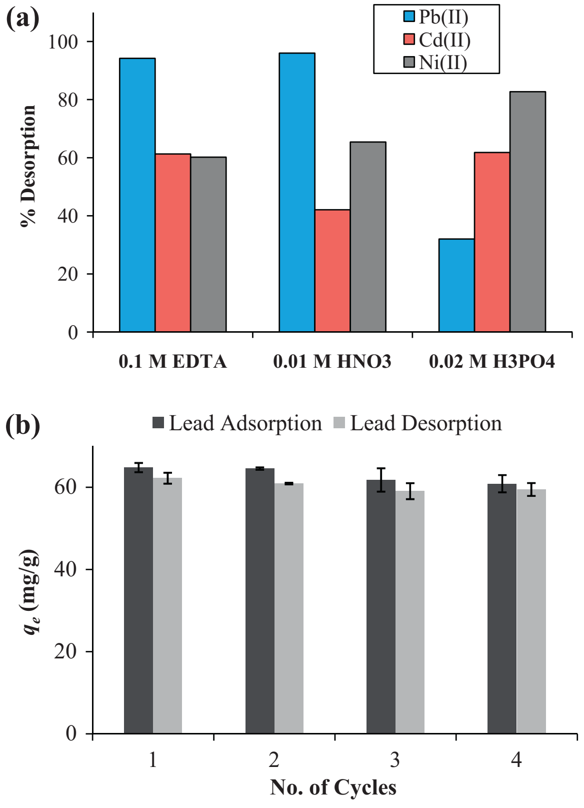


Fig. 4. (a) Percentage recovery of Pb^{2+}, Cd^{2+} and Ni^{2+} from CDpoly-MNPs using different desorption eluents, (b) four consecutive adsorption–desorption cycles of CDpoly-MNPs adsorbent for Pb^{2+} (initial concentration: 300 mg L^{-1}, pH: 5.5, desorption agent: 10 mL of 0.01 M HNO_3).

The reusability was checked by following the adsorption–desorption process for four cycles for Pb^{2+} ions and the adsorption efficiency in each cycle was analyzed and presented in Fig. 4(b). As Pb^{2+} ions could be desorbed almost completely from the adsorbent, reusability of the adsorbent was checked with only Pb^{2+} ions in this study. The CDpoly-MNPs adsorbent kept its adsorption capability after repeated adsorption–regeneration cycles with negligible changes, indicating that there are almost no irreversible sites on the surface of CDpoly-MNPs. Our recyclability studies suggest that these nanoadsorbents can be repeatedly used as efficient adsorbents in wastewater treatment.

4. Conclusions

Superparamagnetic magnetite (Fe_3O_4) nanoparticles coated with CM-β-CD polymer were synthesized, which could be used as an efficient adsorbent for the removal of heavy metal ions from wastewater. The adsorption capacities of Fe_3O_4 nanoparticles were enhanced upon the surface modification with CM-β-CD polymer. The CM-β-CD polymer provides numerous surface carboxyl and hydroxyl groups, and hence, generates the strong affinity for metal ions. The solution pH, temperature and ionic strength affected the adsorption of all metal ions onto CDpoly-MNPs. Adsorption reaches equilibrium within 45 min and the kinetics of Pb^{2+}, Cd^{2+} and Ni^{2+} adsorption follows the pseudo-second-order model. The maximum uptake capacities for Pb^{2+}, Cd^{2+} and Ni^{2+} were 64.50, 27.70 and 13.20 mg g^{-1}, respectively at 25 °C and the equilibrium data are fitted well by the Langmuir model. Adsorption of Pb^{2+} ions was preferential to that of Cd^{2+} and Ni^{2+} ions. In multi-metal solutions, CDpoly-MNPs could removed target metal ions with the selectivity order of $Pb^{2+} \gg Cd^{2+} > Ni^{2+}$. Higher selectivity as well as reversibility of the sorption–elution process towards Pb^{2+} ions is the characteristic of these nanoadsorbents. Our results suggest that cyclodextrin polymer/Fe_3O_4 nanocomposites can be used as a reusable absorbent for easy, convenient, and efficient removal of metal ions from wastewater.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2012.08.030.

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