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# Endocrine Disrupters and Toxic Metal Ions Removal by Carboxymethyl-β-Cyclodextrin Polymer Grafted onto Magnetic Nanoadsorbents

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***Abstract***

*In this study, carboxymethyl-β-cyclodextrin (CM-β-CD) polymer modified $Fe_3O_4$ magnetic nanoparticles (CMPCD-MNPs) is fabricated and the feasibility of using these nanoadsorbents for removal of bisphenol A (BPA) and $Pb^{2+}$ ions from aqueous solution was investigated. The properties of the particles were characterized by FTIR and TEM. The CM-β-CD polymer grafted onto nanoparticle surface contributes to an enhancement of the adsorption capacity of $Fe_3O_4$ nanoparticles because of the strong complexation abilities of the multiple hydroxyl/carboxyl groups in CM-β-CD polymer with metal ions and of the hydrophobic cavity with organic contaminants through host-guest interactions. The adsorption of both BPA and $Pb^{2+}$ ions onto CMPCD-MNPs was found to be dependent on pH. Adsorption equilibrium was achieved in 10-30 min and the adsorption kinetics of both contaminants is found to follow a pseudo-second-order kinetic model. Equilibrium adsorption data are fitted well by Langmuir isotherm model. Furthermore, these nanoadsorbents can be used as effective, separable and reusable materials for removal of both organic and inorganic contaminants from wastewater by magnetic separation systems.*

## 1. Introduction

Recently, the environmental pollution such as water and soil pollutions with endocrine disrupting chemicals (EDCs) and various heavy metals has attracted global attention because of their detrimental effects on environmental and human health[1]. EDCs (Bisphenol A, dioxins etc.) are anthropogenic chemicals with the potential to elicit negative effects on the endocrine systems of humans and wildlife. Heavy metal ions (Pb, Cd, As etc.) are also toxic and non-biodegradable and hence, accumulate in human immune system and thereby disrupt function in vital organs and glands such as the heart, brain, kidneys, bone, liver, etc. Therefore, the removal of these pollutants from aquatic environment is necessary and very important.

Various treatment techniques available for the removal of these chemicals from environmental matrices are activated carbon adsorption, electrochemical, ion exchange, reverse osmosis, biological and chemical procedures[2]. However, among all the methods adsorption is highly effective and economical. Recently, functionalized magnetic nanocomposites have received many attentions for use in the adsorption of both organic and inorganic pollutants[3,4]. Magnetic nano-adsorbents have the advantages of both magnetic separation techniques and nano-sized materials, which can be easily recovered or manipulated from complex multiphase systems with an external magnetic field. For the effective removal of toxic contaminants from wastewater, functional magnetic nanomaterials were synthesized by anchoring polymer, inorganic or organic molecules to the surfaces of magnetic nanoparticles including chitosan[5], silica[6], mesoporous carbon[4], alginate[3], gum arabic[7] etc. However, no or less adsorptive study of pollutants on β-cyclodextrin (β-CD) bonded magnetic nanoparticles has been reported, though β-CD complexation has proved an effective method for decontaminating technique.

β-CD is a cyclic oligosaccharide consisting of 7 glucopyranose units, which are joined together by α (1–4) linkage forming a torus-shaped ring structure with a hydrophilic exterior and a hydrophobic cavity[8]. It can form inclusion complexes with a wide variety of organic compounds in its hydrophobic cavity through host-guest interactions. These fascinating properties make them promising for applications in drug carrier systems, nanoreactors, bioactive supramolecular assemblies, molecular recognition, and catalysis[9,10].

In this study, carboxymethyl-β-cyclodextrin polymer modified magnetic nanocomposites were synthesized and used to investigate the adsorption characteristics for removal of bisphenol A (BPA) and $Pb^{2+}$ ions from aqueous solution. CM-β-CD polymers have the ability to form inclusion complexes with organic pollutants in their hydrophobic cavities and also to adsorb metal ions due to the presence of multiple hydroxyl/carboxylic functional groups in the polymer matrix, which can interact with the metal ions by complexation reactions. The adsorption behaviors of CMPCD-MNPs with both pollutants were studied using both equilibrium and kinetic viewpoints.

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# 2. Experimental

## Materials

Iron (II) chloride tetrahydrate (99%), Iron (III) chloride hexahydrate (98%), chloroacetic acid (99%), Bisphenol A (98%) was purchased from Alfa Aesar. Ammonium hydroxide (25%) was purchased from Merck (USA). β-CD (99%) was obtained from Tokyo Kasie Kogyo (Japan). The water in this work was Milli-Q ultrapure water.

# 3. Methods

## Synthesis of CM-β-CD polymer coated magnetic nanoparticles (CMPCD-MNPs)

First, CM-β-CD polymer was prepared following the procedure as described in literature[11]. Briefly, β-CD (5 g) was dissolved in 50 ml of 10% (w/v) NaOH and 10 ml of epichlorohydrin were added. The system was vigorously stirred for 8 h, another 5 ml of epichlorohydrin added with stirring and the mixture kept overnight at room temperature. The solution was concentrated and precipitated by addition of cold ethanol (500 ml). The gummy precipitate was then washed with ethanol and acetone and dried under high vacuum overnight. Then, two grams of the above polymer were further dissolved in 50 ml 5% (w/v) NaOH and 2 g of monochloroacetic acid were 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 and then washed again with ethanol and acetone and dried under high vacuum overnight.

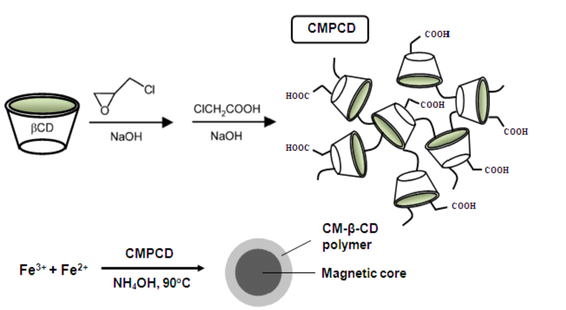


Fig.1. Scheme representation of CM-β-CD polymer coating on bare magnetic nanoparticles.

CMPCD-MNPs were fabricated by one step co-precipitation method. Briefly, 0.86 g of $FeCl_2.4H_2O$, 2.36 g $FeCl_3.6H_2O$ and 1.5 g CMPCD were dissolved in 40 ml of de-aerated Milli-Q water with vigorous stirring at a speed of 1,200rpm. 5 ml of $NH_4OH$ was added after the solution was heated to 90ºC. The reaction was continued for 1.5 h at 90ºC under constant stirring and nitrogen environment. The resulting nanoparticles were then washed with Milli-Q water few times to remove any unreacted chemicals and dried in a vacuum oven.

## Adsorption of BPA and $Pb^{2+}$ ions

BPA and $Pb^{2+}$ ions adsorption experiments were carried out using batch equilibrium technique in aqueous solutions at different pH range at 25ºC. In general, 120 mg of wet magnetic nano-adsorbent was added to 10 mL of BPA or $Pb^{2+}$ ions solution of various concentrations and shaken in a thermostatic water-bath shaker operated at 220 rpm for a specific period of time to reach adsorption equilibrium. The magnetic nanoadsorbents were then removed using a strong permanent magnet made of Nd-Fe-B and the supernatant was collected. The amount of BPA in the supernatant was then quantified by UV-vis spectrophotometer. The detection wavelength of BPA was set at 276.4 nm. The concentrations of $Pb^{2+}$ ions were measured using Atomic Absorption Spectrometer (Agilent ICP-MS 7700 series).

# 4. Results & Discussion

## Synthesis and characterization

The step-by-step reaction procedures to synthesize CM-β-CD polymer modified magnetic nanoparticles are shown in Fig. 1 In this method, the carboxyl groups of CM-β-CD polymer directly react with the surface OH groups on the magnetite to form Fe-carboxylate.

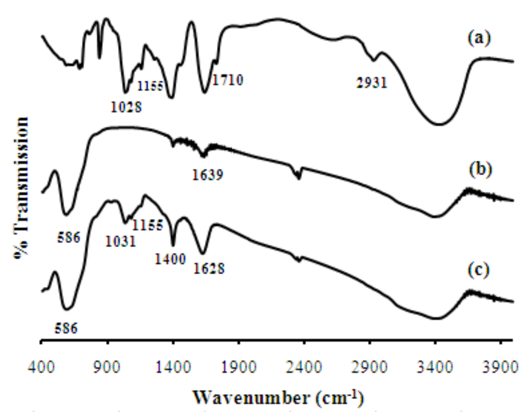


Fig.2. FTIR spectra of (a) CM-β-CD polymer, (b) uncoated MNPs and (b) CMPCD-MNPs.

The grafting of CM-β-CD polymer on magnetic nanoparticles is confirmed by FTIR spectroscopy. Fig.2 shows the FTIR spectra of as-synthesized nanoparticles in the 400-4000 $cm^{-1}$ 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 $cm^{-1}$ corresponded to the antisymmetric glycosidic $\nu_a$(C-O-C) vibrations and coupled ν (C-C/C-O) stretch vibration. The peak at 1710 $cm^{-1}$ corresponds to

Journal of Chemical Engineering, IEB
Vol. ChE. 27, No. 1, June 2012

carbonyl group (=CO) stretching which confirms the incorporation of the carboxymethyl group ($-COOCH_3$) into CM-β-CD polymer. The characteristic adsorption band of Fe–O bonds in the tetrahedral sites is 586 $cm^{-1}$. All the significant peaks of CM-β-CD polymer in the range of 900–1200 $cm^{-1}$ are present in the spectrum of CMPCD-MNPs with a small shift. Moreover, as shown in Fig. 2(c), 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[12].

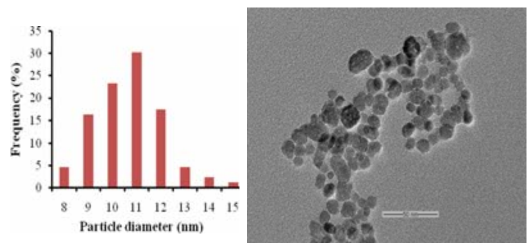

Fig.3. TEM micrograph and size distribution of CM-β-CD polymer coated magnetic nanoparticles. (Scale bar is 50 nm).

Typical TEM image and size distribution of CMPCD-MNPs are shown in Fig. 3. Well-shaped spherical or ellipsoidal magnetic nanoparticles are observed. The mean diameter of CM-β-CD coated magnetic nanoparticles is about 11 nm.

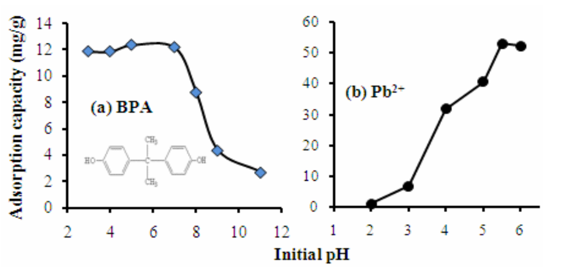

Fig.4. Effect of pH on the adsorption of (a) BPA and (b) $Pb^{2+}$ onto CMPCD-MNPs. (BPA: 0.50 mg/mL and $Pb^{2+}$: 200 mg/L).

## 5. Adsorption results

### Effects of pH

The solution pH plays an important role in the adsorption process. The effects of initial solution pH on CMPCD-MNPs adsorption capacity for BPA and $Pb^{2+}$ are presented in Fig. 4. It can be seen that adsorption of BPA remained roughly unchanged at pH below about 7.0, while increase in pH above about 7.0 resulted in a gradually decreased adsorption. A decreasing trend at a higher pH ranging from 7 to 11 was also observed when insoluble cross-linked cyclodextrin polymers were used as adsorbents[13]. The result could be elucidated by the p*Ka* value of bisphenol-A ranging from 9.6 to 10.5[1], implying that the ionization of bisphenol-A occurred at around pH 8–10 to form the phenolate and bisphenolate anions. The phenolate anions have less tendency to be included in the hydrophobic cavity of cyclodextrin moieties, hence decrease the adsorption capacity of CMPCD-MNPs

From Fig. 4 it is also observed that the $Pb^{2+}$ uptake capacity increases with an increase in pH from 2 to 6. The maximum metal uptake capacity was observed at pH 5.5– 6. At pH below 6, $Pb^{2+}$ is the major species, and with the increase of pH from 6 to 9, Pb(OH)+ dominates[14]. The variation in metal uptake capacity with pH can be explained by considering the differences in the charge state of metal ions, as well as the zero point of charge (ZPC) of CMPCD-MNPs ($pH_{ZPC}$ = 4.5). Generally at pH below the zero point charge, $H^+$ ions compete effectively with $Pb^{2+}$ ions for adsorption sites causing a decrease in uptake capacity. At pH above the zero point charge, the surface of the adsorbent gets negatively charged, which enhances the positively charged $Pb^{2+}$ through electrostatic forces of attraction.

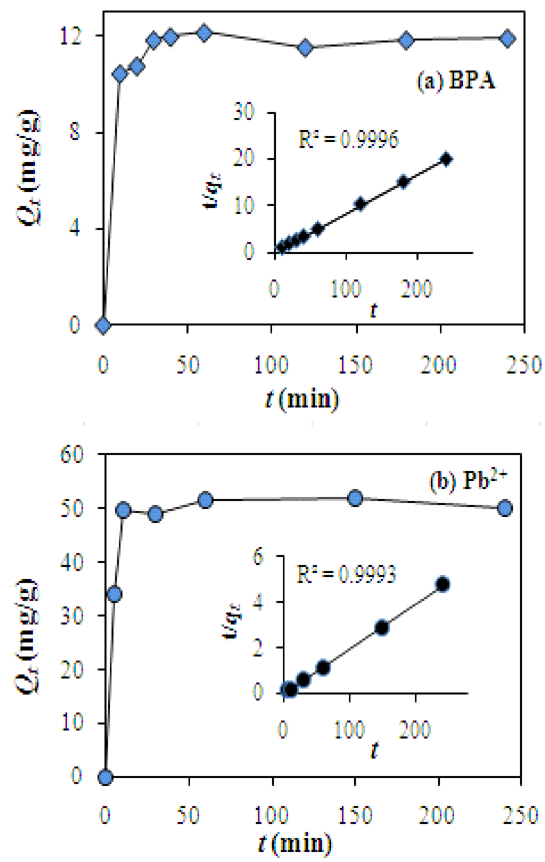

Fig.5. Effect of contact time on BPA (at pH 7 and conc. 0.5 mg/mL) and (b) $Pb^{2+}$ adsorption by CMPCD-MNPs (at pH 5.5 and conc. 200 mg/L). Insets: pseudo-second-order kinetics.

Journal of Chemical Engineering, IEB
Vol. ChE. 27, No. 1, June 2012

## Effect of contact time and kinetics

Fig. 5 illustrates the adsorption of BPA and $Pb^{2+}$ ions on CMPCD-MNPs from aqueous solution as a function of contact time. It can be seen from Fig. 5 that the maximum adsorption of both contaminants was achieved almost within 20-30 min and the adsorption remained nearly constant after that.

The pseudo-second-order rate model is often used to simulate the adsorption kinetic of contaminants on magnetic nanoadsorbents[12]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \qquad (1)$$

Where $k_2$ is the rate constant of pseudo-second-order adsorption (g $mg^{-1}min^{-1}$). The slope and intercept of the plot of $t/Q_t$ versus $t$ are used to calculate $k_2$ and $Q_{e,cal}$ (Fig. 5). The correlation coefficient ($R^2$) for the pseudo-second-order adsorption model has high value (> 99%) which indicates that the kinetic adsorption can be well described by a pseudo-second-order rate equation. The values of $k_2$, $Q_e$ and $R^2$ are 0.91 g/(mg·min), 11.95 mg/g and 0.9996 for BPA and 0.05 g/(mg·min), 50.76 mg/g and 0.9993 for $Pb^{2+}$ ions, respectively.

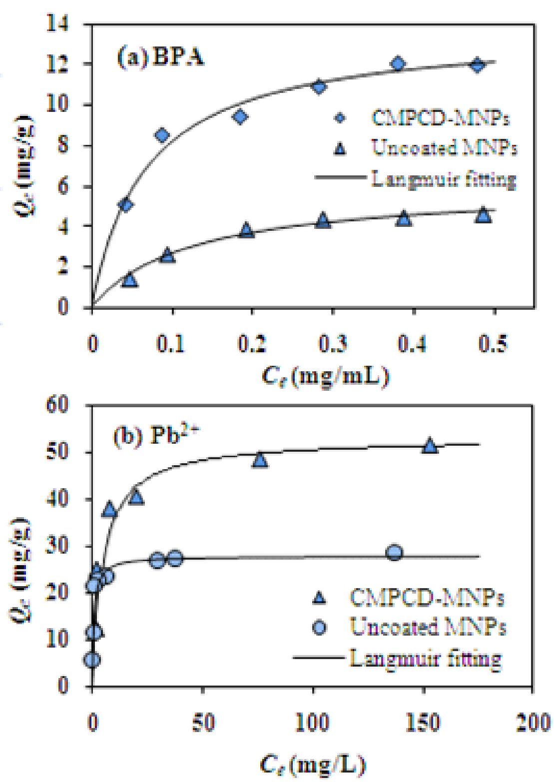


Fig.6. The adsorption isotherm of (a) BPA at pH 7 and (c) $Pb^{2+}$ at pH 5.5 onto uncoated and CMPCD-MNPS at 25$^{o}$C.

## Equilibrium studies

The equilibrium isotherms for the adsorption of BPA and lead ions by uncoated MNPs and CMPCD-MNPs at 25$^{o}$C are shown in Figuer 6. The equilibrium data are fitted by Langmuir and Freundlich isotherm model which can be expressed in eqs 2 and 3, respectively:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \qquad (2)$$

$$\ln Q_e = (1/n)\ln C_e + \ln K_F \qquad (3)$$

where $Q_e$ is the amount of adsorbate adsorbed per mass of adsorbent at equilibrium (mg/g), $C_e$ is the equilibrium concentration of adsorbate in aqueous solution (mg/mL), $Q_m$ is the monolayer adsorption capacity at equilibrium (mg/g), $K_L$ 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).

Table 1. Adsorption isotherm parameters for BPA and $Pb^{2+}$ ions onto uncoated and CMPCD-MNPS.

| Iso-therm Models | Para-meters | Bisphenol A (pH 7) | | $Pb^{2+}$ (pH 5.5) | |
|---|---|---|---|---|---|
| | | CMPCD - MNPs | Bare MNP | CMPCD -MNPs | Bare MNP |
| Lang-muir | $q_m$ (mg/g) | 13.70 | 5.90 | 52.20 | 28.01 |
| | $K_L$ (L/mg) | 0.015 | 0.008 | 0.208 | 1.25 |
| | $R^2$ | 0.995 | 0.988 | 0.999 | 0.999 |
| Freund-lich | $n$ | 3.01 | 2.02 | 3.88 | 4.00 |
| | $K_F$ (L/g) | 0.016 | 0.008 | 16.43 | 13.46 |
| | $R^2$ | 0.919 | 0.919 | 0.853 | 0.731 |

The isotherm parameters and related $R^2$ values are shown in Table 1. The adsorption isotherm data of both contaminants on this adsorbent are better fitted to Langmuir isotherm model ($R^2$ > 0.99) in compared to Freundlich model. Based on Langmuir isotherms, the maximum adsorption capacities ($Q_m$) of CMPCD-MNPs toward BPA and $Pb^{2+}$ are 13.70 and 50.5 mg/g, respectively at 25°C, which are almost or more than twice than those obtained using uncoated MNPs. These results indicate that the modification of magnetite surface by CM-β-CD polymer could enhance the adsorption capabilities of CMPCD-MNPs.

The inner cores of CM-β-CD molecules, with their hydrophobic cavities, easily adsorb BPA through host-guest interactions. The main interactions in the complexation process between cyclodextrin and organic molecule are dipole-dipole, hydrogen bonding, van der

Waals, hydrophobic and charge transfer interaction[8]. On the other hand, the multiple oxygen containing groups (mainly, hydroxyl/carboxyl groups) present in CM-β-CD polymer can form strong complexes with $Pb^{2+}$ ions on the surface of CMPCD-MNPs[12].

# 6. Conclusion

In summary, CM-β-CD polymer modified magnetic nanoparticles with magnetic and inclusion/complexation properties were successfully synthesized. The adsorption of BPA and $Pb^{2+}$ ions on these adsorbents was found to be pH dependant. The kinetics of both pollutants onto CMPCD-MNPs followed the pseudo-second-order model. The equilibrium data were fitted well by the Langmuir isotherm model. The grafted CM-β-CD polymer contributed to enhanced adsorption capacity of CMPCD-MNPs for both BPA and $Pb^{2+}$ ions from aqueous solution. Consequently, the as-obtained magnetic-cyclodextrin nanocomposites can be used as a reusable absorbent for fast, convenient, and highly efficient removal of both organic and inorganic toxic pollutants from the wastewater.

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