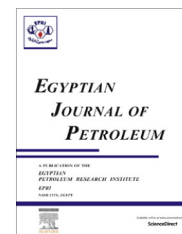


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FULL LENGTH ARTICLE

Adsorbents based on natural polymers for removal of some heavy metals from aqueous solution

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Abstract Heavy metal ions are discharged into water from several industries. They are carcinogenic and they cause severe environmental hazards. In the present work the ability of removal of copper and lead from aqueous solutions has been studied using carboxy methyl β cyclodextrin, poly(ethylene glycol) β cyclodextrin and their magnetic counterparts. Effects of pH, concentration of the metal ion, temperature and contact time have been studied. Equilibrium isotherms for the adsorption of the metals were measured experimentally. Results were analysed at different temperatures and the characteristic parameters for each adsorption isotherm were determined. The adsorption process has been found exothermic in nature and thermodynamic parameters, Gibb's free energy (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS) have been calculated. The paper also includes results on the kinetic measurements of adsorption of the metal on modified β cyclodextrin and their magnetic nano composites at different temperatures. It was found that poly (ethylene glycol) β cyclodextrin showed better performance than carboxy methyl β cyclodextrin.

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1. Introduction

Toxic heavy metals are considered one of the major pollutants that affect man and animals directly. They are not biodegradable and can accumulate in living organisms [1] Industrial wastewater containing lead, copper, cobalt and chromium, etc for example can contaminate groundwater resources and thus lead to a serious groundwater pollution problem [2,3].

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The hazardous effects of some heavy metals are listed below in Table 1. Water of high quality is essential to human life and water of acceptable quality is essential for other activities such as agriculture, industrial, domestic and commercial uses. All these activities pollute the water when thrown to freshwater every day. As known, fresh water resources decrease remarkably day by day [4,5]. The task of providing proper treatment facility for all polluting sources is very difficult and also expensive. Therefore, there is an increased demand for innovative and low cost technologies. The adsorption technique is favoured over other methods since it is environmentally safe, economical and technically easy to separate as the requirement of the control system is minimum [6–9]. Instead

Table 1 The hazardous effects of some heavy metals.

Heavy metal	Toxicities	MCL (mg L ⁻¹)
Arsenic	Skin manifestations, visceral cancers and vascular disease	0.050
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhoea, nausea, vomiting, carcinogen	0.05
Copper	Liver damage Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst	0.80
Lead	Damage to the foetal brain, diseases of the kidneys and circulatory system	0.00003

of using synthetic adsorbents or commercial activated carbon, researchers have worked on inexpensive materials such as egg shell [10], orange peels [11], oil palm shell [12], shrimp shell [13] and other adsorbents [14–17], which have high adsorption capacity and are locally available. Cyclodextrins are molecular chelating agents. They possess a cage-like supra-molecular structure thus they attract attention as strong adsorbents of natural origin [18–20].

Cyclodextrins are cyclic oligosaccharides consisting of six α -cyclodextrin, seven β -cyclodextrin, eight γ -cyclodextrin or more glucopyranose units linked by α -(1,4) bonds. β -Cyclodextrin is the most accessible, the lowest-priced and generally the most useful. Fig. 1 illustrates the chemical structure of β -cyclodextrin [21]. β -cyclodextrin as a renewable and biodegradable compound has the ability to chelate various metal ions and this ability can be improved by chemical modification through esterification, etherification, oxidation reactions and cross-linking of hydroxyls outside the interior cavity [22]. Though β -cyclodextrin/metal complexation has been used in the removal of heavy metals [23], very little attention has been paid to the kinetics of adsorption and selectivity of heavy metal ions on these magnetic adsorbents. In this work, β -cyclodextrin was modified chemically by two methods:

esterification (carboxy methyl β -cyclodextrin) and etherification (poly (ethylene glycol) β -cyclodextrin). A comparative study between the efficiency of the modified β -cyclodextrins and their magnetic counterparts in removing some heavy metals was carried out. The mechanism of metal removal, kinetics of adsorption and the factors affecting the adsorption process were considered.

2. Materials and methods

2.1. Chemicals

All the chemicals used in this work are of analytical grade and purchased from Sigma–Aldrich Company. They include: Iron (II) chloride tetrahydrate, iron (III) chloride hexahydrate, chloroacetic acid, ammonium hydroxide (25%), lead(II) nitrate and copper (II) nitrate, β -Cyclodextrin, β , β' dichloro diethyl ether and poly(ethylene glycol) M.wt 1000. The water in this work was double-distilled water.

2.2. Synthesis of CM- β -CD polymer [24,25]

CM- β -CD polymer was prepared as follows: In a 1 L flat bottom flask, 5 g of β -cyclodextrin was dissolved in 50 ml of 10% NaOH then 10 ml of epichlorohydrin was added. The system was vigorously stirred for 8 h before another 5 ml of epichlorohydrin was added with continuous stirring and the mixture kept overnight at room temperature. The solution was concentrated to about 15 ml and precipitated by addition of 500 ml of cold ethanol. The precipitate was crushed several times with ethanol in a mortar until a fine precipitate was obtained. For further purification, the precipitate was then washed again with ethanol and acetone and dried in a vacuum oven overnight. The yield of β -CD/epichlorohydrin co-polymer was 72%. Five grams of the above polymer was further dissolved in 50 mL 5% NaOH and 5 g of mono chloroacetic acid was added. The system was vigorously stirred for 24 h then 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 500 ml cold ethanol. The precipitate was crushed with ethanol until a fine powder was obtained. The yield of CM- β -CD polymer was 55%. The molecular weight of this polymer (Mp = 10,200,

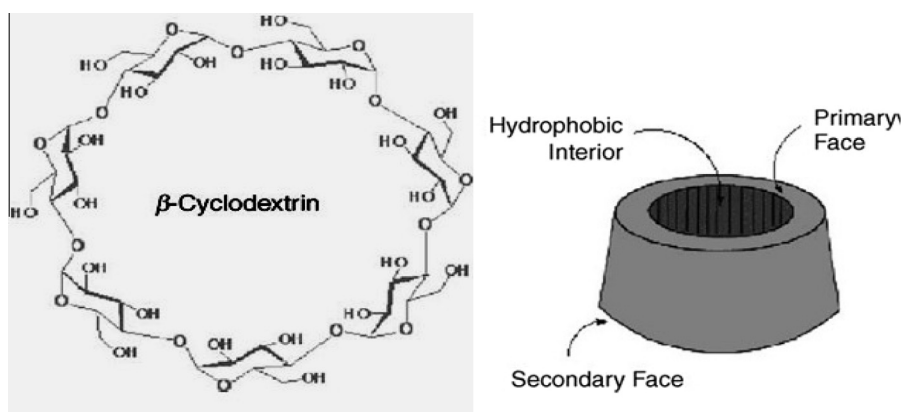


Figure 1 Chemical structure of β -cyclodextrin.

Table 2 Codes and composition of the modified β -CD.

Code	Composition
CM- β -CD	Carboxy methyl β cyclodextrin polymer
M-CM- β -CD	Carboxy methyl β cyclodextrin magnetic nanocomposite
PEG- β -CD	Poly ethylene glycol β cyclodextrin polymer
M-PEG- β -CD	Poly ethylene glycol β cyclodextrin magnetic nanocomposite

Mw = 12,820 and Mn = 12,450) was determined by gel permeation chromatography, Jordi Gel xStream H₂ OTM.

2.3. Synthesis of CM- β -CD magnetic nanocomposite (M-CM- β -CD)

CM- β -CD polymer was fabricated by co-precipitation method. Briefly, 0.92 g of FeCl₂·4H₂O, 2.7 g FeCl₃·6H₂O and 1.9 g CM- β -CD polymer were dissolved in 50 ml of de-ionized water with vigorous stirring at a speed of 1200 rpm. After the solution was heated to 90 °C, 5 ml of NH₄OH (25%) was added. The reaction was continued for 1 h at 90 °C under constant stirring and nitrogen environment. The resulting nanoparticles were then washed several times to remove any unreacted chemicals and dried in a vacuum oven for two hours.

2.4. Synthesis of PEG- β -CD polymer

In a 500-mL round flask fitted with a mechanical stirrer, Dean-Stark side arm, and digital temperature controller (Prolabo S-09), 0.01 mol of β -cyclodextrin is dissolved in a mixture of 0.01 mol of β , β' dichloro diethyl ether, and 0.01 mol of polyethylene glycol. 0.02 mol of NaOH was added

as a catalyst. The reaction temperature was raised gradually and adjusted at 170 °C until the calculated amount of water is collected (0.02 mol). At the end of the reaction, the product is treated with an equal volume of saturated NaCl solution, and then neutralized with dil. HCl. The temperature of the mixture is raised to boiling and maintained for an hour. The upper layer was separated and dried in a vacuum oven at 50 °C to a constant weight.

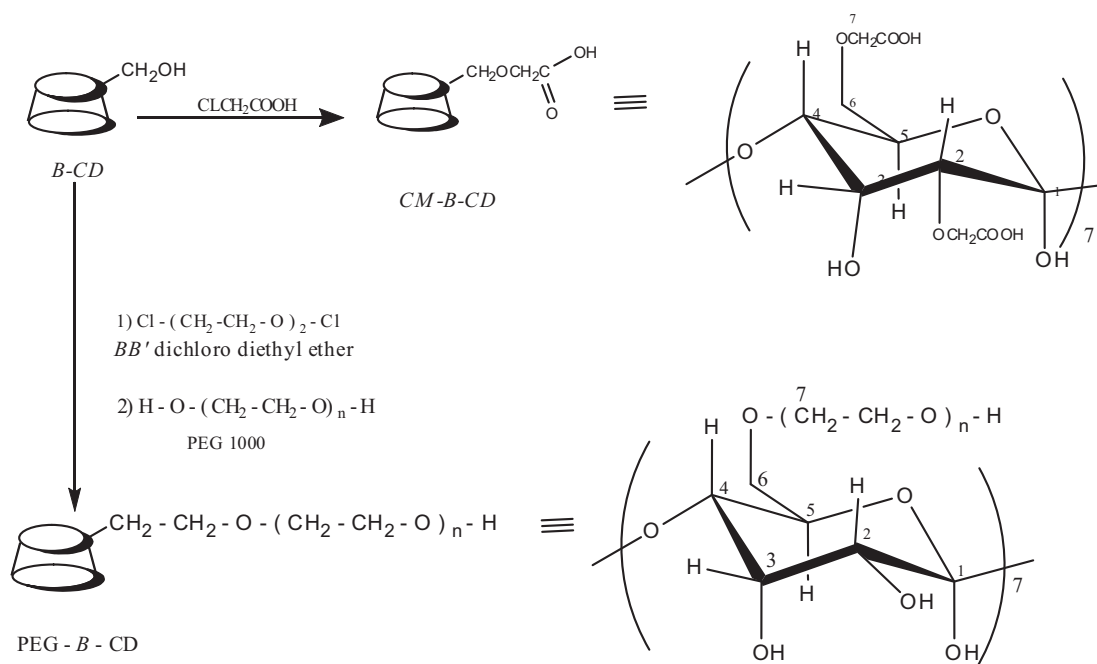
2.5. Synthesis of M-PEG- β -CD polymer

M-PEG- β -CD polymer was prepared by co-precipitation method. Briefly, 1.4 g of FeCl₂·4H₂O, 3.9 g FeCl₃·6H₂O and 12.7 g PEG- β -CD polymer were dissolved in 70 ml of de-ionized water with vigorous stirring at a speed of 1200 rpm. After the solution was heated to 90 °C, 9 ml of NH₄OH (25%) was added. The reaction was continued for 2 h at 90 °C under nitrogen environment. The resulting nanoparticles were rinsed with distilled water several times to remove any unreacted chemicals and dried in a vacuum oven for two hours.

The notation of the prepared compounds and their codes are provided in Table 2, moreover, all the previous reactions are provided in Scheme 1. The codes and composition for the prepared compounds are given in Table 2.

2.6. Adsorption and adsorption kinetics of heavy metal ions [26]

The uptake capability of the β -CD polymer and their nanocomposites for lead and copper ions was studied using the batch equilibrium method at different application conditions. An accurately weighed polymer sample (0.05 g) was suspended in the metal solution and shaken for 4 h (which was enough for achieve equilibrium) in atmospheric conditions. Then, the adsorbents were removed from the solution by

**Scheme 1** Modification reactions of β -CD.

magnetic separation. The concentration of the metal ion in the filtrate was measured by using atomic absorption spectrometer/ZEEnit 700P/Analytikjena Co./Germany.

The amount of adsorbed ions was determined by difference between the initial and final concentration of the metal.

For the kinetic experiments, the initial metal ion concentration used was 300 mg L^{-1} and the pH used was 5.5. At different time intervals, samples were collected after magnetic decantation and the concentrations of studied pollutants were determined. In the binary adsorption experiments, the studied metal ions were added in equal mass concentration (each 150 mg L^{-1}) to a 10 ml solution contained in the vial. The vials were shaken at 800 rpm for 2 h to ensure equilibrium before the magnetic nanoparticles being removed and the concentrations of remaining metal ions were measured as mentioned previously.

2.7. Characterization of the materials

A Field Emission Transmission Electron Microscopy (JEOL2011F) 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 gold grid (200 mesh). The gold film was then dried at room temperature for

24 h before the measurement. The functionalization of β -CD polymer onto the surface of Fe_3O_4 nanoparticle was monitored by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). FTIR measurements were performed using Shimadzu infrared spectrometer (Model400) on KBr disc over the range of $4000\text{--}400 \text{ cm}^{-1}$. X-ray diffraction (XRD) analysis was carried out on Shimadzu XRD 2000.

Thermo gravimetric Analysis (TGA) was carried out to measure the changes in the weight loss of the sample as a function of temperature and time thermal analysis technique is used. The thermo gravimetric analysis (TGA) was performed on a thermal analysis system (Model: TA 2050). For TGA measurements, 7–15 mg of the dried sample was loaded into the system and the mass loss of dried sample was monitored under N_2 at temperatures ranging from room temperature to $800 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C}/\text{min}$.

3. Results and discussion

3.1. Synthesis and characterization of magnetic nanoparticles

The detailed synthesis procedures of modified β -CD are shown in Scheme 1. The characterization of these nano-sized particles and their magnetic counter parts was performed by FTIR,

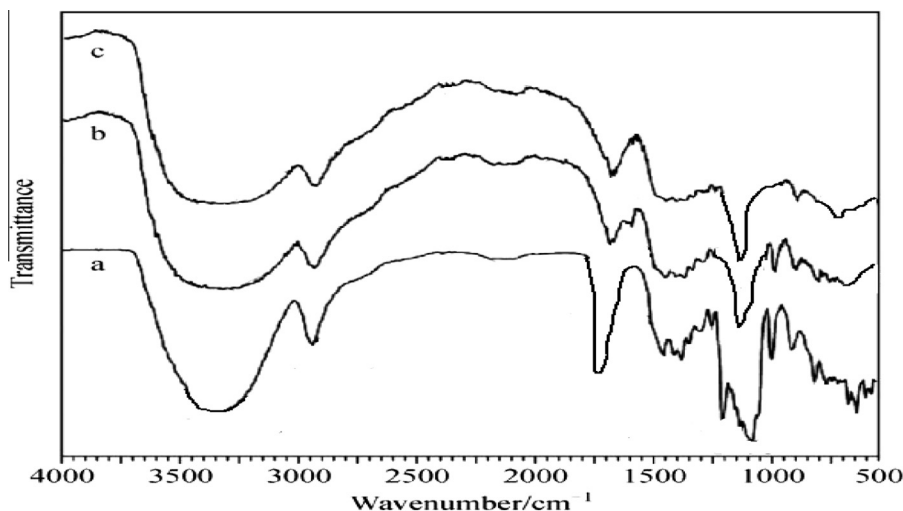


Figure 2 IR spectra of a-CM- β -CD, b-PEG- β -CD and c- β -CD.

Table 3 The most characteristic peaks for the modified β -CDs.

The compound	The most characteristic peaks	Data interpretation
CM- β -CD	<ul style="list-style-type: none"> The broad band at $3300\text{--}3500 \text{ cm}^{-1}$ A strong peak at 2850 cm^{-1} The peak at 950 cm^{-1} Two peaks at 1030 and 1170 cm^{-1} A peak at 1750 cm^{-1} 	<ul style="list-style-type: none"> —OH stretching vibrations C—H aliphatic R-1,4-bond skeleton vibration of β-CD Asymmetric glycosidic (C—O—C) vibrations and coupled $\nu(\text{C—C/C—O})$ [28,29] carbonyl group ($=\text{CO}$)
PEG- β -CD	<ul style="list-style-type: none"> The broad band at $3300\text{--}3500 \text{ cm}^{-1}$ Two peaks at 1070 and 1200 cm^{-1} A peak at 1350 cm^{-1} 	<ul style="list-style-type: none"> —OH stretching vibrations Asymmetric glycosidic (C—O—C) vibrations and coupled $\nu(\text{C—C/C—O})$ [28,29] Methylene group (CH_2)
β -CD	<ul style="list-style-type: none"> The broad band at $3200\text{--}3500 \text{ cm}^{-1}$ Two peaks at 1055 and 1180 cm^{-1} 	<ul style="list-style-type: none"> —OH stretching vibrations Asymmetric glycosidic (C—O—C) vibrations and coupled $\nu(\text{C—C/C—O})$ [28,29]

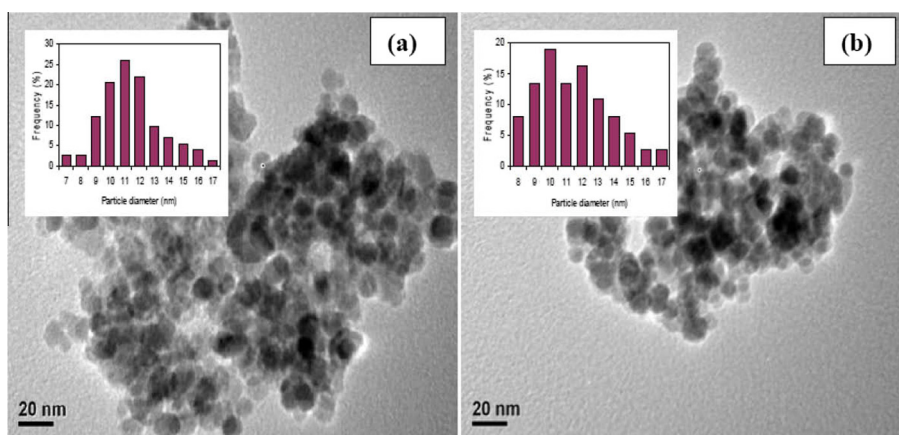


Figure 3 TEM images of a-M-CM-β-CD and b-M-PEG-β-CD.

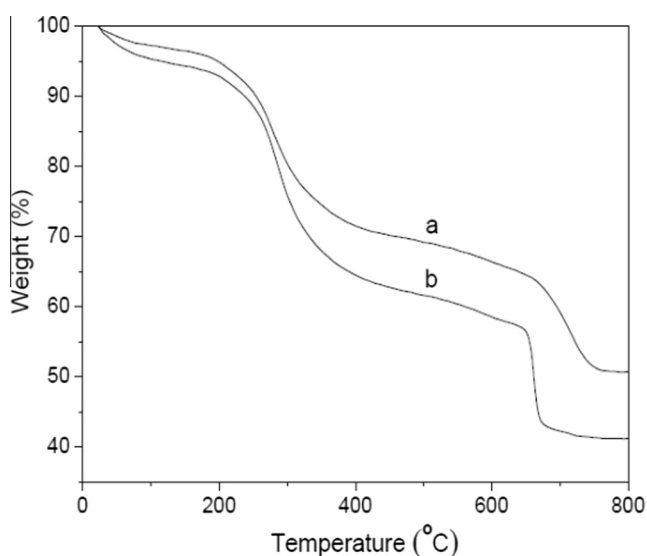


Figure 4 the TGA curves for a-M-PEG-β-CD and b-PEG-β-CD.

TEM and XRD. IR spectra of CM-β-CD, PEG-β-CD and β-CD in the 400–4000 cm^{-1} wave number range are given in Fig. 2a–c respectively. The most characteristic peaks and their interpretation are summarized in Table 3.

TEM images and particle size distributions of M-CM-β-CD and M-PEG-β-CD are shown in Fig. 3(a) and (b) respectively. Spherical or ellipsoidal shaped magnetic nanoparticles can be observed. The mean diameter of both M-CM-β-CD and M-PEG-β-CD is about 11–14 nm. This indicates that binding process did not significantly result in the agglomeration and more changes in their sizes.

The amount of polymer grafted on Fe_3O_4 magnetic nanoparticles is estimated from TGA analyses of uncoated and PEG-β-CD coated magnetic nanoparticles. As shown in Fig. 4 a and b, the TGA curves for M-PEG-β-CD and PEG-β-CD exhibited two steps of weight loss, contributed from the loss of residual water in the sample in 50–220 °C and the loss of PEG-β-CD in the range of 220–450 °C. From the TGA curve for M-PEG-β-CD and PEG-β-CD, a drastic drop of 5% and 13%, respectively can be seen in the range 220–450 °C and it is contributed from the thermal decomposition of PEG-β-CD moieties. Below 220 °C, the rate of weight loss

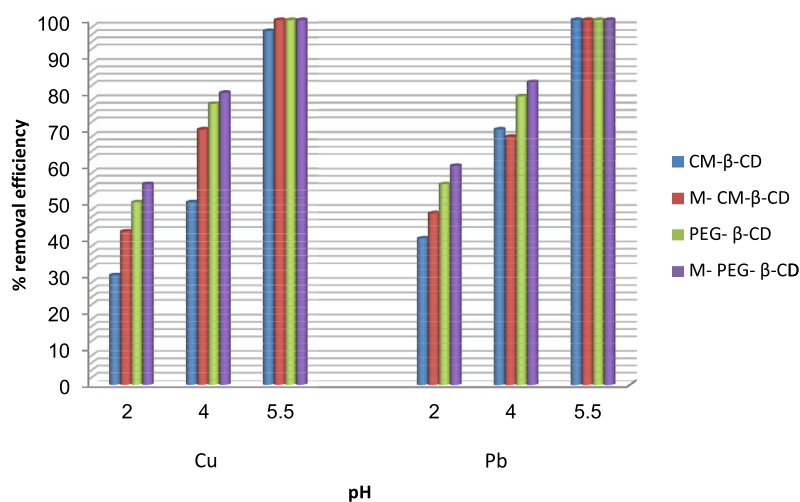


Figure 5 The effects of initial solution pH on Cu^{2+} and Pb^{2+} adsorption onto modified β-CD polymers (pH 2–5.5, 25 °C, and an initial metal ion concentration of 150 ppm).

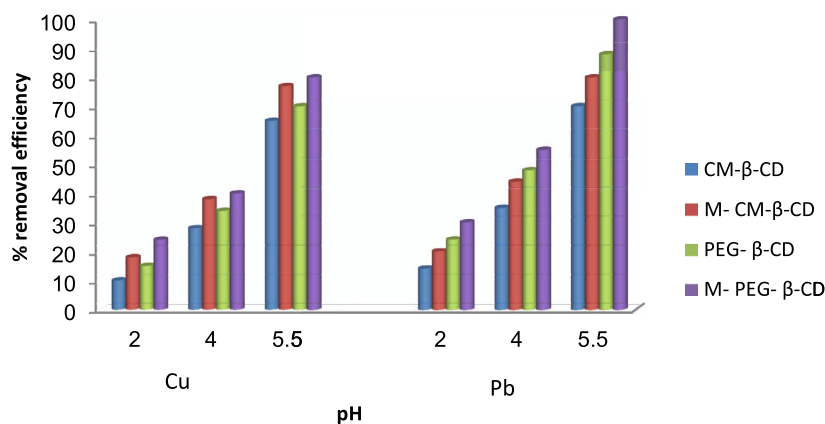


Figure 6 The effects of initial solution pH on Cu^{2+} and Pb^{2+} adsorption onto modified β -CD polymers (pH 2–5.5, 25 °C, and an initial metal ion concentration of 300 ppm).

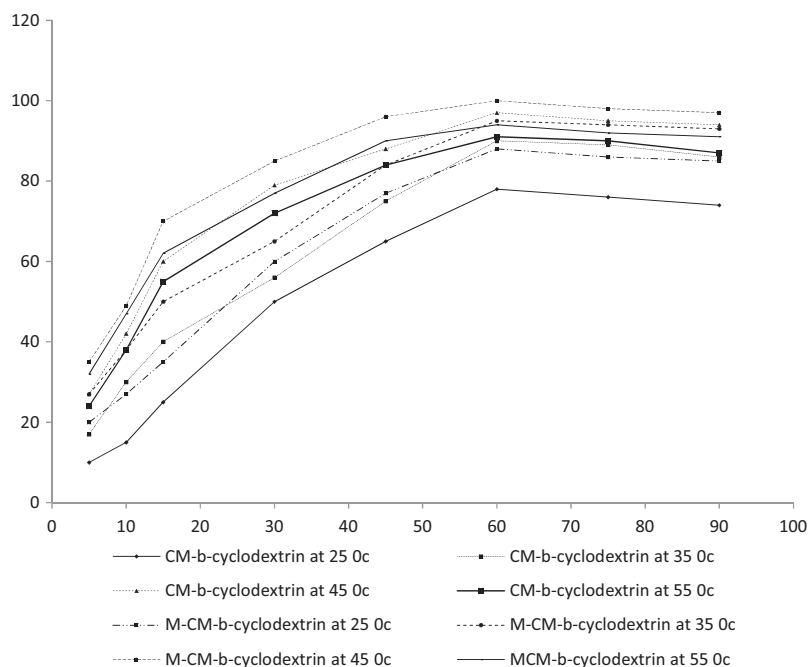


Figure 7 Percentage removal of Cu ion by CM- β -CD and M-CM- β -CD at different temperatures (at pH 5.5 and 50 ppm of the adsorbent).

is relatively slow due to the loss of residual water adhering to the sample surface and adsorbed in the CD cavities and entrapped between PEG chains. Thus, the TGA curves also confirm the successful grafting of PEG- β -CD molecules onto the magnetic surface.

3.2. Adsorption of metal ions on modified β -CD polymers

3.2.1. Effect of pH

The pH of the aqueous solution is a very important parameter in controlling the adsorption process [27–30]. The effects of initial solution pH on Cu^{2+} and Pb^{2+} adsorption onto modified β -CD polymer were investigated at pH 2–6, 25 °C, and an initial metal ion concentration of 150 and 300 mg L^{-1} . As

shown in Figs. 5 and 6, it is noteworthy that the adsorption capacity of metal ions increases with the solution pH at an initial ion concentration of 150 mg L^{-1} . This might be due to the less insignificant competitive adsorption of hydrogen ions [31,32]. At a higher initial ion concentration (300 mg L^{-1}), the adsorption capacity remarkably decreases with decreasing the solution pH due to enhanced competition between the hydrogen ions and the metal ion in the solution. It is obvious that the affinity of the investigated polymers towards lead ions is greater than towards copper ions. It is well known that Cu (II) species can be present in aqueous solution in the forms of Cu^{2+} , $\text{Cu}(\text{OH})^+$, $\text{Cu}(\text{OH})_2$, $\text{Cu}(\text{OH})_3$ and $\text{Cu}(\text{OH})_4$ and the predominant copper species at pH < 6.0 is Cu^{2+} [33,34]. Therefore, less adsorption of Cu^{2+} that takes place can be

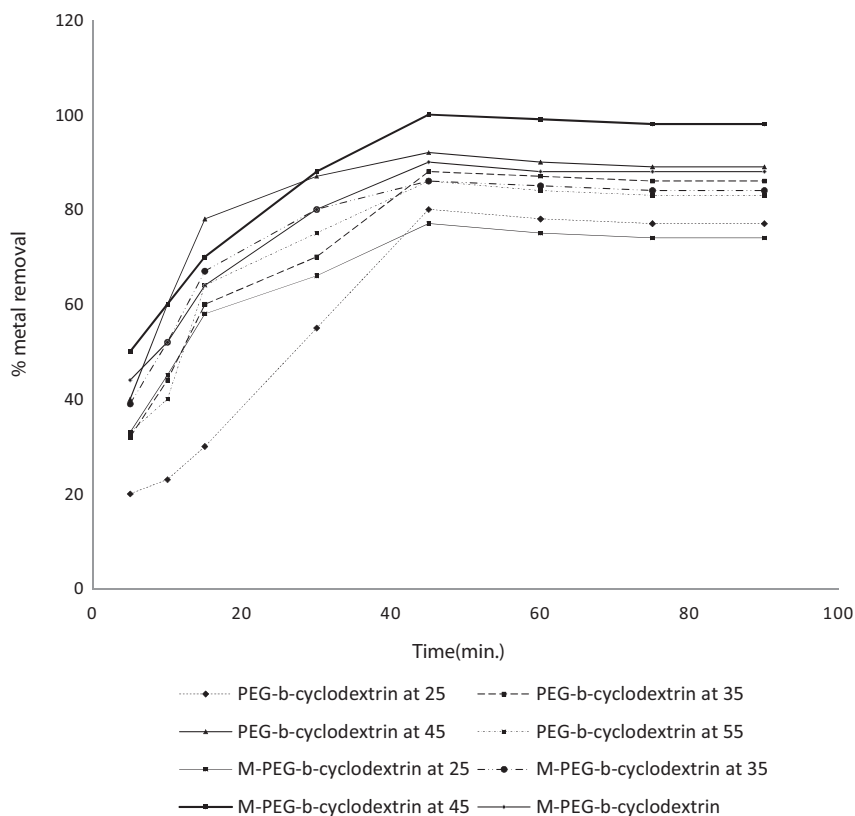


Figure 8 Percentage removal of Cu ion by PEG-β-CD and M-PEG-β-CD at different temperatures (at pH 5.5 and 50 ppm of the adsorbent).

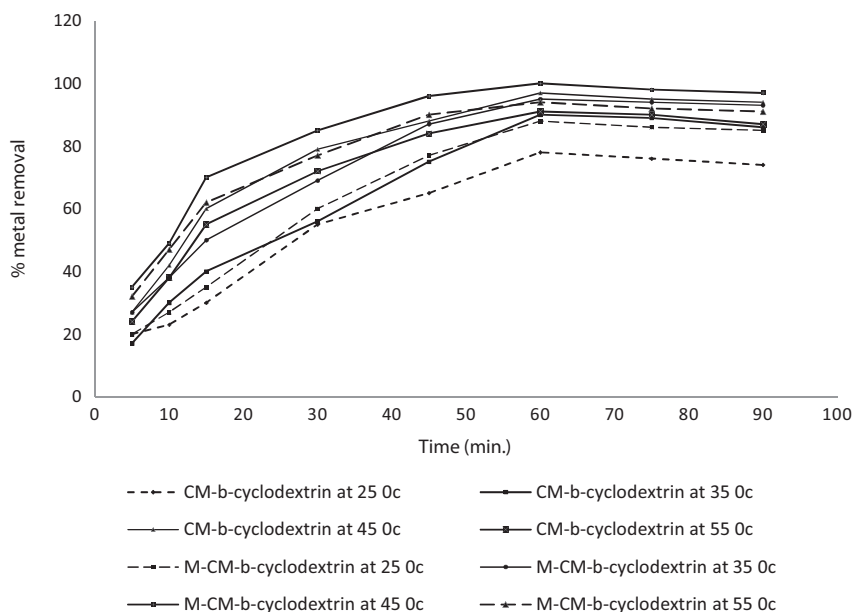


Figure 9 Percentage removal of Pb ion by CM-β-CD and M-CM-β-CD at different temperatures (at pH 5.5 and 50 ppm of the adsorbent).

explained by the fact the H^+ ions compete with copper cations for the same adsorption sites [35]. The adsorption studies at

pH > 6 were not conducted because of the precipitation of $Cu(OH)_2$ from the solution.

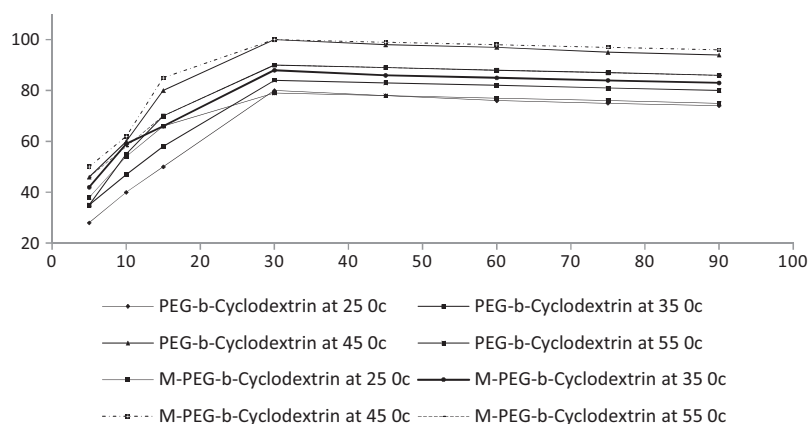


Figure 10 Percentage removal of Pb ion by PEG- β -CD and M-PEG- β -CD at different temperatures (at pH 5.5 and 50 ppm of the adsorbent).

3.2.2. Effect of temperature

The effect of temperature on the adsorption isotherm was investigated under isothermal conditions in the temperature range of 25–55 °C and at pH 5.5. Figs. 7–10 show the effect of temperature on metal removal by the modified β -CD polymers. It is obvious that there is an optimum temperature and time to achieve maximum metal uptake by the investigated samples. For CM- β -CD and M-CM- β -CD, the maximum metal uptake of Copper ions was reached after an hour at 45 °C and after 45 min at the same temperature for Pb ion. It was observed that the percentage ion uptake decreases by increasing the temperature from 45 °C to 55 °C. This may be due to that metal ions may acquire higher kinetic energy on higher temperature. This leads to increase the rate of desorption than the rate of adsorption. Furthermore, at higher temperature, the interaction between the metal and the active sites becomes weaker which cause the metal ions to re-dissolve in the solution. Our finding runs in harmony with the results obtained by Chen et al. [36].

3.2.3. Effect of contact time

Figs. 7–10 show the effect of contact time on adsorption of metal ions onto modified β -CD polymers. It can be seen that a rapid adsorption occurs, with different equilibrium times that differ from sample to another. The minimum equilibrium time was 45 min for β -CD polymers modified with PEG whereas the maximum equilibrium time was 60 min for carboxymethyl β -CD polymer. This suggests that modified β -CD polymers could easily and rapidly abstract metal ions from

aqueous solution due to high specific surface area and the absence of internal diffusion resistance. Rapid adsorption rate for copper removal has also been observed using several magnetic nanoparticle based nano-adsorbents [37,38]. It was found that the adsorption by β -CD modified with PEG reaches equilibrium faster than β -CD modified with the carboxy methyl group. This may be explained by the greater affinity of PEG chains towards the metal ions and their better abstraction power due to the coiling of the chains which provides more adsorption sites. This explains the higher adsorption rate of β -CD – PEG polymers where they achieve complete metal removal at shorter adsorption time. Upon reaching equilibrium, the rate of adsorption equals the rate of desorption.

3.2.4. Rate of adsorption and adsorption kinetics

The plots in Figs. 7–10 show the rate of adsorption of lead ions is faster than that of copper ions. This may be due to the higher ionic strength of lead over copper.

The free energy change (ΔG) for adsorption was calculated using the following equation:

$$\Delta G = -RT \ln K_a = -RT \ln K_c = -RT \ln (C_{ads}/C_e) \quad (1)$$

where T is the temperature (K), R the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), C_e the metal ion concentration in solution at equilibrium and C_{ads} the concentration of metal ion adsorbed at equilibrium. The values of K_a are listed in Tables 4 and 5 for Cu^{+2} and Pb^{+2} respectively.

$$\ln K_a = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (2)$$

Table 4 Adsorption kinetic parameters of Cu^{+2} onto the β -CD modified nano-adsorbents at pH 5.5 and different temperatures.

The adsorbent	The temp. (°C)	K_1 (min^{-1})	$Q_{e,cal}$ (mg/g)	The adsorbent	The temp. (°C)	K_1 (min^{-1})	$Q_{e,cal}$ (mg/g)
CM- β -CD	25	0.0062	18.7	PEG- β -CD	25	0.0067	19.1
	35	0.0091	22.4		35	0.0094	23.6
	45	0.0140	50.0		45	0.0151	50.0
	55	0.0084	34.6		55	0.0086	36.2
M-CM- β -CD	25	0.0074	20.1	M-PEG- β -CD	25	0.0076	23.1
	35	0.0095	24.4		35	0.0097	25.3
	45	0.0156	50.0		45	0.0160	50.0
	55	0.0093	37.7		55	0.0097	38.0

Table 5 Adsorption kinetic parameters of Pb^{+2} onto the β -CD modified nano-adsorbents at pH 5.5 and different temperatures.

The adsorbent	The temp. (°C)	K_a (min ⁻¹)	$Q_{e,cal}$ (mg/g)	The adsorbent	The temp. (°C)	K_a (min ⁻¹)	$Q_{e,cal}$ (mg/g)
CM- β -CD	25	0.0074	20.4	PEG- β -CD	25	0.0082	29.4
	35	0.0101	25.4		35	0.0104	31.6
	45	0.0153	55.0		45	0.0155	57.2
	55	0.0094	44.6		55	0.0097	48.7
M-CM- β -CD	25	0.0079	24.6	M-PEG- β -CD	25	0.0081	30.9
	35	0.0111	27.9		35	0.0115	33.3
	45	0.0158	55.7		45	0.0164	57.2
	55	0.0097	39.4		55	0.0097	40.4

Table 6 Thermodynamic parameters of metal adsorption.

The adsorbent	The temp. (°C)	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹ K ⁻¹)	The adsorbent	The temp. (°C)	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹ K ⁻¹)
CM- β -CD	25	-3.431	-22.21	-0.0523	PEG- β -CD	25	-3.226	-22.78	-0.0561
	35	-3.115	-20.99	-0.0517		35	-3.179	-21.21	-0.0542
	45	-2.994	-19.34	-0.0503		45	-2.846	-19.06	-0.0521
	55	-3.008	-20.78	-0.0512		55	-3.012	-20.18	-0.0509
M-CM- β -CD	25	-3.351	-23.74	-0.0544	M-PEG- β -CD	25	-3.109	-23.77	-0.0511
	35	-3.092	-23.11	-0.0568		35	-2.915	-22.19	-0.0525
	45	-2.875	-22.77	-0.0555		45	-2.878	-21.23	-0.0510
	55	-3.117	-23.08	-0.0570		55	-3.015	-22.56	-0.0546

Values of ΔH and ΔS can be obtained from the van't Hoff plots of $\ln K_a$ versus $1/T$ from the slopes and intercepts, respectively (not provided).

The calculated thermodynamic parameters are listed in Table 6. The negative value of all ΔG indicates the feasibility of the process and spontaneous nature of metal ion adsorption onto modified β -CD adsorbents. Moreover, the magnitude of ΔG increases with increasing temperature from 25 to 45 °C indicating that adsorption is enhanced in this temperature range. Then the magnitude ΔG decreases at 55 °C indicating that the adsorption is not favourable at higher temperatures. It can be seen that the adsorption by magnetic nanoparticles is enhanced over non-magnetic counterparts. The changes of enthalpy (ΔH) and entropy (ΔS) at 25–55 °C were also determined. The negative value of ΔH confirms the exothermic nature of adsorption, i.e. spontaneous adsorption.

3.3. Mechanism of adsorption

It is reported that due to its specific characteristics (the presence of cyclodextrin moieties and complexing chemical groups), the sorption mechanism of cyclodextrin based materials is different from those of other materials [39]. The main interactions in the complexation process between cyclodextrin and other organic molecule are dipole–dipole, hydrogen bonding, electrostatic, van der Waals, hydrophobic and charge transfer interaction [40]. Among these forces, hydrophobic interactions have been mostly recognized as the main factors involved in the inclusion complex with cyclodextrin. In this study, the adsorption of metal ions is found to be pH dependent and the chelation between the active sites in the cyclodextrin and the metal ions depending on various pHs plays an important role in adsorption efficiency. The data in the previous sections reveal that the adsorbents based on β -CD

modified by PEG are more efficient than those based on CM- β -CD. However, the negative values of free energy change (ΔG) confirmed the affinity of adsorbents for the metal ions.

4. Conclusion

In this study, a magnetic novel nano-adsorbent comprising Fe_3O_4 nanoparticles modified with CM- β -CD and PEG- β -CD was prepared. Grafting of CM- β -CD and PEG- β -CD onto the magnetic nano-adsorbents is confirmed by FTIR, TGA, and XPS analyses. These magnetic nano-adsorbents were used to effectively remove Cu^{2+} and Pb^{2+} from aqueous solution. The solution pH greatly influenced the adsorption of metal ions. The optimum temperature of the solution for attaining maximum adsorption was 45 °C. Maximum adsorption of metal ion was reached after 45 min. It was found that the CD modified with PEG is more efficient than those modified with carboxy methyl because the metal affinity of PEG chain is greater than the metal affinity of the carboxy methyl group. Furthermore, the adsorption process is spontaneous and exothermic in nature. The data reveal that the tendency of the modified β -CD towards Pb^{2+} is more pronounced than Cu^{2+} . Both FTIR and XPS analyses clearly reveal that the oxygen atoms on the polymer are the main binding sites for the metal to form surface-complexes.

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