

Chelating modified cellulose bearing pendant heterocyclic moiety for effective removal of heavy metals

R. Saravanan, R. Mahalakshmi, M. S. Karthikeyan and L. Ravikumar

ABSTRACT

Cellulose bearing pendant Schiff base with heterocyclic chelating groups (CMC-Bz) was synthesized, which were fully characterized using various instrumental techniques such as solid state carbon-13 nuclear magnetic resonance ($^{13}\text{C-NMR}$), Fourier transform infrared (FTIR), scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDX) spectra. The adsorption of toxic metals onto cellulosic material was tested in a batch mode operation. The adsorption functional factors such as pH, adsorbent dose, metal ion concentration, equilibrium time and temperature were experimentally optimized for the maximum removal of Cu(II) and Pb(II) ions. Adsorption isotherms were evaluated with Langmuir, Freundlich, Temkin and Redlich–Peterson isotherms. Kinetic parameters and equilibrium adsorption capacities were investigated for pseudo-first-order, pseudo-second-order and intra-particle diffusion models. Thermodynamic parameters and reusability were also evaluated.

Key words | equilibrium, heavy metal removal, modified cellulose, specific oxidation

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INTRODUCTION

Heavy metals are the most toxic pollutant in the aquatic environment. They are generally refractory and non degradable. In the past decades, the presence of heavy metals in water resources has been of great concern to scientists and engineers in terms of their augmented discharge, toxic nature, bioaccumulation and other adverse effects (Anirudhan & Sreekumari 2011). Toxic heavy metals are mainly derived from Pb, Hg, Cd, As, Cu and Cr species etc., owing to the capability of these to pose health threats (Gao *et al.* 2010). They are often discharged by number of industries, such as batteries, smelting, metal plating, mining operations and tanneries, ammunition, fertilizer, ceramic and glass industries etc. This can lead to the contamination of fresh and marine water (Abdel-Halim *et al.* 2011). On an annual basis, significant quantities of various heavy metals are produced from mining of their respective ores. In 2004 USEPA reported that $14,500 \times 10^3$ tons of copper were produced (USEPA 2001).

Many of the heavy metals are essential to human life as micronutrients, but higher concentrations are known to produce a range of toxic effects. High levels of copper and lead in the human body cause encephalopathy, cognitive impairment, behavioural disturbances, damage to both kidney and liver, anaemia, inhibition of the biosynthesis of heme and

toxicity to the reproductive system (Pagliuca *et al.* 1990; Theophanides & Anastassopoulou 2002). The acceptable limit of copper and lead in drinking water is given by the Bureau of Indian Standards (BIS) as 0.2 mg/L and 0.01 mg/L (BIS 1994).

In developed countries, removal of heavy metals from wastewater is normally achieved by advanced technologies including physical and chemical processes such as ion exchange, solvent extraction, evaporation, membrane separation, reverse osmosis, chemical precipitation, ultra filtration, electrochemical deposition and adsorption.

Among these methods adsorption is one of the most popular and effective approaches for removing toxic heavy metals and recalcitrant pollutants from aqueous systems. Adsorption techniques are very successful for copper and lead removal from wastewater (O'Connell *et al.* 2008). The substantial drawbacks of existing adsorbents are high capital and operational costs, low efficiency and an exhausted adsorbents disposal problem, which causes serious environmental issues. This has encouraged researchers worldwide to research new materials that are both efficient and cheap.

Recently, modified cellulose has been found to be a cheaper and more efficient adsorbent. Cellulose is an eco-friendly, renewable, non toxic and plentiful material,

which also has many primary active hydroxyls that easily trigger many reactions, such as oxidation, esterification, halogenation and etherification (O'Connell *et al.* 2008). Moreover, annually 10^{11} – 10^{12} tons of relatively pure form of cellulose are synthesised by photosynthesis.

Modified cellulose with chelating groups such as quaternary ammonium groups (Zhou *et al.* 2011), succinic anhydride (Gurgel *et al.* 2008), thio and amine (Takagai *et al.* 2011), carboxyl (Marchetti *et al.* 2000; Low *et al.* 2004; Liu 2007), hydroxyl (Aoki *et al.* 1999), imidazole (O'Connell 2006; O'Connell *et al.* 2006a), amino (Maekawa & Koshijima 1990; Navarro *et al.* 1996) and amidoxime (Saliba *et al.* 2005) have been used as potential adsorbents for heavy metal ions such as Cu^{2+} , Pb^{2+} , Ni^{2+} , Cd^{2+} , Hg^{2+} , Cr^{3+} , Co^{2+} and Fe^{3+} .

Therefore, the direct chemical modification of cellulose can provide adequate structural stability and competent adsorption capacity. The periodate oxidation of cellulose under mild aqueous conditions leads to specific cleavage of the C2–C3 bond of the glucopyranose ring, which results in the formation of two aldehyde groups (Kim *et al.* 2000; Kim & Kuga 2001; Saravanan & Ravikumar 2016).

Recently, we have reported a series of modified cellulose-bearing pendant groups such as benzalaniline (Ravikumar & Saravanan 2015), pyridine (Saravanan & Ravikumar 2017b), hydroxyl (Saravanan & Ravikumar 2017a) and carboxylic acid (Saravanan & Ravikumar 2016), which act as chelating sites for the successful removal of heavy metals from aqueous solution.

The novelty of the present investigation concerns the synthesis of modified cellulose-bearing benzothiazole chelating groups possessing metal-complexing ligands like sulphur and nitrogen atoms. If these chelating functionalities are present in cellulose, they are expected to show enhanced metal ion adsorbing capacity and stability for re-use.

Fourier transform infrared (FTIR) and solid-state carbon-13 nuclear magnetic resonance (^{13}C -NMR) spectra at 100.62 MHz on a Bruker AMX-200 spectrometer were applied in order to determine the chelating groups that are responsible for complexation of synthesised chemically modified cellulose (CMC-Bz) adsorbent with the metal ions. The surface morphologies of the adsorbent and metal-chelated adsorbent were analysed using a Leo Gemini 1,530 microscope. Energy dispersive X-ray analysis (EDX) analysis was employed to validate the adsorption of metal ions onto CMC-Bz adsorbent. The concentrations of Cu(II) and Pb(II) in the solutions, before and after equilibrium, was determined by atomic absorption spectrometer (AAS) (AA6300-Shimadzu, Japan).

MATERIALS AND METHODS

Materials

Chemicals such as natural cellulose (Loba), 2-aminobenzothiazole and sodium metaperiodate (NaIO_4) (Sigma-Aldrich, St Louis, Missouri) were used without further purification. Copper and lead salts were procured from Aldrich–Sigma Chemicals. All other solvents used were purified according to standard procedures (Vogal 1989). Metal salts $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$ (Loba) were used for preparing stock Cu(II) and Pb(II) metal ion solutions.

Synthesis of modified cellulose bearing heterocyclic moiety

The periodate oxidation onto cellulose was performed with the oxidising agent NaIO_4 . The reaction of periodate oxidation that cleaves the C2–C3 bond of the glucosidic ring of cellulose and converts 2,3-dihydroxyl groups into 2,3-dialdehydic groups following the Malaprade reaction, without side reactions before the Schiff base formation (Kim *et al.* 2000; Saravanan & Ravikumar 2016).

The dialdehyde cellulose (DAC) was synthesised according to reported procedure and shown in Figure 1 (Saravanan & Ravikumar 2016, 2017a, 2017b). The NaIO_4 solutions were prepared by dissolving the stoichiometric quantities of salt in deionised water. Cellulose powder were added to closed vessels and treated with NaIO_4 in the dark at ambient temperature and under continuous stirring. The concentration of NaIO_4 was kept at 0.1 M at room temperature in the dark for 4 hours, so as to have 30 carbonyl groups per 100 glucose units (Princi *et al.* 2006).

The dried DAC reacted with amines by forming amine derivatives (Maekawa & Koshijima 1990; Kim *et al.* 2000; Saravanan & Ravikumar 2016). The CMC-Bz bearing Schiff base with benzothiazole chelating groups was synthesised by condensation of dialdehyde cellulose with heterocyclic aromatic amines and shown in Figure 1. The 2-aminobenzothiazole (1.5 g) dissolved in 20 ml of *N,N*-dimethylformamide (DMF) was mixed with DAC (0.5 g) and a few drops of concentrated HCl were added as a catalyst and constantly stirred at 60–70 °C for 5 hours. A brown gel was obtained which was then poured into absolute ethanol. The precipitate formed was cooled, filtered and washed several times with hot water and dried under vacuum.

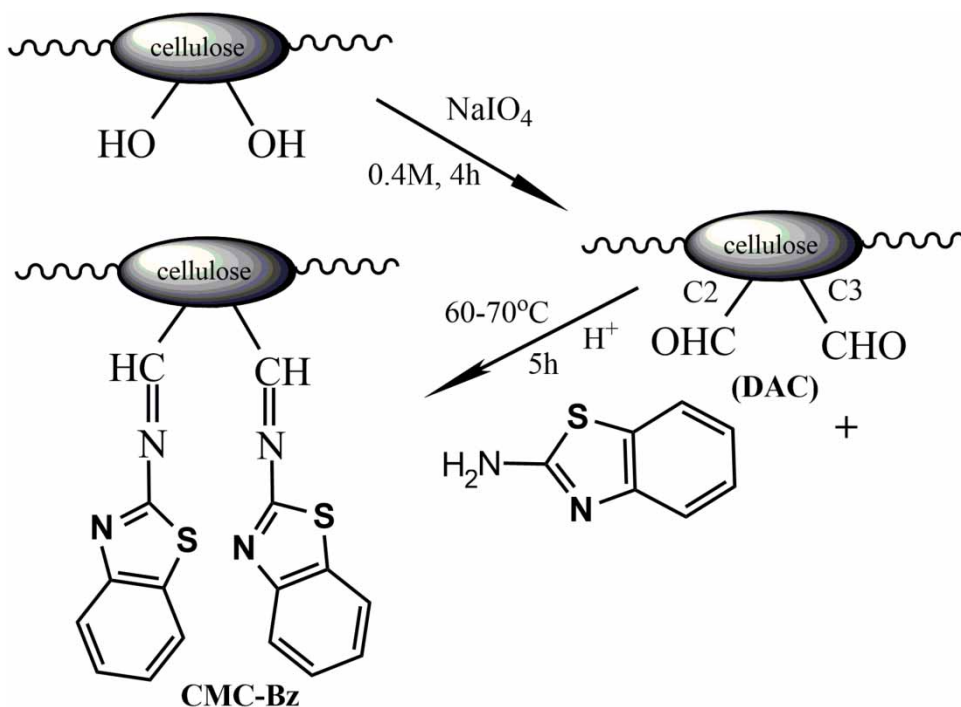


Figure 1 | Scheme of CMC-Bz.

Batch adsorption experiments

In the present study, batch adsorption experiments were carried out to investigate the adsorption isotherms, kinetics, mechanism and thermodynamics for the maximum removal of Cu(II) and Pb(II) ions in optimum conditions. A calculated amount of adsorbent was added to the 100 mL of Cu(II) and Pb(II) ions solution with a concentration in the range of 100–500 mg/L and shaken in a horizontal bench shaker at 200 r/min (Orbitek-Teqip-ACT/EQ/454, Tamil Nadu, India). After equilibrium had been reached, the supernatant was analysed.

The various operating parameters such as pH, contact time, adsorbent dose, initial metal ion concentration, temperature and regeneration performance were investigated to find the most favourable conditions for the removal of Cu(II) and Pb(II) ions onto CMC-Bz.

The percentage removal (% *E*) and amount of metal ions adsorbed onto CMC-Bz at equilibrium time (*q*, mg/g) was calculated using the following equations:

$$\% E = \left(1 - \frac{C_e}{C_0}\right) \times 100 \quad (1)$$

$$q = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 and C_e are initial and equilibrium final concentrations (mg/L) of the metal solutions, V is the volume of the solution (L), and m is the mass of the CMC-Bz adsorbent (g), respectively.

Batch desorption experiments

The desorption of metal ions from the adsorbent was performed by leaching spent CMC-Bz in various concentrations of acid solution. The metal adsorbate was treated with different concentration of acids in a thermostatic shaker under agitation of 200 r/min at 30 °C. The filtrate was evaluated to determine the metal recovery by the AAS.

RESULTS AND DISCUSSION

Spectroscopy of CMC-Bz

CMC-Bz was produced by specific oxidation of cellulose and condensation with aminobenzothiazole. The scheme of CMC-Bz synthesis is shown in Figure 1.

The chemical modification of cellulose was confirmed by FTIR and ^{13}C -NMR spectra and the spectrum of CMC-Bz is shown in Figure 2. Several peaks were observed in

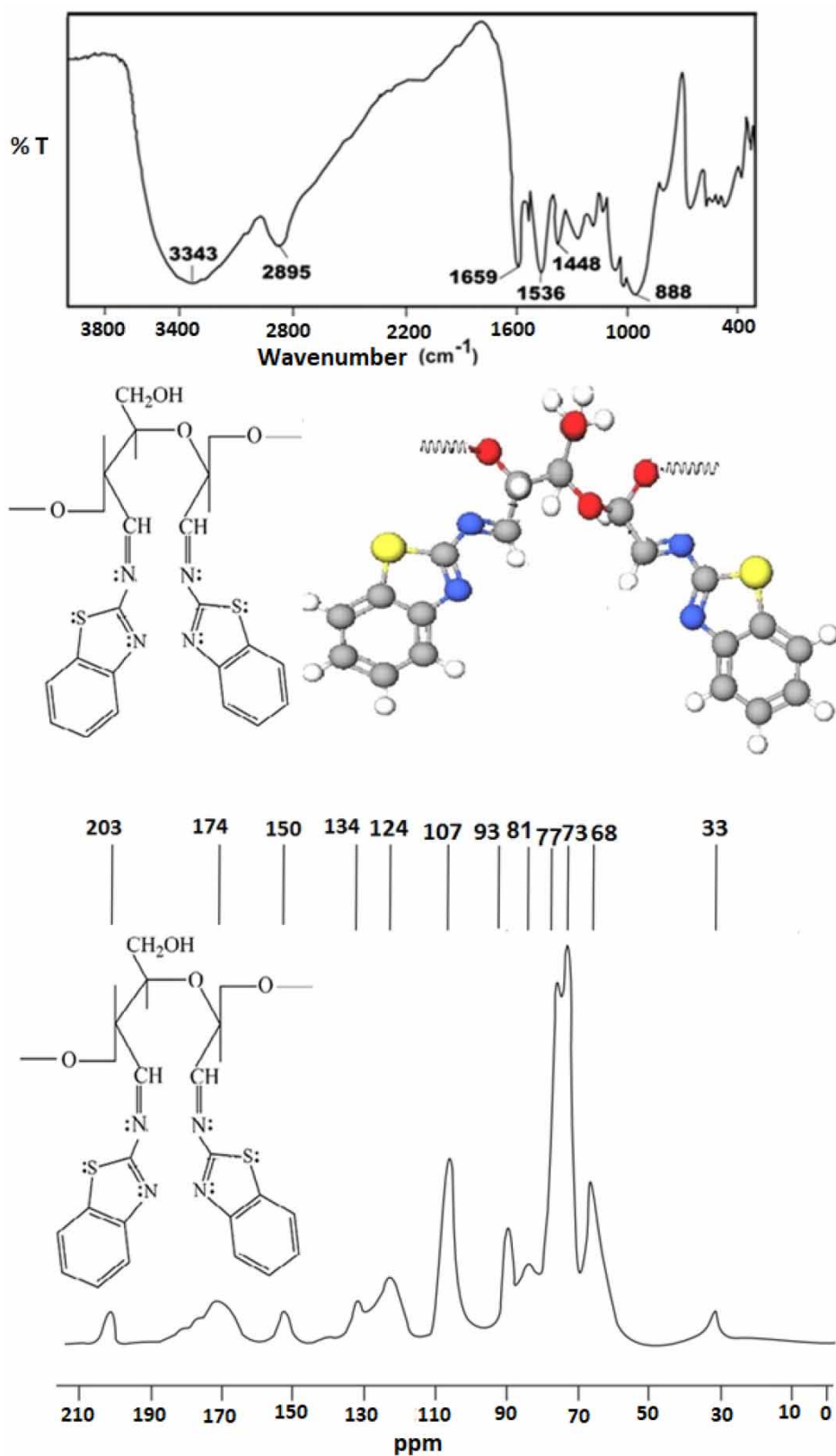


Figure 2 | FTIR and ¹³C-NMR spectra of CMC-Bz.

the spectrum of natural cellulose, indicating that cellulose is composed of various functional groups. The intense main characteristic bands at $3,348\text{ cm}^{-1}$ attributed to $-\text{OH}$ stretching, $2,903\text{ cm}^{-1}$ (C-H), $1,664\text{ cm}^{-1}$ (C-C ring), $1,430\text{ cm}^{-1}$ ($-\text{CH}_2$), $1,371\text{ cm}^{-1}$ ($-\text{CH}$ bend) and $1,058\text{ cm}^{-1}$ (C-O-C) are in good agreement with the reported values (El-Khouly *et al.* 2011; Saravanan & Ravikumar 2016, 2017a, 2017b).

In the CMC-Bz, the $-\text{OH}$ stretching frequency appeared at $3,343\text{ cm}^{-1}$, while the imine- CH stretching frequency appeared at $2,895\text{ cm}^{-1}$, $1,536\text{ cm}^{-1}$ (C-N), $1,448\text{ cm}^{-1}$ ($-\text{CH}_2$ bend), 888 cm^{-1} (C-S). The C-C ring stretching frequency was not observed in the modified cellulose due to cleavage of the pyranose ring. A strong absorption peak at $1,659\text{ cm}^{-1}$ is clear and it is due to the $-\text{N}=\text{CH}$ - (azomethine) stretching frequency, which supports the configuration of pendent benzothiazole groups in the CMC-Bz shown in Figure 2.

The spectrum of natural cellulose shows signals vibrated around $\delta = 62.2\text{--}102.4$ ppm for carbons of the pyranose ring and the carbon of $-\text{CH}_2\text{-OH}$ signal visible at $\delta = 44.2$ ppm are in agreement with the reported values. In the modified cellulose pyranose ring carbons exhibited signals between $\delta = 68$ and 107 . Apart from the descriptive signals, the aromatic ring carbons appeared at $\delta = 124$ ppm, 134 ppm and 150 ppm. The imine ($-\text{CH}=\text{N}-$) carbon showed at $\delta = 174$ ppm. The carbon of $-\text{CH}_2\text{-OH}$ group were shifted to $\delta = 33$ ppm. The pendant benzothiazole groups showed as a broad signal at $\delta = 203$ ppm. The assessment of solid state $^{13}\text{C-NMR}$ and FTIR spectrum of natural and modified cellulose clearly showed that the formation of azomethine linkage and all the principal functional groups were present in the CMC-Bz backbone.

Adsorption studies of CMC-Bz

Effect of initial pH

The acidity of a solution affect both the aqueous chemistry and the active sites of the adsorbent. The adsorption of metal ions was studied in the pH range of 2.0–8.0. At low pH, the chelating sites on the CMC-Bz surface are protonated, and fewer metal ions can be adsorbed because of electrostatic repulsive forces (Saravanan & Ravikumar 2017a). If the pH was increased then the ability of metal ions to compete with protons was also increased. At high pH, free imine and chelating sites are accessible on the adsorbent for metal complexation up to $\text{pH} = 6$, but complexation decreases beyond this value due to precipitation

of metal hydroxides; the results are shown Figure 3(a). Hence, an optimum $\text{pH} = 6$ was used for all batch adsorption studies.

Effect of CMC-Bz dose

The CMC-Bz dose is an important parameter in the removal of metal ions. The number of available sites and exchangeable ions for the adsorption depends upon the amount of adsorbent.

As seen in Figure 3(b), the removal of metal ions increases sharply with an increase in the CMC-Bz dose. Beyond a CMC-Bz dose of 60 mg the percentage removal almost reaches a stable value. This leads to the conclusion that effective adsorption is attained at 60 mg dosage and this was chosen as the optimum dose for further studies.

Modelling effect of agitation time

The influence of the adsorption time on the removal of metal ions by CMC-Bz chelating adsorbent is presented in Figure 3(c). With the increase in adsorption time, the removal of metal ions was increased, and the maximum removal of Cu(II) and Pb(II) ions was gained at 60 min .

At first, the fast removal of metal ions was due to the availability of a higher number of imine sites and adequate chelating groups. These groups may actively take part in the adsorption of metal ions up to 60 min , beyond which no significant change in adsorption marked the attainment of equilibrium. Thus, the agitation time was fixed as 60 min for further adsorption studies.

The experimental data obtained from agitation time factors was used to establish the mechanism of the adsorption system using Lagergren pseudo-first-order (Lagergren 1898), Ho's pseudo-second-order (Ho & McKay 2002), Weber and Morris intra-particle diffusion (Weber & Morris 1963) and Elovich kinetic models (Ho & McKay 2002). All the kinetic models parameters of CMC-Bz-metal ion system are given in Table 1.

The Lagergren linear form of the pseudo-first-order equation is:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

where q_e and q_t are the equilibrium adsorption capacities (mg/g) at time t , and k_1 is the rate constant. The k_1 and q_e values were obtained from $\ln(q_e - q_t)$ versus t .

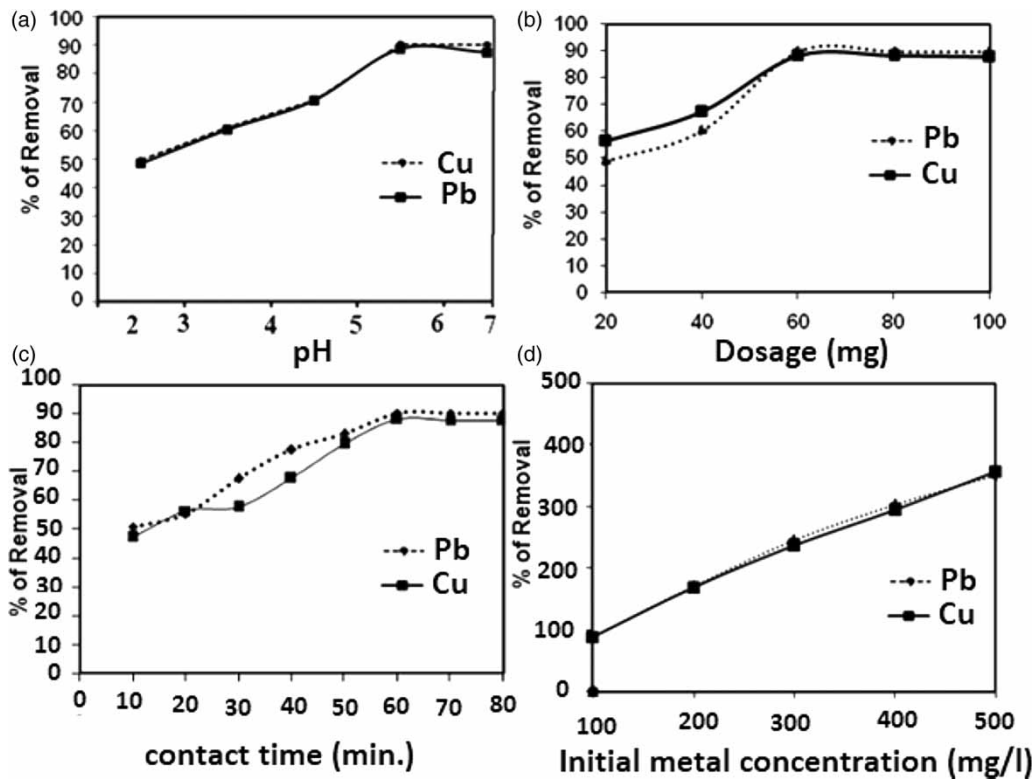


Figure 3 | Effect of adsorption parameters on adsorption.

Table 1 | Kinetic parameters for the adsorption of Cu(II) and Pb(II) onto CMC-BZ

Kinetic model	Parameter	Metal ion solution	
		Cu(II)	Pb(II)
Pseudo-first-order	$K(\text{mg}^{-1})$	0.0282	0.0321
	$q_e, \text{cal}(\text{mg}/\text{g})$	2.0399	2.0567
	R^2	0.9798	0.9502
Pseudo-second-order	$K(\text{g mg}^{-1} \text{min}^{-1})$	0.0098	0.0097
	$q_e, \text{Cal}(\text{mg}/\text{g})$	0.1292	0.1122
	R^2	0.9946	0.9952
Elovich model	$\alpha(\text{mg}/\text{g min})$	20.645	19.686
	$\beta(\text{g}/\text{mg})$	1.427	4.6282
	R^2	0.9431	0.9392
Intra-particle diffusion model	$K_p(\text{mg}/\text{g}\cdot\text{min}^{1/2})$	6.5053	6.1877
	C	31.073	35.728
	R^2	0.8747	0.8668

Ho's linear form of the pseudo-second-order model is:

$$t/q_t = 1/k_2 q_e^2 + (1/q_e)t \quad (4)$$

where k_2 is the rate constant calculated from t/q_t versus t for second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$).

The Weber and Morris intra-particle diffusion model was expressed as:

$$Q = k t^{1/2} + C \quad (5)$$

where C is the intercept and k is the rate constant ($\text{mg}/\text{g min}^{1/2}$) for intra-particle diffusion, determined from graphical interpretation of q versus $t^{1/2}$.

The linear form of the Elovich equation is given by:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (6)$$

where α and β are the Elovich coefficients; α represents the initial sorption rate in $\text{mg}/(\text{g min})$ and β is related to the extent of the surface coverage and activation energy for chemisorption (g/mg). They can be computed from the plot of qt versus $\ln t$.

The kinetic results show that the adsorption process does not proceed well with the pseudo-first-order kinetics. The correlation coefficients (R^2) of both pseudo-first-order and pseudo-second-order did not differ much but extremely high correlation coefficients were achieved for the pseudo-second-order kinetics (Table 1).

If the regressions in the plot of qt versus $t^{1/2}$ are linear and pass through the origin, then the diffusion model is the rate-limiting step. However, the linear plot at each concentration did not pass through the origin. Recorded R^2 values were low, which indicated that the experimental data did not fit the Elovich kinetic model and CMC-Bz system could not be studied under this model.

The pseudo-second-order kinetic model best fitted the experimental data with a correlation coefficient ($R^2 = 0.9946$

and 0.9952 for Cu(II) and Pb(II)) value close to 1 as compared to the pseudo-first-order kinetics, intra-particle diffusion and Elovich models.

Effect of initial metal ion concentration

The adsorption isotherms are important in designing the adsorption system and for anticipation of the characteristic relationship between the adsorbate and the adsorbent. The

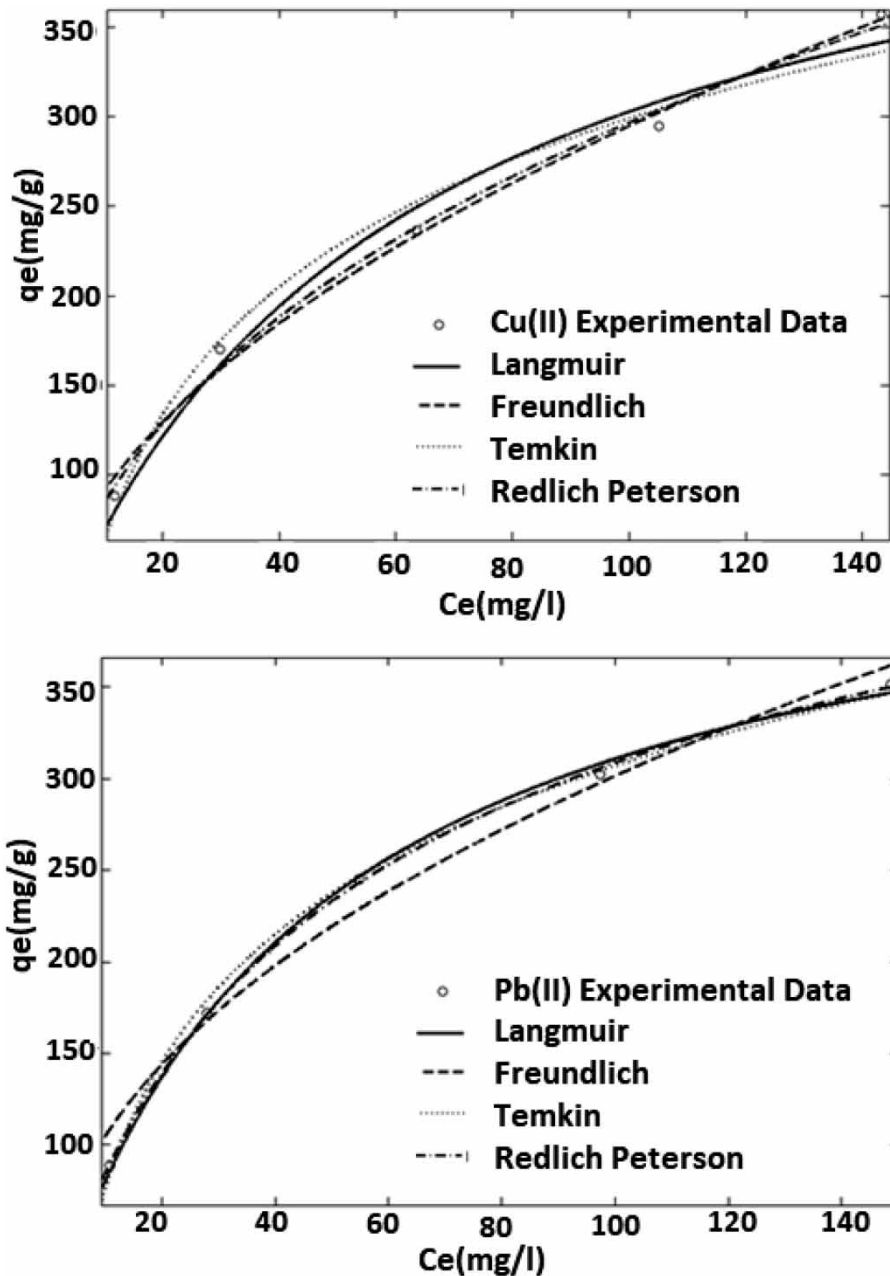


Figure 4 | Non-linear adsorption isotherm for Cu(II) and Pb(II) ions with CMC-Bz.

adsorption of metal ions at different initial metal ion concentrations (100–500 mg/L) using CMC-Bz is represented in Figure 3(d).

The results clearly indicate that with an increase of initial metal ion concentration, the adsorption capacity of both metal ions increased significantly. At lower initial metal ion concentrations, the adsorption capacities increased linearly with the concentration, signifying that there were plenty of adsorption sites on the CMC-Bz. At higher initial metal ion concentrations, the adsorption capacities no longer increase proportionally, indicating that the number of adsorption sites on the surfaces of the adsorbent actually limited the adsorption capacities (Saravanan & Ravikumar 2016, 2017a).

The experimental data on the effect of initial Cu(II) and Pb(II) ion concentrations on the CMC-Bz medium were applied to the various non-linear adsorption isotherm models such as Langmuir (Langmuir 1918), Freundlich (Freundlich 1906), Temkin (Temkin & Pyzhev 1940) and Redlich–Peterson (Redlich & Peterson 1959), and the results are shown in Figure 4.

The non-linear form of Langmuir isotherm model is:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (7)$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount metal adsorbed (mg/g), q_m is the maximum adsorption capacity (mg/g) and K_L is the Langmuir constant. The Langmuir model separation factor R_L can be calculated using following equation:

$$R_L = \frac{1}{1 + bC_0} \quad (8)$$

where b is the Langmuir adsorption equilibrium constant (L/mg) and C_0 is the initial metal ion concentration (mg/L). For favourable adsorption $0 < R_L < 1$, unfavourable $R_L > 1$, linear $R_L = 1$ and irreversible $R_L = 0$.

The non-linear form of the Freundlich equation is given by:

$$q_e = K_f C_e^{1/n} \quad (9)$$

where K_f is the Freundlich constant ((mg/g) (L/mg)^{1/n}), $1/n$ is the heterogeneity factor and n is a measure of the deviation from the linearity of adsorption process (g/L).

The linear form of Temkin equation is:

$$q_e = \frac{RT}{b} \ln(AC_e) \quad (10)$$

where q_e is the adsorbed value of the metal ion at equilibrium concentration (mg/g), A and RT/b (B) are the Temkin constants related to heat of absorption, R is the gas constant (8.314 J·K⁻¹·mol⁻¹) and T is temperature at 298 K.

The non-linear Redlich–Peterson isotherm model equation is:

$$q_e = \frac{q_m K_R C_e}{1 + \alpha_R C_e^\beta} \quad (11)$$

where K_R (L/g) and α_R (L/mg) are the Redlich–Peterson constants and β is the Redlich–Peterson isotherm exponent, which lies between 0 and 1.

The calculated R^2 values were 0.9831 and 0.9985 for Cu(II) and Pb(II) based on the Langmuir isotherm constants. The maximum adsorption capacity of Cu(II) and Pb(II) metal ions were found to be 483.2 and 455.3 mg/g, respectively, indicating high adsorption. The values of R_L lie between 0.060 and 0.021, indicating the of suitability of the CMC-Bz as adsorbent for Cu(II) and Pb(II) from aqueous solution.

Redlich–Peterson isotherm fits better compared to the other isotherms (β is near to 1). In addition, the Redlich–Peterson isotherm model also follows the Freundlich isotherm, since its constant K_R values are greater than 1.

Table 2 | Isotherm parameters for the adsorption of Cu(II) and Pb(II) ions onto CMC-Bz

Isotherm model	Parameters and constants	Metal ion conc. 100 mg/L	
		Cu(II)	Pb(II)
Langmuir	q_m (mg/g)	483.2	455.3
	k_L (L/mg)	0.0168	0.0215
	R^2	0.9831	0.9985
	R_L	0.060	0.021
Freundlich	K_f (mg/g)	28	36.25
	n (g/L)	1.956	2.17
	R^2	0.9931	0.9817
Temkin	A (L/mg)	0.1832	0.2127
	B (mg ⁻¹)	44.65	43.58
	R^2	0.9899	0.9975
Redlich-Peterson	K_{RP} (L/g)	20.79	11.35
	α_{RP} (L/mg)	0.0356	0.0429
	β_{RP}	0.8135	0.8979
	R^2	0.9947	0.9996

Table 3 | Thermodynamic parameters for the adsorption of Cu(II) and Pb(II) onto CMC-Bz

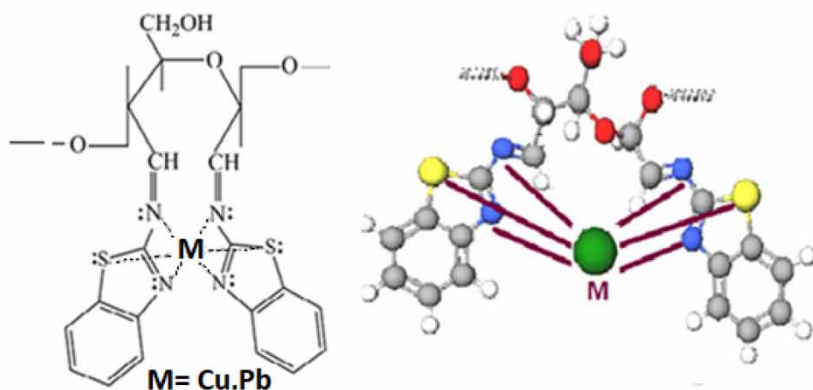
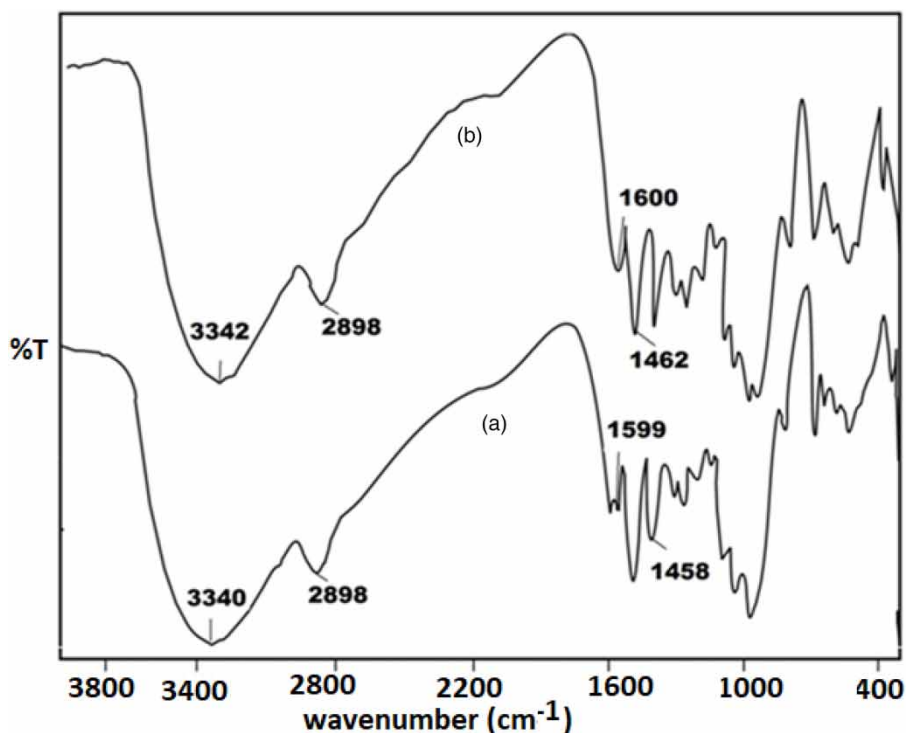
Parameters	Cu(II)	Pb(II)
$-\Delta H^\circ$ (kJ mol ⁻¹)	-26.27	-27.38
ΔS° (kJ mol ⁻¹)	0.795	0.828
$-\Delta G^\circ$ (kJ mol ⁻¹)		
308 K	-42.16	-44.49
313 K	-56.84	-60.30
318 K	-80.41	-86.26
328 K	-123.17	-134.33

Also, the R^2 values for Cu(II) (0.9931) and Pb(II) (0.9817) and the n value for Cu(II) (1.956) and Pb(II) (2.17) was

found to be greater than 1, which indicates that the adsorption system is a favourable one.

The representation of the experimental data by all the models resulted in a non-linear curve with the R^2 values (Cu(II) (0.9947) and Pb(II) (0.9996) for Redlich–Peterson), as shown in Table 2. The experimental data fit based on its correlation coefficient values follows the order: Redlich–Peterson > Temkin > Freundlich > Langmuir for the Cu(II) and Pb(II) ions from aqueous solution.

Based on these results, it can be indicated that the adsorption process is a heterogeneous surface adsorption rather than a monolayer one, which may be due to the heterogeneous distribution of the active sites on the CMC-Bz adsorbent.

**Figure 5** | FTIR spectrum of (a) CMC-Bz-Cu and (b) CMC-Bz-Pb.

Effect of temperature

Adsorption of Cu(II) and Pb(II) ions using CMC-Bz adsorbent was investigated with the temperature ranging from 35 °C to 55 °C. The changes in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) parameters were calculated to find the feasibility of the adsorption of the CMC-Bz system. Adsorption of metal ions onto CMC-Bz decreased when the temperature was increased.

$$K_C = \frac{C_{Ae}}{C_e} \quad (12)$$

$$\Delta G^\circ = -RT \ln K_C \quad (13)$$

$$\log K_C = \frac{\Delta S^\circ}{2.303 R} - \frac{\Delta H^\circ}{2.303 RT} \quad (14)$$

where K_C is the equilibrium constant, C_e is the equilibrium metal ion concentration in solution (mg/L), C_{Ae} is the

amount of metal ion adsorbed on the adsorbent/litre of solution at equilibrium (mg/L), R is the gas constant 8.314 J/mol/K and T (K) is the absolute temperature.

The thermodynamic parameters were evaluated from the van 't Hoff plot and the results are shown in Table 3. The ΔG° of the adsorption process at all temperatures is negative for both ions. The ΔG° decreases with an increase in temperature which indicates that the adsorption is spontaneous in nature and the spontaneity increases with the rise in temperature. The negative ΔH° value indicates the exothermic nature of adsorption, and the ΔS° value can be used to reveal the randomness at the CMC-Bz/solution interface during adsorption. The thermodynamic studies suggest that CMC-Bz can be used as an effective adsorbent for the removal of metal ions at ambient temperature.

The complexation of CMC-Bz with Cu(II) and Pb(II) metal ions caused frequency a shift from 1,659 cm^{-1}

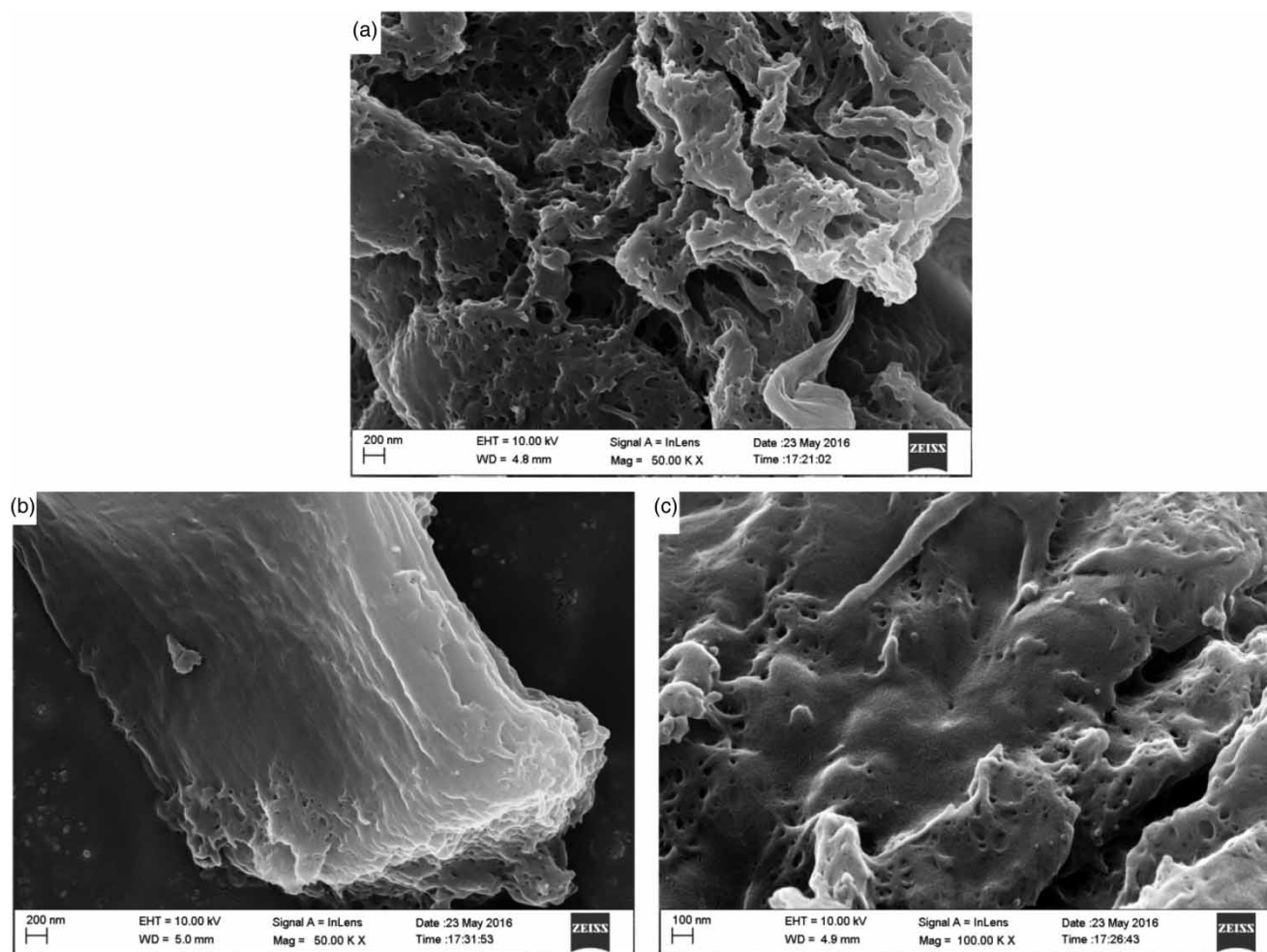


Figure 6 | SEM morphology of (a) CMC-Bz, (b) Cu, (c) Pb metal chelated CMC-Bz.

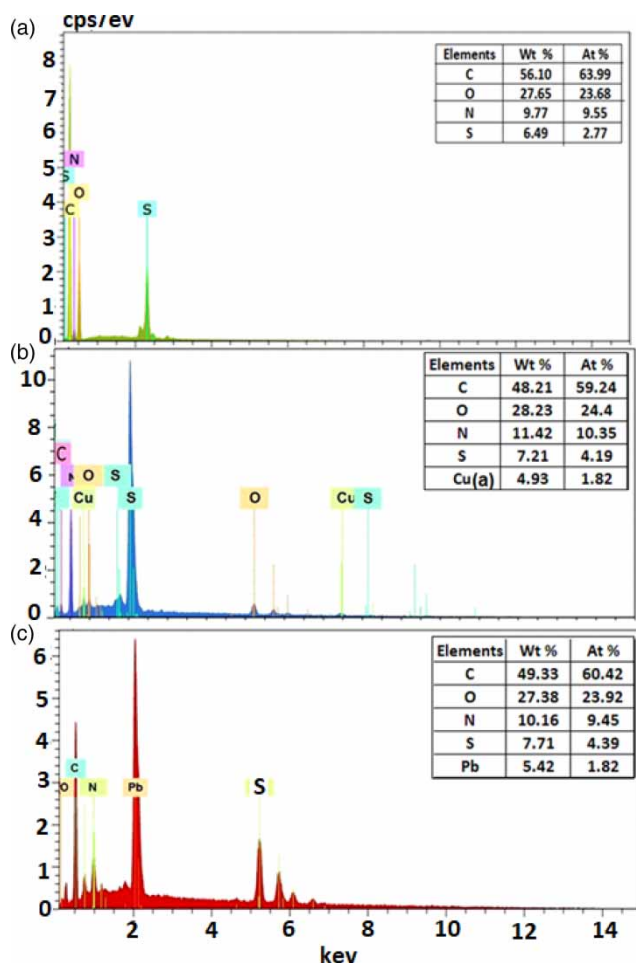


Figure 7 | EDX spectra of (a) CMC-Bz, (b) CMC-Bz-Cu, (c) CMC-Bz-Pb.

(-CH=N- stretching) to $1,599\text{ cm}^{-1}$ and $1,600\text{ cm}^{-1}$. The peak at $1,448\text{ cm}^{-1}$ vibration of $-\text{CH}_2$ shifted to $1,458$ and $1,462\text{ cm}^{-1}$ in the metal chelated CMC-Bz (Figure 5). The complexation mechanism involved electron pair sharing between electron donor atoms and metal ions. In addition, the absorption intensity and shape of -OH and C-S stretching band was found to be significantly changed. Based on the above observations it is likely that chelating groups such as $-\text{CH}=\text{N}-$, -OH and C-S groups are the key sites in CMC-Bz for adsorption of Cu(II) and Pb(II) metal ions.

This statement is further confirmed through the scanning electron microscope (SEM) images of metal chelated CMC-Bz (Figure 6(a)–6(c)). The modified cellulose has a rough and open permeable structure compared to the metal chelated cellulose. On that basis, the adsorbent has an adequate morphology with disordered distribution of sizes which could be the main reason for their high surface area for the removal of metal ions. The surface texture of CMC-Bz changed after complexation with Cu(II) and Pb(II) ions.

Furthermore, the EDX spectra of Cu(II) and Pb(II) onto CMC-Bz illustrate the presence of corresponding peaks to the elements in the spectrum (Figure 7(a)–7(c)), supporting the adsorption of metal ions onto modified CMC-Bz. Schiff base with benzothiazole group is confirmed by the high N content of 9.77 wt % and S content of 6.49 wt % (Figure 7(c)) in the EDX of CMC-Bz. The adsorption competency of the present adsorbent (CMC-Bz)

Table 4 | Comparison of adsorption competency with other adsorbents

Adsorbent used	Adsorption capacity (mg/g)		
	Cu(II) ion	Pb(II) ion	References
6-Deoxy-6-mercaptocellulose	22.0	28.0	Aoki <i>et al.</i> (1999)
Citric acid modified cellulose	24.0	64.3	Low <i>et al.</i> (2004)
Acrylic acid grafted cellulose	17.2	55.9	Guclu <i>et al.</i> (2003)
Amidoximated bacterial cellulose	46.2	52.6	Chen <i>et al.</i> (2009)
Succinylated mercerised AQ cellulose	56.8	147.1	Vinicius <i>et al.</i> (2009)
Cellulose-glycidyl methacrylate	60.0	–	Navarro <i>et al.</i> (1999)
Hyperbranched aliphatic polyester grafted cellulose	9.8	–	Liu (2007)
Cellulose bearing Schiff base and benzalaniline groups	157.3	153.5	Ravikumar & Saravanan (2015)
Cellulose bearing Schiff base and carboxylic acid chelating groups	87.00	85.43	Saravanan & Ravikumar (2016)
Cellulose bearing Schiff base and hydroxyl chelating groups	80.35	81.32	Saravanan & Ravikumar (2017a)
Cellulose bearing Schiff base and pyridine chelating groups	83.35	82.43	Saravanan & Ravikumar (2017b)
Cellulose bearing Schiff base and pyridine chelating groups	483.2	455.3	Present work

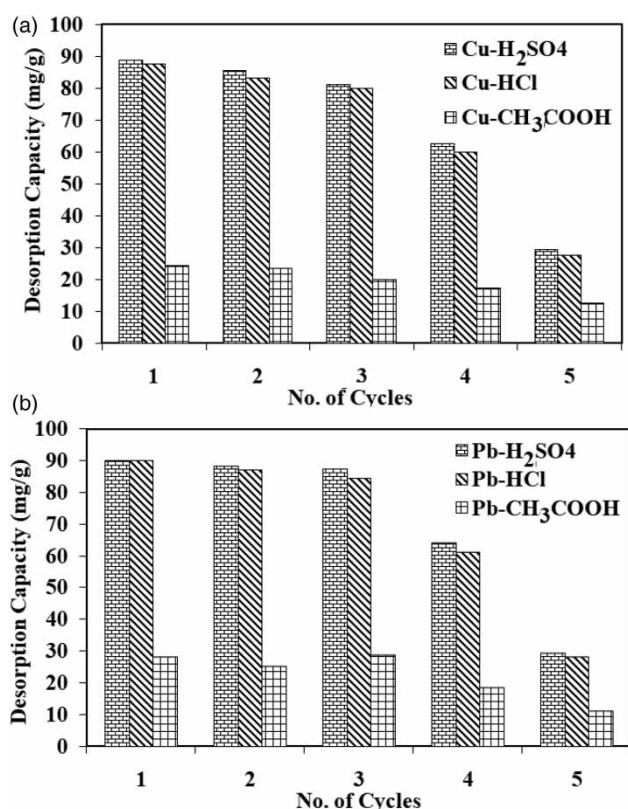


Figure 8 | Recyclability of (a) Cu(II) (b) Pb(II) ions onto CMC-Bz.

containing Schiff base and benzothiazole functional groups is clearly superior to conventional adsorbents presented in Table 4.

Recyclability of CMC-Bz

Reusability tests on CMC-Bz were carried out several times with strong acids (HCl, H₂SO₄) and weak acid (CH₃COOH) as the eluents, and the results are shown in Figure 8(a) and 8(b). The metal chelated CMC-Bz was treated with 0.1 M H₂SO₄ solutions for an hour, and the filtrate concentration was evaluated to determine the metal concentration using the AAS. As evident, the capacity of the recycled CMC-Bz for Cu(II) and Pb(II) ions removal is almost 80% of adsorption even after five cycles. The obtained results confirmed that the desorption process of CMC-Bz is viable and that the adsorbent contains the acid resistant of Schiff base group.

CONCLUSION

The results of present research show that modified cellulose (CMC-Bz) adsorbent has a significant potential for the

removal of Cu(II) and Pb(II) metal ions from aqueous solutions. The adsorption of metal ions onto CMC-Bz was found to be highly dependent on the solution pH. The mechanism, equilibrium, thermodynamics and kinetics of Cu(II) and Pb(II) sorption on CMC-Bz were studied and the following results were obtained. The equilibrium data yielded excellent fits with the following isotherms for Cu(II) and Pb(II) in the following order: Redlich–Peterson > Temkin > Freundlich > Langmuir isotherms based on their R² values. The maximum adsorption values were found to be 483.2 and 455.3 mg/g for Cu(II) and Pb(II), respectively. The adsorption kinetics closely followed the pseudo-second-order kinetic model. The negative values of ΔG° and ΔH° led to the conclusion that the CMC-Bz adsorption system is a spontaneous process. Also, ΔG° values suggest that adsorption is due to chemisorption. Repeated absorption and desorption cycles showed the feasibility of reusing CMC-Bz adsorbent. The Schiff base and benzothiazole chelating sites in the cellulose backbone, which can complex with metal ions, are responsible for the higher adsorption efficiency and recyclability. The proposed green adsorbent has the potential to control heavy metal pollution in natural and industrial waters or biomedical wastewater.

REFERENCES

- Abdel-Halim, E. S., El-Rafie, M. H. & Al-Deyab, S. S. 2011 Polyacrylamide/guar gum graft copolymer for preparation of silver nanoparticles. *Carbohydr. Polym.* **85**, 692–697.
- Anirudhan, T. S. & Sreekumari, S. S. 2011 Adsorptive removal of heavy metal ions from industrial effluents using activated carbon derived from waste coconut buttons. *J. Environ. Sci.* **23**, 1989–1998.
- Aoki, N., Fukushima, K., Kurakata, H., Sakamoto, M. & Furuhashi, K. 1999 6-Deoxy-6-Mercaptocellulose and Its S-Substituted derivatives as sorbents for metal ions. *React. Funct. Polym.* **42**, 223–233.
- BIS 1994 Methods of sampling and test (physical and chemical) for water and waste water: Part 47 lead. In: IS No. 3025 (Part 47). BIS.
- Chen, S., Shen, W., Yu, F. & Wang, H. 2009 Kinetic and thermodynamic studies of adsorption of Cu²⁺ and Pb²⁺ onto amidoximated bacterial cellulose. *Polym. Bull.* **63**, 283–297.
- El-Khouly, A. S., Kenawy, E., Safaan, A. A., Takahashi, Y., Hafiz, Y. A., Sonomoto, K. & Zendo, T. 2011 Synthesis, characterization and antimicrobial activity of modified cellulose-graft-polyacrylonitrile with some aromatic aldehyde derivatives. *Carbohydr. Polym.* **83**, 346–353.
- Freundlich, H. M. F. 1906 Over the adsorption in solution. *J. Phys. Chem.* **57**, 385–470.
- Gao, B., Gao, Y. & Li, Y. 2010 Preparation and chelation adsorption property of composite chelating material

- poly(amidoxime)/SiO₂ towards heavy metal ions. *Chem. Eng. J.* **58**, 542–549.
- Gucclu, G., Gurdag, G. & Ozgumus, S. 2003 Competitive removal of heavy metal ions by cellulose graft copolymers. *J. Appl. Polym. Sci.* **90**, 2034–2039.
- Gurgel, L. V. A., Freitas, R. P. & Gil, L. F. 2008 Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by sugarcane bagasse and mercerized sugarcane bagasse chemically modified with succinic anhydride. *Carbohydr. Polym.* **74**, 922.
- Ho, Y. S. & McKay, G. 2002 Application of kinetic models to the sorption of copper(II) onto peat. *Adsorpt. Sci. Technol.* **20**, 797–815.
- Kim, U. J. & Kuga, S. 2001 Thermal decomposition of dialdehyde cellulose and its nitrogen-containing derivatives. *Thermochim. Acta* **369**, 79–85.
- Kim, U. J., Kuga, S., Wada, M., Okano, T. & Kondo, T. 2000 Periodate oxidation of crystalline cellulose. *Biomacromolecules* **1**, 488–492.
- Lagergren, S. 1898 About the theory of so-called adsorption of soluble substances. *Kungliga Sven. Vetensk. Handl.* **24**, 1–39.
- Langmuir, I. 1918 The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* **40**, 1361–1403.
- Liu, P. 2007 A novel degradable adsorbent of the hyper branched aliphatic polyester grafted cellulose for heavy metal ions. *Turk. J. Chem.* **31**, 457–462.
- Low, K. S., Lee, C. K. & Mak, S. M. 2004 Sorption of copper and lead by citric acid modified wood. *Wood Sci. Technol.* **38**, 629–640.
- Maekawa, E. & Koshijima, T. 1990 Preparation and characterisation of hydroxamic acid derivatives and its metal complexes derived from cellulose. *J. Appl. Polym. Sci.* **40**, 1601–1613.
- Marchetti, M., Clement, A., Loubinoux, B. & Gerardin, P. 2000 Decontamination of synthetic solutions containing heavy metals using chemically modified sawdusts bearing polyacrylic acid chains. *J. Wood Sci.* **4**, 331–333.
- Navarro, R. R., Sumi, K., Fujii, N. & Matsumura, M. 1996 Mercury removal from wastewater using porous cellulose carrier modified with polyethyleneimine. *Water Res.* **30**, 2488–2494.
- Navarro, R. R., Sumi, K. & Matsumura, M. 1999 Improved metal affinity of chelating adsorbents through graft polymerization. *Water Res.* **33** (9), 2037–2044.
- O'Connell, D. W. 2006 *Development of A Modified Cellulose Material and Assessment of Its Adsorption Capabilities in the Removal of Heavy Metals From Aqueous Solutions*. PhD Thesis, University of Limerick, Ireland, pp. 244–263.
- O'Connell, D. W., Birkinshaw, C. & O'Dwyer, T. F. 2006a A chelating cellulose adsorbent for the removal of Cu(II) from aqueous solutions. *J. Appl. Polym. Sci.* **99**, 2888–2897.
- O'Connell, D. W., Birkinshaw, C. & O'Dwyer, T. F. 2008 Heavy metal adsorbents prepared from the modification of cellulose: a review. *Bioresour. Technol.* **99**, 6709–6724.
- Pagliuca, G. J., Mufti, D., Baldwin, A. N., Lestas, R., Wallis, M. & Bellingham, A. J. 1990 Lead poisoning: clinical, biochemical, and haematological aspects of a recent outbreak. *J. Clin. Pathol.* **43**, 277–281.
- Princi, E., Vicini, S., Pedemonte, E., Gentile, G., Cocca, M. & Martuscelli, E. 2006 Synthesis and mechanical characterisation of cellulose based textiles grafted with acrylic monomers. *Eur. Polym. J.* **42**, 51–60.
- Ravikumar, L. & Saravanan, R. 2015 The use of new chemically modified cellulose for heavy metal ion adsorption and antimicrobial activities. *J. Water Resour. Prot.* **7**, 530–545.
- Redlich, O. & Peterson, D. L. 1959 A useful adsorption isotherm. *J. Phys. Chem.* **63**, 1024–1026.
- Saliba, R., Gauthier, H. & Gauthier, R. 2005 Adsorption of heavy metal ions on virgin and chemically-modified lingo cellulosic materials. *Adsorpt. Sci. Technol.* **23**, 313–322.
- Saravanan, R. & Ravikumar, L. 2016 Cellulose bearing Schiff base and carboxylic acid chelating groups a low cost and green adsorbent for heavy metal ion removal from aqueous solution. *Water Sci. Technol.* **74**, 1780–1792.
- Saravanan, R. & Ravikumar, L. 2017a Renewable modified cellulose bearing chelating Schiff base for adsorptive removal of heavy metal ions and antibacterial action. *Water Environ. Res.* **89**, 626–640.
- Saravanan, R. & Ravikumar, L. 2017b Adsorption equilibrium and kinetic studies on effective removal of heavy metals onto modified cellulose bearing Schiff base with pyridine chelating groups from aqueous solution. *Int. J. Mater. Prod. Technol.* **55**, 188–209.
- Takagai, Y., Shibata, A., Kiyokawa, S. & Takase, T. 2011 Synthesis and evaluation of different thio-modified cellulose resins for the removal of mercury (II) ion from highly acidic aqueous solutions. *J. Colloid Interface Sci.* **353**, 593–597.
- Temkin, M. J. & Pyzhev, V. 1940 Recent modifications to Langmuir isotherms. *Acta Physico Chim. URSS.* **12**, 217–225.
- Theophanides, T. & Anastassopoulou, J. 2002 Copper and carcinogenesis critical reviews. *Oncology/Haematology* **42**, 57–64.
- US Environmental Protection Agency (USEPA) 2001 *Lead: Identification of Dangerous Levels of Lead*. final rule, Vol. 66. US Government Printing Office, Washington, DC.
- Vinicius, L., Gurgel, A. & Gil, L. F. 2009 Adsorption of Cu(II), Cd(II) and Pb(II) from aqueous single metal solutions by succinylated mercerized cellulose modified with triethylenetetramine. *Carbohydr. Polym.* **77**, 142–149.
- Vogel, A. I. 1989 *Text Book of Practical Organic Chemistry*, 5th edn. Longman, London.
- Weber, W. J. & Morris, J. C. 1963 Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.* **89**, 31–60.
- Zhou, Y. M., Jin, Q., Zhu, T. W. & Akama, Y. 2011 Adsorption of chromium (VI) from aqueous solutions by cellulose modified with β -CD and quaternary ammonium groups. *J. Hazard. Mater.* **187**, 303–310.

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