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Optimization of Cd(II), Cu(II) and Ni(II) biosorption by chemically modified *Moringa oleifera* leaves powder

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ABSTRACT

A cation exchange biosorbent was developed by chemically modifying the *Moringa oleifera* leaves powder by esterifying with NaOH followed by citric acid treatment. The modified biosorbent was characterized by FTIR, SEM and XRD techniques and was used for the removal of Cd(II), Cu(II) and Ni(II) from aqueous solution. Different operational parameters such as the effect of pH, biomass dose, equilibrium time and temperature and initial metal ion concentrations were studied. Experimental data were analyzed by kinetic parameters and found that biosorption of three metal ions followed pseudo-second-order. Equilibrium data were analyzed using the Langmuir, Freundlich, Dubinin–Radushkevich and Temkin isotherm models. The thermodynamic properties, ΔG°, ΔH° and ΔS° showed that biosorption of Cd(II), Cu(II) and Ni(II) onto CAMOL were spontaneous, endothermic and feasible in the temperature range of 293–313 K. Furthermore, the CAMOL can be regenerated and reused for the metal removal.

1. Introduction

Solid waste generated due to agricultural by-products as a whole is estimated exceeds by 320,000,000,000 kg annually (Wing, 1996), creating significant disposal problem. Agricultural by-products are high volume, low value and underutilized lignocellulosic biomaterials; contain high level of cellulose, hemicelluloses and lignin (Sud, Mahajan, & Kaur, 2008). So it will be a significant contribution in the field of environmental protection if suitable methods are developed for utilization of agricultural by-products thereby minimizing the disposal problem. The potential of agricultural waste in removing a number of metal ions by adsorption process is gaining importance. Agricultural byproducts being rich in cellulosic and lignin materials, show a strong tendency to attract and remove heavy metal ions from aqueous solution. The components of agricultural by-products that compose hydroxyl, carbonyl, carboxylic and ether functional groups bind heavy metals by the donation of an electron pair and form complexes or exchange hydrogen ions for heavy metal ions in solution (Ofomaja, Naidoo, & Modise, 2010a). Heavy metal binding onto an agro biomass involves complex processes that comprise a number of mechanisms like adsorption, complexation, chelation and entrapment in capillaries and spaces with in polysaccharide network due to concentration causing diffusion through the cell walls and membrane (Farooq, Kozinski, Khan, & Athar, 2010). However, adsorption capacity of crude agricultural by-products in general is low. In order to increase the ion exchange capacity and physical stability (partial solubility) of agricultural residues, it must be chemically modified, co-polymerized and cross-linked. Chemical modification has shown great promise in improving the adsorption and the cation exchange capacity of agricultural by-products (Karnitz et al., 2007).

Incorporation of acidic groups onto the complex polysaccharide matrix of agricultural residues will result in the formation of low-cost cation exchange resins (Marshall, Wartelle, Boler, Johns, & Toles, 1999). Chemical modification of agricultural materials via cross-linking has been studied by several workers (Marshall, Chatters, Wartelle, & McAloon, 2001; Marshall & Wartelle, 2006). In these studies, the low cost citric acid has been used as a modification agent in order to attach free carboxyl groups onto the hydroxyl of polysaccharide matrix of cellulosic waste materials. The additional carboxyl groups conferred higher sorption capacity for positively charged metal ions. Hence, modification of low-cost biological materials with citric acid would provide improved metal binding capacity and higher mechanical strength due to cross-linking. Citric acid modification of NaOH treated soybean hulls

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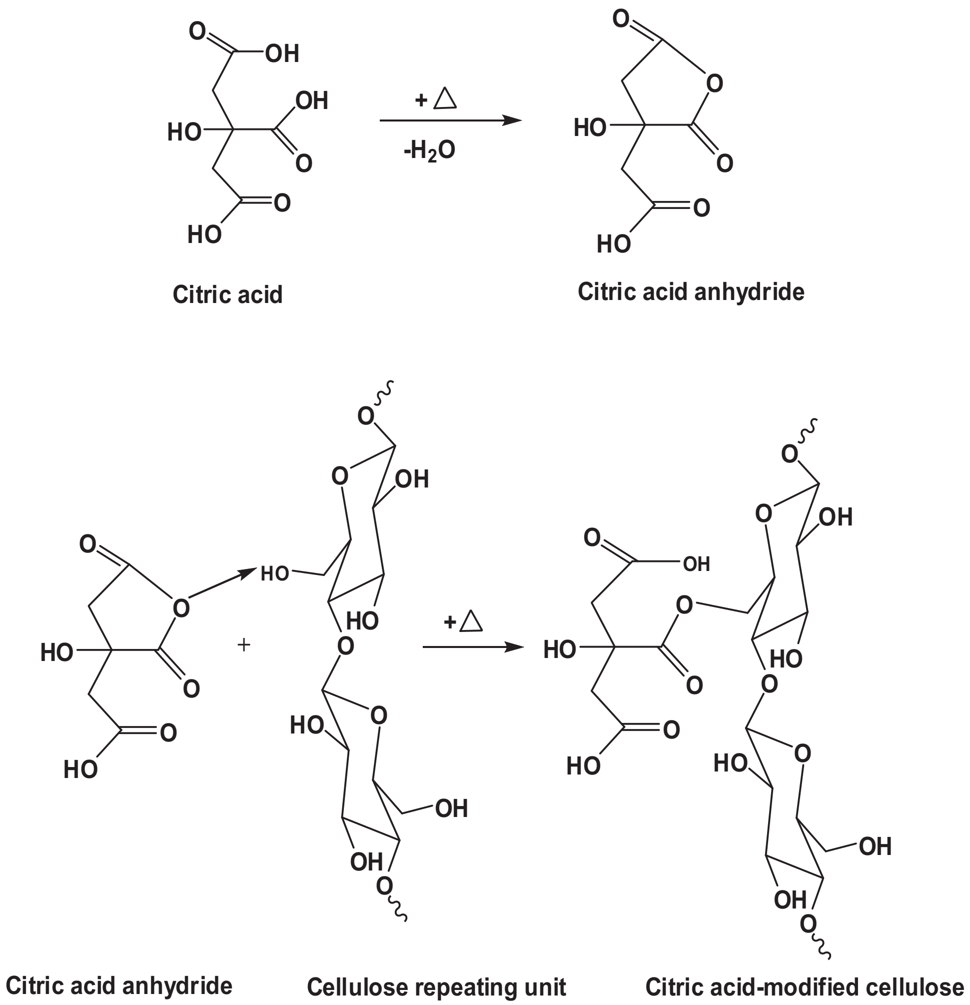

Fig. 1. Proposed reaction between citric acid and the cellulose in MOL to produce citric acid-modified MOL.

(Marshall et al., 1999) and citric or phosphoric acid treated corncobs (Vaughan, Seo, & Marshall, 2001) showed sorption enhancement of metal ions. In our earlier study carboxyl groups-rich sorbent which is effective for the removal of Pb(II) from aqueous solution, was developed from *Moringa oleifera* leaves powder (Reddy, Harinath, Seshaiah, & Reddy, 2010).

M. oleifera is the most widely cultivated species of a monogeneric family, the Moringaceae, it is widely cultivated and has become naturalized in many locations in the tropics. The main chemical ingredients present in various segments of the *M. oleifera* leaves are fairly unique group of glycoside compounds called glucosinolates and isothiocyanates (Doerr, Wade, Stephenson, Reed, & Fahey, 2009). *M. oleifera* leaves contain 4-(R-L-rhamnopyranosyloxy)-benzylglucosinolate and three monoacetyl isomers of this glucosinolate (Bennett et al., 2003). In addition quercetin-3-O-glucoside and quercetin-3-O-(6″-malonyl-glucoside), lower amounts of kaempferol-3-O-glucoside and kaempferol-3-O-(6″-malonyl-glucoside) also 3-caffeoylquinic acid and 5-caffeoylquinic acid (Bennett et al., 2003) are identified. The presence of polar groups on the surface of *M. oleifera* leaves powder is likely to improve considerable cation exchange capacity.

The objective of the present work is to investigate the potential of the Citric Acid Modified *Moringa oleifera* Leaves powder (CAMOL) in removing Cd(II), Cu(II) and Ni(II) ions from an aqueous solution by biosorption in the batch method. Optimum biosorption conditions were investigated as a function of pH, biomass dosage, contact time, and temperature. The Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Temkin models were used to analyze equilibrium isotherms. The biosorption mechanisms of metal ions onto *CAMOL* biomass were also evaluated in terms of thermodynamic and kinetic parameters.

2. Materials and methods

2.1. Materials

M. oleifera leaves were collected from Punganur, Chittoor district, Andhra Pradesh, India. All the chemicals used were of analytical grade and obtained from M/S Qualigens Fine Chemicals, Mumbai, India. Atomic absorption spectrophotometer (AAS) (Model AA 6300, Shimadzu, Japan) was used for determination of Cd(II), Cu(II) and Ni(II) before and after biosorption. The synthetic solutions were prepared by diluting Cd(II), Cu(II) and Ni(II) standard stock solutions (concentration $1000 \pm 2\,\mathrm{mg\,L^{-1}}$). Fresh dilutions were used in each experiment.

2.2. Synthesis of CAMOL

Base treatment of MOL and subsequent citric acid modification was done by adopting previous method by Marshall et al. (1999). Chemical modification of *M. oleifera* leaves (MOL) using NaOH followed by citric acid treatment was shown in Fig. 1. The study of the synthesis of CAMOL was carried out as followed (Reddy et al., 2010).

The precursor was washed several times with distilled water to remove all the dirt and other particulate matter and air dried for 12 h. MOL leaves were sieved to 20–30 mesh fractions. Two hundred grams of sieved leaves powder was placed in 4 L of 0.1 N NaOH. The slurry was stirred at 300 rpm for 1 h at 23 °C to remove excess base. The washed leaves powder was taken onto a 40 mesh sieve, rinsed with water and added to 4 L of distilled water. This procedure was repeated twice to ensure removal of base from the leaves powder. This biomass named as BW-MOL, was mixed with citric acid (CA) in a ratio of 1.0 g leaves powder to 7.0 mL of CA. Leaves powder readily absorbed the acid and this ratio of leaves powder to acid was required to ensure the complete absorption of liquid by leaves powder. The acid/leaves powder slurry was dried overnight at 50 °C.

CA treated BW-MOL leaves powder was placed on Whatman 41 filter paper and washed in a Buchner funnel under vacuum with 150–200 mL of distilled water per gram of the product to remove excess CA. This volume of water was sufficient to remove unreacted CA since no turbidity from lead citrate was observed when the washed leaves powder was suspended in 10 mL of water to which 10 mL of 0.1 M lead nitrate was added. The modified leaves powder was dried at 50 °C overnight and sieved to retain the 20–30 mesh fractions. Treating with a base like NaOH and a subsequent citric acid modification stabilizes the MOL due to insertion and cross linking of carboxyl groups and thus increases its cation uptake ability (Zhu, Fan, & Zhang, 2008). This modified MOL, named as CAMOL was used in the present studies.

2.3. CAMOL characterization

The functional groups present in CAMOL were analyzed by Thermo-Nicolet FT-IR, Nicolet IR-200, USA, using potassium bromide discs. Scanning Electron Microscopy Evo15, Carl Zeiss, England, was used to study the surface morphology of the biosorbent. Wide angle X-ray diffraction patterns of samples were recorded on XRD-6000, Shimadzu, by using Cu Kα radiation (λ = 1.5406 Å) at 40 kV and 30 mA with a scan rate of 5° min^{-1} in the range of 2θ from 10 to 70°.

Point of Zero Charge (PZC) of biosorbent was determined by the following procedure (Leyva-Ramos, Bernal-Jacome, & Acosta-Rodriguez, 2005): The pH or point of zero charge (abbreviated as PZC) for the CAMOL was determined by boiling 100 mL deionized water for 20 min to eliminate dissolved CO_2 and quickly cooling and capping the solution. 0.2 g of CAMOL was placed in 15 mL of the CO_2-free water, then sealed and continuously agitated for 48 h at room temperature before measuring the solution pH – taken as the point of zero charge.

2.4. Biosorption experiments

The biosorption tests were performed by batch technique in single system using stoppered conical flasks on a temperature-controlled water bath shaker set at 200 rpm and maintained at the desired temperature. In order to optimize the experimental conditions, the batch studies were performed for different metal concentrations (10–1000 mg L^{-1}), contact time (0–100 min), pH (2.0–9.0), biosorbent dosage from (0.010–0.140 g) and temperatures (293–313 K). Isotherms were obtained by equilibrating metal ion solutions of different initial concentrations at different temperatures (293–313 K) using a thermostatic shaking water bath. After prescribed contact time, the solutions were filtered through Whatmann filter paper No. 41 and the concentration of metal in the filtrate was measured using AAS. The extent of biosorption was calculated as follows:

$$\text{Biosorption}\,(\%) = \frac{(C_i - C_f)}{C_i} \times 100 \qquad (1)$$

where C_i and C_f are the initial and equilibrium metal ion concentrations respectively.

2.5. Desorption and reusability studies

The desorption studies of Cd(II), Cu(II) and Ni(II) from CAMOL was carried out by using 0.1 M HCl. After determination of metal contents of the final solutions, the biosorbent was washed with excess of acid solution and distilled water in order to reuse for next experiment. Consecutive sorption–desorption cycles were repeated five times to establish the reusability of the biosorbent.

2.6. Statistical analysis

All the experiments were carried out in triplicate and data presented are the mean values of three independent experiments. Standard deviation and error bars are shown wherever necessary. All statistical analysis was done using Origin Pro.7.5 where it is possible to evaluate whether the effect and the interaction among the investigated factors are significant with respect to the experimental error.

2.7. Chi-square (χ^2) analysis

In order to evaluate the fit of the isotherm models to the experimental equilibrium data, an error function is required to enable the optimization procedure (Reddy, Ramana, Seshaiah, & Reddy, 2011). Chi-square (χ^2) test was carried out to find out the best fit among the adsorption isotherm models used. The Chi-square test statistic is basically the sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models. The equivalent mathematical statement is:

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \qquad (2)$$

$q_{e,m}$ equilibrium capacity obtained by calculating from a model (mg g^{-1}) and q_e experimental data of equilibrium capacity (mg g^{-1}).

3. Results and discussion

3.1. Characterization of biosorbent

3.1.1. FTIR analysis

FTIR analysis was used to identify the characteristic functional groups on the surface of biosorbents and the spectra of MOL and CAMOL are shown in Fig. 2. The FTIR spectrum of raw MOL biomass exhibited a broad peak at 3422 cm^{-1} which is indicative of the existence of macromolecular association (cellulose, pectin, etc.) and may denote the presence of both H-bonded amine and OH groups. The FTIR spectrum exhibited characteristic main skeleton cellulose peak in the finger print region of 1000–1200 cm^{-1}. The doublet peaks appeared in all the spectra at wave numbers 2921–2918 cm^{-1} and 2853–2850 cm^{-1} are due to the asymmetric and symmetric stretch of aliphatic chains (—CH) respectively. Comparison of the IR spectra of samples of MOL and CA modified MOL revealed that a strong characteristic stretching vibration absorption band of carboxyl group at 1742 cm^{-1} is present in the IR spectrum of CAMOL samples. This confirms the esterification between alcohol groups of cellulose in MOL and citric acid. The broad absorptions around 2500–3500 cm^{-1} confirm the existence of carboxylic O—H groups and free COOH groups after CA modification.

It appears from Supplementary Fig. 1 that different functional groups on CAMOL are responsible for biosorption of Cd(II), Cu(II) and Ni(II). A change in peak position at 3422 cm^{-1} in the spectrum

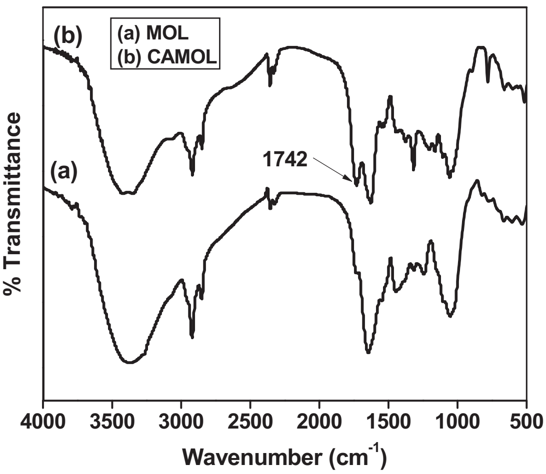

Fig. 2. FTIR spectra of (a) MOL and (b) CAMOL.

of the cadmium, copper and nickel loaded CAMOL indicates the binding of these metal ions with hydroxyl groups. Further shift in the peak at 1732 cm^{-1} of CAMOL on Cd(II), Cu(II) and Ni(II) biosorption indicating the binding of metal ions to carboxylic groups also. From these findings, it is presumed that Cd(II), Cu(II) and Ni(II) adsorbed mainly to the active groups such as hydroxyl groups (—OH) and carboxylic groups (COO^-).

3.1.2. X-ray diffraction

Fig. 3 shows the X-ray diffraction patterns of CAMOL biosorbent powder. Diffraction peaks corresponding to crystallinity was not observed, whereas, amorphous form is identified in the biosorbent. The amorphous nature of the biosorbents suggested that the metal ion could more easily penetrate into the surface of the CAMOL biosorbent on the amorphous.

3.1.3. Microscopy

The scanning electron microscope (SEM) has been used by many researchers for the characterization of the biosorbents. After the esterification process, it was evident that the biosorbent had suffered some degree of degradation, since it was smaller and darker in color. Thus the samples, MOL and CAMOL were analyzed by SEM in order to determine the morphological changes experienced by the biosorbent on the treatment. Supplementary Fig. 2 shows SEM micrographs of MOL and modified MOL (CAMOL). Supplementary Fig. 2a represents the micrograph of raw-MOL biosorbent. The micrograph clearly shows the presence of an assemblage of fine particles, which did not have regular, fixed shape and size. The particles were of various dimensions and all of them contained a large number of steps and kinks on the external surface, with broken edges. As it can be seen from Supplementary Fig. 2b CAMOL surface is smoother than that of MOL. This was attributed to the friction effect induced by the rotor and the chamber surface during the reaction. When lignocellulosics are chemically treated, some of their components can be affected, depending on the treatment. In the present study, the effect of the chemicals was evident, since after treatment CAMOL was darker, as a result of the degradation of the hemicellulose, cellulose and lignin. The size of the voids in the MOL was reduced after citric acid treatment and some distortion of the shape could be seen in the SEM of CAMOL. The surface morphology of MOL is different from that of CAMOL, irregular and porous surface could be observed. On the basis of this fact, it can be concluded that the biosorbent CAMOL present and adequate morphology for metal biosorption.

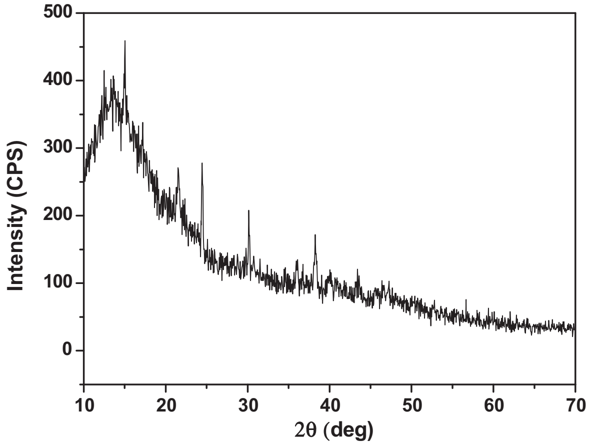

Fig. 3. X-ray diffraction patterns of CAMOL.

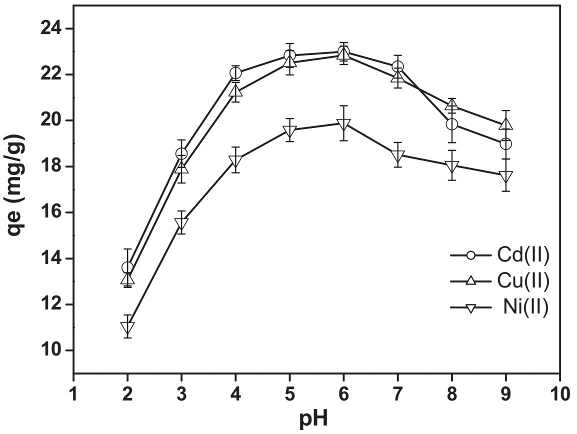

Fig. 4. Effect of pH on the biosorption of Cd(II), Cu(II) and Ni(II) onto CAMOL. (Initial conc.: 50 $mg L^{-1}$, contact time: 2 h, agitation rate: 200 rpm, biosorbent dose: 0.200 g. Error bars represent ±S.D.)

3.2. Effect of pH on biosorption

Since pH is one of the main variables affecting the biosorption process, the optimum pH value for the uptake of metals was determined using 50 $mg L^{-1}$ concentration of Cd (II), Cu(II), and Ni(II). In Fig. 4, the amount of metal removed by CAMOL versus initial solution pH varying from 2 to 9 has been plotted. As elucidated in Fig. 4, the biosorption capacities for all the metal ions were minimum at the initial pH 2 and metal removal increased with increasing solution pH. A trend of increasing metal ion binding with increasing pH could be observed for pH values above 2. The maximum removal efficiency of three metals was observed in the pH range 4–6. The results revealed that the optimum biosorption pH value for Cd(II), Cu(II), and Ni(II) onto CAMOL was 5.0. It is important to note here that the uptakes for some metals may decrease when pH is higher than the optimum pH. So each biomass has its own optimum pH for metal ion uptake. These different behaviors provide a preliminary indication of different metals to be effectively removed at certain pH value.

The pH dependence of metal uptake can be explained considering the nature of biosorbents. For CAMOL its practical functional group is carboxyl group and the pK_a value of carboxyl group is about 3. When pH < 3, the non-ionic form of carboxyl group, —COOH, was presented, metal adsorption was small because of the absence of electrostatic interaction. When pH was above 3, carboxyl group was turned into $—COO^-$, metal adsorption was increased and a plateau was reached at around pH 4.0–6.0. At low pH, cell wall ligands were closely associated with hydronium ions and hence the access of the metal ions to the biosorbent was restricted. With increasing pH, carboxyl groups were exposed leading to attraction between the negative charges and the metal ions and hence increased in biosorption onto the cell surface. The pH effect may be further explained in relation to the competition between H_3O^+ and metal ions. At low pH values, the concentration of H_3O^+ far exceeds that of metal ions and hence, occupying the binding sites on the cell walls, leaving metal ions unbound. When the pH was increased, the competing effect of H_3O^+ decreased and the positively charged metal ions took up the free binding sites. The metal uptake capacity was hence increased. At higher pH, the solubility of metal complexes decreases to a great extent allowing metal hydroxide precipitation, which may complicate the sorption process. Hence pH 5.0 was chosen optimum pH for all metal ions for further studies.

Point of zero charge determination of biosorbent is important in elucidating biosorption mechanism. PZC of CAMOL is 3.72 ± 0.21 this can be used to explain the effect of pH on Cd(II), Cu(II) and Ni(II) biosorption. The pH at PZC, the surface charge of adsorbents is neutral and the electrostatic forces between metal ions and surface of adsorbent are balanced. This balance is disturbed when pH is deviated from PZC. At pH < PZC, the adsorbents surface charge is positive which results in an electrostatic repulsion with metal ion and causes low sorption. At pH > PZC, the surface charge of adsorbents becomes negative and metal ions in solution are attracted to this surface. Maximum sorption is likely to occur at pH values greater than PZC when biosorbent have a net negative charge. The rule of PZC agrees with the biosorption behaviors of biosorbent for three metal ions.

3.3. *Effect of biosorbent dosage*

The optimum dosage of CAMOL to achieve the highest biosorption capacity was determined at pH 5.0 for all metal ions. The amount of CAMOL added to the metal solutions varied between 0.01 and 0.140 g, while the total volume, initial concentration of the metal solution, temperature and the pH value were kept constant. The result of variation of biosorption capacity with dosage of CAMOL is shown in Supplementary Fig. 3. The amount of Cd(II), Cu(II) and Ni(II) biosorption increased with an increase in biosorbent dosage. This result can be explained by the fact that for optimum biosorption, extra sites must be available for biosorption reaction, whereas by increasing the biomass concentration, number of sites available for biosorption site increased; this is in agreement with the results published by different authors. The maximum biosorption percentage reached >90% for all metal ions as biomass concentration was 0.04 g as shown in Supplementary Fig. 3. However, further increase in sorbent mass beyond 0.04 g did not result in significant improvement in the percentage removal of metal ions by CAMOL. Therefore, the optimum biomass concentration was taken as 0.040 g for further batch experiments.

3.4. *The effect of contact time and kinetics of biosorption*

After fixing the pH, sorbent dosage, the effect of contact time on biosorption capacity of CAMOL for Cd(II), Cu(II) and Ni(II) ions was investigated at various initial concentration (10–40 mg L^{-1}) shown in Supplementary Fig. 4. Biosorption increased sharply with contact time in the first 20 min and equilibrium biosorption was established within 50 min. For all the three metal ions it was observed that 50 min was enough to reach biosorption equilibrium. As contact time increases, metal uptakes increase initially, and then become almost stable, denoting attainment of equilibrium. These changes in metal uptake may be due to the fact that, initially, all adsorbent sites were vacant and the solute concentration was high. After that period, only a very low increase in the metal uptake was observed because there were few surface active sites on the cell wall of CAMOL.

The kinetics of the CAMOL and three metal ion interactions was tested with different kinetic models including pseudo-first order, pseudo-second-order, and intraparticle diffusion models. The pseudo-first order kinetic model equation is written as (Ho & Ofomaja, 2006):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

where q_t and q_e are the amount sorbed at time t and at equilibrium and k_1 is the rate constant of the pseudo-first-order sorption process. On integration under the boundary conditions of $t = 0$ and $t = t$ and $q_t = 0$ to $q_t = q_t$, gives a linear expression:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{4}$$

where q_t (mg g^{-1}) is the amount of the metal ion biosorbed at time t. The value of k_1 can be obtained from the slope of the plot of log $(q_e - q_t)$ versus t.

The pseudo-second order kinetic equation (Ho and McKay, 1999) is expressed in Eq. (4):

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

In Eq. (3) q_e^2 is the maximum adsorption capacity (mg g^{-1}) and k_2 (g mg^{-1} min^{-1}) is the adsorption rate constant of pseudo-second-order. From the plots of t/q_t against t, q_e and k_2 can be evaluated. The initial sorption rate h_0 (mg g^{-1} min^{-1}) is defined as (Ho and McKay, 2000):

$$h_0 = k_2 q_e^2 \tag{6}$$

Plotting t/q_t versus "t" at different adsorbate concentrations provided the second-order sorption rate constant (k_2) and q_e values from slopes and intercepts.

The pseudo-first-order data do not fall on straight line indicating that this model is not appropriate. The experimental and calculated q_e values, pseudo-first-order rate constant and coefficient of determination (R^2) values are given in Table 1. The theoretic values ($q_{e,cal}$) are far lower than the corresponding experimental data, $q_{e,exp}$ implying that the biosorption process does not follow fully the pseudo-first-order biosorption rate expansion.

The dependence of t/q_t versus t gives an excellent straight line relation for all the experimental concentrations (Supplementary Fig. 5), and all the R^2 values are close to 1 (Table 1), confirming the applicability of the pseudo-second-order equation. In addition, there is only little difference between the $q_{e,exp}$ and $q_{e,cal}$ (Table 1), reinforcing the applicability of this model. It can also be seen in Table 1 that, with an increase in initial metal concentration, the initial sorption rate (h_0) increases while the rate constant of adsorption (k_2) decreases. The lower correlation factors obtained for pseudo-first-order model as compared with that obtained for the pseudo-second-order model for the biosorption of all metal ions, implies that the pseudo-first-order model is not very good in explaining the kinetics of the biosorption of the metal. Therefore, the pseudo-second-order model better represented the sorption kinetics and thus supports the assumption behind the model. The obtained results are supporting that the chemical sorption as rate-limiting step of adsorption mechanism and a mass transfer was not involved in solution.

The kinetic data were analyzed by an intra-particle diffusion model to elucidate the diffusion mechanism (Weber & Morris, 1963):

$$q = k_{id} t^{1/2} + c \tag{7}$$

where k_{id} (mg g^{-1} $min^{-1/2}$) is the intraparticle diffusion rate constant and c (mg g^{-1}) a constant that gives idea about the thickness

Table 1
Parameters of pseudo-first-order, pseudo-second-order, and intraparticle diffusion models.

Initial concentration (mg L^{-1})	Experimental		Pseudo-first-order			Pseduo-second-order			Weber and Morris		
	$q_{e,exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	$k_1 \times 10^{-2}$ (mg g^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	$k_2 \times 10^{-2}$ (mg g^{-1} min^{-1})	h_0 (mg g^{-1} min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	K_{id} (mg g^{-1} min$^{-1/2}$)	R^2
Cd(II)											
10	13.54 ± 0.04	10.99 ± 1.52	5.74 ± 0.26	0.9638	14.32 ± 0.64	1.39 ± 0.37	2.73 ± 0.53	0.9951	3.27 ± 0.54	1.21 ± 0.99	0.8488
25	13.80 ± 0.18	10.90 ± 0.74	6.31 ± 0.64	0.9597	14.54 ± 0.23	1.46 ± 0.04	3.09 ± 0.01	0.9969	3.79 ± 0.07	1.18 ± 0.07	0.8324
40	20.86 ± 0.57	15.24 ± 1.22	6.70 ± 0.72	0.9666	21.57 ± 0.60	1.22 ± 0.17	5.61 ± 0.52	0.9981	6.36 ± 0.32	1.73 ± 0.07	0.7929
Cu(II)											
10	11.92 ± 0.65	11.03 ± 0.60	3.36 ± 0.43	0.9598	12.81 ± 0.98	3.40 ± 2.27	5.58 ± 0.02	0.99928	2.33 ± 0.09	1.02 ± 0.04	0.8981
25	13.55 ± 0.45	12.45 ± 2.22	7.64 ± 0.43	0.9238	14.23 ± 0.75	1.66 ± 0.50	3.37 ± 0.01	0.9958	3.64 ± 0.47	1.18 ± 0.10	0.8232
40	16.01 ± 0.31	12.86 ± 1.17	5.11 ± 2.25	0.9531	16.59 ± 0.32	1.56 ± 0.17	4.31 ± 0.01	0.9977	4.98 ± 0.18	1.32 ± 0.03	0.7923
Ni(II)											
10	10.24 ± 0.47	10.14 ± 0.01	5.11 ± 1.60	0.9356	10.86 ± 0.67	1.51 ± 0.35	1.70 ± 0.25	0.9951	2.54 ± 0.16	0.93 ± 0.06	0.866
25	12.49 ± 0.24	11.71 ± 0.48	6.80 ± 0.55	0.9430	13.29 ± 0.38	1.31 ± 0.14	2.29 ± 0.15	0.9952	2.84 ± 0.17	1.15 ± 0.04	0.8661
40	14.07 ± 0.35	12.10 ± 0.62	3.78 ± 1.92	0.9189	14.75 ± 0.46	1.52 ± 0.23	3.27 ± 0.33	0.9967	3.90 ± 0.31	1.22 ± 0.07	0.724

of the boundary layer. Supplementary Fig. 6 shows the amount of metal sorbed versus $t^{1/2}$ at three different concentrations with a fixed biosorbent dose. According to this model, if the plot of q_t versus $t^{1/2}$ gives a straight line, then the sorption process is controlled by intra-particle diffusion, while, if the data exhibit multi-linear plots, the two or more steps influence the adsorption process (Bilgili, 2006). In the present study, the plots present multi-linearity indicating three steps taking in biosorption. At the first, sharper portion may be considered as external surface adsorption or faster adsorption stage. The second portion describes the gradual adsorption stage, where the intra-particle diffusion is rate-controlled. The third portion is attributed to the final equilibrium stage, where intra-particle diffusion starts to slow down due to the extremely low adsorbate concentration in the solution (Bilgili, 2006). In the intermediate stage where the adsorption is gradual, the process may be controlled by intra-particle diffusion. This indicates that intra-particle diffusion involved in the sorption of metal ions onto CAMOL, but it was not the sole rate-controlling step. The k_{id} values were obtained from the slope of the linear portions of the curve of different initial concentrations and shown in Table 1.

As a result compared to the pseudo-first-order, second-order and intraparticle diffusion kinetics models, a good correlation coefficient was obtained for pseudo-second-order kinetic model, which indicates the Cd(II), Cu(II) and Ni(II) biosorption onto CAMOL follows pseudo-second-order rate expression. When comparing the obtained values for the sorption rate constant, *k*, Cd(II) presented the highest value, followed by the other metals in the following order: Cd > Cu > Ni.

3.5. Biosorption isotherms

The analysis of the isotherm data is important to develop an equation which accurately represents the results and could be used for designing purposes. In order to investigate the sorption isotherm, four models were used: the Langmuir, the Freundlich, the Dubinin–Raduskovich and Temkin the isotherm. Isotherm plots were drawn for the experimental data of the amount of Cd(II), Cu(II) and Ni(II) biosorbed per unit mass (mg g^{-1}) versus equilibrium solution concentration for the biosorption of Cd(II), Cu(II) and Ni(II) from solutions of concentration ranging from 10 to 1000 mg L^{-1} at three different temperatures 293, 303 and 313 K keeping the other conditions constant.

The Langmuir sorption isotherm (Langmuir, 1916) is perhaps the best known of all isotherms describing sorption. The theoretical Langmuir isotherm is often used to describe sorption of a solute from a liquid solution as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{8}$$

where C_e is the equilibrium solute concentration (mg L^{-1}); q_e is the amount of metal ion sorbed (mg g^{-1}); q_m is q_e for a complete monolayer (mg g^{-1}); K_L is sorption constant (L mg^{-1}). The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (R_L), which is defined as:

$$R_L = \frac{1}{(1 + K_L C_0)} \tag{9}$$

where K_L is the Langmuir constant (L mg^{-1}) and C_0 is the initial adsorbate concentration (mg L^{-1}). The value of R_L indicates the types of isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Freundlich isotherm (Freundlich, 1906) is an empirical relationship established upon sorption onto a heterogeneous surface on the assumption that different sites with several adsorption energies are involved, which is given by Eq. (10)

$$q_e = K_F C_e^{1/n} \tag{10}$$

where K_F (mg g^{-1}) and n are the Freundlich constants related to the sorption capacity of the adsorbent and the energy of adsorption respectively.

The equilibrium data were examined using the D–R isotherm (Dubinin & Radushkevich, 1947) model in order to determine the nature of biosorption processes as physical or chemical. The non-linear presentation of the equation is given as

$$q_e = Q_m \ \exp\left(-K\left[RT\ln\left(1+\frac{1}{C_e}\right)\right]\right) = Q_m \exp(-k\varepsilon^2) \tag{11}$$

where Q_m is the maximum amount of the ion that can be sorbed onto unit weight of sorbent (mg g^{-1}), ε is the Polanyi potential which is equal to RT $\ln(1+1/C_e)$, where R and T are the universal gas constant (kJ mol^{-1} K^{-1}) and the absolute temperature (K), respectively. K is related to the mean free energy of sorption per mole (E) of the sorbate when it is transferred to the surface of the solid from infinity in the solution and E can be computed using the following relationship:

$$E = \frac{1}{\sqrt{2K}} \tag{12}$$

The Temkin isotherm (Temkin and Pyzhev, 1940) is represented by the following equation:

$$q_e = \frac{\mathrm{RT}}{b}\ \ln(K_T C_e) = B_1 \ln(K_T C_e) \tag{13}$$

where constant $B_1 = RT/b$, which is related to the heat of adsorption, R is the universal gas constant (J mol^{-1} K^{-1}), T is the temperature (K), b is the variation of adsorption energy (J mol^{-1}) and K_T is the equilibrium binding constant (L mg^{-1}) corresponding to the maximum binding energy. A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants B_1 and K_T from the slope and the intercept, respectively.

Langmuir model serves to estimate the complete monolayer biosorption capacity (q_m). The parameters for the Langmuir isotherms models are summarized in Table 2. The values of q_m appear to be significantly higher for biosorption of Cd(II) in comparison with Cu(II) and Ni(II) ions onto CAMOL. The maximum biosorption values are 171.37, 167.90 and 163.88 for Cd(II), Cu(II) and Ni(II) ions, respectively, and showing the following capacity order: Cd(II) > Cu(II) > Ni(II). While this outcome is contradictory to the studies involving Cd(II), Cu(II) and Ni(II) biosorption (Hawari & Mulligan, 2006; Saeed, Iqbal, & Akhtar, 2005). It is found that the complete monolayer biosorption capacity, q_m and b increased in the order of increasing temperature. It is found that the regression coefficients R^2 obtained from Langmuir model for Cd(II), Cu(II) and Ni(II) ions were greater than 0.99, which implied that Langmuir model could be used to describe the biosorption of Cd(II), Cu(II) and Ni(II) onto CAMOL at the temperature range of 293–313 K. In addition, the values of R_L varied in the range between 0 and 1. This demonstrated that Langmuir model is suitable favorable for the biosorption of Cd(II), Cu(II) and Ni(II) onto CAMOL at the temperature range of 293–313 K.

The Freundlich constants were calculated along with the coefficient of determination, R^2, in Table 2 and Supplementary Table 1. The results revealed that the constants, n, and K_F were found to be higher for cadmium(II) than copper(II) and nickel(II) ions. The n value of Freundlich equation can give an indication on the favorability of sorption. It is generally stated that values of n in the range of 2–10 represent good, 1–2 moderately difficult, and less than 1 poor sorption characteristics. The results showed that the numerical values of n for Cd(II), Cu(II) and Ni(II) were 3.12, 3.01 and 2.91

Table 2
Isotherm parameters for Cd(II), Cu(II) and Ni(II) biosorption onto CAMOL at different temperatures.

Metal ion	Temp. (K)	Langmuir		Freundlich		Dubinin–Raduskovich		Temkin	
		q_m (mg g^{-1})	b (L mg^{-1})	K_F (mg g^{-1})	n	Q (mg g^{-1})	K	b	K
Cd(II)	293	159.88 ± 5.16	0.027 ± 0.0006	5.54 ± 1.30	2.02 ± 0.16	111.79 ± 8.20	1.68 ± 0.51	1.29 ± 0.08	0.13 ± 0.02
	303	166.24 ± 5.64	0.034 ± 0.001	10.85 ± 1.94	2.40 ± 0.17	139.16 ± 11.72	2.92 ± 1.35	1.16 ± 0.07	0.31 ± 0.06
	313	171.37 ± 4.22	0.037 ± 0.004	23.53 ± 5.26	3.12 ± 0.38	151.68 ± 11.49	0.18 ± 0.09	1.13 ± 0.03	0.82 ± 0.09
Cu(II)	293	146.87 ± 6.19	0.024 ± 0.001	2.99 ± 0.56	1.80 ± 0.10	102.66 ± 9.21	12.51 ± 5.24	1.30 ± 0.09	0.09 ± 0.01
	303	151.29 ± 3.85	0.028 ± 0.001	9.88 ± 2.18	2.42 ± 0.22	118.35 ± 8.84	0.96 ± 0.34	1.22 ± 0.07	0.25 ± 0.04
	313	167.90 ± 4.39	0.029 ± 0.001	21.23 ± 5.20	3.01 ± 0.39	147.36 ± 11.10	0.20 ± 0.09	1.09 ± 0.03	0.60 ± 0.07
Ni(II)	293	138.04 ± 4.50	0.021 ± 0.001	2.65 ± 0.64	1.78 ± 0.12	97.01 ± 8.16	14.97 ± 5.68	1.37 ± 0.10	0.08 ± 0.01
	303	148.76 ± 4.18	0.022 ± 0.001	8.94 ± 2.05	2.36 ± 0.21	117.69 ± 8.87	1.52 ± 0.58	1.21 ± 0.06	0.21 ± 0.03
	313	163.88 ± 4.16	0.023 ± 0.003	18.87 ± 4.98	2.91 ± 0.39	143.62 ± 10.28	0.28 ± 0.11	1.08 ± 0.03	0.45 ± 0.05

Table 3
Thermodynamic parameters for the biosorption of Cd(II), Cu(II) and Ni(II) ions onto CAMOL at different temperatures.

Metal ions	Temperature (K)	$-\Delta G^\circ$ (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	ΔH° (kJ mol^{-1})
Cd(II)	293	3.68	62.57	15.27
	303	4.50		
	313	4.95		
Cu(II)	293	3.17	52.60	12.76
	303	3.75		
	313	4.25		
Ni(II)	293	2.68	42.92	10.32
	303	3.08		
	313	3.56		

respectively at 313 K. The values for n were greater than 2 indicating that Cd(II), Cu(II) and Ni(II) ion are favorably biosorbed by CAMOL. This is in great agreement with the findings to R_L value. Also the values of n calculated from Freundlich isotherms at different temperatures were found to be very close to each other, indicating that the adsorption intensity was not affected by changing the temperature of adsorption medium.

The equilibrium data were also subjected to the D–R isotherm model to determine the nature of biosorption process as physical or chemical. The Dubinin–Radushkevich isotherm parameters are shown in Table 2. The E values obtained in this study are greater than 8 kJ mol^{-1}, indicating ion-exchange mechanism.

The equilibrium isotherm data were finally analyzed using the Temkin isotherm model. The values of the Temkin constants and the correlation coefficient calculated and are listed in Table 2 and Supplementary Table 1. As seen from Table 2, the Temkin constant b (the heat of adsorption) decreased with the increasing temperature from 293 to 313 K.

Consequently, among the four isotherm models used, the Langmuir model offers the best correlation factors. By comparing the correlation coefficients (Supplementary Table 1) and other parameters determined by these four isotherms, Langmuir isotherm model is better fit than Freundlich, D–R and Temkin isotherms.

3.6. Thermodynamic analysis

In environmental engineering practice, both energy and entropy factors must be considered in order to determine the processes that occur spontaneously. In the present study, the biosorption experiments were carried out in the temperature range of 209–313 °C. The effect of temperature on Cu(II), Cd(II) and Ni(II) biosorption can be inferred from Supplementary Fig. 7. Thermodynamic parameters ΔG°, ΔH° and ΔS°, that describe Cu(II), Cd(II) and Ni(II) biosorption onto CAMOL were calculated using the following thermodynamic equations

$$\Delta G^\circ = -RT \ln K \tag{14}$$

where R is the universal gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}), T is an absolute temperature (K) and K (L g^{-1}) an equilibrium constant obtained by multiplying the Langmuir constant q_m and K_L (Aksu & Isoglu, 2005).

The enthalpy (ΔH°) and entropy (ΔS°) values were estimated from the following equations:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{15}$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{16}$$

The values of ΔG° were calculated from Eq. (14). Reciprocal of temperature ($1/T$) was plotted against $\ln K$, which was a straight line shown in Supplementary Fig. 7. The values of ΔH° and ΔS° were evaluated from the slope and intercept of the line in Supplementary Fig. 7. The values of ΔH° and ΔS° and ΔG° are shown in Table 3. The negative values of ΔG° at different temperatures are due to the fact that the sorption process is spontaneous with high preference of metal ions for the sorbent prepared from CAMOL. The magnitude of ΔH gives an idea about the type of sorption. The positive value of the enthalpy change indicates that the biosorption is endothermic in nature. The positive values of ΔS° show increased randomness at the solid/solution interface with some structural changes in the sorbate (hydrated metal ions) and biosorbent (CAMOL)

Table 4
Langmuir based maximum biosorption capacity of several biosorbents for heavy metal biosorption at ambient temperature.

Biosorbent	q_m (mg g^{-1})	T (K)	pH	Reference
Cd(II)				
Modified orange peel	293.3	303	5.5	Feng, Guo, Liang, Zhu, & Liu (2011)
Coffee husk	6.9	298	4	Oliveira, Franca, Oliveira, & Rocha (2008)
Heartwood powder of Areca catechu	10.66	303	6	Chakravarty et al. (2010)
Fennel biomass	26.59	323	4.3	Rao, Khan, and Rehman (2010)
CAMOL	171.37	323	5	This study
Cu(II)				
Leaves of salt bush	68.0	297	5.0	Sawalha, Peralta-Videa, Romero-González, Duarte-Gardea, & Gardea-Torresdey (2007)
NaOH treated pine cone	26.32	291	5	Ofomaja, Naidoo, & Modise (2010b)
Sugar beet pulp	28.5	298	4	Aksu and Isoglu (2005)
Peanut hull	21.25	303	5.5	Zhu et al. (2009)
CAMOL	167.90	323	6	This study
Ni(II)				
Modified orange peel	162.6	303	5.5	Feng et al. (2011)
Irish peat moss	14.5	298	4.5	Gupta, Curran, Hasan, & Ghosh (2009)
Coir pith	9.5	303	3.9	Ewecharoen, Thiravetyan, & Nakbanpote (2008)
Black carrot residues	6.51	333	5.2	Guzel, Yakut, & Topal (2008)
CAMOL	163.88	323	6	This study

3.7. Comparison of CAMOL with other biosorbents

In order to assess the performance of CAMOL as biosorbent for Cd(II), Cu(II) and Ni(II) ions, a comparison with other types of biosorbents that are used for removal of metal ions was made (Table 4). CAMOL is an effective biosorbent for the removal of Cd(II), Cu(II) and Ni(II) from aqueous solutions, its biosorptive capacity being clearly superior to some of the biosorbents (Table 4). Difference in metal uptake by various biosorbents is due to the properties of each biosorbent such as structure, functional groups and surface area.

3.8. Desorption and regeneration

To keep the processing cost down and to open the possibility of recovering the metal(s) extracted from the liquid phase, it is desirable to regenerate the biosorbent material. To test the suitability and stability of the biosorbent, it was subjected to successive biosorption and desorption cycles. A strong desorption agent HCl acid is usually used to recover quantities of metals from metal-loaded biosorbent. Desorption experiments were first carried out through various concentrations of HCl (0.1–0.6 M), respectively (data now shown). It was found that the desorption efficiency was almost same when HCl concentration was higher than 0.4 M. Hence, 0.4 M HCl solution was chosen as a suitable concentration for the regeneration of metal ions. In each cycle, the biosorbent was filtered and repeatedly washed with deionized water after each desorption to eliminate the excess of acid. The biosorbent was washed with water before each measurement. The results showed that CAMOL can be used repeatedly at least four times without significantly losing the biosorption capacity for Cd(II), Cu(II) and Ni(II) (Supplementary Fig. 8). These results show promising regeneration potential of the CAMOL. Interestingly, the biomass was able to sustain its biosorption capacity and remained rigid even after repeated exposure to acidic conditions. This property of CAMOL may be utilized by small scale commercial units to remove Cd(II), Cu(II) and Ni(II) from their discharging effluents in an economical and efficient way.

3.9. The effect of alkali metal ions on the biosorption

During practical applications, the interference of alkali metal ions such as Na^+ and K^+, and alkaline earth metal ions such as Mg^{2+} and Ca^{2+} has an important influence on biosorption. Calcium and magnesium are particularly important in the area where the hardness of water is high. Hence the extent of Cd(II), Cu(II) and Ni(II) biosorption in presence of coexisting cation such as Ca^{2+}, Mg^{2+}, Na^+ and K^+, was examined under the optimum conditions described above. The biosorption studies were performed by adding 100 mg L^{-1} of Na^+, K^+, Mg^{2+} and Ca^{2+} individually in 100 mg L^{-1} Cd(II), Cu(II) and Ni(II) solutions containing 100 mg of CAMOL. The results showed that the ions Ca^{2+}, Mg^{2+}, Na^+, K^+ had no noticeable effect on biosorption of three metal ions.

4. Conclusion

This study illustrates the performance of CAMOL biomass prepared from acid modified MOL, in sequestering Cd(II), Cu(II) and Ni(II) ions from aqueous solution. The analysis of experimental data led to the following conclusions:

1. Heavy metal sorption onto esterified MOL sorbent is highly dependent upon solution pH. Metal removal sharply decreases with decreasing pH which indicates that metals may be recovered by a desorption process.
2. Kinetic test demonstrated that sorption equilibrium is reached within 50 min for Cd(II), Cu(II) and Ni(II). Moreover, a pseudo-second-order model has better fit to heavy metal uptake vs. time profiles.
3. The biosorption data are better fitted by the Langmuir and Temkin adsorption isotherm models as compared to the Freundlich and D-R models. The monolayer capacity (q_m) was calculated using the Langmuir isotherm for the sorbent and the metal sorption capacity was found to be in the general order of Cd(II) > Cu(II) > Ni(II).
4. The metal sorption capacities were found to increase with increasing temperature, indicating the endothermic nature of the process.
5. Regeneration studies showed that CAMOL can be effectively utilized for the recovery of Cd(II), Cu(II) and Ni(II) ions and reuse of biosorbents upto five cycles.

Overall, the results of this study showed that the CAMOL can be used as a sorbent to remove heavy metals from the aqueous solutions. Especially, leaves having low commercial values may be utilized for the preparation of low cost biosorbent.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbpol.2012.01.073.

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