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Equilibrium, kinetic and thermodynamic studies on biosorption of Cu(II), Cd(II), Pb(II) and Ni(II) from aqueous solution by chitosan-abrus precatorius blended beads

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ABSTRACT

Chitosan-abrus precatorius blended beads were used as a biosorbing agent for the removal of Cu(II), Cd(II), Pb(II) and Ni(II) ions from aqueous solutions. The adsorption studies were conducted as a function of pH, contact time, adsorbent dosage, initial metal ion concentration and temperature. Optimum adsorption of Cu(II), Cd(II), Pb(II) and Ni(II) took place at pH values of 6.0, 4.0, 5.0 and 4.0, respectively. Further, the biosorbent was characterized by Fourier Transform Infrared Spectroscopy (FTIR) and BET Surface area analysis. The adsorption data of metal ions at the temperature of 30, 40 and 50°C are fitted to Langmuir and Freundlich isotherm models. Langmuir model fitted the equilibrium data better than the Freundlich isotherm. Experimental data were used to predict biosorption kinetics using pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models. The results showed that the biosorption processes of metal ions followed well pseudo-second order kinetics. The calculated thermodynamic parameters (ΔG° , ΔH° and ΔS°) showed that the biosorption of Cu(II), Cd(II), Pb(II) and Ni(II) onto chitosan-abrus precatorius blended beads was feasible, spontaneous and endothermic.

Key words: Biosorption; Chitosan-abrus precatorius blended beads; Isotherms; Kinetics; Thermodynamics

INTRODUCTION

Concentration of many trace metals in the aquatic environment have been reduced over the last few decades, through the implementation of Environmental Quality Standards. Owing to their

adverse effects on human beings, a number of techniques such as filtration, reverse osmosis, chemical precipitation, ion exchange, electro-deposition and adsorption have been used to remove the toxic metals from aquatic environment [1]. However, these technologies are most suitable in situations where the concentrations of heavy metal ions are relatively high. They are either ineffective or expensive when heavy metals are present in wastewater at low concentrations [2]. Adsorption is an alternative technology and is highly effective, cheap and easy method among the physicochemical treatment processes. Adsorption on activated carbon has been found to be an effective process for metal removal, but it is too expensive. Consequently numerous low cost alternatives have been studied including activated carbon [3], activated slag [4], natural zeolites [5], *acacia leucocephala* bark [6], mungbean husk [7], red mud [8, 9], brewery's waste biomass [10], microbial and plant derived biomass [11], living and non-living algal biomass [12-17], chitosan-calcium pectinate pellets [18], chitin and chitosan [19, 20].

Chitosan is polycationic polymer derived from chitin, a major component of arthropods and is readily available from sea food processing wastes [21]. Because chitosan has unique physiological and biological properties, it has been widely used as a versatile starting material for the preparation of various products in biomedical engineering [22]. In recent years, chitosan has also increasingly been studied as an adsorbent for the removal of heavy metal ions from aqueous solutions because the amino and hydroxyl groups on the chitosan chain act as a chelation or reaction sites for the substances to be removed [23,24]. Several investigators have attempted to modify chitosan to facilitate mass transfer and to expose the active binding sites to enhance the adsorption capacity. Grafting specific functional groups onto native chitosan backbone allows its sorption properties to be enhanced [25]. To overcome some of the problems associated with the use of pure chitosan, it is chemically modified by cross-linking or coating and is used as adsorbent [26,27].

The present study was aimed to prepare chitosan-abrus precatorius blended beads and to investigate the ability of these blended beads in removing Cu(II), Cd(II), Pb(II) and Ni(II) from aqueous medium. The effects of pH, contact time, initial metal concentration, adsorbent dosage and temperature on the extent of adsorption. In addition, the biosorption kinetics was evaluated using the pseudo-first-order, pseudo-second-order and intraparticle diffusion models. Isotherms and thermodynamics of the biosorption at various temperatures were also studied.

EXPERIMENTAL SECTION

Materials

Chitosan, having an average molecular weight of 300 000 was purchased from Aldrich Chemical Corporation, USA. Fresh seeds of abrus precatorius were collected from a local source, Pullampet, Andhra Pradesh, India. The seeds were cleaned and ground to fine powder with a high speed blender. All chemical compounds used for preparation of the reagent solutions were of analytical grade (S.D. Fine Chemicals, Mumbai, India). Four types of metal stock solutions (1000 mg/L) used in this study were prepared by dissolving weighed quantities of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$ and $\text{Ni}(\text{NO}_3)_2$ salts in twice-distilled water.

Preparation of biosorbent

Chitosan gel was prepared by adding 3 g of chitosan to 100 mL of 5% oxalic acid. To 100 mL of chitosan gel, 1.5 g *abrus precatorius* was added to form intense gummy gel. This gel was stirred for a period of 1 h for homogeneity at room temperature and kept aside for 1 h to obtain a bubble-free solution. Spherical shaped beads were then prepared by drop wise addition of chitosan *abrus precatorius* blended gel into a 10% NaOH precipitation bath. The purpose of adding acidic chitosan *abrus precatorius* mixture to NaOH solution is to assist rapid neutralization of oxalic acid. These spherical beads were taken from the NaOH bath and washed several times with deionized water to a neutral pH.

Preparation of Cu(II), Cd(II), Pb(II) and Ni(II) standards

The stock solutions containing 1000 mg/L of Cu(II), Cd(II), Pb(II) and Ni(II) were prepared by dissolving 3.801g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 2.744g of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 1.598g of $\text{Pb}(\text{NO}_3)_2$ and 4.954g of $\text{Ni}(\text{NO}_3)_2$. The desired concentrations were prepared from stock solutions for carrying out experiments.

Batch adsorption studies and instruments

The metal solutions were prepared by diluting 1000 mg/L stock solutions. Adsorption experiments were carried out in 250 mL Erlenmeyer flasks using 100 mL metal bearing solution with a known quantity of the chitosan *abrus precatorius* blended beads. Before mixing these solutions with the adsorbent, test solutions were prepared with pH values ranging from 3 to 7 by adding 0.1 N NaOH or 0.1 N HCl. After we selected the optimal pH, one pH value was tested in all subsequent adsorption tests. The adsorption medium was placed in a mechanical platform shaker (ZHWHY-200B, ZHICHENG Analytical Co., Ltd) and stirred for different time intervals and at a fixed agitation speed of 200 rpm. The metal solution was filtered through 0.45 μm pore size membrane filters (Millipore Corp., Bedford). It was then analysed using an atomic absorption spectrophotometer (Shimadzu AA-6300, Japan) Infrared spectra of the beads in solid phase were performed using a Fourier Transform Infrared Spectrometer (Spectrum 2000 Explorer, Perkin-Elmer, USA). The BET surface area of the beads was measured by N_2/BET method using Micromeritics surface analyzer (Model ASAP-2000, USA). The pH was measured using a Beckman 32 pH meter (Beckman Instruments, Fullerton, CA).

The sorption capacity of metal ion is the concentration of metal ion on the adsorbent, and it can be calculated based on the mass balance principle where;

$$q_e = \frac{(C_i - C_e)V}{M} \quad (1)$$

where q_e (mg/g) is the adsorption capacity of the biosorbent at any time, M (g) is the biomass dosage, and V (L) is the volume of the solution.

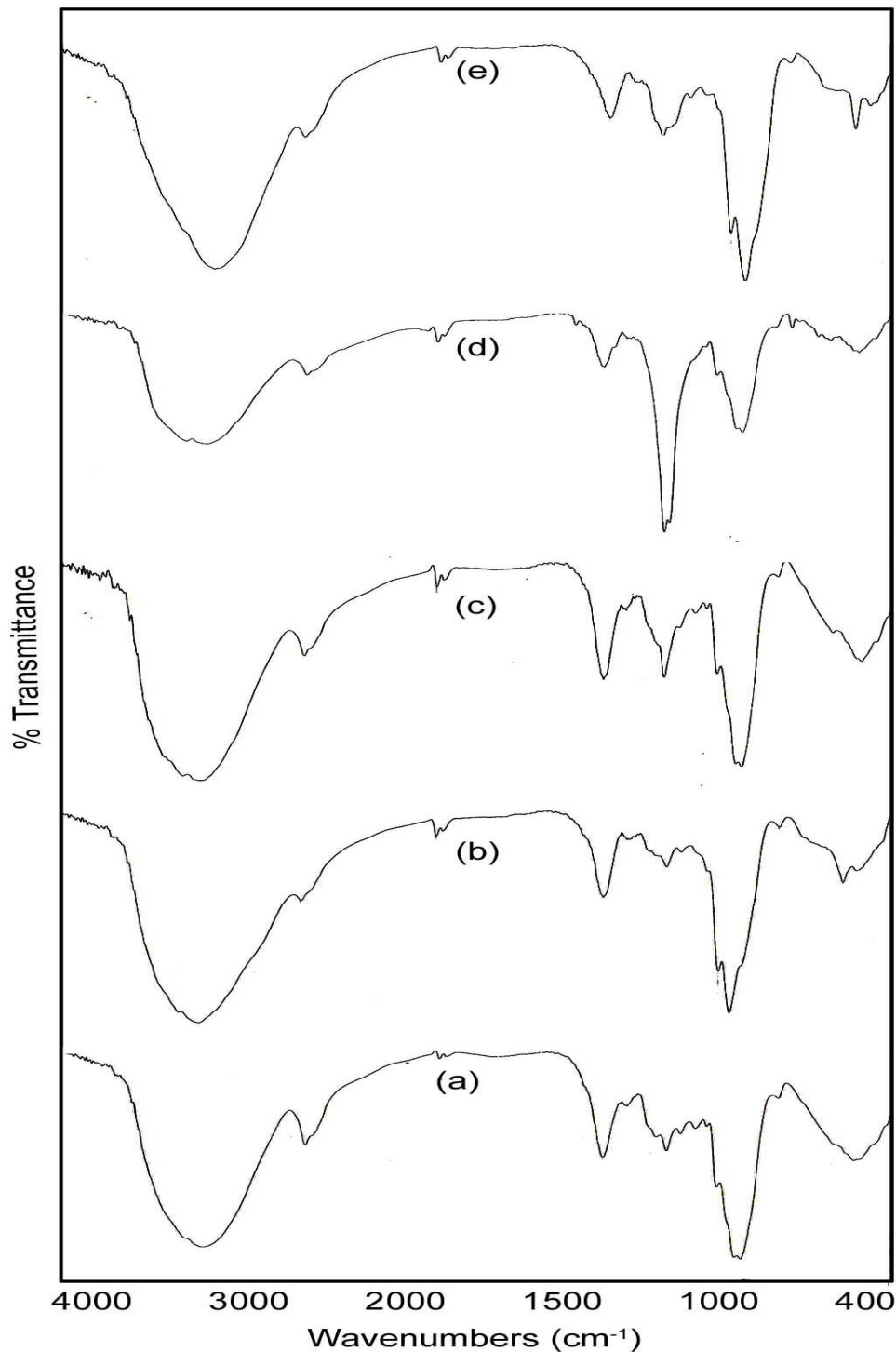
RESULTS AND DISCUSSION**Characterization of the chitosan abrus precatorius blended beads**

Fig. 1: FTIR Spectra of Chitosan-abrus precatorius blended beads: (a) Unloaded (b) loaded with Cu(II) (c) loaded with Cd(II) (d) loaded with Pb(II) and (e) loaded with Ni(II).

FTIR analysis

The FTIR spectra of dried unloaded and loaded with Cu(II), Cd(II), Pb(II) and Ni(II) ions chitosan-abrus precatorius blended beads in the range of 400-4000 cm^{-1} were recorded in order to obtain information on the nature of the possible adsorbent-metal ion interactions. The spectra are presented in Fig. 1a-e. The FTIR spectrum of unloaded chitosan-abrus precatorius blended beads in Fig. 1a indicates the presence of predominant peaks at 3360 cm^{-1} (-OH and -NH stretching vibrations), 2898-2990 cm^{-1} (-CH stretching vibration in -CH and -CH₂), 1655 cm^{-1} (-C=O stretching vibration), 1380-1460 cm^{-1} (-CH₂ bending vibration), and 1043 cm^{-1} (C-O stretching vibration). The peaks at these wave numbers are intact, indicating that the functional groups are not disturbed during the coating process and are available for interaction with the metal ions. The intensity of transmittance of the peaks are relatively more in case of metal ions (*viz.*, Cu(II), Cd(II), Pb(II) and Ni(II))-loaded chitosan-abrus precatorius blended beads (Fig. 1b-e) compared with unloaded chitosan-abrus precatorius blended beads. This may be attributed to the interaction between the functional groups and metal ions during the adsorption process. These observations provide evidence for the involvement of functional groups such as -NH₂, -OH and -CO in binding the metal ions to chitosan-abrus precatorius blended beads.

Surface area analysis

Surface area, pore volume and pore diameter of the chitosan-abrus precatorius blended beads were determined on the basis of the Brunauer, Emmet and Teller (BET) method. Surface area was measured assuming that the adsorbed nitrogen forms a monolayer and possesses a molecular cross sectional area of 16.2 \AA^2 per molecule. The shape of the adsorbent is nearly spherical with particle diameter ranging from 100-150 μm . The influence of the surface properties on the extent of adsorption was evaluated by measuring the surface area (99.5 m^2/g), total pore volume 0.067 cm^3/g , and the average pore diameter 26.8 \AA . The isotherm plots were used to calculate the specific surface area (N_2 /BET method) and average pore diameter of chitosan-abrus precatorius blended beads. Micropore volume was calculated from the volume of nitrogen adsorbed at P/P_0 0.9966.

Effect of pH

The pH of the aqueous solution was an important variable, which controls the adsorption of the metals at the solid-water interfaces. The pH affects the availability of metal ions in solution and the metal binding sites of the adsorbent [28]. The effect of hydrogen ion concentration on the extent of adsorption was studied by varying pH of the solution from 3 to 7. The equilibrium concentration of each metal ion was determined and the amount adsorbed per unit weight of sorbent at different pH values was determined. These results are graphically presented in Fig. 2. The results indicate that the extent of adsorption varies with pH. Since below pH 3 the chitosan undergoes dissolution [29] the experiments were conducted above pH 3. The maximum biosorption was observed at pH 6.0, 4.0, 5.0 and 4.0 for Cu(II), Cd(II), Pb(II) and Ni(II), respectively. Therefore, the remaining all experiments were carried out at these pH values. At highly acidic pH ($\text{pH} < 3.0$), the overall surface charge on the active sites became positive and metal cations and protons compete for binding sites on cell wall, which results in lower uptake of metal. The biosorbent surface was more negatively charged as the pH of solution increased from 3.0 to 6.0. The functional groups of the chitosan-abrus precatorius blended beads deprotonated and thus available for the metal ions. Decrease in biosorption yield at higher pH ($\text{pH} > 6$) is not only related to the formation of soluble hydroxylated complexes of the metal ions but also to the

ionized nature of the cell wall surface of the chitosan-abrus precatorius blended beads under the studied pH.

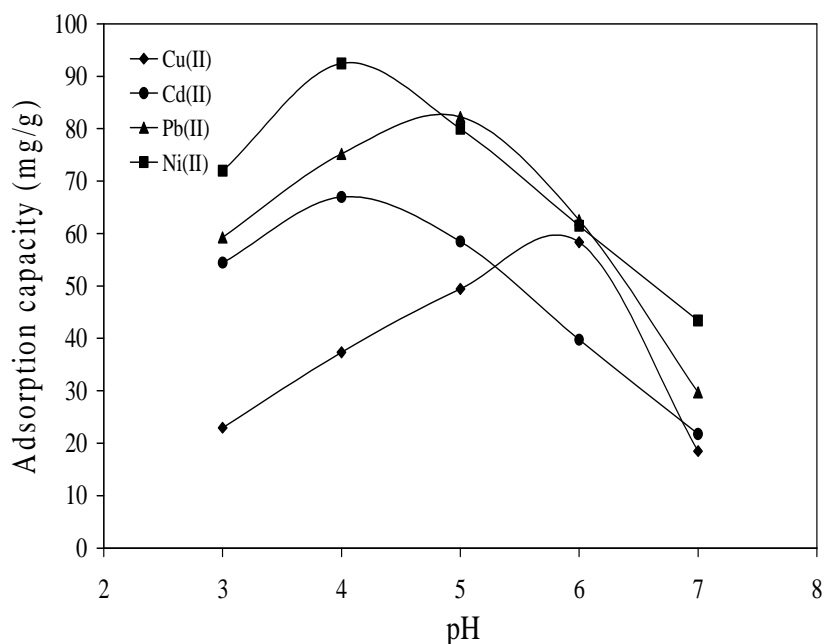


Fig. 2: Effect of pH on adsorption of Cu(II), Cd(II), Pb(II) and Ni(II) on Chitosan-abrus precatorius blended beads

Effect of contact time

The effect of time on the extent of adsorption of Cu(II), Cd(II), Pb(II) and Ni(II) at different initial concentrations of metal ions was investigated. The extent of adsorption of Cu(II), Cd(II), Pb(II) and Ni(II) increases with time and attains equilibrium at 210 min. Further increase in contact time did not enhance the biosorption, so, the optimum contact time was selected as 210 min for further experiments.

Sorption Dynamics

Successful application of the adsorption technique demands development of inexpensive, nontoxic, readily available adsorbents of known kinetic parameters and sorption characteristics. Therefore, kinetic studies of adsorption are carried out at various initial concentrations 50-200 mg/L.

Reaction based models

In order to investigate the mechanism of sorption the rate constants of sorption process were determined by using Lagergren first order [30,31] and a pseudo-second order [32] kinetics models, which are represented as,

$$\log(q_e - q) = \log q_e - \frac{K_1}{2.303} t \quad (2)$$

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

A straight line of $\log(q_e - q)$ versus t suggests the applicability of this kinetic model. q_e and K_1 are determined from the intercept and slope of the plot, respectively. In many cases the first order equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption process [33]. The second order rate constant K_2 is determined by plotting t/q_t against t . In many cases, the adsorption data could be well correlated by second order rate equation over the entire period of contact time. The values of the constants along with the R^2 values are given in Table 1. The results of the present study indicate that the adsorption of metal ions on chitosan-abrus precatorius blended beads follows pseudo-second-order kinetics.

Diffusion based model

The results were also analyzed in terms intraparticle diffusion model to investigate whether the intraparticle diffusion was the rate controlling step in adsorption of metal ions on chitosan-abrus precatorius blended beads. The model proposed by Weber and Morris [34] can be written as,

$$q = K_{id}t^{0.5} + C \quad (4)$$

where K_{id} is the intraparticle diffusion rate constant ($\text{mg}/(\text{g min}^{0.5})$) and C is the intercept.

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

Metal ion	Lagergren first-order			Pseudo-second-order			Weber and Morris		
	K_1 (min^{-1})	R^2	SSE	K_2 ($(\text{g}/\text{mg})\text{min}$)	R^2	SSE	K_{id} ($(\text{mg}/\text{g})\text{min}^{0.5}$)	R^2	SSE
Cu(II)	0.01	0.986	0.998	0.0007	0.997	0.027	1.476	0.943	0.908
	0.008	0.953	0.998	0.0006	0.998	0.011	2.122	0.948	0.927
	0.007	0.994	0.999	0.0007	0.997	0.007	2.424	0.987	0.942
	0.005	0.992	0.999	0.0007	0.995	0.006	2.786	0.985	0.944
Cd(II)	0.007	0.976	0.999	0.0006	0.994	0.007	0.964	0.964	0.942
	0.008	0.994	0.999	0.0007	0.995	0.003	1.377	0.969	0.957
	0.005	0.988	0.998	0.0006	0.997	0.005	2.298	0.987	0.947
	0.003	0.984	0.999	0.0006	0.997	0.003	2.442	0.984	0.956
Pb(II)	0.006	0.962	0.998	0.0005	0.989	0.022	1.199	0.963	0.917
	0.008	0.895	0.999	0.0005	0.993	0.004	2.138	0.964	0.951
	0.008	0.998	0.999	0.0004	0.990	0.012	4.325	0.931	0.931
	0.009	0.995	0.998	0.0005	0.996	0.011	5.186	0.930	0.930
Ni(II)	0.011	0.604	0.998	0.0002	0.999	0.004	1.253	0.985	0.947
	0.014	0.915	0.999	0.0002	0.999	0.004	2.199	0.984	0.955
	0.011	0.993	0.999	0.0002	0.996	0.014	5.151	0.979	0.927
	0.013	0.992	0.998	0.0002	0.998	0.021	7.822	0.962	0.918

It can be seen that all the plots have an initial curved portion, followed by a linear portion and a plateau regions. The initial curve of the plot is due to the diffusion of metal ion through the solution to the external surface of chitosan-abrus precatorius blended beads. The linear portion of curves describes the gradual adsorption stage, where intraparticle diffusion of metal ion on chitosan-abrus precatorius blended beads takes place and final plateau region indicates

equilibrium uptake. The rate constants of Weber-Morris intraparticle diffusion model are shown in Table 1. Based on the results it may be concluded that intraparticle diffusion is not only the rate determining factor.

Fitness of the kinetic models

The best fit among the kinetic models is assessed by the squared sum of error (SSE) values. It is assumed that the model which gives the lower SSE values is the best model for metal ion sorption on chitosan-abrus precatorius blended beads. The SSE values are calculated by the equation:

$$SSE = \sum \frac{(q_{t,e} - q_{t,m})^2}{q_{t,e}^2} \quad (5)$$

where $q_{t,e}$ and $q_{t,m}$ are the experimental adsorption capacities of metal ions (mg/g) at time t and the corresponding values that are obtained from the kinetic models. SSE values for all the kinetic models are calculated and are summarized in Table 1. Pseudo-second-order model has lower SSE values indicating that the adsorption of Cu(II), Cd(II), Pb(II) and Ni(II) on the biosorbent follows second order kinetic model.

Effect of adsorbent dose

One of the parameters that strongly affect the biosorption capacity is the amount of the biosorbent. The dependence of Cu(II), Cd(II), Pb(II) and Ni(II) sorption on chitosan-abrus precatorius blended beads was studied by varying the amount of the adsorbent from 0.1 to 0.7g while keeping the other parameters such as pH, metal solution volume (100 mL), concentration (100 mg/L), and contact time (210 min) constant. The removal efficiency of Cu(II), Cd(II), Pb(II) and Ni(II) ions increased with increasing adsorbent dosage. The maximum removal efficiency was attained as the dosage was 0.6 g/0.1L. The increase in the adsorption percentage with rise in adsorbent dosage is due to increase in active sites on the adsorbent and thus making easier penetration of the metal ions to the sorption sites. Based on this observation it may be concluded that the optimum biosorbent dosage is 0.6 g/0.1L for further experiments.

Adsorption isotherms

Two equilibrium models, namely Langmuir and Freundlich isotherm models are used to analyze the equilibrium experimental data. Initial concentration of Cu(II), Cd(II), Pb(II) and Ni(II) ions are varied from 20 to 100 mg/L while the weight of chitosan-abrus precatorius blended beads and pH are kept constant. The adsorption capacity of the chitosan-abrus precatorius blended beads increases with increase of initial metal ion concentration from 20 to 100 mg/L.

The Langmuir model suggests monolayer sorption on a homogeneous surface without interaction between sorbed molecules. In addition, the model assumes uniform energies of sorption onto the surface and no transmigration of the sorbate. This model can be written as follows [35].

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad (6)$$

where C_e is the equilibrium aqueous metal ions concentration (mg/L), q_e the amount of metal ions adsorbed per gram of adsorbent at equilibrium (mg/g), q_m and K_L are Langmuir constants related to the maximum adsorption capacity (mg/g) and the energy of adsorption (mg/L),

respectively. The plots of $1/C_e$ versus $1/q_e$ at different temperatures are found to be linear, indicating the applicability of the Langmuir model. The statistical significance of the correlation coefficient (R^2) for $1/C_e$ versus $1/q_e$ is the criteria by which the fitting of the data to Langmuir isotherm. It demonstrates monolayer coverage of adsorbate at the outer surface of the adsorbent. The parameters q_m and K_L have been calculated and the results are represented in Table 2. As seen from Table 2, Langmuir isotherm fits well with the experimental data.

On the other hand, Table 3 presents the comparison of adsorption capacity (q_m : mg/g) of chitosan-abrus precatorius blended beads for Cu(II), Cd(II), Pb(II) and Ni(II) ions with that of various biosorbents reported in literature [29, 36-50]. The adsorption capacity of chitosan-abrus precatorius blended beads for Cu(II), Cd(II), Pb(II) and Ni(II) is higher than that of the majority of other biosorbents mentioned. Therefore, it can be noteworthy that the chitosan-abrus precatorius blended beads have important potential for the removal of Cu(II), Cd(II), Pb(II) and Ni(II) ions from aqueous solution.

Table 3: Comparison of maximum adsorption capacity of Cu(II), Cd(II), Pb(II) and Ni(II) on different adsorbents in the literature

Biosorbent	Maximum adsorption capacity (mg/g)				References
	Cu(II)	Cd(II)	Pb(II)	Ni(II)	
Chitosan coated on perlite	196.07			114.94	[29]
Chitosan	16.8			2.4	[36]
Chitosan acetate crown ether (CCTS-1)	23.9			0.7	[37]
Chitosan diacetate crown either (CCTS-2)	31.3			4.1	[37]
Epichlorohydrine cross-linked chitosan (CCTS)	16.8			6.4	[37]
Chitosan-coated onto polyvinyl chloride (PVC) beads	87.9			120.5	[38]
Crab shell	19.83		38.62		[39]
Arcs shell	18.33		17.64		[39]
Chitosan-H ₂ SO ₄	225.73		346.18		[40]
Chitosan-alginate beads			60.27		[41]
Xanthated chitosan		357.1			[42]
Chitin		14			[43]
Chitosan		5.93			[44]
Porous-magnetic chitosan beads		188-518			[45]
Chitosan obtained from silkworm chrysalides (ChSC)	87.0				[46]
Carboxylgrafted chitosan	318.0				[47]
Aminated chitosan				30.2	[48]
EDTA-Chitosan				123.3	[49]
DTPA-Chitosan				117.4	[50]
Chitosan-abrus precatorius blended beads	97.1	108.6	161.3	196.1	Present Study

The equilibrium data are also fitted Freundlich [51] equation, which takes the form:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

where q_e is the amount of metal ion adsorbed per unit mass of adsorbent (mg/g) at equilibrium, C_e is the equilibrium concentration of heavy metal ion (mg/L); K_f and $1/n$ are Freundlich constant related to adsorption capacity and adsorption intensity, respectively. The plots of $\log C_e$ versus $\log q_e$ at different temperatures are found to be linear indicating the applicability of the Freundlich model. The Freundlich parameters are represented in Table 2.

Table 2: Parameters of Langmuir and Freundlich isotherms for adsorption of Cu(II), Cd(II), Pb(II) and Ni(II) onto Chitosan-abrus precatorius blended beads at different temperatures

Metal ions	Temp. K	Langmuir constants				Freundlich constants			
		q_m (mg/g)	K_L (L/mg)	R^2	χ^2	K_f (mg/g)	$1/n$	R^2	χ^2
Cu(II)	303	83.3	2.33	0.997	16.04	3.94	0.592	0.972	294.9
	313	88.5	2.61	0.997	18.03	4.88	0.625	0.971	390.8
	323	97.1	2.98	0.996	23.64	5.71	0.676	0.971	519.5
Cd(II)	303	93.5	2.61	0.996	13.95	4.21	0.609	0.972	429.8
	313	98.1	3.04	0.998	18.27	5.15	0.645	0.976	495.3
	323	108.6	3.55	0.997	26.39	6.11	0.694	0.979	616.1
Pb(II)	303	131.6	3.36	0.997	26.38	4.40	0.694	0.987	586.4
	313	144.9	3.85	0.998	39.36	5.24	0.763	0.996	785.1
	323	161.3	4.57	0.998	53.21	7.29	0.787	0.993	939.5
Ni(II)	303	169.5	3.95	0.999	50.58	3.91	0.775	0.996	743.1
	313	185.2	4.95	0.998	68.24	4.72	0.826	0.999	979.2
	323	196.1	5.77	0.997	80.28	6.64	0.855	0.998	1139.1

χ^2 analysis

To identify the suitable isotherm for biosorption of metal ions onto chitosan-abrus precatorius blended beads, the χ^2 analysis is carried out. The mathematical statement for χ^2 analysis is written as;

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \quad (8)$$

where $q_{e,m}$ is the equilibrium capacity obtained by calculating from the model (mg/g) and q_e is the experimental data on the equilibrium capacity (mg/g). The χ^2 values are presented in Table 2. If the data from the model are similar to the experimental data, χ^2 will be a small number, while if they differ; χ^2 will be a larger number. Therefore, it is necessary to analyze the data set using the non-linear Chi-square test to confirm the best-fit isotherm for the sorption process. The χ^2 values of both the isotherms are comparable and hence the adsorption of metal ions follows both Freundlich and Langmuir isotherms and relatively better fit is observed with Langmuir model as its χ^2 value is less than that of Freundlich model.

Thermodynamic parameters

Thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) can be estimated from equilibrium constants determined at different temperatures. The Gibbs free energy change of the sorption process is given by the following equation [52]:

$$\Delta G^\circ = -RT \ln K_L \quad (9)$$

$$\ln K_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (10)$$

where R is the universal gas constant (8.314 J/mol K), T is temperature (K) and K_L is the Langmuir constant. ΔH° and ΔS° are obtained from the slope and intercept of van't Hoff plot of $\ln K_L$ versus $1/T$ (Fig. 3). The values of ΔG° , ΔH° and ΔS° are given in Table 4.

Table 4: Values of thermodynamic parameters for the adsorption of Cu(II), Cd(II), Pb(II) and Ni(II) onto Chitosan-abrus precatorius blended beads

Metal ions	Temperature (K)	ΔG° (kJ/mol)	ΔS° (J/mol K)	ΔH° (kJ/mol)
Cu(II)	303	-2.128	40.6	10.3
	313	-2.485		
	323	-2.927		
Cd(II)	303	-2.496	50.1	12.7
	313	-2.894		
	323	-3.399		
Pb(II)	303	-3.053	51.2	12.8
	313	-3.508		
	323	-4.079		
Ni(II)	303	-3.459	63.4	15.6
	313	-4.161		
	323	-4.708		

The negative ΔG° values indicated thermodynamically feasible and spontaneous nature of the adsorption process. The decrease in ΔG° with increase in temperature shows a decrease in feasibility of adsorption at high temperatures. The positive value of ΔH° illuminated the endothermic nature of biosorption. The positive value of ΔS° suggested the increase randomness at the solid/solution interface during the biosorption of metal ions of chitosan-abrus precatorius blended beads.

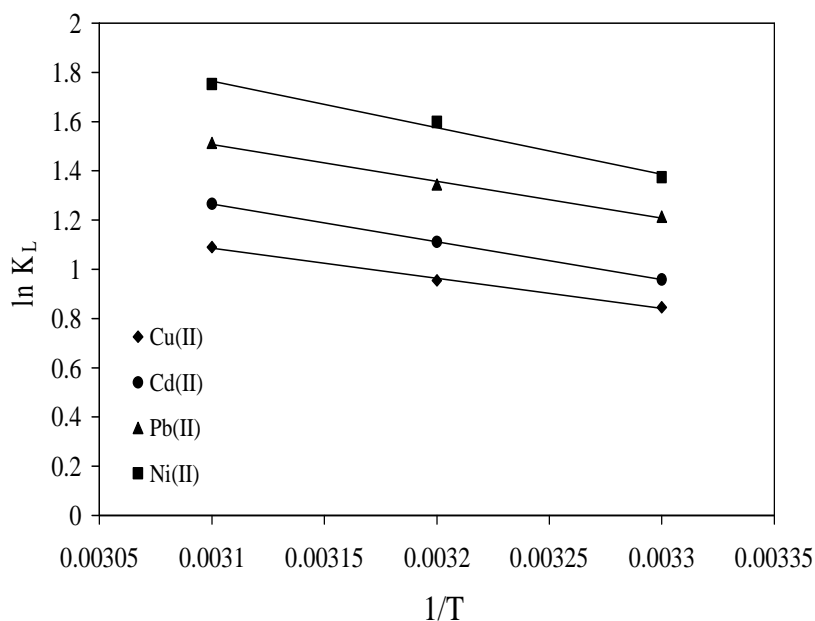


Fig. 3: Plot of $\ln K_L$ vs. $1/T$ for adsorption of Cu(II), Cd(II), Pb(II) and Ni(II) onto Chitosan-abrus precatorius blended beads

CONCLUSION

This study focused on the biosorption of Cu(II), Cd(II), Pb(II) and Ni(II) ions onto chitosan-abrus precatorius blended beads from aqueous solution. The operating parameters such as pH of solution, contact time, adsorbent dosage, initial metal ion concentration and temperature influence the uptake of Cu(II), Cd(II), Pb(II) and Ni(II) on to the sorbent. The kinetic data signified that the biosorption of Cu(II), Cd(II), Pb(II) and Ni(II) ions onto chitosan-abrus precatorius blended beads follow well the pseudo-second-order kinetic model. Biosorption equilibrium is better described by the Langmuir isotherm model than the Freundlich model. The biosorption capacity of chitosan-abrus precatorius blended beads follow the order; Ni(II)>Pb(II)>Cd(II)>Cu(II) at optimum conditions of pH 5.0, 4.0, 5.0 and 6.0, respectively. Further, the biosorbent is characterized by Fourier Transform Infrared Spectroscopy (FTIR), BET Surface area analysis. The calculated thermodynamic parameters indicated the feasibility, endothermic and spontaneous nature of the biosorption of Cu(II), Cd(II), Pb(II) and Ni(II) ions onto chitosan-abrus precatorius blended beads. Thus, it may be concluded that chitosan-abrus precatorius blended beads is a good adsorbent for Cu(II), Cd(II), Pb(II) and Ni(II) removal from aqueous solution.

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