Utilization of Fennel biomass (*Foeniculum vulgari*) a medicinal herb for the biosorption of Cd(II) from aqueous phase

Rifaqat Ali Khan Rao *, Moonis Ali Khan, Fouzia Rehman

Environmental Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh 202002, UP, India

ABSTRACT

This work presents the biosorption potential of Fennel biomass for the effective removal of Cd(II) ions. The biosorption was maximum (92%) at pH 4.3. Maximum biosorption capacities of Cd(II) at 30, 40 and 50 °C temperatures were 21, 24 and 30 mg/g, respectively. The biosorption of Cd(II) was concentration dependent and increases from 0.49 to 9.3 mg/g with increase in concentration from 5 to 100 mg/L. Biosorption follows Freundlich isotherm at 50 °C. Mean free energies at different temperatures were in between 7.1 and 11.95 kJ/mol indicating chemical nature of biosorption process. Kinetics studies showed that pseudo-second-order kinetics model was applicable to the data. The process was endothermic and spontaneous, the spontaneity of the process increases with increase in temperature. Regeneration studies showed a decrease in the recovery of Cd(II) from 99.8% to 41.7% in five consecutive cycles. 80% of the Cd(II) in single and multi-metal systems was recovered in 10 mL. Breakthrough and exhaustive capacities of Cd(II) in single metal system were 10 and 40 mg/g. For multi-metal systems in double distilled water the breakthrough and exhaustive capacities of Cd(II) were 2 and 12 mg/g. In saline solution the breakthrough and exhaustive capacities of Cd(II) were 0.8 and 4 mg/g.

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1. Introduction

"Biosorption" refers to a specific type of sorption based on the use of solid phase (sorbent) that is derived from various types of bio-materials or biomass. It could be considered for its economic edge as a possible alternative technique for metal removal/recovery. The performance of biosorbents is comparable to its closest commercially used competitors, namely the ion-exchange process. While commercially available ion-exchange resins are rather costly, the price tag of biosorbents can be one tenth of that of an ion-exchange resins. The cost effectiveness constitutes the main attraction of biosorption.

Today the greatest demand for the metal sequestration comes from the need for immobilizing the metals mobilized by and partially lost as a result of human technological activities. It has been established beyond any doubt that dissolved heavy metals escaping into the environment pose a serious health hazard. They accumulate in living tissues throughout the food chain with humans at the top.

The chronic toxicity of Cd(II) to the humans and the environment has been well documented. In U.S., maximum permissible limit of Cd(II) in drinking water has been set at 0.01 mg/L [1]. WHO's recommended maximum permissible limit of Cd(II) in drinking water as 0.005 mg/L [2]. The significant anthropogenic sources of Cd(II) in the environment are metalliferous mining, fertilizers, manures, sewage sludge, metallurgical industries, land fill leachate, batteries [3]. Long-term effects of Cd(II) poisoning includes kidney damage, and changes to the constitution of the bones, liver and blood. Short term effects includes nausea, vomiting, diarrhea, cramps [4].

The objective of this work is to explore the biosorption efficiency of Fennel seeds for the removal and recovery of Cd(II) by batch and column process. Fennel plant (*Foeniculum vulgari*) belongs to Apiaceae (Umbelliferae) family. Fennel is a perennial herb, meaning that it grows year round. It is erect, glaucous green, and grows to heights of up to 2.5 m, with hollow stems. The fruit is a dry seed from 4 to 10 mm long, half as wide or less, and grooved [5]. These plants are abundantly grown in India because of their use in traditional Indian medicine and spices. Fennel contains anethole, which act as phytoestrogens [6]. Fennel water is an important constituent of the domestic 'Gripe Water,' used to correct the flatulence of infants. It can be made into syrup to treat babies with colic or painful teething. Fennel seeds or tea can relax the intestines and reduce bloating caused by digestive disorders. Fennel is also largely used for cattle condiments. It is one of the plants which is said to be disliked by fleas, and powdered Fennel has the effect of driving away fleas from kennels and stables. In the Indian subcontinent,

Fennel seeds are also eaten raw, sometimes with some sweetener, to improve eyesight. Fennel is also used as flavoring in some natural toothpaste. Some people employ it as a diuretic. A tea made from Fennel seeds can be used as an eye tonic, applied directly like eye drops or as a compress, to reduce soreness and inflammation of the eye. Others use it to improve the milk supply of lactating mothers [7].

2. Experimental procedure

2.1. Preparation of biosorbent

Waste seeds of Fennel (*Foeniculum vulgaris*) biomass were collected from local Unani medicine manufacturing unit at Aligarh. The biomass was washed several times with double distilled water (DDW) to remove dirt and dust. The washed biomass was dried in an oven at 60–70 °C. The dried biomass was then crushed and sieved to 300–100 μm particle size. Sieved biomass was stored in an airtight container in order to avoid moisture and used as such for the biosorption studies.

2.2. Preparation of sorbate solution

Single metal aqueous stock solutions of Cd(II), Ni(II), Zn(II) and Cu(II) were prepared (1000 mg/L) by dissolving the desired amount of their nitrate or chloride (AR grade) salts.

2.3. Characterization of biosorbent

Scanning electron microscopy (SEM) analysis technique was employed to observe the surface physical morphology of the biosorbent with 3500× magnification. The type of binding groups present on the biosorbent were identified by Fourier transform infrared spectroscopy (FTIR) analysis using Perkin Elmer 1600 infrared spectrometer with pellets of powdered KBr and biomass.

2.4. Determination of active sites

Active sites present on the surface of the biosorbent were determined by acid–base titration method [8] at room temperature (30 °C) in a shaker and was left for 5 days. Afterwards, a sample of 10 mL was titrated with 0.1 M HCl solution to its neutralization point. The titration was done in triplicate.

2.5. Biosorption studies

Batch experiments were carried out at different temperatures (30, 40, and 50 °C). 25 mL of metal solution of initial concentration (C_0) (5–500 mg/L) were shaken in water bath shaker at a constant agitation speed (120 rpm) with 0.25 g of the biosorbent dose for an specified period of contact time (0.5–480 min), varying initial pH of the solutions (2–9.3). The pH of the solutions was adjusted to the required value by adding either 0.1 M HCl or 0.1 M NaOH solution. After attaining equilibrium, the sorbate was filtered by using Whatman filter paper no. 41. Final concentration (C_e) in the filtrate was determined by atomic absorption spectrophotometer (AAS) (GBC 902). %Biosorption and biosorption capacity were calculated using the following relationships:

$$\%\text{Biosorption} = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

$$\text{Biosorption capacity}\,(q_e)\,(\text{mg/g}) = [(C_0 - C_e)] \times \frac{V}{W} \tag{2}$$

where C_0 is the initial concentration of sorbate (mg/L), C_e is equilibrium sorbate concentration (mg/L), V is the volume of the solution (L) and W is the mass of the biosorbent (g).

2.6. Desorption studies

Desorption studies were carried out for single and multi-metal system in a continuous flow column (0.6 cm internal diameter) with a glass wool support. 50 mL of 50 mg/L Cd(II) solution was passed through the column containing 0.25 g biosorbent. The effluent was collected at a flow rate of 1 mL/min. In multi-metal system 50 mL mixture of Cd(II), Ni(II), Cr(VI), Zn(II), Cu(II) containing 10 mg/L of each metal was passed through the column at a flow rate of 1 mL/min. The column was washed several times with DDW (pH 6.5) in order to remove traces of metal ions remained unsorbed. 0.1 M HCl solution was then passed through the column as an eluent. The effluent was collected in 10 mL fractions in each case with a flow rate 1 mL/min and the metal ions desorbed were determined in each fraction.

2.7. Breakthrough studies

Breakthrough studies were carried out both in single and multi-metal systems containing Cd(II), Ni(II), Cr(VI), Zn(II), Cu(II). 0.25 g of biosorbent was taken in glass column (0.6 cm internal diameter) with glass wool support. 1000 mL single metal solution of each metal and multi-metal solutions and solutions prepared in 0.1 M NaCl were passed through the column at 1 mL/min. flow rate. The initial metal ions concentration (C_0) in single metal system was 50 mg/L and in multi-metal system was 10 mg/L. First 50 mL of the effluent was collected in 10 mL fractions, thereafter the effluent was collected in 50 mL fractions in each case. The amount of metal ions (C) in single and multi-metal systems were determined by AAS. The breakthrough curves were obtained by plotting C/C_0 versus volume of the effluent.

2.8. Regeneration studies

The regeneration of biosorbent is directly related to the application potential of biosorption technology. Column process was employed for the regeneration of the biosorbent. 25 mL of the Cd(II) solution with initial concentration 50 mg/L was passed through the column containing 0.25 g of biosorbent on glass wool support at 1 mL/min flow rate. The column was washed several times with DDW to remove unsorbed traces of Cd(II) ions. To regenerate the column 25 mL of 0.1 M HCl solution was passed through the column as an eluent at 1 mL/min flow rate. The column was washed with DDW until the column was neutralized. The same procedure was repeated for five cycles or five times.

3. Results and discussion

3.1. Characterization of biosorbent

3.1.1. Scanning electron microscope (SEM) analysis

A scanning electron microscope (SEM) was used to examine the surface of the biosorbent before and after biosorption of Cd(II) ions. The surface of the biosorbent appears to be irregular and porous (figures not shown). The pores are prominent on the surface of biosorbent before biosorption. After biosorption of Cd(II) the pores are filled showing adherence of sorbate ions on the surface.

3.1.2. FTIR analysis

FTIR spectra of Fennel before and after Cd(II) biosorption are shown in Fig. 1a and b, respectively. Spectra show the presence of ionizable functional groups (carboxylic, phenolic and
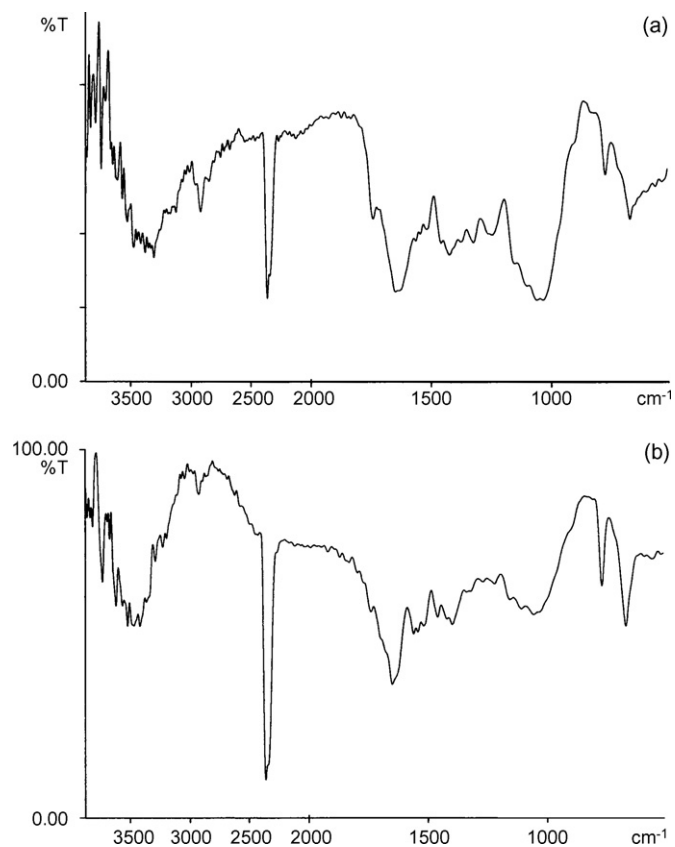
Fig. 1. (a) FTIR spectrum of Fennel before Cd(II) biosorption. (b) FTIR spectrum of Fennel after Cd(II) biosorption.

Fig. 2. Effect of pH on the biosorption of Cd(II) on Fennel.

hydroxyl) able to interact with metal ions. These spectra show prominent peaks at 2918–2925 cm^{-1} (phenolic and carboxylic groups), 2362–2361 cm^{-1} (NH$_2$ group), 1649–1650 cm^{-1} (due to C=O group), 1322–1459 cm^{-1} (COO group), and 1058–1056 cm^{-1} (C–O stretch due to CH$_2$–OH of primary alcohols) [9]. There is a sharp decrease in the biosorption at 1058, 2918–2925 and 1322–1422 cm^{-1} after Cd(II) biosorption indicating that Cd(II) binding occurs at carboxylic and phenolic functional groups.

3.2. Determination of active sites

The total number of acidic sites matching carboxylic, phenolic, and lactonic sites were neutralized using alkaline solutions (0.1 M NaOH, 0.1 M NaHCO$_3$, 0.1 M Na$_2$CO$_3$). The carboxylic and lactonic sites were titrated with 0.1 M Na$_2$CO$_3$ solution, the carboxylic sites were determined with 0.1 M NaHCO$_3$ solution and the phenolic sites were estimated by the difference [8] (Table 1).

3.3. Effect of pH on biosorption

The %biosorption of Cd(II) increases with increase in initial pH of the solution. The maximum sorption occurs at pH 4.3 (Fig. 2). It is usual that acidic solution inhibits metal uptake because of high concentration of H$^+$ ions competing with metal ions due to the

protonation of various functional groups (carboxylic and phenolic groups) present on the surface of the biosorbent. At pH greater than 3 carboxylic groups were ionized or deprotonated [10] thus attraction of positively charged Cd(II) ions were enhanced. Free carboxylic groups were protonated below pH 3 hence reduces the metal uptake. Fig. 2 shows how initial pH is changed after attaining equilibrium. When initial pH is adjusted to 2 the final pH or equilibrium pH remains the same showing that functional groups on the biosorbent surface are protonated hence biosorption of Cd(II) is negligible. However, when initial pH is adjusted to 3 the final pH increases sharply to 4.8 and at the same time biosorption increases to 60% indicating that fairly large amount of Cd(II) ions are sorbed along with H$^+$ ions that is responsible for the increase in final or equilibrium pH. This process continues up to pH 4.3 and above that %biosorption becomes constant (90%). The initial pH changes from 4.3 to 7. When initial pH is adjusted to 7 and above, the final pH is decreased showing that some more functional groups are deprotonated releasing H$^+$ ions in the solution.

3.4. Effect of concentration and biosorption isotherms

Biosorption of Cd(II) on Fennel can be successfully represented by a good description of the equilibrium separation of Cd(II) between two phases. Fig. 3 presents the amount of Cd(II) sorbed at 30, 40 and 50 °C plotted against the concentration of Cd(II) at equilibrium. Increase in concentration of Cd(II) from 5 to 500 mg/L at different temperatures showed an increase in the biosorption capacity. The maximum biosorption capacity of Cd(II) at 30, 40 and 50 °C was 21, 24 and 30 mg/g, respectively (Fig. 3). The increase in the biosorption capacity of Cd(II) with increase in temperature indicates the process is endothermic in nature [11]. The adsorption capacity (q_m) of Fennel towards Cd(II) is comparable with other biosorbents used earlier. The maximum biosoption capacities of various biosorbents are listed in Table 2.

Table 1
Concentration of active sites on Fennel surface.

Acidic sites	Concentration (meq./g)
Carboxylic	0.027
Phenolic	0.113
Carboxylic + lactonic	0.140

Table 2
Biosorption capacities of various biosorbents for the biosorption Cd(II).

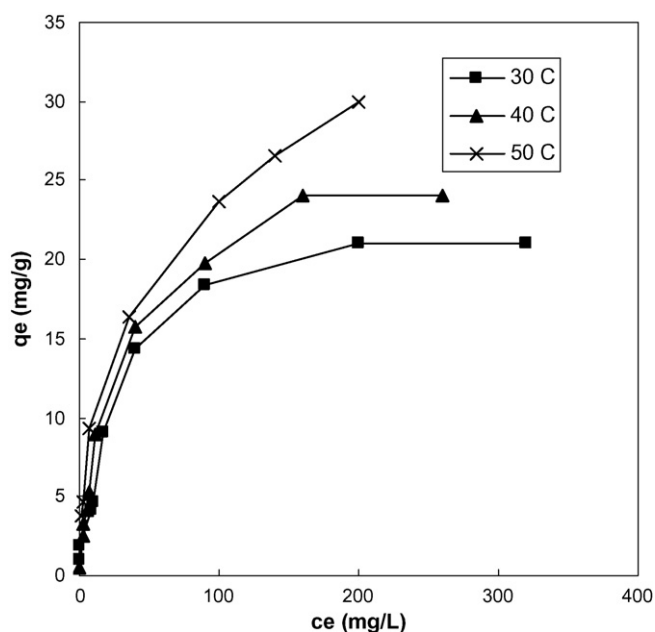| Biosorbent	Biosorption capacity (mg/g)	Reference
Date pits	6.50	[21]
Untreated Juniper fiber	9.18	[22]
Black gram husk	39.99	[23]
Parthenium hysterophorous	27.00	[2]
Neem Oil Cake	11.82	[12]
Fennel	26.59	Present study

Fig. 3. Effect of concentration of Cd(II) on the biosorption capacity of Fennel at different temperature.

The equilibrium data at 30, 40 and 50 °C was modeled with Langmuir, Freundlich and D–R isotherms.

3.4.1. Langmuir isotherm

The linear form of Langmuir isotherm is expressed as [12]

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e} \tag{3}$$

where q_e is the amount of Cd(II) sorbed per unit weight of biosorbent (mg/g), C_e is the equilibrium concentration of Cd(II) in solution (mg/L), q_m is the maximum biosorption capacity determined by the number of reactive sites in an ideal monolayer system (mg/g) and b is related to the binding energy with a pH dependent equilibrium constant (L/mg). A plot of $1/q_e$ versus $1/C_e$ (figure not shown) yields a straight line. The values of b and q_m calculated from the slope and intercept are reported in Table 3.

The non-linear form of Langmuir plots at different temperatures indicates that for the temperature range 30–50 °C the minimum deviation is at lower initial concentrations. However, deviation from experimental q_e values with calculated q_e becomes more prominent when experiments were carried out at higher initial concentrations of Cd(II).

Table 3
Parameters of the biosorption isotherms obtained at different temperature.

Isotherms	Parameters	Temperature (°C)		
		30	40	50
Langmuir	b (L/mg)	0.34	0.11	0.08
	q_m (mg/g)	10.16	13.92	26.59
	r^2	0.9624	0.9971	0.9878
Freundlich	n	1.98	2.18	2.29
	K_f (mg/g)(L/mg)$^{1/n}$	1.84	2.14	3.16
	r^2	0.9641	0.9347	0.9807
D–R	q_m ($\times 10^{-3}$ mol/g)	1.39	0.85	0.76
	E_a (kJ/mol)	7.1	10.54	11.95
	r^2	0.9503	0.9845	0.9899

3.4.2. Freundlich isotherm

In principle, the Freundlich equation is an empirical approach for biosorbent with very uneven adsorbing surface, and is applicable to the biosorption of single solutes within a fixed range of concentration [13]. A linear form of the Freundlich isotherm is given by expression

$$\log q_e = \log K_f + \frac{1}{n} \times \log C_e \tag{4}$$

A plot of $\log q_e$ versus $\log C_e$ (figure not shown) enables the constant K_f and exponent n to be determined. K_f can be defined as biosorption of distribution coefficient and represents the quantity of Cd(II) sorbed onto biosorbent for an equilibrium concentration. The value of n is not only a measure of the deviation from linearity, but informs about the heterogeneity degree of the biosorption sites. The values of $n > 1$ for the biosorption of Cd(II) on Fennel showing favorable biosorption at different temperatures (Table 3).

The non-linear form of Freundlich isotherms at different temperatures (figure not shown) indicate least deviation from q_e experimental with q_e calculated at 50 °C. This is also evident from the correlation coefficient value ($r^2 = 0.9807$) obtained at 50 °C (Table 3). The biosorption capacity increases with increase in temperature and maximum value (K_f) is obtained at 50 °C (3.16 (mg/g)(L/mg)$^{1/n}$) with sufficiently high affinity (n) of 2.29 that represents favorable biosorption.

3.4.3. Dubinin–Radushkevich isotherm

Dubinin–Radushkevich isotherm equation has been used to determine the mean free energy of biosorption. The D–R equation assume heterogenous surface. The linear presentation of the equation is given as [14].

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{5}$$

and

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \tag{6}$$

where q_e is the biosorption capacity (mol/g), β is activity coefficient constant (mol^2/J^2) related to biosorption energy, q_m is the maximum biosorption capacity (mol/g) to form monolayer, ε is Polyanyi potential, T is absolute temperature (K), R is gas constant (J/mol K), C_e is the equilibrium concentration (mol/L). The values of q_m and β can be obtained from the intercept and slope of the $\ln q_e$ versus ε^2 plot (figure not shown). The mean free energy E_a can be calculated from the following relation [14].

$$E_a = \frac{1}{\sqrt{(-2\beta)}} \tag{7}$$

The D–R parameters and mean free energy values are given in Table 3. The magnitude of E_a indicates the type of biosorption reaction. E_a values obtained are in between 7.1 and 11.95 kJ/mol showing that biosorption process is chemical in nature [15].

3.5. Effect of contact time and biosorption kinetics

Biosorption of Cd(II) onto Fennel at various initial concentrations was carried at different time intervals (0.5–240 min). The equilibrium uptake (q_e) for Cd(II) was found to be 0.49, 2.46, 4.9 and 9.3 mg/g at 5, 25, 50 and 100 mg/L initial Cd(II) concentrations (Fig. 4), respectively. When the initial concentration of Cd(II) increased, the rate of biosorption decreased, but the amount of biosorption increased. The biosorption of Cd(II) was concentration dependant and it could be seen that the amount of biosorption enhanced with the increase of initial concentration. In the first stage, the rate of biosorption was rapid and then attains an equilibrium value. The equilibrium was achieved easily when the initial
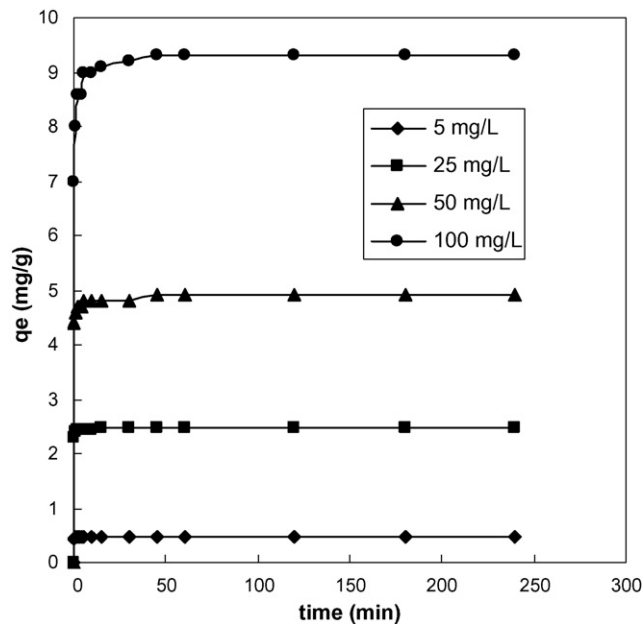
Fig. 4. Effect of contact time on the biosorption of Cd(II) at different concentration on Fennel.

Fig. 5. Pseudo-second-order kinetics for the biosorption of Cd(II) at different concentrations.

concentration waslow, because at the first stage the ratio of available surface of biosorbent was large for the biosorption of Cd(II) and as the contact time increases it gradually decreases until it attains equilibrium [16].

In order to analyze the biosorption kinetics of Cd(II) onto the Fennel, the pseudo-first-order and pseudo-second-order kinetics model were tested using experimental data and rate constants were calculated at different concentrations. Pseudo-first-order kinetics equation as expressed by Lagergren [12] can be written as

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} \times t \tag{8}$$

where q_e and q_t are the amount of metal sorbed (mg/g) at equilibrium and at time t, respectively and K_1 is the pseudo-first-order equilibrium rate constant (1/min). A plot of $\log(q_e - q_t)$ versus t gives straight line and rate constant K_1 can be calculated from the slope (figure not shown).

Pseudo-second-order kinetics equation may be expressed as [12]

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \times t \tag{9}$$

where K_2 is the pseudo-second-order biosorption rate constant (g/mg min). A plot of t/q_t versus t gives straight line (at different concentrations) (Fig. 5). The values of K_2 can be calculated from the intercept of the plot.

The data show that the correlation coefficient values (r^2) for pseudo-first-order kinetics are very low in comparison to pseudo-second-order kinetics (Table 4). The values of theoretical biosorption capacity $q_{e(\text{theo})}$ are very near to experimental values $q_{e(\text{exp})}$ for second-order kinetics but for first-order kinetics equa-
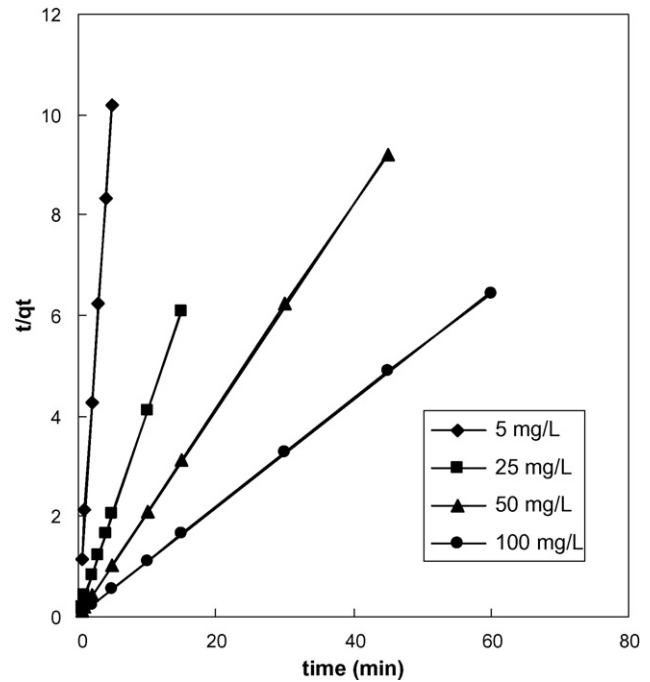
tion these values are very different. Higher correlation coefficient (r^2) values and similar $q_{e(\text{cal})}$ and $q_{e(\text{exp})}$ values indicate the better applicability of pseudo-second-order kinetics model.

For batch process the temporal approach to equilibrium can be illustrated by a plot of the fractional uptake F against time t (figure not shown), where $F = q_t/q_e$. The time needed to reach equilibrium increases with increasing the initial Cd(II) concentration. It also shows that the fractional uptake F decreases with increasing the initial Cd(II) concentration, although this tendency is not so obvious within the high concentration range at short biosorption times. These observations are corroborated by examining the values of K_1 in Table 4, where the values of the rate constant K_1 decrease with increasing the initial concentration of Cd(II) from 5 to 100 mg/L. A larger K_1 value implies that it will take a shorter time for the biosorption system to reach the same fractional uptake. Therefore, the trend that K_1 decreases with increasing initial concentration in the range 5–100 mg/L means that it is faster for biosorption system with a lower initial concentration to reach a specific fractional uptake [17].

Boyd [18] and Webber [19] models are widely used for predicting the nature of biosorption. Boyd's model determines whether the main resistance to mass transfer is in the thin film (boundary layer) surrounding the biosorbent particle, or the resistance to diffusion inside the pores. This model is expressed as

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 Bt) \tag{10}$$

where B is diffusivity constant.

Table 4
Kinetics parameters for the biosorption of Cd(II) at different concentrations on Fennel.

Conc. (mg/L)	$q_{e(\text{exp})}$ (mg/g)	Pseudo-first-order kinetics			Pseudo-second-order kinetics			
		$q_{e(\text{theo})}$ (mg/g)	K_1 (1/min)	r^2	$q_{e(\text{theo})}$ (mg/g)	K_2 (g/mg min)	h	r^2
5	0.49	0.057	0.490	0.9204	0.49	28.7	6.89	0.9997
25	2.46	0.071	0.248	0.9336	2.46	10.2	61.72	1
50	4.9	0.290	0.107	0.9213	4.9	1.54	37.02	0.9999
100	9.3	0.901	0.081	0.9043	9.3	0.476	41.15	1

Table 5
Thermodynamic parameters for the biosorption of Cd(II) on Fennel.

Temperature (°C)	K_c	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)
30	7.33	−5.017	10.34	0.051
40	8.25	−5.470		
50	9.41	−6.016		

From Eq. (10), it is not possible to calculate the values of Bt for each fraction adsorbed. By applying the Fourier transform and then integration, Reichenberg [20] obtained the following approximation

$$\text{For } F > 0.85, \quad Bt = -0.4977 - \ln(1 - F) \tag{11}$$

and

$$\text{for } F < 0.85, \quad Bt = \left(\sqrt{\pi} - \sqrt{(\pi - (\pi^2 F/3))}\right)^2 \tag{12}$$

The values of F obtained were $F > 0.85$. This shows that Eq. (11) is applicable in this case.

If the plot Bt versus time is linear and passes through the origin then pore-diffusion controls the rate of mass transfer. If the plot is non-linear or linear but does not pass through the origin, then it is concluded that film-diffusion or chemical reaction controls the adsorption rate. The plot of Bt versus time for the biosorption of Cd(II) on Fennel at different concentrations shows that the line does not pass through the origin. Initially the plot is linear but with time the plot becomes non-linear (figure not shown). These observations suggest that film-diffusion or chemical reaction controls the rate of adsorption during this period.

3.6. Thermodynamics of biosorption

The temperatures used in this study were 30, 40 and 50 °C. The equilibrium constant at different temperatures can be calculated with the following relations

$$K_c = \frac{C_{Ae}}{C_e} \tag{13}$$

where K_c is the equilibrium constant. C_{Ae} (mg/L) is the amount adsorbed on solid at equilibrium and C_e (mg/L) is the equilibrium concentration of Cd(II) in the solution, respectively. The values of free energy change (ΔG°) at different temperatures were calculated from the following relation

$$\Delta G^\circ = -RT \ln K_c \tag{14}$$
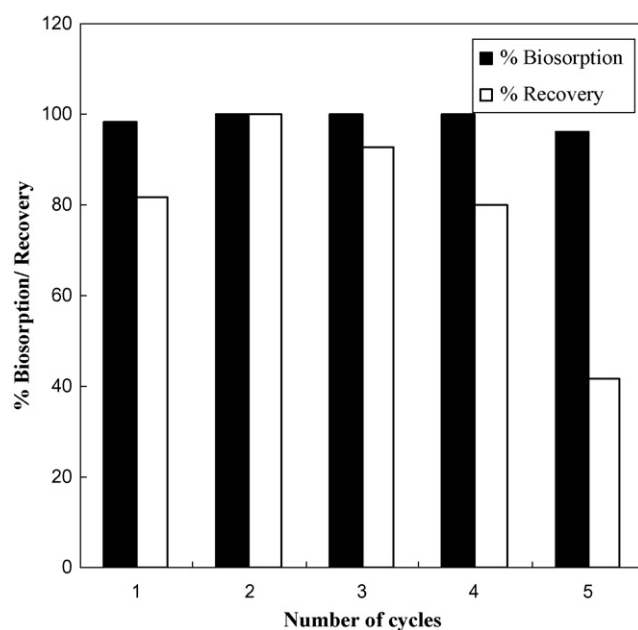
where R is gas constant and T is absolute temperature.

Van't Hoff equation was applied to calculate the enthalpy change (ΔH°) and entropy change (ΔS°).

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \times \frac{1}{T} \tag{15}$$

ΔS° and ΔH° can be calculated from the intercept and slope of the linear plot of $\ln K_c$ versus $1/T$ (figure not shown). The values are reported in Table 5. Positive value of ΔH° indicates endothermic nature of the biosorption process. ΔG° is negative and decreases with increase in temperature showing that biosorption of Cd(II) is

Fig. 6. Column studies to regenerate the sorbent column by using 0.1 M HCl as an eluent.

spontaneous and spontaneity increases with increase in temperature. Positive value of ΔS° indicates increased randomness at the solid/solute interface.

3.7. Regeneration studies

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. 0.1 M HCl was used in this study as a regenerating agent (or eluent). The results show slight increase in the biosorption of Cd(II) from 98.2% to 99.8% in the second cycle (Fig. 6). This increase in the biosorption may be due to the activation of some more surface active sites present on the biosorbent surface when it comes in contact with 0.1 M HCl during elution. The recovery of Cd(II) decreased to 41.7% from 99.8% in five consecutive cycles (Fig. 6). These results show promising regeneration potential of the Fennel. This property of Fennel may be utilized by small scale commercial units to remove Cd(II) from their discharging effluents in an economical and efficient way.

3.8. Desorption studies

Column process was used to check the practical utility of the biosorbent for the recovery of Cd(II) ions in single and multi-metal systems. The biosorption of Cd(II) with 50 mg/L initial concentration in single metal system was 97% (Table 6). 87.8% of Cd(II) was eluted by using 0.1 M HCl. In multi-metal system containing 10 mg/L each of Cd(II), Ni(II), Zn(II), Cu(II), the sorption of Cd(II) was 96% (Table 6). Recovery of Cd(II) by 0.1 M HCl in multi-metal
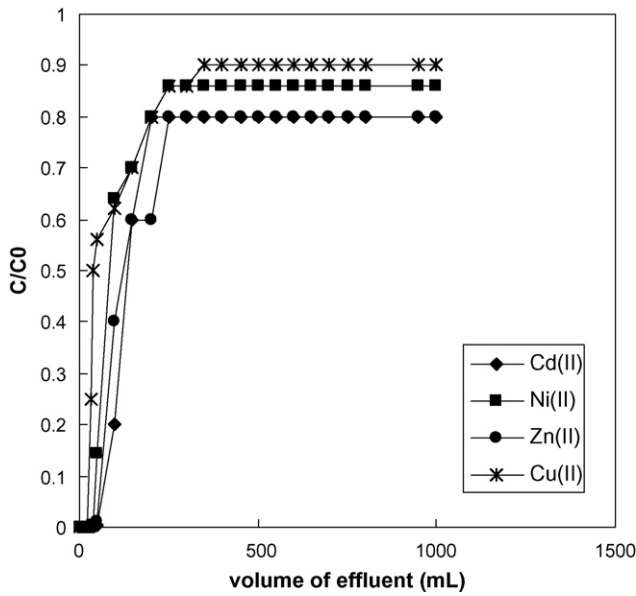
Table 6
Biosorption and desorption of Cd(II) in single and multi-metal systems on Fennel by column process.

Metal solutions	Metals	Amount loaded (mg)	Amount sorbed (mg)	%Biosorption	Amount recovered (mg)	%Recovery
Single metal system	Cd(II)	2.5	2.425	97	2.130	87.8
Multi-metal system	Cu(II)	0.5	0.39	78	0.305	78.2
	Cd(II)	0.5	0.48	96	0.48	100
	Ni(II)	0.5	0.3	60	0.265	88.3
	Zn(II)	0.5	0.38	76	0.053	14.1

Fig. 7. Breakthrough capacity curve for the biosorption of metal ions in single metal system on Fennel.
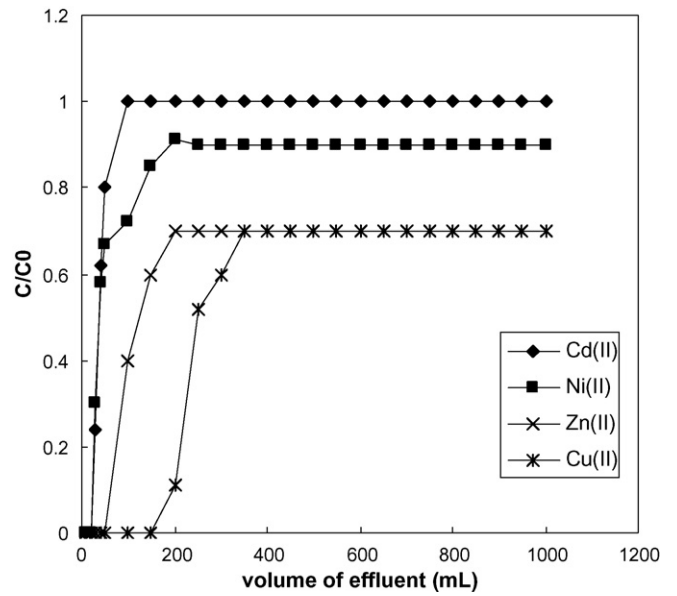

Fig. 8. Breakthrough capacity curve for the biosorption of ions in multi-metal system in 0.1 M NaCl solution on Fennel.

system was 100%. It was observed that 80% of the metal in single and multi-metal systems was recovered in 10 mL. This property of the biosorbent can be utilized for preconcentration.

3.9. Breakthrough studies

Breakthrough curves of a single metal system indicates that 50 mL of Cd(II) and Zn(II), 40 mL of Ni(II), 20 mL of Cu(II) solution containing 50 mg/L of metal ions could be passed through the column without detecting traces of any metal ions in the effluent (Fig. 7). To check the hindrance caused on the biosorption of Cd(II) by other metal ions present in the influent, multi-metal solutions containing 10 mg/L each of Cd(II), Ni(II), Zn(II) and Cu(II) were prepared in DDW and to check the effect of salinity on the biosorption, 0.1 M NaCl solution was used as solvent. Result shows that 50 mL of the influent containing metal ions could be passed through the column without detecting traces of metal ions in the effluent (Figs. 8 and 9). The breakthrough capacities of metals in single and multi-metal system are reported in Table 7. The breakthrough capacities of Cd(II) in single and multi-metal system in DDW and 0.1 M NaCl were 10, 2 and 0.8 mg/g, respectively (Table 7). The decrease in the breakthrough capacities of these metals in presence of Na$^+$ ions indicate that ion-exchange mechanism is involved during biosorption.
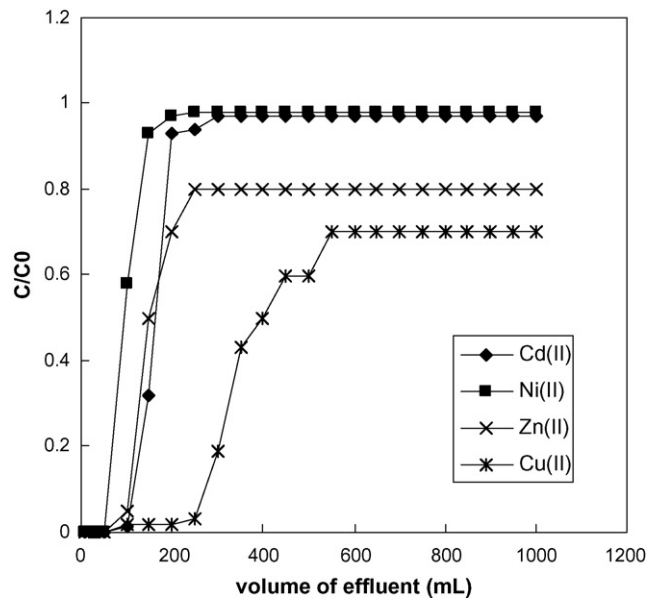

Fig. 9. Breakthrough capacity curve for the biosorption of ions in multi-metal system in DDW solution on Fennel.

Table 7
Breakthrough capacity and exhaustive capacity of metal ions on Fennel in single and multi-metal systems.

Metal solutions	Metal ions	Initial conc. (mg/L)	Breakthrough capacity (mg/g)	Exhaustive capacity (mg/g)
Single metal system	Cd(II)	50	10	40
	Ni(II)	50	8	50
	Zn(II)	50	10	50
	Cu(II)	50	4	70
Multi-metal system in DDW	Cd(II)	10	2	12
	Ni(II)	10	2	10
	Zn(II)	10	2	10
	Cu(II)	10	2	22
Multi-metal system in 0.1 M NaCl	Cd(II)	10	0.8	4
	Ni(II)	10	0.8	10
	Zn(II)	10	2	8
	Cu(II)	10	6	14

4. Conclusions

Fennel is a perennial herb available in abundance in India. It is used in traditional Indian medicines. The discarded biomass obtained after extraction of juice can be utilized satisfactorily for sequestering Cd(II) ions from wastewater. Regeneration studies showed that Fennel can be effectively utilized for the removal of Cd(II) ions upto five cycles. Breakthrough studies showed that in single and multi-metal system with Cd(II) concentrations of 50 and 10 mg/L, respectively, 50 mL of the effluent could be passed through the column without detecting traces of Cd(II) ions. But in case of multi-metal solution in saline medium with 10 mg/L Cd(II) concentration only 20 mL of the effluent becomes free from Cd(II).

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