CHAPTER-2

Utilization of Fennel biomass (Foeniculum vulgari) a Medicinal herb for the Biosorption of Cd(II) from Aqueous phase
2.1. Introduction

“Biosorption” refers to a specific type of sorption based on the use of solid phase (sorbent) that is derived from various types of biomaterials 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 exchangers. 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 has 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 4–10 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].
2.2. Experimental procedure

2.2.1. Preparation of biosorbent

Waste seeds of Fennel (*Foeniculum vulgare*) 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 100-300 µm particle size. Sieved biomass was stored in an airtight container in order to avoid moisture and used as such for the biosorption studies.

2.2.2. 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. While aqueous stock solution of Cr(VI) was prepared by dissolving desired quantity of K₂Cr₂O₇.

2.2.3. Characterization of biosorbent

Scanning electron microscopy (SEM) analysis technique was employed to observe the surface physical morphology of the biosorbent with 3500x 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.

2.2.4. Determination of active sites

Active sites present on the surface of the biosorbent were determined by acid-base titration method [8]. The flask was slowly agitated and partially immersed in a
constant temperature water bath set at 30\(^0\)C and it was left there for 5 days. Afterwards, a sample of 10 mL was titrated with 0.1N HCl. The titration was done in triplicate by using pH meter (ELICO LI 120).

### 2.2.5. Biosorption studies

Batch experiments were carried out at different temperatures (30\(^0\), 40\(^0\), and 50\(^0\)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 0.25g 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 0.1N HCl or 0.1N NaOH solution. After attaining equilibrium, the sorbate was filtered by using Whatman filter paper no. 41. Final concentration (C\(_e\)) of metal in the filtrate was determined by atomic absorption spectrophotometer (AAS) (GBC 902). % Biosorption and biosorption capacity were calculated using the following relationships.

\[
\% \text{ Biosorption} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]

\[
\text{Biosorption capacity (q}e\text{)} (\text{mg/g}) = \left( \frac{[C_0 - C_e]}{V/W} \right)
\]

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).

### 2.2.6. 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 0.25g biosorbent. The effluent was collected at a flow rate of 1mL/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 1mL/min. The column was washed several times with DDW (pH 6.5) in order to remove traces of metal ions remained unsorbed. 0.1N 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.

2.2.7. 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). 0.25g 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 0.1N NaCl were passed through the column at 1mL/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 concentration of metal ions in the effluent ($C$) in single and multi-metal systems was determined by AAS. The breakthrough curves were obtained by plotting $C/C_0$ versus volume of the effluent.

2.2.8. 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 0.1N 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.
2.3. Results and discussion

2.3.1. Characterization of biosorbent

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.

FTIR Analysis:

FTIR spectra of Fennel before and after Cd(II) biosorption are shown in Fig. 2.1a and b respectively. Spectra show the presence of ionizable functional groups (carboxylic, phenolic and 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 peak intensity 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.

2.3.2. Determination of active sites

The total numbers of acidic sites matching carboxylic, phenolic, and lactonic sites were neutralized using alkaline solutions (0.1N NaOH, 0.1N NaHCO\(_3\), and 0.1N Na\(_2\)CO\(_3\)). The carboxylic and lactonic sites were titrated with 0.1N Na\(_2\)CO\(_3\) solution,
the carboxylic sites were determined with 0.1N NaHCO$_3$ solution and the phenolic sites were estimated by the difference [8] (Table 2.1).

2.3.3. 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. 2.2). 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 was enhanced. Free carboxylic groups were protonated below pH 3 hence reduces the metal uptake. Fig. 2.2 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.

2.3.4. 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. 2.3
presents the amount of Cd(II) sorbed at 30\(^0\), 40\(^0\) and 50\(^0\)C plotted against the concentration of Cd(II) at equilibrium \(C_e\). 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\(^0\), 40\(^0\) and 50\(^0\)C was 21, 24 and 30 mg/g respectively (Fig. 2.3). The increase in the biosorption capacity of Cd(II) with increase in temperature indicates the process is endothermic in nature [11]. The biosorption capacity \(q_m\) of Fennel towards Cd(II) is comparable with other biosorbents used earlier. The maximum biosorption capacities of various biosorbents are listed in Table 2.2.

The equilibrium data at 30\(^0\), 40\(^0\) and 50\(^0\)C were modeled with Langmuir, Freundlich and D-R isotherms.

**Langmuir isotherm**

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

\[
\frac{1}{q_e} = \left(\frac{1}{b}\right) \times \left(\frac{1}{q_m}\right) \times \left(\frac{1}{C_e}\right) + \left(\frac{1}{q_m}\right) \tag{3}
\]

where \(q_e\) is the amount of Cd(II) sorbed per unit weight of sorbent (mg/g), \(C_e\) is the equilibrium concentration of Cd(II) in solution (mg/L), \(q_m\) is the maximum sorption 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 \(1/C_e\) (Fig. 2.4) yields a straight line. The values of \(b\) and \(q_m\) calculated from the slope and intercept are reported in Table 2.3.

The non-linear Langmuir plots at different temperatures indicate that for the temperature range 30-50\(^0\)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).

**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 solute 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 \( \log C_e \) (Fig. 2.5) 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 2.3).

The non-linear Freundlich isotherms at different temperatures indicate least deviation from \( q_e \) experimental (\( q_{e(\text{exp})} \)) with \( q_e \) calculated (\( q_{e(\text{cal})} \)) at 50\(^0\)C. This is also evident from the correlation coefficient value (\( R^2 = 0.9807 \)) obtained at 50\(^0\)C (Table 2.3). The maximum value (\( K_f \)) is obtained at 50\(^0\)C (3.16 (mg/g) (L/mg) \(^{1/n}\)) with sufficiently high affinity (\( n \)) of 2.29 that represents favorable biosorption.
Dubinin–Radushkevich isotherm

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

\[
\ln q_e = \ln q_m - \beta \Box^2 \quad \quad \quad \quad \quad (5)
\]

and

\[
\Box = RT \ln (1 + 1/C_e) \quad \quad \quad \quad \quad (6)
\]

Where \( q_e \) is the biosorption capacity (mol/g), \( \beta \) is activity coefficient constant (mol²/kJ²) related to biosorption energy, \( q_m \) is the maximum biosorption capacity (mol/g) to form monolayer, \( \Box \) is Polanyi 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 \( \beta \) can be obtained from the intercept and slope of the \( \ln q_e \) versus \( \epsilon^2 \) plot (Fig.2.6). The mean free energy \( E \) can be calculated from the following relation [14].

\[
E = 1 / \sqrt{(-2\beta)} \quad \quad \quad \quad \quad (7)
\]

The D-R parameters and mean free energy values are given in Table 2.3. The magnitude of \( E \) indicates the type of biosorption reaction. \( E \) values obtained are in between 7.1 - 11.95 kJ/mol showing that biosorption is chemical in nature [15].

2.3.5. 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. 2.7) 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 concentration was low, 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

\[
\log (q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303}\right) \times t \quad (8)
\]

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 (Fig. 2.8).

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

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \times t \quad (9)
\]

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. 2.9). 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
2.4). The values of biosorption capacity calculated from the model ($q_{e\text{exp}}$) are very near to experimental values $q_{e\text{exp}}$ for second-order-kinetics but for first-order-kinetics equation these values are very different. Higher correlation coefficient ($R^2$) values and similar $q_{e\text{cal}}$ and $q_{e\text{exp}}$ values indicates 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 $t$, 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 2.4, 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

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

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

For $F > 0.85$, $B_t = -0.4977 - \ln(1 - F)$ \hspace{1cm} (11)

and for $F < 0.85$, $B_t = \left(\sqrt{\pi} - \sqrt{(\pi - (\pi^2 F/3))}\right)^2$ \hspace{1cm} (12)

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

If the plot $B_t$ versus time is linear and passes through the origin then pore-diffusion controls the rate of mass transfer. If the plot is nonlinear or linear but does not pass through the origin, then it is concluded that film-diffusion or chemical reaction controls the adsorption rate. The plots of $B_t$ versus time for the biosorption of Cd(II) on Fennel at different concentrations show that the lines do not pass through the origin. These observations suggest that film diffusion or chemical reaction controls the rate of adsorption during this period.

2.3.6. Thermodynamics of biosorption

The temperatures used in this study were $30^0$, $40^0$ and $50^0$C. The equilibrium constant at different temperatures can be calculated with the following relations

$$K_c = \frac{C_{Ae}}{C_e} \hspace{1cm} (13)$$

Where $K_c$ is the equilibrium constant. $C_{Ae}$ (mg/L) is the amount sorbed on solid at equilibrium and $C_e$ (mg/L) is the equilibrium concentration of Cd(II) in the solution. The values of free energy change ($\Delta G^0$) at different temperatures were calculated from the following relation
\[ \Delta G^0 = -RT \ln K_c \] (14)

Where \( R \) is gas constant and \( T \) is absolute temperature.

Van’t Hoff equation is applied to calculate the enthalpy change (\( \Delta H^0 \)) and entropy change (\( \Delta S^0 \)).

\[ \ln K_c = (\Delta S^0/R) - (\Delta H^0/R) \times (1/T) \] (15)

\( \Delta S^0 \) and \( \Delta H^0 \) can be calculated from the intercept and slope of the linear plot of \( \ln K_c \) versus \( 1/T \) (Fig. 2.10). The values are reported in Table 2.5. Positive value of \( \Delta H^0 \) indicates endothermic nature of the biosorption process. \( \Delta G^0 \) is negative and decreases with increase in temperature showing that biosorption of Cd(II) is spontaneous and spontaneity increases with increase in temperature. Positive value of \( \Delta S^0 \) indicates increased randomness at the solid/solute interface.

### 2.3.7. 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. 0.1N 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. 2.11). 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 0.1N HCl during elution. The recovery of Cd(II) is decreased from 99.8% to 41.7% in fifth consecutive cycle (Fig. 2.11). 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.
2.3.8. Desorption studies

Column process was used to check the practical utility of the sorbent 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 2.6). 87.8% of Cd(II) was eluted by using 0.1N 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 2.6). Recovery of Cd(II) by 0.1N HCl in multi-metal system was 100%. It was observed that 80% of the metal in single and multi-metal systems was recovered within 10 mL. This property of the biosorbent can be utilized for preconcentration.

2.3.9. 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) solutions containing 50 mg/L of metal ions could be passed through the column without detecting traces of any metal ions in the effluent (Fig. 2.12). 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, 0.1N 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 2.13 and 2.14). The breakthrough capacities of metals in single and multi-metal system are reported in the Table 2.7. The breakthrough capacity of Cd(II) in single and multi-metal system in DDW and 0.1N NaCl is 10 mg/g, 2 mg/g and 0.8 mg/g respectively (Table 2.7). The decrease in the breakthrough capacities of these metals in presence of Na$^+$ ions indicate that ion-exchange mechanism is involved during biosorption.
2.4. 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 show that Fennel can be effectively utilized for the removal of Cd(II) ions upto five cycles. Breakthrough studies show that in single and multi-metal system with Cd(II) concentrations of 50 mg/L 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).
Table 2.1. Concentration of active sites on fennel surface

<table>
<thead>
<tr>
<th>Acidic sites</th>
<th>Concentration (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylic</td>
<td>0.027</td>
</tr>
<tr>
<td>Phenolic</td>
<td>0.113</td>
</tr>
<tr>
<td>Carboxylic+ Lactonic</td>
<td>0.140</td>
</tr>
</tbody>
</table>

Table 2.2. Biosorption capacities of various biosorbents for the biosorption Cd(II)

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

Table 2.3. Parameters of the biosorption isotherms obtained at different temperature.

<table>
<thead>
<tr>
<th>Isotherms</th>
<th>Parameters</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b (L/mg)</td>
</tr>
<tr>
<td>Langmuir</td>
<td></td>
<td>0.3400</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.1100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0800</td>
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<tr>
<td></td>
<td></td>
<td>0.7600</td>
</tr>
</tbody>
</table>

The table provides the concentration of active sites on fennel surface, the biosorption capacities of various biosorbents for the biosorption Cd(II), and the parameters of the biosorption isotherms obtained at different temperatures.
Table 2.4. Kinetics Parameters for the biosorption of Cd(II) at different concentrations on fennel

<table>
<thead>
<tr>
<th>Conc. (mg/L)</th>
<th>$q_{e(\text{exp})}$ (mg/g)</th>
<th>$q_{e(\text{cal})}$ (mg/g)</th>
<th>$K_1$ (1/min)</th>
<th>$R^2$</th>
<th>$q_{e(\text{cal})}$ (mg/g)</th>
<th>$K_2$ (g/mg-min)</th>
<th>h</th>
<th>$R^2$</th>
</tr>
</thead>
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<tr>
<td>5</td>
<td>0.49</td>
<td>0.057</td>
<td>0.490</td>
<td>0.9204</td>
<td>0.49</td>
<td>28.700</td>
<td>6.89</td>
<td>0.9997</td>
</tr>
<tr>
<td>25</td>
<td>2.46</td>
<td>0.071</td>
<td>0.248</td>
<td>0.9336</td>
<td>2.46</td>
<td>10.200</td>
<td>61.72</td>
<td>1.0000</td>
</tr>
<tr>
<td>50</td>
<td>4.90</td>
<td>0.290</td>
<td>0.107</td>
<td>0.9213</td>
<td>4.90</td>
<td>1.540</td>
<td>37.02</td>
<td>0.9999</td>
</tr>
<tr>
<td>100</td>
<td>9.30</td>
<td>0.901</td>
<td>0.081</td>
<td>0.9043</td>
<td>9.30</td>
<td>0.476</td>
<td>41.15</td>
<td>1.0000</td>
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</tbody>
</table>

Table 2.5. Thermodynamic parameters for the biosorption of Cd(II) on fennel

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$K_c$</th>
<th>$\Delta G^0$ (kJ/mol)</th>
<th>$\Delta H^0$ (kJ/mol)</th>
<th>$\Delta S^0$ (kJ/mol-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>7.33</td>
<td>-5.017</td>
<td>10.34</td>
<td>0.051</td>
</tr>
<tr>
<td>40</td>
<td>8.25</td>
<td>-5.470</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>9.41</td>
<td>-6.016</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2.6. Biosorption and desorption of Cd(II) in single and multi-metal systems on fennel by column process

<table>
<thead>
<tr>
<th>Metal solutions</th>
<th>Metals</th>
<th>Amount loaded (mg)</th>
<th>Amount sorbed (mg)</th>
<th>% Biosorption</th>
<th>Amount recovered (mg)</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single metal system</td>
<td>Cd(II)</td>
<td>2.5</td>
<td>2.425</td>
<td>97</td>
<td>2.130</td>
<td>87.8</td>
</tr>
<tr>
<td>Multi-metal system</td>
<td>Cu(II)</td>
<td>0.5</td>
<td>0.39</td>
<td>78</td>
<td>0.305</td>
<td>78.2</td>
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<tr>
<td></td>
<td>Cd(II)</td>
<td>0.5</td>
<td>0.48</td>
<td>96</td>
<td>0.480</td>
<td>100.0</td>
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<tr>
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<td>Ni(II)</td>
<td>0.5</td>
<td>0.30</td>
<td>60</td>
<td>0.265</td>
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<tr>
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<td>Zn(II)</td>
<td>0.5</td>
<td>0.38</td>
<td>76</td>
<td>0.053</td>
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</table>

Table 2.7. Breakthrough capacity and exhaustive capacity of metal ions on fennel in single and multi-metal systems

<table>
<thead>
<tr>
<th>Metal solutions</th>
<th>Metal ions</th>
<th>Initial Conc. (mg/L)</th>
<th>Breakthrough capacity (mg/g)</th>
<th>Exhaustive capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single metal system</td>
<td>Cd(II)</td>
<td>50</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>Ni(II)</td>
<td>50</td>
<td>8</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>Zn(II)</td>
<td>50</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>Cu(II)</td>
<td>50</td>
<td>4</td>
<td>70</td>
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<tr>
<td>Multi-metal system in DDW</td>
<td>Cd(II)</td>
<td>10</td>
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<td>12</td>
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<tr>
<td></td>
<td>Ni(II)</td>
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<td>2</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Zn(II)</td>
<td>10</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Cu(II)</td>
<td>10</td>
<td>2</td>
<td>22</td>
</tr>
<tr>
<td>Multi-metal system in 0.1N NaCl</td>
<td>Cd(II)</td>
<td>10</td>
<td>0.8</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Ni(II)</td>
<td>10</td>
<td>0.8</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Zn(II)</td>
<td>10</td>
<td>2.0</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Cu(II)</td>
<td>10</td>
<td>6.0</td>
<td>14</td>
</tr>
</tbody>
</table>
Fig. 2.1a FTIR spectrum of Fennel before Cd(II) biosorption

Fig. 2.1b FTIR spectrum of Fennel after Cd(II) biosorption
Fig. 2.2 Effect of pH

Fig. 2.3 Effect of concentration at different temperatures
Fig. 2.4 Langmuir isotherms

Fig. 2.5 Freundlich isotherms
Fig. 2.6 D-R plots for the adsorption of Cd (II)

Fig. 2.7 Effect of contact time
Fig. 2.8 Pseudo-first order kinetic model

Fig. 2.9 Pseudo-second order kinetic model
Fig. 2.10 Van't Hoff plot

Fig. 2.11 Column studies to regenerate the biosorbent column by using HCl as eluent
Fig. 2.12 Breakthrough capacity curve for the biosorption of metal ions in single metal system on Fennel

Fig. 2.13 Breakthrough capacity curve for the biosorption of metal ions in multi-metal system in DDW on Fennel
Fig 2. 14 Breakthrough capacity curve for the biosorption of ions in multi-metal system in 0.1N NaCl solution on Fennel
Reference:


