Chapter- IV

EXPERIMENTAL PROCEDURE

The present experimentation is carried out both batch-wise and column, on biosorption of chromium and cadmium metals from aqueous solutions onto two separate biosorbents - *Syzigium cumini* seed powder and *Caulerpa taxifolia* (green algae) powder.

The experimental procedure consists of the following steps:

4.1. Preparation of the biosorbent

4.2. Characterization of biosorbent

4.3. Preparation of the stock solutions

4.4. Analysis of metal ion concentration

4.5. Batch studies

   - Effect of agitation time
   - Effect of pH
   - Effect of initial metal ion concentration
   - Effect of biosorption dosage
   - Effect of temperature

4.6. Central Composite Design

4.7. Studies on biosorption kinetics

4.8. Studies on equilibrium biosorption

4.9. Studies on thermodynamics

4.10. Column studies

   - Effect of flow rate
   - Effect of bed height
The experimental scheme adopted for the present investigation is given in fig. 4.1

![Experimental scheme](image)

**Fig. 4.1 Experimental scheme adopted for the present investigation**
4.1. Preparation of the biosorbent

*Syzigium cumini* seeds were collected from Andhra University College of Engineering, Visakhapatnam and *Caulerpa taxifolia* was collected from Visakhapatnam coastal area, India. The collected biosorbents were washed with water several times until the dirt is removed and finally washed with distilled water. The biosorbents were dried in sun light for ten days, cut into small pieces, powdered and sieved. In the present study, 53 μm size seed powder was used as biosorbent without any pretreatment.

4.2. Characterization of biosorbent

FTIR studies

Biosorbents were characterized by FTIR spectrometry using Spectrum GX of Perkin Elmer, USA spectrophotometer from 400 to 4000 cm$^{-1}$ with a resolution of 1 cm$^{-1}$ using 4 scans with background subtraction. After obtaining the spectra, the peaks were identified by comparing with the spectra reported in literature.

X-ray diffraction analysis (XRD)

XRD of the powder samples were taken using a Philips PW 1830. The diffracted X-ray intensities were recorded as a function of 2θ by using cobalt target (Co-Kα radiation with $\lambda = 1.7890$ Å) at a scan speed of 1.2$^0$/ min. XRD patterns were recorded from 10 to 70$^0$. Different phases in the samples were identified by comparing a set of ‘d’ values and the corresponding intensities with the standards from the JCPDS (Joint Committee on Powder Diffraction Data, Swathmore, PA, USA) data files.
SEM studies

The dried powders and the corresponding metal loaded powders were first coated with ultra thin film of gold by an ion sputter JFC-1100 and then were exposed under a Japanese make electron microscope (JEOL, JXA-8100). For this purpose the working height was kept 15 mm with working voltage ranging between 10 kV to 25 kV. The compositional image analyses of samples were also taken up using the same equipment in which the working voltage was kept 20 kV with beam current as 40-100 nA.

4.3. Preparation of stock solution

The standard stock solution of chromium (1000 mg/L) was prepared by dissolving 2.828 g of 99.9 % analytical grade K₂Cr₂O₇ in 1000 mL of distilled water. The standard stock solution of cadmium (1000 mg/L) was also prepared by dissolving 2.284 g of 100% 3CdSO₄·8H₂O in 1000 mL of distilled water. The concentration of both metals in the aqueous solution was varied by diluting the stock solutions with required quantity of deionized water. The pH of the working solution was adjusted using either 0.1 N HCL or 0.1N NaOH.

Metal equivalent to 1 g = [Molecular wt. of metal salt x 100] / [Molecular wt. of metal x purity]

4.4. Analysis of metal ion concentration

The concentrations of metal ions were determined using an Atomic Absorption Spectrophotometer (AAS - Perkin Elmer AAnalyst 200 model). Air-acetylene flame was used at a wave length of 357.87 nm for chromium and 259 nm for cadmium with a slit width of 0.7 nm and sensitivity of 0.078 mg/L.
4.5. Batch studies

Effect of agitation time

Known amount of biosorbent was added to 50 mL of known amount of (chromium or cadmium) metal ion solution in each of 250 mL Erlenmeyer flasks. The flasks were incubated in shaker at a speed of 180 rpm at 30°C for different agitation times (1, 5, 10, 20, 30, 40, 50, 60, 90, 120, 150, 180 min). The samples were filtered separately by Whatman filter papers and analyzed in AAS to obtain final concentrations of metal.

% biosorption is calculated from the relation = \[\frac{(C_o - C_i)}{C_o}\] \times 100

\(C_o=\) initial concentration of metal in the aqueous solution (mg/L)
\(C_i=\) final concentration of metal in the aqueous solution (mg/L)

Metal uptake = \[\frac{V (C_o - C_i)}{W \times 1000}\]

V = volume of the metal ion solution taken
w = amount of biosorbent taken

Effect of pH

The effect of initial solution pH on the equilibrium uptake was analyzed over a different pH range. The pH of the solutions are adjusted by adding required amounts of 0.1 N HCL or 0.1N NaOH. To these, known amount of biosorbent is added. The flasks were incubated in shaker at a speed of 180 rpm at 30°C for optimum agitation time. The sample were allowed to settle, filtered and analyzed in AAS to obtain final concentration of metal.
Effect of initial metal ion concentration

Keeping pH at optimum value, known amount of biosorbent was added to 50 mL of aqueous solution containing different metal ion concentrations are incubated in shaker at room temperature for optimum agitation time. The sample were allowed to settle, filtered and analyzed in AAS to obtain final concentration of metal.

Effect of biosorption dosage

Keeping pH and initial metal ion concentration fixed at optimum value, 50 mL of aqueous solution is taken in a 250 mL flask with different amounts of biosorbents. The sample is kept in continuous contact for optimum agitation time by incubating at 30°C. The sample were allowed to settle, filtered and analyzed in AAS to obtain final concentration of metal.

Effect of temperature

Keeping pH, initial metal ion concentration and biosorbent at optimum values, 50 mL of aqueous solution is taken in a 250 mL flask at different temperature. The samples were filtered by Whatman filter paper and analyzed in AAS to obtain final concentration of metal.

4.6. Central Composite Design (CCD)

Once the parameters having the greatest influence on the responses were identified, a CCD was used to optimize the levels of these parameters. The full CCD, based on three basic principles of an ideal experimental design, primarily consists of (1) a complete $2^n$ factorial design, where $n$ is the number of test parameters, (2) $n_0$ center points ($n_0 \geq 1$) and (3) two axial points on the axis of
each design parameter at a distance of $2^n/4$ from the design center. Hence, the total number of design points is $N = 2^n + 2n + n_0$. For statistical calculations the parameters $X_i$ are coded as $x_i$ according to eq. (4.1):

$$x_i = \frac{X_i - \bar{x}_i}{\Delta x_i}, \quad (i = 1, 2, 3, \ldots, k) \quad (4.1)$$

where $x_i$ is dimensionless value of an independent parameter, $X_i$ is the real value of an independent parameter, $\bar{x}_i$ the is real value of the independent parameter at the center point and $\Delta x_i$ is the step change.

The second degree polynomials (eq. 4.2) were calculated with the statistical package (Stat-Ease Inc., Minneapolis, MN, USA) to estimate the response of the dependent parameter:

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_4 X_4 + b_{11} X_1^2 + b_{22} X_2^2 + b_{33} X_3^2 + b_{44} X_4^2 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{14} X_1 X_4 + b_{23} X_2 X_3 + b_{24} X_2 X_4 + b_{34} X_3 X_4 \quad (4.2)$$

where $Y$ is predicted response, $X_1, X_2, X_3, X_4$ are independent parameters, $b_0$ is offset term, $b_{b_1}, b_{b_2}, b_{b_3}, b_{b_4}$ are linear effects, $b_{b_{11}}, b_{b_{22}}, b_{b_{33}}, b_{b_{44}}$ are squared effects and $b_{b_{12}}, b_{b_{13}}, b_{b_{14}}, b_{b_{23}}, b_{b_{24}}, b_{b_{34}}$ are interaction terms.

### 4.7. Studies on kinetics

In order to determine the order of the rate of biosorption, 50 mL of known amount of metal ion concentration is taken in thirteen flasks. To these known amount of biosorbent is taken in each flask and incubated in shaker at 30°C at a speed of 180 rpm for different time intervals (1, 5, 10, 20, 30, 40, 50, 60, 90, 120, 150, 180
min). They are then settled, filtered and the filtrates are analysed to find the final concentrations of metal.

**4.8. Studies on isotherms**

In order to determine the isotherms, 50 mL of known amount of metal ion concentration is taken in 250 mL conical flask and to this known amount of biosorbent is added and kept for shaking at 30°C at a speed of 180 rpm for optimum time. They are then settled, filtered and the filtrates are analyzed to find the final concentrations of metal. The experiment is repeated for different metal ion concentration.

**4.9. Studies on thermodynamics**

To evaluate thermodynamic parameters, 50 mL of aqueous solution containing known amount of metal ion concentration is taken in each of 250 mL flasks. Optimum amount of biosorbent is added to each of these flasks. These flasks are incubated in shaker at room temperature at a speed of 180 rpm for optimum time. They are then settled, filtered and the filtrates are analyzed to find the final concentrations of metal.

**4.10. Column studies**

For industrial water treatment, fixed bed column are generally used. Column adsorption studies were carried out using *Caulerpa taxifolia* powder. Flow rate and bed height are the parameters chosen for these studies. Column studies were carried out using glass column having 2.5 cm internal diameter (ID) of 30 cm length. Glass wool was placed at inlet and outlet of the column to avoid any loss of biosorbent material. The cadmium solution was fed through the bottom of the
column with the help of a Watson Marlow metering pump and output was collected from the top of the column at regular intervals for analysis. The flow rate was checked regularly. The pumping was continued till there was no further biosorption of cadmium i.e., inlet and outlet cadmium concentrations became same.

The experimental data were tested for four different kinetic models namely Bohart-Adams model, Thomas model, BDST model and Yoon-Nelson model to find out the best fit. Break through and saturation periods were used to compare and evaluate the adsorption performance of the biosorbent under various conditions. The break through point was defined as the time interval at which the ratio of output concentration of the column \((C_2)\) to the input concentration \((C_1)\) was 0.1. The bed volume was obtained as the ratio of volume of solution treated to volume of bed depth.

The amount of Cd (II) adsorbed per unit mass of \textit{Caulerpa taxifolia} \((q_i, \text{mg/g})\) in the column was calculated using eq. (4.3).

\[
q_i = \frac{\sum_{i=1}^{n} v(t_i - t_{i-1})[1 - \left(\frac{C_2}{C_1}\right)_i]C_1}{m_s}
\]  
\text{(4.3)}

where \(m_s\) is the mass of biosorbent in the column and the rest of the quantities have been already been defined.
The experimental conditions for biosorption of chromium onto *Syzigium cumini* seed powder and *Caulerpa taxifolia* powder are given in Table 4.1.

**Table 4.1**

Experimental conditions for biosorption of chromium

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Parameter</th>
<th>Values Investigated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Agitation time, t, min</td>
<td>1, 5, 10, 20, 30, 40, 50, 60, 90, 120, 150 and 180</td>
</tr>
<tr>
<td>2</td>
<td>pH of the aqueous solution</td>
<td>2, 3, 4, 5, 6 and 7</td>
</tr>
<tr>
<td>3</td>
<td>Initial metal concentration, C&lt;sub&gt;o&lt;/sub&gt;, mg/L</td>
<td>20, 40, 60, 120 and 160</td>
</tr>
<tr>
<td>4</td>
<td>Biosorbent dosage, w, g/L</td>
<td>10, 20, 40 and 80</td>
</tr>
<tr>
<td>5</td>
<td>Temperature, K</td>
<td>293, 303, 313 and 323</td>
</tr>
</tbody>
</table>

The experimental conditions for biosorption of cadmium onto *Syzigium cumini* seeds powder and *Caulerpa taxifolia* powder are given in Table 4.2

**Table 4.2**

Experimental conditions for biosorption of cadmium

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Parameter</th>
<th>Values Investigated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Agitation time, t, min</td>
<td>1, 5, 10, 20, 30, 40, 50, 60, 90, 120, 150 and 180</td>
</tr>
<tr>
<td>2</td>
<td>pH of the aqueous solution</td>
<td>2, 3, 4, 5, 5.5, 6 and 7</td>
</tr>
<tr>
<td>3</td>
<td>Initial metal concentration, C&lt;sub&gt;o&lt;/sub&gt;, mg/L</td>
<td>20, 40, 60, 120 and 160</td>
</tr>
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<td>4</td>
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<td>293, 303, 313 and 323</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

In the present investigation, the potentials of two biosorbents namely *Syzigium cumini* seed powder and *Caulerpa taxifolia* algae powder are investigated for biosorption of chromium and cadmium from aqueous solutions.

The effects of various parameters on biosorption of chromium and cadmium by the biosorbents were studied. The measured data consist of agitation time, pH, initial and final concentrations of metal, biosorbent dosage and temperature of the aqueous solution. The experimental data are obtained by conducting both batch and continuous experimentations.

**Chapter–V** prescribes results and discussion for biosorption of chromium onto biosorbents mentioned below.

- Section–I deal with biosorption of chromium onto *Syzigium cumini* seed powder.
- Section–II deals with biosorption of chromium onto *Caulerpa taxifolia* powder.

**Chapter–VI** prescribes results and discussion on biosorption of cadmium onto biosorbents mentioned below.

- Section–A deals with biosorption of cadmium onto *Syzigium cumini* seed powder.
- Section–B deals with biosorption of cadmium onto *Caulerpa taxifolia* powder.

**Chapter–VII** presents continuous column data for biosorption of cadmium using *Caulerpa taxifolia* powder.