BIOSORPTION OF NI (II) FROM INDUSTRIAL EFFLUENT BY CAULERPA RACEMOSA AND ULVA LACTUCA

Krishna Y. Pandya1,2, Rinku V. Patel1,2, Rakesh T. Jasrai3 and Nayana Brahmbhatt2*

ABSTRACT: Environmental pollution is serious global problem; it leads research towards remediation technique by applying biological method. Marine algal treatment for the biosorption of metal is found promising technique because of its availability and low cost, it absorbs toxic metals from the waste water. The biosorption capacity of the seaweed is depend on chemical constitution of their cell wall and presence of molecules with various functional groups which interacts with metal ions. This research paper focuses on biosorption of nickel (II) by using marine algal biomass of Caulerpa racemosa and Ulva lactuca (Chlorophyceae) and study of Langmuir and Freundlich adsorption isotherms and kinetics. The study indicates both the isotherm models observed favorable; the Freundlich model indicates higher adsorption capacity of the biomass. This study shows Ulva lactuca gives higher biosorption yield as compare to Caulerpa racemosa. The kinetic study indicates the reaction follows pseudo second order model observed in both marine algal biomass. Thus, it can be used as an effective technique in heavy metal removal from the contaminated environment.

KEYWORDS: Biosorption, Caulerpa racemosa, Effluent, Isotherm, Nickel, Ulva lactuca

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1. INTRODUCTION
The heavy metal pollution is serious environmental issue which creates adverse effects to living organisms and earth ecosystem [1][2] therefore it is important to mitigate heavy metals such as cadmium (Cd), copper (Cu), zinc (Zn), nickel (Ni), chromium (Cr) as they are carcinogenic and
persistent in nature and toxic which cause severe health problems in human such as nervous system breakdown, brain function disorder, kidney damage etc. The adverse effect of nickel (Ni) cause allergies, lung disorders and cancer [3][4]. They also cause toxic symptoms such as anemia, insomnia, irritability, muscles weakness, dizziness etc [5]. There are number of treatment technologies available for the waste water treatment such as ion exchange mechanisms, chemical precipitation, evaporation, membrane filtration, activated carbon, [6][7] these methods having high operational costs and high consumption of energy therefore the biosorption treatment have been found most promising technique because of low cost of adsorbent biomaterials with potential capability to absorb heavy metals from the waste water [8]. The biosorption is the result of the metal ion interaction with functional group of the adsorbent biomass. These functional groups are responsible for metal ion adsorption such as carboxylate, hydroxyl, amino, amide, sulfonate, phosphate etc [9]. It also involves several other interactions such as complexation, ion-exchange, coordination, chelation, precipitation etc [10][11]. An application of living and nonliving biomass is an interesting approach to reduce toxicity problems from waste due to non-requirement of nutritional supplements and maintenance [12]. Marine algae are most suitable biomass for their application as biosorbents because of their maximum abundance in oceans; it can be used in bioremediation of pollutant from waste water [13][14]. This method is low cost and having high metal binding efficacy. The selected algae biomass has good capability of biosorption of metals due to presence of active sites of functional group inside tissues of the cell wall. Marine algae also give result for the color removal, fluoride removal and removal of phosphate from the industrial waste water. [15][16][17][18]. The aim of this article is to study the biosorption of nickel (II) by green marine algae Caulerpa racemosa and Ulva lactuca (Chlorophyceae) with the equilibrium isotherm and kinetics study.

2. MATERIALS AND METHODS

Biomass Collection

The biomass of Caulerpa racemosa and Ulva lactuca (Chlorophyta) were collected from Okha coast of Gujarat, India (Longitude - 68°20´ E to 70°40´ E Latitude - 22°15´ N to 23°40´ N). They were washed with marine water at source to remove unwanted debris, epiphytes and sand particles then kept in icebox and transferred to laboratory. This biomass were washed with distilled water two to four times to remove impurities and salt and identified by method described by M. Umamaheswara Rao [19]. Then it was sundried and pulverized in grinder which goes under sieving through a screen with 0.5 mm of mesh size. This powdered biomass was then kept inside airtight plastic bags and stored at room temperature. This both biomass Caulerpa racemosa and Ulva lactuca were entitled as A and B and they were further analyzed for SEM (Scanning electron microscopy) analysis.
**Effluent Sample collection and Analysis**

The industrial effluent samples were collected from various dye industries entitled as E1, E4 and E6; they are composed of dye components. The heavy metals of effluent sample were analyzed using ICP-OES (Model- Optima 3300 RL, Make- Perkin Elmer). The biosorption of chromium and copper by the biomass were studied in author’s previous article [20]. The present paper investigates biosorption of Ni(II) by *Caulerpa racemosa* and *Ulva lactuca*. The concentration of Ni(II) is indicated in Table-1.

**Scanning Electron Microscopy (SEM):**

The morphology of both the biomass surface for before and after treatment of effluents E1, E4 & E6 were studied by Field Emission Gun-Scanning Electron Microscopy (Make: FEI Ltd., Model: Nova NanoSEM 450)

<table>
<thead>
<tr>
<th>Heavy Metal</th>
<th>Nickel(Ni) ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>0.174</td>
</tr>
<tr>
<td>E4</td>
<td>0.2054</td>
</tr>
<tr>
<td>E6</td>
<td>0.1754</td>
</tr>
</tbody>
</table>

(E1, E4 & E6 is industrial dyes effluent samples)

**Biosorption of Ni(II) by Batch Experiments:**

The 2 g of the biomass in 200 ml of dye effluents was inoculated in 500 ml of conical flask at pH 8; the batch adsorption experiment was carried out in flask shaker at constant agitation speed of 80 rpm for the better contact of biomass with effluents at room temperature (28°C). The effluent samples were analyzed after every 10 minutes of gap up to 90 minutes of the time period. The samples were filtered with Whatman filter paper No. 40 to make it adsorbent free. The left over heavy metal Ni(II) in filtered effluent samples were analyzed by atomic absorption spectrophotometer (Make: shimadzu, Model: 1800). The equilibrium biosorption qe (mg/g) was calculated by
\[ q_e = \frac{(C_0 - C_e)V}{W} \]  

(1)

Where, Co and Ce are initial & equilibrium of the effluent respectively; V & W are the volume (ml) & weight of the seaweed biomass (g). The concentration of Ni(II) adsorbed at time t as qt was calculated as per the following equation (2) [21]

\[ q_t = \frac{(C_0 - C_t)V}{W} \]  

(2)

Where, Co is the initial concentration (ppm) and Ct is the Ni(II) concentration (ppm) in filtrate effluent sample taken at time t; W is the weight (g) of the biomass and V is the volume (ml). The metal removal yield was determined by the below equation (3) [22]

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

(3)

3. RESULT AND DISCUSSION

The Figure-2 shows quantity absorbed in ppm as function of contact time by biomass of Caulerpa racemosa and Ulva lactuca which reveals that the biomass shows rapid absorption initially and reaches equilibrium at 50 minutes and 60 minutes time periods respectively, then slowly decreased afterwards. Because of maximum vacant space available initially on the surface of the biomass therefore the absorption rate becomes rapid. Then the process reaches equilibrium because of intra-particle diffusion in the cells of the biomass from bulk to surface and then it slowly decreased because of repulsive forces of molecules lowers the rate of reaction and lowest vacant space available in biomass [22]. Thus the biosorption process is depends on vacant space availability, attraction and repulsion forces & diffusion process in molecules, the similar work reported by various scientists on biosorption of copper, lead, cadmium, chromium, nickel by algal biomass [23][24][25][26][27][28]. Figure-3 shows biosorption yield in percentage for Ni(II) by both Caulerpa racemosa and Ulva lactuca from the E1, E4 and E6 effluents. The maximum 28.84 % and 36.71 % Ni(II) removal observed from waste water by Caulerpa racemosa and Ulva lactuca respectively. The attraction towards heavy metal is depending on ionic size, ionic charge and hydrolysis constant of the metal [29]. Ulva lactuca indicates maximum affinity towards Ni(II) and gives higher metal removal yield as compare to Caulerpa racemosa.
Figure-2: Biosorption capacity of *Caulerpa racemosa* and *Ulva lactuca* as function of contact time

![Biosorption capacity of Caulerpa racemosa and Ulva lactuca](image)

Figure-3: Biosorption yield (%) of *Caulerpa racemosa* and *Ulva lactuca*

Biosorption Isotherms: -

The (Langmuir and Freundlich) adsorption isotherms used to determine the wide range of concentration of sorbent to investigate characteristics of adsorption such as equilibrium concentration of adsorbate in the mass and accumulation of metal onto the surface of adsorbent biomass. Langmuir and Freundlich isotherms are commonly used for sorption study and successfully applied to explain the adsorption of metal; thus they have been applied in the present study [30][31][32]. The Langmuir equation [33] illustrated in linerized form:

\[
\frac{C_e}{Q_e} = \frac{b}{Q_o} + \frac{C_e}{Q_o}
\]  

(4)

The linear plot of specific adsorption \((C_e/q_e)\) verses equilibrium concentration \((C_e)\) indicated in Figure-4 (1,2,3,4,5,6) and Figure-5 (7,8,9,10,11,12) signifies the adsorption follow Freundlich model. The Table-2 represents the values of \(Q_m\) and \(b\). The Langmuir isotherm can be expressed by constant separation factor \(R_L\) which is shown in the below equation [34]:

\[
R_L = \frac{1}{1 + bC_0}
\]  

(5)

Where the \(R_L\) value shows the characteristics of adsorption to be either unfavorable \((R_L > 1)\), linear \((R_L = 1)\), favorable \((0 < R_L < 1)\), or irreversible \((R_L = 0)\).

The Freundlich isotherm [35] is illustrated by the below equation:

\[
\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e
\]  

(6)

Where equation indicates the Freundlich constants as \(K_f\) and \(n\); which can be studied by intercept and slope of the Figure-4 and Figure-5 (4,5,6,10,11,12) represents the adsorption capacity and intensity respectively. The values indicated in Table-2.
Equilibrium Studies:

The Langmuir and Freundlich isotherm plots are shown in Fig-4 and Fig-5 which indicates the adsorption of Ni(II) on both the seaweed biomass. The straight lines satisfactorily explain Langmuir and Freundlich model for the equilibrium adsorption process. Both the isotherm models were observed favorable for all effluent samples shown in Table-2. The Freundlich values shows the adsorption of Ni(II) on adsorbent biomass has high adsorption capacity with rapid progression.

Figure-4: Langmuir and Freundlich isotherm of Ni(II) by Caulerpa racemosa (1-6).

Figure-5: Langmuir and Freundlich isotherm of Ni(II) by Ulva lactuca (7-12)
Table 2: - Biosorption isotherm parameter in *Caulerpa racemosa* and *Ulva lactuca*

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Metal</th>
<th>Parameter</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td><strong>Caulerpa racemosa</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>Ulva lactuca</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Langmuir</td>
<td>Nickel</td>
<td>R2</td>
<td>0.987</td>
<td>0.798</td>
<td>0.982</td>
<td>0.880</td>
<td>0.949</td>
<td>0.883</td>
</tr>
<tr>
<td>Isotherm</td>
<td></td>
<td>qmax(mg/g)</td>
<td>5.78</td>
<td>0.07</td>
<td>1.14</td>
<td>6.45</td>
<td>0.86</td>
<td>5.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B</td>
<td>0.11</td>
<td>0.19</td>
<td>0.14</td>
<td>0.10</td>
<td>0.16</td>
<td>0.11</td>
</tr>
<tr>
<td>Freundlich</td>
<td>Nickel</td>
<td>R2</td>
<td>0.995</td>
<td>0.898</td>
<td>0.987</td>
<td>0.955</td>
<td>0.942</td>
<td>0.949</td>
</tr>
<tr>
<td>Isotherm</td>
<td></td>
<td>qmax(mg/g)</td>
<td>4.27</td>
<td>33.33</td>
<td>9.34</td>
<td>3.75</td>
<td>27.27</td>
<td>4.25</td>
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<td></td>
<td></td>
<td>B</td>
<td>0.59</td>
<td>0.61</td>
<td>0.55</td>
<td>0.59</td>
<td>0.61</td>
<td>0.58</td>
</tr>
</tbody>
</table>

**Biosorption Kinetics:** -

During the first few minutes the Ni(II) is attached with functional group of seaweed rapidly because of availability of vacant space in the biomass followed by slowly increase till the equilibrium stage is reached at 50 and 60 minutes in *Caulerpa racemosa* and *Ulva lactuca* respectively. The kinetics was studied for pseudo first order and pseudo second order models. Lagergren’s model is known as pseudo first order model and applied to study adsorption rate of the biomass. The pseudo first order model in linear form is as below [36]:

\[
\ln (q_e - q_t) = \ln (q_e - K_1 t)
\]  

The pseudo second order model given by the [37] is as below:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}
\]  

Where, the K represents rate constant of pseudo-second order for adsorption (g/mg/time) & q_e & q_t were the Ni(II) content (mg/g) adsorbed at equilibrium & time t respectively. The linear plot of t vs t/qt was studied which shows the kinetic data fitted well in pseudo-second order model. The Figure-6 and Figure-7 indicates linear plot of ln (qe-qt) vs t and t/qt vs t for pseudo-first order reaction and for pseudo-second order reaction respectively for the adsorption of Ni(II) onto *Caulerpa racemosa* and *Ulva lactuca*. The correlation coefficient of second-order model are nearer to correlation coefficient of pseudo first order models suggests that the pseudo second order model was followed by *Caulerpa racemosa* and *Ulva lactuca*.
Figure 6: Pseudo-first order & Pseudo-second order plot for Ni (II) by Caulerpa racemose (13-18).

Figure 7: Pseudo-first order & Pseudo-second order plot for Ni (II) by Ulva lactuca (19-24).

The scanning electron microscopy explains the surface characteristics of the seaweed biomass of Caulerpa racemosa and Ulva lactuca before and after exposure with Ni (II) containing effluents represented in Image-1 and Image-2. The images were scanned under 100 µm range. After effluent treatment the scanned images were represented as E1, E4 and E6 in both the biomass. It was observed damaged, broken, swollen and uneven surface of the biomass indicates the linking of metal with the functional group and accumulation of the metal inside the biomass cells which exchange cations by
occupying the free binding sites inside the cell wall indicates strong cross linking and ion exchange mechanisms [38]. Thus, the biosorption of metal by marine algae is found promising technique because of its availability and low cost, it absorbs toxic metals from the waste water. The biosorption capacity of the seaweed is depend on chemical constitution of their cell wall and presence of molecules with various functional groups which interacts with metal ions. The study indicates both the isotherm models observed favourable, the Freundlich model indicates higher adsorption capacity of the biomass. *Ulva lactuca* gives higher biosorption as compare to *Caulerpa racemosa*. The kinetic study indicates the reaction follows pseudo second order model observed in both marine biomass. Finally, this present study concludes that both the marine algal biomass of *Caulerpa racemosa* and *Ulva lactuca* can be applied as an effective technique for metal removal from contaminated waste water.

**Image-1:** Scanning electron microscopy (SEM) of Untreated & Treated *Caulerpa racemosa*

![Image-1](attachment:SEM_Caulerpa_racemosa.png)

**Image-2:** Scanning electron microscopy (SEM) of Untreated & Treated *Ulva lactuca*

![Image-2](attachment:SEM_Ulva_lactuca.png)

**ACKNOWLEDGEMENT**
I am thankful to my Co-authors, Bharuch Enviro Infrastructure Ltd. (BEIL), Ankleshwar and Sophisticated Instrumentation Centre for Applied Research and Testing (SICART), Vallabh Vidhyanagar for the successfully completion of the work support.

**CONFLICT OF INTEREST**
Authors have no conflict of interest
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