Adsorption of Nickel(II) Ion From Aqueous Solution onto ZnCl₂ Activated Carbon Prepared From Delonix Regia Pods (Flame Tree)

RAJAPPA A,¹ RAMESH. K ², NANDHAKUMAR. V ³.

¹ Department of chemistry, Sri Manakula Vinayagar Engg. College, Madagadipet, Puducherry, India.
² Department of chemistry, Arasu Engineering college, Kumbakonam, Thanjavur, India.
³ Department of chemistry, A.V.V.M Sri Pushpam college, Poondi, Thanjavur, India.
Corresponding email: vnchem13@gmail.com

Abstract

Adsorption of Nickel(II) ion onto Activated Carbon prepared from Delonix regia pods activated with Zinc chloride (DRZAC) under various experimental conditions were studied. Batch mode adsorption experiments were conducted. The characteristics of the DRZAC were determined by SEM, XRD, FTIR, BET analysis and pHZPC. The maximum removal efficiency of Ni(II) ion is 85% at pH 6. Under the chosen conditions, Experimental data obtained were fitted with linearised forms of Legergren and Ho kinetic models. The Sum of Error Squares Percentage (SSE %) for first order and second order kinetics were 1.56 & 0.72 respectively. Thus this adsorption followed second order kinetics. The equilibrium adsorption data were analyzed with four isotherm models. Order of best fitting isotherm models were found to be Freundlich >Temkin >Langmuir >Dubinin Raduskevich. The results in this study indicated that DRZAC could be employed as an adsorbent for the removal of Ni(II) ion from an aqueous solution.

Keywords: Adsorption; Delonix regia ZnCl₂ activated carbon; Nickel(II) ion removal; Kinetics; Isotherms.

Introduction

The progressive increase of industrial technology results in a continuous increase of pollution, so that a great effort has been devoted to minimizing these hazardous pollutants and therefore, avoiding their dangerous effects on animals, plants and humans. Metals can pose health hazards if their concentrations exceed allowable limits. Even when the concentrations of metals do not exceed these limits, there is still a potential for long-term contamination, since heavy metals are known to be accumulative within biological systems [1, 2, 3]. These heavy metals are not biodegradable and their presence in streams and lakes leads to bioaccumulation in living organisms, causing health problems in animals, plants and human beings [1, 4]. Heavy metal ions are reported as priority pollutants, due to their mobility in natural water ecosystems and due to their toxicity [5]. Cadmium, zinc, copper, nickel, mercury, and chromium are often detected in industrial wastewaters, which are originated from metal plating, mining activities, smelting, battery manufacture, pesticides, nuclear industry, etc.

Nickel salts are commonly used in metal plating and its concentration in industrial wastewater varies between 6 to12 mg/L, which is above the safe limit (0.15 mg/L) [6]. The chronic toxicity of nickel
to humans and the environment is well known and high nickel concentration causes gastrointestinal irritation and lung and bone cancers [7].

Among several chemical and physical methods, the adsorption onto activated carbon has been found to be superior to other techniques because of its capability of adsorbing a broad range of different types of adsorbates efficiently and its simplicity of design [9]. However, commercially available activated carbons are still considered expensive [10]. As a result, many researchers have studied cheaper substitutes, which are relatively inexpensive and at the same time endowed with reasonable adsorption capacity. These studies include the use of coal [11], fly ash [8, 12-13], activated clay [14], palm fruit bunch [15], rice husk [16], hazelnut shell [17], coconut shell [18] and peat [19, 20].

The objective of this study is to evaluate the feasibility of using the adsorbent prepared from Delonix Regia pods for the removal of Nickel(II) ion from aqueous solution. The influence of experimental parameter such as contact time, adsorbent dosage and initial Ni(II) ion concentrations were studied. Kinetic and equilibrium aspects of the adsorption process were studied.

Table 1: Nomenclature

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>C&lt;sub&gt;i&lt;/sub&gt;</td>
<td>Liquid phase initial concentrations of the adsorbate (mg/L)</td>
</tr>
<tr>
<td>C&lt;sub&gt;t&lt;/sub&gt;</td>
<td>Liquid phase concentrations of the adsorbate at time “t” (mg/L)</td>
</tr>
<tr>
<td>C&lt;sub&gt;e&lt;/sub&gt;</td>
<td>Liquid phase concentrations of the adsorbate at equilibrium (mg/L)</td>
</tr>
<tr>
<td>V</td>
<td>Volume of the adsorbate solutions in liter (L)</td>
</tr>
<tr>
<td>W</td>
<td>Mass of the adsorbent (g)</td>
</tr>
<tr>
<td>q&lt;sub&gt;e&lt;/sub&gt;</td>
<td>Quantity adsorbed at equilibrium (mg/g)</td>
</tr>
<tr>
<td>q&lt;sub&gt;t&lt;/sub&gt;</td>
<td>Quantity adsorbed at time “t” (mg/g)</td>
</tr>
<tr>
<td>T</td>
<td>Time in minutes</td>
</tr>
<tr>
<td>Q&lt;sub&gt;e&lt;/sub&gt;</td>
<td>Amount of solute adsorbed per unit weight of adsorbent (mg/g)</td>
</tr>
<tr>
<td>C&lt;sub&gt;e&lt;/sub&gt;</td>
<td>Equilibrium concentration of solute in the bulk solution (mg/L)</td>
</tr>
<tr>
<td>Q&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Langmuir adsorption efficiency</td>
</tr>
<tr>
<td>b</td>
<td>Langmuir adsorption energy</td>
</tr>
<tr>
<td>R&lt;sub&gt;L&lt;/sub&gt;</td>
<td>Langmuir separation factor</td>
</tr>
<tr>
<td>C&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Initial concentration of the adsorbate</td>
</tr>
<tr>
<td>K&lt;sub&gt;f&lt;/sub&gt; and n</td>
<td>Freundlich constants incorporating all factors affecting the adsorption capacity and intensity of adsorption respectively</td>
</tr>
<tr>
<td>B&lt;sub&gt;1&lt;/sub&gt;</td>
<td>Tempkin constant related to heat of sorption (J/mol)</td>
</tr>
<tr>
<td>K&lt;sub&gt;T&lt;/sub&gt;</td>
<td>Tempkin equilibrium binding constant</td>
</tr>
</tbody>
</table>
Material and Methods:

Materials

All the chemicals used for this experiments are of analytical grade. Activated Carbon was prepared from Delonix Regia pods. (NH₄)₂.Ni.(SO₄)₂.6H₂O, complexing reagent such as Bromine water, Ammonia and Dimethyl glyoxime purchased from Merck Company.

Preparation of Stock solution

Stock solution 500mg/L of Ni(II) ion was prepared by dissolving 0.3360g of (NH₄)₂.Ni. (SO₄)₂.6H₂O in double distilled water. The solution was further diluted to the required concentrations. Before mixing the adsorbent, the pH of each Ni(II) ion solution was adjusted to the required value by 0.1 M NaOH or 0.1 M HCl solution. The Ni(II) ion optical density of the solution measuring at 450 nm.

Preparation of Adsorbent

Delonix Regia pods were collected from Kumbakonam region, Thanjavur District. Delonix Regia pods were repeatedly washed with distilled water to remove dirt, dust and impurities. The washed shells materials were then dried in sunlight for a month. The dried shells were chopped into small chips. Chemical activation of the Delonix Regia pods was carried out with ZnCl₂ solution. 20g of dried Delonix Regia pods were well mixed with 20ml desired concentration (20%,40%) of ZnCl₂ 1:1 w/v aqueous solution. The slurry was kept in an air oven at 100°C for 24 hours. The resulting product was then subjected to carbonization and activation process in a muffle furnace at 400°C for 1 hour. Then the sample was cooled and subsequently washed with 0.05M HCl and then with deionized water for several times. It was ground and sieved. The particle size ranged between 110 mm & 90 mm were taken and kept in a desiccator for further use.
Physico-chemical Characterization of DRZAC

The properties of DRZAC were given in Table 2. The total surface areas were calculated using the BET equation[^21].

Table 2 Physico-chemical characteristics of DRZAC

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Properties</th>
<th>DRZAC Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PHzpc</td>
<td>6.0</td>
</tr>
<tr>
<td>2.</td>
<td>Particle size, mm</td>
<td>90-110</td>
</tr>
<tr>
<td>3.</td>
<td>Surface area (BET), m²/g</td>
<td>916.1234</td>
</tr>
<tr>
<td>4.</td>
<td>Pore volume, cm³/g</td>
<td>0.3986</td>
</tr>
<tr>
<td>5.</td>
<td>Pore size (Pore width), nm</td>
<td>2.7174</td>
</tr>
<tr>
<td>6.</td>
<td>Bulk density, g/Ml</td>
<td>0.52</td>
</tr>
<tr>
<td>7.</td>
<td>Fixed Carbon, %</td>
<td>71.11</td>
</tr>
<tr>
<td>8.</td>
<td>Moisture content, %</td>
<td>4.36</td>
</tr>
</tbody>
</table>

Table 3 Data processing Tools

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Parameters</th>
<th>Formulae</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Kinetic Models &amp; SSE %</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pseudo First order kinetics (Legergren equation)</td>
<td>[ \log (q_e - q_t) = \log q_e - k_1/2.303 \times t ]</td>
</tr>
<tr>
<td></td>
<td>Pseudo Second order kinetics (Ho equation)</td>
<td>[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e t} ]</td>
</tr>
<tr>
<td></td>
<td>The initial adsorption rate h</td>
<td>[ h = k_2 q_e^2 ]</td>
</tr>
<tr>
<td></td>
<td>Sum of error squares</td>
<td>[ \text{SSE} (%) = \sqrt{\frac{\sum (q_{e,exp} - q_{e,cal})^2}{N}} ]</td>
</tr>
<tr>
<td>2.</td>
<td>Isotherms</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Langmuir Separation factor</td>
<td>[ \frac{C_e}{Q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} ]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[ R_L = \frac{1}{1 + b C_0} ]</td>
</tr>
<tr>
<td></td>
<td>Freundlich Separation factor</td>
<td>[ \log Q_e = \log K_f + \frac{1}{n} \log C_e ]</td>
</tr>
<tr>
<td></td>
<td>Tempkin Separation factor</td>
<td>[ q_e = B_1 \ln K_T + B_1 \ln C_e ]</td>
</tr>
<tr>
<td></td>
<td>Dubinin – Raduskevich, Polanyi potential Separation factor</td>
<td>[ \ln q_e = \ln q_0 - \frac{B \varepsilon^2}{\varepsilon} ]</td>
</tr>
<tr>
<td></td>
<td>Mean free energy of adsorption</td>
<td>[ \varepsilon = RT \ln (1 + 1/C_e) ]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[ E = 1/ (2B)^{1/2} ]</td>
</tr>
</tbody>
</table>

Batch Adsorption procedure:

Batch adsorption studies were carried out in 250 mL iodine flasks with 50 mL of the working Ni(II) ion solution of different concentrations ranging from 10 mg/L to 20 mg/L. Known amount of adsorbent was
added to the solution. The flasks were agitated at a constant speed of 180 rpm. Samples were collected from the flasks at predetermined time intervals for analyzing the residual Ni(II) ion concentration in the solution. The amount of Ni(II) ions adsorbed in milligram per gram of adsorbent was determined by using the following mass balance equation:

\[ q_e = \frac{(C_i - C_e)V}{W} \]

Where \( C_i \) and \( C_e \) are Ni(II) ion concentrations (mg/L) before and after adsorption, respectively, \( V \) is the volume of adsorbate in litre and \( m \) is the weight of the adsorbent in grams. The percentage of removal of Ni(II) ions was calculated using the following equation:

\[ \text{Removal (\%)} = \frac{(C_i - C_e)}{C_i} \times 100 \]

RESULT AND DISCUSSION

Effect of Contact time and initial concentration

The effect of contact time on percentage removal of Ni(II) ion for different initial concentration have been shown in figure 1. Adsorption of Ni(II) ion from the solution increases with the time and finally attains equilibrium at 60, 80 and 100 minutes for the initial concentrations 10, 15 and 20 mg/L respectively. The percentage of removal increased with the increase in contact time and decreased with the increase of initial concentration of the Ni(II) ion. However the amount of metal ion adsorbed on the adsorbent increased with the increase of initial concentration of the Ni(II) ion solution [22], which is depicted in figure 1 and given in table 4.
Effect of pH:

The pH of the adsorbate solutions has been identified as the most important parameter governing sorption of metal ion on different adsorbents. This is partly due to the fact that hydrogen ions themselves are a strong competing sorbate and partly to the fact that the solution pH influences the chemical speciation of metal ion. The effect of pH on adsorption of Ni(II) ion onto DRZAC is shown in Figure 2. As shown in this figure, at low pH values, the adsorption percentage is low due to the increase in positive charge density (protons) on the surface sites, resulting in electrostatic repulsion between the Ni(II) ion and positive charge on the surface. Electrostatic repulsion decreases with increasing pH because of the reduction of positive charge density on the sorption edges. In an alkaline medium, percentage of removal was not good. This may be due to the role of inter ionic attraction between the OH⁻ ion and the metal ion. According to Figure 2, the maximum adsorption of metal ion were found at pH 6.0, which is the pHzpc of the carbon where the surface of the adsorbent is neutral. Therefore, an optimum pH 6.0 was selected for further experiments [23].

Effect of Temperature:

It is well known that temperature plays an important role in the adsorption process. The metal ions removal increase rapidly from 303K, 313K and 323K this result suggests that the experimental
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Temperature had a greater effect on the adsorption process implying that the surface coverage increased at higher temperatures. This may be attributed to the increased penetration of metal ions inside micro pores or the creation of new active sites at higher temperatures. This indicates the endothermic nature of the controlled adsorption process. Similar result has been reported in the literature.

**Adsorption Kinetics:**

The adsorption kinetics shows the evolution of the adsorption capacity through time and it is necessary to identify the types of adsorption mechanism in a given system. Plots of different kinetic models applied were given in the Figure 3 and the kinetic parameters calculated were given in the Table 5. Between the first order and second order, second order kinetic model seems to best describe the above adsorption system as its R² values were very close to unity. Moreover, difference between qe (cal) and qe (exp) values of second order is small when compared to first order kinetic model. Statistically it is tested with the tool Sum of error squares (SSE%) [25]. The Δqe and SSE % values were given in the Table 5 from which it was concluded that second order kinetic model was more appropriate rather than first order kinetic model.

![Figure:3 Pseudo first and second order kinetics](image)

<table>
<thead>
<tr>
<th>Ci (mg/L)</th>
<th>Rate constants</th>
<th>qe(cal) mg/g</th>
<th>qe(exp) mg/g</th>
<th>Δqe</th>
<th>R²</th>
<th>(SSE %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k₁ (10⁻²) (min⁻¹)</td>
<td>k₂ (10⁻³) (gmg⁻¹ min⁻¹)</td>
<td>First Order</td>
<td>Second Order</td>
<td>First Order</td>
<td>Second Order</td>
</tr>
<tr>
<td>10</td>
<td>4.61</td>
<td>5.08</td>
<td>8.25</td>
<td>8.25</td>
<td>9.79</td>
<td>8.77</td>
</tr>
<tr>
<td>15</td>
<td>4.53</td>
<td>2.28</td>
<td>11.25</td>
<td>11.25</td>
<td>12.82</td>
<td>12.5</td>
</tr>
<tr>
<td>20</td>
<td>4.38</td>
<td>1.47</td>
<td>14.0</td>
<td>14.0</td>
<td>12.42</td>
<td>14.39</td>
</tr>
</tbody>
</table>

![Table:5 Kinetic parameters](image)
Adsorption Isotherm Studies:

The existence of equilibrium between the liquid and solid phase is well described by adsorption isotherms. Equilibrium data collected at different temperatures were fitted in Langmuir, Freundlich, Tempkin and Dubinin-Raduskevich adsorption isotherm models [24]. These isotherms are depicted in Figure 4.

$R^2$ values of these isotherm plots reveal that Freundlich isotherm well describes the present system that is the possibility of multilayer adsorption. $R^2$ value of Dubinin-Raduskevich isotherm is very low. In Dubinin-Raduskevich isotherm, the very low value of the constant ‘B’ related to the mean free energy of adsorption per mole of the adsorbate and the adsorption is physical in nature. Results of various isotherms are presented in Table 6.

<table>
<thead>
<tr>
<th>Isotherm Models</th>
<th>Temp (K)</th>
<th>Parameters and their results</th>
<th>$Q_0$ (mg/g)</th>
<th>$b$</th>
<th>$R_L$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>303</td>
<td></td>
<td>12.05</td>
<td>2.07</td>
<td>0.1768</td>
<td>0.989</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td></td>
<td>15.38</td>
<td>1.86</td>
<td>0.2351</td>
<td>0.989</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td></td>
<td>34.48</td>
<td>1.00</td>
<td>0.4348</td>
<td>0.996</td>
</tr>
<tr>
<td>Freundlich</td>
<td>303</td>
<td>$K_f$ (mg/g$^{-1}$)</td>
<td>9.75</td>
<td>2.91</td>
<td>0.999</td>
<td></td>
</tr>
<tr>
<td></td>
<td>313</td>
<td></td>
<td>11.12</td>
<td>2.67</td>
<td>0.999</td>
<td></td>
</tr>
<tr>
<td></td>
<td>323</td>
<td></td>
<td>13.0</td>
<td>2.37</td>
<td>0.999</td>
<td></td>
</tr>
<tr>
<td>Tempkin</td>
<td>303</td>
<td>$B_1$ (J/mol)</td>
<td>459.02</td>
<td>4.53</td>
<td>0.997</td>
<td></td>
</tr>
<tr>
<td></td>
<td>313</td>
<td></td>
<td>394.22</td>
<td>4.48</td>
<td>0.994</td>
<td></td>
</tr>
<tr>
<td></td>
<td>323</td>
<td></td>
<td>305.79</td>
<td>3.77</td>
<td>0.991</td>
<td></td>
</tr>
<tr>
<td>Dubinin Raduskevich</td>
<td>303</td>
<td>$q_D$ (mg/g)</td>
<td>19.95</td>
<td>6.86</td>
<td>0.0013</td>
<td>0.924</td>
</tr>
<tr>
<td></td>
<td>313</td>
<td></td>
<td>22.39</td>
<td>5.66</td>
<td>0.0025</td>
<td>0.941</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td></td>
<td>26.91</td>
<td>3.16</td>
<td>0.0038</td>
<td>0.992</td>
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</table>
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Analysis of Isotherm

Langmuir isotherm

In the present study $Q_0$ value ranges from 12.05 to 34.48, as the temperature increases the monolayer adsorption capacity also found to increase. This kind of results were obtained in various similar studies [25]. The separation factor $R_L$ values were in between 0 to 1 which indicates the favourable adsorption. $R^2$ values of isotherm ranged between 0.989 to 0.996.

Freundlich isotherm

The values of $n$ were between 1 and 10 which indicates cooperative adsorption [26]. The $R^2$ values were close to unity which revealed the good fitting into freundlich isotherm.

Temkin Isotherm

$B_1$-Temkin constant is related to the heat of adsorption. This $B_1$ value increased from 305.79 to 459.02 as the temperature of adsorption increased. The temkin parameter $K_T$ value give an idea about nature of adsorption [27]. In our present study the $K_T$ values ranged from 3.77 to 4.53 which indicate the adsorption is physical nature. The $R^2$ value was low compared to freundlich isotherm.
Dubinin-Raduskevich

The activation energy $E$ value ranges from 3.16 to 6.86 and $B$ value from 0.0013 to 0.0038 indicates the physisorption. The $R^2$ value was very low when compared to other three isotherms.

In general the fitting data in isotherm equation were in the following order: Freundlich>Temkin>Langmuir > Dubinin-Raduskevich.

Conclusion

The present investigation shows that DRZAC is an effective adsorbent for the removal of Ni(II) ion from aqueous solutions. From the kinetic studies, it is observed that adsorption of Ni(II) ion is very rapid in the initial stage and decreases while approaching equilibrium. The equilibrium time increases with initial concentration. The percentage removal of Ni(II) ion increases with the increase in adsorbent dosage and decreases with increase in initial concentration. Experimental results are in good agreement with Freundlich isotherm when compared to other three isotherm models. Adsorption of Ni(II) ion obeys pseudo-second order equation with good correlation.

References

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