Kinetic and Equilibrium Studies on Removal of Nickel Ions onto Pomegranate Peel

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Abstract
In this work, pomegranate peel (PGP) was investigated as adsorbent for removal of nickel ions from aqueous solution. It was found that maximum adsorption occur at PH7. Their equilibrium data were fitted with the Freundich and Langmuir isotherms. The adsorption kinetics data were best fitted with the pseudo–second order.


Introduction
Industrial, agricultural and domestic waste pollute water bodies with heavy metals, which reach tissues through the food chain. The toxicity of heavy metals to aquatic organisms has been a subject of interest to biologist for many years. Adsorption of trace metals onto natural particulate matter can play an important role in determining trace metal speciation in many aquatic systems [1–4]. Among different types of pollution, the industrial waste constitutes the major source of various kinds of metal pollution in natural water [5]. The important toxic metals, i.e. Cd, Zn, Cr, Pb and Cu finds its way to the water bodies through wastewater from such industries as metal-plating industries of cadmium, nickel batteries, pigment, stabilizers, alloys [6].

Nickel is used in plating plants and is present in their wastewater [7]. About 40% of the nickel produced are used in steel factories, Ni batteries and in the production of some alloys[8]. Manifestation of dermatitis in some workers engaged in electroplating, polishing, paints and pigments may be attributed to nickel poisoning.

The conventional methods for heavy metal removal from wastewater includes reduction, precipitation, ion exchange, reaction with silica, electrochemical reduction, evaporation, reverse osmosis and direct precipitation. Most of these methods involve high capital cost with recurring expenses, which are not suitable for small-scale industries. Studies on treatment of effluents bearing heavy metals have revealed adsorption to be a highly effective, cheap and easy method among the physicochemical treatment processes. Owing to the high cost and difficult procurement of activated carbon, efforts are being directed towards finding efficient and low-cost materials. Removal of nickel by adsorption using solid residue form olive mill products [9], Mangifera indica seed shell [10], humic acid type purifying agents [11], coal-based adsorbents [12], burned clay and root [13], furnace gas cleaning sludge [14], hydrous oxides of iron(II) [15] have been reported. The aim of this work is to study the ability of pomegranate peel to clean water from nickel, the pH of maximum adsorption and the effect of PGP concentration as well as the kinetic model that fit to the experimental data and the best isotherm that fitted to the experimental data will be investigated.

Experimental
Biomass
Pomegranate peel (PGP) was collected in the Baghdad district which was dried, then milled and sieved to particle size of 300-500 μm. The PGP was shake with distilled water for overnight then filtered, this process was repeated about ten times or until we get rid off all colored or soluble materials, then filtered and dried in an air oven at 80 °C for overnight.

Preparation of Nickel solution and analysis
A stock solution of Ni(II), 500 mg/L, was obtained by dissolving 2.272g of Ni(NO₃)₂.H₂O in 1L of deionized water, and the solution was used for further experimental solution preparation. The pH values were adjusted with 0.1 M HNO₃ or 0.1M NaOH. Analytical grade reagents were used throughout this study. The Ni(II) content in the
sorption solutions was determined by atomic absorption spectrophotometer type (phoenix-986).

**Batch adsorption studies**

*Effect of pH*

The initial pH values were adjusted to 5.0, 6.0, 7.0 and 8.0 with 0.1M HNO₃ and 0.1 M NaOH. The effect of initial pH on the Nickel ions adsorption onto PGP was determined using 0.1 g of adsorbent in 50 mL of Ni solution of 20 mg/L at 30°C for 90 minutes and 140 rpm agitation. The amount of Ni(II) adsorbed onto the PGP, qₑ mg/g, was calculated using the following equation:

\[ qₑ = (Cᵢ – Cₑ)V/W \] .................................(1)

where \( Cᵢ \) and \( Cₑ \) are the initial and equilibrium liquid phase concentration of Ni(II) respectively. \( V \) is the volume of the solution (L) and \( W \) is the weight of the PGP used (g).

The Nickel percent removal (R%) was calculated using the following equation:

\[ R% = \frac{Cᵢ – Cₑ}{Cᵢ} \times 100 \] .................................(2)

*Kinetic studies*

Kinetic studies were carried out at solution pH 7.0. Nickel solution of 20 mg/L agitated at 30 and 40°C. The samples were collected from duplicate flasks at different time intervals, filtered by filter paper, the filtrate was analyzed for residual Ni(II) concentration using atomic absorption spectrophotometer.

**Result and Discussion**

*Effect of pH on Nickel(II) Adsorption*

pH is an important parameter influencing heavy metal adsorption from aqueous solutions. It affects both the surface charge of adsorbent and the degree of ionization of the heavy metal in solution [16]. Plot of pH versus quantity of metal ion adsorbed on gram of adsorbent \( qₑ \) was shown in Fig.(1). The optimum pH was found to be pH 7. The maximum removal efficiency was 84.5%. At pH values higher than 6.0, insoluble Nickel hydroxide start precipitating from the solutions making true sorption studies impossible [17].

![Fig.(1) pH versus quantity of metal ion (Ni⁺²).](image)

*Effect of adsorbent concentration*

The effect of PGP dosage on the adsorption of Ni(II) from aqueous solutions was investigated using four different adsorbent concentrations. The extent of adsorption is proportional to specific area, which can be defined as that portion of the total area that is available for adsorption. Concentrations of PGP were varied from 2 to 16 g/L. The results are presented in Fig.(2) which indicate that the \( qₑ \) decreased with increasing PGP concentration, while the R% increases with increasing PGP concentration. This result may be attributed to the fact that the higher sorbent doses provide the more sorbent surface area and pores volume which will be available
Adsorption kinetic

The study of adsorption kinetic describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of Ni(II) adsorption on the PGP were analyzed using pseudo first-order and pseudo second-order. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients ($R^2$).
and the coincidence between the experimental and calculated $q_e$. A relatively high ($R^2$) value indicates that the model successfully describes the kinetics of Ni(II) adsorption.

The pseudo first-order equation [19] is generally expressed in it linear form as follows:

$$\log (q_e - q_t) = \log q_e - (k_1 / 2.303) t \text{ ...............}(3)$$

The linear form of pseudo second-order adsorption kinetic equation is expressed as [20]:

$$t / q_t = 1 / k_2 q_e^2 + 1 / q_e (t) \text{ .........................}(4)$$

Where $k_1$ and $k_2$ are the rate constants of Pseudo-first-order and Pseudo-second-order kinetics, $q_e$ and $q_t$ are the adsorption capacity at equilibrium and time $t$ respectively. From the plot of first-order kinetic, $\log(q_e-q_t)$ versus time, the rate constants and the adsorption capacity $q_e$ can be calculated which was presented in Table (1). It is obvious from the correlation constants and the calculated $q_e$ that the adsorption process did not follow the first–order kinetic. When the experimental data were applied to the second-order kinetic it was obvious from Fig.(4) and Table (1) that the calculated $q_e$ in good agreement with experimental one, and the correlation coefficient was higher than that of the first order kinetic.

**Table (1)**

<table>
<thead>
<tr>
<th>Kinetic parameters of 1st-order and 2nd-order models at 40&amp;50 °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pseudo-first-order kinetic</strong></td>
</tr>
<tr>
<td>$q_e$ (exp.)</td>
</tr>
<tr>
<td>$q_e$ (cal.)</td>
</tr>
<tr>
<td>$k_1$</td>
</tr>
<tr>
<td>$R^2$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Pseudo-second-order kinetic</strong></th>
<th><strong>40°C</strong></th>
<th><strong>50°C</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_e$ (cal.)</td>
<td>7.496</td>
<td>8.562</td>
</tr>
<tr>
<td>$k_2$</td>
<td>0.028</td>
<td>0.011</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9995</td>
<td>0.9877</td>
</tr>
</tbody>
</table>

**Fig.(4)** 2nd-order kinetic at 40 °C.
Adsorption isotherms

Adsorption isotherms are essential for the description of how metal ion concentration will interact with the adsorbent surface and are useful to optimize the adsorbent for the removal of Ni(II) ions. Isotherms are one of the most important data to understand the mechanism of the sorption. Several isotherm equations are available and two important isotherms are selected in this study. They are namely the Langmuir, and Freundlich models.

The **Langmuir equation** equation is valid for monolayer adsorption onto a completely homogenous surface with a finite number of identical sites and with negligible interaction between adsorbed molecules, the linear form can be written as follow [21]:

\[
\frac{C_e}{q_e} = \left( \frac{1}{Q_m b} \right) + \left( \frac{1}{Q_m} \right) C_e
\]

Where \( Q_m \) is the theoretical maximum adsorption capacity (mg g\(^{-1}\)), \( b \) is the Langmuir adsorption constant (L mg\(^{-1}\)). Plot of \( C_e/q_e \) versus \( C_e \) is presented in Fig. (5). The values of Langmuir isotherm constants and correlation coefficients are found in Table (2). The correlation coefficients of the isotherm were found to be linear over the whole concentration indicating that the Langmuir isotherm is applicable. The \( Q_m \) value is presented in table 2 and found to be 26.8 mg/g.

The **Freundlich isotherm** [22] is derived by assuming a heterogenous surface with a non-uniform distribution of heat of sorption over the surface, the linear form is:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

Where \( K_F \) (L mg\(^{-1}\)) and \( n \) are isotherm constants indicate the capacity and intensity of the adsorption respectively. The linear plot of \( \log q_e \) versus \( \log C_e \) indicate that the adsorption of Ni(II) onto PGP also follows Freundlich equation Fig.(6), the Freundlich constants and correlation coefficients are listed in Table (2). The value of \( 1/n \) was found to lie between zero and one, indicating that the Ni(II) is favourably adsorbed by PGP at the studied temperature[23]. On the other hand, the value of \( n \) are higher than one indicating that the adsorption may be physical [24].

**Table (2)**

<table>
<thead>
<tr>
<th>Isotherms</th>
<th>Constant of adsorption Ni(^{2+})onto PGP at 30 °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir</strong></td>
<td></td>
</tr>
<tr>
<td>( Q_{max} )</td>
<td>26.8</td>
</tr>
<tr>
<td>( b )</td>
<td>0.103</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.9906</td>
</tr>
<tr>
<td><strong>Freundlich</strong></td>
<td></td>
</tr>
<tr>
<td>( K_F )</td>
<td>5.55</td>
</tr>
<tr>
<td>( n )</td>
<td>2.833</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.9413</td>
</tr>
</tbody>
</table>

**Fig.(5) Adsorption isotherm from Langmuir equation.**
Fig. (6) Adsorption isotherm from Freundlich equation at 30 °C.

References


الخلاصة
في هذا البحث تم استخدام قشور الرمان كمادة امتزاز لازالة ايونات النيكل (II) من محليل المائي، وقد وجد ان أفضل امتزاز حصل عند pH7. قيم التوازن الحراري تتفق مع معادلات فريندش ولينكماير، حيث ان دراسة حركية الامتزاز تتفق مع مرتبة التفاعل الثانية الكاذبة.