Orange Peels as a Low Cost Adsorbent for the Removal of Pb(II) from Aqueous Solution: Equilibrium and Kinetic Studies

Atif S. Alzaydien

Department of Chemistry, Mutah University, P.O. Box 7, Jordan

Abstract: In this study, the potential of low-cost agricultural by product, namely, orange peel in the removal of lead(II) ions from aqueous solutions was investigated. Adsorption of lead(II) ions onto a powder prepared from orange peel was investigated with the variation in the parameters of pH, contact time, the amount of adsorbent and lead(II) ions concentration at ambient temperature. Four kinetic models are the pseudo-first-order, pseudo-second-order, Elowich and intraparticle diffusion equations, were selected to interpret the adsorption data. Kinetic parameters such as the rate constants, equilibrium adsorption capacities and related correlation coefficients, for each kinetic model were calculated and discussed. The linear Langmuir and Freundlich models were applied to describe equilibrium isotherms and both models fitted well. The monolayer adsorption capacity was found as 21.1 mg g⁻¹ at pH 6 and 20°C. The dimensionless separation factor (Rₛ) has shown that orange peel can be used for removal of Pb(II) from aqueous solutions. The negative free energy of adsorption indicated that the adsorption of lead(II) ions onto orange peel was feasible and spontaneous. The sorption capacity of the orange peel is comparable to the other available adsorbents and it is quite cheaper.

Key words: Pb(II) · Orange peel · Kinetics · Diffusion · Adsorption isotherm

INTRODUCTION

Ecotoxicological effects of heavy metals are a major concern nowadays due to their accumulation through food chain and persistence in nature [1]. Since levels of heavy metals in the environment have increased because of the industrial pollution [2,3], the elimination of such ions from water is essential to protect public health. In addition, these toxic elements can seriously affect plants and animals, causing a large number of afflictions.

It is well documented that lead is one of contaminants of industrial wastewaters and its pollution exists in the wastewater of many industries. The main industrial sources for lead include metal finishing, mining and mineral processes and oil refining industries as well as motor vehicles use leaded petrol [4].

Lead poisoning in human causes severe damage to the kidney, nervous system, reproductive system, liver and brain. Severe exposure to lead has been associated with sterility, abortion, stillbirths and neonatal deaths [5,6]. The permissible level for lead in drinking water is 0.05 mg L⁻¹ according to the World Health Organization [7]. Therefore, a very low concentration of lead in water is very toxic. Hence, the safe and effective disposal of wastewater containing heavy metals is always a challenge to industrialists and environmentalists.

Conventional methods for removing metals from industrial effluents include chemical precipitation, coagulation, solvent extraction, electrolytic processes, membrane separation, ion-exchange [8-11], reverse osmosis, ultra filtration, biological systems [12,13] and adsorption [14-20]. Conventional technologies for the removal of heavy metal are often neither effective nor economical. Among the physico-chemical treatment process adsorption is found to be highly effective, cheap and easy to adapt. Activated carbon in most cases has been used as an adsorbent for reclamation of municipal and industrial wastewater for almost last few decades [21-24]. But the high cost of activated carbon has inspired the investigators especially in developing countries to search for suitable low-cost adsorbents. As a result, recent research has focused on the development of cost effective alternatives using various natural sources and

Corresponding Author: Atif S. Alzaydien, Department of Chemistry, Mutah University, P.O. Box 7, Jordan
ndustrial wastes [25-33]. In this setting, the use of low-cost agricultural materials, waste and residues for recovering heavy metals from contaminated industrial effluent has emerged as a potential alternative method to high cost adsorbents. For example, some of the non-conventional low cost adsorbents recently used for the removal of heavy metals are hazelnut shell, apple residues, banana pith, tree leaves, mandarin peels, rice polish, seeds of Capsicum annuum and Cerba pentandra hulls [34-42].

In the present study, adsorption of lead(II) ions onto orange peel (OP), a typical agricultural byproduct, has been investigated systematically with the variation in the parameters of pH, sorbent dosage, contact time and the initial concentration of adsorbate. Langmuir and Freundlich isotherms were used to analyze the equilibrium data. Kinetic and thermodynamic parameters were also calculated to describe the adsorption mechanism.

**EXPERIMENTAL**

**Orange Peel:** The orange peel (OP) was obtained from a local market in the south of Jordan. The orange peel was cut into small pieces using scissors. Then OP was dried at 100°C for 24 h using hot air oven. The dried materials were then ground using a domestic Sunneet mixer. The ground OP were then sieved through to get uniform geometrical size for use. The resulting powder was washed with doubly distilled water and then dried in an oven at 333 K for 24 h. Powdered material containing particle sizes = 0.6 nm was used for the adsorption studies.

**Characterization of the Biosorbent**

**Infrared Measurements:** Qualitative analyses of the main functional groups involved in metal adsorption were performed using a Fourier transformed infrared spectrometer (Mattson 5000). The experiment was carried out using Kbr discs to prepare the OP sample and the spectral range varied from 4000 to 400 cm⁻¹.

**SEM Studies:** The surface images of orange peel before adsorption process were captured by scanning electron microscopy (SEM). The SEM used was a Philips XL30.

**Determination of the Point of Zero Charge:** The point of zero change (PZC) for the OP was determined by the following procedure: 100 mL of deionized water was added to an Erlenmeyer flask, which was then capped with cotton. The deionized water was heated until boiling for 20 min to eliminate the CO₂ dissolved in the water. The CO₂-free water was cooled down as soon as possible and the flask was immediately capped. On the other hand, 0.5 g of OP was weighed and placed in a 25 mL Erlenmeyer flask to which 10 mL of CO₂-free water was added. The flask was sealed with a rubber stopper and left in continuous agitation for 48 h at 25°C. Then the solution pH was measured and this value is the point of zero charge. This method has been used satisfactorily by Leon y Leon and Radovic [43] and Moreno-Castilla et al. [44].

**Surface Area:** OP surface area was measured experimentally using acetic acid adsorption [45,46], assuming monolayer coverage, according to Langmuir isotherms. Accurately weighed 1.00 g samples of OP, taken from the same particle size range, were placed into each of the seven pre-treated bottles. To each bottle was then added an acetic acid solution (100 mL), with concentrations ranging from 0.015 to 0.15 M. The stoppered, thermostated (25°C) mixtures were then periodically shaken for 60 min to reach equilibrium. Each mixture was then filtered and titrated with NaOH(aq) (0.1 M), using phenolphthalein indicator. The total number of moles of acetic acid adsorbed per gram of carbon (N) was then measured for different acetic acid concentrations at equilibrium (Ce). Plots of Ce/N vs. Ce were then constructed, according to the equation Ce/N = Ce/Nm + 1/k,Nm and the slope showed the number of acetic acid moles adsorbed per gram OP assuming a monolayer coverage (Nm). The total surface area g⁻¹ AC was then calculated knowing the area for the acetic acid molecule as 2.1x10⁻⁹ m² molecule⁻¹.

**Adsorption Studies:** Biosorption experiments were carried out in a thermostatic shaker at 180 rpm and at an ambient temperature (20±2°C) using 250 mL shaking flasks containing 100 mL of different concentrations and initial pH values of Pb(II) solutions, prepared from reagent grade salt Pb(NO₃)₂ (Merck). The initial pH values of the solutions were previously adjusted with 0.1 M HNO₃ or NaOH and measured using a hand held pH meters (315i/SET). The sorbent (0.2-1.0 g) was added to each flask and then the flasks were sealed up to prevent change of volume of the solution during the experiments. After shaking the flasks for predetermined time intervals, the samples were withdrawn from the flasks and filtered through a Whatman filter paper. The filtrate was analyzed by AAS (Perkin Elmer Analyst 300). The amounts of Pb(II) sorbed by the biomass were calculated using the following equation:
where \( Q \) (mg g\(^{-1}\)) is the amount of Pb(II) sorbed by biomass, \( C_i \) and \( C_e \) (mg L\(^{-1}\)) are the initial and equilibrium liquid-phase concentration of Pb(II), respectively, \( V \) (L) the initial volume of Pb(II) solution and \( M \) (g) the weight of the biomass.

The percent adsorption (%) was calculated using the following equation:

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

The effect of each parameter was studied by fixing the values of other parameters. The experiments were conducted in duplicate and the negative controls (with no sorbent) were simultaneously carried out to ensure that sorption was by OP biomass and not by the container.

**RESULTS AND DISCUSSION**

**Characterization of the Biosorbent:** In order to determine which functional groups were responsible for metal uptake, an FTIR analysis in solid phase was performed on the biomass prepared in a KBr disk. As shown in Fig. 1, the broad, intense absorption peaks around 3433 cm\(^{-1}\) are indicative of the existence of bounded hydroxyl groups. The peaks around 1643 cm\(^{-1}\) are due to the C-C stretching that can be attributed to the aromatic C-C bond, while the intense band at 1064 cm\(^{-1}\) can be assigned to the C-O of alcohols and carboxylic acids.

Based on analysis of the images of OP taken by SEM (Fig. 2), highly heterogeneous pores within orange peel particles were observed.

The point of zero charge (PZC) of an adsorbent is a very important characteristic that determines the pH at which the adsorbent surface has net electrical neutrality. At this value, the acidic or basic functional groups no longer contribute to the pH of the solution. Cations adsorption will be more favourable at pH value higher than PZC. The value of PZC found for OP is 4.4. The surface area for OP obtained was 17 m\(^2\) g\(^{-1}\).

**Effect of pH:** The pH of an aqueous solution is an important controlling parameter in the process of adsorption. Solution pH affects both aqueous chemistry and surface binding sites of the adsorbent. Change of pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of adsorption process.

Figure 3 shows the pH dependence of Pb (II) adsorption on OP. The adsorption of Pb (II) is strongly dependent on pH values, which affect the surface charge of the adsorbent and the relative distribution of Pb (II) species in aqueous solution [47]. The percent removal of Pb (II) by OP was increased with increase in pH, the maximum removal of lead appeared at pH = 5.9. The PZC of OP was found to be 4.4. Above this value the surface of OP is negatively charged. This will enhance the adsorption of Pb (II) by electrostatic interaction. A similar theory was proposed by several earlier workers for metal adsorption on different adsorbents [48,49]. From other side, Fig. 4 gives the relative distribution of Pb(II) species in the aqueous solution as a function of pH at 298 K and in 0.01 M NaNO\(_3\) solutions. As can be seen from Fig. 4, at pH < 6 the free ion Pb\(^{2+}\) is the predominating species. At pH < 6, positively charged metal ions are attracted to the surface of OP by coulombic forces [50]. In alkaline medium, lead tends to hydrolyze and precipitate instead of adsorption and adsorbent was deteriorated with accumulation of metal ions, making true adsorption studies impossible [51-53]. Finally, the strong pH dependent adsorption of Pb(II) on OP suggests that surface complexation of Pb(II) with carboxyl and hydroxyl functional groups contributes mainly to the adsorption of Pb(II) onto OP [54].

**Effect of OP Dose:** The adsorption of Pb(II) on OP was studied by changing the quantity of adsorbent (0.2, 0.4, 0.6, 0.8 and 1.0 g/100 mL) in the test solution while keeping the initial Pb(II) concentration (200 mg L\(^{-1}\)), temperature (20±2°C) and pH (6.0) constant at contact times for 120 min.

The adsorption of Pb(II) on OP as a function of OP dose is shown in Fig. 5. The adsorption percentage of Pb(II) increases with increasing OP dose. The adsorption percentage of Pb(II) increased from 66 to 89% for OP dose of 0.2 and 1.0 g. This trend is expected because as the adsorbent dose increases the number of adsorbent particles increases and thus more Pb(II) is attached to their surfaces. The increase of Pb(II) adsorption is easily explained by an increase in the surface area of OP samples. With increasing surface area, the available sites for binding Pb(II) increases.
Fig. 1: FTIR spectrum of orange peel

Fig. 2: SEM images for orange peel

Fig. 3: Variation in adsorption of Pb (II) onto OP as a function of pH initial Pb (II) concentration=200 mg/l, T= 20±2 °C
Fig. 4: Distribution of Pb (II) species as a function of pH

Fig. 5: Variation in adsorption of Pb (II) onto OP as a function of OP dose initial Pb (II) concentration=200 mg/l, T= 20±2 °C, pH = 6.0

Fig. 6: Variation in adsorption of Pb (II) onto OP as a function of initial Pb (II) concentration, T= 20±2 °C, pH = 6.0

Fig. 7: Plot of the amount of Pb(II) adsorbed versus time, initial Pb (II) concentration=100 mg/l, T = 20±2 °C, pH = 6.0
and thereby enhances the adsorption of Pb(II) from solution to solid [55].

**Effect of Initial Pb(II) Concentration:** Effect of initial Pb(II) concentration on adsorption of lead by OP is presented in Fig. 6. The percent removal of Pb(II) increased from 36 to 92% as the initial Pb(II) concentration increased from 50 to 200 mg L\(^{-1}\). The increase in adsorption capacity with increasing copper concentration could be due to higher probability of collision between Cu(II) ions and adsorbent surface [56].

The diffusion of Pb(II) ions through the solution to the surface of adsorbents is affected by the lead concentration, since agitation speed is constant. An increase of the lead concentration accelerates the diffusion of Pb(II) from the lead solution onto adsorbent active sites due to the increase in the driving force of the concentration gradient [57,58].

**Effect of Contact Time:** The adsorption data of lead versus contact time is presented in Fig. 7. The sorbate concentrations in solution were determined at different times from initial solutions of 100 mg L\(^{-1}\) and a sorbent dosage of 1.0 g/100 mL. All the experiments conducted here were at pH \(~ 6\). The plot representing adsorption of lead on OP, visualize three distinct phases: the first phase indicates the instantaneous sorption of the Pb(II) within 10 min of contact time, the second one shows a gradual equilibrium and the third one indicates the final equilibrium. The uptake of lead on OP reaches equilibrium in 85 min with 84% of metal removal. These changes in lead uptake may be due to the fact that all adsorbent sites were vacant and the solute concentration was high at the beginning. After that, only a very low increase in the lead uptake was observed because there are few surface active sites on the orange peel. The quick equilibrium time is due to the small particle size because the effective surface area is high for small particles.

**Adsorption Kinetics:** The prediction of kinetics is necessary for the design of adsorption systems. The kinetic parameter, which is helpful for the prediction of adsorption rate, gives important information for designing and modeling the processes.

Four kinetic models, i.e. the Lagergren-first-order, pseudo-second-order, Elovich and the intraparticle diffusion equations, were considered to interpret the time dependent experimental data.

The Lagergren-first-order rate expression [59] is given as:

\[
\ln (Q_t - Q_e) = \ln Q_e - k_1 t
\]

(3)

The pseudo-second-order kinetic model equation [60] is given as:

\[
uQ_t = \frac{1}{k_2Q_e^2} + \frac{t}{Q_e}
\]

(4)

Half-adsorption time, \(t_{1/2}\), is defined as the time required for the adsorption to take up half as much OP as its equilibrium value. This time is often used as a measure of the adsorption rate

\[t_{1/2} = \frac{1}{k_2Q_e}\]

(5)

The Elovich equation is given as follows [61]:

\[
dQ_t/dt = \alpha \exp (-\beta Q_t)
\]

(6)

where \(\alpha\) is the initial sorption rate (mol/g min) and \(\beta\) is the desorption constant (g/mol). To simplify the Elovich equation, it is assumed that \(\alpha \beta t << 1\) and by applying the boundary conditions \(Q = 0\) at \(t = 0\), this equation becomes

\[Q_t = \beta \ln(\alpha \beta) + \beta \ln t\]

(7)

Thus, the constants can be obtained from the slope and intercept of a straight line plot of \(Q_t\) versus \(\ln t\).

The intraparticle diffusion equation [64] can be written by the following:

\[Q_t = k_i t^{1/2} + C\]

(8)

where \(Q_e\) and \(Q_t\) are the amounts of lead(II) ions adsorbed on the adsorbent at equilibrium and at various times \(t\) (mg g\(^{-1}\)), \(k_i\) is the rate constant of the Lagergren-first-order model for the adsorption process (min\(^{-1}\)); \(Q_e\) is the maximum adsorption capacity (mg g\(^{-1}\)) and \(k_1\) is the rate constant for the pseudo-second-order model (gm g\(^{-1}\) min\(^{-1}\)); \(\alpha\) is the initial adsorption rate (mg g\(^{-1}\) min\(^{-1}\)) and \(\beta\) is the desorption constant (gm g\(^{-1}\)) for Elovich model; \(C\) is the intercept and \(k_i\) is the intraparticle diffusion rate constant (mg g\(^{-1}\) min\(^{-1/2}\)) for the intraparticle diffusion model. The straight-line plots of \(ln (Q_t - Q_e)\) versus \(t\) for the Lagergren-first-order model, \(t/Q_e\) against \(t\) for the pseudo-second-order model and the
plots of $Q$, versus $\ln(t)$ (Fig. 10) for the Elovich model for the adsorption of lead(II) ions onto OP have been drawn to obtain the rate parameters.

The rates of adsorption were first tested with the pseudo first order mechanism of Lagergren by plotting $\ln (Q_i/Q)$ vs time (Fig. 8). This plot has good linearity ($R^2 = 0.97$) and the first order rate constant obtained from this plot has value of 0.0185 min$^{-1}$. Good linearity of the Lagergren plots is no guarantee that the interactions will follow first order kinetics.

In order to find a more reliable description of the kinetics, second order kinetic equation was applied to the adsorption data by plotting $t/Q$ against $t$ (Fig. 9). The plots are now of better linearity ($R^2 = 0.9944$) and the second order rate constant, $k_2$, has value of 0.0313 g mg$^{-1}$ min$^{-1}$.

Elovich equation is also very often used to interpret the kinetics of adsorption. Elovich equation has been found useful in describing predominantly chemical adsorption on highly heterogeneous adsorbents, but no definite mechanism for adsorbate-adsorbent interaction could be worked out. Plot of $Q$ vs $\ln t$ yielded very good linearity (Fig. 10) with correlation coefficient of 0.98. The Elovich constants, $\alpha$ and $\beta$, had values of 5.223 mg g$^{-1}$ min$^{-1}$ and 1.2702 mg (g min) respectively. The constants depended significantly on the amount of adsorbent with the adsorption rate constant, $\alpha$, being much more sensitive. Since $\alpha$ represents the initial rate of adsorption, the results indicate that the rate could be enhanced many times by increasing the adsorbent amount, i.e. by providing a large surface area for interaction.

Diffusion from the solid-liquid interface to the interior of the solid particles plays a very important role. The Lagergren first-order, pseudo-second-order and Elovich models cannot identify the diffusion mechanism and the results were then subjected to analyze by the intraparticle diffusion model. If the plot of uptake, $Q_i$ versus square root of time, $t^{1/2}$, passes through the origin then the intraparticle diffusion will be the sole rate-controlling process [65, 66]. The plot of $q$ vs $t^{1/2}$ (Fig. 11) was linear with regression coefficient of $\sim 0.94$. The intraparticle diffusion rate constant, $k_{iii}$, has value of 0.4354 mg g$^{-1}$ min$^{-1/2}$. However, the plot did not pass through the origin. This indicates that although the intraparticle diffusion was involved in the adsorption process, it was not only the rate-controlling step for the whole adsorption process [67].

The kinetic parameters of lead(II) ions onto OP were calculated from these plots and are given in Table 1. It can be easily seen from Table 1, the correlation coefficients ($R^2$), for the Lagergren-first-order and the Elovich kinetic models are lower than that of the pseudo-second-order kinetic model. This is probable that the adsorption system is not followed by the Lagergren-first-order or Elovich kinetic models, it is fitted the pseudo-second-order kinetic model. The calculated $Q_i$ values agree with experimental $Q_i$ values and also, the correlation coefficients for the pseudo-second-order kinetic plots were very high than the $R^2$ values of the other kinetic models.

**Sorption Isotherms:** In a two-component system (sorbed and solution), at equilibrium there is always a defined distribution of the solute between the liquid and the solid phase, which can generally be expressed by one or more isotherms [68]. In the present study, the equilibrium sorption of Pb(II) onto OP was studied in concentration range 50-250 mg l$^{-1}$ at room temperature.

There are several isotherm equations available for analyzing experimental sorption equilibrium data. In the present study experimental data were fitted to well-known and widely applied isotherm models of Langmuir [69] and Freundlich [70]. The linear equations are given below:

\[
\text{Langmuir} : Q_i = \frac{1}{K_L} + \left( \frac{1}{K_L} \right) C_e \\
\text{Freundlich} : \ln Q_i = \ln K_F + \left( \frac{1}{n_F} \right) \ln C_e
\]

Where, $C_i$ (mg L$^{-1}$) and $Q_i$ (mg g$^{-1}$) are the liquid phase concentration and solid phase concentration of adsorbate at equilibrium, respectively; $K_L$ (L$^{-1}$ mg) and $a_i$ (L$^{-1}$ mg) are the Langmuir isotherm constants; $K_F$ is the Freundlich constant (L$^{-1}$ mg) and $1/n_F$ is the heterogeneity factor.

The Freundlich isotherm, the earliest known relationship describing the adsorption process, is an empirical equation employed to describe heterogeneous systems. Its application suggests that adsorption energy exponentially decreases on completion of the sorptional
Fig. 8: Lagergren-first-order kinetic plot for the adsorption of Pb(II) onto OP initial Pb (II) concentration = 100 mg/l, OP dose 1.0g, pH 6.0, at 20±2°C

\[ y = -0.0185x + 0.9334 \]
\[ R^2 = 0.9944 \]

![Lagergren-first-order kinetic plot](image)

Fig. 9: Pseudo-second-order kinetic plot for the adsorption of Pb(II) onto OP initial Pb (II) concentration=100 mg/l, OP dose 1.0g, pH 6.0, at 20±2°C

\[ y = 0.1114x + 2.3999 \]
\[ R^2 = 0.9817 \]

![Pseudo-second-order kinetic plot](image)

Fig. 10: Plot of Elovich equation for adsorption of Pb(II) onto OP: initial Pb(II) concentration 100 mg/L, OP dose 1.0g, pH 6.0, at 22°C

\[ y = -0.0185x + 1.3928 \]
\[ R^2 = 0.9706 \]

![Elovich equation plot](image)
Fig. 11: Intraparticle diffusion kinetics for adsorption of Pb(II) onto OP: initial concentration 100 mg/L, OP dose 1.0 g, pH 6.0, at 22°C

Fig. 12: Langmuir plots for the adsorption of Pb(II) onto OP

Fig. 13: Freundlich isotherm for Pb(II) uptake by OP
Table 2: Summary of the Langmuir and Freundlich isotherm constants, separation factor (R_L) and linear (R^2) regression coefficients

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>R^2</th>
<th>Coefficient L^-1</th>
<th>R_L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>Q_max = 21.1 (mg g^-1), K_L = 0.120 (L g^-1), a_L = 0.058 (L mg^-1)</td>
<td>0.9022</td>
<td>50 0.256</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>100 0.147</td>
<td>150 0.103</td>
<td>200 0.079</td>
</tr>
<tr>
<td>Freundlich</td>
<td>K_0 = 2.36 (L g^-1), n_0 = 2.01</td>
<td>0.9608</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Comparison of adsorption capacity of Orange peel with various adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorption capacity (mg g^-1)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon prepared from coconut shell</td>
<td>12.64</td>
<td>[72]</td>
</tr>
<tr>
<td>Rice husk ash</td>
<td>10.86</td>
<td>[73]</td>
</tr>
<tr>
<td>Biosorbent (Cephalosporum aphidicola)</td>
<td>9.24</td>
<td>[74]</td>
</tr>
<tr>
<td>Turkish sidette</td>
<td>10.32</td>
<td>[75]</td>
</tr>
<tr>
<td>Fly ash</td>
<td>15.08</td>
<td></td>
</tr>
<tr>
<td>Oryza sativa L. husk</td>
<td>8.6</td>
<td>[76]</td>
</tr>
<tr>
<td>Corn</td>
<td>18.9</td>
<td>[77]</td>
</tr>
<tr>
<td>Bituminous coal</td>
<td>8.89</td>
<td>[78]</td>
</tr>
<tr>
<td>Nile rose plant power (water hyacinth)</td>
<td>27.4</td>
<td>[79]</td>
</tr>
<tr>
<td>Bone powder</td>
<td>55.3</td>
<td>[80]</td>
</tr>
<tr>
<td>Orange peel</td>
<td>21.1</td>
<td>Present study</td>
</tr>
</tbody>
</table>

centres of an adsorbent. The Langmuir equation is applicable to homogeneous adsorption, where the adsorption of each molecule onto the surface has equal adsorption activation energy.

By plotting C_s/Q_e against C_s (Fig. 12), it was possible to obtain the value of K_L from the intercept which was 1/K_L, and the value of a_L from the slope which was a_L/K_L. The maximum adsorption capacity of the adsorbent (Q_max) is numerically equal to K_L/a_L. The plot of lnQ_e versus C_s was employed to generate the intercept value of K_L and the slope 1/m_L (Fig. 13). 1/m_L is a measure of the deviation from linearity of the adsorption. The value ranges between 0 and 1 and indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value of 1/m_L is equal to unity, the adsorption is linear; if the value is below unity, this implies that adsorption process is chemical; if value is above unity, adsorption is a favorable physical process. The more heterogeneous the surface, the closer 1/m_L value is to 0 [71]. The adsorption behavior of was analyzed using linear regression.

The linearized forms of Langmuir and Freundlich isotherms are found to be linear over the whole concentration range studied. Apparently, the plots in Fig. 12 and 13 and the R^2 values (>0.96) showed that the two equations provided a reasonable description of the experimental data. The Langmuir and Freundlich isotherm parameters for the adsorption of lead(II) ions onto OP are listed in Table 2. On the basis of the Langmuir analysis, the maximum adsorption capacity was determined to be 21.2 mg of Pb (II) per gram of OP. This value demonstrated that OP exhibited interesting sorption properties. Compared with some recent data in the literature (Table 3), the results also revealed the potential of OP to be an effective adsorbent for removing Pb (II).

The effect of isotherm shape has been discussed with a view to predict whether an adsorption system is favorable or unfavorable. The essential feature of the Langmuir isotherm can be expressed by means of 'R_L', a dimensionless constant referred to as separation factor or equilibrium parameter R_L is calculated using the following equation:

\[ R_L = \frac{1}{1 + K_L C_0} \]  

where C_0 is the initial lead (II) ions concentration (mg dm^-3). The values of R_L calculated as above equation are incorporated in Table 2. As the R_L values lie between 0 and 1, the related adsorption process is favorable [81] and [82]. Further, the R_L values for lead(II) ions onto OP lie between 0.065 and 0.256, therefore, its adsorption is favorable. Also higher R_L values at lower Pb(II) concentrations showed that adsorption was more favorable at higher concentration.

The free energy change (\( \Delta G \)) for adsorption at 22°C was calculated using the following equation:

\[ \Delta G = -RT \ln K_L \]  

where T is the temperature, R the gas constant and K_L the Langmuir constant.

The calculated \( \Delta G \) value was found to be -17.2 kJ mol^-1. The negative value of free energy change indicated the spontaneous nature of sorption and confirmed affinity of OP for the Pb (II) ions.

**CONCLUSIONS**

In this study, batch adsorption experiments for the removal of Pb(II) from aqueous solution by using Orange peel have been carried out. The obtained results can be summarized as follows:
1. For the maximum adsorption, the optimal operating parameters, pH of solution, adsorbent dosage and contact time was selected as pH 6, 1.0 g, 90 min at 20°C and agitation speed 180 rpm.

2. By applying the kinetic models to the experimental data, it was found that the adsorption of Pb(II) onto Orange peel follows the pseudo-second-order rate kinetics.

3. The linear Langmuir and Freundlich isotherm models were used to represent the experimental data. Both models were fitted well. The monolayer adsorption capacity was obtained 21.1 mg g⁻¹ at optimal experimental conditions.

4. The negative ΔG° value showed that the adsorption of Pb(II) onto orange peel was feasible and spontaneous.

5. The sorption capacity of the orange peel is comparable to the other available adsorbents and it is quite cheaper.

REFERENCES


