Adsorption of Pb(II) from aqueous solutions using activated carbon developed from Apricot stone

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Abstract

Low-cost activated carbon was prepared from Apricot stone material by chemical activation with sulphuric acid for the adsorption of Pb(II) from dilute aqueous solution. The activated carbon developed shows substantial capacity to adsorb Pb(II) from dilute aqueous solutions. The parameters studied include physical and chemical properties of adsorbent, pH, adsorbent dose, contact time and initial concentrations. The percent removal increased with pH from 1.5 to 5. The optimum pH required for maximum adsorption was found to be 6.0. Adsorption kinetics data were modeled using the pseudo-first and pseudo-second-order models. The results indicate that the second-order model best describes adsorption kinetic data. The isotherm equilibrium data were well fitted by the Langmuir and Freundlich models. The estimated maximum capacities of lead ions adsorbed by Apricot stone activated with sulphuric acid were 21.38 mg g−1. The adsorbent derived from this material is expected to be an economical product for metal ion remediation from water and wastewater.

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1. Introduction

Heavy metal contamination is recognized as a priority problem at hazardous waste sites. The contamination by metals can occur in both soils and groundwater as a result of industrial activities such as mining, metal plating, tanneries, and petroleum refining [1–3]. Another source of groundwater metal contamination is related to the migration of leachates from uncontrolled landfill sites. Because of their strong complexing capacity (because of the high concentration of organic and inorganic ligands), metals can be strongly extracted by the dumped wastes and move easily to the groundwater [4]. With respect to the other categories of contaminants, heavy metals are particularly dangerous because they are not biodegradable and accumulate in living organisms.

Lead poisoning causes damage to liver, kidney and reduction in hemoglobin formation, mental retardation, infertility and abnormalities in pregnant women. Due to the hazardous nature of lead (II), it directly or indirectly may cause anemia, headache, chills, diarrhea and poisoning leading to the dysfunction of kidneys, reproductive system, liver, brain and central nervous system also.

Available technologies for heavy metal-contaminated waste stream and soil treatments are usually carbon adsorption, ion exchange, precipitation, membrane filtration, reverse osmosis, and solidification/stabilization. Sorbent-based processes are probably the most used, although the cost of substrate materials and regeneration is a limiting factor. Thus, great attention is given to the characterization of the sorption properties of alternative low-cost materials that range from natural sorbent phases to dead biomass [5]. Disposal of agricultural by-products has become a major, costly waste disposal problem. Produced activated carbons are used for removing organic chemicals and metals from wastewater. A wide variety of materials such as rice husk [6], modified cellulolic materials [7], wheat brean [8], modified bark [9], sawdust [6] and pine bark [10], are being used as low-cost alternatives to expensive adsorbents. Most of the activated carbons are produced by a two-stage process carbonization followed by activation. The first step is to enrich the carbon content and to create an initial porosity and the activation process helps in enhancing the pore structure. Basically, the activation can be done by two different processes: physical and chemical. In fact, there are two important advantages of chemical activation in comparison to physical activation. One is the lower temperature in which the process is accomplished. The other is that the global yield of the chemical activation tends to be greater since burn off char is not required. Among the numerous dehydrating agents, sulphuric acid in particular is the widely used chemical agent in the preparation of activated carbon. In the present work the sorption of lead ion from aqueous solution by using activated carbon produced from Apricot stone was investigated. The adsorption capacity of adsorbent was investigated using batch experiments. The influence of pH, contact time, metal ions and adsorbent concentrations were investigated and the experimental data obtained were evaluated and fitted using adsorbent equilibrium isotherms, and kinetic models.

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2. Experimental technique

2.1. Preparation of activated carbon

Apricot fruits are widely consumed fresh and in processed forms as juice and jams. Apricot stone, as a by-product of the Apricot juice industry is therefore an inexpensive material. Sulfuric acid, as a chemical reagent, added during the activation process help to produce more specific area. The activation procedure was accomplished as follow: Apricot stone was impregnated with a solution of 50% H₂SO₄ in water. Then this suspension (H₂SO₄ and untreated Apricot stone) was heated at 200 °C for 2 h and then filtered. After 20–25 times washing carbon was treated with liquid aqueous ammonia solution in such a fashion that it does not affect the surface properties. Then activated carbon was dried at 60 °C [11]. The carbonized material was sieved (250–125 μm size) and used for adsorption experiments. The specific surface area of the activated carbon was measured by N₂ gas adsorption at –196 °C (COULTER-SA3100). BET equation was used to calculate the specific surface area. The physical characteristics of the adsorbent are given in Table 1.

2.2. Method of experiment

Batch reactor tests were carried out to study the effect of various operating parameters on the adsorption rate. Adsorption experiments of Pb(II) on activated carbon were conducted containing different initial concentrations of heavy metal solutions from 10 to 100 mg/l for lead. A known amount of different activated carbons is varied the initial concentrations of heavy metal solutions from 10 to 100 mg/l for lead. A known amount of different activated carbons is added into solutions followed by agitating the mixture at 150 rpm till equilibrium. The adsorption capacity qₑ (mg/g) after equilibrium was calculated by mass balance relationship equation as follows:

\[ qₑ = \frac{(C₀−Cₑ) \times V}{m} \] (2)

Where C₀ and Cₑ represent initial and equilibrium concentrations respectively; (mg/l) of lead. Isotherm studies were recorded by varying the initial concentrations of heavy metal solutions from 10 to 100 mg/l for lead. A known amount of different activated carbons is added into solutions followed by agitating the mixture at 150 rpm till equilibrium. The adsorption capacity qₑ (mg/g) after equilibrium was calculated by mass balance relationship equation as follows:

\[ \text{Removal} \% = \frac{(C₀−Cₑ)}{C₀} \times 100 \] (1)

Where C₀ and Cₑ represent initial and equilibrium concentrations respectively; (mg/l) of lead. Isotherm studies were recorded by varying the initial concentrations of heavy metal solutions from 10 to 100 mg/l for lead. A known amount of different activated carbons is added into solutions followed by agitating the mixture at 150 rpm till equilibrium. The adsorption capacity qₑ (mg/g) after equilibrium was calculated by mass balance relationship equation as follows:

\[ qₑ = \frac{(C₀−Cₑ) \times V}{m} \] (2)

Where V is the volume of the solution (L) and m is the mass of the adsorbent (g).

3. Results and discussions

3.1. Effect of agitation time and initial concentration on Pb (II) adsorption

Fig. 1 shows the effects of agitation time and Pb(II) concentration on adsorption capacity. We note that the adsorption of Pb (II) increases with an increase in agitation time and attains equilibrium in 10 min for 10 mg/l Pb(II) and 20 min for 30, 50, 80 and 100 mg/l Pb(II). This result is interesting because equilibrium time is one of the parameters for economical wastewater treatment plant applications. According to these results, the agitation time was fixed at 5 h for the rest of the batch experiments to make sure that equilibrium was reached. It also shows that increases in metal ion concentration increased the amount of metal ion uptake per unit weight of carbon (mg/g).

Table 1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>ASAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore volume (cm² g⁻¹)</td>
<td>0.192</td>
</tr>
<tr>
<td>BET surface area (m² g⁻¹)</td>
<td>393.2</td>
</tr>
<tr>
<td>Iodine number (mg g⁻¹)</td>
<td>154</td>
</tr>
<tr>
<td>Methylene blue number (mg g⁻¹)</td>
<td>91</td>
</tr>
<tr>
<td>Bulk density</td>
<td>0.81</td>
</tr>
<tr>
<td>Acidity surface functional groups (mmol g⁻¹)</td>
<td>0.78</td>
</tr>
</tbody>
</table>

* BET surface area corresponds to the particle size 250–125 μm.
3.2. Effect of adsorbent concentrations

One of the parameters that strongly affect the sorption capacity is the concentration of the adsorbents. At a fixed metal concentration, it can easily be inferred that the percent removal of metal ions increases with increasing weight of the adsorbents as shown from Fig. 2. This is due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent.

For the complete removal of Pb (II) from 1000 ml solution at 50 and 100 mg/l concentration, a maximum carbon concentration of 1.5 and 2.0 g/l, is required respectively.

3.3. Effect of particle size on Pb (II) removal

The percent removal of Pb (II) decreased with increasing adsorbent particle size. The percent removal for particle size ranges of 750–500, 500–250 μm and 250–125 μm was 76.4%, 81.6% and 86.7%, respectively. The adsorption of Pb (II) attains equilibrium in 120, 90 and 60 min for particle size ranges of 750–500, 500–250 μm, and 250–125 μm with specific areas equal to 212, 278 and 393 m² g⁻¹, respectively. This is because adsorption is a surface controlled phenomenon, so the smaller adsorbent particle size offers a comparatively larger and more accessible surface and hence, higher adsorption occurs at equilibrium.

3.4. Effect of pH

The pH of the solution has a significant impact on the uptake of heavy metals, since it determines the surface charge of the adsorbent. In order to establish the effect of pH on the biosorption of lead (II) ion, the batch equilibrium studies at different pH values were carried out in the range of 1.5–9 (Fig. 3). We note that the uptake is quite low at lesser pH. However, with the increase in pH, a significant enhancement in adsorption is recorded. The optimum pH for ASAC-Pb system was found to be 6.0 with the removal of about 88.3% Pb(II) from the solution with initial lead concentration of 50 mg/l. At lower pH, Pb(II) uptake decreased because the surface area of the adsorbent was more protonated and competitive adsorption occurred between H⁺ protons and free Pb(II) ions and their hydroxides towards the fixation sites [12]. Therefore, H⁺ ions react with anionic functional groups on the surface of ASAC and results on the reduction of the number of binding sites available for the adsorption of Pb(II). However, a favorable increase in adsorption was observed above pH 5. The amount adsorbed increased as pH increased from 1.5 to 6.0. This increase may be due to the presence of negative charge on the surface of the adsorbent that may be responsible for metal binding. However, as the pH is lowered, the hydrogen ions compete with the metal ions for the sorption sites in the sorbent; the overall surface charge on the adsorbent becomes positive, and hinders the binding of positively charged metal ions [13]. At pH 8.0, a decrease in adsorption of Pb(II) was observed due to the formation of soluble hydroxyl complexes. So all the experiments were carried out at pH 6.0.

3.5. Kinetic models

In order to investigate the mechanism of adsorption, two kinetic models were considered as follows. Lagergren proposed a pseudo-first-order kinetic model. The integral form of the model is:

\[ \ln(qe - qt) = \ln qe - K_p t. \]  

Where \( q_t \) is the amount adsorbed (mg/g) at time \( t \) (min), \( q_e \) is the amount adsorbed (mg/g) at equilibrium, and \( K_p \) is the equilibrium rate constant of pseudo-first-order adsorption (1 min⁻¹). The straight line of the plot of \( \ln(qe - qt) \) versus time suggest the applicability of the Lagergren equation for the present system [14]. The values of \( K_p \) were determined from the slope of the plots and are given in Table 2 (Fig. 4). Recently, Ho and Mc Kay [15] have reported that most of the sorption systems followed a second-order kinetic model which can be expressed as:

\[ \frac{t}{q_t} = \frac{1}{K_{ps}q_e} + \frac{1}{q_e} t \]  

Where \( K_{ps} \) is the pseudo-second-order rate constant of adsorption. The plots of \( t/q_t \) versus \( t \) (Fig. 4) were used to determine the rate constants and correlation coefficients. Table 2 shows the pseudo-second-order rate constants and correlation coefficients for removal of lead from aqueous solutions.

The calculated correlation coefficients are less than 0.963 for the first-order kinetic model, whereas the values of the correlation coefficient are greater than 0.999 for the pseudo-second-order kinetic model. Therefore, the adsorption kinetics could be well explained and approximated by the pseudo-second-order kinetic model for the activated carbon from Apricot stone. These results suggest that the
pseudo-second-order mechanism is predominant and that chemisorption might be the rate-limiting step that controls the adsorption process. Kinetic parameters for the adsorption of Pb\(^{2+}\) ions onto activated carbon by Apricot stone at various initial concentrations.

### 3.6. Adsorption isotherms

In order to successfully represent the equilibrium adsorptive behavior, it is important to have a satisfactory description of the equation state between the two phases constituting the adsorption system. Two kinds of several isotherms equations were tested to fit the experimental data [16]:

**Langmuir isotherm**: 
\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}}} b + \frac{C_e}{q_{\text{max}}}
\]  
(5)

**Freundlich isotherm**: 
\[
\ln q_e = \ln K + \frac{1}{n} \ln C_e
\]  
(6)

where \(q_e\) is the amount adsorbed at equilibrium (mg/g) and \(C_e\) is the equilibrium concentration of metal ions in solution (mg/l). The other parameters are different isotherm constants, which can be determined by linear regression of the experimental data. In the Langmuir equation, \(q_{\text{max}}\) (mg/g) represents the maximal adsorption capacity under the experimental conditions and \(b\) is a constant related to the energy of adsorption. The maximal adsorption capacity calculated from the Langmuir isotherm is equal to 21.38 mg/g at an initial pH of 6.0. Freundlich model gives the parameters, \(n\), indicative of bond energies between metal ion and the adsorbent and \(K\), related to bond strength. The linearized Langmuir and Freundlich isotherms of lead are shown in Figs. 5 and 6. The estimated model parameters with correlation coefficient (\(R^2\)) for the different models are shown in Table 3. From the values of \(R^2\) summarized in Table 3 it may be concluded that both equations fit reasonably well the experimental data. However the Langmuir equation provides a better fit than the Freundlich one. The essential feature of the Langmuir isotherm can be expressed in terms of dimensionless separation parameter \(R_L\), which is indicative of the isotherm shape as follows:

\[
R_L = \frac{1}{1 + bC_0}
\]  
(7)

Where \(b\) is the Langmuir constant. The parameter \(R_L\) indicates the shape of the isotherm as follows:

- \(R_L > 1\) : unfavorable
- \(R_L = 1\) : linear
- \(0 < R_L < 1\) : favorable
- \(R_L = 0\) : irreversible

### Table 3

<table>
<thead>
<tr>
<th>Metals</th>
<th>Freundlich constants</th>
<th>Langmuir constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(^{2+})</td>
<td>(K)</td>
<td>(1/n)</td>
</tr>
<tr>
<td>Pb(^{2+})</td>
<td>21.123</td>
<td>0.4385</td>
</tr>
</tbody>
</table>
According to McKay et al. [18], $R_0$ values between 0 and 1 indicate favorable adsorption. The $R_0$ values were found to be between 0.0017 and 0.0172 (Table 4) for concentrations of 10, 30, 50, 80 and 100 mg/l Pb(II).

The calculated maximum adsorption capacity for lead was 21.38 mg g$^{-1}$. Freundlich model is characterized by $1/n$ heterogeneity factor; hence, it is applicable to sorption on heterogeneous surfaces, i.e., surface with non-energetically equivalent sites. The values of $1/n$ between 0.1 $< 1/n < 1.0$ represent good adsorption of metal onto the sorbent [19].

Values of the adsorption capacity of other adsorbents from the literature are given in Table 5 for comparison. The value for lead sorption observed in this work is in good agreement with values found by other researchers. Differences of metal uptake are due to the properties of each adsorbent such as structure, functional groups and surface area.

3.7. Effect of sodium chloride concentration on Pb(II) removal

The presence of complexing ions is one of the most important influencing factors in solution adsorption processes. The effect of different concentrations of NaCl on lead removal was studied. The effect of complex formation on sorption of a metal ion depends on the relative stability of the cation–ligand in solution and the cationic surface and on whether the surface has an affinity for the complexed form [29]. Increasing chloride ion concentration considerably decreases the adsorption of lead for the carbon studied (Fig. 7). In the absence of NaCl, maximum removal has been observed due to formation of Pb(OH)$_2$ which is higher at pH above 3.0 and it seems to be better adsorbed than PbCl$_2$ [30]. At higher Cl concentrations the low adsorption is likely to be due to the formation of more stable Pb–Cl complexes which are poorly adsorbed [30]. The observed variations in Pb sorption with ionic strength may be explained by the formation of outer–sphere complexes since Na$^+$ in the background electrolyte. This last could compete with the metal ions adsorbed on the outer-sphere sorption sites and reduce the adsorption capacity. Whereas Na$^+$ would not have competed for the inner–sphere sites. This independence of sorption with background electrolyte concentration has been interpreted to indicate that the sorption process is primarily non-electrostatic in nature [31]. Additionally, the presence of salts may compress the electric double layer surrounding negatively charged surfaces [32], which contribute to the release of adsorbed lead.

![Fig. 7. Effect of concentration of NaCl on removal of P(II) from aqueous solution. Conditions: Pb(II) = 50 mg/l; S/L = 1 g/1 l; pH = 6; temperature = 20 °C.](image)

### Table 4

<table>
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<tr>
<th>Metals</th>
<th>Concentrations (mg/l)</th>
<th>$R_0$</th>
</tr>
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<tr>
<td>Pb$^{2+}$</td>
<td>10</td>
<td>0.0172</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.0058</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.0035</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.0021</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.0017</td>
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### Table 5

<table>
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<tr>
<th>Adsorbent</th>
<th>Lead(II)</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Red mud</td>
<td>88.2</td>
<td>Gupta et al. [20]</td>
</tr>
<tr>
<td>Caur</td>
<td>18.9</td>
<td>Conrad and Hansen [21]</td>
</tr>
<tr>
<td>Crushed concrete fines</td>
<td>37</td>
<td>Coleman et al. [22]</td>
</tr>
<tr>
<td>Fly ash</td>
<td>15.08</td>
<td>Cho et al. [23]</td>
</tr>
<tr>
<td>Peat</td>
<td>95.2</td>
<td>Ho and McKay [24]</td>
</tr>
<tr>
<td>Oryza sativa L. husk</td>
<td>8.6</td>
<td>Zhu et al. [25]</td>
</tr>
<tr>
<td>Turkish low rank coal</td>
<td>13.58</td>
<td>Arpa et al. [26]</td>
</tr>
<tr>
<td>Bituminous coal</td>
<td>8.89</td>
<td>Rawat et al. [27]</td>
</tr>
<tr>
<td>Sawdust</td>
<td>3.19</td>
<td>Yu et al. [28]</td>
</tr>
<tr>
<td>Apricot stone activated carbon</td>
<td>21.38</td>
<td>Present study</td>
</tr>
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</table>

### References


