Adsorption of Lead from Aqueous Solution by Modified Beech Sawdust

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ABSTRACT: Sawdust is now being investigated as an adsorbent to remove contaminants from aqueous solution. Heavy metals can be decreased very effectively with the organic material. In this research, adsorption of Pb (II) onto modified beech sawdust in a batch system was investigated. Sawdust was collected from timber mill of Qom, Iran, and modified with H2SO4 and NaOH. Then, the effects of various parameters such as initial concentration, contact time, adsorbent dosage, and pH were evaluated. Finally, the residual concentrations of Pb (II) were determined by atomic absorption spectrophotometer (A.A.S). The maximum and minimum efficiency of Pb (II) removal occurred at pH 5 and 7 in optimum conditions which were reported 91.3% and 28.04%, respectively. The maximum adsorption capacity (qe) was found to be 0.3941 mg/g. Findings revealed that by increasing the concentration of Pb (II) from 1 to 7 mg/L, the removal efficiency was declined from 91.3% to 33.86%. It was also obvious that by increasing the adsorbent dose from 2 to 8 g/L, the removal efficiency was improved from 50% to 97.3%. The removal efficiency had a decreasing trend after the equilibrium. Obtained data can be explained with both of Langmuir and Freundlich isotherm models.

KEYWORDS: Pb (II), Aqueous Solution, Modified Beech Sawdust, Adsorption, Water

Introduction

The depletion of heavy metals into water resources is a drastic environmental problem which deteriorates the quality of water resources. These metals can be discharged into the surface waters and groundwater via industries such as mining, metallurgical, tannery, electrical, smelters, jewelry, electroplating, dyes, chemical, textiles, oil refineries, pulp and paper production, battery manufacturing processes, metal plating facilities, production of paints and pigments, mining operations, glass production industry, ceramics,fungicides, rubber, fertilizers, and Aircraft industry [1–4]. Lead is applied to produce solder, lead–acid batteries, and alloys. The service organ lead compounds tetaethyl and tetraethyl lead have also been used extensively as antiknock and lubricating agents in gasoline [5].

Lead from natural sources can seldom be detected in drinking water. Its presence may be related to material of plumbing system containing lead. Guideline value for Pb (II) concentration in drinking water is 0.01 mg/L [6]. Lead has widely spread in soil, water, air, and food. World production exceed 3 million tons per year. Lead results in health effects such as irreversible brain damage and injury to the blood forming systems [6].

With confirming the toxic effects of heavy metals on humans and the environment various methods for removing heavy metals from water and wastewater has been considered such as coagulation and flocculation, chemical and electrochemical precipitation, electrochemical deposition, complexation/sequestration, ion exchange resins, membrane filtration, reverse osmosis, solvent extraction, oxidation, biological treatment, cementation and adsorption on adsorbents which do not seems these methods to be economical and in huge scales, most of the methods for removal only at relatively low concentrations of heavy metals are cost–effective [1–4, 7, 8]. For example, Ion–exchange has the advantage of allowing the recovery of metallic ions, but it is expensive and sophisticated [9]. Although, the chemical and electrochemical precipitation have become prevalent [2], but precipitation methods require large settling tanks for the precipitation of high quantity of alkaline sludge and a subsequent treatment. Also, it needs to control pH and further coagulation process is needed [9]. Therefore, it requires more investment and high costs operating [1, 8].

Chemical precipitation is not suitable for removing low concentrations of heavy metal ions [1]. Because of its easy handling, high efficiency, cost–effectiveness, and the accessibility of different adsorbents, adsorption is a suitable process. In addition, the recoveries of pure metal for recycling as well as reuse of the adsorbent are the added advantages [10]. The synthetic and natural adsorbents are used to treat the water and wastewater. An adsorbent creates the chemical bonds or physical attractions with the heavy metals presented in aqueous solutions [8].

Scheele et al. (1773) governed the first quantitative studies about the uptake of various gasses by charcoal and clay adsorbents. However, the term "adsorption" indicates the process has been widely used for the removal of solutes from solutions and pollutant gasses from the air [7]. Among the different adsorbents, activated carbon has been used as a highly efficient alternative to the removal of numerous trace elements from water. But the high cost of activated carbon inhibits its large–scale applications [10]. If the adsorption process is to be selective adsorbent, absorbing the natural elements play an important role to play in the separation of water systems [2, 10].

Sawdust (SD) is a waste by–product of the timber industry which is produced in large quantities and is used as cooking fuel, packing agent in furniture and heating in boilers [2, 8]. Various chemical treatments can be done to improve the heavy metal binding capacity of sawdust [8, 11].

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The adsorption can be classified to chemical, physical, and electrostatic mechanisms. The physical adsorption is the most common mechanism in nature [13].

In this study Pb (II) removal efficiency and effective parameters such as pH, contact time, and initial concentration of Pb (II) on its adsorption from synthetic solution by beech sawdust has been investigated and concluded. Experimental data were analyzed with Langmuir and Freundlich.

Materials and methods

Treatment of sawdust with NaOH and H₂SO₄

Beech sawdust was collected from a timber mill in Qom, Iran and sieved to 30 ASTM mesh size and it was washed with deionized water and dried in an oven at 70 °C for 16 h. Because the use of wood–based materials such as sawdust and bark increases the COD of water, modification of these adsorbents decreases this problem. The raw sawdust was completely immersed in 2 N NaOH aqueous solution for a period of 4 h. Thereafter, it was rinsed several times with distilled water to eliminate the lignin content and excess of NaOH and then dried. It was then immersed in 0.2 N H₂SO₄ for a period of 4 h to remove traces of alkalinity and other impurities. Double distilled water was used to washout and eliminate excess of sulphuric acid and other coloring materials from the acid treated sawdust material till the wash water was colorless and finally dried in an oven. Fig. 1 shows modified sawdust (a) and unmodified sawdust (b).

Preparation of Pb (II) Solution

All chemicals used in this study were provided by Merck Company (Germany). The stock solution of Pb (II) was further diluted with deionized water to desire concentration for obtaining the test solutions.

Adsorption experiments

The experimental parameters used in this study is shown in Table 1. First of all, the equilibrium time should be calculated according to the Eq. 1.

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

Where, \(q_e\) is the adsorption capacity (mg/g), \(C_i\) is the initial concentration of metal in solution (mg/L), \(C_f\) is the equilibrium concentration of metal in solution (mg/L), \(V\) is the volume of metal ion solution (L) and \(W\) is the weight of the adsorbent (g).

According to the equilibrium time, optimum condition was considered as follows: pH= 5, Pb (II) concentration= 1 mg/L, adsorbent dosage= 0.5 g/250 mL, the maximum contact time= 40 min. After determination of equilibrium time, the effect of the various parameters on removal efficiency can be examined by varying one parameter and keeping steady the other conditions. Adjusting the pH was done by using either 0.1 M HCl or NaOH solutions. The adsorption experiments were performed in a batch reactor using pyrex glass flasks. After every step of experiments, a Whatman No. 1 filter was used to separate the suspension of the adsorbent from the solution. The concentration of heavy metal ions remaining in solution was measured by atomic absorption spectrometer using the flame method in \(\lambda= 290\) nm.

Table 1. Experimental parameters

<table>
<thead>
<tr>
<th>Contact Time (min)</th>
<th>5, 10, 15, 20, 30, 40, 70, 110</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye Concentration (mg/L)</td>
<td>1, 3, 5, 7</td>
</tr>
<tr>
<td>Adsorbents Dose (g/250 mL)</td>
<td>0.5, 1, 1.5, 2</td>
</tr>
<tr>
<td>pH</td>
<td>5, 6, 7</td>
</tr>
</tbody>
</table>

The Lead removal efficiency of Pb (II) (R%) is calculated using Eq. 2:

\[
R(\%) = \frac{(C_i - C_f)}{C_i} \times 100
\]

Where, \(C_i\) and \(C_f\) are the initial and final concentrations of Pb (II) (mg/L), respectively.

Adsorption isotherms

The obtained data from equilibrium sorption of Pb (II) on beech sawdust was analyzed in terms of Freundlich and Langmuir isotherm models. The Langmuir isotherm equation could be expressed as (Eq. 3):

\[
\frac{q_e}{Q_m} = \frac{K_L C_e}{1+K_L C_e}
\]

Where, \(q_e\) is the equilibrium concentration on adsorbent (mg/g), \(C_e\) is equilibrium concentration in solution (mg/L), \(Q_m\) is maximum adsorption capacity (mg/L) and \(K_L\) is adsorption equilibrium concentration (mg/L).

This model is based on the assumption that the forces of interactions among adsorbed molecules are tiny and when a molecule occupies a site no more sorption happens.
The percent of adsorption of heavy metal increased by increasing adsorbent dose that can be attributed to increased surface area and more adsorption sites [14]. M. S. Siboni et al. showed that the removal efficiency of Cr (VI) was increased from 59.4% to 74.6% with an increase in the mass of adsorbent from 15 to 30 g that can be attributed to increasing more binding sites for the adsorption [15]. The maximum of removal Pb (II) in this experiment was determinate 97.3% at 30 min and with initial concentration 1 mg/L at pH 5. Biosorbents (e.g. sawdust) usually contains organic functional groups such as alcohol, aldehydes, ketones, carboxylic, phenolic, and ether groups on their surface. These groups participate in cation binding due to their ability to ionize in an aqueous solution [16, 17]. The cellwalls of such these adsorbents mainly consist of cellulose, hemicellulose, and many hydroxyl groups such as tannins and lignin. Lignin is the third major component of the wood that is usually in the range of 18 – 35% and is built up from the phenylpropane nucleus; an aromatic ring with a three carbon side chain is promptly available to interact with cationic metal ions [2, 8, 18, 19]. Tannins are complex polyhydric phenols that they occur chiefly in hardwoods. All those components are active ion exchange compounds [8].

The non-linear form of the Freundlich equation is as (Eq. 4):

$$q_e = K_F C_e^n$$  \hspace{1cm} (4)

Where, $K_F$ is adsorption capacity and $n$ is reaction energy. The linearized form of Freundlich isotherm is given as (Eq. 5):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$  \hspace{1cm} (5)

By plotting $\ln q_e$ versus $C_e$, $K_F$ and $n$ can be determined if a straight line is achieved.

Finally, in order to find out the optimum condition, the results of each examination were statistically analyzed.

**Results and discussion**

**The effect of adsorbent dose on removal efficiency**

As it is shown in Fig. 2 by increasing the adsorbent dose from 0.5 g/250 mL to 2 g/250 mL at 5 min, the removal efficiency reached from 50% to 95.2%. In other researches, the same results were obtained [2, 3, 12, 13].

The possible sites on sawdust for specific adsorption include H$^+$ ions in –OH and –COOH functional groups in which H$^+$ ions can be exchanged for cations in solution. Other sites present adsorbent surface is negatively charged and the adsorbate species still remains positively charged. The adsorbent surface is negatively charged and increases electrostatic attraction of metal ions. The decrease in the removal of metal ions at lower pH is apparently due to the higher concentration of H$^+$ ions present in the reaction mixture, which compete with the Pb (II) ions for the adsorption sites on sawdust. At higher pH, the production of soluble hydroxyl complexes decreases the adsorption which causes less efficiency [7, 8, 10, 18].

**The effect of pH on removal efficiency**

Fig. 3 shows the effect of pH on this heavy metal removal efficiency of treated sawdust. The pH is one of the parameters that controls the removal of heavy metals from aqueous solutions. Fig. 3 presents that maximum removal efficiency has occurred in pH 5 about 91.3% at 40 min. The removal percentage is decreased by increasing pH toward 6 and 7. At contact time 5 min, Pb (II) removal was 50% that was reached to 28.04% at pH 7. In other studies, the maximum percentage of adsorption was obtained at pH 6 and thereafter decreased with additional increase in pH [2, 10]. In another research by F. Kaczala et al., a remarkable increase of the removal efficiency was observed from 32% to 99% for Pb and from 43% to 95% for V, respectively, when the initial pH was reduced from 7.4 to 4.0 [3].

**The effect of contact time on removal efficiency**

Fig. 4 shows the variation in the percentage removal of Pb (II) with a contact time of treated beech sawdust at pH 5. For an optimum adsorbent dose of 0.5 g/250 mL, removal of lead increases with the increase of contact time from 5 to 40 min and after that is decreased. At 5 min of the reaction time, removal percentage was 50% that till reaching to equilibrium time is...
The effect of contact time on removal efficiency

For a fixed concentration of heavy metals and a fixed adsorbent mass, the adsorption rate of heavy metals at primary times of experiment is high due to more availability areas. By adding more contact time the removal efficiency is increased [20, 22, 23] because contact time between adsorbent and adsorbate and reaching adsorption sites are increased. A similar result has been found by other researchers [1, 24]. Fig. 5 gives the evidence that the equilibrium takes a few minutes (about 15 min) to occur at concentration 1 mg/L for all adsorbent doses. After reaching equilibrium, the removal efficiencies decreased by about 1 – 3% with increase in contact time. This may be resulted from the process of adsorption and desorption that takes place after adsorbent surface saturation by Pb (II) ions.

The effect of initial concentration on removal efficiency

Fig. 6 shows the effect of initial concentration on the percentage removal of Pb (II). Fig. 6 reveals by increasing initial concentration of Pb (II) from 1 toward 7 mg/L, the removal efficiency had been decreased. The highest removal of the contaminant was 91.3% in 1 mg/L Pb (II) and time 40 min. The least removal was allocated to 7 mg/L that was 43.45% at the same time. The decrease in the percentage removal can be explained by the fact that the active sites of adsorbent was limited, which could become saturated above a given concentration [25]. In other studies, the same results were obtained [9, 26, 27].

Adsorption isotherms

The isotherm of equilibrium adsorption is mainly being applied to design adsorption processes since it can demonstrate how metal ions are distributed between the solid and liquid phases at equilibrium as a function of metal concentration. Table 2 has presented the characteristics of adsorption isotherms models.

Table 2. Characteristics of adsorption isotherms

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$R^2$</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>0.994</td>
<td>0.406</td>
<td>2.46</td>
</tr>
<tr>
<td></td>
<td>0.979</td>
<td>0.737</td>
<td>1.13</td>
</tr>
</tbody>
</table>

The isotherm of equilibrium adsorption is mainly being applied to design adsorption processes. If an adsorbent is exposed to a solution containing a species of metal ions, the metal ions will be adsorbed on the adsorbent surface and their concentration will increase on adsorbent surface up to an equilibrium is reached. As shown in Fig. 7 and Fig. 8, the Langmuir and Freundlich isotherm models were applied to model the experimental adsorption data.
The Langmuir isotherm model ($R^2 = 0.9944$) provided a better fit to the experimental data than Freundlich adsorption model ($R^2 = 0.9797$). Following equilibrium adsorption data from the Langmuir isotherm means that the adsorption takes place at given homogeneous sites on the adsorbent and is based on the monolayer adsorption of ions on the surface of sites [19, 28]. The Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption [28].

Conclusion

- The maximum and minimum of Pb (II) removal efficiency occurred at pH 5 and 7, respectively, were 91.3% and 28.04% in optimum condition.
- The maximum adsorption capacity ($q_m$) was earned 0.3841 mg/g.
- By increasing Pb (II) concentration from 1 to 7 mg/L, removal efficiency was declined from 91.3% to 33.88%.
- By increasing adsorbent from 0.5 to 2 g/250 mL, the removal was decreased from 50% to 97.3%.
- With increasing time to reaching equilibrium time, the removal efficiency was increased and after that was decreased.
- Obtained data can be explained with both of Langmuir and Freundlich isotherm models.
- According to the results, sawdust can be used as a low cost, natural and abundant availability adsorbent for removal of lead ions from aqueous solution.

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Reference


Fig. 8. Langmuir adsorption isotherm of Pb (II) ions on beech sawdust particles
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