Adsorption of Lead Ions from Solution by Modified Wheat Straw in Batch Mode

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Abstract. It is essential to remove lead ions from solution. In this research, wheat straw was modified by diethylenetriamine and adsorption property of modified wheat straw (MWS) toward lead ions was evaluated at 303 K. Several experimental factors like initial pH, adsorbent dose, contact time were presented to study the effect of adsorption quantity. Solution pH near 5 was in favor of adsorption. The adsorption capacity from experiment was up to 69.4 mg/g. Pseudo-second order equation was best to describe the kinetic process while Langmuir model was best available to fit the adsorption equilibrium data. It was concluded that MWS may be good adsorbent to remove Pb(II) from solution.

Introduction

Water pollution can be attributed to excessively release of industrial effluent, discharge of toxic industrial wastes, and runoff from agricultural field, which due to population expansion and rapid pace of industrialization [1]. Most significant problem in water pollution is mainly caused by heavy metal ions, such as zinc, copper, lead, chromium, cadmium, mercury, nickel and so on, which have lethal effects on all forms of life, thus, the removal of metal ions from wastewaters is of a great concern nowadays.

Numerous studies already utilized low-cost adsorbents, including biomaterials, natural inorganic material, and waste materials from agriculture and industry, as alternative sorbent to remove heavy metal ions [2,3]. Wheat straw contains abundant floristic fiber, protein, and some functional groups (carboxyl, hydroxy, and amidogen, etc.), which make the adsorption processes possible. Furthermore, wheat straw as agricultural by-products was cheap and vastness. But adsorption capacity toward pollutants was lower. Natural or modified wheat straw (MWS) has been used as an available adsorbent to remove heavy metals and dyes from water/wastewater [4,5]. The aim of this work was to prepare modified wheat straw (MWS) using diethylenetriamine and study its adsorption property toward Pb(II) from aqueous solution. Adsorption models were applied to fit the experimental data.
Materials and Methods

Materials

The raw wheat straw collected from local countryside of Zhengzhou City was treated according to published work [3] and 40-60 mesh size of particle was selected. All chemicals were of analytical reagent grade, and only diethylenetriamine is chemically pure. A 1.0 g/L Pb stock solution was prepared by dissolving Pb(NO\textsubscript{3})\textsubscript{2}.

Then approximately 1.5 g of wheat straw was mixed with 150 ml of 2 m NaOH solution, 30 ml of epichlorohydrin, 30ml of ethanol solution. The mixture was stirred at room temperature for 5 h. The obtained straw product was washed thoroughly with deionized water to remove excess alkali and any other soluble substances until neutrality. The straw was dipped into 200 ml distilled water with dissolving 3.0 g Na\textsubscript{2}CO\textsubscript{3}, added with 15 ml of diethylenetriamine, and then added with 30 ml of ethanol solution. Then the mixture was further shaken for 3 h at room temperature, and then left still overnight. It was filtered and washed several times with deionized water until neutral pH. The product was dried in an oven at 353 k for 3 h and modified wheat straw (MWS) was obtained. The content of nitrogen was 0.59% about MWS and not detected about wheat straw. This showed diethylenetriamine was grafted on the surface of wheat straw.

Methods

Adsorption experiments were carried out in a rotary shaker at 100 rpm using 50 ml shaking flasks containing 20 mL of desired lead ion concentrations with 0.02 g of MWS (except the effect of dose) within a constant temperature shaker bath (303 K). After adsorption, the mixture were filtered, and the Pb(II) concentration in solution was determined using flam atomic absorption spectrometer (AAS) (Analyst 300, Perkin Elmer). Each experiment was repeated three times and the results given were the average values.

The adsorption quantity of Pb(II) \((q_e, \text{mg/g})\) at the equilibrium and removal efficiencyy \(p\) (\% removal) were calculated as equation (1) and (2), respectively:

\[
q_e = \frac{V(C_0 - C_e)}{m}.
\]

\[
p = \frac{(C_0 - C_e)}{C_0} \times 100\%
\]

Where: \(q_e\) (mg/g) is the biomass adsorption equilibrium metal ion uptake capacity, \(V\) (L) is the solution volume, \(C_0\) (mg/L) is the initial metal ion concentration, \(C_e\)(mg/L) is the metal ion concentration after equilibrium, and \(m\) (g) is the dry weight of the adsorbent.

Results and Discussions

Effect of MWS Dose on Adsorption Quantity

The adsorption amount and the removal of metal ions is a function adsorbent dosage, so the efficiency of MWS adsorbents was evaluated at different adsorbent doses. The experiments were
conducted at pH 5, contact time (1 h) with varying adsorbent dose (0.4–5.0 g/L). The adsorption quantity (mg/g) and percentage removal of Pb ions were shown in Fig. 1.

Percentage removal of Pb(II) increased from 30% to 93% when the adsorbent dose was increased from 0.4 to 5.0 g/L. This was due to the availability of more adsorption sites or the number of surface area with the increase of adsorbent dose and hence resulted in a higher percent of Pb removal. However, values of $q_e$ decreased from 71.1 mg/g to 19.2 mg/g with the increase of the adsorbent dose. This was because that the amount of lead ions was changeless in the system; the more the MWS dose used, the little the adsorptive quantity adsorbed for per gram MWS.

![Figure 1. The effect of MWS dose on Pb ion adsorption ($C_0$=100 mg/L).](image1)

![Figure 2. The effect of the pH values on adsorption quantity ($C_0$=100 mg/L).](image2)

**Effect of Solution pH Values on Adsorption Quantity**

The pH of the medium has a significant effect on the adsorption process of metal ions. The solution pH affected the surface charge of the adsorbent, the degree of ionization and speciation of adsorbate during adsorption. Therefore, for adsorption of Pb(II), experiments were carried out at different initial pH ranging from 1 to 5.6. The results are shown in Fig. 2.

Form Fig. 2, it was observed that the maximum adsorption capacities in the pH range 4.5-5.5. At pH 1-2.5 range the adsorption quantity increased very slightly and increased was very quick between pH 2.5-4.5. When the value of pH was from 4.5 to 5.5, the adsorption quantity was approximately no change. As there were some amine groups as protonation at lower pH, the surface of MWS should be positively charged in acid solution. There was existed an electrostatic repulsive force attraction between Pb(II) cations and MWS. So pH 5.0 was chosen in next section.

**Effect of Contact Time on Adsorption Quantity**

The effect of contact time on adsorption of lead ion by MWS was performed, and the results are depicted in Fig. 3.

As can be seen from the Fig. 3, the whole process was divided by three stages: (1) first initial rapid stage (to 20 min) where adsorption rate was fast, (2) a second stage where adsorption rate became lower (20–50 min), and (3) a third equilibrium adsorption stage. At the first process of adsorption, the driving force of Pb concentration between MWS and Pb solution was largest, and adsorption speed was relative fastest. The value of $q_t$ increased significantly. In second stage, the driving force became smaller, and value of $q_t$ increase with small range. This result may be an indication that external mass transfer (first) and intraparticle diffusion mass transfer may be controlled Pb adsorption onto MWS.
The adsorption quantity of Pb(II) onto MWS was up to 31.3 mg/g (from Fig. 3) value, much higher than that was obtained when WS was used as adsorbent in the same working conditions ($q_e=5.66$ mg/g). This showed that adsorption capacity for Pb(II) was significantly enhanced through modification. Adsorption kinetics models were used to explain the adsorption mechanism and adsorption characteristics. To evaluate the adsorption kinetics of Pb(II) ions, two kinetic models, pseudo-first-order model, pseudo-second-order model were applied for the experimental data. The equations were represented as following [6,7]:

$$q_t = q_e \left(1 - e^{-k_1t}\right). \quad (3)$$

$$q_t = \frac{k_2q_e^2t}{1 + k_2q_e^2t}. \quad (4)$$

Where $k_1$(1/min$^1$) is the pseudo-first-order rate constant of adsorption, $k_2$($(g/((mg \text{ min}))$) is the pseudo-second-order rate constant of adsorption, $q_e$ and $q_t$ (mg/g) are the adsorption capacity at equilibrium and at time t, respectively.

Nonlinear regressive analysis was conducted using the Origin 7.5 software. The regression coefficients ($R^2$) and rate constants obtained from the application of kinetic models were presented in Table 1. Sum of difference square ($SS$) was also listed in Table 1. The fitted curves were shown in Fig. 3.

According to Fig. 3 and Table 1, the pseudo-second-order reaction model was better to describe the kinetic process as there were higher $R^2$ and lower $SS$ while the fitted curve was very close to experimental curve. This indicated that the process may be chemical process. Complexation and ion exchange may be the mechanism [6].
Table 1. Kinetic parameters for the adsorption of Pb(II) by MWS.

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Parameter Value</th>
<th>Parameter Value</th>
<th>Parameter Value</th>
<th>$R^2$</th>
<th>SS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first order</td>
<td>$k_1$ (1/min)$^1$</td>
<td>$0.147±0.013$</td>
<td>$q_e$(mg/g)</td>
<td>30.4±0.50</td>
<td>0.91</td>
</tr>
<tr>
<td>order equation</td>
<td></td>
<td></td>
<td></td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>Pseudo-second order</td>
<td>$k_2$ (g/mg·min$^{-3}$)</td>
<td>(7.08±0.49)×1</td>
<td>$q_e$(mg/g)</td>
<td>32.9±0.31</td>
<td>0.98</td>
</tr>
<tr>
<td>order equation</td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>5</td>
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</tbody>
</table>

Note: $SS = \sum (q_e - q_t)^2$, where $q_e$ and $q_t$ is from calculation and experiment, respectively.

Effect of Equilibrium Lead Concentration on Adsorption

The equilibrium adsorption of Pb (II) was studied as a function of different concentrations ranging from 10 to 200 mg/L. The results of this series of experiments are presented in Fig. 4 (adsorption isotherm).

As seen in Fig. 4, the adsorption capacity of MWS was increased with an increase in the equilibrium lead concentration. At low concentration, the ratio of available surface to the initial lead concentration was larger, so the adsorption amount was smaller due to not saturation of the adsorbent. High initial concentration provided an important driving force between the aqueous and solid phases. Therefore, a high initial concentration of lead ion enhanced the adsorption amount.

Analysis of experimental sorption data is important for developing an equation that can be used to understand the adsorption process and investigate the adsorption mechanisms. Two isotherm equations namely, Freundlich, Langmuir, models have been applied. These equations were presented as following [8,9]:

The Freundlich model:

$$ q_e = K_F c_e^{1/n}. \tag{5} $$

The Langmuir model:

$$ q_e = \frac{q_m K_L c_e}{1 + K_L c_e}. \tag{6} $$

Where $K_F$ and $1/n$ are the Freundlich constants; $q_m$ (mg/g) is a constant related to adsorption capacity; $K_L$ (L/mg) is the Langmuir constant related to the affinity of the binding sites and energy of adsorption.

Table 2. Isotherms parameters for the adsorption of Pb(II) by MWS.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Parameter Value</th>
<th>Parameter Value</th>
<th>Parameter Value</th>
<th>$R^2$</th>
<th>SS</th>
</tr>
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<tbody>
<tr>
<td>Freundlich</td>
<td>$K_F$</td>
<td>8.68±0.875</td>
<td>$1/n$</td>
<td>0.430±0.023</td>
<td>0.992</td>
</tr>
<tr>
<td></td>
<td>$K_L$(L/mg)</td>
<td>0.031±0.006</td>
<td>$q_m$(mg/g)</td>
<td>83.05±5.34</td>
<td>0.984</td>
</tr>
</tbody>
</table>

All relative parameters of the isotherm equations, the correlation coefficient, isotherm constants, and $SS$ were listed in Table 2. Compared to the data shown in Table 2, the value of $R^2$ about the Freundlich isotherm was higher than others while the relative value of SS was lower. This suggested
the adsorption of lead ion on MWS was well fitted to the Freundlich isotherm model and $1/n$ values lied between 0 and 1 indicating favorable adsorption [10,11].

**Summary**

The MWS as a good adsorbent can effectively adsorb lead ions from aqueous solutions. The kinetic process follows pseudo second-order model while the equilibrium data can be better fitted by the Freundlich model. The mechanism may be a chemisorption process.

**Acknowledgements**

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**References**


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