Adsorption of Heavy Metals from Aqueous Solution onto Sawdust Activated Carbon

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Abstract

In this study, sawdust as a cheap method and abundant raw material was utilized to produce active carbon (SDAC). Physiochemical activation was utilized where potassium hydroxide used as a chemical activating agent and carbon dioxide was used as a physical activating agent. Taguchi method of experimental design was used to find the optimum conditions of SDAC production. The produced SDAC was characterized using SEM to investigate surface morphology and BET to estimate the specific surface area. SDAC was used in aqueous lead ions adsorption. Adsorption process was modeled statistically and represented by an empirical model. The highest specific surface area of SDAC was 688.3 m²/gm. Langmuir and Freundlich isotherms were used to fit the adsorption process, where equilibrium data was best represented by Langmuir isotherm model. Pseudo-first order and pseudo-second order equations were used to study adsorption kinetics, lead adsorption on SDAC fitted pseudo-second order more adequately. Best removal efficiency was found to be 99.63% with highest adsorption capacity of 19.92 mg/g.

Keywords: Adsorption, activated carbon, sawdust, lead, physiochemical activation.

1. Introduction

Due to the wide range and the exaggerated uses of organic solvents, oxidizing agents, phenols and heavy metals in industry, they were accumulated in the environment which caused ecosystems deterioration.

Heavy metals category is one of the most lethal pollutants of surface and ground waters. Industrial effluents are the major source. Since most of heavy metals could not be degraded into benign components, removing the heavy metals before discharging waste waters into rivers becomes necessary. Otherwise they could be harmful to the health and/or reduce drinking water quality [1].

According to the World Health Organization (WHO, 1984) and International Program of Chemical Safety (IPCS, 1988), the most poisonous metals are aluminum, zinc, mercury, arsenic, chromium, nickel, copper, cadmium and lead. The drinking water guideline value recommended by World Health Organization (WHO) and Iraqi standard regulation is 0.01 and 0.015 mg Pb/L.

Lead is found in freshwaters due to its wide uses in petroleum refining, batteries industry, preparation of nuclear fuels and electroplating. Lead causes severe damage to human organs e.g. kidneys, the brain, reproductive system, the liver and the nervous system [2].

As a result of the toxicity of the lead and its compounds, removal method has become an
important priority. There are various available means to reduce heavy metals levels from water including ion exchange, membrane filtration, chemical precipitation and reverse osmosis, but these methods generally require high cost and produce more lethal by products [3].

Adsorption on solid materials is one of the best existing methods for improving the water quality and the regulation of atmospheric and aquatic pollution, with active carbon being the most used adsorbent in industry. In the last years, worldwide consumption of active carbon has increased by an annual average of 5.5% , and it is anticipated to continue to do so at a higher rate in next years (8.1% in 2018)[4]. Thus, locally produced wastes such as saw dust, cow bones, and others were examined for preparing active carbon. Because of the low cost of those wastes, high percentage of carbonaceous contents and their abundancy, they were found to be of high potency in heavy metals adsorption.

The aim of this study is to optimize the production of activated carbon from sawdust by physiochemical activation method and to evaluate its adsorption potential for the lead ions aqueous solution. Adsorption isotherm fitting and kinetics studies were conducted to understand the behavior of lead ions onto SDAC. Effective parameters such as initial pH of the metal solutions, contact time, initial metal concentrations and temperature were investigated.

2. Materials and Methods

2.1. Adsorbate

Technical grade Lead nitrate (Pb(NO₃)₂) of 99.8% purity provided by Himedia- India was used to prepare stock solution of the Lead. Distilled water was used to prepare all solutions. A stock of 1000 mg/L was prepared by adding (1.68) gm of Pb(NO₃)₂ to a liter of distilled water. Other solutions were prepared by diluting the stock solution to the required concentrations. NaOH and HNO₃ solutions each of 0.1 M concentration were used to adjust pH value.

2.2. Preparation and Characterization of Activated Carbon

Saw Dust (SD) was obtained from local furniture workshops, Baghdad, Iraq as waste. The preparation methodology of SDAC is concisely illustrated in figure.1. The surface area was analyzed using Brunaure- Emmett-Teller (BET: HORIBA, SA-900 series, USA) through nitrogen adsorption isotherm at 77 K. In order to determine the shape of SDAC surface and pore characteristics, the samples were scanned using Scanning Electron Microscope (TESCAN, Vega III, Czech Republic).

2.3. Design of Experiments

Experimental design usually used to efficiently map the set of experiments to be conducted and to serve the following: understand the effect of the factors and/or model the relationship between response and factors with a minimum number of experiments [5]. Taguchi method was used in the optimization of SDAC production and in modelling of adsorption process due to its efficiency compared to other methodologies and its robustness. STATISTICA 10 (Stat Soft, Inc. USA) was used to design the set of experiments. Where L9 orthogonal array was chosen (2 factors, 3 levels) in SDAC preparation, and L25 array (4 factors, 4 levels) for adsorption process modelling.
Batch Equilibrium Studies

Batch mode adsorption experiments were conducted by adding specific amount of adsorbent to a 100 ml lead solution contained in 125 ml capped plastic containers. The containers were placed in an isothermal shaker (JSSI-300CL, JSR, Korea) at agitation speed of 180 rpm. After adsorption time was completed, all samples were filtered from the adsorbent with Whatmen filter paper to make it carbon free. The remaining concentration of the lead in each sample after adsorption was determined by atomic-absorption spectroscopy (Shimadzu AA6200, Japan). The lead adsorption capacity on SDAC was predicted according to:

\[ q_e = \frac{(C_0-C_e)W}{W} \]  

where \( C_0 \) and \( C_e \) are the concentrations of the Lead at initial and equilibrium conditions (mg/L) respectively; \( V \) is the volume (L); and \( W \) is the weight (g) of SDAC.

2.5. Adsorption Isotherm

Langmuir and Freundlich isotherm models were used to fit the equilibrium data. The linear form of the Langmuir [6] model is:

\[ \frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{(K_aq_m)} \frac{1}{C_e} \]  

where \( C_e \) (mg/L) is the concentration of the lead at equilibrium; \( q_e \) (mg/g) is the equilibrium adsorption capacity; \( q_m \) is the adsorption capacity for a complete monolayer (mg/g); \( K_a \) (L/mg) is the constant of adsorption equilibrium. The linear form of Freundlich [7] isotherm is:

\[ \ln q_e = \ln K_F + \left( \frac{1}{n} \right) \ln C_e \]  

The constants \( K_F \) (mg/g) and \( n \) are Freundlich constants.

2.6. Kinetic Studies

The adsorption rate constants were predicted from the pseudo first-order and pseudo second-order kinetic equations. Pseudo first-order [8] expression is:

\[ \log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \]  

where \( q_e \) and \( q_t \) (mg/g) are the adsorption capacities at equilibrium and at time \( t \) (min), respectively and \( k_1 \) (1/min) is the adsorption constant. The linear form of the pseudo second-order kinetic model [9] can give by:

\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t \]  

where \( q_e \) is the adsorption capacity of equilibrium and the constant of second order \( k_2 \) (g/mg h) can be determined experimentally from the intercept and slope of \( t/q_t \) versus \( t \) plot.
3. Results and Discussion

3.1. SDAC Production and Optimization

The experiments that were conducted are shown in Table 1.

Table 1, 
Preparation of SDAC experimental design array and the results for SSA and yield.

<table>
<thead>
<tr>
<th>Runs</th>
<th>SDAC preparation variables</th>
<th>SDAC preparation responses</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IR</td>
<td>Activation Temperature (°C)</td>
</tr>
<tr>
<td>1</td>
<td>1:2</td>
<td>600</td>
</tr>
<tr>
<td>2</td>
<td>1:2</td>
<td>700</td>
</tr>
<tr>
<td>3</td>
<td>1:2</td>
<td>800</td>
</tr>
<tr>
<td>4</td>
<td>1:3</td>
<td>600</td>
</tr>
<tr>
<td>5</td>
<td>1:3</td>
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<tr>
<td>7</td>
<td>1:4</td>
<td>600</td>
</tr>
<tr>
<td>8</td>
<td>1:4</td>
<td>700</td>
</tr>
<tr>
<td>9</td>
<td>1:4</td>
<td>800</td>
</tr>
</tbody>
</table>

In SDAC preparation, the SSA increases as IR rises from 1:2 to 1:3. The clarification of this result is that the reduction of KOH occurs during activation process was transformed to potassium oxide by dehydration reaction. Potassium oxide reacts with carbon dioxide that is provided during physical activation to form K₂CO₃ which aids to form new pores and widen pores that formed during chemical activation. So it was recognized that above 420 °C (melting point of KOH), the surface area of carbon activated by KOH is more than the area of carbon activated by K₂CO₃ [10]. But when the IR reached to 1:4 the SSA decreased. This was probably due to excessive potassium hydroxide molecules decomposing into metal. As a result, metal deposition on the already developed pores might occur and lead to reduction of the surface area [11].

Regarding the activation temperature effect, it was perceived that as the temperature rises from 600 °C to 700 °C SSA increases. These results can be explained by the following: as the temperature increases, more KOH evaporates which enhances the surface porosity [12]. On the other hand, SSA decreased as the temperature reached to 800 °C, this is due to the fact that elevated activation temperatures cause pore dilation which lead to explosion/collapse of pores, that led to the lower values of specific surface area [13].

In general, the SDAC yield was found to be inversely proportional to both temperatures of activation and IR. As the temperature elevates more volatile components will be released due to intensified dehydration and elimination reaction that increase C-KOH and C-CO₂ reaction rate which causes lower weights of SDAC [14]. Moreover, the yield decreased with increasing IR. Potassium hydroxide promotes the oxidation process, with high KOH ratio, the gasification of surface carbon atoms is the predominant reaction leading to increase in the weight loss of carbon [15].

3.2. SEM and BET Analysis

Fig. 2 shows the SEM images of SD and SDAC. It can be noticed that SDAC surface has developed pores in which there is a good probability for the lead to be adsorbed. BET surface area was 688.62m²/g. Average pore diameter for SDAC was 5.675µm where it is larger than 50 nm that agrees with IUPAC categories of macro porous materials within the stated range [16]. The high SSA of the SDAC was a result of the used technique of activation. The activation process involved chemical and physical activating agents which are KOH and CO₂ respectively. However, the developed pores during carbonization enhanced the surface area by diffusing more CO₂ and KOH molecules inside the pores, therefore, the reaction between KOH-carbon and CO₂-carbon promoted leading to more pores in the activated carbon.
3.3. Batch Equilibrium Studies

Batch adsorption experiments were conducted by adding 0.25 g of SDAC with 100 ml of prepared lead solution of various concentration (10, 20, 30, 50mg/l) with different initial solution pH ranging from 2 to 5. The experiments were accomplished in different contact times within the range of 10-40 minutes. The temperature range was 20-50 °C where the temperature was controlled by using thermal shaker.

Another set of experiments with time ranging from 30-300 minutes was conducted. Results showed that almost all of the experiments that have contact time larger than 30 minutes with no lead was remained, time range was change to 10-40 minutes.

3.4. Experimental Design and Empirical Model

The set of experiments that was designed by Taguchi method and their results are shown in Table 2.

![Fig. 2. SEM images (A) precursor and (B) SDAC (magnifications: 1000X)](image)

<table>
<thead>
<tr>
<th>initial concentration (mg/L)</th>
<th>time (min)</th>
<th>Temperature (°C)</th>
<th>pH</th>
<th>equilibrium concentration (mg/L)</th>
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</thead>
<tbody>
<tr>
<td>10</td>
<td>10</td>
<td>20</td>
<td>2</td>
<td>10</td>
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<tr>
<td>10</td>
<td>20</td>
<td>30</td>
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<tr>
<td>10</td>
<td>30</td>
<td>40</td>
<td>4</td>
<td>1.911</td>
</tr>
<tr>
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<td>40</td>
<td>50</td>
<td>5</td>
<td>2.132</td>
</tr>
<tr>
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<td>3.175</td>
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<td>20</td>
<td>20</td>
<td>5</td>
<td>2.402</td>
</tr>
<tr>
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<td>30</td>
<td>50</td>
<td>2</td>
<td>13.322</td>
</tr>
<tr>
<td>20</td>
<td>40</td>
<td>40</td>
<td>3</td>
<td>3.131</td>
</tr>
<tr>
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<td>2.707</td>
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<td>4</td>
<td>3.539</td>
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<tr>
<td>50</td>
<td>10</td>
<td>50</td>
<td>3</td>
<td>3.701</td>
</tr>
<tr>
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<td>20</td>
<td>40</td>
<td>2</td>
<td>3.304</td>
</tr>
<tr>
<td>50</td>
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<td>30</td>
<td>5</td>
<td>3.5</td>
</tr>
<tr>
<td>50</td>
<td>40</td>
<td>20</td>
<td>4</td>
<td>3.202</td>
</tr>
</tbody>
</table>
The obtained model with its four factors and their interaction is represented by:

\[
Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + b_4 X_4 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{14} X_1 X_4 + b_{23} X_2 X_3 + b_{24} X_2 X_4 + b_{34} X_3 X_4 + b_{11} X_1^2 + b_{22} X_2^2 + b_{33} X_3^2 + b_{44} X_4^2 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{14} X_1 X_4 + b_{23} X_2 X_3 + b_{24} X_2 X_4 + b_{34} X_3 X_4 + b_{11} X_1^2 + b_{22} X_2^2 + b_{33} X_3^2 + b_{44} X_4^2 \] 

where \( b_0, b_1, b_2, b_3 \) and \( b_4 \) are the linear coefficients, \( b_{12}, b_{13}, b_{14}, b_{23}, b_{24} \) and \( b_{34} \) are the second-order interaction terms, and \( b_{11}, b_{22}, b_{33} \) and \( b_{44} \) are the quadratic terms of each factor. \( Y, X_1, X_2, X_3 \) and \( X_4 \) are the coded terms of equilibrium concentration, initial Lead concentration, time, temperature and pH, respectively.

The estimated values of the model coefficient, standard error of each model term, and its p value are shown in Table 3.

Table 4. Model coefficients, standard error and terms p-values

<table>
<thead>
<tr>
<th>Estimate</th>
<th>Standard error</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>b0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>b1</td>
<td>1.928</td>
<td>0.257</td>
</tr>
<tr>
<td>b2</td>
<td>-1.033</td>
<td>0.203</td>
</tr>
<tr>
<td>b3</td>
<td>3.079</td>
<td>0.352</td>
</tr>
<tr>
<td>b4</td>
<td>-24.723</td>
<td>2.942</td>
</tr>
<tr>
<td>b12</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>b13</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>b14</td>
<td>0.031</td>
<td>0.002</td>
</tr>
<tr>
<td>b23</td>
<td>0.004</td>
<td>0.00</td>
</tr>
<tr>
<td>b24</td>
<td>0.049</td>
<td>0.00</td>
</tr>
<tr>
<td>b34</td>
<td>0.037</td>
<td>0.003</td>
</tr>
<tr>
<td>b11</td>
<td>0.004</td>
<td>0.001</td>
</tr>
<tr>
<td>b22</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>b33</td>
<td>-0.022</td>
<td>0.005</td>
</tr>
<tr>
<td>b44</td>
<td>1.603</td>
<td>0.466</td>
</tr>
</tbody>
</table>

\( b_0, b_{12}, b_{13}, b_{22} \) were eliminated from the model due to their insignificant values compared to others. Their elimination did not affect the accuracy of the predicted model.

3.5 Effects of Factors

3.5.1 Effect of Contact Time and Pb(II) Initial Concentration

The influence of adsorption time on the lead ions adsorbed by SDAC was investigated and presented in Fig. 2. It was observed that removing the lead ions was fast through the first 20 min and removing efficiency of SDAC increased with the initial lead ion concentration. The adsorption was fast at the initial stage because of the high driving force which induced the metal ions to transfer rapidly from the bulk solution to the surface of SDAC [17]. With further increasing time, the availability of the uncovered surface area and the remaining active sites diminish and the decrease in the driving force makes it take long time to reach equilibrium for metal ions, and slowly diffusing into the intraparticle pores of the adsorbent. Thus, the adsorption rate becomes slower [18].

It is also clear from Fig. 2 that adsorption efficiency improved as the initial concentration of Pb (II) increased. This can be due to the fact that higher adsorbate concentration acts as a driving force for higher adsorption efficiency onto SDAC [13]. Similar trend of heavy metal adsorption, as a function of initial concentration, has also been reported previously by Igberase [19] and Trang [20].

![Fig. 2. Effect of contact time and initial concentration on removal efficiency.](image)

3.5.2. Effect of pH and Temperature

The initial solution pH is the most significant factor to investigate the adsorption characteristic of an adsorbent because it affects not only surface charge of the adsorbent, but also the ionization degree and adsorbate speciation [21]. The effect of initial solution pH on the lead ion removal by SDAC is presented in Fig. 3. As the negative charge density on SDAC surface increases due to COOH ionization, the adsorbed lead will rise rapidly [22].
At pH = 5, the efficiency on adsorption reached its maximum value. In order to assure a true investigation of adsorption characteristics of SDAC and to avoid precipitation of the lead ions, all the experiments were run at pH <=5.0. This result is in line with Al-malack and Basaleh [23] and Shi [24].

As temperature rises, the solution viscosity will slightly decrease which enhances the diffusion rate of the lead into the pores of SDAC [25]. In addition to that, the high temperatures will break internal bonds at the edges of the active sites [26] which aids the enhancement of adsorption efficiency of the SDAC. Fig. 3 illustrates the direct proportion between temperature and efficiency of adsorption. As it can be seen from fig.3 that lead adsorption on SDAC is endothermic process. This result corresponds with Sulaymon [27] and Adebisi [3].

3.6 Adsorption Isotherm Studies

The adsorption data of Pb(II) on SDAC fitted Langmuir isotherm more adequately with R² value of 0.996. Fig.4 shows the plot of 1/Cₑ versus 1/qₑ. The results confirmed that the lead had formed a monolayer on the SDAC outer surface with monolayer full coverage adsorption capacity of 13.65 mg/g. Other studies had also confirmed the same results [28] and [29].

Fig. 3. Effect of initial pH and temperature on adsorption efficiency.

Fig. 4. Adsorption data fitted into Langmuir isotherm.

3.7. Kinetics Studies

To figure out the mechanism that controls the adsorption of the lead on SDAC, such as physical interactions and chemical reaction, pseudo-first-order and pseudo-second-order equations were utilized to model the kinetics of adsorption. Fits better the experimental data (R² = 0.996) than the pseudo-first-order model (R² =0.974). The equilibrium adsorption capacity obtained from pseudo- second order (qₑ) was 24.19 mg/g and second order constant k₂ = 0.0053 (g/mg h). Other researches had confirmed the same results [30] and [29].

4. Conclusion

The results of this study showed the active carbon that prepared from sawdust using physiochemical activation is a favorable adsorbent for the lead adsorption from aqueous solution over a wide range of conditions. Langmuir and Freundlich isotherm models were utilized to fit the data of equilibrium and the equilibrium data for SDAC were found to be well represented by the Langmuir isotherm. The kinetics of adsorption followed the pseudo second- order kinetic model. The empirical model represented the adsorption process accurately with R² value of 0.988. Based on the high range of removal efficiencies, SDAC can be used as a cost effective, and inexpensive substitute to the commercial activated carbons.
5. References


أمتزاز المعادن الثقيلة من محلول ماني على كربون منشط من نشارة الخشب

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الخلاصة

نتيجة للأعمال الوراثية للرصاص في الصناعة، بالإضافة إلى أن اثار الخطرة، وجب البحث عن طريقة فعالة واقتصادية إزالتها من المياه العادية. في هذه الدراسة، تم اتخاذ نشارة الخشب كمادة أولية رخيصة، لإنتاج الكربون المنشط. تم اتخاذ طريقة فربانين، كعامل تعديل كيميائي وثاني أوكسيد الكربون كعامل تعديل فيزيائي. تم اتخاذ طريقة تفاعل ثانوي للتحضير لتنشيط الكربون المنشط، ثم تشير خاصيات الخشب في الخلاصة. تم اتخاذ الكربون المنشط من نشارة الخشب لامتزاز ايونات الرصاص من المحلول المائي. تم تحليل عملية الامتزاز، وتم قياس أساطير عينة ثانيوكستات، حيث كانت العملية مناسبة بصورة كبيرة مع معادلة الدرجة الثانية. أظهر كفاءة الامتزاز الحصول عليها 94.48% مع أعلى نسبة الامتزاز تصل إلى 13.21 ملغ/غم.