Adsorption of Lead(II) and Cadmium(II) ions from aqueous solutions by adsorption on activated carbon prepared from cashew nut shells

S. Tangujunk, N. Insuk, J. Tontrakoon, V. Udeye

Abstract—Cashew nut shells were converted into activated carbon powders using KOH activation plus CO2 gasification at 1027 K. The increase both of impregnation ratio and activation time, there was swiftly the development of mesoporous structure with increasing of mesopore volume ratio from 20-28% and 27-45% for activated carbon with ratio of KOH per char equal to 1 and 4, respectively. Activated carbon derived from KOH/char ratio equal to 1 and CO2 gasification time from 20 to 150 minutes were exhibited the BET surface area increasing from 222 to 627 m².g⁻¹. And those were derived from KOH/char ratio of 4 with activation time from 20 to 150 minutes exhibited high BET surface area from 682 to 1026 m².g⁻¹. The adsorption of Lead(II) and Cadmium(II) ion was investigated. This adsorbent exhibited excellent adsorption for Lead(II) and Cadmium(II) ion. Maximum adsorption presented at 99.61% at pH 6.5 and 98.87% at optimum conditions. The experimental data was calculated from Freundlich isotherm and Langmuir isotherm model. The maximum capacity of Pb²⁺ and Cd²⁺ ions was found to be 28.90 m².g⁻¹ and 14.29 m².g⁻¹, respectively.

Keywords—Activated carbon, Cashew nut shell, Heavy metals, Adsorption

1. INTRODUCTION

Water pollution is serious problem of the environment. The increasing in the use of major 20 heavy metals from over the past few decades has inevitably resulted an increasing flux of metallic substances in natural source of water. Resulting from many industries such as tannery, mining, alloying and battery produce significantly major hazardous heavy metal ions such as lead, cadmium and mercury [1]. All lead compounds are considered cumulative poisons. Acute lead poisoning can effect nervous system and gastrointestinal track [2]. The harmful of cadmium include number of acute and chronic disorders such as “itai-itai” disease, emphysema and hypertension [3]. Conventional technique for heavy metals removal water and wastewater including electrolating, evaporating, oxidation, reduction, membrane separation, ion exchange and adsorption. Among these methods, adsorption is worthy economical and effective [4]. Various adsorbents such as silica gel, alumina clay, synthetics polymer resins and carbonaceous materials are used in adsorption method [5]. The activated carbon is the major applying for removal heavy metals adsorption [6], [7]. Agriculture wasted is highly uses as raw material for produce the activated carbon because large quantity of unused and low cost on the production [8]. In recently, activated carbons can be commonly produced from coal, wood or agricultural wastes such as coconut and palm shell, corn cob, rich husk, etc., activated by physical or chemical process. Because of their special pore structure, they have super adsorption capacity and are generally used in variety industrial and domestic fields, such water treatment, solvent decolourization, catalyst supports of fuel cell and supercapacitors [9]. In recent years, there is growing interest in the production of activated carbons from agricultural by-products and residual wastes. In previous studies, many researchers found that activated carbons from coconut shells [10], and pistachio shells [11] by KOH activation and CO2 gasification are essentially microporous with a fairly high surface area [12]. Chemical carbonization of bagasse with concentrated sulfuric acid at a 4: 3 ratio and subsequent CO2 activation at 900°C produced activated carbons with high surface areas (403-1433 m².g⁻¹) [13]. The above mentioned studies show that KOH activation and CO2 gasification enhance high surface area in activated carbon. However, there are few reports on the preparation and characterization of activated carbons derived from cashew nut shells [14] - [16] but the study about how to prepare activated carbon from cashew nut shells with large surface area is scarce in literature. The cashew tree, Anacardium occidentale Linn., is a native plant of eastern Brazil and is introduced into other tropical countries such as India, Africa, Indonesia and South East Asia in the 16th century. It is now found widely in other parts of Central America and the Southern of Thailand, cashew nut shells are usually neglected and abundant agricultural waste. The cashew nut shells have found important commercial usage as the phenolic raw material for the manufacture of certain resins and plastics having unusual electric and frictional properties. Therefore, it is interesting to develop the cashew nut shells as activated carbons with large surface area.

The objectives of this work are to prepare activated carbons from cashew nut shells using KOH activation under N2 and CO2 atmosphere. The prepared activated carbon which characterized their properties from typical technique was use for removal of lead(II) and...
copper(II) ions in aqueous solutions by batch method. The parameters such as effect of initial pH of heavy metal solution, contact time, dosage of activated carbon, and initial concentration of heavy metals were studied.

2. EXPERIMENTAL

2.1. Preparation of activated carbon

Chars were prepared from cashew nut shells by carbonization in the absence of air. These chars were well mixed with water and KOH in a grass beaker with the weight ratios of KOH per char equal to 1 and 4. The mixed chars were dried in oven at 120°C for 24 h to obtain the dried mixtures consisting of chars and KOH. The dried mixtures were heated in oven from room temperature to 850°C (1027 K) with a rate of 15 °C min⁻¹, and temperatures for 20 to 150 minutes. When the time was up, the nitrogen gas was switch off and CO₂ immediately flowed into the oven. The activated carbons obtained were thoroughly washed with distilled water several times, dried at 110°C, cooled at room temperature and stored in desiccators for activated carbon characterization.

2.2. Characterization of the produced activated carbon

FT-IR spectrometer (Spectrum GH, Perkin Elmer) was employed to determine the presence of surface functional groups in samples and samples were analyzed as KBr pellets. The change of crystal structures was characterized by X-ray diffractometer (XRD) with CuK-α radiation (Siemens, D-500). The microstructure of activated carbon was investigated with Scanning electron microscope (LEO, Model 1455VP). The BET surface area of the activated carbon was obtained from the N₂ adsorption isotherm at 77K with adsorption meter (Micromeritics, Porous Materials, BET-2020). The yield was calculated by the following formula as in (1):

\% yield = \frac{\text{(weight of the final products)(weight of the initial samples)}}{\times 100} \quad (1)

2.3. Adsorption experiments

The activated carbon which has highest BET surface area (1127 m² g⁻¹) were chosen as adsorbent for adsorption of heavy metals solution. The adsorption of Pb(II) and Cd(II) ions from aqueous solution was investigated by batch method. The effect of initial pH, contact time and activated carbon dosage and initial heavy metal concentrations were studied. The aqueous which aliquots of 50 mL of Pb(II) and Cd(II) solution of 40 mg L⁻¹ were poured into Erlenmeyer flask(100 mL) containing accurately weight amount of activated carbon which used as adsorbents. The required initial pH of solution were adjusted by adding 0.1 M HCl or NaOH. Then, the flasks were shaken continuously at 200 rpm by auto-shaker for prescribed length of time attain to equilibrium. After filtration through Whatman filter paper, Pb(II) and Cd(II) ions remaining in the solution were determined by atomic adsorption spectrometer(Varian SpectrAA 220).

The amount of metals ion adsorbed[17] was calculated in percentaget(%) and metal uptake(qe) as in (2) and (3):

\% Adsorption = \frac{(C_i - C_e)}{C_e} \times 100 \quad (2)

\[ q_e = \frac{(C_i - C_e) V}{w} \quad (3) \]

where \( C_i \) is the initial concentration (mg L⁻¹), \( C_e \) is metal concentrations at various time interval (mg L⁻¹), \( V \) is the volume of the heavy metal solution (mL), \( w \) is the mass of adsorbent(g)

The Freundlich equation [18]-[21] is in the linearise form as in (5):

\[
\log q_e = \frac{1}{n} \log C_e + \log k
\]

where \( q_e \) is the metal ions adsorbed(mg g⁻¹) at equilibrium, \( C_e \) are the equilibrium concentration(mg L⁻¹), \( k \) is Freundlich constant with multilayer adsorption, \( n \) is adsorption intensity.

The Langmuir equation [22] is in the form as in (6):

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

where \( q_e \) is the metal ions adsorbed(mg g⁻¹), \( C_e \) are the equilibrium concentration(mg L⁻¹), \( q_{max} \) is monolayer adsorption capacity(mg g⁻¹), \( K_L \) is Langmuir adsorption constant.

Langmuir and Freundlich isotherms were obtain from the experiments.

3. RESULTS AND DISCUSSION

3.1. Effects of KOH/char and activation time

Fig. 1 shows the effects of the activation time on the yield of activated carbons. It can be seen that, an increase of activation time decreases the yield of activated carbons. For the activated carbons of group with KOH/char ratio equal to 4, the yield decreased from 82-64% with the increase of the activation time from 20–150 minutes. For the activated carbons of group with KOH/char ratio equal to 1, the yield decreased from 77-60% with the increase of the activation time from 20–150 minutes. The results indicate that with increase of the activation time the yield of group with KOH/char ratio equal to 1 are lower than that of group with KOH/char ratio equal to 4. This is due to the occurrence of the activation reaction between CO₂ and carbons, so the longer activation time favors the progress of activation reaction, which increases in the degree of burning of the produced carbon. However, a large amount of KOH enveloped the carbon, thus lowered the reaction between CO₂ and carbon, resulting of decrease in the degree of burning of the produced carbon.

3.2. Surface chemistry

The adsorptive capacity of the activated carbon is influenced by its surface chemical structure. The functional groups suggested most
often in activated carbon are carboxyl groups, phenolic hydroxyl groups, carbonyl groups and lactone groups [24]. The FTIR spectra of activated carbon are shown in Fig. 2. The spectra were recorded from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\). The FTIR spectrum of the raw cashew nut shell (Fig. 2a) was quite similar to that of rockrose [25], which is also a type of lignocellulosic materials. The band at about 3436 cm\(^{-1}\) was attributed to \(\nu\)(O-H) vibrations in hydroxyl groups or surface-bonded water. The location of hydrogen-bonded OH groups is usually in the range of 3200-3650 cm\(^{-1}\) for alcohols and phenols. The band located around 2923 and 2852 cm\(^{-1}\) corresponded to \(\nu\)(C-H) vibrations in methyl and methylene groups [26], [27]. The \(\nu\)(C=C) vibrations can also be inferred from peak in the region of 1631 cm\(^{-1}\). The band around 1457 cm\(^{-1}\) corresponded to carboxylic groups (-COOH). The band shows around 1113 cm\(^{-1}\) referred to the vibration of the C-O group in lactones [28]. The band at 1384 cm\(^{-1}\) could be attributed to \(\nu\)(C-O) vibrations in carboxylic groups. The appearance of bands between 1300 and 900 cm\(^{-1}\) could be assigned to C-O stretching vibrations. Absorption due to \(\gamma\)(C-H) bending occurred at 776 cm\(^{-1}\) whilst \(\gamma\)(O-H) bending attributed to the absorptions at 579 cm\(^{-1}\). For activated carbons with KOH/char ratio equal to 1 with activation time 20 min (Fig. 2b) and 60 min (Fig.2c), appearance of bands located at 2335 and 1740 cm\(^{-1}\) which could be assigned to the C=O stretching vibrations in ketones or carbonyl groups [29] while the bands at 2923 and 2852 cm\(^{-1}\) disappeared. The decreasing of the intensity of the peaks between 3436 cm\(^{-1}\) indicated a decomposition of the cellulose-based cashew nut shell structure and the loss of surface-bonded moisture. Besides these peaks, the other bands in all activated carbons were quite similar even though the magnitude of the bands decreased with increasing activation time, which suggested that they have similar structures. These trends were also consistent with the activated carbons with KOH/char ratio equal to 4 (Fig. 2d-2e). These results agree with the surface chemistries of other agricultural by-products, such as peach stones [30] and pistachio-nut shell [31].

Fig. 2. FTIR spectra of the cashew nut shell and activated carbons; (a) the cashew nut shell, (b) KOH/Char = 1 with activation time 20 min, (c) KOH/Char = 1 with activation time 60 min, (d) KOH/Char = 4 with activation time 20 min, (e) KOH/Char = 4 with activation time 60 min.

3.3. X-ray analysis

Fig. 3 shows the X-ray diffraction profile of the raw cashew nut shell and the prepared activated carbons at different times and KOH/Char ratios. The raw material (Fig.3a) had a less organized structure with no indication of any specific crystalline structure probably due to the various organic impurities and volatile matters present within the structure. For char (Fig. 3b), there appeared to have a peak at around 20 = 26°. Whilst at a furnace temperature of 850 °C, much of the volatiles and other impurities would have been released and therefore there was formation of any crystalline structures for activated carbons (Fig. 3c-3f). The results indicated that the diffraction profiles of all activated carbons exhibited broad peaks and the absence of a sharp peak revealed a predominantly amorphous structure, and two broad peaks seemed to appear at around 20 = 26° and 43° which were similar to the peaks of crystalline carbonate structure such as graphite (JCPDS). In addition, increasing activation time (Fig. 3c-3f) resulted in slightly sharper peak at around 43°, signified an increasing regularity of crystal structure and resulted in better layer alignment. However, the XRD peaks of group of KOH/char ratio equal to 1 (Fig. 3e and 3d) and 4 (Fig. 3e and 3f) were very similar. This indicated that the KOH effect was not significant for development structure.

Fig.3. XRD patterns of the cashew nut shell, char and activated carbons: (a) Cashew nut shell, (b) Char, (c) KOH/Char = 1 with activation time 20 min, (d) KOH/Char = 1 with activation time 60 min, (e) KOH/Char = 4 with activation time 20 min, (f) KOH/Char = 4 with activation time 60 min.

3.4. Microstructure

Typical SEM microstructures of various conditions of activated carbon from cashew nut shell are shown in Fig. 4a-4g. The char surface (Fig. 4a) shows the irregular structure with prolonged slit pores of the order of 10 μm. Activation of the sample for KOH/Char equal to 1 produced the irregular structure with rough texture and a large number of shallow cavities on the surface (Fig. 4b-4d). With the increase of activation time from 20 to 120 minutes, the random arrays of pore structures had more appeared due to the progress of activation reaction between CO\(_2\) and carbon and the release of the volatile. On the other hand, the increasing both of impregnation ratio and activation time, more pores appear in the interporous areas. With increasing of ratio of KOH/char from 1 to 4 resulted in significantly different of surface and pore structures as observed in Fig. 4e - 4g. For the ratio of KOH/Char equal to 4 with activated time 20 min (Fig. 4e), the surface was enveloped with an amount of KOH and interspersed with generally large pores due to some of the volatiles being evolved. When the activation time was increased from 20 to 120 minutes, decreased the amount of KOH on the surface (analogous to release of volatiles), and there are many uniformly pore structures and becoming honeycomb shape as shown in Fig. 4f-4g. This is because at prolonged activation time favours the progress of activation reaction between CO\(_2\) and carbon, the surface was destroyed by violent activation and large pore numbers were created with increased activation time (analogous to release of volatiles) [32]. Meantime, there were the development of porosity due to reaction between KOH and carbon. This is attributed to the fact that the most of KOH seeped deeply into the interior of char; while at higher KOH/Char ratio, the more severe etch of the wall takes place to create a great quantity of micropores, resulting in an increase in the pore volume [33]. This difference in the development of pore structure can also exhibit the apparently larger BET surface area of the resulting activated carbons produces with higher impregnation ratio of KOH. Furthermore, the SEM result shows that the activated carbon appears to have well developed macropores of the order of 10-30 μm.
mesopores, which make them more suitable for liquid-phase adsorption for example wastewater treatment or drinking water purification. It was found that the KOH activation could provide the activated carbon with relatively high levels of BET surface area when compared to other activation methods. Based on this observation, it can suggest that cashew nut shell is a good material for the preparation of a high quality activated carbon.

Table 1  Physical properties of activated carbons derived from cashew nut shells under different.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gasification time (min.)</th>
<th>BET (m²/g)</th>
<th>Por volume (cm³/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH/Char</td>
<td>0.1127</td>
<td>20.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>222</td>
<td>0.1321</td>
<td>20.11</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>272</td>
<td>0.1389</td>
<td>20.48</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>285</td>
<td>0.1450</td>
<td>20.36</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>553</td>
<td>0.2802</td>
<td>20.26</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>627</td>
<td>0.3142</td>
<td>21.46</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>682</td>
<td>0.3675</td>
<td>21.57</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>KOH/Char = 4 with activation time 60 min.</td>
<td>4</td>
<td>KOH/Char = 4 with activation time 120 min.</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>828</td>
<td>0.4431</td>
<td>21.42</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>995</td>
<td>0.5677</td>
<td>21.63</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>1120</td>
<td>0.5789</td>
<td>22.57</td>
<td></td>
</tr>
</tbody>
</table>

3.6. Adsorption Efficiency

The pH of the aqueous solution is an important controlling parameter in the adsorption process. The effect of initial pH on the adsorption is exhibited in Fig. 4. The result of Pb(II) and Cd(II) ions from Fig. 5 exhibited in the high range 97.50 to 99.13 %. The maximum adsorption efficiency for both of Pb(II) and Cd(II) ion was obtained at pH 6.0-6.5 respectively. The pH of the solution at the equilibrium increased initial pH from 6.0-6.5 to 7.0-7.75. The pH of the initial solution are affected variables in the adsorption process that treated surface charge of the adsorbent and degree of specification and ionization of activated carbon. Between pH 6.0-6.5, the surface is negative charge on the surface of the adsorbent increase there for Pb²⁺ and Cd²⁺ could be enhanced the physical sorption on active site. Thus, the optimum condition value were chosen at 6.0 for Cd(II) and 6.5 for Pb(II) adsorption for further experiments.

Fig. 5. Effect of initial pH on adsorption of Pb(II) and Cd(II) solutions(initial concentration 40 mg.L⁻¹, contact time 30 min. , 0.6 g Activated carbon/solution 50 mL and temp. 303 K).

The effect of the contact time on adsorption of Cd(II) and Pb(II) ions is presented in Fig. 6. For Cd(II), the adsorption equilibrium are obtained at 30 to 120 minutes which showed high range of adsorption of 99.68-99.83%, respectively. The percentage removal of Cd(II) ions increase rapidly from 5 to 30 minutes and then
close to constant value of adsorption efficiency although further increasing contact time till 120 minutes. Thus, the equilibrium contact time of 30 minutes for Cd\textsuperscript{2+} adsorption could be required because of the adsorbate diffused around adsorbent particle and penetrated into internal pore. Though, the equilibrium of the contact time on adsorption of Pb(II) ion was attained after shaking 5 to 30 minutes, then desorption are received. However, it could be re-adsorbed at high efficiency are shown at 90 to 120 minutes. However, from the results, the agitation time required for uptake of Pb(II) ions and Cd(II) ion were fixed at 30 minutes for another next parameter to make sure that the equilibrium was accomplished. As seen from Fig. 5, Pb\textsuperscript{2+} ions exhibited greater attributed than Cd\textsuperscript{2+} ions.

The effect of initial concentration on the percentage removal of Pb(II) and Cd(II) ions by activated carbon prepared from cashew nut shell is shown in Fig. 8, where it is seen that the adsorption of Pb(II) ions decreases from 99.9% to 99.28% and Cd(II) ions is decrease from 99.6% to 91.45%, respectively. For this case, the increase of solution concentration leads to a significantly decrease of the adsorption. Cadmium ions has significantly decrease of adsorption capacity more than Pb(II) ions. This was due to high initial concentrations the number of mole of heavy Pb(II) and Cd(II) ions available to the surface are very high, so functional adsorption become dependent on initial concentration. This characteristic indicated that surface saturation was dependent on initial metal ions concentration.

![Fig. 6](image_url)  
Fig. 6. Effect of contact time on adsorption of Pb(II) and Cd(II) ions (initial concentration 40 mg·L\textsuperscript{-1}, initial pH of heavy solution of Pb(II) 6.5 and Cd(II) 6.0, 0.6 g Activated carbon/solution 50 mL and temp. 303 K).

![Fig. 7](image_url)  
Fig. 7. Effect of activated carbon dosage on adsorption of Pb(II) and Cd(II) ions (initial concentration 40 mg·L\textsuperscript{-1}, initial pH of heavy solution of Pb(II) 6.5 and Cd(II) 6.0, contact time 30 min. and temp. 303 K).

![Fig. 8](image_url)  
Fig. 8. Effect of initial concentration of heavy metals solution on adsorption of Pb(II) and Cd(II) ions (initial pH of heavy solution of Pb(II) 6.5 and Cd(II) 6.0, contact time 30 min., 0.6 g Activated carbon/solution 50 mL and temp. 303 K).

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Freundlich constant</th>
<th>Langmuir constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>q\textsubscript{max}</td>
<td>K</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>1.320</td>
<td>0.859</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>1.390</td>
<td>0.289</td>
</tr>
</tbody>
</table>

Table 2 Values of Freundlich and Langmuir constants for adsorption of Pb(II) and Cd(II) ions.

The comparison of adsorption capacity of various adsorbents for lead and cadmium ions taken from literatures are showed in Table 3. From these results could be assess the quantitatively the binding capacities of prepared activated carbon from cashew nut are competitive when compare other adsorbent. However, prepared activated carbon exhibited preferred Pb(II) ions adsorption more than Cd(II) ions adsorption.
Table 3 Comparison of adsorption capacity of various sorbent for Pb(II) and Cd(II).

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Pb(II) Adsorption capacity (mg/g)</th>
<th>pH</th>
<th>Cd(II) C (mg/L)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut shell carbon</td>
<td>26.50</td>
<td>4.5</td>
<td>50</td>
<td>[35]</td>
</tr>
<tr>
<td>Eichhornia activation</td>
<td>16.58</td>
<td>9.3</td>
<td>3.0</td>
<td>[1]</td>
</tr>
<tr>
<td>Hazelnut husk A.C.</td>
<td>13.05</td>
<td>5.7</td>
<td>40</td>
<td>[17]</td>
</tr>
<tr>
<td>Ceiba Pentandra hulls</td>
<td>-</td>
<td>19.50</td>
<td>5.7</td>
<td>80</td>
</tr>
<tr>
<td>Cashew nut shells A.C.</td>
<td>28.90</td>
<td>14.29</td>
<td>6.0-6.5</td>
<td></td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

A high BET surface area activated carbons could be prepared from cashew nut shells by KOH activation plus CO2 gasification. FTIR spectrum of activated carbons exhibited the presence of different oxygen groups, and aromatic carbon structures. The X-ray diffraction profiles showed a predominantly amorphous structure, and two broad peaks seemed to appear at around 20 = 26° and 43° which were similar to the peaks of crystalline carboaceous structure such as graphite. SEM photographs showed that the structure of activated carbons composed of a great porous with honeycomb shaped and increased with increase of KOH/char ratio and gasification time. Increasing activation time from 20 to 150 min resulted in higher values of BET surface area, pore volume and ratio of mesopore volume. The activated carbons prepared at an activation time of 150 minutes with KOH/char ratio to 4 yielded the highest BET surface area(1120 m² g⁻¹). The optimum conditions of lead and lead showed highly 99.90% and 98.87%, respectively. The adsorption capacity of both of heavy metals exhibited high values that use as beneficial adsorbent. The study indicated that activated carbon prepared from cashew nut shells could be use as an effective adsorbent for the treatment of lead and cadmium aqueous wastewater.

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