Production of Activated Carbon from Cocoa (Theobroma cacao) Pod Husk

Gerardo Cruz*, Minna Pirilä, Mika Huuhtanen, Lili Carrión, Emilio Alvarenga and Riitta L Keiski

1 National University of Tumbes, Department of Forestry Engineering and Environmental Management, Environmental Analysis Laboratory, Av. Universitaria s/n Campus Universitario - Universidad Nacional de Tumbes, Peru
2 University of Oulu, Department of Process and Environmental Engineering, Mass and Heat Transfer Process Laboratory, P.O. Box 4300, FI-90014 University of Oulu, Finland

Abstract

Activated carbons were obtained from cocoa pod husk using two different initial particle sizes (ranges 0.25 – 0.50mm and 0.50 – 1.00mm), three chemical activation agents (K2CO3, KOH and ZnCl2) and carbonization under nitrogen atmosphere during two hours at three different temperatures (500°C, 650°C and 800°C).

The prepared activated carbons were characterized using Brunauer–Emmett–Teller (BET) and Langmuir surface areas, pore volume, average pore size, bulk density, moisture, ash content, and yield. The five best activated carbons were selected for further experiments according to the chemical activation agent used, high BET surface area, high pore volume and low ash content. Additionally, content of impurities, carbon content and FE-SEM micrographs were determined for these five best activated carbons. As adsorption tests were also carried out with these samples.

Results of the experiments show that cocoa pod husk is a material that can be used to produce activated carbon by chemical activation and ZnCl2 showed to be the best chemical activation agent based on the highest BET surface area (780 m²/g in the best case) and pore volume (0.58 m³/g in the best case), the lowest ash content (6.14% in the best case), and the highest carbon content (86.1% in the best case), compared with others chemicals. Carbons activated by ZnCl2 are capable to adsorb As(V), getting As(V) removal levels up to 80% in less than 1 hour in the experimental conditions applied (initial pH 6-7, activated carbon concentration 0.1 g/l and 0.5 g/l, initial As concentration 100 ppb).

Keywords: Activated carbon; Cocoa pod husk; Chemical activation; Physical-chemical characterization; Adsorption

Introduction

Adsorption with activated carbon is a useful treatment method to remove pollutants from waters and wastewaters. However, commercial activated carbons are expensive and it is important to find out new low cost materials available for use as adsorbents. A wide range of studies have been conducted to reach this aim, using cocoa pod husk [1-3] and different agricultural and forest wastes as raw materials, e.g. macadamia nutshell [4], rice husk [5-7], jatropha husk [8], wood apple shell [9], pine nutshell [10], oil palm shell [11], seed shell of the palm tree [12], sago waste [13], guava seed [14], almond shell, pistachio shell, walnut shell [15], olive mill waste [16] and others.

Besides economic implications, the use of agricultural byproducts has environmental advantages [17]. In Peru agricultural wastes as cocoa pod husk are disposed in unsuitable conditions, generating bad smell, microorganisms, pollution of water stream and considerable impacts on the landscape. Another advantage from the environmental point of view is that cocoa pod husk may be considered as a renewable resource because it has been replenished continuously.

Cocoa pod husk represents between 70 to 75% of the whole weight of the cocoa fruit, i.e. per each ton of cocoa fruit there will be between 700 to 750 Kg of waste. Nevertheless, some alternatives have been carried out to avoid the final disposal as well as to create valuable products, e.g. food antioxidants [18], dietary fibers [19], animal feed [20]. Cocoa pod husk shows good features to be used as a precursor in the activated carbon production due to its cellulosic and hemicellulosic content [21].

Cellulosic, hemicellulosic and lignocellulosic materials may be activated using two groups of methods, physical activation and chemical activation. Physical activation involves the use of steam, air, CO2 or a combination of those as an activation agent, while chemical activation uses reagents such as ZnCl2 [7,8], H3PO4 [8], KOH [8,22], K2S, KCNS or K2CO3 [5]. However, chemical activation shows several advantages when compared to physical activation. It uses lower temperatures than pyrolysis, it usually needs only one step, in general it leads to a much higher yield than the physical activation, it allows to obtain activated carbons with very high surface areas and well developed micro porosities, and there is an important reduction of the mineral matter content in the activated carbons obtained.

The adsorption of heavy metals from waters and wastewaters using activated carbon as the treatment method has been studied by several authors; Shukla and Sakhdarenre [23] studied Hg and Pb adsorption, Orhan and Buyukgungor [24] Cd and Cr adsorption, Kumar and Bandypadhyay [25] Cd and Hg adsorption, Jameel and Hussain [6] Pb, Cu, Ni and Cr adsorption, Tangjuank et al. [22] Pbl(II) and Cd(II) adsorption, Khan et al. [7] Cu (II) adsorption, Cem et al. [26] Zn, Cu and Pb adsorption, among others.

Arsenic (As) is one of the pollutants that have several environmental and health implications. The main concern of arsenic is that it can be introduced in food chain e.g. via contaminated drinking water, causing several health effects especially cancer [27]. Arsenic has always been a problem in groundwater pollution; however, nowadays there is also an emerging problem in surface waters. For example in Tumbes River, Peru, arsenic has been found in levels much higher than Peruvian water quality standard allows [28]. Thus, it has become a severe problem since people in rural areas drink this water without any treatment.

*Corresponding author: Gerardo Cruz, National University of Tumbes, Department of Forestry Engineering and Environmental Management, Environmental Analysis Laboratory, Av. Universitaria s/n Campus Universitario - Universidad Nacional de Tumbes, Peru, E-mail: gcrucz@untumbes.edu.pe

Received January 10, 2012; Accepted February 23, 2012; Published February 25, 2012


Copyright: © 2012 Cruz G, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.
This study aims to produce a low-cost activated carbon from cocoa pod husk using three different chemical activation agents, three different carbonization temperatures and two different particle sizes of the raw material. The prepared adsorption materials were characterized by different surface science methods and their performance was compared by testing the preliminarily As adsorption capability of the five best activated carbons.

**Material and Methods**

**Raw material**

Cocoa pod husk samples were collected from four different areas in Tumbes, Peru. Based on Oladayo [21], the characteristics of cocoa pod husk are: moisture content 10.04±0.03 %, ash content 12.67±0.19 %, crude fiber content 33.60±0.15 %, hemi-cellulose content 35.26±0.05 %, lignin content 0.95±0.04 %, and cellulose content 41.92±0.09 %. In addition, the following compounds in cocoa pod husk have also been reported by Aregheore [20]: crude protein 6.2 %, ether extract 1.4 %, calcium 1.63 g/kg, phosphorus 0.17 g/kg, potassium 2.18 g/kg, sodium 0.36 g/kg, magnesium 0.24 g/kg, copper 135.2 mg/kg, manganese 45.6 mg/kg, and zinc 90.3 mg/kg.

**Reagents**

All the chemicals were of analytical reagent grade and used without further purification. The activation chemicals used were K₂CO₃, ZnCl₂, both purchased from Merck, and KOH purchased from Sigma-Aldrich. Sodium arsenate dibasic heptahydrate (HASNa O₇H₇O) from Sigma-Aldrich was used for preparing the 100 mg/l As stock solution for adsorption experiments. The stock solution was preserved with ultrapure concentrated (65 %) nitric acid (HNO₃) in order to have a final acid concentration of 0.2 % in the solution. De-ionized water from a Millipore Milli-Q water system was used for all dilutions of the stock solution.

**Carbonization equipment**

The equipment for the activation of cocoa pod husk is seen in Figure 1. The equipment contained a nitrogen supply, a nitrogen mass flow controller, a furnace, a tubular reactor, a ceramic container for the sample and a trap for gaseous compounds.

**Production of activated carbon**

Cocoa pod husk was dried at 80°C until a constant weight was obtained, ground and sieved to two fractions: 0.25 – 0.5 mm and 0.5 – 1 mm. K₂CO₃, KOH and ZnCl₂ were used as activation chemicals for raw material in a weight proportion 1/1. In the case of K₂CO₃ and KOH water was added to the samples in a weight proportion 1/1 (water/mix), dried at 100°C overnight and carbonized at different temperatures 500, 650 and 800°C. In the case of ZnCl₂, samples were carbonized directly without water addition and dried.

The heating rate of 10°C/min was applied to reach the carbonization temperature, in which the samples were kept for two hours and then cooled down to room temperature. The whole process of carbonization was done under nitrogen atmosphere (150 ml/min).

After carbonization, the samples activated with K₂CO₃ were washed with boiled distilled water and room temperature water. The samples activated with KOH and ZnCl₂ were washed with a dilute solution of HCl (0.5 N) and room temperature water. Finally, all samples were dried at 100°C overnight, ground and sieved on a mesh of 0.25 mm pore size. Table 1 presents the conditions during the activations and the names used for the activated carbons produced.

**Characterization of activated carbon**

Activated carbons obtained were characterized using BET surface area (m²/g), Langmuir surface area (m²/g), pore volume (m³/g), average pore size (nm), moisture content (%), dry matter content (%), ash content (%), yield (%) and bulk density (kg/l) measurements.

Micromeritics ASAP 2020 Surface area and porosity analyzer was used to determine BET surface area, Langmuir surface area, pore volume and average pore size. The BET method was used to calculate the surface area, based on the N₂ adsorption data within the p/p₀ range of 0.057–0.203. The total pore volume and the average pore size were derived using the BJH (Barret-Joyner-Halenda) method. Moisture was determined by a gravimetric method and ash content of the carbons was determined using the standard ASTM procedure D2866-94. The yield was calculated by the following equation

\[
Yield(\%) = \frac{FW}{IW} \times 100\%
\]

where FW is the final weight after carbonization process and IW is the initial raw material weight used before the addition of a chemical activation agent.

The best five samples according to the chemical activation agent, surface area and ash content were selected to carry out deeper analysis such as carbon content (%), impurities content (mg/kg) and existence of impurities and surface uniformity (Fe-SEM images). Impurities were analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) Perkin Elmer Optical Emission Spectrometer Optima 5300 DV. The samples were first dissolved with a mixture of HNO₃, H₂O₂, HF and HCl in microwave oven before analysis with ICP-OES. Fe-SEM images were obtained using a Field Emission Scanning Electron Microscopy ZEISS ULTRA plus equipped with Oxford Instruments INCA-X-act EDS detector.

![Figure 1: Carbonization equipment.](image-url)

<table>
<thead>
<tr>
<th>Chemical Activator</th>
<th>K₂CO₃</th>
<th>KOH</th>
<th>ZnCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>Party size (mm)</td>
<td>Particle size (mm)</td>
<td>Particle size (mm)</td>
</tr>
<tr>
<td>500</td>
<td>0.25 – 0.5</td>
<td>0.5 – 1</td>
<td>0.25 – 0.5</td>
</tr>
<tr>
<td>650</td>
<td>0.25 – 0.5</td>
<td>0.5 – 1</td>
<td>0.25 – 0.5</td>
</tr>
<tr>
<td>800</td>
<td>0.25 – 0.5</td>
<td>0.5 – 1</td>
<td>0.25 – 0.5</td>
</tr>
</tbody>
</table>

Table 1: Description of conditions during the activation process.
Adsorption experiments

Batch adsorption experiments were carried out to test the arsenic adsorption capability of the five best activated carbons obtained. The experiments were conducted at room temperature. The initial arsenic concentration of 100 µg/l in the 200 ml batches was achieved by diluting the As stock solution with Milli-Q water. The initial pH of the arsenic solution was between 6 and 7 and the experiments were conducted without adjusting the solution pH during the test. The activated carbon loadings were 0.5 g/l and 1.0 g/l. The solutions were shaken with a mechanical shaker Certomat at 175 rpm for six hours. Samples were taken periodically at the initial time, 5, 15, 30, 60, 120, 180, and 240 minutes, filtered through 0.45 µm syringe filters and acidified with p.a. nitric acid in order to maintain the preservation of the samples. Arsenic concentration of the samples was analyzed using Graphite Furnace Atomic Absorption Spectrometry (GF-AAS) Perkin Elmer A Analyst 600.

Results and Discussion

Characterization of activated carbons

The characterization results for activated carbons obtained are shown in Table 2. For the samples CPH-07, CPH-08 and CPH-10 it was not possible to obtain results because the yields were insignificant, due to the following reasons: cocoa pod husk particles between 0.25 – 0.5 mm were digested by KOH, high volatilization took place during the carbonization stage or/and the material losses during the washing stage were high because of very low particle size and water solubility of the material.

In the case of KOH the best results of surface area, pore volume and ash content were obtained at 800°C (the highest temperature applied). At 500°C and 650°C, high surface areas were not obtained. This tendency may be because the activation mechanism of KOH in order to generate high porosity needs high temperatures, i.e. temperatures around 800°C. Similar behavior was found by Ahmadpour [4] in the preparation of activated carbon from Macadia Nutshell.

The best results in the samples activated by K2CO3 were obtained at 800°C, and the results show that the quality of activated carbons improves with an increase in the carbonization temperature in the range between 500°C to 800°C. Hayashi et al. [15] found the same results working with various nutshells, however, this behavior changes at carbonization temperatures higher than 900°C.

In general, ZnCl2 was apparently the most effective chemical agent to activate cocoa pod husk, obtaining for all temperatures and particle sizes (all the experiments) the highest BET surface area, highest pore volume and the lowest ash content. Samples prepared by ZnCl2 at 500°C and 650°C showed the best results of surface area and pore volume, while samples prepared at 800°C had lower quality which may be a consequence of ZnCl2 evaporation during carbonization [4].

ZnCl2 activated carbons obtained the highest final yield, then K2CO3 activated carbons and finally KOH activated carbon. It is because of the difference between impregnation methods applied; impregnation in ZnCl2 activation was only for minutes in dry conditions and at room temperature, while in K2CO3 and KOH the impregnation was in wet conditions and overnight at 100°C. Different reaction mechanisms in the activation are another cause for these yields. According to Ahmadpour [4] ZnCl2 (a Lewis acid) promotes the aromatic condensation reactions, which produce an increase in the yield; while KOH (a strong base) catalyzes the oxidation reactions, which results in further carbon gasification. Reaction mechanism of K2CO3 at temperatures above 600°C involves its conversion into CO2 and the significant loss in yield.

The five best activated carbons according to chemical activation agent, BET surface area, pore volume, and ash content were: CPH-09 (0.5-1 mm/KOH/800°C), CPH-13 (0.25-0.5 mm/K2CO3/800°C), CPH-14 (0.5-1 mm/K2CO3/800°C), CPH-21 (0.5-1 mm/ZnCl2/500°C) and CPH-22 (0.25-0.5 mm/ZnCl2/650°C), respectively. These criteria were chosen because these parameters are the most important parameters in the quality of activated carbons. The chemical impurities for contents for these five samples were analyzed with ICP-OES and are shown in Table 3.

The content of impurities was high in the samples analyzed; CPH-09, CPH-13 and CPH-14 have high K levels because of reagents KOH and K2CO3 used in the activation; CPH-21 and CPH-22 show high levels of Zn as impurity, also because of the chemical activation reagent ZnCl2. It will be necessary to adjust the washing in order to reduce the amounts of these impurities [29,30]. Some of these impurities are originating from the natural composition of the cocoa pod husk.

The average carbon content in the samples was 72.9 % for CPH-

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Temp. (°C)</th>
<th>Chemical activator</th>
<th>Particle size(*) (mm)</th>
<th>Final yield (%)</th>
<th>Bulk Density (Kg/l)</th>
<th>Ash (%)</th>
<th>Moisture (%)</th>
<th>Dry matter (%)</th>
<th>BET surface area (m²/g)</th>
<th>Langmuir Surface Area (m²/g)</th>
<th>Pore Volume (m³/g)</th>
<th>Average Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPH – 09</td>
<td>800</td>
<td>KOH</td>
<td>0.5 -1</td>
<td>13.5</td>
<td>0.1</td>
<td>22.3</td>
<td>6.8</td>
<td>93.2</td>
<td>490</td>
<td>648</td>
<td>0.24</td>
<td>2.0</td>
</tr>
<tr>
<td>CPH – 11</td>
<td>650</td>
<td>KOH</td>
<td>0.5 - 1.0</td>
<td>20.7</td>
<td>0.23</td>
<td>53.0</td>
<td>9.0</td>
<td>91.0</td>
<td>8</td>
<td>10</td>
<td>0.02</td>
<td>7.9</td>
</tr>
<tr>
<td>CPH – 12</td>
<td>500</td>
<td>KOH</td>
<td>0.5 - 1.0</td>
<td>21.0</td>
<td>0.22</td>
<td>51.5</td>
<td>8.7</td>
<td>91.3</td>
<td>7</td>
<td>9</td>
<td>0.01</td>
<td>7.0</td>
</tr>
<tr>
<td>CPH – 13</td>
<td>800</td>
<td>K2CO3</td>
<td>0.25 – 0.5</td>
<td>24.2</td>
<td>0.12</td>
<td>20.5</td>
<td>6.9</td>
<td>93.1</td>
<td>615</td>
<td>811</td>
<td>0.31</td>
<td>2.0</td>
</tr>
<tr>
<td>CPH – 14</td>
<td>800</td>
<td>K2CO3</td>
<td>0.5 - 1</td>
<td>19.9</td>
<td>0.1</td>
<td>11.4</td>
<td>6.0</td>
<td>94.0</td>
<td>614</td>
<td>811</td>
<td>0.31</td>
<td>2.0</td>
</tr>
<tr>
<td>CPH – 15</td>
<td>500</td>
<td>K2CO3</td>
<td>0.5 - 1</td>
<td>28.5</td>
<td>0.21</td>
<td>20.2</td>
<td>8.8</td>
<td>93.3</td>
<td>8</td>
<td>12</td>
<td>0.01</td>
<td>5.2</td>
</tr>
<tr>
<td>CPH – 16</td>
<td>650</td>
<td>K2CO3</td>
<td>0.25 - 0.5</td>
<td>14.8</td>
<td>0.15</td>
<td>13.2</td>
<td>8.9</td>
<td>91.1</td>
<td>320</td>
<td>424</td>
<td>0.17</td>
<td>2.1</td>
</tr>
<tr>
<td>CPH – 17</td>
<td>650</td>
<td>K2CO3</td>
<td>0.25 - 0.5</td>
<td>31.3</td>
<td>0.15</td>
<td>17.7</td>
<td>7.0</td>
<td>93.0</td>
<td>8</td>
<td>12</td>
<td>0.02</td>
<td>7.3</td>
</tr>
<tr>
<td>CPH – 18</td>
<td>500</td>
<td>K2CO3</td>
<td>0.25 - 0.5</td>
<td>21.7</td>
<td>0.13</td>
<td>10.7</td>
<td>5.8</td>
<td>94.2</td>
<td>12</td>
<td>17</td>
<td>0.02</td>
<td>6.4</td>
</tr>
<tr>
<td>CPH – 19</td>
<td>800</td>
<td>ZnCl2</td>
<td>0.5 - 1</td>
<td>36.6</td>
<td>0.41</td>
<td>8.8</td>
<td>4.3</td>
<td>95.7</td>
<td>562</td>
<td>771</td>
<td>0.42</td>
<td>3.0</td>
</tr>
<tr>
<td>CPH – 20</td>
<td>800</td>
<td>ZnCl2</td>
<td>0.25 - 0.5</td>
<td>35.3</td>
<td>0.36</td>
<td>6.4</td>
<td>4.3</td>
<td>95.7</td>
<td>574</td>
<td>782</td>
<td>0.38</td>
<td>2.6</td>
</tr>
<tr>
<td>CPH – 21</td>
<td>500</td>
<td>ZnCl2</td>
<td>0.5 - 1</td>
<td>42.5</td>
<td>0.28</td>
<td>8.1</td>
<td>3.3</td>
<td>96.7</td>
<td>724</td>
<td>993</td>
<td>0.53</td>
<td>2.9</td>
</tr>
<tr>
<td>CPH – 22</td>
<td>650</td>
<td>ZnCl2</td>
<td>0.25 - 0.5</td>
<td>37.3</td>
<td>0.32</td>
<td>11.9</td>
<td>3.0</td>
<td>97.0</td>
<td>780</td>
<td>1084</td>
<td>0.58</td>
<td>2.9</td>
</tr>
<tr>
<td>CPH – 23</td>
<td>650</td>
<td>ZnCl2</td>
<td>0.5 - 1</td>
<td>44.9</td>
<td>0.33</td>
<td>11.5</td>
<td>4.5</td>
<td>95.5</td>
<td>663</td>
<td>912</td>
<td>0.57</td>
<td>3.4</td>
</tr>
<tr>
<td>CPH – 24</td>
<td>500</td>
<td>ZnCl2</td>
<td>0.25 - 0.5</td>
<td>47.2</td>
<td>0.32</td>
<td>12.8</td>
<td>4.4</td>
<td>95.6</td>
<td>599</td>
<td>817</td>
<td>0.43</td>
<td>2.9</td>
</tr>
</tbody>
</table>

(*)Particle size of the raw material

Table 2: Results of characterization of activated carbons obtained.
Theobroma cacao

2

d) CPH-21, 1 g/l

2

When the loading of the activated carbon is increased. Aggregation of active sites at the initial period.

According to Jameel and Hussain [6] this is due to adequate availability of active sites at the initial state (between 0 – 50 minutes) then the rate decreases rapidly. These ACs might work in adsorbing As at lower pH values.

Fe-SEM micrographs also show the impurities found with ICP-OES analysis including the presence of charged particles (bright ones) evolved from chemical activation agents.

Adsorption experiments

Redox potential and pH are the most important parameters in the heavy metal speciation in aqueous solutions. Values of pH between 6 – 7 and oxidizing conditions were chosen for the adsorption experiments because of river water conditions in the north of Peru, the place where the future adsorption experiments will be done. In these experimental conditions, the aqueous speciation of arsenic is dominated by As(V), and more specifically oxyanions HAsO$_2^-$ and AsO$_4^{3-}$ are the predominant aqueous forms [32].

Only the activated carbons activated with ZnCl$_2$, (CPH-21 and CPH-22) were capable to adsorb arsenic in the experimental conditions (initial pH 6-7, activated carbon concentration 0.5 g/l and 1.0 g/l, initial As concentration 100 ppb).

Regarding the prepared materials activated by KOH and K$_2$CO$_3$, the problem was the increase of pH; both these activated carbons were basic and when they were added to the initial As solution the pH increased up to 8 or 9. The impurities content in the activated carbon is a negative factor for the adsorption of As(V), since the chemical activation agents are still remaining in the surface of the samples, which is the reason for the increase of pH. Since the surface charge of AC is presumably positive at lower pH values and negative at higher pHs, there may be repulsive forces at basic conditions between the negatively charged activated carbons and anionic As(V) species, and the adsorption does not occur. These ACs might work in adsorbing As at lower pH values.

Figure 3 shows that the rate of adsorption of As(V) is high at the initial state (between 0 – 50 minutes) then the rate decreases rapidly. According to Jameel and Hussain [6] this is due to adequate availability of active sites at the initial period.

As seen from Figure 3 the adsorption of arsenic with CPH-22 decreases remarkably from approximately 70 % to 30 % removal when the loading of the activated carbon is increased. Aggregation of adsorption sites might cause this behavior resulting in decrease in total adsorbent surface area available for As(V) adsorption and an increase in diffusion path length [33]. With CPH-21 the effect is not the same and the removal of arsenic stays at the same level with both the loadings of activated carbon.

Different kinetic models were applied to the experimental data obtained from batch experiments in order to estimate the adsorption mechanism. It was found out that the results followed the best the pseudo-second-order model, which assumes that the rate-limiting step is a chemical sorption between the adsorbate and adsorbent. The integrated form of that model can be written as follows [34]:

\[ q_{\text{e}} = \frac{1}{k_2 q_m} + \frac{1}{q_m} \cdot t \]

09, 76.6 % for CPH-13, 69.6 % for CPH-14, 86.0 % for CPH-21 and 82.9 % for CPH-22. Samples activated by ZnCl$_2$ have the highest carbon content, which is good for the quality of activated carbon in order to adsorb pollutants.

Fe-SEM micrographs in Figure 2 show the development of porosity of the five best samples. However, the structure and size of the pores vary according to the chemical activation agent. For the five best samples, the average pore size is low, because of the predominance of structure of micro pores. However, activated carbons activated by KOH and K$_2$CO$_3$ (2 nm in average, see Table 2) have pores smaller than activated carbons activated by ZnCl$_2$ (3 nm in average, see Table 2). Cocoa pod husk is a material with high content of cellulose and low content of lignin; this is the reason to get predominantly micro porous structure [31].

The pore size distribution of activated carbons activated by ZnCl$_2$, shows a well developed mesoporous structure. It is possible to find micropores inside of these mesopores. This is very important from the water treatment point of view, because mesoporous structure allows water or wastewater to penetrate into activated carbon and to get in contact with the micropores in order to permit the adsorption of heavy metals and pollutants of high molecular weight such as organic compounds.

Fe-SEM micrographs also show the impurities found with ICP-OES analysis including the presence of charged particles (bright ones) evolved from chemical activation agents.
\[
\frac{t}{q_i} = \frac{1}{k_2 q_e} + \frac{t}{q_e}
\]

where \(t\) is the adsorption time (h), \(q_i\) is the amount adsorbed at time \(t\) (mg of As / g of AC), \(k_2\) is the pseudo-second-order rate constant (gm/(g·h)) and \(q_e\) is the calculated equilibrium adsorption capacity (mg of As / g of AC). The amount of arsenic adsorbed at time \(t\) was calculated by using the following mass balance equation:

\[
q_i = \frac{(c_i - c_e)V}{m_{AC}}
\]

where \(c_i\) and \(c_e\) are the initial and the concentration at time \(t\) of arsenic in solution (mg/l), respectively. V is the total volume of solution (l) and \(m_{AC}\) is the mass of activated carbon (g). In Figure 4, \((t/q_i)\) was plotted as a function of time giving linear correlations with all the experimental results.

The second-order adsorption rate constant \((k_2)\) and \(q_e\) values were obtained from the slopes and the intercepts. The values of the correlation coefficients, \(R^2\), \(k_2\) and \(q_e\) are presented in Table 4.

Conclusions

This research studied the utilization of waste biomass, cocoa pod husk, as a precursor for activated carbon production. The raw material was chemically activated with three different activation agents and characterized for the physico-chemical properties. Five best samples were further studied for the adsorption of arsenic. It was found out that cocoa pod husk is a material that can be used to prepare activated carbon by chemical activation and to obtain adsorption materials with high surface areas.

\(\text{ZnCl}_2\) showed to be the best chemical activation agent in the preparation of activated carbon from cocoa pod husk according to the highest BET surface area (780 m\(^2\)/g in the best case) and pore volume (0.58 m\(^3\)/g in the best case), lowest ash content (6.14 % in the best case), and highest carbon content (86.1 % in the best case), compared with other chemicals.

Activated carbons activated by \(\text{ZnCl}_2\) are capable to adsorb As(V), up to removal levels of 80 % in less than one hour at the experimental conditions applied (initial pH 6-7, activated carbon concentration 0.5 g/l and 1.0 g/l, initial As concentration 100 ppb).

Acknowledgements

The project CIMO North-South-South “PROENV2” and the Finnish Graduate School of Environmental Science and Technology are acknowledged for financial support.

References


