In-situ evaluation of the degradable carbon influence for industrial waste water treatment

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Abstract. A photochemical investigation and synergetic blend for wastewater purification was carried out. Blends of different peels: Potato-, Apple and Pineapples-peals (PAP-peals) were impregnated with aqueous solutions of ZnCl2 following the variant of the incipient wetness method for activation of activated carbon (AC). Different concentrations were used to produce impregnation ratios. Activation was carried out in a tube furnace by heating to 700°C with 1 hour soaking time. Scanning Electron Microscopic with attached energy dispersive spectrometer (SEM/EDS), Atomic Adsorption Spectrometry (AAS) and Fourier Transform Infrared spectrometer (FTIS) equipments were used for the characterization of the AC produced. The result shows that PAP-peals derived activated carbons had micro porous characteristics. The study revealed that these new combined adsorbents materials are inexpensive, easily available and they have applications for the removal of Cu, Pb and Cr contained in industrial effluents.

Keywords: Wastewater, Activated Carbon, Potato-peal, Apple-peal, Pineapple-peal, SEM

INTRODUCTION

Industries have been forced to reduce to acceptable level, contents of heavy metal in water and industrial wastewaters [1]. Cr, Cd, Cu and Pb are among those hazardous materials that are most commonly found in industrial wastewaters; therefore, their removal is of most importance [1,2]. Different wastewater treatment techniques have been developed to decrease the amount of wastewater produced [2-4]. Although various treatment techniques can be employed to remove heavy metals from contaminated wastewater, they have their inherent advantages and limitations in application [1-6]. The techniques include chemical precipitation, ion-exchange, adsorption, membrane processes and electrolytic methods [1-9]. In recent years, researchers have studied the production of Activated Carbon (ACs) from cheap and renewable raw materials such as coconut shells, egg shell, wood, maize cob, rice husk, fruit stones, coir pith, used tyres, cotton stalks and bamboo as adsorbents for heavy metals in wastewater treatment [10-12]. In this study, a blend of activated carbon prepared from potato, apple- and pineapple peels induced for removal of heavy metals in wastewater was investigated, using the chemical activation process in which monitoring of the activation time, temperature and impregnation ratio was put in to consideration.
**METHODOLOGY**

**Experimental Procedure**

Process used in this experiment is the chemical reactivation in which a carbon content material is impregnated with a strong base, strong acid or a salt then carbonized at a lower temperature (450-900) °C in the furnace. The advantage of the preparation of activated carbon using chemical activation process is that low activation temperature and shorter time is required for activating the carbon content material.

**Preparation of the Substrate**

Peels obtained from fresh pineapples, apples and potatoes were washed separately with distilled water to remove inorganic impurities then oven dried for few minutes to remove moisture content. These peels were then weighed and initial mass were recorded, followed by oven dry for 24h at 119°C. The peels were then crushed and sieved to required sizes of (1-2) mm, before soaking them in phosphoric acid for 24 hours. They were then washed with distilled water until residual liquid reached pH of 7. Figure 1 shows the chopped oven dried peels soaked in phosphoric acid.

*Figure 1: Potato-, Apple- and Pineapple-peels soaked in phosphoric acid for 24hr*

**Impregnation of the Substrate**

The impregnation ratio of these peels was based on mass ratio of zinc chloride to peels in ratio of 2:1 and 1:2. 32g of peels was impregnated with the solution of zinc chloride and was kept agitated for 1 hour at 80°C the slurry was then filtered and then oven dried for 24hrs at 100°C and labelled 1AC500 2AC500. According to the impregnation ratio and amount of time to be carbonised, impregnation ratio was calculated using equation 1

\[
IR = \frac{w(ZnCl_2)}{w(Char)}
\]

The photochemical and synergetic blend for wastewater purification was investigated. Blends of different peels were used for activation of activated carbon. Potato- apple- and pineapples-peels were impregnated with aqueous solutions of ZnCl₂ following a variant of the incipient wetness method. The impregnation ratio had a strong influence on the pore structure of these ACs, which was easily controlled by simply varying the proportion of ZnCl₂ used in the activation. High impregnation ratios yielded essentially mesoporous carbons with high surface area and pore volume. Thus, low impregnation ratio led to essentially microporous ACs.
Carbonization of the Substrate

The carbonization temperature was carried out in two different temperatures that is 500°C and 700°C in a tube furnace. Each sample was heated in a different temperature for 1hr and then allowed to cool for 30 minutes in the tube furnace after heating. 1AC500 and 2AC500 labelled activated carbon samples were heated separately with a temperature 500°C for 1hr. The final products of activated carbon were then washed with distilled water and dried for a few minutes in an oven to remove moisture then stored in labelled desiccators. Table 1 shows the experimental preparation conditions of the ACs.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>IMPREGNATION RATIO (%w)</th>
<th>CARBONIZATION TEMPERATURE °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1AC500</td>
<td>78.22</td>
<td>500</td>
</tr>
<tr>
<td>2AC500</td>
<td>156.52</td>
<td>500</td>
</tr>
</tbody>
</table>

Characteristics of Potatoes, Apple and Pineapple Peels (PAP-Peels)

Potato peels contain an array of nutritionally and pharmacologically active components such as phenolic compounds, glycol alkaloids, and cell wall polysaccharides, which may be used as antioxidants, precursors of steroids hormones and dietary fiber [13]. Apple peels contain greater amount of crude fiber, ash and caloric value with great amount of moisture found in the peel. Mineral elements composition revealed that apple peels contains greater amount of potassium and zinc. On the other side, pineapple solid waste constitutes about 40-50% of fresh pineapple fruit and core [14]. Pineapple waste contains valuable components which are mainly sucrose, glucose, fructose and other nutrients [15-16].

Adsorption in Wastewater Treatment

Adsorption is a natural process by which molecules of a dissolved compound collect on and adhere to the surface of an adsorbent solid. Carbon has been used as an adsorbent for centuries; powder activated carbon is a particularly good adsorbent medium due to its high surface area to volume ratio and it has been also found to be superior compared to other chemical and physical methods for wastewater treatment in terms of its capability for efficiently adsorbing a broad range of pollutants, fast adsorption kinetics and its simplicity of design [17]. The properties of different carbons can have profound effects on both rate and capacity for adsorption [18]. The percentage adsorption can be calculated by the expression in equation 2.

\[
\text{Percentage adsorption (PA)} = \frac{C_i - C_e}{C_i} \times 100
\]

Therefore the sorption capacity \( q \) is obtained from

\[
q = \left( C_i - C_e \right) \frac{v}{m}
\]

where \( v \) is the volume of the solution (l), \( m \) is the amount of sorbent (g), \( C_i \) and \( C_e \) are the initial and equilibrium concentration in the solution e.g. (Cu, mgL\(^{-1}\)).
Scanning Electron Microscopic (SEM)

SEM was used to study the external morphology of the adsorbent [19]. The electron microscope produces images of samples by scanning it with a focused beam of electron. This electron beam was actually scanned in a raster scan pattern, and the beam’s position was combined with the detected signal to produce an image.

RESULTS AND DISCUSSION

SEM Micrographs Analysis

Figure 2: SEM micrograph and the EDS spectra of 1:2 at 1AC500

Figure 3: SEM micrograph and the EDS spectra of 2:1 at 2AC500

Figure 2 and 3 shows the morphology study by SEM micrographs of activated carbons, in which cavities, pores and rough surfaces were observed on the surface of the prepared activated carbon. It again shows the effect of the
activation temperature and the activating agent influencing the topographical characteristics of the carbon surface. Figure 2 shows the SEM image of activated carbon prepared under optimum conditions (500°C activation temperature, 1 hr activation time and 78.22 w% ZnCl). Small developed pores were found on the surface of the activated carbon which may be due to the lower activation temperature used for activation which significantly resulted to less formation of micropores. Comparatively, Figure 3 also showed very small pores on the surface of the activated carbon, thus low activation temperature was used for activation. A well-developed micropores structure which may be favorable to adsorb larger molecules in comparison to other carbons prepared were seen in activated carbon.

**Adsorption Capacity of Heavy Metals in Industrial Wastewater**

Figure 4 shows the graphs of adsorption capacity of the heavy metals in industrial wastewater. From these graphs, it was observed that the highest metal uptake was copper in which low concentration of this metal is depicted by the results in Figure 4. Lead is the metal that also had considerable low concentration after adsorption, followed by chromium which experienced lower adsorption capacities.

![Figure 4: Concentration of adsorbed heavy metals by 1AC500](image)

![Figure 5: Concentration of adsorbed heavy metals by 2AC500](image)
Table 2 shows the adsorption percentage and the adsorption capacity of Cr (III), Cu (II) and Pb (II) from wastewater adsorbed by AC at different activation ratio and carbonisation temperature 1:2 at 500°C. Based on batch equilibrium studies, the uptake capacity of the three heavy metals appears to be greatest for Cu, followed by Lb and then Cr.

<table>
<thead>
<tr>
<th>Sorbent/metal</th>
<th>Adsorption capacity</th>
<th>Percentage adsorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1AC500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>1.16</td>
<td>78.41</td>
</tr>
<tr>
<td>Cr</td>
<td>0.03</td>
<td>11.64</td>
</tr>
<tr>
<td>Pb</td>
<td>0.3</td>
<td>44.69</td>
</tr>
<tr>
<td>2AC500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.8</td>
<td>57.23</td>
</tr>
<tr>
<td>Cr</td>
<td>0.013</td>
<td>3.85</td>
</tr>
<tr>
<td>Pb</td>
<td>0.36</td>
<td>47.35</td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

From the result obtained, the following conclusion can be drawn:

a). The pyrolysis of potato, pine apple and apple peels impregnated with ZnCl produces materials with a developed structure and adsorption capacities able to adsorb;

b). The impregnation ratio has a strong influence on the pore structure of this activated carbon (ACs), which are easily controlled by simple varying the proportion of zinc chloride used in the activation.

c).The experiment revealed that this new combined adsorbents are inexpensive, easily available materials and they have applications for the removal of Cu, Pb and Cr contained in industrial effluents.

**REFERENCES**