Improvement of Methylene Blue Removal Using Mixed Solid Waste Activated Carbon

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ABSTRACT
Solid wastes have great potential for the removal of pollutants from aqueous solution. So this work aimed to improve the efficiency of mixed solid wastes activated carbon (AC) via chemical activation. AC was prepared by the copyrolysis of mixed solid wastes (palm wastes, paper and plastic wastes). Chemical activation using calcium hydroxide was tested, final activation temperature was 500°C and the adsorption capacity of the produced AC was determined. Results showed that the carbon content of activated carbon increased as the calcium hydroxide concentration increased from 0.0 to 2 M. Also volatile matter and ash content was reduced as the concentration of calcium hydroxide was increased from 0.0 to 2.0M. The adsorption capacity of the prepared AC samples towards methylene blue was increased as the Ca(OH)₂ concentration increased from 0.5 to 2 M at carbonization temperature of 400°C for 2 hr and final activation temperature of 500°C for 1 hr. Scanning electron microscope images showed the micro-porosity activated carbon produced from mixed wastes and confirm that chemical activation and physical activation with calcium hydroxide widens the pores and promotes porosity in carbon which explain the improvement in the adsorption capacity. The methylene blue removal efficiency of the prepared AC is very high (109 mg/g) compared to other adsorbent from the literature.

1. INTRODUCTION
Activated carbons are carbonaceous material that can be distinguished from elemental carbon by the oxidation of the carbon atoms found on the outer and inner surfaces (Mattson 1971). These materials have high internal surface area (that can reach 3000m² g⁻¹), porosity and tunable surface functional groups and cannot be represented by any distinctive chemical formula (Baker 1992; Jiang 2003). These unique properties make activated carbon as versatile material, which has been widely used in various industries. It is used as adsorbent for the removal of heavy metal ions, and toxic organic chemicals from industrial effluents, wastewater, air and gases. It is also used in separation and purification of air, vehicle exhaust emission control, solvent recovery and catalyst support. The large surface area results in high capacity for adsorbing chemicals from gases and liquids (Zanzi 2001).

Due to rapid urbanization, increasing industrial activities and the expansion of crop yields causing an ascending accumulation of different types of solid wastes which if not managed properly, would cause serious degradation to the urban environment. Saudi Arabia domestic solid waste production hits 12 million tons/year; organic, paper, cartons, clothes and plastic waste represents the highest proportional of this waste (79%).
Agricultural wastes originated from different activities including planting, harvest, packaging and marketing therefore various residues, by-product and remains are generated. Plant stems and corn cobs are considered major solid wastes from agricultural activities (Tchobanoglous 2002). Each year the date palm trees are pruned to remove old dead or broken leaves. In the kingdom of Saudi Arabia this practice produces approximately 75,000 tons of date palm fronts (DPF) and 25,000 tons of date palm leaves (DPL) are produced (Al-Jurf 1988). There are several options for proper solid waste management. Disposal of plastic waste is one of the important environmental challenges and its recycling has encountered problems more than any other solid wastes due to their non-degradable feature. More than 80% of the solid wastes are subjected to land filling. Date palm leaves as agricultural waste generated from regular pruning of older leaves have low economic utilization values. Normally, farmers leave this waste outdoors which could provide good environment for certain pests like rodents and insects. The disposed Solid wastes contain materials which could be recycled or safely reused as precursor for low cost adsorbent to treat wastewater contaminated with heavy metals and refractory compounds (Babel 2003). The conversion of these locally available solid wastes such as biomass, waste cartoons, waste news papers, plastics and industrial byproducts into activated carbon for wastewater treatment would improve economic value by providing a potential alternative to costly activated carbon (Kurniawan 2006a; ALOthman 2011; Kurniawan 2006b).

The pyrolysis process can be used as a form of thermal treatment to reduce waste volumes and produce a high economic by-product such as charcoal, gases and tar. The application of pyrolysis to waste management has been gaining acceptance along with other advanced waste treatment technologies. Pyrolysis enables safely solid waste degradation and reduction of green house gases which may result from other treatment methods such as incineration and dumping. The main product of pyrolysis is charcoal and its character differs due to the treatment condition as reported by Helleur (2001). Many authors have used biomass and plastic wastes and proved that they can be converted to suitable adsorbents (Kim 1997; Scott 1990; Conesa 1997; Williams 1997; Tuzen 2009). Williams and Williams (1997) and Fortuna (1997) studied the pyrolysis of waste tires and obtaining around 33% of solid residue, 35% of oil fraction, 12% of scrap and 20% of gases. The typical slow pyrolysis method of carbonization was used to produce char (Bridgwater 2002; Demirbas 2002; Karaca 2006; Tang 2005; Onay 2003). Some researchers (Paradela 2009) have pyrolysed the mixtures of plastics and pine residues to study the effect of the experimental conditions on products composition and yield.

The aim of this study was to convert some organic solid waste into activated carbon for environmental applications. Activated carbon was prepared from mixed organic solid wastes (palm wastes, paper wastes and plastic wastes) by chemical activation with calcium hydroxide and to investigate the effect of activation time and concentration of the impregnating agent on the surface properties and to find the optimum conditions in making AC with well developed porosity. The adsorptive properties of the prepared AC samples were also evaluated by a model compound, Methylene Blue
(MB) which is a cationic dye that dissociate in aqueous solutions into Methylene Blue cation and chloride ion (El Qada 2006).

2. MATERIAL AND METHODS

2.1. Materials

The precursors used in this study were palm wastes, paper wastes and plastic wastes collected from a municipal solid waste station in Riyadh, Saudi Arabia. The elemental analysis of the precursor materials are showed in Table 1.

Table 1. The elemental analysis of the precursor materials.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Palm stem</th>
<th>Waste paper</th>
<th>plastic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon %</td>
<td>45.56</td>
<td>37.83</td>
<td>91.42</td>
</tr>
<tr>
<td>Hydrogen %</td>
<td>5.91</td>
<td>5.57</td>
<td>7.82</td>
</tr>
<tr>
<td>Nitrogen %</td>
<td>0.82</td>
<td>0.08</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Methylene blue (MB), C16H18CIN3S·3H2O supplied by Sigma Aldrich was used as an adsorbate. Stock solution was prepared by dissolving 1.0 g of methylene blue (MB) in 2 L distilled water.

2.2. Activated carbon preparation and characterization

In this study, the three-stage process (Diao 2002) was used for the preparation of activated carbon from mixed wastes. In this process, the precursors are carbonized, impregnated, and then activated for a specific period of time.

For scanning electron microscope (SEM) analysis, samples were mounted on an aluminum stub, coated with a thin layer of gold and then examined using Jeol (JSM-6380 LA) Japan. Fourier transformation infrared (FTIR) spectra of samples were recorded using a spectrophotometer (Thermo Scientific USA). Elemental analysis was performed using a Perkin Elmer Series II CHN analyzer.
2.3. Adsorption studies

Known volumes (80 ml) of each methylene blue solution (50 ppm) were placed in 100-ml Erlenmeyer flasks containing 0.03 g of adsorbent. The contents were shaken at 150 rpm for 4 h in a thermostatic shaking water bath at 25°C. At the end of 4 h, the solutions were separated by filtration. Blank experiments without added adsorbents were performed at the same time. The procedure was repeated for temperatures 40 and 50 °C. MB concentrations were determined by spectrometry at the wavelength of maximum absorbance, 665nm using a double beam UV–Vis spectrophotometer (thermo scientific, USA).

The adsorption capacity of the AC samples was evaluated using eq. (1).

\[ Q_e = (C_0 - C_e) \times \frac{V}{M} \]

where, \( Q_e \) is the adsorption capacity (mg/g), \( C_0 \) is the initial concentration of methylene blue, \( C_e \) is the equilibrium concentration of methylene blue, \( V \) is the volume of the solution (L), and \( M \) is the mass of the adsorbent (g).

3. RESULTS AND DISCUSSION

3.1. Properties of the prepared adsorbents

The thermal properties of the wastes raw material were investigated by TGA and DSC. The TGA of the raw materials was carried out at a heating rate of 10°C/min with a temperature range of 25°C to 1000°C. Above 500°C no further weight loss was observed. Therefore, 500°C was selected as the activation temperature in this study. The overall yield of activated carbon increased as the calcium hydroxide concentration increased from 0.0 to 2 M. The higher yield of activated carbon may be due to the inhibition of the formation of volatile matter by the activating agent (calcium hydroxide). The inhibiting effect chemical activation on volatile matter increases with higher concentration, thereby increasing the carbon yield, enhancing the aromatic condensation reactions and facilitating the evolution of molecular hydrogen from the hydroaromatic structure of the precursor and thereby leaving some active sites on adjacent molecules that can undergo aromatization (polymerization) reactions. As a result of these reactions, the volatile molecules are stabilized, and the carbon yield is increased.

The FTIR spectra of the activated carbon prepared from mixed wastes showed bands at 3650 and 3629 cm\(^{-1}\), arising from the O-H stretching vibration in alcohols; 2928 cm\(^{-1}\), arising from the -CH stretch of a methylene; and 1700cm\(^{-1}\), arising from the C=O stretching vibration in carboxylic acid. There are strong bands around 1600, 1585 and 1514- 1450 cm\(^{-1}\), due to C=C stretching in an aromatic ring.

Table 2 showed ultimate and proximate analysis of the AC samples obtained from the co-pyrolysis of mixed wastes and activated with different concentrations of calcium hydroxide. Results showed a reduction in volatile matter and ash content as the concentration (impregnation ratio) of calcium hydroxide was increased from 0.0 to 2.0 M. This may have been caused by the inhibition of excessive burn-off as the concentration calcium hydroxide increased, resulting in a higher yield of carbon and fixed carbon and a lower content of volatile matter and ash. The same trend was observed by increasing the activation time at 500°C. Also, as can be seen, the carbon content (fixed carbon and elemental carbon) increased with calcium hydroxide
concentration. The value of elemental carbon was consistent with that of fixed carbon, and for each sample the fixed carbon was lower than that of the elemental carbon.

Table 2. Proximate and ultimate analysis of carbon samples obtained from copyrolysis of mixed wastes

<table>
<thead>
<tr>
<th>Activation condition</th>
<th>Proximate analysis (Wt %, dry)</th>
<th>Ultimate analysis (Wt %, dry basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Activation time (min)</td>
<td>Moisture</td>
</tr>
<tr>
<td>0 60</td>
<td>2.354 26.667 5.912 65.067</td>
<td>67.56 2.84 1.23 28.37</td>
</tr>
<tr>
<td>0.5 60</td>
<td>2.742 24.443 10.487 62.328</td>
<td>71.88 5.14 0.86 22.12</td>
</tr>
<tr>
<td>1 60</td>
<td>2.807 21.761 10.828 64.604</td>
<td>72.06 4.54 1.05 22.36</td>
</tr>
<tr>
<td>2 60</td>
<td>2.874 17.556 9.664 69.906</td>
<td>75.34 3.22 0.84 20.60</td>
</tr>
<tr>
<td>1 30</td>
<td>3.191 23.443 7.692 65.674</td>
<td>70.59 3.31 1.02 25.08</td>
</tr>
<tr>
<td>1 60</td>
<td>3.328 21.997 8.211 66.464</td>
<td>73.68 6.33 0.45 19.54</td>
</tr>
<tr>
<td>1 90</td>
<td>3.481 18.766 8.836 68.907</td>
<td>74.03 3.14 1.14 21.69</td>
</tr>
<tr>
<td>1 120</td>
<td>3.846 15.33 11.158 69.666</td>
<td>74.85 2.77 1.12 21.26</td>
</tr>
</tbody>
</table>
3.2. Methylene Blue Adsorption Capacity

Conversion of solid wastes to activated carbon will serve a double purpose. First, unwanted wastes is converted to useful, value-added adsorbent and second, the use as a potential source of adsorbents which will contribute to solving part of the wastewater treatment problems. As shown in Figure 1, the efficiency in removal of methylene blue is enhanced by using mixed wastes co-pyrolysis condition. Also the adsorption capacity of the prepared activated carbon (AC) samples towards methylene blue was increased as the calcium hydroxide concentration increased from 0.5 to 2 M at carbonization temperature of at 400°C for 2hr and final activation temperature of 500°C for 1 hr (Figure 3). The same trend was observed by increasing the time from 30 – 120 minute at final activation temperature of 500°C (Figure 5). These results were correlated with the properties of activated carbon which showed in table 2. The increasing in the adsorption capacity for methylene blue removal with increasing calcium hydroxide concentration and also by increasing activation time at 500°C is due to chemical and physical activation promotes porosity in the carbon. Greater carbon porosity makes it more accessible to the bulky molecules of MB, thereby raising its removal efficiency (Caturla 1991; Kutahyal 2004). Scanning electron microscope images (Figures 2, 4 and 6)) showed the micro-porosity activated carbon produced from mixed wastes and confirm that chemical activation and physical activation with calcium hydroxide widens the pores and promotes porosity in carbon which explain the improvement in the adsorption capacity. Adsorption capacity was high compared to other adsorbent from the literature (Table 3).

![Figure 1](image-url) Methylene blue adsorption capacity (mg/g) of activated carbon prepared from palm wastes and co-pyrolysis of mixed wastes. (carbonization temperature of 400°C for 2hr, chemical activation with 0.5 M calcium hydroxide and final activation temperature of 500°C for 1 hr)
Figure 2 Scanning electron microscope of activated carbon prepared from (a) palm wastes and (b) copyrolysis of mixed wastes. (carbonization temperature of 400°C for 2 hr, chemical activation with 0.5 M calcium hydroxide and final activation temperature of 500°C for 1 hr).

Figure 3. Effect of calcium hydroxide concentration on the methylene blue adsorption capacity (mg/g) of activated carbon prepared by copyrolysis of mixed wastes. (Carbonisation temperature 400°C for 2 hr and final activation temperature 500°C for 1 hr).
Figure 4. Scanning electron microscope of activated carbon prepared from copyrolysis of mixed wastes at carbonization temperature of 400°C for 2hr, chemically activated with (a) 0.0M, (b) 0.5M, (c) 1.5M and (d) 2M calcium hydroxide and final activation temperature of 500°C for 1 hr.

Figure 5. Effect of final activation time at 500°C on the methylene blue adsorption capacity (mg/g) of activated carbon prepared by copyrolysis of mixed wastes. (Carbonization temperature of 400°C for 2hr, chemically activated with 0.5M calcium hydroxide)
Figure 6. Scanning electron microscope of activated carbon prepared from copyrolysis of mixed wastes at carbonization temperature of 400°C for 2hr, chemically activated with 0.5M calcium hydroxide and final activation temperature of 500°C for (a) 0.5, (b) 1.0 (c) 1.5 and (d) 2hr.

Table 3. Comparison of adsorption capacity of various modified adsorbant for methylene blue

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$q_{\text{max}}$ (mg/g) (temperature $^\circ\text{C}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Activated carbon from mixed wastes</td>
<td>93 (30)</td>
<td>This study</td>
</tr>
<tr>
<td>• Coffee husks</td>
<td>90.1 (30)</td>
<td>(Oliveira 2008)</td>
</tr>
<tr>
<td>• Yellow passion fruit waste</td>
<td>44.7 (25)</td>
<td>(Pavan 2008)</td>
</tr>
<tr>
<td>• Rice husks</td>
<td>40.6 (32)</td>
<td>(Vadivelan 2005)</td>
</tr>
<tr>
<td>• Banana peel</td>
<td>20.8 (30)</td>
<td>(Annadurai 2002)</td>
</tr>
<tr>
<td>• Cereal chaff</td>
<td>20.3 (25)</td>
<td>(Han 2006)</td>
</tr>
<tr>
<td>• Spent coffee grounds</td>
<td>18.7 (25)</td>
<td>(Franca 2009)</td>
</tr>
<tr>
<td>• Orange peel</td>
<td>18.6 (30)</td>
<td>(Annadurai 2002)</td>
</tr>
<tr>
<td>• Wheat shells</td>
<td>16.6 (30)</td>
<td>(Bulut 2006)</td>
</tr>
<tr>
<td>• Posidonia oceanica (L.) fibres</td>
<td>5.6 (30)</td>
<td>(Ncibi 2007)</td>
</tr>
</tbody>
</table>
4. CONCLUSION

Activated carbon was prepared by the co-pyrolysis of palm wastes, paper and plastic wastes by chemical activation and physical activation. The effect of calcium hydroxide concentration and the activation time for the final activation temperature at 500°C on properties and the adsorption capacity of activated carbon were investigated. The volatile matter and moisture content of the activated carbons was found to be decreased with increasing calcium hydroxide concentration from 0.5 to 2 m and also with increasing the activation time for the final activation temperature at 500°C from 30 to 120 minute, while the carbon content and fixed carbon increased. The methylene blue removal efficiency of the prepared activated carbon is very high (93 mg/g).

5. ACKNOWLEDGMENTS

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6. REFERENCES


