The preparation of activated carbon from agroforestry waste for wastewater treatment

Hesham R. Lotfy*, Jane Misihairabgwi and Mary Mulela Mutwa

Chemistry and Biochemistry Department, Science Faculty, University of Namibia, P. Bag 13301, Windhoek, Namibia.

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The scope of this study was to produce activated carbon from local agroforestry wastes (marula fruit stones, jackalberry seeds, eembe seeds, efukwa shells and eembu seeds) and assess the efficiency of the produced carbons in removing dyes and metal ions from wastewater. Preparation of activated carbons from efukwa shells, marula fruit stones, jackalberry seeds, eembe seeds and eembu seeds are described in this study. The carbons were chemically activated by treatment with 50% phosphoric acid. The dyes tested in this study were methylene blue and methyl orange and the metal ions tested were lead and zinc. The carbons produced in this study were compared to commercially powdered activated carbon (PAC) and granular activated carbon (GAC). In case of Lead ion and Powdered Activated Carbon (PAC) produced, the removal efficiency for Eembe, Eembu and Jackalberry was 100%, so as for the commercial powdered activated carbon, 100%. In case of Lead ion and granular activated carbon (GAC) produced, the removal efficiency for Eembu and Marula was 100% and for the commercial granular activated carbon was also 100%. In case of Zinc ion and granular activated carbon (GAC) produced, the removal efficiency for Eembu was 91% and Eembe had zero removal and for the commercial granular activated carbon was 89%. In case of Zinc ion and powdered activated carbon (PAC) produced, the removal efficiency for Eembe, Eembu and Efukwa was around 60%, while the powdered activated carbon (PAC) produced from Jackalberry and Marula had zero removal and for the commercial powdered activated carbon (PAC) the removal was 90%. In case of methyl orange dye and powdered activated carbon (PAC) produced, the removal efficiency for Eembe, Marula and Efukwa was 84% and for the commercial powdered activated carbon was 92%. In case of methyl orange dye and granular activated carbon produced, the removal efficiency for Eembu and Marula was 78% and for the commercial granular activated carbon was 87.5%. In case of methylene blue dye and powdered activated carbon (PAC) produced, the removal efficiency for Jackalberry, 84.4%; Marula, 83% and Eembe was 81.3 % and for the commercial powdered activated carbon was 84.4%. In case of methylene blue dye and granular activated carbon (GAC) produced, the removal efficiency for Jackalberry, 83%; Eembu was 81.25% and for the commercial granular activated carbon was 92.2%. The effectiveness of the produced activated carbon in most of the cases is comparable and in some cases equivalent to that of the commercial carbons.

Key words: Activated carbon (AC), powdered activated carbon (PAC), granular activated carbon (GAC), adsorption.

INTRODUCTION

Agricultural by-products represent a considerable quantity of harvested commodity crops. The use of by-products as precursors for the production of widely used adsorbents, such as activated carbons, may impart a value-added component of the overall biomass harvested. In most developing countries, the activated carbon is imported at high cost, limiting the quantities of safe...
drinking water available to the people (Misihairabgwi et al., 2007).

In recent years, there has been research focusing on the use of appropriate, low cost technology for the treatment of drinking water in the developing world. Research has also been focused on the indigenous production of water treatment chemicals using locally available raw materials (Warhurst et al., 1997). Generally, the raw materials for the production of Activated Carbon (AC) are those with high carbon but low inorganic contents such as wood, lignite, peat and coal (Jabit, 2007).

Activated carbons form a large and important class of porous solids, which have found a wide range of technological applications. The characteristics of activated carbon depend on the physical and chemical properties of the precursor as well as on the activation method. In addition to the starting material and the oxidizing agent, activation time and temperature affect the structural properties of the resulting activated carbon. There are two different ways of preparing activated carbon: physical and chemical activation. The physical activation method involves: carbonization of raw material and activation at high temperature in carbon dioxide or water vapor (Petrov et al., 1999). Chemical activation is a well-known method for the preparation of activated carbon, which has been the objective of numerous studies within the last few years (Karim et al., 2006; Wu et al., 2006; Yang et al., 2006; Haimour and Emeish, 2006; Shalaby et al., 2006; Fierro et al., 2006; Pérez et al., 2006) as it presents several advantages compared to the physical activation. The advantage of chemical activation over physical activation is that it is performed in one step and at relatively low temperatures. The most important and commonly used activating agents are phosphoric acid, zinc chloride and alkaline metal compounds, such as KOH (Serrano-Gomez et al., 2005; Dabrowski et al., 2005; Li et al., 2008).

Acid activation of carbons made from wood and coal under a nitrogen atmosphere was investigated by Jagtoyen et al. (1992) and Jagtoyen and Derbyshire (1993) but no attempt was made to investigate cationic metal uptake. It was determined that the oxidation of the carbon surface was important as it produced a negative surface charge, which contributed to its ability to adsorb cations, and a linear relationship between surface charge and metal adsorptive capacity has already been demonstrated by Lima et al. (2004). The process was further evaluated and the predicted cost of producing phosphoric acid activated carbons from agricultural by-products was estimated at $2.89/kg (Ng et al., 2003).

A wide range of carbonaceous materials can be used as the carbon precursors such as coal, peat, wood and various agricultural by-products. Recently, agricultural by-products have received an increasing attention for the production of activated carbon due to their low-cost, renewability and wide prevalence (Kadivelu et al., 2003; Yang and Lua, 2003; Ahmedna et al., 2004; Zhang et al., 2004; Cox et al., 2000; Kadivelu et al., 2004; Gurses et al., 2006; Mohanty et al., 2005). The production of value-added products such as activated carbon will enlarge its application, reduce waste materials and generate income to rural communities in Namibia.

Heavy metal contamination exists in aqueous waste streams of many industries such as metal plating facilities, mining operations and tanners (Özçimen and Ersoy-Merigboyu, 2009). Activated carbons were used as adsorbent materials because of their extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity. Furthermore, the presence of different surface functional groups on activated carbon, especially oxygen groups, leads to the adsorption of ions of heavy metals (Al-Asheh et al., 2003; Naseem and Tahir, 2001).

One of the fastest growing research areas is the environmental applications of activated carbon, such as wastewater treatment. In the treatment of wastewater, it is used for purification, decolorization and the removal of toxic organics and heavy metal ions (Jabit, 2007; Lotfy, 2006; Dastgheib and Rockstraw, 2001; Wartelle and Marshall, 2001).

The demand of activated carbon increased over the years and the market growth was estimated at 4.6 % per year (Jabit, 2007). This demand can be satisfied considering the large number of raw material available for the production of activated carbon (Jabit, 2007).

The aim of the study was to produce activated carbon from local agroforestry wastes (Eefukwa shells, marula fruit stones, jackalberry seeds, eembe seeds and eembu seeds) and assess the efficiency of the produced carbons in removing dyes and metal ions from wastewater.

**MATERIALS AND METHODS**

The shells and seeds which were used as the carbon source were obtained from the northern regions of Namibia during April 2011.

**Sample preparation**

The raw material was washed with deionized water and dried at 120 °C for 4 h. The dried raw material was then ground to particle size of 125 to 250 µm. The particle size was determined using a laboratory test sieve.

**Chemical activation and carbonization**

Six grams of each ground raw material was soaked in 50 ml of 50 % phosphoric acid at 30 °C for 48 h. After 48 h, the phosphoric acid was filtered out and the activated raw material was carbonized in a muffle furnace at 300 °C for 2 h in nitrogen atmosphere. After cooling each of the carbonized materials was washed with 200 ml hot distilled water, then dried for 2 h at 120 °C. The dried carbon was then weighed to determine percentage yield. This procedure
was used to prepare both powdered activated carbon (PAC) and granular activated carbon (GAC).

**Calibration curves**

Dye solutions with concentrations of 10, 20, 30, 40, 50, 60, 70, and 80 mg/L were prepared, maximum wavelength was determined using UV-spectrophotometer and calibration curves were drawn.

**The removal efficiency**

**Removal of dyes**

A solution of 32 mg/L of each dye was prepared in a 100 ml volumetric flask. 20 ml of the dye solution was poured in 50 ml beaker and mixed with 0.01 g PAC, and in another set of experiments, mixed with 0.03 g GAC. The mixture was stirred for 15 minutes and allowed to settle for 10 minutes before filtration. Residual dye concentration was determined in each case.

**Removal of metal ions**

Solutions of 100 mg/L lead and Zinc were prepared in two different 100 ml volumetric flasks. A 20 ml of each was mixed in 50ml beakers with 0.01 g PAC, and in another set of experiments, mixed with 0.03 g GAC, the mixtures were stirred for 15 min and allowed to settle for 10 min before they were filtered. The residual metal ion concentration of the filtrate was determined.

**RESULTS AND DISCUSSION**

The percentage yield for the powdered activated carbon (PAC) is shown in Table 1. Table 2 shows the percentage yield of GAC.

Figure 1 shows the lead ion concentration before and after removals with PAC while the lead ion concentration before and after removal with GAC is shown in Figure 2.

For Zinc ion concentration before and after removals with PAC and GAC are shown in Figures 3 and 4, respectively. Removal of Methyl orange using PAC and GAC are shown in Figures 5 and 6. Figures 7 and 8 shows the removal of Methylene blue using PAC and GAC, respectively.

Agricultural by-products are receiving an increasing attention for the production of activated carbon due to their low-cost, renewability and wide prevalence. The production of value-added products such as activated carbon will enlarge its application and help to deal with wastewater treatment challenges in Namibia.

**Percentage yield**

The percentage yield of the prepared powdered activated carbons were, Eembe, 71.5%; Marula, 66.5%; Eembu, 51.5%; Jackleberry, 61.2% and Eefukwa, 54.7%. In case of granular activated carbon, Eembu, 54.3%; Marula, 59.6%; Eembe, 38.6%; Jackleberry, 37.4%. Efukwa has soft shells which cannot be ground into granulars. Most of the mass loss was during the carbonization process in the muffle furnace.

**Adsorption efficiency**

In case of Lead ion and PAC produced, the removal efficiency for Eembe, Eembu and Jackalberry was 100% and for the commercial PAC was also 100%. In case of Lead ion and GAC produced, the removal efficiency for Eembu and Marula was 100% and for the commercial GAC was 100% as well. In case of Zinc ion and GAC produced, the removal efficiency for Eembu was 91% but for Eembe, there was zero removal and for the
commercial GAC was 89%, in this case the removal efficiency of the GAC produced from Eembe is higher than that of the commercial GAC. In case of Zinc ion and PAC produced, the removal efficiency for Eembe, Eembu and Efukwa was around 60%. The PAC produced from Jackalberry and Marula had zero removal and for the commercial PAC the removal was 90%. In case of methyl orange dye and PAC produced, the removal efficiency for Eembu, Eembe, Marula and Efukwa was 84% and for the commercial PAC was 92%. In case of methyl orange dye and GAC produced, the removal efficiency for Eembu, Eembe and Marula was 78% and for the commercial GAC was 87.5%. In case of methylene blue dye and PAC produced, the removal efficiency for Jackalberry, 84.4%; Marula, 83% and Eembe was 81.3% and for the commercial PAC was 84.4%, in this case the removal efficiency of the PAC produced from Jackalberry is equal to that of the commercial PAC. In case of methylene blue dye and GAC produced, the removal efficiency for Jackalberry, 83%; Eembe was 81.25% and for the commercial GAC was 92.2%.

All the adsorbents used namely; marula, jackalberry, eembe, eembu and efukwa were found to have (varying) adsorptive capacities, that can be attributed to the fact that the characteristics of activated carbon depend on the physical and chemical properties of the precursor. In general PAC was found to have higher adsorptive capacity compared to GAC, which is attributed to the
Figure 3. Zinc ion concentration before and after removal with PAC.

Figure 4. Zinc ion concentration before and after removal with GAC.

Figure 5. Concentration of Methyl orange before and after removal with PAC.
Figure 6. Concentration of methyl orange before and after removal with GAC.

Figure 7. Concentration of Methylene blue before and after removal with PAC.

Figure 8. Concentration of Methylene blue before and after removal with GAC.
larger surface area of the PAC.

**Conclusion**

This study proved the possibility of producing activated carbons from the studied agriculture by-products (efukwa shells, marula fruit stones, jackalberry seeds, eembe seeds and eembu seeds). The study showed that PAC produced from Eembe, Eembu and Jackalberry and GAC produced from Eembu and Marula can completely remove lead ions from a solution containing 100 mg/L Pb²⁺. The PAC produced from Jackalberry is equivalent to the commercial PAC in removing methylene blue dye. The GAC produced from Eembu is better than the commercial GAC in removing Zinc.

If the carbons prepared in this study are produced on a large scale, the cost of water treatment in Namibia will be greatly reduced. The predicted cost of producing phosphoric acid activated carbons from agricultural by-products was estimated at US$2.89/kg (Ng et al., 2003), which is much cheaper than the imported activated carbon. Therefore, consideration should be given to process scale-up for the local manufacturing of these carbons.

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