Sustainable waste management by production of activated carbon from agroforestry residues

Agroforestry waste presents a problem for disposal and negatively impacts on the environment if left to rot or burn. The aim of this study was to reduce environmental problems associated with agroforestry waste by promoting the innovative use of such waste in the production of activated carbons (ACs) using a low-cost production technique, and ultimately delivering more affordable water and effluent treatment adsorbents. Four varieties of ACs from four different agroforestry materials – pine (Pinus contorta) cones (PC), Abies (Abies cilicica) seeds (AS), maple (Acer ginnala) seeds (MS) and peach (Prunus persica) stones (PS) – were prepared by single-step steam pyrolysis and characterised. The raw materials were evaluated for AC yield while the respective ACs were evaluated on the basis of iodine number, phenol specific area, ash content, pH, moisture content and removal of metal ions, nitrates and sulphates from aqueous solution. The AC yields for PS, PC, AS and MS were found to be 23.0%, 18.0%, 17.8% and 14.6%, respectively. The yield for PS (23%) is within the specified commercial limits of 20% to 40%. The phenol specific areas of the ACs ranged between 381 m²/g and 415 m²/g higher than the commercial lower limit (300 m²/g) generally specified. The ACs also showed the capacity to remove heavy metal ions from their aqueous solutions. Removal of both nitrates and sulphates in raw water was greater than 50%. Although no quantitative analysis has been performed to date, it is envisaged that the production of AC from agroforestry wastes can contribute to the sustainable management of environmental pollution by these residues and the concomitant delivery of cheaper adsorbents.

Introduction

A large volume of agroforestry waste is one of the global environmental problems of our time.1 The waste tends to accumulate in water sources, resulting in pollution such as unpleasant odours, eutrophication, high levels of biological oxygen demand and chemical oxygen demand.2 In response to rising costs associated with waste disposal and increasing environmental demands, the sustainable conversion of wastes into useful products is becoming increasingly important.3,4 Conventionally, agroforestry wastes are disposed of by thermal treatment, landfilling and decomposition.5 Despite numerous means of disposal, these wastes still have adverse impacts on the environment.6 Thermal treatment processes involve combustion which results in gaseous emissions (CO₂, CO, CH₄, SO₂, NOₓ, ashes, etc.), many of which are greenhouse gases; combustion is therefore a controversial method of waste disposal.4 On the other hand, landfill waste management commonly results in environmental odours, emission of greenhouse gases – CH₄ and CO₂ – and pollution of both underground and surface waters.8 The quest for environmentally friendly and sustainable ways of disposing of carbonaceous wastes, such as agroforestry wastes, has triggered research focusing on their potential as raw materials for the production of activated carbons.

Activated carbon (AC) is carbonaceous material with a highly developed internal surface area and porosity. The large surface area gives a high capacity for adsorbing chemicals from gases or liquids.10 The specific surface areas of ACs vary widely, with reported values ranging from 250 m²/g to over 2000 m²/g, making them versatile adsorbents with a wide range of applications.10-14 A large volume of ACs is used in water treatment, in which ACs are added primarily to remove organics and other compounds that affect the taste and odour of the water.11-14 In some instances, removal of metals and biological elements may be intended. Other applications include industrial wastewater and gas treatment; removal of compounds that affect colour, taste and odour in the food industry; recovery of metallic minerals such as gold from leached liquors in the mineral processing industry; medicinal and pharmaceutical uses; catalysis; and air filtration and conditioning.11-13

In developing countries, particularly in Africa, the costs associated with the production and/or importation of ACs for water treatment is very high. For example, 1 ton of coconut shell based activated carbon costs about US$950–1400 before shipment.14 This high cost is one of the many contributing factors to a lack of access to commercially treated water for a significant fraction of the population in developing countries. On the other hand, contamination of global water sources is worsening because of increasing industrial activities and population growth and the concomitant increase in waste generation.15 Recent research has established that 70–80% of all illnesses in developing countries is related to water contamination.15 AC is considered a universal adsorbent for the removal of diverse types of pollutants from water; however, its use remains restricted by its relatively high cost, given the low per capita incomes in developing countries.15 The high cost of adsorbents also limits the capacity of industries to treat their effluents to required environmental standards before disposal – with some industries operating outside legal limits – thus exacerbating environmental pollution. Therefore, the need for development of sustainable, cheap and user-friendly water-treatment substances and/or technologies cannot be overemphasised. In particular, increasing demand for adsorption processes in the water-treatment industry is driving research into the production of AC from alternative precursors, such as industrial wastes and agricultural by-products.16 The potential of various agroforestry residues as water treatment adsorbents10,17 and as raw materials for production of AC18,19 has been a subject of investigation for more than two decades. Utilisation of single-step steam pyrolysis as a relatively cheap technique for producing AC from agroforestry residues has also been a subject of keen interest.10,11,13,16,19 Traditionally, commercial activation of carbon is conducted at temperatures above 800 °C in a
mixture of steam and carbon dioxide; and the main raw materials are coal, lignite, coconut shell and wood peat. Steam pyrolysis is a physical activation process in which the precursor material is heat-treated in the presence of steam to form AC. The physical activation process involves two main steps: carbonisation of the carbonaceous raw material to a carbonaceous char; and activation of the char in the presence of a suitable activating medium such as carbon dioxide, steam, air or their mixture. Carbonisation occurs between 400 °C and 800 °C, while activation usually occurs between 600 °C and 900 °C. Several research studies have shown that steam activation is capable of delivering ACs of comparable properties to those of commercial ACs. [11,13,14,18,19]

Although numerous studies have been devoted to investigating the potential of various agroforestry wastes as sources of AC, [11,13,14,22] each particular material and method of production deserves special attention before any commercial viability is recommended. This specificity is necessary because both the raw material and the activation process determine the quality and the cost of producing the ACs. Currently, coconut shells are typical agroforestry residues used commercially in the production of activated carbons intended for drinking water treatment. The byproduct of agroforestry waste makes it a potentially cheaper raw material for production of AC. Single-step steam pyrolysis, by virtue of its simplicity and low cost, is one of the most appropriate technologies for this purpose in developing countries. The aim of the present study was to evaluate the potential of converting agroforestry waste to commercial-grade AC, as an economic waste-management measure, using the low-cost single-step steam pyrolysis process.

**Materials and methods**

**Raw materials**

A total of 5 kg of each of pine (Pinus contorta) cones (PC), Abies (Abies cilicica) seeds (AS), maple (Acer ginnala) seeds (MS) and peach (Prunus persica) stones (PS) was collected around Roma, about 35 km southeast of Maseru, Lesotho. The raw materials were thoroughly cleaned by scraping off surface adherents and washing in distilled water before drying in an oven at 60 °C for 24 h.

**Preparation of activated carbons**

Production of activated carbons was done following the method described in Hapazari et al. [20] The dried raw materials were carbonised and activated using single-step steam pyrolysis. Samples (250 g) of each material were crushed into small pieces and placed in a stainless-steel tray (22 cm × 15 cm × 10 cm) and inserted into a size 1 Gallenkamp box furnace (Griffin and George Limited, Leicestershire, England), fitted with a regulated steam generation system. Steam was generated by injecting water into the furnace at a rate of 20 mL/min, starting when the furnace temperature was at 100 °C until the end of the soak period (30 min). Softer raw materials (MS and AS) were treated at 500 °C while harder raw materials (PC and PS) were treated at 800 °C. The treatment temperatures were selected to ensure minimum ashing and good adsorption properties of the ACs. At the end of the soak period, samples were allowed to cool in a furnace to 100 °C before removing the ACs for washing. The ACs were washed with distilled water for 30 min at 60 °C to remove ash, then dried in the oven at 60 °C for 24 h and weighed. The ACs were then ground to powder and sieved through an 80-mesh (0.177-mm) sieve.

**Characterisation of activated carbons**

The four experimentally produced ACs and a commercially available activated carbon (CAC) were characterised according to five parameters: phenol adsorption (which reflects the surface area of AC), iodine number (which indicates adsorption capacity), pH, ash content and moisture content.

**Phenol adsorption**

Phenol adsorption isotherms were determined and in turn were used to calculate specific surface area of the ACs. Five-point, single-adsorbate isotherms were constructed for a phenol concentration range of 0.2–0.6 mM. Samples of approximately 0.1 g AC were added to 100 mL adsorbate solution in 250-mL stoppered flasks. The flasks were then sealed and shaken at 100 rpm in a temperature-controlled shaker bath (Gallenkamp, Griffin and George Limited) at 25 °C for 24 h. The suspensions were then filtered through Whatman No.1 size 15 filter paper. Residual adsorbate concentrations were determined using a UV spectrophotometer (Shimadzu UV-160A, Sydney, Australia) at 270 nm. The adsorption isotherms were analysed using the Langmuir aqueous phase adsorption model that applies Equation 1 (below) to establish best fit. The model assumes formation of a monolayer of the adsorbate on the carbon surface and is represented by Equation 1:

\[
q_e = \frac{q_m C_e}{1 + b C_e}
\]

where \(q_e\) is the amount of solute adsorbed on the carbon (mol/g); \(C_e\) is the equilibrium concentration of solute (mol/L); \(q_m\) is the Langmuir monolayer coverage constant (mol/g) and \(b\) is the Langmuir adsorption coefficient. \(q_m\) and \(b\) can be derived from a linear plot of \(1/C_e\) against \(1/q_e\).

**Iodine numbers**

Iodine numbers were determined according to the standard procedures of the American Society for Testing and Materials. [26]

**pH**

Slurries of the ACs were prepared by adding 0.2 g AC samples to 100 mL distilled water in 250-mL flasks, and shaking at 200 rpm using a shaker (Vacutec Cat N° 10 × 400 × 2) for 2 h under ambient conditions. The slurries were filtered and the pH of each filtrate was measured.

**Ash content**

For ash content, 2-g samples were ashed at 900 °C for 12 h in a furnace (Gallenkamp box) and the residue cooled to room temperature in a desiccator. The ash content was calculated as the weight ratio of the residues to the original sample.

**Moisture content**

A thermogravimetric method was used to determine moisture content. [27]

**Application of pine cone activated carbon**

Pine cone activated carbon (PCAC) was used to investigate the effectiveness of the experimental ACs for the removal of metal ions (Cd (II), Cu (II), Hg (II), Mn (II) and Pb (II)), nitrates and sulphates from water. The selection of PCAC was based on its superior performance, in terms of adsorption properties, compared to the other experimental ACs.

**Removal of nitrates and sulphates from water**

Analysis of nitrates and sulphates was done before and after treating water with activated carbon. A sample of untreated water (100 mL) was mixed with PCAC (0.1 g) in a 250-mL Erlenmeyer flask. The mixture was shaken at 200 rpm in a temperature-controlled shaker (Vacutec Cat N° 10 × 400 × 2) at 25±2 °C for 2 h. After the specified time, the mixture was filtered using Whatman filter paper No. 1 size 15 to remove the carbon. Nitrates were determined using a UV spectrophotometer (Shimadzu UV 160 A, Sydney, Australia). The nitrate assay relied on a reaction between nitrate ions and sodium salicylate in the presence of tetraoxosulphate (VI) acid medium to produce sodium nitrosalicylate, which is yellow in colour. The intensity of the yellow colour is directly proportional to the nitrate concentration in the sample. The minimum detectable concentration by this method is 0.01 mg/L. Calibration standards ranging from 0.25 mg/L to 2.00 mg/L nitrate solution were prepared and were used to plot a standard curve. Absorbance of the sample was read on the spectrophotometer using quartz cuvettes at 420 nm. The concentration of nitrates in each water sample was calculated from the calibration curve. [28]
For sulphate determination, calibration standards were prepared from sulphate solution stock ranging from 10 mg/L to 80 mg/L sulphate. The standards were then used to plot a calibration graph. A photometer (Spectronic 20 Genesys, Burlington, USA) was used to measure turbidity of the sulphates in the samples. A sample (100 mL) was mixed well into an Erlenmeyer flask with citrate buffer solution (20 mL) using a stirrer at constant speed. While stirring, a spoonful of barium chloride was added, after which stirring continued for 60 s. After stirring, the solution was poured into an absorption cell of the photometer and turbidity was measured at 450 nm. The concentration of sulphates in the sample was then calculated from the calibration curve.

### Removal of metal ions from water

The removal of metal ions – Cd (II), Cu (II), Hg (II), Mn (II) and Pb (II) – from water by the PCAC was determined using a flame atomic adsorption spectrophotometer (FAAS). All the adsorption experiments were carried out in triplicate using a batch adsorption technique. For each metal, a stock solution of metal ion concentration of 1000 mg/L was prepared by dissolving equivalent amounts of analytical reagent grade metal salts (CdCl₂·H₂O, CuCl₂·2H₂O, HgCl₂, MnCl₂·4H₂O and PbCl₂) in 250 mL deionised water. Experimental solutions were prepared by diluting stock solutions of (1) five single-element solutions of 50 mg/L metal ions and (2) a multi-element solution containing 7.14 mg/L of each of the metal ions. Approximately 0.1 g of PCAC was added to each of the six flasks containing 100 mL metal-ion solutions and continuously shaken for 3 h at room temperature. After the adsorption step, the aqueous phase was filtered through Whatman No.1 size 15 filter paper and the final concentration of metal ions was determined by FAAS (Varian Spectra AA-100, Melbourne, Australia).

### Statistical analysis

Determinations of concentration were carried out in triplicate and standard errors were calculated for all results. Data obtained for the removal of metal ions were analysed by SPSS (version 16.0) using a one-tailed Student t-test to determine differences in the removal of metal ions between single- and multi-element solutions. p < 0.05 was considered significant.

### Results and discussion

#### Suitability of raw materials

The AC yields for MS, AS, PC and PS were found to be 14.6%, 17.8%, 18.0% and 23.0%, respectively (Figure 1). The yield for PS was not considered significant.

### Properties of activated carbons

Each of the ACs has its own characteristic properties and variation exists in the efficiency of removal of a range of impurities from water or any other media. Characterisation of the carbons is important in the formulation of a consistent quality carbon applicable for specific uses.

### Ash content and pH

Ash contents for PCAC, MSAC, PSAC and ASAC were 3.03%, 3.90%, 5.35% and 61.4%, respectively (Table 1). The ash content is directly indicative of soluble inorganic material, which, for specific uses such as medical and pharmaceutical applications, may need to be removed for the carbon to be used.

#### Table 1: Characteristics of the experimental carbons and a commercially available activated carbon

<table>
<thead>
<tr>
<th>Carbon sample</th>
<th>Ash content (%)</th>
<th>pH</th>
<th>Moisture content (%)</th>
<th>Water solubility (%)</th>
<th>Solubility in 0.2 M HCl (%)</th>
<th>Iodine value (g/100g)</th>
<th>Phenol specific area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASAC</td>
<td>5.35±0.13</td>
<td>9.76±0.28</td>
<td>0.59±0.06</td>
<td>5.0±0.16</td>
<td>4.7±0.18</td>
<td>52.2±0.23</td>
<td>381±0.66</td>
</tr>
<tr>
<td>MSAC</td>
<td>3.90±0.09</td>
<td>8.64±0.17</td>
<td>0.68±0.05</td>
<td>3.0±0.19</td>
<td>4.0±0.11</td>
<td>61.4±0.07</td>
<td>388±0.45</td>
</tr>
<tr>
<td>PCAC</td>
<td>3.03±0.16</td>
<td>8.34±0.10</td>
<td>0.82±0.08</td>
<td>2.3±0.10</td>
<td>2.7±0.03</td>
<td>100.3±0.11</td>
<td>415±0.10</td>
</tr>
<tr>
<td>PSAC</td>
<td>3.03±0.11</td>
<td>8.58±0.25</td>
<td>1.19±0.03</td>
<td>2.5±0.24</td>
<td>2.2±0.14</td>
<td>73.6±0.20</td>
<td>399±0.06</td>
</tr>
<tr>
<td>CAC</td>
<td>2.00±0.22</td>
<td>8.20±0.13</td>
<td>0.11±0.03</td>
<td>1.8±0.04</td>
<td>1.0±0.03</td>
<td>172.9±0.32</td>
<td>600±0.50</td>
</tr>
</tbody>
</table>

ASAC, activated carbon produced from Abies seeds; MSAC, activated carbon produced from maple seeds; PCAC, activated carbon produced from pine cones; PSAC, activated carbon produced from peach stones; CAC, commercial activated carbon.
Moisture content

The prepared ACs exhibited low moisture contents of 0.59–1.19%, which are ideal for storage (Table 1). Generally, the recommended AC storage moisture content is less than 3%.[3] The higher the moisture content, the more susceptible the carbon is to fungal growth, thus the lower the storage and shelf-life of activated carbon. High moisture contents encourage the growth of AC microorganisms (fungi) within the macropores and micropores of the AC, blocking the pores and thereby reducing the adsorptive capacity of the carbon.[3]

Iodine value

The iodine value is a convenient indicator of carbon adsorption activity and is even relied upon in the water treatment industry for selection of AC from suppliers. The experimental carbons gave iodine values ranging from 52.2 g/100g to 100.3 g/100g, while the CAC gave an iodine value of 172.9 g/100g (Table 1). The experimental carbons exhibit inferior adsorption activities relative to CAC with the best of them, PC, being approximately 1.7 times less than CAC. However, the activities are technically viable and are not necessarily unique. Elsewhere, comparable results have been reported on evaluating ACs from agricultural wastes such as almond shells, cherry stones and peach stones, in which the iodine values ranged from 75 g/100g to 145 g/100 g.[10]

Specific surface area

Adsorption isotherms (Figure 2) were used to assess the adsorptive capacity of carbons by estimating the surface area available for a monolayer of a molecule of phenol. A higher phenol specific area indicates a large micropore volume of the carbon. The phenol specific areas ranged between 318 m²/g (for PSAC) and 415 m²/g (for PCAC). The shape of the adsorption isotherms can provide preliminary qualitative information on the adsorption mechanism and on the porous structure of the carbons. At low phenol concentrations, less than 0.3 mM, all isotherms present a sharp increase typical of adsorption taking place by primary filling of micropores. Between 0.3 mM and 0.4 mM, curves exhibit a levelling off (or adsorption equilibrium), presumably marking the end of primary filling of micropores. Above 0.4 mM, the curves increase sharply again, which presumably shows the onset of secondary filling of super-micropores. Based on the shape of the graphs in Figure 2, the characteristics resemble Langmuir isotherms, also reported by Ntuli et al.[8], Okeola and Odebumi[9] and Aliko and Adebayo.[10] The surface area of AC is generally proportional to its adsorptive capacity. Surface area is dependent on the mass removed during activation of the carbon, which creates pores in the material. The surface area of AC is also influenced by the ash content of the raw material. A high ash content is indicative of high levels of non-carbonaceous matter (impurities) that tend to block the pores during activation, thus lowering the surface area. All raw materials used in this study exhibited low ash contents, which are ideal for attainment of large surface areas in their AC derivatives.

Adsorption of nitrates and sulphates

The PCAC adsorbed both nitrates and sulphates in water and these were reduced from 2.1 mg/L to 0.8 mg/L and 680 mg/L to 200 mg/L, respectively (Table 2; Figure 3). Nitrates and sulphates pose a problem of eutrophication in the aquatic ecosystem, which results in bad odours in water if found exceeding the maximum limit of 600 mg/mL.[11]

Table 2: Nitrate and sulphate values (mg/L) for untreated water and water treated with pine cone activated carbon

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Untreated</th>
<th>Treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrates</td>
<td>2.1±0.05</td>
<td>0.8±0.02</td>
</tr>
<tr>
<td>Sulphates</td>
<td>680±10.5</td>
<td>200±3.1</td>
</tr>
</tbody>
</table>

Generally, percentage adsorption of impurities is proportional to the surface area of AC.14,15 PCAC demonstrated a well-developed surface area (internal pore structure) as removal of nitrates and sulphates was above 50% (Figure 3).

Adsorption of metal ions

Although we did not investigate the parameters known to influence the adsorption process, such as contact time, pH and adsorbent dose, the results still present a positive illustration of the capacity of the tested ACs to adsorb metals from water (Figure 4). The differences in percentage removal of specific elements from single-element and the multi-element solutions can be attributed to the competition for active sites by the elements. In a single-element solution, only one element is available for adsorption by the active sites, while in a multi-element solution, the five elements compete for the active sites for adsorption at constant adsorbent dose. This competition resulted in significantly lower...
percentages adsorptions ($p < 0.05$) from the multi-element solution than from the single-element solutions.

Figure 4: Percentage adsorption values for metal ions in single-element and multi-element solutions. The error bars shown are at a 5% confidence level. There was a significant difference in percentage adsorption between single-element and multi-element solutions ($p < 0.05$).

Conclusions
We demonstrated the technical potential of using a combination of agroforestry wastes and the single-step steam pyrolysis technique to produce activated carbons of acceptable functional properties. We also envisaged that the application of such a process at an industrial scale could contribute towards agroforestry waste reduction in the environment as well as deliver economically competitive ACs. On the basis of AC yields, the use of PS gave a commercially viable yield of 23.0% (above the commercially recommended lower limit of 20%). Two other raw materials – AS and PC – gave yields of 17.8% and 18.0%, which were scattered around the 20% minimum limit, making them also promising raw materials for commercial production. All the investigated agroforestry wastes gave ACs of good quality based on the analysed characteristics. The ACs were by and large suitable for drinking water treatment, as well as any other application of comparatively less stringent requirements.

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Authors’ contributions
V.N. and I.H. contributed equally to the experimental design, data collection and writing of the manuscript.

References
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