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Full Length Research Paper

Adsorption of heavy metals by agroforestry waste derived activated carbons applied to aqueous solutions

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Activated carbons prepared from macadamia nut shells, baobab shells, pigeon pea husks, rice husks, *Moringa oleifera* husks, and marula stones were investigated for their abilities to adsorb Pb(II), Zn(II), Cu(II), Ni(II), Fe(II), Mn(II), Hg(II), Cr(III), As(III) and Cd(II) from aqueous solutions. Batch adsorption experiments were conducted at pH values of 4, 5 and 6. Metal ion adsorption generally increased as the pH was increased from 4 to 6. Percentage adsorption values were above 60% for adsorption of Hg(II) by all the activated carbons at pH 6. The adsorption of Pb(II) by carbons from Baobab shells, pigeon pea husks, *Moringa oleifera* husks and Marula stones was at least 22% higher than that of the commercial carbons used for comparison. Carbons derived from pigeon pea husks and baobab shells showed better metal ion adsorption compared to the other carbons and were used to determine the effects of initial metal concentration, contact time and adsorbent quantity on metal adsorption. The metal ion adsorption data fitted the Langmuir adsorption model.

Key words: Agroforestry, wastes, activated, carbon, adsorption, metals.

INTRODUCTION

The removal of heavy metals from industrial effluents is a major challenge of wastewater treatment. Heavy metals occur as contaminants of liquid waste discharged from various industries such as electroplating, tanneries, textiles, radiator manufacturing, chloralkali, oil refineries, mining and smelting (Kula et al., 2008; Garcia-Reyes et al., 2010; Kantali and Yanik, 2010). The most common toxic metals found in industrial wastewater are chromium, nickel, manganese, mercury, cadmium, lead, copper and zinc (Kazemipour et al., 2008). Potential exists for the

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accumulation and exposure of the metals to humans and other biological systems via water or food (Farooq et al., 2010; Ye and Du, 2010; Zakhama et al., 2011). When heavy metals exceed tolerance levels, they have a harmful effect on human physiology causing various diseases and disorders among which are nervous and renal breakdown, brain damage and convulsions (Kula et al., 2008; Kazemipour et al., 2008; Farooq et al., 2010).

Conventional techniques used for the removal of metals from wastewater include precipitation, membrane filtration, flocculation, ion exchange, reverse osmosis and adsorption (Chang et al., 2002; Kantarli et al., 2010). The methods tend to have relatively high capital and operating costs and are therefore not suitable for developing countries and small-scale industries in developed countries.

Worldwide, research has been focused on the indigenous production of water treatment chemicals using locally available raw materials (Farooq et al., 2010; Mussatto et al., 2010; Rivera-Utrilla et al., 2011). Among many water treatment technologies, utilizing plant residues as adsorbents for the removal of dyes and metal ions from wastewater is a prominent technology (Kadirvelu et al., 2001).

Activated carbon, due to its high surface area, micro porous character and surface chemistry, has been proven to be an effective adsorbent for the removal of heavy metals from industrial wastewater (Avelar et al., 2010; Mussato et al., 2010; Utrilla et al., 2011). Despite its frequent use in the water and waste industries, activated carbon remains an expensive material (Farooq et al., 2010; Mussatto et al., 2010). In view of the high cost of activated carbon, a lot of research has been directed to the development of low-cost activated carbon from cheap and readily available materials. Among the low-cost raw materials are the agroforestry and agro-industrial residues. A wide variety of carbons have been prepared from agricultural wastes such as olive seeds, rice husks, walnut shells, palm shells, hazelnut shells, almond shells, pistachio nut shells and apricot stone (Kula et al., 2008; Kazemipour et al., 2008; Ye and Du, 2010; Zabihi et al., 2010; Owlad et al., 2010; Ozcimen and Ersoy-Mericboyu, 2009). Each of the carbons has characteristic properties and variation exists in the efficiency of removal of a range of heavy metal ions from solution. There is a constant need to investigate the potential of various raw materials as activated carbon precursors, depending on their costs and availability.

We report in this study, the efficiencies of agroforestry waste-derived activated carbons in the removal of heavy metal ions from aqueous solutions. Common heavy metals found in industrial wastewater, Pb(II), Zn(II), Cu(II), Ni(II), Fe(II), Mn(II), Hg(II), Cr(III), As(II) and Cd(II) were used in the study.

MATERIALS AND METHODS

Activated carbon

Activated carbons prepared from macadamia nut shells (MNS), *Adansonia digitata* (Baobab) fruit shells (BBB), pigeon pea husks (PPH), rice husks (RH), *Moringa oleifera* husks (MH) and *Sclerocarya birrea* (Marula) fruit stones (AML) were used in this study. The carbons were prepared at the Centre for Water Sanitation and Hygiene, Malawi Polytechnic, University of Malawi. All the biomass samples were activated and carbonized in a one-step pyrolysis method in the presence of steam at 750°C and final soak time of 30 min (Warhurst et al., 1997). Pyrolysis was carried out in a cube furnace (Podmore and Sons Ltd, Type J2HT, S/N 5655) at a temperature of 750°C, a soak time of 30 min and a water flow rate of 30 ml/min. A stainless steel box, 240 mm high, 210 mm wide and 400 mm deep, with three trays in which the raw materials were placed, was inserted into the furnace and water was injected at a rate of 30 ml/min using a pump (Watson Marlow Ltd. Type 501 S170, S/N 70256). After carbonization, the carbons were ground using a pestle and mortar and sieved to a size of <250 µm, dried in an oven at 110°C then stored in a desiccator until use. All the agroforestry derived carbons were compared against the commercially produced carbon typically used at municipal water treatment works in Harare, Zimbabwe, and with Eurocarbon PHO 14 x 45 from Eurocarbon Products Ltd., England.

Effect of pH on metal ion adsorption

Batch adsorption experiments were conducted in triplicate to investigate the effect of pH on the adsorption of metal ions by activated carbons. Solutions containing 10 mg/l of each heavy metal ion (Pb(II), Zn(II), Cu(II), Ni(II), Fe(II), Mn(II), Hg(II), Cr(III), As(III) and Cd(II) were prepared from the dilution of 1000 mg/L metal ion standard solutions (Fisher Scientific, Loughborough, UK). Metal ion solutions were prepared in acetate buffer (0.1 M) at pH values of 4, 5 and 6. The initial pH values of the solutions were measured using a Mettler Toledo 340 pH meter (Leicester, UK). Powdered activated carbon (100 mg) (<200 µm) from the various agroforestry wastes was added to solutions of the metal ions (20 ml) at different initial pH values. Mixtures were agitated on a flask shaker (Barlowworld Ltd., Staffordshire, UK) at 500 strokes/min at room temperature (25 ± 2°C) for 120 min. The mixtures were then centrifuged at 3000 rpm for 10 min (ALC Centrifuge, model PK130, Cologne, Germany) and the supernatants were filtered through 0.45 µm syringe filters (Millipore Corporation, USA). The concentration of residual metal ions in the supernatants were determined by ICP-OES using a Perkin Elmer Optima 5300 DV instrument (Perkin Elmer, UK) at an RF power of 1300 W and with plasma, auxiliary and nebuliser argon gas flows of 15, 0.2 and 0.75 L min^{-1} respectively, and a pump flow rate of 1.5 ml/min. Multi-element calibration standards in the concentration range 1 - 10 mg/L were used and the emission intensity measured at appropriate wavelengths. For all elements, analytical precision (RSD) was typically 1 to 5% for individual aliquots (n=3).

Effect of contact time on metal ion adsorption by BBB and PPH

Activated carbons pigeon pea husks (PPH) and baobab shells

(BBB) were used to determine the effect of contact time and quantity of adsorbent on metal ion adsorption. Batch adsorption experiments were carried out as described for the determination of initial pH, for contact times of 15, 30, 60, 90 and 120 min, with a fixed quantity of adsorbent of 5 g/L at pH 6 for solutions of mixtures of the metal ions at a concentration of 10 mg/L and for solutions containing Pb(II) ions only at a level of 10 mg/L.

Effect of quantity of carbon on metal ion adsorption

To investigate the effect of varying the quantity of carbon on metal ion adsorption, the quantity of carbon was varied from 0.5 to 10 g/L, whilst keeping all the other experimental variables constant, that is, pH 6.0, initial metal concentration of 10 mg/L and contact time 60 min.

Langmuir adsorption isotherm

The adsorption isotherm data produced from varying quantities of BBB in the adsorption of Pb(II) was analyzed using a Langmuir aqueous phase adsorption model. The Langmuir adsorption model assumes that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface (Bansode et al., 2003). The Langmuir equation can be described by the linearized form:

$$C_e/q_e = 1/Q_o b + C_e/Q_o \quad (1)$$

Where, q_e is the amount of solute adsorbed on the carbon (mg/g), C_e is the equilibrium concentration of solute (mg/l). The adsorption capacity, Q_o; and the energy of adsorption capacity, b; can be derived from a linear plot of C_e/q_e against C_e.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by the equation:

$$R_L = 1/(1+bC_o) \quad (2)$$

R_L values between 0 and 1 indicate favorable adsorption of Pb(II) onto BBB (Bansode et al., 2003).

RESULTS AND DISCUSSION

Effect of pH on adsorption of metal ions

The adsorption efficiency of the carbons was initially determined at pH values of 4, 5 and 6 and a contact time of 120 min, which was considered as adequate for an efficient adsorbent to reach equilibrium. The adsorption of all target metal ions by macadamia nut shells (MNS), rice husks (RH), *Moringa oleifera* husks (MH) and marula stones (AML) increased as initial pH increased from 4 to 6 (Tables 1, 2 and 3). The trend is consistent with the results obtained for the adsorption of Pb(II) using activated carbon prepared from various agricultural wastes (Ayyappan et al., 2005), for the adsorption of heavy metal ions using activated carbon prepared from apricot stone (Kobya et al., 2005) and for the adsorption of nickel by activated carbon prepared from almond husk (Hasar, 2003). For all the carbons used in this study, maximum metal ion adsorption was observed at pH 6 (Table 3) and on raising the pH above 6, precipitation occurred. The removal of metals from solution is dependent on the pH of the solution, which affects the surface charge of adsorbents, the degree of ionization and the species of adsorbate (Ayyappan et al., 2005; Karagoz et al., 2008; Dermibas et al., 2008). The increase in metal removal as pH increased can be attributed to the decrease in competition between H^+ ions and positively charged metal ions at the surface sites of the activated carbon (Hasar, 2003). Also, the binding of metal ions to the adsorbent should increase as the surface of the adsorbent changes from positive to negative, a transition which is influenced by the equilibrium pH. As the equilibration pH is varied, a point of zero charges (pH_{ZPC}) is attained, which is a pH value where the net charge on the surface of the adsorbent is zero (Noh and Schwarz, 1989). It is expected that as equilibrium pH is increased from 4 to 6, the transition towards negative charge on the carbons takes place as the pH moves towards or above pH_{ZPC} and therefore the carbon surfaces become more negatively charged resulting in increased binding of the metal ions.

Under all the pH conditions, RH had adsorption efficiencies below 42% for most of the metal ions. Adsorption efficiencies of Cd(II) and Zn(II) were less than 40% for all the adsorbents under all the pH conditions investigated, except PPH, which had 63% adsorption of Zn(II) at pH 6. On comparing the metal ion adsorption efficiencies of the various adsorbents at pH 6, it was observed that the percentage adsorption values were above 60% for adsorption of Hg(II) by all the activated carbons (Table 3). MNS had adsorption efficiencies of above 60% for Cu(II) and Hg(II) under all the pH conditions investigated, with a relatively high value of 97% for Hg(II) at pH 6. At the same pH, BBB was able to adsorb more than 84% of Pb(II), Cu(II), Fe(II) and Hg(II). Adsorption efficiencies higher than 68% were observed for adsorption of Pb(II), Cu(II), Fe(II), Hg(II) and As(III) using PPH. Heavy metal ion adsorption efficiencies of the experimental carbons were compared with commercially available carbons. In comparison with the two commercial carbons, the adsorption of Pb(II) by BBB, PPH, MH and AML was at least 22% higher than that of commercial carbons. The differences in adsorption efficiencies of the carbons can be attributed to possible differences in the pH_{ZPC} of the carbons. The pH_{ZPC} is in-turn influenced by the nature of the active groups on the carbon, an aspect that will vary depending on the precursor material (Al-Degs et al., 2000).

Table 1. Percentage adsorption of metal ions onto various adsorbents at pH 4.

Metal ion	Adsorbent							
	MNS	BBB	PPH	RH	MH	AML	CC 1	CC 2
Pb(II)	19.3	51.2 ± 0.1	49.2	12.8 ± 0.1	51.9 ± 0.1	28.2 ± 0.1	14.2±0.1	7.4 ± 0.5
Zn(II)	12.6 ± 0.2	19.1 ± 0.2	19.8 ± 0.3	1.5 ± 0.1	4.7 ± 0.1	1.7 ± 0.1	1.3	17.9 ± 0.3
Cu(II)	78.2	90.7	61.8 ± 0.1	16.1 ± 0.2	34.9 ± 0.2	35.7 ± 0.1	17.7	43.3 ± 0.6
Ni(II)	13.6	30.7 ± 0.1	16.9 ± 0.2	0.3	3.1	1.9	0	14.5 ± 0.2
Fe(II)	38.6 ± 0.2	50.1 ± 0.1	68.3 ± 0.1	8.2	28.4 ± 0.1	9.1	0	13 ± 0.1
Mn(II)	0	12.3 ± 0.1	16.7 ± 0.1	2 ± 0.1	6 ± 0.1	1.6	1.4	2.3 ± 0.2
Hg(II)	62.4 ± 0.1	43.7 ± 0.1	39.2 ± 0.1	22 ± 0.3	66.7	45.6 ± 0.1	100	50.8 ± 0.7
Cr(III)	22.8 ± 0.1	35.3 ± 0.1	31	9.4 ± 0.2	17	9.5 ± 0.6	6.2	13.6
As(III)	9.5 ± 0.1	18.6 ± 0.2	17.4 ± 0.1	5.2	5.4	7.5	5.8	13.8 ± 0.1
Cd(II)	10.7 ± 0.2	20.6 ± 0.2	22.9	2.3	7.3	3.2 ± 0.1	6.1	13 ± 0.4

MNS: Macadamia nut shells activated carbon, BBB: baobab shells activated carbon, PPH: pigeon pea husks activated carbon, RH: rice husks activated carbon, MH: *Moringaoleifera* husks activated carbon, AML: marula stones activated carbon, CC1: commercial carbon 1, CC2: commercial carbon 2

Table 2. Percentage adsorption of metal ions onto various adsorbents at pH 5.

Metal ion	Adsorbent							
	MNS	BBB	PPH	RH	MH	AML	CC 1	CC 2
Pb(II)	28.7±0.1	38.3±0.1	35.1±0.1	14.3	54	36.1±0.1	17.8	26.2±0.1
Zn(II)	6.9±0.1	14.2±0.1	6.6±0.2	1.6	7±0.1	4.1	2.5	8.6±0.2
Cu(II)	75.3±0.1	84.3	48	25.8±0.4	47.9±0.1	51.2±0.1	29.1	43.3±0.4
Ni(II)	11.4±0.1	24.1±0.1	8.9±0.1	2.8±0.1	6.6±0.1	8.2±0.1	2.3±0.1	7.1
Fe(II)	47.7±0.1	48.5±0.1	50.8	16±0.1	12.3±0.1	17.6±0.1	20.6±0.1	17.2±0.2
Mn(II)	0±0.1	5.7	8.6	2.8±0.1	5.4±0.1	2.8	0.7	0.7
Hg(II)	61±0.2	41.7±0.1	37.7±0.1	29.2±0.2	72.2±0.1	57.2	92.8±0.1	51.3±0.2
Cr(III)	30.2±0.1	34.5	27.4	7.7±0.5	18.3±0.1	18±0.1	21.9±0.1	17±0.1
As(III)	0.3±0.1	3.4±0.1	3.6±0.1	6.9	8.3±0.1	7±0.1	8.4	0.7
Cd(II)	0±0.1	6±0.1	10.9±0.1	0.4	6.5±0.1	2.7	3.6	1.2±0.1

MNS: Macadamia nut shells activated carbon, BBB: baobab shells activated carbon, PPH: pigeon pea husks activated carbon, RH: rice husks activated carbon, MH: *Moringaoleifera* husks activated carbon, AML: marula stones activated carbon, CC1: commercial carbon 1, CC2: commercial carbon 2

Effect of contact time on adsorption of metal ions

On monitoring the adsorption of the metal ions by the most efficient carbons, PPH and BBB, over time, percentage adsorption increased up to 60 min then reached a plateau for adsorption of Pb(II), Cu(II), Hg(II), Zn(II), Cr(III), Ni(II) and As(III) onto PPH (Figures 1 and 2). The adsorption of Fe(II) remained constant at the different contact times while percentage adsorption continued to increase slightly for the adsorption of Mn(II), As(III) and Cd(II). Apparently, there was competitive binding of the metal ions onto the carbon in the decreasing order of Fe(II)>Pb(II)>Hg(II)>Cu(II)>Zn(II)> Cr(III)>As(III)>Ni(II)>Mg(II)>Cd(II). When BBB was used as the adsorbent, there was no apparent effect of increasing contact time on the adsorption of all the metals except for Cr(III), where a slight increase in adsorption was adsorbed, reaching equilibrium at 90 min (Figure 2). Yu et al. (2001), reported that removal of Cr(VI) from aqueous solution increased with time and attained saturation in about 100 to 200 min. In adsorption of nickel by activated carbon prepared from almond husks, Hasar

Table 3. Percentage adsorption of metal ions onto various adsorbents at pH 6.

Metal ion	Adsorbent							
	MNS	BBB	PPH	RH	MH	AML	CC 1	CC 2
Pb(II)	66.3	84.3	94.2±0.1	40.2 ± 0.1	76.2	64.8	40.8 ± 0.1	61.8
Zn(II)	11.7	36.6	62.8	7.9 ± 0.2	28.4 ± 0.1	16.3 ± 0.1	0 ± 0.2	14.5 ± 0.1
Cu(II)	87.7 ± 0.2	98.3±0.1	87.5 ± 0.1	42.2 ± 0.2	62.7 ± 0.1	75.9 ± 0.1	59.9	79.5 ± 0.1
Ni(II)	17.6	61.4	38.4	12.7 ± 0.1	19.8 ± 0.1	19.5 ± 0.1	0 ± 0.2	19.9 ± 0.1
Fe(II)	80.9	88.6	98.5	58.8 ± 0.1	58.0	63.8	83.3	73.3
Mn(II)	6.9	26.1±0.1	34.7±0.1	11.5 ± 0.1	24.8 ± 0.1	12.9 ± 0.1	0	6.6
Hg(II)	97.3	89.3±0.1	95.5±0.1	64.5	95.1	90.9	100 ± 0.1	88.0 ± 0.1
Cr(III)	59	48.8	51.8	24.8 ± 0.1	28.4 ± 0.1	36.0 ± 0.1	61.3 ± 0.1	56.3 ± 0.1
As(III)	50.5	57.2	68.5	40.1 ± 0.2	34.5 ± 0.1	41.5 ± 0.1	57.8 ± 0.2	46.0 ± 0.1
Cd(II)	4.9	16.5	25.5±0.1	5.0 ± 0.2	18.1 ± 0.1	8.3 ± 0.1	0	4.4 ± 0.2

MNS: Macadamia nut shells activated carbon, BBB: baobab shells activated carbon, PPH: pigeon pea husks activated carbon, RH: rice husks activated carbon, MH: *Moringaoleifera* husks activated carbon, AML: marula stones activated carbon, CC1: commercial carbon 1, CC2: commercial carbon 2

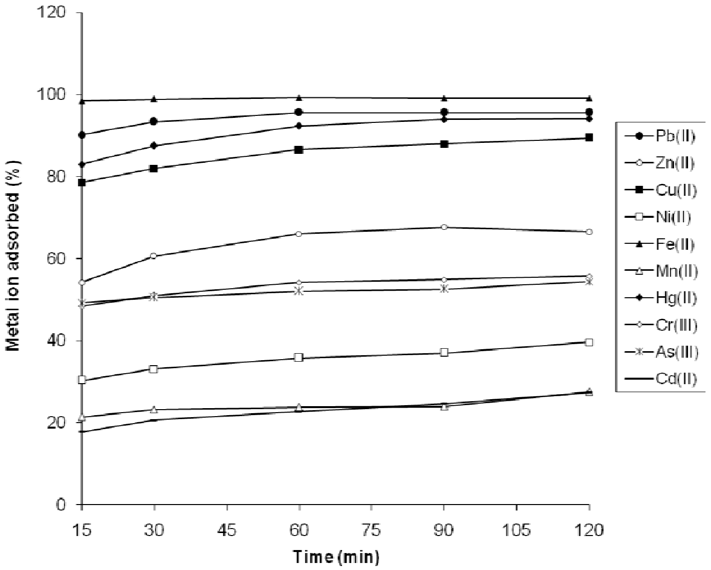

Figure 1. Effect of contact time on metal ion adsorption onto carbon prepared from pigeon pea husks. (Contact times: 15-20 min, carbon dose: 5 g/l, pH:6, metal ion concentration: 10 mg/l each in a mixture of the ions).

(2003) established that at 50 min, equilibrium had been attained. Apparently, the adsorption of most metal ions by activated carbon generally reaches equilibrium within 120 min (Ayyappan et al., 2005; Yu et al., 2001; Hasar, 2003). When BBB was used to adsorb Pb(II) from a solution containing Pb(II) only, percentage adsorption of Pb(II) was higher than the values obtained when Pb(II) was adsorbed from a mixture of metal ions (Figure 3).

Effect of quantity of carbon on adsorption of Pb(II)

The effect of increasing the quantity of adsorbent on the adsorption of Pb(II) by PPH and BBB is shown in Figure

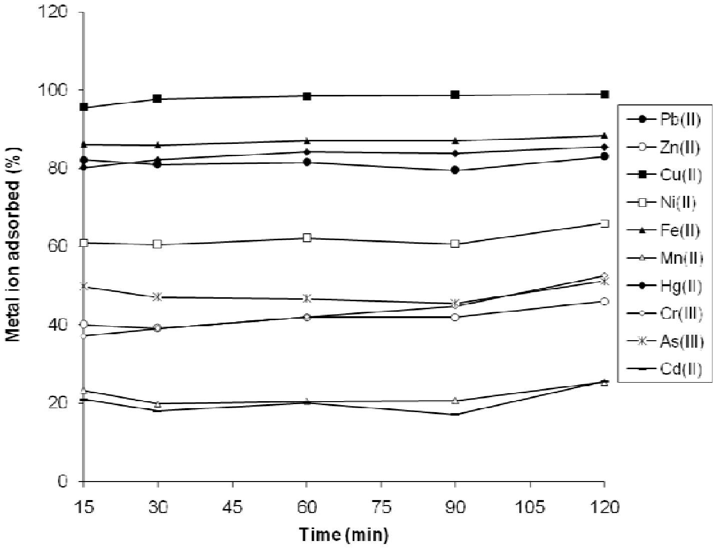

Figure 2. Effect of contact time on metal ion adsorption onto carbon prepared from baobab shells. (Contact times: 15-20 min, carbon dose: 5g/l, pH:6, metal ion concentration: 10 mg/l each in a mixture of the ions).

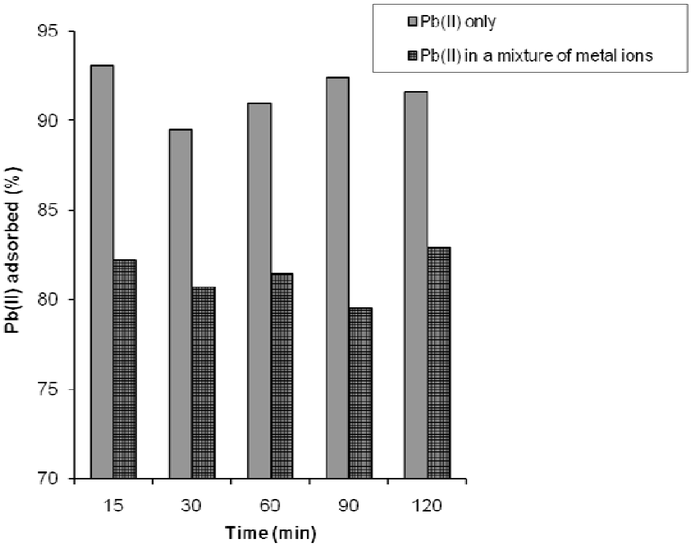

Figure 3. Comparison of the adsorption of Pb(II) onto carbon prepared from baobab shells while alone in solution and in a mixture with other metal ions. (Contact times: 15-20 min, carbon dose: 5g/l, pH:6, metal ion concentration: 10 mg/l).

4. On increasing the quantity of carbon from 0.5 g/l, the percentage removal of Pb(II) increased up to carbon quantities of 4 g/l and 6 g/l for PPH and BBB respectively then remained constant as the adsorbent quantities increased. The trend is consistent with results obtained by Hasar (2003), who observed an increase in adsorption

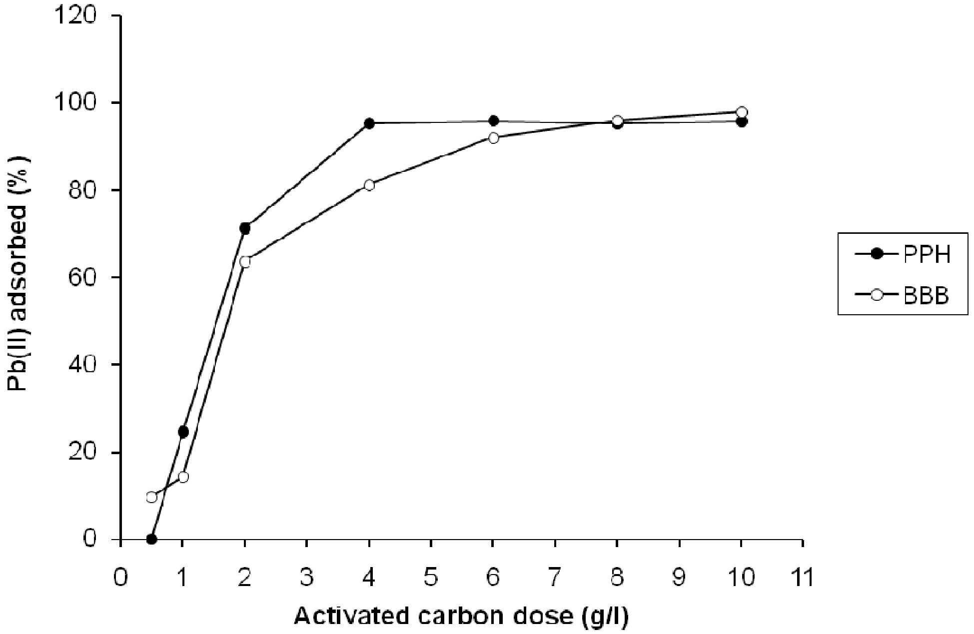

Figure 4. Effect of adsorbent dose on the adsorption of Pb(II) onto carbon prepared from pigeon pea husks and baobab shells. (Contact times: 15-20 min, carbon dose: 5g/l, pH:6, Pb(II) concentration: 10 mg/l).

of Ni(II) onto activated carbon prepared from almond husks as quantity of carbon was increased from 0.5 to 10 g/L then the adsorption remained constant upon further increase in carbon quantity. Ayyappan et al. (2005), recorded that percent sorption of Pb(II) onto activated carbon prepared from various agroforestry wastes increased with the increase in quantity of carbon from 0.5 to 2.0 g and remained constant on further increase in the quantity of the carbon.

Adsorption isotherms

The linear plot of C_e/q_e versus C_e for the adsorption of Pb(II) onto BBB shows that the adsorption obeys the Langmuir adsorption isotherm and indicates the formation of monolayer coverage of the adsorbate at the outer surface of the adsorbent (Figure 5). Q_o and b values of 1.52 and 1.96 respectively were determined from the linear plot. The R_L value was 0.05, indicating favorable adsorption of Pb(II) onto BBB (Bansode, 2003). The implications of this trend are that the adsorption of Pb(II) is due to specific interactions of the metal ion with groups on the surface of the carbon. Thus, when the monolayer covers these groups, there is no further adsorption of the metal ions.

Conclusion

The results of this study demonstrate the efficacy of carbon derived from agroforestry waste products in the removal of heavy metal ions from aqueous solutions. The optimum pH for removal of most of the ions by adsorption on all the carbons studied was 6. Equilibrium adsorption data for Pb(II) adsorption onto BBB followed the Langmuir isotherm. The results of this study show great potential for the removal of toxic metals from water bodies using low cost, domestic and environmentally safe technology. It is possible to desorb the metal ions so as to regenerate the carbons by equilibrating the metal ion-carbon complexes in acid solutions. Since the raw materials obtained from agroforestry wastes are freely available and abundant, the cost of preparation of the carbons is expected to be low and the method should be adopted with ease.

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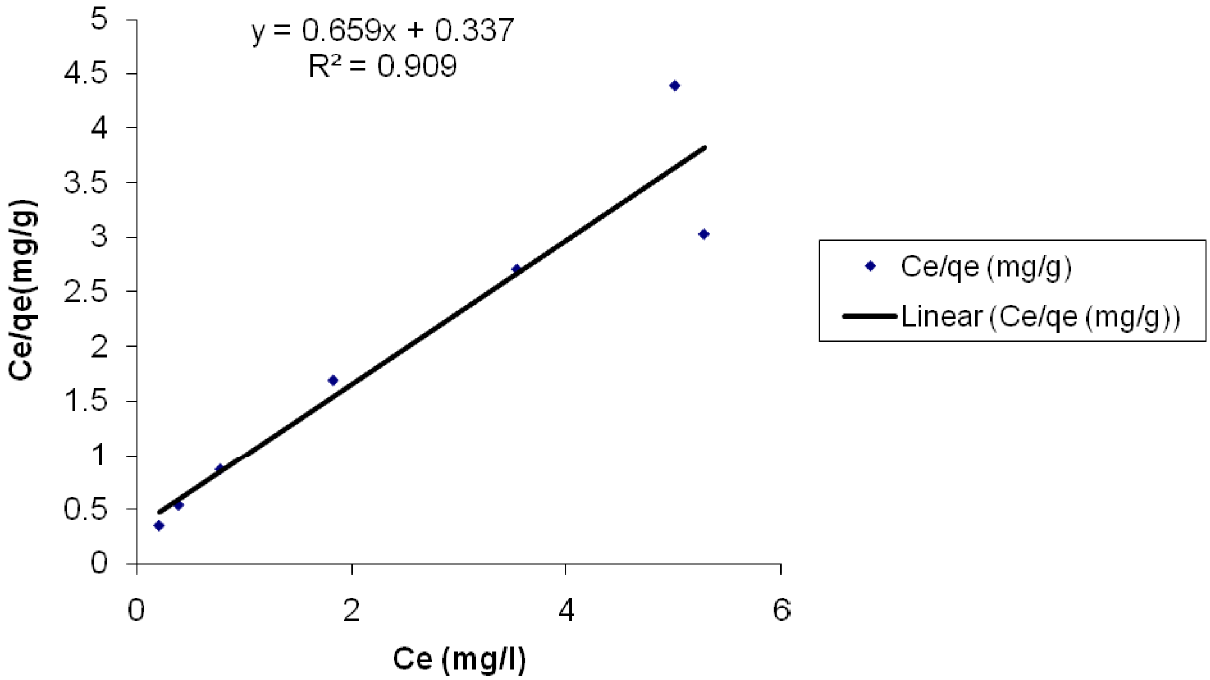

Figure 5. Langmuir isotherm for Pb(II) adsorption onto carbon prepared from baobab shells.

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Conflict of Interests

The author(s) have not declared any conflict of interests.

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