



ARTOCARPUS ALTILIS PROVING ITS WORTH IN TOXIC METAL REMOVAL FROM THE ENVIRONMENT

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ABSTRACT

Nuts of breadfruit tree (*Artocarpus altilis*) obtained from Ugbowo Campus of University of Benin, Benin City, were dehusked and the husk thoroughly washed with distilled water, air-dried, pulverized and sieved to obtain the particulate sizes of 63 μ m, 300 μ m and 600 μ m. These particulate sizes were oven-dried at 105°C to constant weight and preserved in a desiccator. The pulverized husk hereafter was referred to as adsorbent. Adsorbent (1.0g) of each particulate size was weighed into 100cm³ conical flask containing 50cm³ of 2.0, 4.0, 6.0, 8.0 and 10.0mgL⁻¹ Pb²⁺ ions, respectively. These mixtures were shaken for 30 min after which they were filtered and the filtrate used for Atomic Absorption Spectrophotometric (AAS) analysis. The same process was repeated using Cd²⁺ and Ni²⁺ ions, respectively. The effects of particulate size (surface area), temperature, initial metal ion (adsorbate) concentration and pH, on the extent of sorption, were studied; the infrared (IR) spectra of the adsorbent was also studied. Results indicate that sorption capacity is best at pH 4.0 for all metal ions (Cd²⁺, Pb²⁺ and Ni²⁺) studied. The effect of temperature revealed that maximum sorption occurs at 29°C compared to other temperatures of 60°C and 90°C. There was a general increase in adsorption of Cd²⁺, Pb²⁺, and Ni²⁺ ions as their initial concentrations increased. The adsorbent particulate size of 63 μ m had the greatest adsorptive capacity compared to other sizes. IR analysis of the adsorbent suggested the presence of C = O, OH, N-H, N = O, C=N, and COOH functional groups.

Keywords: *Artocarpus altilis*, sorption, toxic metals.

INTRODUCTION

Research to ensure clean and healthy environment has now assumed central stage in modern scientific endeavors. This is because the industrial revolution (which takes the credit for modern civilization) has inadvertently brought with it waste products most of which have deleterious effects on humans, plants and animals (Saha and Hossain, 2011). Toxic metals are among such waste products. They may originate from municipal wastewater treatment plants, manufacturing industries, mining, and agricultural cultivation and fertilization. Toxic metals are transported as either dissolved species in water or as an integral part of suspended sediments. They may be volatilized to the atmosphere, especially during dry seasons (Okolo and Okolo, 2011); others may end up in riverbed sediments. Toxic metals are taken up by man and other organisms through the food chain, and the ones dissolved in water have the greatest potential of causing the most deleterious effects (Lagrana *et al*, 2011; Garbarino *et al*, 1995; Manahan, 1994).

Treatment of wastewater to remove toxic metals include chemical precipitation, membrane filtration, ion exchange, and co-precipitation. These methods, though effective, require high technology, laborious procedures and are expensive (Ricordel *et al*, 2001; Garadea *et al*, 2000; Arpa *et al*, 2000; Mofa, 1995; Gardea *et al*, 1996; Abia *et al*, 2002). Workers are presently exploring the use of agricultural by-products as effective and cheap methods of isolating toxic metals from aqueous systems (Abia, *et al*, 2002; Mofa, 1995; Kamel *et al*, 2004; Lihan and Faut, 2000;

Yesim and Izzet, 2005; Singh *et al*, 2005; Jideonwo *et al*, 2006; Chi *et al*, 2009; Chio *et al*, 2009; Okolo and Okuo, 2011). In this work, the husks obtained from breadfruit nuts have been applied in its natural form for the biosorption removal of some toxic (heavy) metal ions (Cd²⁺, Pb²⁺ and Ni²⁺) from aqueous systems. Since it is suspected that polar functional groups could be a strong factor in the biosorption of toxic metal ions (Ricordel *et al*, 2011), the infrared (IR) spectra of the adsorbent was also investigated. Our aim was to employ the cheap, renewable and environmentally-friendly biomass (husk of *Artocarpus altilis* seed) for the removal of some toxic (heavy) metals from our environment.

MATERIALS AND METHODS

Breadfruit nuts (*Artocarpus altilis*) obtained from Ugbowo Campus of University of Benin, Benin City, Nigeria, was dehusked and the husk thoroughly washed with distilled water, air-dried, pulverized and sieved to obtain the following particulate sizes: 63 μ m, 300 μ m and 600 μ m. These particulate sizes were oven-dried at 105°C to constant weight (Ricordel *et al*, 2001). They were preserved in a desiccator for the experiment. The pulverized husk hereafter is referred to as adsorbent, while the metal ions are adsorbates. Analytical grade of the following (from BDH) were used: iodine crystals, sodium thiosulphate, starch, potassium iodate, potassium iodide, sodium hydroxide, hydrochloric acid, lead nitrate, nickel hexachloride and calcium chloride.

Atomic Absorption Spectrophotometer(AAS):model 969 Solar Spectrophotometer Unicam series; and Maltson Genesis Fourier Transformed Infrared Spectrophotometer (FIIR) were employed.

Measurement of Surface Area

The iodine number method was used to calculate the surface area of each particulate size of the adsorbent (Vogel, 1989; Meacabe, 1989; Murphy and Lawrence, 1990). 0.5g of each particulate size was transferred into a centrifuge tube and 30cm³ of 0.952M iodine solution (earlier standardized against sodium thiosulphate) was added. The tube was immediately covered and shaken for two minutes while being held horizontally and centrifuged for another two minutes. 10 cm³ of the adsorbent-free aliquot was titrated with 0.1M sodium thiosulphate (earlier standardized against pure potassium iodate) using 5cm³ of freshly prepared starch solution as indicator. The blank was titrated in the same manner. All titrations were made in triplicates and average results recorded.

The surface area of each particulate size of the adsorbent (63µm, 300µm and 600µm) was computed using the inverse of the iodine value (i.v.) (Vogel, 1989; Meacabe, 1989; Murphy and Lawrence, 1990):

$$i.v. = (y - x_o / y)(v / w).M.126.91mg \text{ iodine/g}$$

sample,

where x_o = volume of thiosulphate used for adsorbent-free aliquote,

y = volume of thiosulphate used for blank titration,

v = volume of iodine solution used for titration,

w = weight of sample (adsorbent) used, and

M = molarity of iodine solution used for titration.

Sorption of Metal Ions onto Adsorbent (Sample)

Equilibrium sorption of Cd²⁺, Pb²⁺ and Ni²⁺ on the adsorbent from aqueous solution was carried out by shaking 1.0g of adsorbent in 50cm³ of different concentrations (2.0, 4.0, 6.0, 8.0, and 10.0 mgL⁻¹) of each metal ion (Ricordel *et al*, 2001). The adsorbent and the metal ion solution were shaken, using mechanical shaker at 310rev./min., for a contact period of 30min after which the mixture was filtered and the residual concentration of the metal ion in the filtrate was determined by atomic absorption spectrophotometer (AAS). Triplicate readings were taken and the average results recorded. The difference between the initial and residual concentrations was recorded as the amount of metal ion adsorbed onto the adsorbent. The ambient pH and temperature of adsorbent-metal ion mixture were 6.8 and 29°C, respectively. The effects of pH and temperature on sorption were studied by varying the pH (4, 7, 10, using 1.0M NaOH or 1.0M HCl) of the adsorbent-metal ion mixture, and at different temperatures (29°C, 60°C and 90°C) (Ricordel *et al*, 2001).

Infrared (IR) Spectra

The IR spectra were generated by grinding the adsorbent to very fine powder in an agate mortar for

a minimum of 12min. This was dried at 100°C for about 2h, diluted and thoroughly mixed with KBr (spectroscopic grade) to produce 0.05%(w/w), with additional grinding. The percent transmittance was recorded between 4000cm⁻¹ to 500 cm⁻¹ wave number (Fig.1).

RESULTS AND DISCUSSION

The formular,

$$i.v. = (y - x_o / y)(v / w).M.126.91mg \text{ iodine/g}$$

sample, was used to calculate the surface area of the adsorbent (Vogel, 1989 and Meacabe, 1989). Here, the inverse of the iodine value(i.v.) is a function of the surface area of the adsorbent. Table 1 presents the iodine value (i.v.) and inverse of i.v. for the three particulate sizes (63µm, 300µm and 600µm) of the adsorbent.

Table 1 clearly shows that, given the same adsorbent weight for the three particulate sizes (63µm, 300µm and 600µm), the particulate size of 63µm provides the smallest surface area per adsorbent-particle and so makes available the largest number of adsorption sites, the overall effect being highest adsorption capacity. This was found to be true for the adsorption of Cd²⁺, Pb²⁺ and Ni²⁺ ions onto the same weight of the particulate sizes under the same experimental conditions (Table 2). For example, at initial metal ion concentration of 2.00mgL⁻¹, the adsorbent particulate size of 63µm tend to be the most effective in removing all three toxic metal ions studied from the aqueous system, the second best was 300µm and the least was 600µm, although the three particulate sizes generally removed not less than 75% of each toxic metal ion from the aqueous system. Ricordel *et al*, 2001, observed a similar trend when they established that, for peanut husk carbon, the particulate size of 0.25-0.50mm was more effective in removing Cd²⁺ from aqueous system than that of 1.25mm and above.

A careful study of Tables 2 and 3 reveals that at all three particulate sizes, the adsorbent removed Cd²⁺ ions more effectively from the aqueous system than Pb²⁺ and Ni²⁺, irrespective of pH and initial metal ion concentrations studied. This may be due to the fact that Cd²⁺ is the most electropositive of the three metals as reported by Chris (2002) and Lee (1996). Generally, adsorption was most effective at pH 4.00 for the three metal ions studied. This may be that at higher pH of 10.0, the metal ions, instead of complexing with the functional groups of the adsorbent, form precipitate with the OH⁻ groups now predominant in the solution, though Cd²⁺ is less susceptible to the OH⁻ attacks because Cd²⁺ complexes with OH⁻ are more difficult to form (Mahan and Meyers, 1987). The excellent sorption capacity of the adsorbent in its natural state, for some toxic metals (Pb²⁺, Cd²⁺, and Ni²⁺) from aqueous system could be mainly due to the nature of the functional groups inherent in its structure.

The IR spectra (Fig.1) suggest the presence of the following functional groups: carbonyls(C=O), carboxylic acids(COOH), amides/amines(N-H), alcohols/phenols(OH), nitro(N=O), and nitriles (C≡N) (Pavia *et al*, 2001). These functional groups would tend to form stable complexes with the metal ions (Mahan and Meyers, 1987).

Table 4 reveals that Cd²⁺ ion is the most effectively adsorbed by the adsorbent at the three temperatures (29°C, 60°C and 90°C), and at prevailing experimental conditions indicated in the Table. Furthermore, for each metal ion, adsorption is best at 29°C, suggesting a decrease in adsorption with increase in temperature. This may be due to desorption (instead of adsorption) occasioned by high kinetic energy of the system associated with high temperature. Also, an increase in temperature may lead to decrease in the stability of metal ion-adsorbent complex (Atkins, 1995; Glasstone, 1964).

CONCLUSION

Without modifications, the adsorbent (husks of *Artocarpus altilis* seed) was found to have very high

sorption capacity - at least 80% (w/w) of the toxic metal ions studied (Pb²⁺, Cd²⁺, and Ni²⁺) was removed, respectively from the aqueous system, at the optimum experimental conditions (earlier work by Jideonwo *et al*, 2006, using chitosan grafted with acrylamide as adsorbent achieved sorption capacity of 61.80%(w/w) for Pb²⁺, 64.8 %(w/w) for Ni²⁺ and 97.90%(w/w) for Cd²⁺ at optimum experimental conditions). Sorption capacity was found to be a function of temperature, pH, surface area of the adsorbent, initial metal ion concentration, in addition to the innate chemical make-up of the adsorbent such as polar functional groups. It would be recommended that the husk of *Artocarpus altilis* seed, in its natural state, be a component of filter-bed for the treatment of both potable water and industrial wastewater contaminated with certain toxic metals. This may prove to be a veritable contribution to rid the environment of some toxic metals (at minimum cost) which has hitherto defied natural means of purification. The husk of *Artocarpus altilis* seed is nontoxic because the seed is edible.

Table 1: Surface area of three particulate sizes of the adsorbent (sample)

Particulate size of sample, µm	Iodine value (i.v.), mg iodine/g sample	Surface area of sample, (i.v.) ⁻¹
63	2.165	0.462
300	0.199	5.025
600	0.119	8.403

Table 2: Effect of surface area of adsorbent and initial metal ion concentration

Particulate size(μm)/surface area(mg/g)	Initial metal ion conc. (mgL^{-1})	Residual metal ion conc. (mgL^{-1})			Conc. (mgL^{-1}) of metal ion adsorbed			% Adsorption			Amount of metal ion adsorbed per weight of adsorbent, mg/g		
		Pb ²⁺	Cd ²⁺	Ni ²⁺	Pb ²⁺	Cd ²⁺	Ni ²⁺	Pb ²⁺	Cd ²⁺	Ni ²⁺	Pb ²⁺	Cd ²⁺	Ni ²⁺
		63/0.462	2.00	0.382	0.010	0.248	1.618	1.990	1.752	80.90	99.50	87.60	0.0809
	4.00	0.358	0.022	0.388	3.642	3.978	3.612	91.05	99.45	90.30	0.1821	0.1989	0.1806
	6.00	0.201	0.006	0.557	5.799	5.943	5.443	96.65	99.05	90.72	0.2900	0.2997	0.2722
	8.00	0.113	0.089	0.715	7.887	7.911	7.285	98.59	98.89	91.06	0.3944	0.3956	0.3643
	10.00	0.106	0.098	0.792	9.894	9.902	9.208	98.94	99.02	92.08	0.4947	0.4951	0.4604
300/5.025	2.00	0.247	0.039	0.292	1.753	1.961	1.708	87.65	98.05	85.40	0.0877	0.0981	0.0854
	4.00	0.585	0.025	0.398	3.415	3.975	3.602	85.38	99.38	90.05	0.1708	0.1987	0.1801
	6.00	0.689	0.078	0.633	5.311	5.922	5.367	88.50	98.70	89.45	0.2655	0.2961	0.2683
	8.00	0.793	0.105	0.781	7.207	7.895	7.219	90.09	98.69	90.24	0.3603	0.3947	0.3609
	10.00	0.873	0.035	0.849	9.127	9.965	9.151	91.27	99.65	91.51	0.4563	0.4982	0.4575
600(8.403)	2.00	0.740	0.070	0.317	1.260	1.930	1.683	63.00	96.50	84.15	0.0630	0.0965	0.0841
	4.00	1.107	0.096	0.445	2.893	3.904	3.555	72.33	97.60	88.86	0.1446	0.1952	0.1777
	6.00	1.238	0.098	0.735	4.762	5.902	5.265	79.37	98.37	87.75	0.2381	0.2951	0.2632
	8.00	1.406	0.112	0.897	6.594	7.888	7.103	82.43	98.60	88.79	0.3297	0.3944	0.3551
	10.00	1.549	0.154	0.937	8.451	9.846	9.063	84.51	98.46	90.63	0.4225	0.4923	0.4531

$\% \text{ Adsorption} = \frac{C_o - C_e}{C_o} \times 100\%$; where C_o = initial metal ion conc., mg/L ; C_e = residual metal ion conc., mg/L .

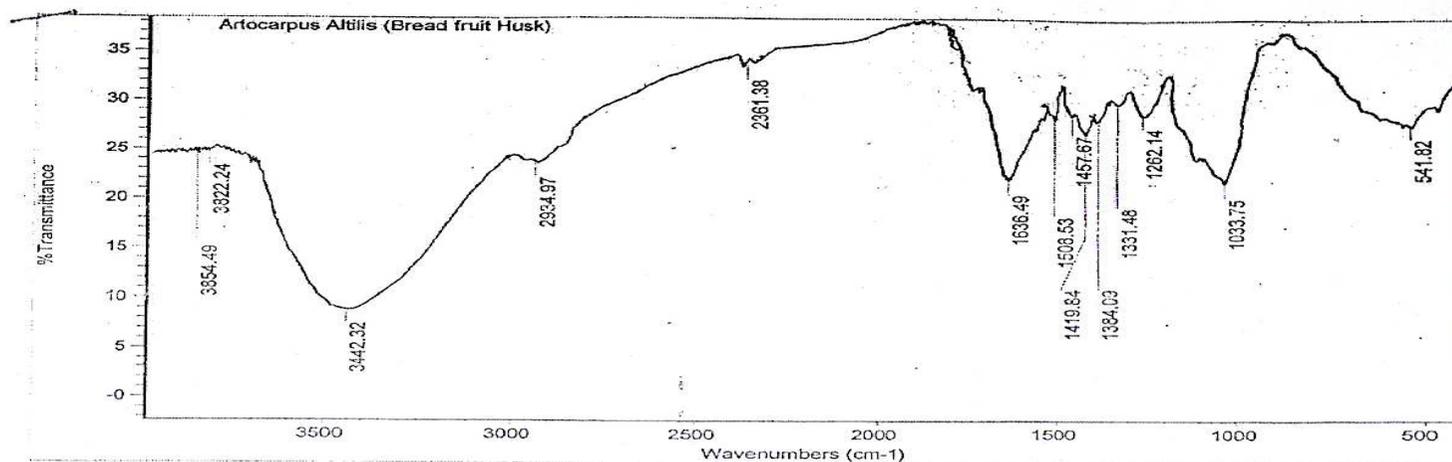
Amount of metal ion adsorbed per weight of adsorbent, $\text{mg/g} = q_e = \frac{C_o - C_e}{w} \times V$; where V = vol.(L) of metal ion solution(0.05L); w = weight (g) of adsorbent(1.0g).

Table 3: Effect of pH

Particulate size, μm	Amt(g) of adsorbent (sample) Used	Initial metal ion conc, mgL^{-1}	pH of adsorbent/ metal ion mixture	Residual metal ion conc, mgL^{-1}			Conc. (mgL^{-1}) of metal ion adsorbed			% Adsorption			Amount of metal ion adsorbed per weight of adsorbent, mg/g		
				Pb ²⁺	Cd ²⁺	Ni ²⁺	Pb ²⁺	Cd ²⁺	Ni ²⁺	Pb ²⁺	Cd ²⁺	Ni ²⁺	Pb ²⁺	Cd ²⁺	Ni ²⁺
				63	1.00	4.00	4.00	0.509	0.005	0.413	3.491	3.995	3.569	87.275	99.875
			7.00	0.640	0.006	0.525	3.336	3.994	3.475	84.000	99.850	86.875	0.1680	0.1997	0.1737
			10.00	1.201	0.019	1.698	2.799	3.981	2.302	69.975	99.525	57.550	0.1399	0.1990	0.1151

Table 4: Effect of Temperature.

Particulate size, μm	Amt(g) of adsorbent (sample) used	Initial metal ion conc, mgL^{-1}	Temp($^{\circ}\text{C}$) of adsorbent/metal ion mixture	Residual metal ion conc, mgL^{-1}						% Adsorption			Amount of metal ion adsorbed per weight of adsorbent, mg/g		
				Pb^{2+}	Cd^{2+}	Ni^{2+}	Cd^{2+}	Cd^{2+}	Ni^{2+}	Pb^{2+}	Cd^{2+}	Ni^{2+}	Pb^{2+}	Cd^{2+}	Ni^{2+}
63	1.00	4.00	29	0.113	0.023	0.388	3.887	3.977	3.612	97.180	99.425	90.300	0.1943	0.1988	0.1806
			60	0.476	0.136	0.823	3.524	3.864	3.177	88.100	96.600	79.425	0.1762	0.1932	0.1588
			90	0.650	0.199	0.920	3.350	3.801	3.080	83.750	95.025	77.000	0.1675	0.1900	0.1540



Thu Sep 27 09:42:26 2007 (GMT+02:00)
 FIND PEAKS:
 Spectrum: Artocarpus Altilis (Bread fruit Husk)
 Region: 3999.84 400.00
 Absolute threshold: 38.142
 Sensitivity: 65
 Peak list:

Position:	541.82	Intensity:	27.660
Position:	1033.75	Intensity:	21.683
Position:	1262.14	Intensity:	28.811
Position:	1331.48	Intensity:	29.848
Position:	1384.09	Intensity:	27.832
Position:	1419.84	Intensity:	26.565
Position:	1457.67	Intensity:	28.352
Position:	1508.53	Intensity:	28.011

Figure 1: Spectra for the adsorbent

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