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Efficacy of Locust Beans Husk Char in Heavy Metal Sequestration

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Most solid waste management schemes minimally consider low concentration biodegradable agricultural waste management, though the environmental impact of this waste category is significant over a time frame. The column-mode study seeks to address the issue by suggesting potential utilisation of post-harvest waste for heavy metal sequestering. Locust beans husk char of 100 and 200 g was employed to inspect removal efficiency, isotherm and kinetic models of some heavy metals at 30, 60, 90, 120 and 150 min contact time. Elemental composition of the biosorbent was investigated using the SEM-EDX machine. The results obtained depict that over 85% aluminium and nickel removal was achieved at 150 min detention time. The Freundlich isotherm well described most of the sorbates sorption ($R^2 \geq 0.91$). The sorption rate equally fitted into the second-order pseudo kinetic model ($R^2 \geq 0.88$). Ion exchange took place during the sorption. Locust beans husk has promising adsorption potential in heavy metal ions removal from fouled surface water.

Keywords*: post-harvest waste, removal efficiency, isotherm, kinetic sorption, locust beans husk char (LHC).*

1 Introduction

Solid waste management is a topical issue due to rate and volume of daily solid waste generation and subsequent effects on the ecosystem. The estimated global municipal solid waste generation per capita per year is 0.1 to 0.8 t (Bogner *et al.*, 2007). The principal reaction to the growing and poorly managed subject particularly in the developing and underdeveloped world is attributed to environmental concern in all its extant forms. The forms are inert, toxic, biodegradable or non-biodegradable. The compositions are metal, food, wood, plastic, glass and paper. Most of the aforementioned constituents are harnessed with modern technologies through recycling, energy recovery and reuse. However, some post-harvest wastes have not gained such interest. Post-harvest wastes are unwanted materials that enclose or are part of the useful crop materials often transported to the processing unit after harvest. The wastes are left bare with little or no good management practice administered mainly because of low concentration in terms of odour and subsequent natural biodegradation, yet the wastes are valuable if correctly utilised. Areas of interest in the application of post-harvest wastes are woodchip in composting (Hanc *et al.*, 2012), pozzolanic material in concrete production (Ndububa & Uloko, 2015) and contaminants removal (Sivakumar & Palanisamy, 2009; Omotosho & Sangodoyin, 2013). The latter application could be streamlined to undesirable substances removal from air and water by the adhesion on the adsorbent produced from post-harvest waste. This treatment method is called adsorption. Contaminants are attached to the adsorbent so that it becomes component of the molecular structure. A number of biomass materials and agricultural wastes have been investigated through this eco-friendly treatment method with remarkable percent removal obtained. Maize tassel (Sekhula *et al*., 2012), lignin (Bailey *et al*., 1999) and wood ash (Chojnacka & Michalak, 2009) are examples of such materials. Other adsorption assessment tools are isotherm and adsorption kinetic. These evaluation tools examine adsorbent effectiveness in relation to the selected sorbate. Hence, the study investigates carbonised post-harvest waste (locust beans husk char) usability as biosorbent in some heavy metal removal from mildly polluted surface water.

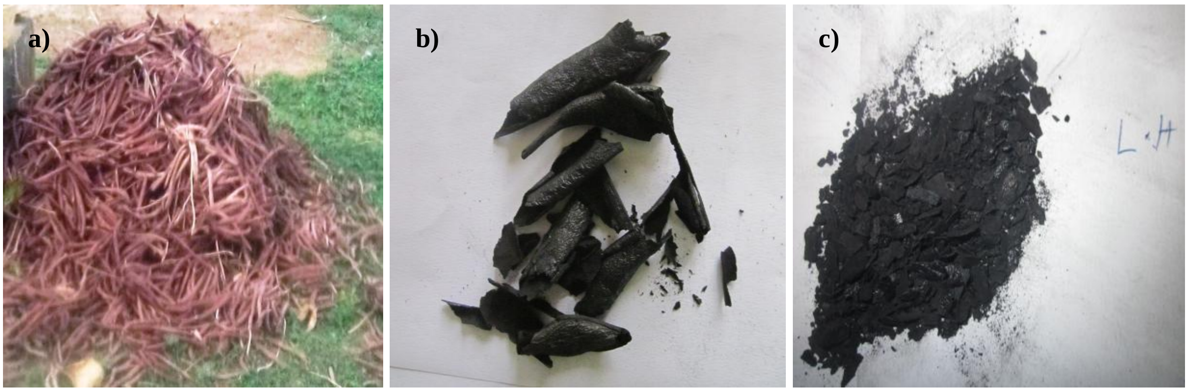

Figure 1. Different structures of locust beans husk: a) pile of locust beans husk; b) carbonised locust beans husk; c) granulated locust beans husk char.

2 Materials and methods

Locust beans husks obtained from a local farmer (Figure 1a) were cleaned and wrapped with doubled-layer aluminium foil to ensure carbonisation under hermetic conditions. The biomass was pyrolysed at 350 °C for a period of 60 min. Char produced was reduced in size for adsorption rate enhancement and sorted with 1,400 microns sieve before storage (Figure 1b, 1c). The sorbent was examined with the EDX machine for variation in chemical composition before and after carbonisation. Two plastic cylindrical reactors of 41 cm in height and 11 cm in diameter were underlaid with 50 g of an absorbent (cotton wool) before the introduction of a biosorbent and then overlaid with another 50 g of an absorbent. The choice of a cylindrical reactor was to prevent pocket formation at the angles of the system wall (Ajayi-Banji, 2012). Granulated locust beans husk char (LHC) of 100 and 200 g was placed in the 1,300 cm^3 mean volumetric capacity reactors. The water sample was collected under stringent conditions along Pipeline Road in Ilorin, Kwara State, Nigeria. The choice of the source was due to its location, which made it a discharge point for surrounding industrial and residential buildings. The water source equally serves irrigation purposes. The collected surface water (18 L) was gradually injected into the reactor at a suitable flow rate (14 mL/min) to ensure the efficient biosorption process. Kumar *et al.* (2007) recommended a flow rate within this limit for good adsorbability. The treated influent was discharged into receiving containers after detention times of 30, 60, 90, 120 and 150 min for heavy metal inspection. Contaminant analysis in the treated and untreated water samples was carried out in replicates twice to cater for possible variations.

2.1 Experimental calculation

Removal efficiency, Freundlich and Langmuir models in linear representation and pseudo first- and second-order kinetic models after integration with boundary conditions are expressed by equations 1-6.

$$Removal\ efficiecy = (C_o - C_t)C_o \times 100 \tag{1}$$

$$Q_t = \frac{(C_o - C_t)V_t}{W_b} \tag{2}$$

$$LogQ_t = Log\ K + \left(\frac{1}{n}\right)LogC_t \tag{3}$$

$$\frac{C_t}{Q_t} = -\frac{1}{Q_m.K_L} + \frac{C_t}{Q_m} \tag{4}$$

$$Log(Q_e - Q_t) = LogQ_e - \left(\frac{K_Q}{2.3038}\right)t \tag{5}$$

$$\frac{t}{Q_t} = \frac{1}{K_p {Q_e}^2} + \frac{t}{Q_e} \tag{6}$$

where C_0 indicates the initial concentration of a heavy metal in a water sample before treatment with LHC (mg/L); C_t indicates the concentration of a heavy metal in effluent after treatment for a particular contact time (mg/L); Q_t indicates the quantity of a heavy metal adsorbed per LHC unit weight at a given detention time (mg/g); Q_e indicates the quantity of a heavy metal adsorbed per adsorbent unit weight equilibrium (mg/g); V_t indicates the volume of water in the adsorption column at a definite contact time (L); W_b is the mass of LHC (g); t indicates retention time in hrs; Q_m signifies the maximum adsorptive capacity of a heavy metal (mg/g) and K is the Freundlich constant related to the extent of adsorption (mg/g); n is related to the adsorption intensity. Values of K and n are constants deduced from the intercept and slope of plot of $Log\ Q_t$ against $Log\ C_t$. K_L and Q_m are obtained from the intercept and slope of plot of C_t/Q_t against C_t. Constants K_Q (L/min) and K_p (g/mg/min) are first- and second-order pseudo kinetic rates calculated from the slope of plot $Log(Q_e – Q_t)$ versus t and slope and intercept of t/Q_t versus t, correspondingly.

3 Results and discussion

3.1 *Biosorbent composition*

Carbon, chlorine, potassium, calcium and oxygen are elements noteworthy in the precursor and biosorbent (Figure 2a, 2b). Carbonisation influenced the chemical properties of the adsorbent. Calcium and potassium quantity per mass of elemental constituents increased by 57% and 30%, respectively, while carbon decreased by 5.4% after carbonisation. Calcium ion in biosorbents plays an important role during adsorption. According to Wilson *et al*. (2003), ions trade-in occurs with the biosorbent that contains some level of calcium. Hence, the high locust beans husk char calcium content will possibly boost heavy metal removal.

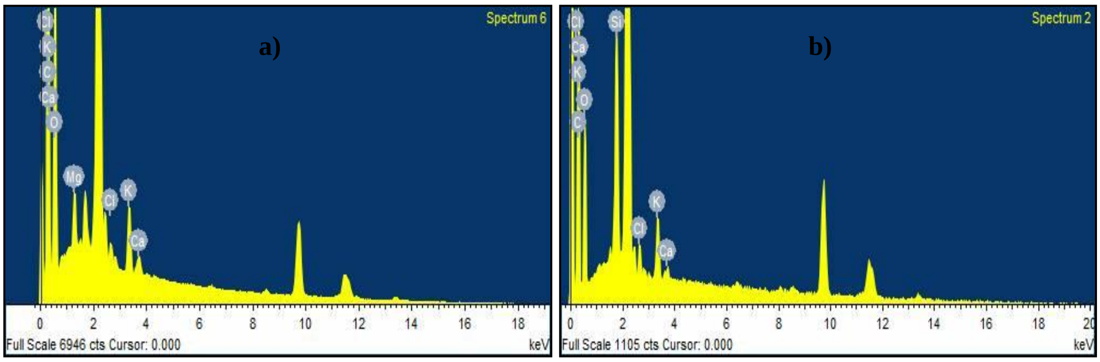

Figure 2. EDX for locust beans: a) husk; b) char.

3.2 *Removal efficiency*

Removal percentage was high at the first 30 min of the sorption process for iron, copper, nickel and manganese at 100 g LHC. The similar result was obtained for aluminium, manganese and nickel at 200 g LHC. This might be attributed to more active sites within the biosorbent at the initial stage and strong interaction between the adsorbent and sorbates. Low sorbate sorption observed for some metals despite active biosorbent sites infers that other factors influence heavy metal removal (Tables 1 & 2). Factors documented in literature include sorbate type, detention time, activation, biosorbent dose and adsorbent type (Emmanuel & Veerabhadra Rao, 2009; Ijaola *et al*., 2013). Removal efficiency was high in aluminium and nickel between 85–89% at 150 min retention time. This is an indication that LHC has high affinity for aluminium and nickel sequestration in polluted surface water. Optimal removal efficiency was not achieved for the sorbates within this contact period for this study. Sangodoyin and Ajayi-Banji (2013) recommended higher contact time for metal removal by biosorbents. Lurtwitayapont and Srisatit (2010) also led credence to this finding in a study of lead removal on bone char. Adsorbent dosage has a declining effect on percent removal for most heavy metals after 30 min retention time except nickel. An increase in LHC dosage from 100 to 200 g does not result in a proportionate increase in removal efficiency. This is an indication of weak interaction between increased mass of LHC (200 g) and adsorbate (Tables 1 & 2). This confirms that retention time does not have autonomous influence on the contaminant sorption rate.

Table 1. Removal efficiency for 100 g LHC.

Heavy metal	**Removal efficiency (%)**				
	30 min	**60 min**	**90 min**	**120 min**	**150 min**
Iron	31.43	36.67	38.57	48.57	53.33
Zinc	5.833	38.33	38.33	42.50	45.83
Copper	26.67	36.67	43.33	50.00	56.67
Aluminium	3.700	67.41	74.82	76.30	86.67
Manganese	25.00	50.00	66.66	79.17	82.00
Nickel	42.86	66.67	71.43	76.19	85.71

Table 2. Removal efficiency for 200 g LHC.

Heavy metal	**Removal efficiency (%)**				
	30 min	**60 min**	**90 min**	**120 min**	**150 min**
Iron	10.95	24.76	26.19	39.52	39.52
Zinc	11.67	20.83	35.83	40.83	60.83
Copper	6.670	13.33	20.00	30.00	33.33
Aluminium	44.44	67.41	68.15	72.59	88.89
Manganese	33.33	37.50	41.67	54.17	54.17
Nickel	66.67	76.19	80.95	85.71	85.71

3.3 Freundlich and Langmuir isotherm models

Isotherm suitability investigated shows that Freundlich well described heavy metal sorption on LHC surface with correlation coefficient values greater than 0.91 in all cases. This trend differs for Langmuir, where the correlation coefficient values were less than 0.81 except for iron and manganese at 100 and 200 g LHC dosage, respectively (Tables 3 & 4). This infers that the sorption process was principally multilayer and applies to heterogeneous surface (Lurtwitayapont and Srisatit, 2010). According to Moreno *et al.* (2010), n value less than unity under a multilayer condition is an indication of considerable adsorption of heavy metals at higher sorbate concentration. Table 3 follows this pattern ($n < 1$); hence, LHC at 100 and 200 g has the tendency to adsorb more heavy metals at higher sorbate concentration. Adsorption intensity is denoted by k value, and high k value depicts high adsorption intensity. The high k values for aluminium, nickel and manganese compared with other metals (Table 3) substantiate the obtained removal efficiency result. Biosorbent dosage has no significant influence on adsorption intensity. It can be deduced that the inspected metal ions have higher k value at 100 g compared with a 200 g sorbent dose (Table 3).

Table 3. Freundlich isotherm parameters for LHC.

Heavy Metal	**100 g**			**200 g**		
	R^2	k ($\times10^{-3}$)	n	R^2	k ($\times10^{-3}$)	n
Iron	0.9989	21.980	0.9103	0.9965	7.6000	0.6282
Zinc	0.9407	14.700	0.4174	0.9933	12.100	0.5738
Copper	0.9999	22.000	0.7682	0.9986	5.1600	0.6036
Aluminium	0.9153	151.00	0.1730	0.9932	85.900	0.6248
Manganese	0.9914	525.20	0.4379	0.9975	31.100	0.8950
Nickel	0.9981	371.30	0.5755	0.9996	308.00	0.5260

Table 4. Langmuir isotherm correlation coefficient for LHC.

Heavy Metal	**100 g R^2**	**200 g R^2**
Iron	0.9051	0.4338
Zinc	0.1331	0.3652
Copper	0.8030	0.4330
Aluminium	0.5726	0.4788
Manganese	0.0546	0.9058
Nickel	0.3260	0.7556

3.4 Pseudo kinetic sorption

Metals kinetic sorption did not follow first-order kinetics ($R^2 < 0.35$). On the contrary, the second-order pseudo kinetic model gave better representation for most metals except zinc and aluminium at a 100 g LHC dose. The correlation coefficient values were greater than 0.88 (Tables 5 & 6). LHC sorbate sorption described by pseudo-second-order rate equation shows close values of calculated Q_t and experimental Q_e values computed from the plot of t/Q_t against t (Table 6). Minimal disparity between calculated and experimental values of adsorption kinetics validates the applicability of pseudo second order. The consistency is an indication of the chemisorption process (*Dizadji et. al.*, 2011).

Table 5. First-order pseudo kinetics parameters for LHC.

Heavy metal	**100 g**		**200 g**	
	R^2	K_q	R^2	K_q
Iron	0.1103	0.0258	0.0526	0.0136
Zinc	0.2421	0.0309	0.3206	0.0341
Copper	0.0211	0.0113	0.0108	0.0053
Aluminium	0.2417	0.0316	0.1531	0.0228
Manganese	0.0290	0.0145	0.1796	0.0359
Nickel	0.1448	0.0297	0.0068	0.0069

Table 6. Second-order pseudo kinetics parameters for LHC.

Heavy Metal	**100 g**			**200 g**		
	R^2	Q_e	Q_t	R^2	Q_e	Q_t
Iron	0.9923	0.0094	0.0092	0.8972	0.0094	0.0076
Zinc	0.1444	0.0136	0.0056	0.8802	0.0110	0.0059
Copper	0.9912	0.0075	0.0073	0.8801	0.0083	0.0045
Aluminium	0.2297	0.0071	0.0030	0.9855	0.0098	0.0095
Manganese	0.9337	0.0023	0.0019	0.9737	0.0011	0.0011
Nickel	0.9774	0.0015	0.0015	0.9691	0.0014	0.0013

4 Conclusions and recommendations

The study shows that locust beans husk char has strong affinity for aluminium, manganese and nickel removal from contaminated surface water at a 100 g adsorbent dosage. Removal efficiency for manganese and nickel was greater than 85% after 150 min retention time. The removal efficiency pattern for all the heavy metals indicates the relationship among detention time, biosorbent dosage and sorbate under consideration. Further studies could be conducted to inspect this relationship. Effect of activated locust beans husk on heavy metal removal could also be investigated. Calcium composition in a biosorbent suggests that the ion exchange mechanism took place during sorption, and chemisorption was equally noted at some point in the process. The Freundlich isotherm provides a close fit for all the heavy metals considered in the removal process study ($R^2 > 0.91$). Second-order kinetics proves to be a better adsorption process description tool particularly for manganese and nickel under both adsorbent dosage conditions ($R^2 > 0.93$). The feasibility and suitability of locust beans husk char, a low cost and environment-friendly post-harvest waste, as the biosorbent in aluminium, manganese and nickel diminution from polluted surface water were established in this study.

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Sunkiųjų metalų atskyrimo panaudojant baltosios Amerikos akacijos pupų lukštų nuodėgulius efektyvumas

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Dauguma kietųjų atliekų tvarkymo sistemų mažai atsižvelgia į mažos koncentracijos bioskaidžias žemės ūkio atliekų tvarkymą, nors šios atliekų kategorijos aplinkosauginis poveikis per tam tikrą laiką yra žymus. Stulpelinis tyrimu siekiama spręsti problemą, pasiūlant potencialų po derliaus nuėmimo likusias atliekas naudoti sunkiesiems metalams atskirti. 100 ir 200 g baltosios Amerikos akacijos pupų lukštų nuodėguliai buvo panaudoti ištirti kai kurių metalų šalinimo efektyvumą, izoterminius ir kinetinius modelius, kai kontaktinis laikas buvo 30, 60, 90, 120 ir 150 min. Biosorbento elementinė sudėtis buvo ištirta naudojant SEM-EDX įrenginiu. Gauti rezultatai rodo, kad aliuminio ir nikelio šalinimo efektyvumas siekė daugiau nei 85 %, kai išlaikymo laikas buvo 150 min. Froindlicho izoterma išsamiai apibūdino daugelio sorbatų sorbciją (R2 >= 0.91). Sorbcijos dydis vienodai tiko į antrinį pseudo kinetinį modelį (R2 >= 0.88). Jonų kaita vyko sorbcijos metu. Baltosios Amerikos akacijos pupų lukštai turi perspektyvų adsorbcijos potencialą šalinant sunkiųjų metalų jonus iš nešvaraus paviršinio vandens.

Raktiniai žodžiai: *po derliaus nuėmimo likusios atliekos, šalinimo efektyvumas, izoterma, kinetinė sorbcija, baltosios Amerikos akacijos pupų lukštų nuodėguliai*.