doi: 10.17221/44/2015-RAE

Investigation of locust bean husk char adsorbability in heavy metal removal

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Abstract

Ajayi-Banji A., Ogunlela A., Ogunwande G. (2017): Investigation of locust bean husk char adsorbability in heavy metal removal. Res Agr. Eng., 63: 29–35.

The column adsorption study examines irrigation water treatment prior to its application in order to ensure water-crop-consumer heavy metal transfer reduction to the safe level using locust bean husk char (LBHC) as biosorbent. Char structural pattern was investigated with SEM-EDX machine. Contaminated surface water was introduced simultaneously into the bioreactors containing 100 and 200 g of LBHC and collected after 30, 60, 90 120 and 150 min of detention time. Removal efficiency, isotherm and kinetic sorption model were the evaluation tools for the study. Percent of Cr, Cd and As removal at 150 min retention time were 83.33, 100 and 100%, respectively for 100 g biosorbents. A similar trend was observed for Cr and As removal at the same retention time for 200 g of LBHC. Metals sorption conforms to the Freundlich isotherm with correlation coefficient values greater than 0.92. Experimental kinetics had a good fit for pseudo second order ($R^2 > 0.94$ for most cases). Removal efficiency is a function of contact time, biosorbent dosage and metal concerned. Locust bean husk char has good and effective treatability for some heavy metals in mildly polluted water.

Keywords: locust bean husk char; biosorption; heavy metal; removal efficiency; isotherm, kinetic sorption

Demand for food has increased tremendously with population growth despite recent agro-technologies that has enhanced productivity especially through mechanization. For instance, total grain consumption increased by 12.5% from 1995 to 2007 (World Bank 2009). Furthermore, the solely linked influence to world's food demand, population, has increased by over 14.7% between this period and it is expected to increase by 19.6% between now and 2050 (Van der Mensbrugghe et. al. 2009). This progressive and projected increase in population and concomitantly demand for food crops has motivated both peasant and especially commercial farmers to adopt means of cultivating crops all year round. Most farmers in the underdeveloped and developing nations cultivate along streams, flowing rivers, wetlands or waterlogged areas in dry seasons or off seasons (personal interview) while others distant from these water sources irrigate in such periods. This approach has proven efficient, however, the level of irrigation water contamination due to anthropogenic activities raises concern as these harmful contaminants have infiltrated into crops and plants (Khurana, Singh 2012; Liao et al. 2013). The effects are carcinogenic cum mutagenic modification and other health risk of ingestion by both primary and secondary consumers especially in robust quantity (WHO 2008; Flora 2009). Hence, irrigation water quality investigation is paramount in a bid to complement limited available quality water with surface or waste water. Treatment methods which sooth irrigation

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purpose without the introduction of secondary contaminants should be administered when fouled water sources are to be harnessed. Biosorption is one of such efficient, cost and time effective decontamination methods (Qian et al. 2007). The process adhere pollutants into the surface and interface of biosorbent. Researches on this process with the use of plant materials as adsorbents have produced significant results. Bamboo (Ijaola et al. 2013), maize leaf (Babarinde et al. 2006), rice husk (Bhattachaya et al. 2006), rice straw, *Moringa indica* and pecan nut shell (Habuda-Stanić et al. 2014) are some plant materials used as precursors in biochar production for mostly contaminants removal. The positive outcomes from the biochars use have encouraged more research focused on pollutants removal with environment-friendly flora materials particularly crop-based waste with less competitive values. Different models have equally been harnessed to further study contaminants sorption on biosorbents. Most employed are isotherm and kinetic models that describe the extent of adsorption favourability (Kumar 2006; Dizadji et al. 2011). Hence, this study inspects locust bean husk char (LBHC) potential in some heavy metals removal from polluted surface water utilized for irrigation.

MATERIAL AND METHODS

Locust bean husk was sourced locally from farmers after harvest in Ilorin, Kwara State of Nigeria (Fig. 1). The precursor (husk) was cleaned from external materials such as sand and other aggregates and weighed (Fig. 1b). Weighed locust bean husks were wrapped with aluminium foil to ensure complete deoxygenated condition during carbonization. The wrapped husks were subjected to varying carbonization temperatures and times in a pre-set muffle furnace (Model SXL) to determine the suitable carbonization temperature and time based on char quality and energy expended. The temperatures were 300°C, 350°C, at 30 and 60 minutes. Pyrolyzed precursor (Fig. 1c) was crushed into granular particle and washed thoroughly in distilled water to prevent cross-contamination. The wet char was then oven dried at 105°C for 6 h, allowed to cool and sorted with 1,400 micron sieve before storage. Locust bean husk structural pattern was examined before and after carbonization using the SEM-EDX machine (TESCAN, South Africa). Two adsorbers were underlaid with 50 g of cotton wool, filled with 100 and 200 g of the non-activated char, respectively, before being overlaid with another 50 g of cotton wool for the experimental set-up. Effluent was collected under stringent condition from a flowing stream channelled through Pipeline, Ilorin-South Local Government, Ilorin, Kwara State. The water source is used by local farmers and horticulturists for irrigation of crops such as plantain, banana, maize, coconut, vegetable and flowers. Eighteen litres of the surface water was introduced through the temporary storage tank into the reactors at flow rate below 14 ml/min in order to enhance biosorbent treatability. Treated influent was collected under safe and hygienic conditions after 30, 60, 90, 120 and 150 min retention. Sorbates (metals) concentration in surface water sample prior to treatment and after treatment was investigated in replicates using standard methods. Average values of replicates were analysed in the study. Adsorbent pH was equally examined before and after washing using standard methods.

Experimental calculation. Removal efficiency, linearized representation of the Freundlich and

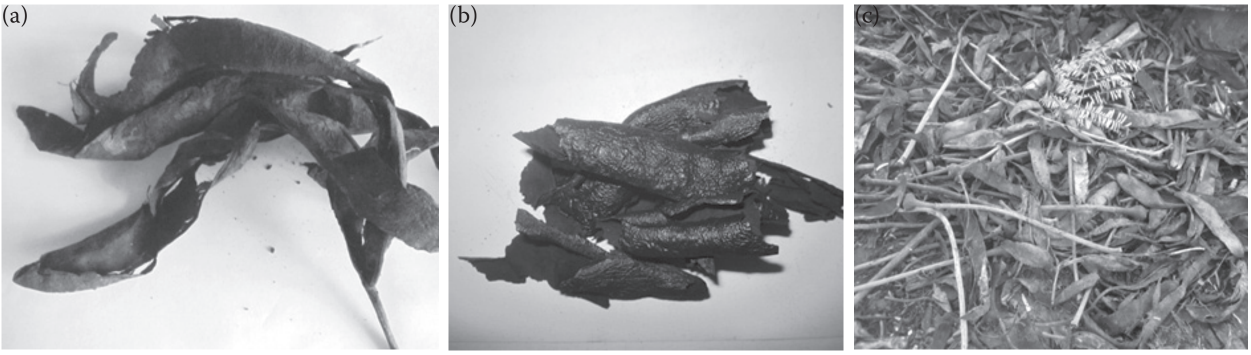

Fig. 1. Locust bean husks pile (a), locust bean husks after cleaning (b) and locust bean husk chars (c)

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Langmuir isotherms and pseudo kinetic models after integration with boundary conditions are expressed by Eqs (1–5):

$$\textit{Removal efficiency} = (C_0 - C_t)C_0 \times 100 \tag{1}$$

where: C_0 – initial concentration of heavy metal in water sample before treatment (mg/l); C_t – concentration of heavy metal in effluent after treatment for a specific contact time (mg/l)

$$Q_t = (C_0 - C_t)V_t/W_b \tag{2}$$

where: Q_t – quantity of heavy metal adsorbed per adsorbent unit weight at a given retention time (mg/g); V_t – volume of water in adsorption column at a definite retention time (l); W_b – mass of biosorbent (g)

$$\log Q_t = \log K + (1/n)\log C_t \tag{3}$$

$$C_t/Q_t = -1/(Q \times K_L) + C_t/Q_m \tag{4}$$

where: Q_m – maximum adsorptive capacity of heavy metal (mg/g); K – the Freundlich constant related to the extent of adsorption (mg/g); n – related to adsorption intensity; K_L – Langmuir parameter related to the energy of adsorption (l/mg)

Values of K and n are constants deduced from the intercept and slope of plot of $\log Q_t$ against $\log C_t$. The intercept and slope denoted with K_L and Q_m, respectively, are obtained from the plot of C_t/Q_t against C_t.

$$\log(Q_e - Q_t) = \log Q_e - (K_Q/2.3038)t \tag{5}$$

$$t/Q_t = 1/K_pQ_e^2 + t/Q_e \tag{6}$$

where: Q_e – quantity of heavy metal adsorbed per adsorbent unit weight equilibrium (mg/g); K_Q (l/min), K_p (g/mg/min) – first and second-order pseudo kinetic rates calculated form the slope plot $\log(Q_e - Q_t)$ versus t and slope and intercept of t/Q_t versus t correspondingly

RESULTS AND DISCUSSION

Weight and carbonization parameters

The weight of the husk after removal of internal material ranges from 1.3–5.3 g and weight loss after carbonization with muffle furnace (Model SXL) for 30 and 60 min was 29.1% at 300°C, 38.7–48.3% at 350°C and 40.7% at 350°C. Despite high energy input into the process, locust husk carbonized at 350°C under 60 min produced the best char quality with odourless, shining black- brown colour and thorough carbonization of the packed husk mass was achieved at this specification.

pH modification in precursor and biosorbent

Washing biosorbent improves adsorbability. This is linked with dirt, basic and water-soluble substance removal from adsorbent surface and interfaces (Ahmadpour, Do 1996; Teng, Yeh 1998). The process tends to results in enhanced pH value suitable for adsorption. pH was inclined towards alkalinity after carbonization (from 5.4 to 7.3) and approaches light acidity (from 7.3 to 6.6) after washing in distilled water. Most documented biosorbent pH for suitable metal sorption is between 5.0–7.0 (Sud et al. 2008; Zhu et al. 2011). This is because H_3O^+ competes with metallic ions at lower pH values and at higher values metal ions precipitate (Taty-Costodes et al. 2003; Mehrasbi et al. 2008).

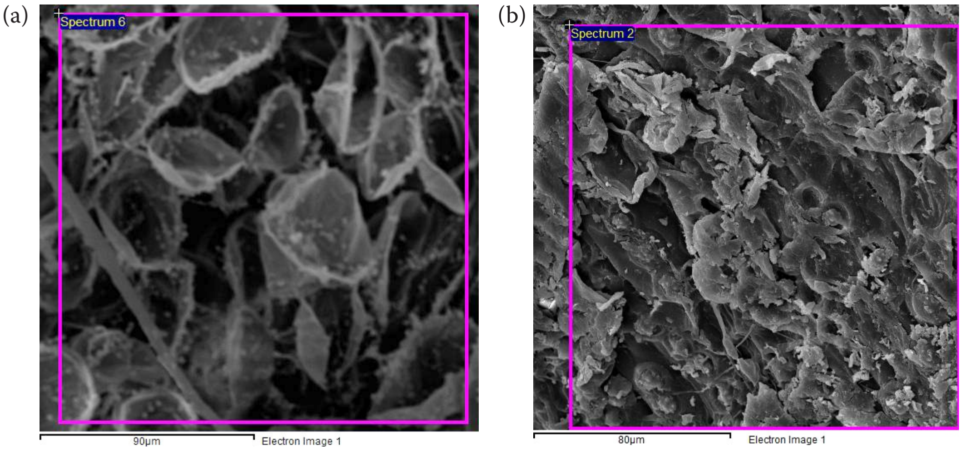

Fig. 2. SEM before (a) and (b) after locust bean husk carbonization

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Table 1. Removal efficiency (%)

	Detention time				
	30 min	60 min	90 min	120 min	150 min
			100 g LBHC		
Pb	12.82	69.23	69.23	69.23	82.05
Cd	33.33	66.67	80.00	86.67	100.00
Cr	61.11	72.22	72.22	77.78	83.33
Ar	33.33	100.00	100.00	100.00	100.00
Co	66.67	76.19	5.71	85.71	100.00
			200 g LBHC		
Pb	12.82	69.23	69.23	69.23	82.05
Cd	33.33	66.67	80.00	86.67	100.00
Cr	61.11	72.22	72.22	77.78	83.33
Ar	33.33	100.00	100.00	100.00	100.00
Co	66.67	76.19	85.71	85.71	100.00

LBHC – locust bean husk char

Table 2. Freundlich isotherm parameters obtained for LBHC at different dosage

	100 g			200 g		
	R^2	k	n	R^2	k	n
Pb	0.9296	1.4168	0.3018	0.9999	13.800	0.9978
Cd	0.9826	10.617	0.3531	0.9988	10.050	0.9206
Cr	0.9982	6.1560	0.8223	0.9623	1.1749	0.5667
Co	0.9787	1.5042	0.6478	0.9890	2.5103	0.7641

R^2 – correlation coeficient; k – Freundlich constant related to extent of adsorption; n – adsorption intensity; LBHC – locust bean husk char

Structural pattern

The micrograph reveals irregularities and heterogeneous particle morphology (Fig. 2a). Though this was pronounced after carbonization with more interconnected pores and enlarged porosity (Fig. 2b). This confirms that pyrolysis improves biosorptivity as documented by Lurtwitayapont and Srisatit (2010). Furthermore, structural state description for this type of adsorption process is not a surface diffusion process (Bruce et al. 2005).

Removal efficiency and adsorbent dosage.

Removal efficiency. Metal removal increased with detention time in most cases. Removal efficiency was the most effective with arsenic when treated with 100 g of biosorbent. Arsenic was completely removed after 60 min retention time. This indicates high treatability for arsenic in polluted surface water by LBHC. High removal efficiencies were also observed for cadmium, chromium, lead and cobalt though at higher contact times. Metal percent removal was influenced by detention time, biosorbent dosage and pollutant involved (Tables 1). In this study, optimal contact time for arsenic, cadmium and cobalt removal at 100 g adsorbent dosage was 60, 150 and 150 min in that order; for 200 g LBHC the optimal retention time for arsenic and cobalt removal was at 150 minutes. Optimal contact time for other investigated metals under this

Table 3. Langmuir isotherm correlation coefficient (R^2) values for LBHC at different dosage

	R^2 (100 g)	R^2 (200 g)
Pb	0.2970	0.9138
Cd	0.3438	0.8860
Cr	0.8195	0.3123
Co	0.5863	0.7856

LBHC – locust bean husk char

Table 4. First order pseudo kinetic parameters obtained for LBHC at different dosage

	100 g		200 g	
	R^2	K_q	R^2	K_q
Pb	0.2153	0.0309	0.3411	0.0412
Cd	0.0100	0.0085	0.2491	0.0440
Cr	0.0348	0.1498	0.0000	0.0005
Co	0.0133	0.0104	0.3222	0.0454

LBHC – locust bean husk char; R^2 – correlation coeficient; K_q – the first-order pseudo kinetic rate

experimental condition was beyond 150 minutes. Sangodoyin and Ajayi-Banji (2013) recommended higher detention time of over 360 min for efficient metal diminution in column biosorption experiment. Metal removal kinetic reveals rapid sorption process at 30 min for chromium, cadmium, arsenic and cobalt. Similar trend was observed for lead, cadmium and arsenic at 60 min contact time and subsequently slower sorption process for 100 g biosorbent. At this contact period, approximately between 50–82% removal was noted. Kinetics for 200 g biosorbent was very rapid at the initial 30 min retention time and afterward a subsequent slow and steady sorption process for other detention times was observed (Tables 1 and 2). According to Zhu et al. (2009), the rapid initial metals sorption was traced to fast ions transport to the LBHC surfaces while the slow and steady sorption process was linked to slow diffusion of contaminants ions into LBHC intra-particle pores.

Adsorbent dosage. Percent of the metal removal increased between 12.4–79.3% when biosorbent dosage was doubled at 30 min contact time except with chromium (Table 1). This is an indication that increased adsorbent sites influence metal sorption and subsequent percent removals were due to interactions between LBHC and sorbates at specified retention time. Obviously, at other detention times, such as chromium percent removal at 30 min retention time, an increase in LBHC dosage does not imply a commensurate increase in contaminant removal (Table 1). A similar result was documented by Mehrasbi et al. (2008) in a study on lead and cadmium biosorption. The disproportionate increase in metal removal with increased adsorbent dosage was tied to a decrease in the amount of metal ion per unit mass of pre-treated almond shell. Adsorbent dosage influences removal efficiency with respect to contact time and contaminant involved.

Isotherm models

The Freundlich isotherm model had good fit in metal removal description at both dosages. Correlation coefficient values were greater than 0.929 for all the cases (Table 2). R-squared value of this range is considered good in most metal adsorption studies (Guedes et al. 2007; Pan et al. 2009; Habuda-Stanić et al. 2014). This suggests the adsorption process is multi-layer and depicts the applicability of the Freundlich isotherm model in the description of heavy metal removal with respect to retention time and LBHC dosage. Values of n were less than unity, which infers that significant adsorption occurred at high concentration and an increase in amount sorbed with concentration was significant at higher concentration (Moreno et al. 2010). *K* value for cadmium and chromium at 100 g biosorbent dose was high. This implies high adsorption intensity (Table 2). Conversely, the Langmuir model provided poor representation for most metallic sorption processes in linearized form except in Pb removal at 200 g biosorbent dosage (Table 3). Hence, the latter is not applicable in LBHC metal removal description.

Table 5. Second order pseudo kinetic parameters obtained for LBHC at different dosage

	100 g				200 g			
	R^2	$Q_e(\times10^{-3})$	$Q_t(\times10^{-3})$	K_p	R^2	$Q_e(\times10^{-3})$	$Q_t(\times10^{-3})$	K_p
Pb	0.0000	4.980	4.980	2.1100	0.9819	2.267	2.227	25.898
Cd	0.9490	1.447	1.447	47.160	0.9905	9.390	0.939	74.680
Cr	0.9845	1.178	1.178	56.110	0.9918	1.264	1.264	333.95
Co	0.9888	1.654	1.654	53.060	0.9547	1.340	1.340	46.760

R^2 – correlation coeficient; $Q_{e,}$ – quantity of heavy metal adsorbed per adsorbent unit weight at a given retention time; Q_t – quantity of heavy metal adsorbed per adsorbent unit weight at equilibrium; K_p – second-order pseudo kinetic rate; LBHC – locust bean husk char

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Kinetic sorption

Pseudo first order kinetic sorption gave poor representation of the kinetic sorption with correlation coefficient values less than 0.4 (Table 4). On the contrary, pseudo second order kinetic suggests good sorption rate fit with all R squared values greater than 0.94 except with Pb at 100 g biosorbent dosage. Minimal disparity between calculated Q_t and experimented Q_e values validates the applicability of pseudo second order kinetics in LBHC sorption description (Table 5). According to Pan et. al. (2009), this suggests chemisorption between LBHC and sorbates during the sorption process.

CONCLUSION

Surface water harnessed to service crop production in order to meet expanding food demand can be treated with locust bean husk char prior to application due to the char adsorption potential in heavy metals diminution. Char treatability was influenced by detention time, sorbate type and adsorbent dosage. Optimal contact time for heavy metal removal varies with LBHC dosage and metal involved. Freundlich isotherm well described the adsorption process ($R^2 \geq 0.92$). Pseudo-second order linearized kinetic well described sorbate sorption ($R^2 \geq 0.94$) and revealed metal sorption was not only physical but a chemical process was involved as well. Locust beans husk char is an effective biosorbent in metal removal from mildly polluted surface water.

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Received for publication June 12, 2015
Accepted after corrections February 8, 2016