

COCONUT HUSK CHAR BIOSORPTIVITY IN HEAVY METAL DIMINUTION FROM CONTAMINATED SURFACE WATER

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Abstract: Applicability of coconut husk char in heavy metal removal was examined in the study. The surface morphology and elemental compositions of the char was investigated with SEM-EDX machine. Heavy metals sorption on 100 g of the char dosage was studied under five different contact times in the column experiment. Isotherm and kinetic models were the probing tools for biosorption mechanism prediction. Results indicated removal efficiency for chromium, cobalt, cadmium, aluminum and arsenic at 60 mins contact time were 72, 80, 86, 89 and 100 % respectively. Contaminate removal depends on metal involved and sorption contact time. Adsorption data are fitted well into Freundlich isotherm model ($R^2 > 0.92$). Pseudo kinetic second order well described the adsorption process, with most R^2 values ≥ 0.94 . Coconut husk char is an effective biosorbent in sequestration of arsenic, cadmium, aluminum and cobalt in contaminated surface water.

Keywords: coconut husk char, removal efficiency, isotherm models, pseudo kinetics

1. INTRODUCTION

Technological advancement pivotal to development has enhanced the utilization of several materials in the production line. The materials principal in the alleviation of societal needs are plastic, steel, iron, rubber, fiber, paper and timber. Use of any type of the materials in the production industries varies with the nature of work, financial resources availability, strength required, material durability, affordability, and availability. Despite the dependents, products derived from the materials deteriorate in value and strength due to physical, chemical and biological influence [1]. The deterioration eventually exceeds the shelf life with the last resort for the product being disposal. The latter is feasible if other waste management options such as reuse and recover are not feasible. Metal is one of the widely utilized materials. The use spans from tiny and simple tool to gigantic and sophisticated equipment and structures. This could be attributed to the superior durability and strength when compared with other materials like plastic and rubber, though on the high side in terms of cost [2]. The additional notable challenge in the utilization of metal-enriched materials is the significant contribution to environmental contamination due to the pronounced susceptibility to wear, rust and corrosion [3].

Chemicals in detergents, disinfectants, mineral lime, pesticides, fertilizers, herbicides, adhesives and from mining activities are equally sources of heavy metals [4-6]. One of the recipients of the contaminants is surface water. The contaminants from anthropogenic activities not only pollute the water source. Studies have also shown that heavy metals concentration in surface water is becoming a subject of concern [7, 8]. Some of the

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identified pollution sources are dump site close to water course [7, 9], industrial waste discharged to surface water [10, 11] and leachate into the nearby stream from pesticides use to ward off insects and mineral fertilizer used as soil nutrient enhancer [12, 13]. An elevated level of heavy metals in surface water poses a risk to aquatic lives. It could lead to the death of aquatic lives [14]. Another drawback in the application of such water for agricultural purposes is an accumulation of heavy metal in crop parts [15]. This might cause health risk when such crop is ingested by fauna and man. This should be of serious concern to farmers in arid and semi-arid regions of developing and underdeveloped countries, who see flowing water as a luxury. Suggested solutions to the challenges are enforcing laws to curb indiscriminate waste and wastewater discharge into a water course, location and relocation of dumpsite from surface water, monitoring activities around water bodies and surface water quality analysis and treatment of affected water sources before usage. The latter is very important in order to ensure stipulated standards are met prior to application. A number of water treatment methods such as precipitation, coagulation, membrane process and activated carbon exist. Though most have been discredited based on the high cost of the method and high volume cum low heavy metal concentration of effluents to be treated [16, 17]. A suitable, effective and environment-friendly physico-chemical surface water treatment method is biosorption. This method is economically efficient because it employs biological materials such as cassava peel [18], maize tassel [19], rice straw [11] and wood waste [20] as biosorbents. Aside the merits, studies have shown that the precursors have effective treatability with respect to column bed height, adsorbent type, dosage and calcium content, sorbate flow rate and concentration, impregnation salt used and contact time [21-23]. Therefore, this study seeks to explore the usability of coconut husk char potential based on retention time in some heavy metals sequestration from mildly polluted surface water.

2. METHODOLOGY

The coconut was sourced from local farmers in Ilorin, Kwara State. The husk (Figure 1) was manually removed from the fruit, cleaned from external materials and weighed. Weighted husk mass was wrapped in double layers of aluminum foil before carbonization to ensure completely deoxygenated condition. The husks were subjected to different carbonization temperatures and times in an electric muffle furnace in order to obtain complete carbonization at optimum level with reference to good quality char. The temperatures at 30 mins carbonization time investigated were 300 and 350 °C. Completely carbonized char produced at 350 °C (Figure 2) was washed in distilled water, filtered and oven dried at 105 °C for 360 mins in an electric oven dryer. The oven dried char was granulated after cooling, sieved to 1400 µm size and stored. Char structure and elemental composition were investigated using SEM-EDX machine. One thousand and three hundred cubic centimeter capacity cylindrical polyvinyl chloride pipe reactor was used for the experiment. The choice of cylindrically shaped adsorber was to avoid pocket formed on the edges of the rectangular reactor during the test (personal observation).



Fig. 1. Coconut husk.



Fig. 2. Carbonized coconut husk.

The system has both inlet and outlet paths. The former receives untreated water from the temporary storage tank at a flow rate of 14 mL/min and the outlet channel discharges the treated effluent. Fifty grams adsorbent (cotton wool) was carefully laid in the reactor to prevent the escape of adsorbent during discharge. The reactor was then loaded with 100 g of granulated coconut husk char before another 50 g of cotton wool was overlaid. Eighteen liters of water sample were collected under stringent condition from surface water channeled through Pipeline area, Tanke, Ilorin. The water is often utilized for ephemeral and annual crop cultivation by farmers especially during the peak period of the dry season in Ilorin, Nigeria. Horticulturist around the vicinity also service flowers with the water source. Influent collected from this source was temporarily stored in the tank before being introduced into the reactor. Samples of treated effluent from this experiment were taken after 30, 60, 90, 120 and

150 mins retention time. Heavy metals investigated before and after treatment using standard method were lead, chromium, arsenic, cadmium, cobalt, aluminum, zinc, and copper. Biosorbent and surface water pH were equally investigated using standard method. Analyses were replicated and the mean values computed.

3. EXPERIMENTAL CALCULATION

The parameters investigated were removal efficiency, Freundlich and Langmuir models in linear representation and pseudo kinetic models after integration with boundary conditions. These are stated in equations (1) – (6). C_o represents the initial concentration of heavy metal in surface water sample before treatment (mg/L); C_t denotes the concentration of heavy metal in effluent after treatment for a specific retention time (mg/L); Q_t connotes the quantity of heavy metal adsorbed per adsorbent unit weight at a given contact time (mg/g); V_t represents the volume of collected surface water in adsorption column at a definite detention time (l); W_b is the mass of biosorbent (g); t represents contact time in hrs. Q_m represents the maximum adsorptive capacity of heavy metal (mg/g); K is the Freundlich constant related to the extent of adsorption (mg/g); n is the Freundlich parameter related to the adsorption intensity; K_L is the 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 $\text{Log } Q_t$ against $\text{Log } C_t$. 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. Q_e represents the quantity of heavy metal adsorbed per adsorbent unit weight equilibrium (mg/g).

$$\text{Removal efficiency} = (C_o - C_t)C_o \times 100 \quad (1)$$

$$Q_t = (C_o - C_t)V_t/W_b \quad (2)$$

$$\text{Log } Q_t = \text{Log } K + (1/n)\text{Log } C_t \quad (3)$$

$$C_t/Q_t = -1/(Q_m \cdot K_L) + C_t/Q_m \quad (4)$$

$$\text{Log}(Q_e - Q_t) = \text{Log } Q_e - (K_Q/2.3038)t \quad (5)$$

$$t/Q_t = 1/(K_p Q_e^2) + t/Q_e \quad (6)$$

4. RESULTS AND DISCUSSION

4.1. Carbonization temperature and time

Percentage mean weight loss after carbonization was 37.0 and 48.3 % for 300 and 350 °C respectively. Statistically, there was no significant difference between weight loss in char at the carbonization temperatures ($P < 0.05$). Quality char was produced under a carbonization temperature and time of 350 °C and 30 mins respectively (Figure 2). The char was odorless and black-brown color. This is a physical pointer to a good carbonized product.

4.2. pH changes in biosorbent

Washing carbonized and granulated char generously in distilled water alters the pH value. Biosorbent pH value adjusted from 4.5 after impregnation and washing in distilled water to 5.6. The pH value is in line with [24] documentation for effective metal sorption. The process equally removes soluble inorganic ions aside dirt [16].

4.3. Structural pattern and elemental composition

EDX result in Figure 3 shows a high proportion of calcium ion with respect to other elements present. The presence of calcium suggests ion exchange mechanism other than biosorption could be responsible for metal diminution in mildly contaminated surface water [25]. Morphological structure of coconut char at 1.09 kx and 50 μm magnification reveals plate-like structural pattern (Figure 4). The pattern is different from irregular structures observed for most biosorbents in terms of porosity [19, 26]. This might be due to precursor employed.

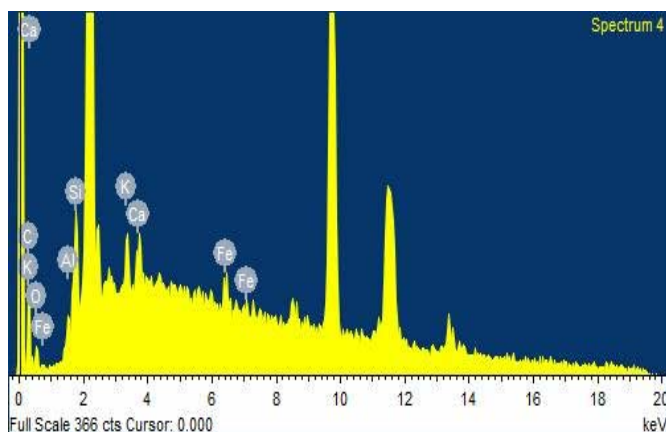


Fig. 3. EDX for carbonized coconut husk.

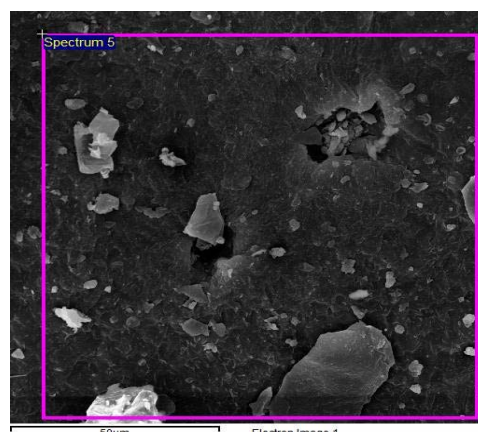


Fig. 4. SEM for carbonized coconut husk.

4.4. Removal efficiency studies

Mean values of treated surface water samples with respect to retention time are shown in Table 1. This is in line with the values obtained from surface water contamination study [7]. Contact time influenced removal efficiency though sorbent displayed different sorption tendencies with respect to heavy metals. In most cases, heavy metal removal increased with detention time. Zinc removal percentage from initial contact time through 30 mins increased by 36.67 %. Cadmium and aluminum demonstrated exceptionally rapid uptake at 30 mins retention time (Table 2). Eighty percent cadmium was sorbed at 30 mins detention time. Higher affinity was achieved with aluminum. This according to [24] is traceable to fast cadmium and aluminum ions mobility to the coconut husk char surfaces. This is an indication that the active sites have rapid uptake rate for cadmium and aluminum at 30 mins detention time. This suggests strong interaction between the adsorbate and adsorbent. Table 2 also shows that lead, chromium, zinc, copper and aluminum require extended detention time before complete adsorption is achieved under this experimental condition. Similar observation was suggested by literature [25, 27].

Table 1. Mean concentration of heavy metals in treated and untreated surface water.

Heavy metal	Untreated (mg/L)	Treated (mg/L)				
		30 mins	60 mins	90 mins	120 mins	150 mins
Lead	0.130	0.087	0.057	0.037	0.030	0.023
Cadmium	0.050	0.010	0.007	0.007	0.000	0.000
Chromium	0.060	0.047	0.017	0.017	0.013	0.010
Arsenic	0.020	0.013	0.000	0.000	0.000	0.000
Cobalt	0.070	0.023	0.013	0.010	0.100	0.000
Zinc	0.400	0.253	0.233	0.177	0.153	0.140
Copper	0.500	0.367	0.317	0.283	0.250	0.233
Aluminum	0.450	0.063	0.047	0.040	0.033	0.020

Table 2. Removal efficiency for the biosorbent dose.

Heavy metal	Removal efficiency (%)				
	30 mins	60 mins	90 mins	120 mins	150 mins
Lead	33.33	54.41	71.80	76.92	82.05
Cadmium	80.00	86.67	86.67	100.00	100.00
Chromium	22.22	72.22	72.22	77.78	83.00
Arsenic	33.33	100.00	100.00	100.00	100.00
Cobalt	66.67	80.95	85.71	85.71	100.00
Zinc	36.67	41.67	55.83	61.67	65.00
Copper	26.67	36.67	43.33	50.00	53.33
Aluminum	85.93	89.63	91.11	92.59	95.56

4.5. Isotherm models studies

Adsorption isotherm data were consistent with Freundlich model with correlation coefficient values greater than 0.92. Therefore, Freundlich isotherm model satisfactorily gave a better description of adsorption process than Langmuir (Table 3). This equally implies the adsorption process is not monolayer [28, 29]. The low k value of

zinc and copper is an indication of low adsorption intensity. This also confirms the low removal efficiencies for these contaminants (Table 2). The value of n less than unity connotes elevated sorption of sorbate at greater concentration [30]. The values of n for all the metals were within this range (Table 3).

Table 3. Isotherm model for coconut char biosorbent in heavy metal removal.

Heavy metal	Freundlich			Langmuir
	n	R^2	K	R^2
Lead	0.9983	0.2448	0.5033	0.0648
Cadmium	0.9248	1.8038	0.6639	0.5770
Chromium	0.9612	5.5450	0.3429	0.1745
Cobalt	0.9877	1.0361	0.6053	0.4523
Zinc	0.9940	0.0359	0.7900	0.8577
Copper	0.9999	0.0219	0.7750	0.8060
Aluminum	0.9992	0.4629	0.8402	0.8301

4.6. Kinetic sorption studies

There exist poor linear relationship between $\log(Q_e - Q_t)$ and t , since regression coefficient values were less than 0.60 (Table 4). Therefore, the process is not pseudo-first order. On the contrary, good linearity exists between t/q and t . Heavy metals biosorption on coconut husk char fitted well into second order kinetic. Most correlation coefficient values were greater than 0.92. According to [31], this indicates chemisorption mechanism involvement in the sorption process. The closely related experimental Q_e and calculated Q_t values from the plot t/q against t confirms the linearity of the second order equation.

Table 4. Kinetic sorption studies for coconut char biosorbent in heavy metal removal.

Heavy metal	First order kinetic		Second order kinetic		
	K_Q	R^2	Q_e	Q_t	R^2
Lead	0.5770	0.0562	0.9487	0.0030	0.0029
Cadmium	0.3136	0.7225	0.9774	0.0019	0.0011
Chromium	0.1921	0.4426	0.8072	0.0016	0.0015
Cobalt	0.0538	0.1239	0.9872	0.0016	0.0015
Zinc	0.0018	0.0042	0.9731	0.0068	0.0067
Copper	0.0090	0.0207	0.9787	0.0070	0.0070
Aluminum	0.2730	0.6289	0.9767	0.0099	0.0087

4. CONCLUSIONS

Surface water contaminants sorption by 100 g of coconut husk char was considered in this study. The study shows that coconut husk char is an effective biosorbent in arsenic, cadmium and cobalt sorption from mildly polluted surface water in column experiment. Removal efficiency at 150 min retention time inspected for all the heavy metals except zinc and copper was greater than 80 %. Removal efficiencies of the heavy metals on coconut husk chars depend on contact time and heavy metal involved. Most kinetics of the heavy metals sorption on coconut husk char conforms to pseudo-second order equation ($R^2 > 0.94$). Chemical sorption of heavy metal was noticed in the process. Freundlich isotherm models well described the heavy metals sorption on the biosorbents ($R^2 > 0.92$).

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