Short Communication

On the Use of Non-Activated Carbon Derived from Abattoir Solid Waste to Adsorb Heavy Metals in Contaminated Surface Water

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Abstract

Heavy metal is a major environmental pollutant with deleterious health effect on man, flora and fauna especially in accumulated form. Possible solution for the attenuation of the contaminant has been examined using various treatment methods. Column biosorption study was carried out to examine the potential of non–activated carbons from abattoir solid wastes in some heavy metals removal. Removal efficiency and isotherm models were tools used to evaluate bone and horn chars potential in metals removal from industrially contaminated surface water. Biosorbents structural pattern was investigated using SEM-EDX machine. Results indicate 100, 67 and 50 % removal of cadmium, lead and chromium respectively after 4 h detention time for both chars, though bone char has higher treatability for iron removal from polluted surface water than horn char. Freundlich isotherm model had a better fit in lead, manganese and chromium removal description with high R^2 value for both chars. Calcium ion exchange occurred during the sorption process without secondary contamination of the treated effluent. The results suggest that abattoir solid wastes are effective biosorbents for iron removal in mildly polluted surface water.

Key Words**:** Heavy metal; abattoir solid waste; non-activated carbon; isotherm model.

Introduction

The trend and extent of heavy metals trace and significant deposition in water and soil is not only alarming but a subject of concern in our society today. This is pronounced in urban settlement due to modernization and increasing industrialization with little orientation on good waste management practices. The primary source of heavy metals could be the uncontrolled disposal of sophisticated and complex items. The wastes stem from different sources, namely, automechanics, chemical, electronics and production industries. The wastes which are recalcitrant in nature contaminate vulnerable soil and surface water and have inherent carcinogenic and mutagenic potentials. Poor management of the wastes could similarly result in leachate percolation thereby ground water contamination, while the secondary effect may be noticed in cultivars consumption. A number of heavy metals, particularly in trace quantities, have nutritional benefits to human, flora and fauna (Raikwar et al., 2008). However, some health challenges have been reportedly traced to indirect and disproportionate ingestion of these substances (IPCS, 1992; Mahtab and Neelam, 2002; WHO, 2008; Flora, 2009).

Heavy metals are becoming ubiquitous due to uncoordinated waste management practices. In WHO (2007) report, cadmium was noticed in crops and aquatic animals exposed to contaminated soil and water. Lead was similarly observed in surface and ground water exposed to anthropogenic activities (UNEP/WHO, 1996). These substantiate and validate claims on environmental pollution attributed to indiscriminate disposal of heavy metal-based wastes (Danny et al., 2000; Esmaeili et al., 2008). Removal of this pollutants have been studied by several authors using a number of biological and synthetic materials such as wood (Chojnacka and Michalak, 2009), silical gel (Ajmal et al., 2001), yeast (Saifuddin and Raziah, 2007) and zeolite (Pandey et al., 2010). While synthetic adsorbents are costly, most of the aforementioned biological materials have established applications. Furthermore, the usability of biological materials for other tasks might leads to resource scarcity and competition. A safe and rational alternative is the consideration of low economic value materials often describe as waste. Waste is any substance considered useless by the end-user. Wastes generated from biological materials are relatively cheap and environment-friendly. Most studies conducted on biowaste utilization for heavy metals attenuation have proven efficient (Aslam et al., 2004, Amuda and Ibrahim, 2006; Mehrasbi et al., 2008; Ajayi-Banji, 2012). Waste from sugarcane (bagasse) was employed in the bioremediation of complex carbon in oil polluted soil with significant contaminant reduction (Goodin and Hudnall, 2001). Over 50 % nickel removal from aqueous solution was achieved using rice husks (Bansal et al., 2009). Lead adsorption on swine bone powder achieved 98 % removal efficiency (Lurtwitayapont and Srisatit, 2010). Chojnacka and Michalak (2009) noted that adsorption using biomaterials including biological wastes have regeneration and reuse advantage for metal removal in several cycles. Further benefit of adsorption over most waste management methods is the drastic reduction of secondary impact on treated water. Although the contaminant removal efficiency of these biosorbents is noteworthy, accurate representation of the adsorbent capacity is often concealed. Studies have shown that adsorption isotherms are effective tools for adsorbent ability assessment and description (Potgieter, 1991; Mkayula and Matunbo, 1994; Zubair and AbdeKhedar, 2007). This study focuses mainly on adsorption potential of unmodified abattoir solid waste chars in heavy metals removal from mildly contaminated surface water.

Methods

Cattle bone and horn were sourced from Bodija Abattoir, one of the major abattoirs in Ibadan in terms of size of daily slaughter. The horn was soaked in tap water for a period of 2 days to ease horn-bone removal from the parent material. Both biowastes were washed and oven dried for 4 h at a temperature of 105 °C. Thereafter the horn was pyrolyzed at 400 °C for 150 mins under deoxygenated condition (wrapped with two layer of aluminium foil) to enhance adsorbent treatability. Cattle bone was carbonized at 450 °C for 120 mins to achieve quality char production. This was equally carried out under hermetic condition. Puangpinyo and Osiriphan (2009) opined that carbon produced under anaerobic state has better adsorption potential compared to chars produced under oxygenated state. Calcium, phosphorus, carbon content, bulk density and colour of the biosorbents were quantified using standard methods. Chars produced were reduced to 850 μm, washed in distilled water and oven dried at 120 °C for 12 h. The flow chart for the methodology is as shown in Figure 1. The structural pattern of the biochars was examined with SEM-EDX machine.

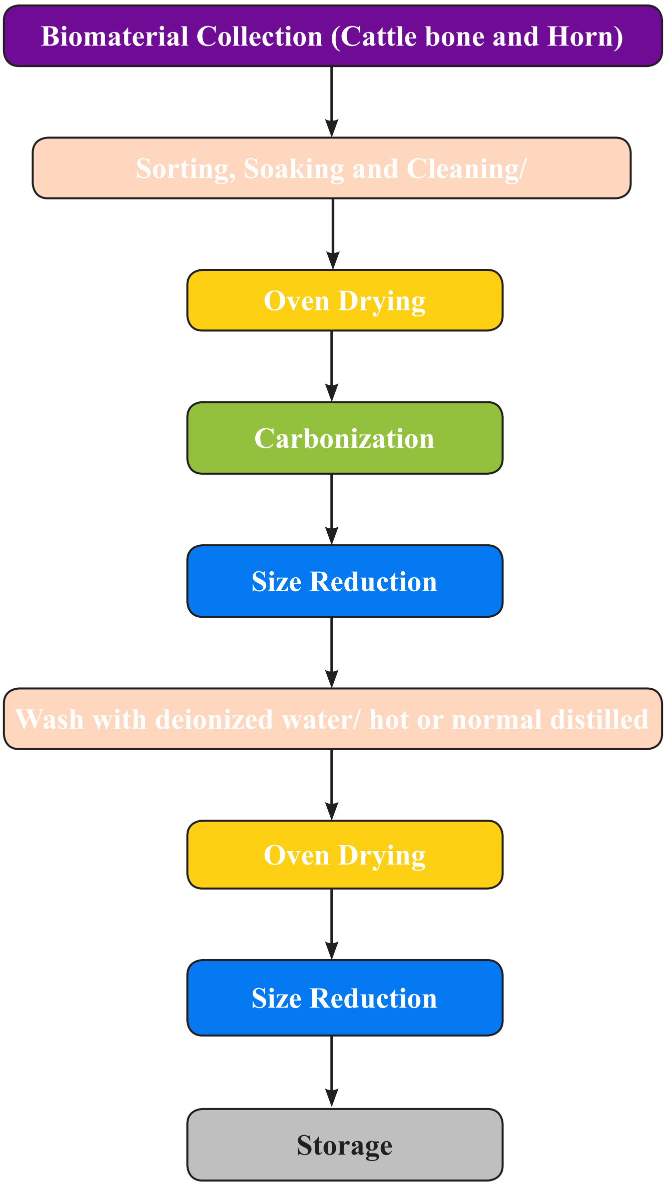

Figure 1 Flow chart for the non-activated carbons production.

Thirty liters of water placidly contaminated with heavy metals were sourced under stringent condition from Oluyole River in Ibadan, Oyo State, Nigeria. The watercourse is a point source discharge of industrial effluent from metal factories, construction companies, drinks and pastries factory in the locality. Although, the river has self-purification ability, indiscriminate discharge of untreated or partially treated industrial effluent impairs its quality. The water was stored in 22.5 L capacity storage tank.

Two composite prism adsorbers were used for the column biosorption experimental set–up. The dimension of the adsorber was 12×12×62 cm. The adsorbers were underlaid with 30 g absorber (cotton wool) each to prevent granulated chars escape alongside the treated effluent and then loaded with 350 g of one of the biosorbents each.

Surface water stored in the 22.5 L capacity storage tank was charged into the adsorber at minimal flow rate of 10 ml/min to enhance adsorbability until the adsorbers were filled to 7200 cm3 capacity (Figure 2). Treated water samples were collected for analysis after 120, 240 and 360 mins detention time. The schematic diagram is as shown in Figure 2.

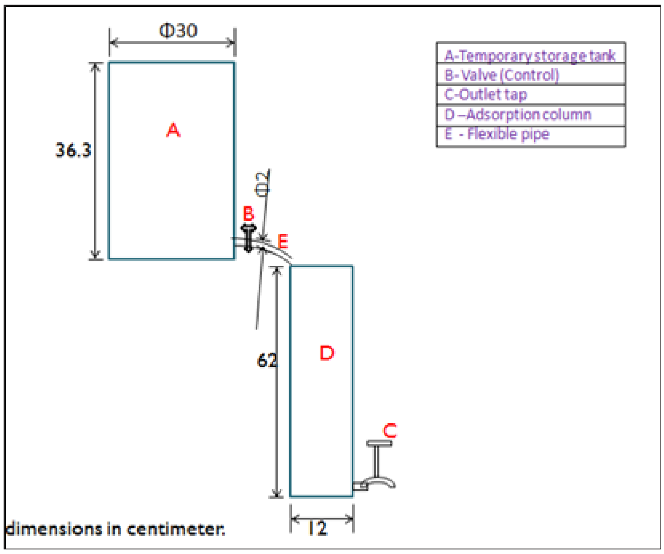

Figure 2 Schematic diagram for the adsorption process.

Heavy metals concentration in samples before and after treatment was determined using atomic absorption spectrophotometer. The analyses were done in triplicates and the average values used for further analysis in the study.

Figure 3 Adsorption process set-up.

Results and Discussion

Biosorbent Properties and Structure

The adsorbents have closely-related elemental composition and properties, but with considerable difference in Ca level (Table 1). Calcium to phosphorus ratio (Ca/P) for cattle bone char was lower than that obtained by Lurtwitayapont and Srisatit (2010) in a study on swine bone as adsorbent in lead removal, though the carbon content was higher. The disparity might be linked with difference in the adsorbent source. The horn char equally has higher carbon content that the one reported by the previous author expect that the Ca/P value was higher than that of bone char reported in this study (Table 1). The bulk densities obtained in this study were greater than the value reported by Nwabanne and Igbokwe (2012) for oil palm fibre. The variation might be attributed to difference in precursor used as biosorbent (Table 1).

The SEM structures show homogeneity morphology of particles for bone and horn char at magnification of 500 X with 20 µm and 1000 X with 10 µm scale bar respectively. Pore spaces were not visible at these magnifications. This observation is similar to Ma et al. (2008) documentation on fluoride removal from drinking water using bone char. Furthermore, internal pore structures for both chars were not extended (Figures 3, 4). According to Bruce et al., (2005) this implies that adsorption process under this structural state was governed by surface diffusion.

Table 1 Physical and Chemical Properties of Biosorbent.

	Bone Char	Horn Char
Ca/P	1.5	1.8
Colour	Dark brown	Light brown
Bulk Density (g/cm^3)	0.93	0.91
Total Carbon (%)	49.0	47.2
Calcium (mg/100g)	266.7	280

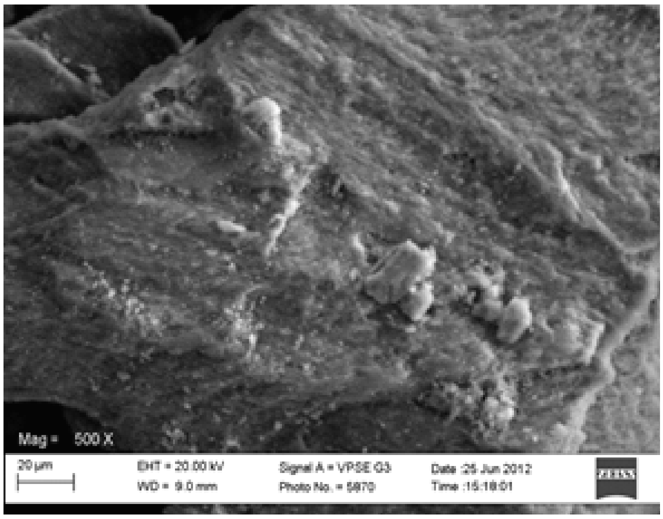

Figure 4 Bone Char

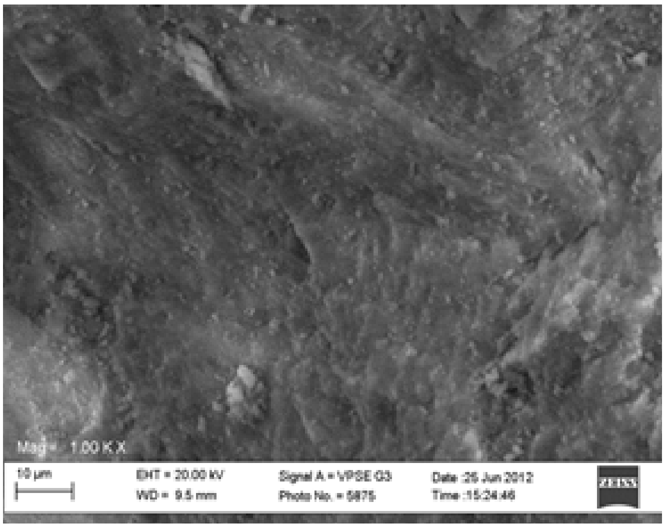

Figure 5 Horn Char

Removal Efficiency

Lead, cadmium, iron, manganese and chromium ions removal were examined using equation 1. Parameter definition is as stated. C_i (mg/l) represents initial concentration of heavy metal in water sample before treatment. C_t (mg/l) represents heavy metal concentration in treated water sample after a detention period.

$$\text{Removal efficiency}=(C_i-C_t)/C_i*100 \quad (1)$$

Result indicates that concentration of heavy metals reduces with detention time, though remain unchanged after 4h detention time (Table 2). Most heavy metals concentration remained constatnt after 2 h retention time. Hundred percent cadmium removal was observed for both chars at 120 mins residence time and over 66 % lead ion removal after 240 mins retention time (Table 3). However, in Lurtwitayapont and Srisatit (2010) study, lead removal efficiency using swine bone char at 4320 mins detention time was higher. This distinction might be due to the considerable difference in contact time and adsorbate source. Similar trend was observed for horn and bone char with respect to all the heavy metal considered in this study except for iron diminution. More iron concentration was removed for bone char compares with horn char. This is an indication that bone char has higher affinity for iron ions.

Table 2 Heavy Metals Concentration for Treated and Untreated Polluted Surface Water.

	Untreated sample (mg/L)	Treated sample (mg/L)					
		Bone Char			Horn Char		
		2h	4h	6h	2h	4h	6h
Pb^{++}	0.03	0.02	0.01	0.01	0.02	0.01	0.01
Cd^{++}	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Fe^{++}	0.65	0.50	0.43	0.40	0.55	0.50	0.43
Mn^{++}	0.03	0.02	0.02	0.02	0.02	0.02	0.02
Cr^{3+}	0.02	0.01	0.01	0.01	0.01	0.01	0.01

Table 3 Biosorbent Cumulative Removal Efficiency of the Metals from Relatively Polluted Water in Percent.

	Bone Char			Horn Char		
	2h	4h	6h	2h	4h	6h
Pb^{++}	33	67	67	33	67	67
Cd^{++}	100	100	100	100	100	100
Fe^{++}	23	34	39	15	23	34
Mn^{++}	33	33	33	33	33	33
Cr^{3+}	50	50	50	50	50	50

Freundlich and Langmuir Isotherm Models

The parameters used in these models are defined as follows. Q_t (mg/g) biosorbent adsorption capacity, V_t (l) represents volume of water in adsorption column and M (g) represents adsorbent mass. Maximum adsorptive capacity of heavy metal is denoted with Q_m(mg/g); K_F represents the Freundlich constant related to the extent of adsorption (mg/g); n represents the adsorption intensity, K_L represents the Langmuir parameter related to the energy of adsorption (L/mg). Values of K_F and n were constants calculated from the intercept and slope of plot of LogQ_t against LogC_t.

The values of K_L and Q_m were obtained from the intercept and slope of plot of C_t/Q_t against C_t. Equations 3 and 4 express linearized form of Freundlich and Langmuir isotherm models respectively.

Adsorption capacity, $Q_t = (C_i - C_t)\, V_t/M$ (2)

$\mathrm{Log}Q_t = \mathrm{Log}\, K_F + (1/n)\, \mathrm{Log}C_t$ (3)

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

Langmuir and Freundlich isotherm models fitted well in describing manganese and chromium ions sorption from polluted surface water with high correlation coefficients ($R^2 > 0.98$). The Freundlich model has better representation for all the metals except iron (Tables 4, 5). Langmuir isotherm model well described iron sorption on bone char surface with correlation coefficient greater than 0.99 (Table 5). Correlation coefficient is a measure of the applicability of the isotherm for adsorption data description. High correlation coefficients imply a nexus between energy responsible for water molecules detachment from ions and interaction of contaminant and biosorbent (Dizadji et al., 2011). According to Lurtwitayapont and Srisatit (2010), high correlation coefficient values from Freundlich isotherm models show that the adsorption process for all the heavy metals except iron was mainly multilayer. Large value of K_f for biosorbent is an indication of high adsorption capacity. Similarly, when 1/n is greater than unity, significant adsorption takes place at low heavy metal concentration with considerable increase in the amount of heavy metal sorbed at higher concentration (Amuda and Ibrahim, 2006; Moreno et al., 2010). In this study, both chars recorded 1/n value greater than 2 for lead though the values for K_f were the least. This confirms higher adsorption rate of Pb compared to other metals (Table 4). Cadmium adsorption could not be modelled with either Freundlich or Langmuir isotherm model as it was completely adsorbed at 120 mins or lesser residence time. Relationship between adsorption capacity and detention time followed the same trend for both biosorbents (Figures 5, 6). This is an indication that both precursors behave similarly during adsorption.

Table 4 Freundlich Isotherm Model for Bone and Horn Char Biosorbent.

	Horn Char			Bone Char		
	R^2	**K_f**	**1/n**	**R^2**	**K_f**	**1/n**
Pb^{++}	0.9812	2.667	2.0275	0.9812	2.667	2.667
Fe^{++}	0.6033	156.8	1.5088	0.2427	255.0	255.0
Mn^{++}	0.3388	290.7	0.8384	0.9988	290.7	290.7
Cr^{3+}	0.9988	162.6	0.8384	0.9988	162.6	162.6

Table 5 Langmuir Isotherm Model for Bone and Horn Char Biosorbent.

	Horn Char		Bone Char	
	R^2	**K_L**	**R^2**	**K_L**
Pb^{++}	0.6611	4.79×10^{-2}	0.661	4.79×10^{-2}
Fe^{++}	0.7367	0.33×10^{-2}	0.9972	0.025×10^{-2}
Mn^{++}	0.9968	5.87×10^{-2}	0.9968	5.87×10^{-2}
Cr^{3+}	0.9968	2.93×10^{-2}	0.6698	2.93×10^{-2}

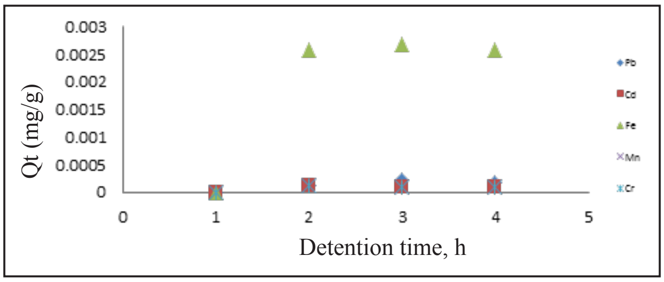

Figure 6 Relationship between adsorption capacity and detention time for horn char.

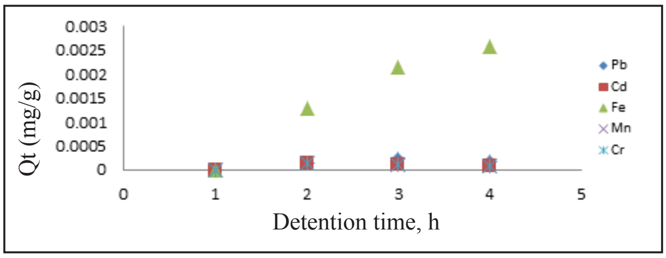

Figure 7 Relationship between adsorption capacity and detention time for born char.

Biosorbent Influence on Calcium and Phosphate ion Sorption

Animal bone and horn-bone contains 65 – 70 % calcium hydroxyl-apatite compound ($Ca_{10}(PO_4)_6(OH)_2$) with the remainder being organic matter (Chonjnacka, 2004). The organic matter mostly composed of protein and collagen disappears after carbonization (Lurtwitayapont and Srisatit, 2010). Hence, calcium and phosphate ions release from the biosorbent could result in secondary contamination beyond permissible limit. Calcium ion desorption occurred at the initial residence time till 120 mins for both chars (Figure 7). Wilson et al., (2003) reported ion exchange mechanism due to calcium release from natural charcoal in a study on heavy metal removal. This suggests ion exchange occurrence with heavy metals trade-in for calcium ion in biosorbents. The present result agrees with a number of studies on biosorption (Brum et al., 2010; Lurtwitayapont and Srisatit, 2010; Moreno-Pirajan et al., 2011). Subsequent trend shows that calcium ion sorption followed adsorption process (Figure 7). On the contrary, secondary contamination from phosphate ion in biosorbent was not noticed even with increasing retention period (Figure 8). This is an indication that phosphate ions were not required for ion exchange during the sorption process. Chonjnacka (2004) observed similar result in a study on bone ash adsorption of metal ions.

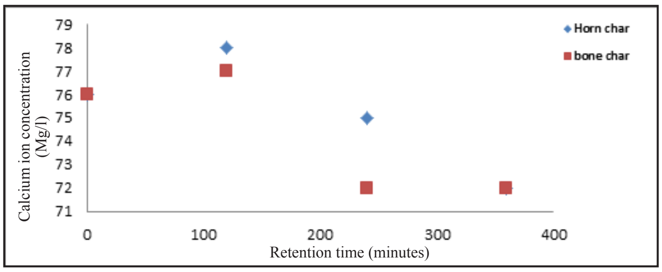

Figure 8 Calcium ion sorption

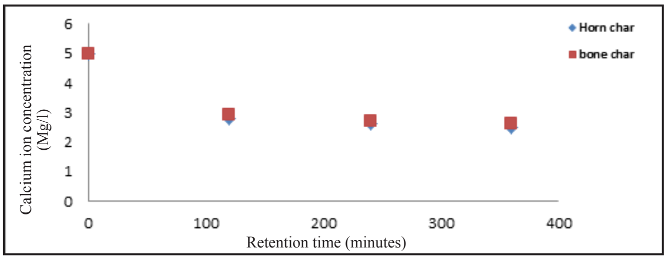

Figure 9 Phosphate ion sorption

Conclusion

Adsorption of heavy metals using cattle bone and horn is a good management practice for abattoir solid wastes. The packed bed column study shows that bone and horn char achieved 100 % cadmium ion removal at 120 mins retention time. There was evidence of ion exchange in heavy metals sorption. Biosorbents investigated in this study do not have secondary contamination effect on treated effluent. Freundlich and Langmuir isotherm fitted most of the metal adsorption process. Pyrolyzed bone and horn chars are suitable biosorbents for iron removal in mildly polluted surface water.

Picture of the project

Figure 10

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16

Reference

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