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Utilization of Abattoir Solid Wastes as Biosorbents for Surface Water Treatment.

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Abstract: *Man's need for proteinaceous foods have led to generation of abattoir solid waste at elevated quantity. This waste could be well managed using an environmentally friendly and cost effective waste management practice such as adsorption to mitigate its impact on man and his environment. This study considered the use of chars and modified chars from cattle bone and horn for treatment of polluted surface water. Cattle horn was carbonized at 350, 400 and 450 ^oC while bone was pyrolyzed at 450 ^oC. Equal portion of the chars was modified using aluminium and zinc chloride salts separately. Removal efficiencies of the six adsorbents were examined. The biosorbents morphology and composition was analysed by SEM-EDX machine. Best quality horn char was obtained at 400 ^oC with virtually no odour impact and minimum energy inputted. Removal percentage of adsorbate varied with contact time, surface water source and biosorbent involved. The highest removal efficiencies at 6 hrs contact time for As, Zn, NO_3, BOD, COD, coliform count, total aerobic and total fungal was 100%, 60%, 65.7%, 50.7%, 52.2%, 97.1%, 98.2% and 99.8% respectively. The study reveal the potential of abattoir non- biodegradable solid wastes as biosorbents for removal of contaminants in mildly polluted surface waters.*
Keywords: *Biosorbents, carbonized-char, pyrolysis, abattoir solid waste.*

I. Introduction

Solid waste generation in most developing nation is on the increase daily with the advent of industrialization and urbanization. Orheruata and Omoyakhi, (2008) noted the trend of population growth as it influence meat consumption, leading to more solid waste generation. De Hean (1996) projected the world's meat production by 2020 to be 310 million tonnes/year. This projection will of course lead to more solid waste generation. Presently, a lot of management practices are in place to combat solid wastes menace. They include incineration, composting, land filling, etc. Though, Raman and Narayanan (2008) considered land filling as the most common disposal method, this is only feasible in locations with sufficient lands for such activities. In urban centres or other densely populated areas where land is becoming luxury and competitive, such method may not be practicable. Other measures such as recycling of the waste will be a realistic and applicable alternative. The conversion of solid wastes to biosorbent was considered by some researchers as an alternative solution to agricultural solid wastes management. Solid wastes from Rambutan seed (Norlia *et. al.*, 2011), Corn cob (Tsai *et. al.*,1998), Marine red algae *Gracilaria* (Esmaeili *et. al.*, 2008), Coconut shell (Amuda and Ibrahim, 2006), Cattle-manure (Qian *et. al*., 2007), brewed tea waste (Dizadji *et. al*., 2011), Cattle bone (Zhu *et. al.*, 2011), etc. were recently used in the adsorption of heavy metals from water, aqueous solution and air with outstanding results obtained. Adsorption as described by Ansari and Mohammed-Khan (2009) is an effective physical method employed to remove dissolved organic and inorganic pollutant. This method can also be defined as the removal of contaminants from a medium (air/water) by binding or adsorbing it on the surface and within the pores of the adsorbent. Compared with most treatment methods, adsorption is less sophisticated, cheap, non-sludge producing, ecofriendly and time effective. Esmaeili *et. al.*, (2008) recommended the use of adsorption in surface water treatment due the adulteration of contaminants concentration in most surface waters. This study was aimed at managing some non-putrescible solid wastes generated from slaughter-house as biosorbents for surface water treatment.

II. Study Area Description

Ibadan is the largest city in West Africa. According to Filani, (1994) Ibadan is located on geographic grid reference longitude 3^o 5E, latitude 7^o 20N. A lot of domestic and industrial establishments are within the Metropolis. This includes the Bodija abattoir, a major slaughter-house in Ibadan, Oyo State. It is located within Bodija market in the Ibadan-North Local Government of South-Western Nigeria. Above 65% of total animal slaughtered in Oyo State are butchered in this abattoir (Abiola, 1995). Amidst the various water sources in Ibadan, industrially and domestically polluted surface waters were collected under stringent condition from Oluyole River and a stream flowing from Yemetu respectively; the River is located in Ibadan South-West Local

Government while the stream is located at Dandaru confluence, Ibadan-North Local Government in Ibadan, Oyo State, South - Western Nigeria.

III. Materials And Methods

Cattle slaughtered at Bodija abattoir are in the range of 200 – 450/day (Personal interview) with the generation of both non-biodegradable and putrescible wastes such as offal, bone, horn, hooves, blood, etc. Precursors from Cattle bones and horns were sourced from the abattoir. The precursors were weighed, soaked in tap water for 48 hrs, rinsed and oven dried at 150 ^{o}C for a period of 4 hrs. The dried samples were wrapped with double layer aluminium foil to ensure minimal oxygen during carbonization. The horn-bone was initially pyrolyzed at 350, 400 and 450 ^{o}C for 120 min to obtain the highest quality horn char, while the bone char was carbonized at 450 ^{o}C under similar conditions. Chars were weighed and granulated after carbonization. Portions of each char were impregnated separately using aluminium and zinc chloride salts with impregnation ratio of 2:1. Five hundred grammes of aluminium salt was dissolved in 1000 ml distilled water with 1 kg of granular bone char saturated in this solution. The solution was left for a period of 2 hours after which it was steadily stirred for 6 hours and then sieved. Zinc chloride modified bone char was produced by dissolving 500 g of zinc salt in 1000 ml distilled water. With the input of 1 kg granules of bone char, the solution was heated to a temperature of 80 ^{o}C and continuously stirred for 1 hour. The impregnation procedures were repeated for zinc and aluminum modified horn chars production. The modified and unmodified chars were generously washed with normal and hot distilled water and afterward oven dried at 120 ^{o}C for 12 hrs. The chars were further crushed into finer particles (≤ 850 microns) and stored. The simple biosorbents production chart underwent is as shown in Figure 1.

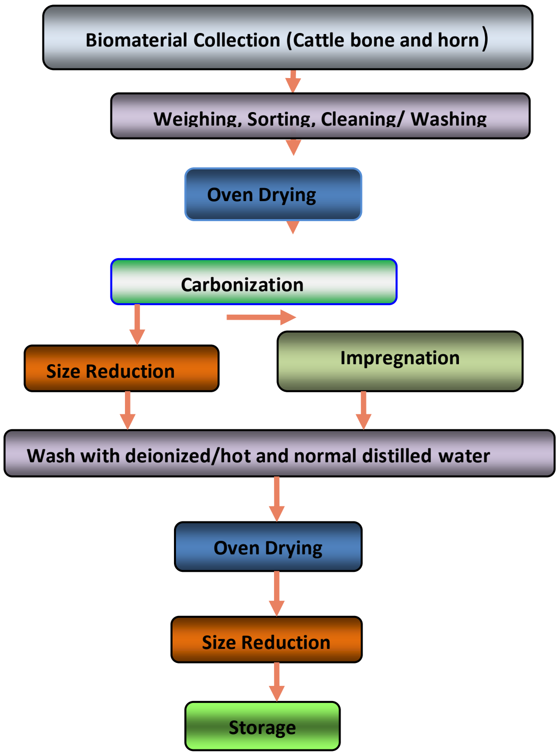

Fig.1: Biosorbents production Processes.

Elemental compositions and physical morphological structure of the adsorbents were examined using the SEM-EDX machine. Six adsorption columns with dimensions 12x12x62 cm underlaid with 30 g absorbent (cotton wool) were filled with 350 g of each biosorbents and then overlaid with 15 g of the absorbent. Flow rate of influent into the column was pre-set below 20 ml/min. Kumar *et. al., (*2007) suggested a flow rate within this range for efficient metal adsorption. Treated water samples were collected at regular intervals of time. The parameters of interest in the surface waters before and after treatment at 2, 4 and 6 hrs contact time were heavy metals, anions, cations, biological and bacteriological. Removal efficiency was calculated by the following equations:

$$Removal\ efficiency = (C_i - C_t)/C_i * 100 \qquad (1)$$

$$Adsorption\ capacity, Q_e = (C_i - C_t)V/W \qquad (2)$$

C_i (mg/l) is initial concentration of contaminant in water before treatment, C_t (mg/l) is contaminant concentration in treated water sample, Q_e (mg/g) adsorption capacity, V (l) is volume of water in adsorption column and W (g) represents adsorbent mass.

IV. Results And Discussions

Quantification of Solid Waste

The weight of cattle horn was in the range 1.32 to 1.37 kg/horned-cattle depending on cattle size. A matured cattle has about 65.4 – 168.2 kg weight of bone depending on its size. This is in line with Buvanendran *et. al.*,(1983) observation as documented by Ikhatua (2000). The bone produced at Bodija abattoir ranges between 13086 and 75690 kg/day. Following meat demand as projected by De Hean (1996) waste from abattoir will continually increase. Therefore, management of abattoir solid waste should be a subject of concern with appropriate measures put in place to reduce the waste menace on the environment.

Weight Variation

Carbonization achieved 57.4% and 55.7% weight loss in bone and horn respectively. This is in agreement with Lurtwitayapont and Srisatit (2010) observation.

Optimal horn carbonization temperature

The horn carbonized at 350 ^oC was blackish in colour with some odour, while at 400 and 450 ^oC the chars were grayish-black with no odour effect. However, more energy was used in producing horn char at 450 ^oC.

pH variation in biosorbents

Increase in pH by most of the adsorbents is a pointer to contaminants removal. Most pH values tend towards alkalinity after washing the biosorbents. Carbonized horn and bone pH values varied from 7.2 to 8.3 and 6.9 to 7.6 respectively after washing in distilled water (Table 1). Washing as observed by Teng and Yeh (1998) increases the surface area of carbon as the pore spaces are free of volatile matter. Ahmadpour and Do (1996) further noted that change in washed biosorbents pH is due to basic and water soluble materials removal. This process eventually increases adsorbents' treatability.

SEM and EDX results

Similar elements were observed in both horn and bone chars though they differ in quantity. The surfaces of all the biosorbents were irregular with rough texture except for the unmodified chars which were smooth with no obvious pores. Activation due to chars' modification altered the surface smoothness. Impregnation created noticeable pore structures and cavities within the aluminium modified bone char. This indicates enlarged surface area at 20µm and 500X magnification (Fig. 2). Demiral and Gündüzoğlu (2010) obtained similar result in the chemical activation of sugar beet bagasse, though with matured macrospores at greater magnification. The colour change in modified chars might be as a result of the activation salts as observed in the micrographs (Fig. 2). Characterization of the biosorbents using EDX shows the presence of alkaline earth metals and some microelements with undetected level of toxic elements (Fig. 3). These biosorbents are better than the ones prepared by Chojnacka and Michalak (2009); the latter released toxic elements, thereby resulting into secondary contamination of surface water.

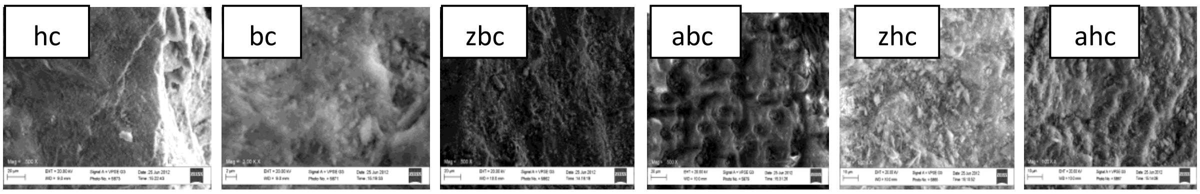

Figure 2: Electron micrograph of biosorbents: hc - horn char, bc - bone char, zbc - zinc modified bone char, abc - aluminium modified bone char, zhc - zinc modified horn char, ahc - aluminium modified horn char.

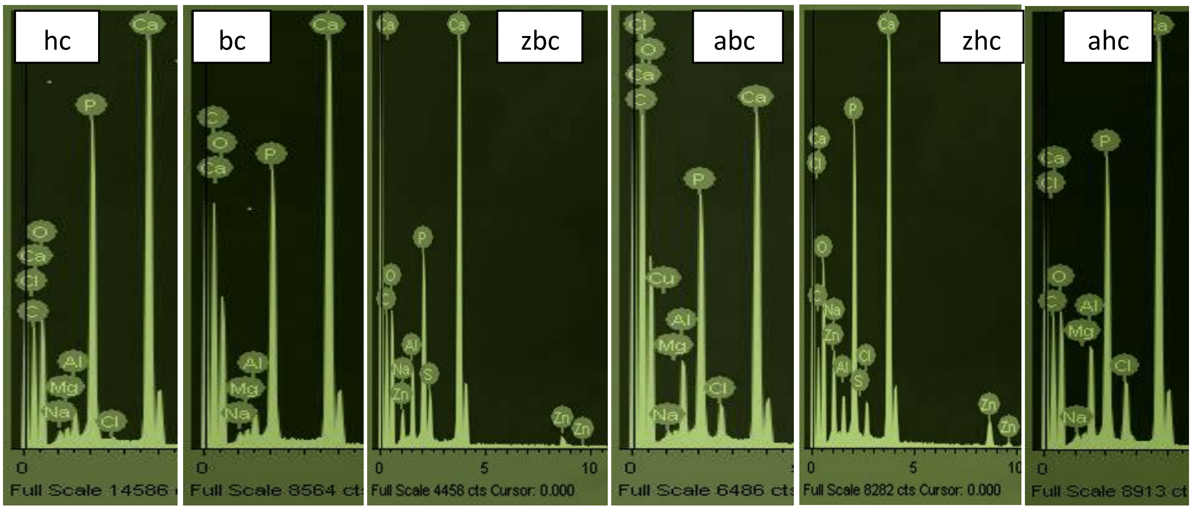

Figure 3: Biosorbents EDX spectrum

Removal Efficiency

The results obtained varied significantly in most cases with water source, contact time and biosorbents involved. Arsenic removal percentages from both water sources were more pronounced and effective with modified chars (Tables 2 - 4). In domestically polluted surface water, 100% Arsenic was removed by modified chars. This might be due to modification effect on the biosorbents. There was no significant difference in zinc removal from unmodified and aluminium modified chars. Activation did not alter the removal capacity of aluminium modified chars. Sixty percent zinc removal was noticed in both instances (Table 2 & 3). Removal percentages of copper, chloride, phosphate, nitrate and sulphate ion, BOD and COD were below 50 % (Tables 2 - 10). For most of the heavy metals, anions and cations removal efficiencies were highest at 6 hrs contact time, though the contact time seems insufficient as compared to that reported by Lurtwitayapont and Srisatit (2010) for maximum sorption of the contaminants. More removal could probably be achieved at higher contact time. Contaminant removal by similar salt modified char was not effective since the adsorbent sorption sites were saturated with the salt. Aluminium was not removed by its modified chars (Table 6). Similar trend was observed in zinc removal (Table 4). Microbial removal was the most efficient by all the adsorbents. Total fungal, coliform and total aerobic removal was over 92, 80 and 76% respectively at 2 hrs contact time. The removal efficiency increased to over 95, 90 and 91% after 6 hours contact time correspondingly (Tables 8 - 10). The amounts of microbial parameters sorbed on the surfaces of biosorbents were noteworthy, though most optimal sorption occurred at the initial contact time. This could be traced to availability of fresh active sites in the biosorbents. Coliform, total aerobic and total fungi sorbed on horn, bone, zinc modified horn, zinc modified bone, aluminium modified horn and aluminium modified bone chars at 2 hours contact time were 39, 37.3 and 40.4 g/g; 41.5, 39.0 and 39.5 g/g; 302, 280.3 and 339.4 g/g; 287.7, 325.3 and 307.3 g/g; 924.4 g, 907.7 and 972.3 g/g; 972.8, 971 and 971.7 g/g respectively.

Table 1: pH of biosorbents from cattle bone and horn

Chars	**Char washing with distilled water**	**Char washing with hot distilled water**
Bone	8.3	7.3
Horn	7.6	7.1
Zinc modified bone	7.2	7
Zinc modified horn	5.8	5.8
Aluminium modified bone	6.5	5.8
Aluminium modified horn	5.9	5.8

N.B. pH of bone and horn after carbonization was 6.9 and 7.2 respectively.

Table 2: Heavy metals removal efficiency for unmodified chars (%)

	Industrially polluted surface water						**Domestically polluted surface water**					
	Bone char			Horn char			Bone char			Horn char		
	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs
Ni	0	50	50	0	50	50	0	50	50	0	50	50
As	0	50	50	0	50	50	0	0	0	0	0	0
Cu	0	25	25	0	25	25	0	0	0	20	20	40
Zn	60	60	60	60	60	60	0	40	40	20	60	60

Table 3: Heavy metals removal efficiency for aluminium modified chars(%)

	Industrially polluted surface water						**Domestically polluted surface water**					
	Aluminum modified bone char			Aluminium modified horn char			Aluminium modified bone char			Aluminium modified horn char		
Contaminants	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs
Ni	0	0	0	50	50	50	0	50	50	50	50	50
As	50	50	100	100	100	100	50	100	100	100	100	100
Cu	25	25	25	0	0	20	0	0	25	0	20	20
Zn	60	60	60	40	40	60	60	60	60	40	60	60

Table 4: Heavy metals removal efficiency for zinc modified chars (%)

	Industrially polluted surface water						**Domestically polluted surface water**					
	Zinc modified horn char			Zinc modified bone char			Zinc modified horn char			Zinc modified bone char		
Contaminants	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs
Ni	0	50	50	0	50	50	50	50	50	50	50	50
As	50	50	50	50	50	100	100	100	100	100	100	100
Cu	25	25	50	25	25	25	0	20	20	0	20	40
Zn	0	0	0	0	0	0	0	0	0	0	0	0

Table 5: Anions and cations removal efficiency for unmodified chars (%)

	Industrially polluted surface water						**Domestically polluted surface water**					
	Bone char			Horn char			Bone char			Horn char		
Contaminants	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs
Cl	21.3	21.3	20.7	25.8	27.1	29	7.4	9.5	10.5	10.5	11.6	11.6
PO_4	39.3	43.5	45.6	25.9	42.6	53.7	41.1	45.6	47.7	33.3	44.4	50
SO_4	27.3	31.8	31.8	16	32	44	36.4	36.4	40.9	28	44	52
NO_3	12	16	24	24	36	40	17.1	28.6	40	48.6	60	62.9
Al	0	0	33	0	33	33	0	0	50	0	50	50

Table 6: Anions and cations removal efficiency for aluminium modified chars (%)

	Industrially polluted surface water						**Domestically polluted surface water**					
	Aluminum modified horn char			Aluminium modified bone char			Aluminium modified horn char			Aluminium modified bone char		
Contaminants	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs
Cl	0	0	0	0	0	0	0	0	0	0	0	0
PO_4	47.7	56.1	49.8	20.4	24.1	25.9	49.8	47.7	54	24.1	25.9	27.8
SO_4	36.4	40.9	45.5	16	16	20	40.9	40.9	45.5	16	20	20
NO_3	24	28	40	20	54.3	60	24	32	36	34.3	57.1	65.7
Al	0	0	0	0	0	0	0	0	0	0	0	0

Table 7: Anions and cations removal efficiency for zinc modified chars (%)

	Industrially polluted surface water						**Domestically polluted surface water**					
	Zinc modified horn char			Zinc modified bone char			Zinc modified horn char			Zinc modified bone char		
Contaminants	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs
Cl	0	0	0	0	0	0	0	0	0	0	0	0
PO_4	37.2	41.4	43.5	45.6	43.5	41.4	24.1	25.9	29.6	25.9	31.5	33.3
SO_4	40.9	45.5	45.5	45.5	50	50	12	24	28	20	28	40
NO_3	36	40	40	40	44	48	45.7	64.9	65.7	51.4	62.9	65.7
Al	0	33	33	33	33	33	0	0	50	0	0	50

Table 8: Microbiological parameters removal efficiency for unmodified chars (%)

	Industrially polluted surface water						**Domestically polluted surface water**					
	Bone char			Horn char			Bone char			Horn char		
Contaminants	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs
TAC	79.3	87.6	92.4	85.5	76.7	97.4	82.8	88.7	92	86.2	90.4	94.9
TFC	92.9	93.4	95.3	94.6	95.7	97.1	98.4	98.6	99.5	99.1	99.6	99.8
CC	86.6	91.6	94	90.5	92.5	95.5	80.7	86.5	91	82.3	89.4	96.8
BOD	34.3	28.7	25.3	40.5	45.9	49.8	31.5	30.9	25.8	41	46.3	50.7
COD	34.8	33.9	28.7	40.8	45.5	51.7	34.2	34.2	35.6	45.5	49.9	52.2

Table 9: Microbiological parameters removal efficiency for aluminium modified chars (%)

	Industrially polluted surface water						Domestically polluted surface water					
	Aluminum modified horn char			Aluminium modified bone char			Aluminium modified horn char			Aluminium modified bone char		
Contaminants	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs
TAC	92	89.1	98.1	85.8	91	91.5	86.9	87.6	97.8	87.4	94.3	94
TFC	99.4	99.5	99.5	88.5	91.4	96.5	99.5	99.5	99.5	89.4	93.7	97.9
CC	90.5	91.1	91.9	93.2	94.5	96.1	91.6	95.5	96.4	90	93.2	97.1
BOD	29.8	32.6	43.8	31.2	37.6	44.9	35.4	35.4	43.8	38.1	40.5	42.4
COD	34.5	36.5	43.7	30.2	35.9	45.5	39.7	38.2	44.8	38.8	40.8	43.9

Table 10: Microbiological parameters removal efficiency for zinc modified chars (%)

	Industrially polluted surface water						Domestically polluted surface water					
	Zinc modified horn char			Zinc modified bone char			Zinc modified horn char			Zinc modified bone char		
Contaminants	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs	2Hrs	4Hrs	6Hrs
TAC	96	96.4	97.2	96.4	97.5	98.1	96.3	98	98.2	93.3	97.7	98.2
TFC	99.5	99.5	99.6	99.6	99.5	99.7	98.2	98.9	99.5	98.7	99.3	99.6
CC	86.6	91.6	94	90.5	92.5	95.5	80.7	86.5	91	82.3	89.4	96.8
BOD	32.6	41	46.6	35.4	43.8	49.4	42.9	45.4	50.2	42.4	44.9	49.8
COD	36.2	42.2	48.3	37.4	45.4	49.7	46.5	46.5	49.6	41.1	46	51.2

V. Conclusion

Contaminant removal is influenced by surface water source, contact time and biosorbent types. Modification has significant impact on contaminant removal. Adsorbate removal efficiency was more effective at 6 hrs contact time, though efficiency might be increased at higher contact time. Cattle bone and horn from abattoir solid waste are good biosorbents for arsenic and microbial parameters removal.

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