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Evaluation of Activated Carbon from Fluted Pumpkin Stem Waste for Phenol and Chlorophenol Adsorption in a Fixed –Bed Micro-Column

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ABSTRACT: Fluted pumpkin stem waste, which is both a waste and pollutant, was chemically modified with ortho-phosphoric acid and used to adsorb phenol and chlorophenol in fixed bed micro column It was found that the carbon bed sorption capacity for phenol and chlorophenol (77.20 and 80.0 mg/g) were higher than the equilibrium sorption studies. The critical bed depth increased with increasing phenol and chlorophenol concentrations. An increase in phenol and chlorophenol concentration from 100 to 200mg/l increased the rate constant, critical bed depth (D_o) and bed sorption capacity, for phenol 77.20 to 160.00mg/g and chlorophenol 80.00 to 173.20mg/g. The breakthrough time, exhaustion time, uptake capacity decreased as the flow rate increased. Chlorophenol and phenol uptake capacity increased with increase in bed height. Experimental data for the change in concentration were correlated using the bed depth service time (BDST) model. In all parameters determined chlorophenol had better adsorption than phenol. Fluted pumpkin is the largest consumed vegetable in the West African sub region and therefore, creates one of the major agro waste problems in Nigeria. Preliminary investigations showed that several tons of these waste are produced daily in market places around the country but scarcely useful and therefore create environmental nuisance. The results obtained could be useful for the application of agricultural wastes for phenol and chlorophenol removal from industrial wastewater. @ JASEM

In the seventies of the last century, the combined global production of phenol and chlorophenols approached 200 million Kg (Atuanya and Chakrabarti, 2003), which has been manufactured in paper, textiles, pharmaceuticals and fertilizer industries. These compounds usually cannot be totally utilised and eventually will be discharged out from industrial processes. Hence a proper waste water treatment method or strategy is needed to tackle industrial effluents. Adsorption has gained increasing popularity in recent years as a unit operation for removing pollutants from effluents (Mall et al., 2006; Wang and Li, 2007), because the process produces a high quality treated effluent which can meet stringent environmental emission standards. In the search for potential low-cost sorbents for pollutant attenuation in aqueous medium, a number of materials have been investigated for their ability for pollutant attenuation. Some of these sorbets are; (cassava waste biomass, tea factory waste, fluted pumpkin stem waste and water spinach (Horsfall et al., 2003; Cay et al., 2004; Ekpete et al., 2010; Tarawou et al., 2010).

Although batch systems produce interesting information in the form of isotherms, adsorption columns, simulate commercial and industrial adsorbers and real world environmental solutions. The advantages of a fixed bed system include little operator attention, easy inspection and cleaning for regeneration of adsorbent, and fewer instances of adsorbent particles in the effluent. Disadvantages include the large physical area needed to operate the fixed bed and higher capital investment.

Fluted pumpkin (*Telfairia occidentalis HOOK F*) is a creeping vegetative shrub that spread low across the ground with large lobed leaves and long twisting tendrils. *T.occidentalis* is grown in some parts of West Africa for its nutritional uses (Horsfall and Spiff, 2005). Several workers have reported the nutritional composition of fluted pumpkin seeds (Fagbemi et al., 2005; Ganiyu, 2005; Agatemor, 2006; Fasuyi, 2008). A single stem with leaves weighing 1.2kg produces less than 200g of leaves, leaving over 1kg stem as waste. Fluted pumpkin is the largest consumed vegetable in the West African sub region and therefore creates one of the major agro waste problems in Nigeria. Preliminary investigations showed that several tons of these waste are produced daily in market places around the country but scarcely useful and there fore create environmental nuisance. Various researches have been conducted for adsorption of phenol and chlorophenol using other adsorbents over the past years. None have been reported on the adsorption of phenol and 2-chlorophenol using activated carbon derived from fluted pumpkin stem waste. The objective of the current investigation was to evaluate the sorption of phenol and chlorophenol on to the fluted activated carbon in a downward flow packed bed column arrangement. The effects of design parameters, such as bed height, initial phenol and chlorophenol concentration and flow rate have been investigated. The breakthrough profiles for the sorption of phenol and chlorophenol were analyzed using bed depth service time (BDST) model.

MATERIALS AND METHODS

The fluted pumpkin stem waste (*Telfairia occidentalis Hook F*) used for this study was obtained from Iwofe market Rumuolumeni Port Harcourt. The

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stems collected were washed thoroughly with water, cut into smaller bits rinsed with distilled water, air dried, and later oven dried at 105°C for 10h. The oven-dried fluted pumpkin was carbonized to obtain the carbonized biomass.

Carbonization: Carbonization was carried out in the Plant Physiology and Anatomy Laboratory of the University of Port Harcourt, using a muffle furnace (Carbolite Sheffield England LMF4) which allows limited supply of air. Carbonization was done at 350°C for two hours and allowed to cool at room temperature for three hours before activation.

Acid activation of the biomass: A carefully weighed 25.00 ± 0.01g carbonized fluted pumpkin was placed in a beaker containing 500cm^3 of 0.3M H_3PO_4. The content of the beaker was thoroughly mixed, heated until it formed a paste. The paste was put in a crucible and placed in a furnace which heated to 300°C for thirty minutes. The fluted activated carbon was washed free of acid to get a pH of 6.7 ± 0.12. This was allowed to cool, washed with distilled water, oven dried at 105°C to constant weight and ground. It was sieved with a 200µm mesh to obtain the activated carbon which was used for the column experiments. The treatment of the adsorbent with 0.3M H_3PO_4 solution aids the removal of any debris or soluble bio molecules that might interact with phenol and chlorophenol during sorption.

Column Sorption Studies: A glass column (20 x 1.4cm) was packed with the activated carbon on a glass wool support. The fixed bed column of activated carbon was prepared by a dry packing technique (Netpradit et al., 2004). In order to yield different bed heights 2.22, 3.45 and 5.0g of activated carbon was added to the glass column to produce bed heights of 3, 6 and 9 cm respectively. The bed was flushed several times with distilled water to ensure a close packing of the activated carbon particles to avoid cracks, channels or void during the transit of the waste water through the column. The bed was allowed to drain completely before the loading of the activated carbon bed with the sorbate. The phenol solution was fed through the bed in a downward flow made under gravity. The effluent from the activated carbon bed was collected at fixed volume (10ml) and the time of each collection noted. The loading of the carbon bed continued until the phenol and chlorophenol concentration in the effluent was 90% of the influent concentration which was regarded as the exhaustion point. Experiments were carried out at varying bed height (3, 6 and 9cm), concentration (100,150 and 200mg/l) and flow rate (2, 3 and 4ml/min) respectively.

Analysis of Column Data: The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and dynamic response of an adsorption column. The breakthrough behaviour shows the loading behaviour of phenol to be removed from solution at a fixed bed usually expressed in terms of adsorbed phenol concentration (C_{ad}) = inlet phenol and chlorophenol concentration (C_0) – outlet phenol and chlorophenol concentration (C_t) or normalized concentration defined as the ratio of effluent phenol concentration to inlet phenol concentration (C_t/C_o) as a function of time or volume of effluent for a given bed height (Aksu and Gonen, 2004). Effluent volume (V_{eff}) can be calculated from Eq (1)

$$V_{eff} = Qt_{total} \qquad (1)$$

Where t_{total} and Q are the total flow time (min) and volumetric flow rates (ml/min). The area under the breakthrough curve (A) obtained by integrating the adsorbed concentration (C_{ad}: mg/l) versus time t (min) plot can be used to find the total adsorbed phenol and chlorophenol quantity (maximum column capacity).Total adsorbed phenol and chlorophenol quantity (qtotal: mg) in the column for a given feed concentration and flow rate (Q) is calculated from Eq. (2):

$$q_{total} = \frac{QA}{1000} = \frac{Q}{1000}\int_{t=0}^{t_{total}} C_{ad}\,dt \qquad (2)$$

Total amount of phenol and chlorophenol sent to column (m_{total}) is calculated from Eq (3).

$$M_{total} = \frac{C_o\, Qt_{total}}{1000} \qquad (3)$$

Total removal is calculated from Eq (4).

$$\text{Total removal } (\%) = \frac{q_{total}}{M_{total}}\, x\ 100 \qquad (4)$$

Equilibrium phenol and chlorophenol uptake (q_{eq}) (or maximum capacity of the column) in the column is defined by Eq. (5) as the total amount of phenol and chlorophenol sorbed (q_{total}) per g of sorbent (X) at the end of total flow time (Malkoc and Nughoglu, 2006).

$$q_{eq} = \frac{q_{total}}{X} \qquad (5)$$

Successful design of a column sorption process required prediction of the concentration –time profile or breakthrough curve for the effluent (Cheng and Wang, 2000; Tarawou et al., 2010).Various mathematical models can be used to describe the fixed bed adsorption. Among these, The BDST model

(1920) is simple to use in the design of a fixed bed adsorption column and the BDST model is one of the most general and widely used method in column performance theory. Therefore, the breakthrough data obtained from the column studies was examined using the BDST model developed by Bohart and Adams (1920).

Bohart and Adams (1920) put the original basis for BDST and proposed that there is a relationship between the bed depth, D and service time t. This relationship was related to the process concentrations and adsorption parameters in a linearlised form (Hutchins, 1973), according to the following equation.

$$\ln\left(\frac{C_o}{C_t}-1\right)=\ln\left(e^{k_a N_0 D/Q}-1\right)-K_a C_o t \quad \ldots\ldots 6$$

Where C_t is the breakthrough phenol and chlorophenol concentration (mg/L), N_o the sorption capacity of bed height (mg/L), Q the solution flow rate (mL/min), and K_a is the rate constant (L/mg/min). D is bed height (m); t is the service time of a column (hr). C_o is initial concentration of sorbate at breakthrough value (mg/dm^3). Since the exponential term $e^{K_a N_0 D/Q}$ is usually much larger than unity, the unity term within the brackets in the right hand side of equation 1 is often neglected and therefore approximation is being made which leads to equation 7 (Ko et al., 1999)

$$t=\frac{N_o}{C_o}\frac{D}{Q}-\frac{1}{K_a C_o}\ln\left(\frac{C_o}{C_t}-1\right) \quad \ldots\ldots\ldots\ldots 7$$

Equation 7 enables the service time t, of an adsorption bed to be determined for a specified bed depth, D, of the adsorbent. The second term on the right hand side of the equation 7 represents the time required for the pollutants to establish its breakthrough curve; that is, it represents that part of the bed which is not saturated when the pollutant concentration in the solution leaving the bed is above the breakthrough value of C_t. The BDST model can predict service time versus bed depth according to the desired percentage breakthrough value and can measure the capacity of the bed at various percentage breakthrough values (Ko et al., 2000). The critical bed depth (D_o) is the theoretical depth of adsorbent sufficient to prevent the sorbate concentration from exceeding breakthrough concentration (C_t) at t =0. By letting t=0, D_o is obtained from equation 6 by solving for D.

$$D_0=\frac{Q}{K_a N_o}\ln\left(\frac{C_o}{C_t}-1\right) \quad \ldots\ldots\ldots 8$$

It is important to mention that the BDST model ignores the intra-particle mass transfer resistance and the external film resistance such that the adsorbate is adsorbed onto the adsorbent surface directly. This model also considered the adsorption capacity N_o to be constant throughout the bed when the adsorption zone was moving at constant speed along the column. It was stated that this model applied well for activated carbon processes and other adsorbents (Walker and Weatherley, 1997; Ko et al., 2000 and Tarawou et al., 2010).

Effect of Initial Concentration: Figures 1 shows the characteristic "S" shape exhibited by breakthrough curves. It was a plot of the dimensionless liquid phase concentration, C_t/C_o versus volume of liquid phenol and chlorophenol treated. It was evident from the curve that, by increasing the initial phenol and chlorophenol concentration, the slope of the breakthrough curve increased and became steeper, thus reducing the volume of phenol and chlorophenol solution treated before the breakthrough. Increasing the initial phenol concentration from 100 to 200mg/l resulted in a decrease in the volume of phenol and chlorophenol solutions treated from 1150 to 400ml and 1200 to 400 at the breakthrough point. Since a constant mass of adsorbent can only absorb a certain amount of phenol and chlorophenol, increasing the initial phenol and chlorophenol concentrations led to a decrease in the breakthrough time.

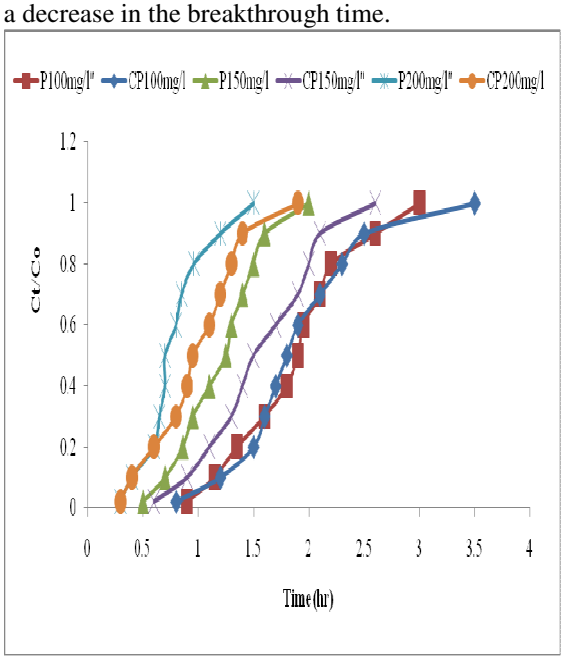

Fig 1 Effect of concentration on packed column for phenol and chlorophenol on FAC: bed height 6cm; Flow rate =2ml/min.P = Phenol, CP = Chlorophenol

Similar trends were observed by Walker and Weatherly, (1997); Kim et al., (2002); Kumar et al., (2006); Al-Degs et al., (2009); Tarawou et al.,

(2010).This may be due to the fact that, by increasing the initial phenol and chlorophenol concentration, the driving forces increased which enhanced the rate of phenol and chlorophenol diffusion within the adsorbent particles and saturated the binding sites more quickly. When the concentration of phenol and chlorophenol was increased from 100 to 200mg/l, the corresponding bed sorption capacity (q_e) increased from 6.60 to 12.52mg/g for phenol and 8.47 to 14.12mg/g for chlorophenol respectively. The total amount of phenol and chlorophenol sent to the column (M_{total}) increased from 22.80 to 43.20 for phenol and 28.80 to 48.00 for chlorophenol respectively. The total removal percentages of phenol and chlorophenol also increased with increasing concentration.

Table 1: Comparison of equilibrium sorption capacity with bed capacity in the sorption of phenol and chlorophenol

Adsorbate	Batch capacities mg/g			Column capacities mg/g
	Langmuir,	Elovich	Dubinin-Radushkevich	
P100	26.31	30.30	6.58	77.2
CP100	26.31	47.62	9.18	80.0

The sorption capacity of the fluted activated carbon obtained from the batch sorption studies of phenol and chlorophenol was compared with the fluted activated carbon bed sorption capacity (N_o) of the column studies. It was found that the carbon bed sorption capacity for phenol and chlorophenol (77.2 and 80.0 mg/g) were higher than the equilibrium sorption studies (Similar results have also been reported earlier (Gupta et al., 2000, Tarawou et al., 2010).This is due to the inherent difference in the nature of continuous and batch operations. A higher capacity of column operation is established by continuously increasing concentration gradient at the interface of the adsorption zone as it passes through the column while the concentration gradient decreases with time in batch adsorption. As seen from the experimental data, 2-chlorophenol is more adsorbed than phenol in all concentrations studied. This shows that solubility seems to play a very significant role in adsorption. A decrease in solubility and pKa is associated to an increase in adsorption capacity. The adsorption capacity for phenol and chlorophenol are a function of molecular weight and cross sectional area. Additionally, it seems that the adsorption capacity is directly proportional to the adsorbate hydrophobicity (Hamdaoui and Naffrechoux, 2007).

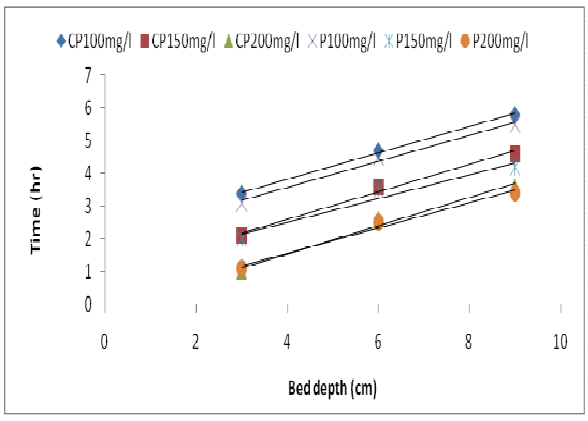

Fig 2: BDST plots at breakthrough concentration of 10% for the sorption of chlorophenol solution by FAC at different concentrations.

Table 2: Effect of concentration on BDST parameters and correlation coefficients for the sorption of phenol and chlorophenol on Fluted activated carbon

Concentration	100mg/l	150mg/l	200mg/l
Bed sorption capacity(N_o)(mg/g)			
Phenol	77.2	114.9	160.0
Chlorophenol	80.00	132.48	173.20
Rate constant (Ka) (Lmg-1hr-1)			
Phenol	0.013	0.017	0.333
Chlorophenol	0.019	0.029	0.109
Critical bed depth, (D_o) (cm)			
Phenol	2.234	2.593	2.786
Chlorophenol	1.379	1.781	2.210
R^2			
Phenol	0.999	0.999	0.990
Chlorophenol	0.997	0.986	0.982

The critical bed depth (D_o) shows an increase with increasing phenol and chlorophenol concentrations. These results correlate well with the observed performance in the breakthrough curves. An increase in chlorophenol concentration increased the rate constant (K_a) of phenol 0.013, 0.017, 0.333 and chlorophenol, 0.019, 0.029 and 0.109 $Lmg^{-1}hr^{-1}$ respectively. This is in line with the findings of (Walker and Weatherley, 1997; Malkoc and Nuhoglu, 2006). The K_a values were higher for phenol than chlorophenol. If K_a is large even a short bed will avoid breakthrough, but as K_a decreases a progressively longer bed is required to avoid breakthrough Walker and Weatherley, (1997). The column adsorption capacity (N_o) using the BDST model also increased with an increase in initial phenol concentrations as follows, 77.2, 114.9, 160.0mg/g and chlorophenol 80.00, 132.48 and 173.2mg/g respectively. The data shows higher bed sorption capacity for chlorophenol with very high correlation coefficient (R^2) ranging from 0.982 to 0.999 for phenol and chlorophenol indicating the validity of BDST model for the present system.

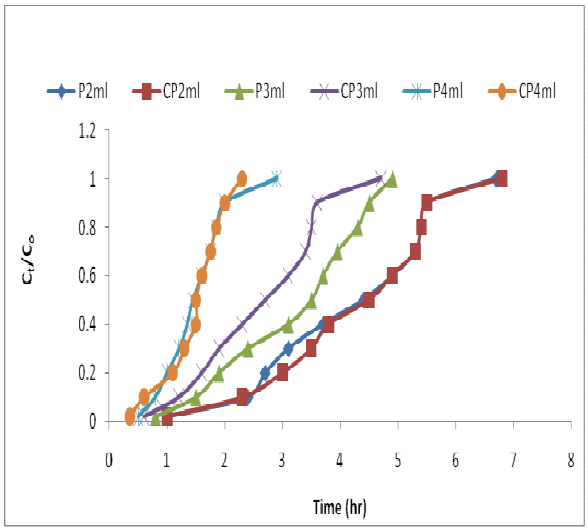

Fig 4: Effect of flow rate on packed bed column for phenol and chlorophenol on FAC: C_o 100mg/l bed height 6cm.

The effect of flow rate on phenol and chlorophenol sorption by FAC was studied by varying the flow rate from 2 to 4ml/min, while the bed height and initial nickel concentration were held constant at 6cm and 100mg/l, respectively. The plots of C_t/C_o versus time at different flow rates are shown in Fig 4, as the flow rate increased, the breakthrough curve becomes steeper. The breakthrough time, exhaustion time, uptake capacity decreased as the flow rate increased. The reason for this behaviour can be explained in the following ways: (1) when the flow rate increased, the residence time of the solute in the column decreased, which causes the chlorophenol and phenol solution in the column to decrease, this makes the chlorophenol and phenol solution to leave the column before equilibration occurs; (2) when the process is intraparticle mass transfer controlled, a slower flow rate favours the sorption and when the process is subjected to external mass transfer control; a higher flow rate decreases the film resistance (Ko et al., 2000).

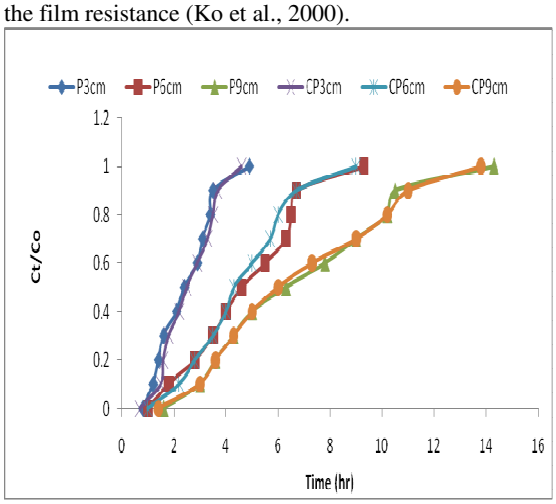

Fig 5: Effect of bed height on packed bed column for phenol and chlorophenol on FAC: C_o 100mg/l flow rate 2ml/min

Both bed capacity and exhaustion time increased with increasing bed height, as more binding sites available for sorption, also resulted in a broadened mass transfer zone as illustrated in figure 5. The increase in adsorption with that in bed depth was due to the increase in adsorbent doses in larger beds which provide greater service area and adsorption sites. The maximum bed capacities for different bed heights of 3, 6 and 9cm for phenol were 21.08, 27.82, 30.48mg/g for chlorophenol 22.16, 28.86, 32.88mg/g respectively. In addition, the chlorophenol uptake capacity of commercial activated carbon (FAC) increased with the increase in bed height due to availability of more binding sites for sorption as observed by Vijayaraghavan et al., (2004) and Tarawou et al., (2010). The chlorophenol and phenol removal percentage was significantly affected by bed height. When the bed height increased from 3 to 9cm, the percentage chlorophenol removal increased as follows 83.66, 89.20, 89.54 % and phenol removal percentage was 84.78, 86.02 and 88.81% respectively.

Conclusion: The study demonstrated that fluted activated carbon could be used for the removal of phenol and chlorophenol from aqueous solution. The increase in flow rate decreased the breakthrough time, exhaustion time and uptake capacity of chlorophenol and phenol, probably due to insufficient residence time of the chlorophenol and phenol in the column. The BDST model was suitable for describing the experimental data generated from the change in concentration in the present study with very high correlation coefficients values. The critical bed depth (D_o) and the column sorption capacity (N_o) were found to increase with an increase in initial phenol concentration. In all parameters determined chlorophenol had better adsorption than phenol.

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REFERENCES

Al-Degs, Y; Khraisheh, M; Allen, S; Ahmad, M 2008. Adsorption characteristics of reactive dyes in columns of activated carbon. Journal of Hazardous Materials, 16: 944-949.

Agatemor, C 2006. Studies of selected physiochemical properties of fluted pumpkin (*Telfairia occidentalis Hook F*) seed oil and tropical almond. (*Terminalia Catappia. L*) Seed Oil. Pak J Nutr 4: 306-307.

Aksu, Z; Gonen, F 2004. Bio sorption of phenol immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves. Process Biochem.39 599-613.

Atuanya, E; Chakrabarti, I 2003. Environ monit, Assess. 83: 283-294.

Bohart, G S; Adams, E O 1920. Some aspects of the behaviour of charcoal with respect to chlorine. J Am Chem Soc 43: 545- 523.

Cay, S; Uyanuk, A; Ozasik, A 2004. Single and binary component adsorption of copper (11) and cadmium (11) from aqueous solutions using tea industry. Waste Sep Purif Technol 38: 273-280.

Cheng, J; Wang, X 2000. Removing copper, zinc, and lead ion by granular activated carbon in pre-treated fixed bed columns. Sep Purif Technol 19: 157-167.

Cooney, D O 1999. Adsorption design for wastewater treatment, CRC Press, Boca Raton

Ekpete, O A; Horsfall M Jnr; Tarawou, T 2010. Potential of fluted and commercial activated carbon for phenol removal in aqueous solutions. ARPN Journal of Engineering and Applied Sciences. 5: 39 - 47.

Vijayaraghavan, K; Jegan, J; Palanivelu, K; Velan, M 2004. Removal of nickel (11) ions from aqueous solution using crab shell particles in a packed bed up-flow column. J Hazard Mater B113: 223-230.

Fagbemi, T; Oshodi, A; Ipinmoroti, K 2005. Processing effects on some anti- nutritional factors and in vitro multi enzyme protein digestibility of three tropical seeds. bread fruit *Atocarpusaltilis*), cashew nut (*Anacardium occidentale*) and fluted pumpkin (*Telfairia occidentalis*): Pak J Nutr 4: 205-256.

Fasuyi, O A 2008. Nutritional potentials of some tropical vegetables leaf meals, chemical characterization and functional properties. Afri J Biotech 5: 44-53.

Ganiyu, A O 2005. Hepatoprotective property of ethanolic and aqueous extracts of fluted pumpkin (*Telfairia occidentalis Hook. F*) leaves against garlic induced oxidative stress. J Med FD 8: 560-563.

Gupta, V K; Srivastava, S E; Renu, T 2000. Design parameters for the treatment of phenolics wastes by carbon columns (obtained from fertilizer waste material). Wat Res 34: 1543-1550.

Gonen, F; Aksu, Z 2003. A comparative adsorption/ bio sorption of phenol to granular activated carbon and immobilized activated sludge in a continuous packed bed reactor. Chemical Engineering Communications 190 (5-8): 763-778.

Hamdaoui, O; Naffrechoux, S 2007. Modelling of adsorption isotherms of phenol and chlorophenol unto granulated activated carbon. part 1, two parameter models and equations allowing determination of thermodynamic parameters. Journal of Hazardous Materials 147: 381-394.

Horsfall, M Jnr; Abia, A; Spiff, A I 2003. Removal of Cu $^{2+}$ and Zn^{2+} ions from wastewater by cassava (*Manihot esculenta Cranz*) waste biomass. African Journal of Biotechnology 2: 969-976.

Horsfall, M Jnr; Spiff, A I 2005. Equilibrium sorption study of Al^{3+}, Co^{2+} and Ag^{+} in aqueous solutions by fluted pumpkin (*Telfairia occidentalis Hook F*) waste biomass. Acta Chim Slov 52:174-181.

Hutchins, R A 1973.New method simplifies design of activated carbon systems. Chem Eng 80 : 133.

Ko, D C; Porter, F J; McKay, G 2000. Adsorption of metal ions on bone char. Chem Eng Sci 55: 819.

Malkoc, E; Nuhoglu, Y 2006. Removal of Ni (Ii) ions from aqueous solutions using waste of tea factory: Adsorption on a fixed bed-column. Journal of hazardous materials B135: 328-336.

Mall, I; Srivastava, V; Agarwal, N 2006. Dyes pigment 9: 210-223

Milhome, M; Keukeleire, D; Ribeiro, J; Nascimente,R; . Carvalho, T; Queiroz, D 2009. Removal of phenol and conventional pollutants from aqueous effluent by chitosan chitin. Quim Nova 32: 8-15

Netpradit, S; Thiravetyan, P; Towprayoon, S 2004. Evaluation of metal hydroxide sludge for reactive dye adsorption in a fixed –bed column system. Water Research 38: 71-78.

Sheng, P; Ying, Y; Chen, J; Hong, L 2005. Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms. J Colloid Interf Sci 275: 131-141.

Tarawou, T; Horsfall, M Jnr; Jose, V 2007. Adsorption of methyl red by water hyacinth (*Eichornia crassipes*) biomass. Chemistry & Biodiversity 4: 2236-2245.

Tarawou, T; Wankasi, D; Horsfall, M Jnr 2010. Sorption kinetic study on the removal of basic blue -9 dye using activated carbon produced from water spinach. Int J Bio Chem Sci **4**: 703-709.

Vijayaraghavan, K; Jegan, J; Panaivelu, K; Velan, M 2004. Removal of Ni (ii) ion on solution using crab shell particles in a packed bed up flow column. Journal of hazardous materials B113: 223-230.

Wang, S; Li, H 2007. Dyes pigment, 72: 308-314.

Walker, G M; Weatherley, L R 1997. Adsorption of acid dyes onto granular activated carbon in fixed beds. Wat Res 8: 2093-2101.