



STUDIES ON NAPHTHALENE ADSORPTION FROM CONTAMINATED WATER USING HYDROXYAPATITE PRODUCED FROM CATFISH BONES

*A. G Farombi, ¹O.S Amuda, ²M.M Raimi, and ¹A. O Olayiwola

*Department of Science Laboratory Technology, Osun State Polytechnic, Iree, Nigeria

1. Department of Pure and Applied Chemistry, LAUTECH, Ogbomoso, Nigeria

2. Department of Applied Science, Osun State Polytechnic, Iree, Nigeria

Corresponding Author's email: gladishbo@gmail.com

ABSTRACT

In this study, adsorption of Naphthalene from water was investigated using hydroxyapatite produced from catfish bones (CFHAP). Characterization of the produced CFHAP was done using Scanning Electron Microscopy (SEM), Fourier Transform Infrared spectroscopy (FTIR), Energy Dispersive X- ray Spectroscopy (EDX) and Brunauer Emmett and Teller (BET). Batch adsorption of naphthalene onto the produced CFHAP was carried out. The batch equilibrium adsorption data obtained for naphthalene was fitted to adsorption isotherm models (Langmuir and Freundlich) and kinetic models. The SEM image of CFHAP revealed no agglomerate with wider pores. The FTIR indicated the presence of OH- and PO₄³⁻ as major functional groups while the EDX revealed the presence of Ca, P, and O. The surface area, pore volume and pore radius of CFHAP produced were 359 m², 146 cm³ and 293 nm for the CFHAP. Batch adsorption studies indicated naphthalene maximum removal of 92% at 70 minutes and the maximum uptake of 93 % at 2 g dosage of CFHAP. The maximum percentage removal of naphthalene was 95.8% at initial concentration of 75mg/L while the maximum removal efficiency of 83% was obtained at pH of 10. Langmuir isotherm model ($R^2 = 0.993$) best correlated the equilibrium adsorption data of naphthalene. Pseudo second order model gave the best fit with the highest correlation coefficient ($R^2= 0.9850$) for naphthalene onto CFHAP. Conclusively, catfish bones were found to be a good raw material for production of catfish bone hydroxyapatite which had good adsorption potential and the produced hydroxyapatite can be used effectively to remove Naphthalene in contaminated water.

Keywords: Naphthalene, Catfish bone hydroxyapatite (CFHAP), Adsorption.

INTRODUCTION

The fate of polycyclic aromatic hydrocarbon (PAHs) in environment is of great concern to researchers due to their toxic, mutagenic carcinogenic and teratogenic properties (Larsson *et al.*, 1983; Seyed *et al.*, 2012; Das and Das, 2015). PAHs are formed mainly through pyrolytic processes which mainly involve incomplete combustion of organic materials during industrial and other human activities, such as coal and crude oil processing, natural

gas combustion, combustion of refuse, cooking and tobacco smoking and other carbonaceous materials (WHO, 1998).

A large number of methods or techniques for removing PAHs in contaminated water have been developed over the years. However, most of these methods have limitations in practice such as high cost, formation of hazardous by-products or intensive energy requirements (Yazdanbakhsh *et al.*, 2011; Tarabi *et al.*, 2012, Amuda *et al.*, 2015). Hence, there is necessity

for efficient inexpensive and environmentally friendly technologies of which adsorption process is one. Adsorption is a process in which a solid surface (adsorbent) is used to remove a soluble component (adsorbate) in a fluid (Amuda *et al.*, 2014).

However, most adsorbents suffer some demerit such as low adsorption capacity, high cost and separation inconveniences (Juan *et al.*, 2010). Owing to this, there is growing interest toward the use of agricultural wastes as adsorbent. Some agricultural waste including animal bones, teeth, shells e.t.c are good sources of adsorbent known as Hydroxyapatite (Anjuran, 2012; Ghorban *et al.*, 2012). Hydroxyapatite belongs to the apatite family. Apatite is the name given to a group of crystals of the general chemical formula $M_{10}(XO_4)_6Y_2$. Where $M = Ca^{2+}, Sr^{2+}, Ba^{2+}, Na^+, Pb^{2+}, La^{3+}$ and many rare earth elements; $XO_4 = PO_4^{3-}, VO_4^{3-}, SiO_4^{4-}, CO_3^{2-}$; $Y = OH^-, Cl^-, F^-, CO_3^{2-}$ and other various anions (Nounnah *et al.*, 1992, Dan *et al.*, 2011).

Hydroxyapatite is a calcium-phosphate compound type of apatite with the chemical formula $Ca_{10}(PO_4)_6OH_2$. It is one of the inorganic components of the hard tissues of living bodies such as bone, teeth, etc. (Elouear *et al.*, 2009; Fernare and Adjiane-Zafour, 2013). Hydroxyapatite is an ideal material for long term containment of contaminants because of its high sorption capacity, low water solubility, high stability under reducing and oxidizing conditions and availability. Hence, it is considered as an excellent adsorption material (Czemiczyniec *et al.*, 2007; Mohammed and Aazam, 2013). Comparing catfish bones to others, it contains higher Calcium-phosphate compound which is the major hydroxyapatite content.

This study focuses on the preparation of hydroxyapatite from catfish bones and its suitability and efficiency as an adsorbent for naphthalene removal in contaminated water.

MATERIALS AND METHODS

The agricultural waste material used in this research work for the production of the adsorbent was catfish bones. The catfish bones

(head and back bones) were obtained freshly from Favour Farm along ring road, Osogbo. Osun State, Nigeria. The material was transported to Chemistry Laboratory, LAUTECH Ogbomosho and kept at 4 °C in the refrigerator prior to the time of use.

Preparation of Adsorbent

Catfish bones stored in the refrigerator were allowed to return to room temperature, then boiled in distilled water for 2 hours and washed in flowing stream of water to remove bulk flesh and fat materials. The remaining bones were then soaked in 30% hydrogen peroxide for a day to remove all residual organic matter after which it was rinsed with distilled water, air-dried for 48 h and then crushed into smaller pieces. These crushed bones were then heated in an oven at 105°C for 3 h and kept in desiccator to prevent adsorption of moisture from the atmosphere (Shyamsunder, 2009).

The crushed catfish bones of 10 g inside crucible was charged into the furnace and heated at the temperature of 300°C and time 1 h. The calcined catfish bone was collected and allowed to cool. Almost all the carbon compounds were given off during the heating. After the calcination, the resultant product formed is a natural hydroxyapatite which is termed catfish bones hydroxyapatite (CFHAP) (Shyamsunder, 2009).

Characterization study of hydroxyapatite (HAP) Produced from Catfish Bone

The hydroxyapatite produced at the temperature of 300°C and time 1 h was characterized using Scanning Electron Microscopy (SEM) (JEOL-JSM – 63335F, TUBITAK, MAM) USA, Brunauer- Emmett- Teller (BET)) surface area analyzer (QUARDROSORB, SI), Energy dispersive X-ray spectroscopy (EDX), Fourier Transform Infrared Spectroscopy (FTIR) (Perkin-Emer Spectrum-100).

Preparation of Adsorbate

Adsorbate was prepared by weighing 1 g of naphthalene and dissolving it in 300 cm³ of acetone in 1000 cm³ standard flask. The mixture was carefully swirled together for 10 min to

allow thorough dissolution of the adsorbate. This was then made up to 1000cm³ mark with distilled water (Crisafully *et al.*, 2008). This makes the stock solutions (1000 mg/L). Different concentrations (50 - 200mg/L) were prepared by serial dilution from the prepared stock Solution.

Adsorption Studies

Batch adsorption study was conducted by weighing (0.5 – 3.0g) of the CFHAP into sample bottle and 100 mL of various concentrations (50 – 200mg/L) of naphthalene maintained at pH (3, 4, 5, 6, 7, 8, 9, 10 and 11) were pour into different sample bottle. The mixture in each of the bottle was covered and placed inside the shaker and agitated for 120rpm at ambient temperature (28⁰C) in water bath shaker (Uniscope SM 101) at different time (30 -150 min). The supernatant solution was allowed to settle and the filtrate was decanted into sample bottles and the absorbance of the solution was measured. Naphthalene concentration was estimated spectrophotometrically, at the wavelength corresponding to maximum absorbance using a spectrophotometer. Then the naphthalene concentration was measured. The q_e is expressed as equation 1:

$$q_e = \left(\frac{C_o - C_e}{M} \right) V \tag{1}$$

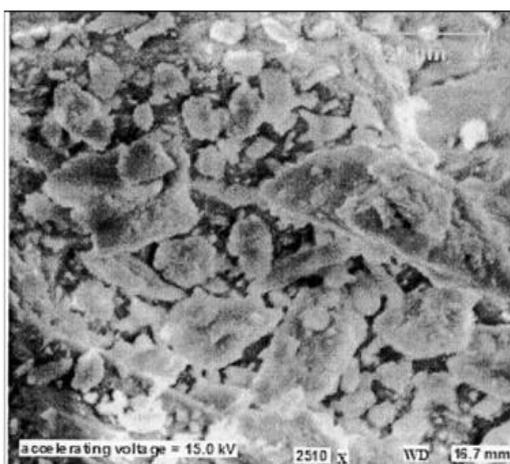


Figure 1: SEM image of catfish bones before calcination

Where q_e = amount of naphthalene adsorbed per unit mass of adsorbent (mg/L), C_o = initial naphthalene concentration (mg/L), C_e = final naphthalene concentration (mg/L), V = volume of naphthalene solution and M = mass of the adsorbent (g).

Removal Efficiency RE(%):

The removal efficiency of CFHAP was calculated according to equation 2. (Amuda *et al.*, 2015).

$$RE(\%) = \left(\frac{C_o - C_e}{C_o} \right) \times 100 \tag{2}$$

RESULTS AND DISCUSSION

Characterization of the produced CFHAP

Characterization of CFHAP was done to investigate the proof of formation of hydroxyapatite and the results obtained are reported below:

The micrograph and the microstructure of catfish bones and CFHAP produced are shown in Figure 1 and 2 respectively. Figure 1 revealed spaced out holes on the surface of the sample. This is in agreement with the observation of Barka *et al.*, (2008), Fernare and Adjiane-Zafour, (2013). In figure 2, present of more open porous structures in the powder was confirm. The microstructure as revealed by the SEM is in well agreement with BET surface area analysis result.

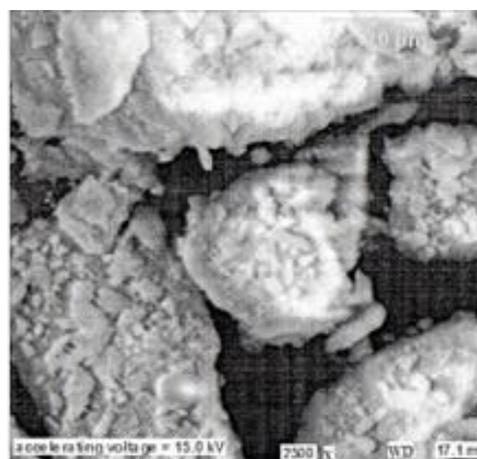


Figure 2: SEM image of CFHAP

Result of surface area analysis by BET analyzer

The specific surface area, pore volume, pore radius of the catfish bone and CFHAP were determined by BET analyzer. The results were obtained using BET plots as shown in Figure 3 and 4. The BET machine did the plotted of the graph and at the same time the values of the total specific surface area, pore volume and pore sizes

were recorded from the machine. From the Table, calcination has influenced the physical properties of the catfish bones. The total specific surface areas increased from $190\text{m}^2/\text{g}$ to $359\text{m}^2/\text{g}$. The total pore volume increased from $119\text{cm}^3/\text{g}$ to $146\text{cm}^3/\text{g}$ and the pore sizes was enlarged from 210nm to 293nm .

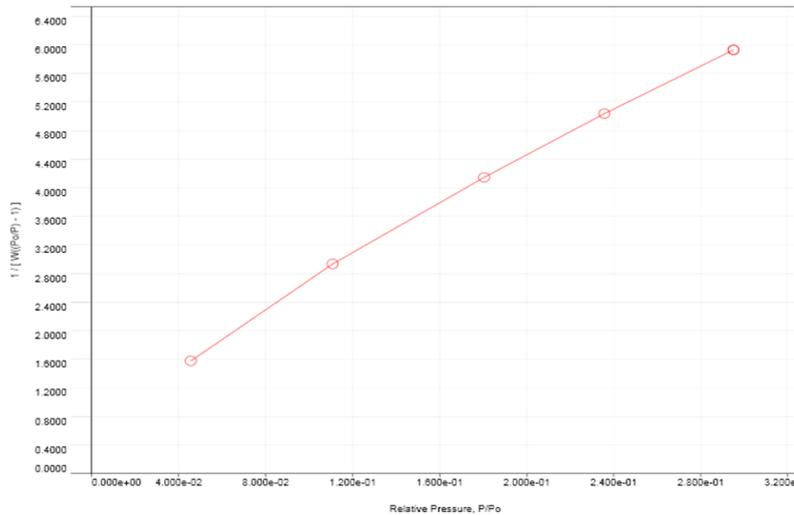


Figure 3: BET plot of the surface area of catfish bones before calcination

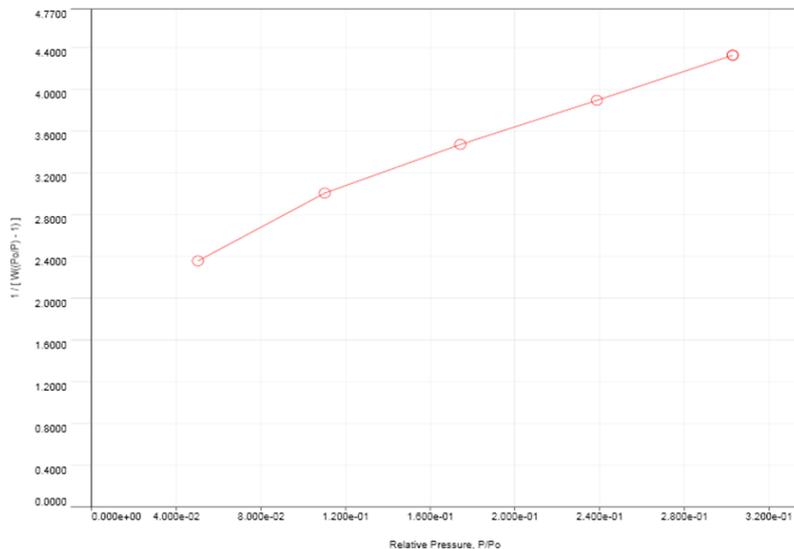


Figure 4: BET plot of the surface area of CFHAP

FTIR characterization results

The FTIR indicated the major functional groups present in the CFHAP produced sample and the raw catfish bones. Figure 5

and 6 show the spectra of raw catfish bones and CFHAP. The main functional groups present in the raw catfish bones were

revealed by spectrum in Figure 5. The sharp vibration observed at 3431.36cm^{-1} indicated the presence of O-H groups, this might be due to the moisture trapped during the process of charging into the FTIR machine (Saeid *et al.*, 2013). The 2941.44cm^{-1} bending vibration found depicts the presence of hydrocarbon (C – H) group. The medium and sharp peak of a phosphorus function in the form of hydrogen bonding to phosphorous (phosphine) was adsorbed at a wavelength of 2353.16cm^{-1} . Similarly, the sharp peak obtained at 1649.143cm^{-1} was attributed to alkene (C=C) and (C=O). The

vibration at 1037.70cm^{-1} is due to presence PO_4^{3-} (Brain-smith, 1998).

The FTIR of the calcined catfish bones at $300^\circ\text{C}/1\text{h}$ (CFHAP) is shown in Figure 6. Some of the bonds that shifted include -OH at 3431.36cm^{-1} which shifted to 3437.15cm^{-1} . The medium and sharp peak of P-H shifted from 2353.16cm^{-1} to 2358.92cm^{-1} and 1649.14cm^{-1} (C-H) peak shifted to 1633.71cm^{-1} in the catfish bones after calcinations (CFHAP). The peak at 2941.44cm^{-1} (C-H) group disappeared. The H_2O revealed at 3776.62 might be due to the moisture trapped.

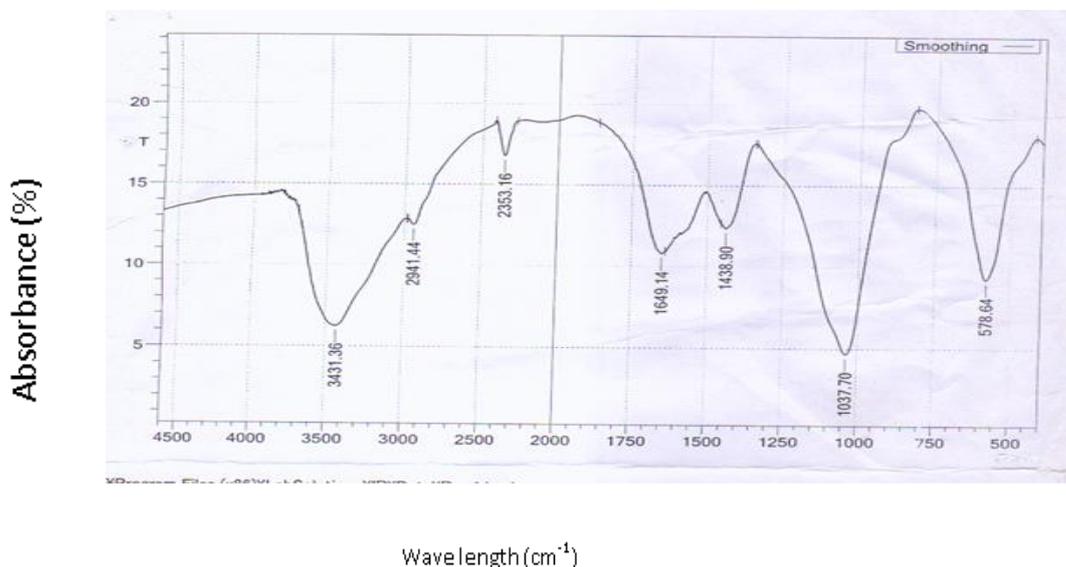


Figure 5: FTIR spectra of catfish bones before calcination

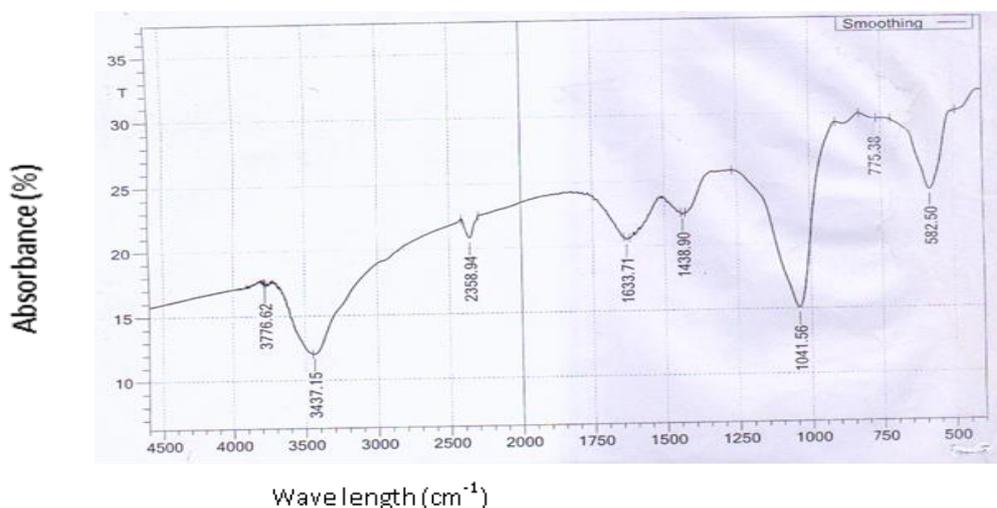


Figure 6: FTIR spectra of catfish bones after calcinations (CFHAP)

Table 1: Peaks Found in the FTIR Spectra of Raw Catfish Bone Optimized CFHAP Samples

Before calcinations		After calcinations	
Wavelength (cm ⁻¹)	Vibration	Wavelength (cm ⁻¹)	Vibration
3431.36	O-H	3776.62	
2941.44	C-H	3437.15	-OH
2353.16	P-H	2358.94	P-H
1649.14	C=O, C=C	1633.71	C=C,C=O
1438.90	S=O	1438.90	S=O
1037.70	PO ₄ ³⁻	1041.56	PO ₄ ³⁻
		582.50	PO ₄ ³⁻

Quantitative analysis of catfish bones and CFHAP by Energy Dispersion Spectroscopy (EDX)

EDX spectra of catfish bones before calcination after calcination (CFHAP) were shown in figure 7 and 8. The EDX revealed calcium, phosphorus and oxygen as the major elements that are present in the samples with (Ca) 38%; 40%, (P)

42%; 40%, (O) 16%; 14% for the raw and calcined catfish bone (CFHAP) respectively. Other elements which are present in trace quantities are zinc, magnesium and barium, they were indicated on the record as shown in Table 3. The introduction of Zn after might be from the apparatus used during the calcination.

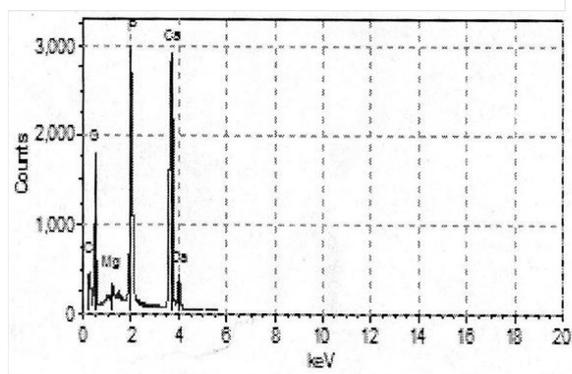


Figure 7: EDX spectra of catfish bones before calcination

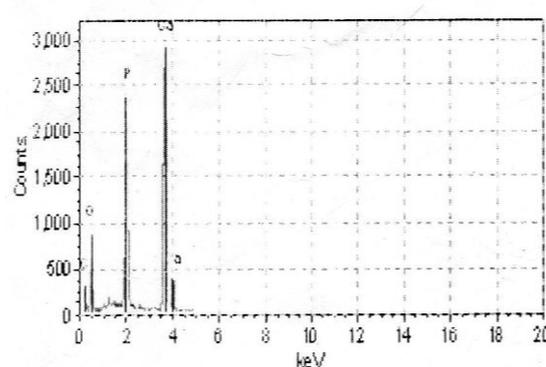


Figure 8: EDX spectra of catfish bone after calcination (CFHAP)

Table 2: Elemental Composition of Catfish bones Before and After Calcination

Sample	Elemental composition (%)					
	Ca	O	P	Zn	Mg	Ba
Catfish bones before Calcination	38	16	42	0.0	2.5	1.0
Catfish bones after Calcination (CFHAP)	40.8	14	40	1.2	2.0	1.7

Adsorption Studies

Effect of solution pH on naphthalene adsorption onto CFHAP

Solution pH is one of the main factors which affect the sorption capacity of a sorbent (Pankay and Sanjee, 2012). The influence of initial naphthalene solution pH (3-11) on the equilibrium uptake capacity was studied at different initial pH at room temperature. The relationship between the initial pH values and the quantities of PAHs adsorbed onto CFHAP was presented in Figure 9 which showed that the naphthalene adsorbed increases as pH increases to 10. It was noticed that at the pH 10, the percentage removal was maximum and the maximum percentage removal efficiency was 83%.

Effects of contact time on naphthalene adsorption onto CFHAP

The effect of contact time on naphthalene adsorption onto CFHAP is shown in Figure 10. Adsorption of 50mg/L of naphthalene onto CFHAP was studied at different contact time interval ranging from 30 to 150 min. From the Figure 9, it was observed initially that the uptake increases with increase in contact time and reaches the contact equilibrium at 70 min and the maximum removal of 92% was attained. From the result, the adsorption takes place rapidly at the initial stage on the external surface of the adsorbent followed by a slower internal diffusion process. This result agreed with the study of Biodegradation of phenanthrene in river sediment by Yuan *et al.*, 2010 study. This may be due to the fact that a large number of surface sites are available for adsorption but owing to the accumulation of naphthalene particles in the vacant sites after a lapse of time, the adsorption rate at later stages decreases because the remaining surface sites are difficult to be occupied, thus make it take long time to reach equilibrium (Mohanmadine-El- Haddad, 2012).

Effect of adsorbent amount (dosage) on the adsorption of naphthalene onto CFHAP

As shown in figure 11, the amount of adsorbed increase rapidly as the initial dosage of the

CFHAP increased from 0.5 to 1.5g. The maximum removal efficiency of 93% was attained at the adsorbent dosage of 2g. Further increase in the CFHAP did not have effect on the adsorption of the naphthalene unto the CFHAP. The insignificant increase in the uptake of naphthalene at CFHAP dosage higher than the maximum percentage removal efficiency could be attributed to the presence of excess pore size for adsorption on the CFHAP than the available naphthalene present in solution at the fixed concentration of 50mg/L. These observations are in agreement with other reports in literature for the sorption of contaminant by different biological materials (Yuan *et al.*, 2010; Bello *et al.*, 2011).

Effect of initial concentration on the adsorption of naphthalene onto CFHAP

The effect of initial concentration on the naphthalene adsorption onto CFHAP is shown in Figure 12. Adsorption capacity was investigated in the range (50 - 200 mg/L) at room temperature without changing the initial pH of the medium which was determined by using pH meter. At 75mg/L the maximum percentage removal of 95.8% for naphthalene was obtained after which percentage removal efficiency decreases with further increase in concentration of the adsorbate to 200 mg/L. The lower uptake at higher concentration resulted from an increased ratio of adsorption number of moles of the naphthalene to the available surface area.

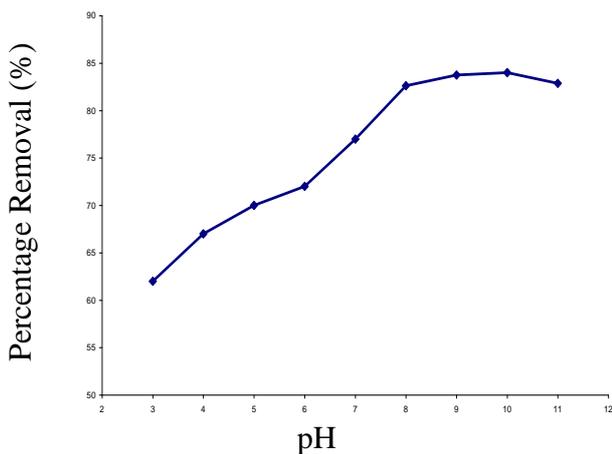


Figure 9: Effect of pH on the removal of naphthalene using CFHAP

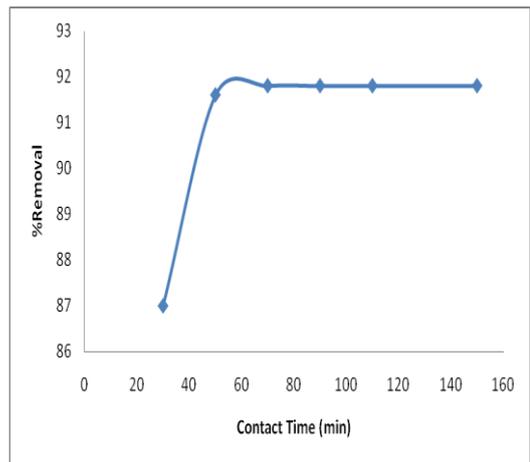


Figure 10: Effect of contact time on the percentage removal of naphthalene using CFHAP

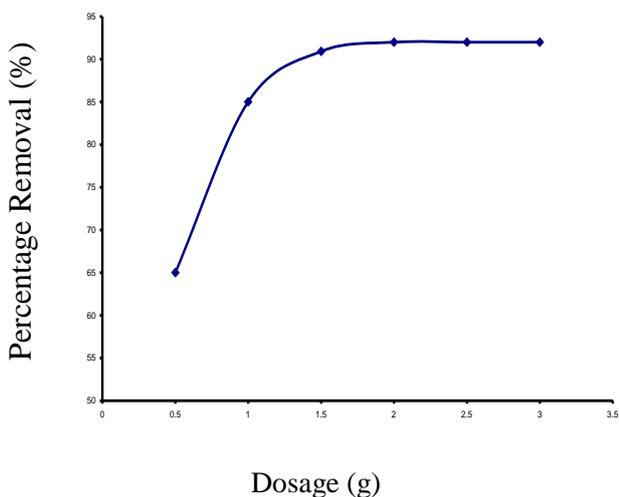


Figure 11: Effect of dosage on the percentage removal of Naphthalene using CFHAP

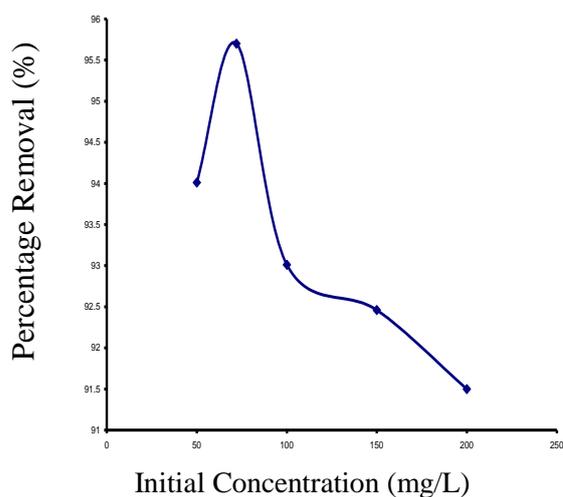


Figure 12: Effect of initial concentration on the percentage removal of naphthalene using CFHAP

Adsorption Isotherm Studies

The obtained data from the adsorption study was used to evaluate isotherm models, which includes Langmuir and Freundlich.

Langmuir isotherm

The values of the Langmuir isotherm parameters as well as the correlation coefficient (R^2) of the Langmuir equation for the adsorption of naphthalene by CFHAP are given in Table 4. The parameters of the Langmuir isotherm equation were obtained by fitting the equation directly to the

equilibrium data using the non-linear curve fitting. Figure 13 shows the plots of $\frac{C_e}{q_e}$ against

C_e using linear method and this was used to determine the Langmuir isotherm parameters for naphthalene adsorption onto catfish bone hydroxyapatite (CFHAP). The parameters of the Langmuir isotherm equation were obtained by fitting the equation directly to the equilibrium data using the linear curve plots. The plot obtained for the isotherm is shown in Figure 13 for the adsorption of naphthalene by CFHAP. The values of correlation coefficient (R^2) 0.993

gotten was close to 0.9700 reported for Oyster shell by Alidoust *et al.*, (2015). The values of the Langmuir isotherm parameters as well as the correlation coefficient (R^2) of the Langmuir equation for the adsorption data of naphthalene by CFHAP are given in Table 4. The value of the separation factor determines the nature of adsorption as follows: $R_L > 1$ unfavorable, $R_L = 1$ linear, $0 < R_L < 1$ favorable and $R_L = 0$ irreversible. For this study, the values of R_L given in Table

4.10 are between 0 and 1 indicating that the adsorption was favorable (Amuda *et al.*, 2014). The high value correlation coefficient (R^2) of 0.993 is an indication particularly for the Langmuir isotherm model that this adsorbent exhibit a monolayer reaction with constant activation energy (Cheung 2009; Han *et al.*, 2009) this showed that the Langmuir model is good for describing the adsorption process of naphthalene.

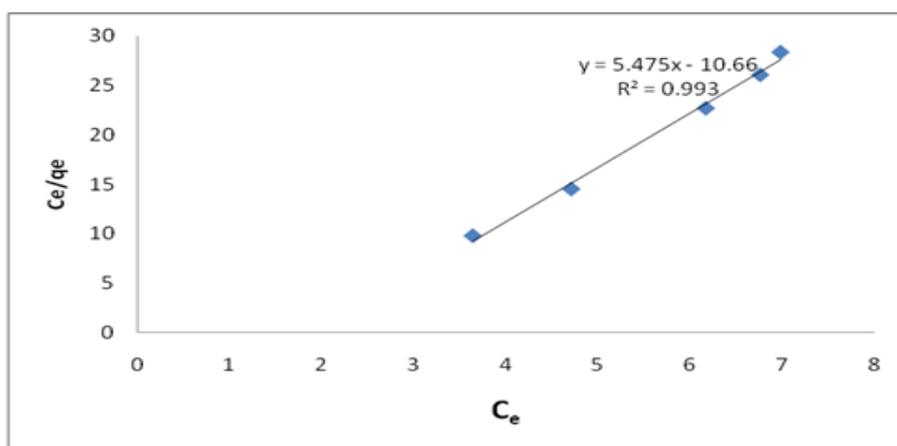


Figure 13: Langmuir isotherm for adsorption of naphthalene

Table 4: Constants and Correlation Coefficients of Langmuir Isotherm Models for Adsorption of Naphthalene onto the CFHAP.

Isotherm Parameters	Values
	Naphthalene
K_L (L/mg)	0.432
Q_m (mg/g)	19.87
R^2	0.993
R_L	0.231

Freundlich isotherm

The Freundlich equation model in non-linear and linear form can be expressed as:

$$q_e = \ln k_F + \frac{1}{n} \ln C_e \tag{3}$$

Where, K_F is the Freundlich characteristics constants and $\frac{1}{n}$ the heterogeneity factor of adsorption obtain from slope of $\ln(q_e)$ vs $\ln(C_e)$.

The value of K_F is an indicator of adsorption capacity and thus can be used for relative measurement of the surface area and $\frac{1}{n}$ are related to enthalpy and intensity of the adsorption. $\frac{1}{n}$ value should be less than unity for high adsorption capacity. Figure 14 shows the plot of $\ln q_e$ versus $\ln C_e$ used for evaluating the Freundlich isotherm parameter for naphthalene adsorption onto CFHAP. Freundlich isotherm parameters

obtained for the adsorption of naphthalene with the CFHAP are shown in Table 5. The Freundlich exponential ‘n’ for the adsorption of naphthalene onto CFHAP was 0.456. This value which never satisfy the condition $1 < n < 10$, this

indicated that the Freundlich isotherm unfavourable. The corresponding large value of correlation coefficient (R^2) 0.9245 shows that Freundlich isotherm can be used to describe the adsorption of naphthalene onto CFHAP.

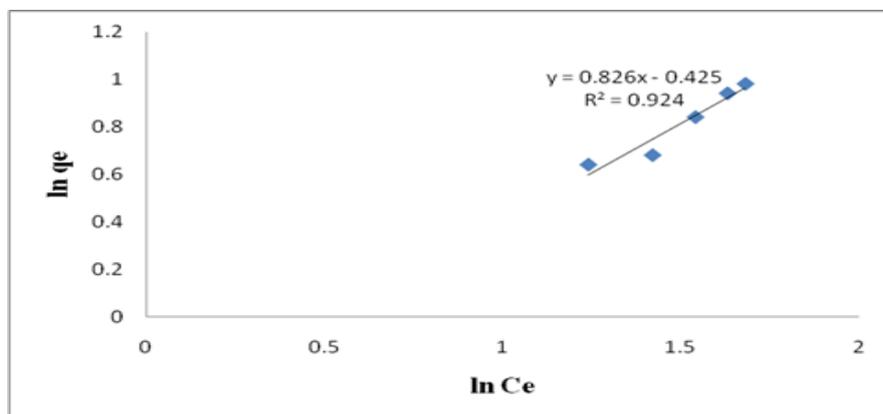


Figure 14: Freundlich isotherm for adsorption of naphthalene

Table 5: Constants and Correlation Coefficients of Freundlich Isotherm Models for Adsorption of Naphthalene onto the CFHAP.

Isotherm Parameters	Values
1/n	0.456
(L/mg)K _F	3.460
R ²	0.924

Kinetics Studies

Pseudo-first order model

The Lagergren pseudo first order kinetic model has been widely used to describe the kinetics of heterogeneous treatment processes. It is expressed in its integrated linear form as in equation below (Malik, 2004).

$$\ln(q_e - q_t) = q_e - K_1 t \tag{4}$$

Where q_e and q_t (mg/g) are adsorption capacities at equilibrium and at time t respectively. K_1 is the rate constant of pseudo first order adsorption (min^{-1}). The values of $\ln(q_e - q_t)$ were linearly correlated, t is rate constant of adsorption. The plot of $\ln(q_e - q_t)$ versus t resulted in a linear relationship from

which K_1 and q_e were determined from the slope and intercept.

As shown in Figure 15, the first order rate constants calculated from the plot are given in Table 6.

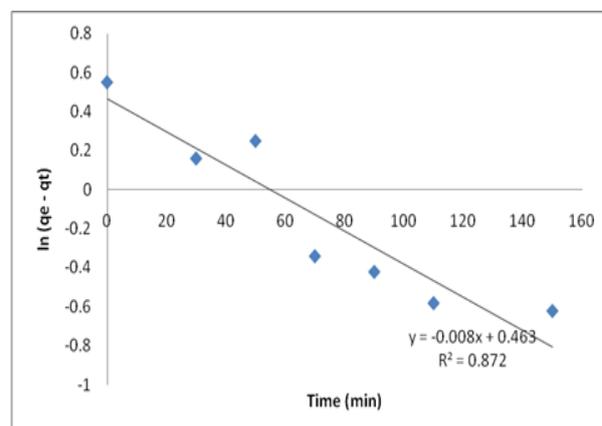


Figure 15: Pseudo first-order kinetics for adsorption of naphthalene

Pseudo-second order model

The pseudo-second order kinetic model assumes that chemisorption is the rate determining step and can be expressed in its integrated linear form as below in equation 5,

$$\frac{t}{qt} - \frac{1}{k_2 q_e} + \frac{t}{q_t} \quad (5)$$

The initial adsorption rate, h ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$) is expressed as follows:

$$h = K_2 q_e \quad (6)$$

Where k_2 is the rate constant of the pseudo second order process ($\text{gmg}^{-1}\text{min}^{-1}$).

The plot of t/qt against t is shown in Figure 16. The kinetic constants calculated from the plot are shown in Table 6 for naphthalene. As seen in Table 6, pseudo-second order has the highest correlation coefficients (R^2). The value of the correlation coefficient (R^2) (Table 2) indicated that the adsorption data for naphthalene onto CFHAP best fit the pseudo-second-order model. This result indicates that the pseudo-second-order model was fitted well to experimental data. The basic assumption behind the pseudo-second-order model, indicate that chemisorption plays a major role and may controls the adsorption process.

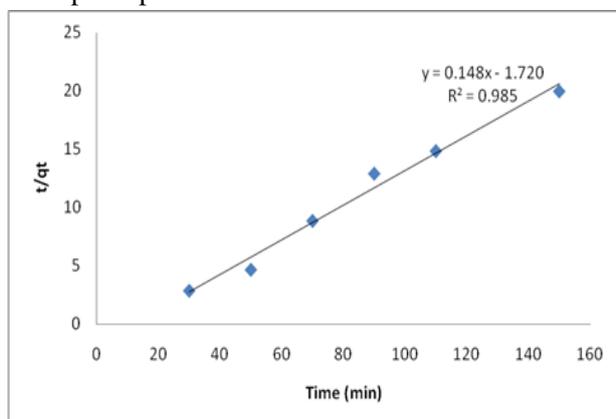


Figure 16: Pseudo Second-order kinetics for adsorption of naphthalene

Intra particle diffusion

The calculated values of the intra particle diffusion rate constant and the boundary layer thickness are shown in Table 6. The plot of q_t vs $t^{1/2}$ as presented in Figure 17 indicates the existence (although not significant) of some boundary layer effects and further showed that intra particle diffusion was not the only rate limiting step. The constant C was increased with increasing the naphthalene concentrations, indicating the increase in the thickness of the boundary layer and decreases in the chance of the external mass transfer and hence increases in the chance of internal mass transfer. The linear portion of the plot for wide range of contact time between adsorbent and adsorbate does not pass through point zero. This deviation may be due to the variation of mass transfer in the initial and final stages of adsorption. Such a deviation indicates that the pore diffusion is the only controlling step and not the film diffusion.

The values of equilibrium rate constant (K_2) are presented in Table 6. In the pseudo-second order model, the slope and intercept of the t/qt vs. t plot were used to calculate the second-order rate constant, K_2 (Figure 17). According to Table 6, the value of R^2 (0.985) naphthalene related to the pseudo-second order model revealed that naphthalene adsorption followed this model, which is in agreement with the results obtained by Karagoz *et al.* (2008), Hamed *et al.* (2007) and Altenor *et al.* (2009). Pseudo-first order and pseudo-second order kinetic models cannot identify the mechanism of diffusion of naphthalene into the adsorbent pores. Therefore, intra-particle diffusion model (Weber and Morris, 1963), which is mostly used for expression of the dependence of surface adsorption process on time, was investigated. Plot of qt against $t^{1/2}$ was illustrated in Figures 17. It showed two separate regions, the initial part is attributed to bulk diffusion while the final part to intra-particle diffusion. The value of R^2 (6) computed for intra-particle diffusion kinetic model showed that the rate of naphthalene adsorption process was not controlled by the stage of diffusion of the adsorbate in the

particles of the CFHAP (Altenor *et al.*, 2009). As Table 6 shows, Pseudo-second order is the best kinetic model, which can describe the adsorption of naphthalene by the CFHAP. This

finding is in line with the results that have been reported previously (Samarghandi *et al.*, 2012, Mall *et al.*, 2006 and Altenor *et al.*, 2009).

Table 6: Constants and Correlation Coefficients of Adsorption Kinetics Models

Kinetics models n	Concentration of naphthalene (mg/L)				
	50	75	100	150	200
Pseudo first –order kinetics					
K ₁	0.028	0.036	0.039	0.041	0.043
q _e (cal)	3.492	3.862	4.654	4.942	6.065
R ²	0.7981	0.8232	0.8727	0.8421	0.8654
Pseudo-second order kinetic					
q _e (cal)	5.856	6.863	8.647	10.462	11.646
K ₂	0.682	0.783	0.894	1.425	1.897
R ²	0.923	0.9584	0.9850	0.9734	0.9835
Intra-particle diffusion					
K ₂	0.386	0.396	0.454	0.587	0.626
C	2.786	3.463	0.454	0.587	0.626
R ²	0.5842	0.596	0.697	0.622	0.6468

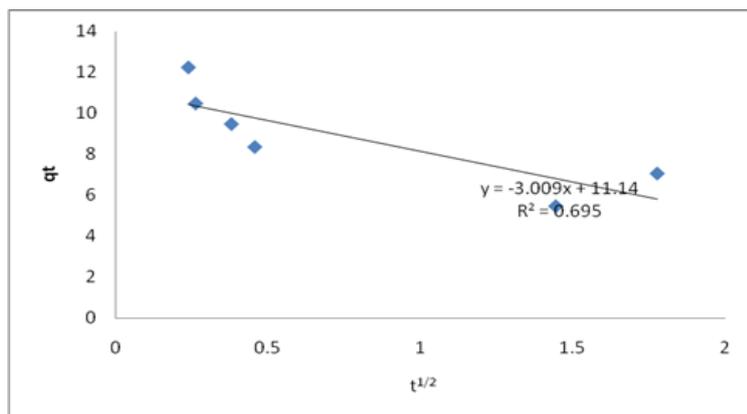


Figure 17: Intra particle diffusion model for adsorption of naphthalene

CONCLUSION

This present investigation showed that catfish bones could be effectively used for the producing of hydroxyapatite which has good adsorption potential for the removal of naphthalene from contaminated water. The fitted batch equilibrium adsorption data obtained for naphthalene fitted into the isotherm models shows that Langmuir isotherm model best correlated the equilibrium adsorption data of naphthalene based on the correlation coefficient (R²). The pseudo second order model result was

the best fit with highest correlation coefficient to describe the adsorption behavior of naphthalene.

REFERENCES

Alidoust, D., Kawahigashi, M., Yoshizawa, S., Sumida, H. and Watanabe, M. (2015). Mechanism of cadmium biosorption from aqueous solution using calcined oyster shells. *Journal of Environmental Management*, 150: 103-110

Amuda, O.S., Olayiwola, A.O., Alade, A.O.,

- Farombi, A.G. and Adebisi, S.A.** (2014). Adsorption of methylene blue from aqueous solution using steam-activated carbon produced from *Lantanacamara* Stem. *Journal of Environmental Protection*, 5: 352-1363.
- Amuda, O.S., Adebisi, S.A., Olayiwola, A.O., Farombi, A. G. and Adejumo, A. L.** (2015). Adsorption isotherms and kinetics studies of the removal of methylene blue from aqueous Solutions using *chrysophyllum albidum* seed shell. *Journal of Applied Chemical Science International*, 6: 63-73.
- Anjuran, S.** (2012), Hydroxyapatite, a biomaterial: Its chemical synthesis characterization and study of biocompatibility prepared from shell of garden nail. *Bioresource Technology*, **92**: 129:124.
- Barka, N., Qoural, S. Assabbane, A., Nounah, A. and Ait-ichou, Y.** (2008). Adsorption of disperse blue dyes SBL dye by synthesized poorly crystalline hydroxyapatite. *Journal of environmental sciences*, **20**: 1268-1272.
- Bello, O. S., Fatoye, F.S., Osulale, O.M and Njoku V. O.** (2011). Adsorption of Eosin dye from aqueous solution using Grounut Hull- Based Activated Carbon: Kinetics, Equilibrium and thermodynamic studies. *Environmental Engineering and Sciences*, **29** (3) :187-195.
- Brian Smith, A. S.** (1998), Infrared spectral interpretation: a systematic approach. CRC Press LLC. 2000 N. W. corporate Blvd., Boca Raton , Florida 33431.
- Cheung, W.H., Szeto, Y.S. and Mckay, G.** (2009). Enhancing the adsorption capacities of acid dyes by Chitosan name particles. *Bioresource Technology* 100: 1143-1148.
- Crisafully, R., Milhome, M.A.A., Cavalcante, R.M., Silveria, R.M., Keukeleire, E.R. and Nascimento, R.F.** (2008). Removal of some polycyclic aromatic hydrocarbon from petrochemical waste using low-cost adsorbents of naturals original. *Bioresource Technology* 99: 9457-4579.
- Czemiczyniec, M., Farias S., Magallanes J. and Cicerone, D.** (2007). Arsenic (V) adsorption onto biogenic hydroxyapatite Solution composition effects. *Water, Air, oil Pollution*, **18**: 75-82.
- Dan, N.U., Nicolae, A., Zorica, B., Elena, V.S and Cristianaa, Z. R.** (2011), Thermal stability of chemically precipitated hydroxyapatite nanopowders. *International Journal of Biology and Biomedical Engineering*, **2**: 57-64.
- Das Nilanjana and Das Devlina** (2015). Strategies for remediation of polycyclic aromatic hydrocarbons from contaminated soil. *Journal of Critical reviews*, **2**: 20 – 25.
- Elouear, Z., Bei Amor, R. and Boujeiben, J.** (2009). The use of phosphate rock for the removal of Ni²⁺ from aqueous solutions: Kinetics and thermodynamics studies. *Journal of Environment Engineering (ASCE)* **135**: 259-265.
- Fernare, F. and Adjiane-Zafour, A. H.** (2013). Treatment of water polluted with heavy metal by sorption of hydroxyapatites. ICOEST-Cappadocia, Turkey, **15**: 18-21.
- Ghorban, A., Ali, R. R., Java, F. and Abdul, M. S.** (2012). Kinetic and isotherm of hexavalent chromium adsorption onto nano hydroxyapatite. *Journal of Research in Health Science*, **12**: 45-53.
- Han, R., Zhang, J. Han, P., Wang, Y., Zhao, Z., and Tan, M.,** (2009). Study of equilibrium, Kinetic and thermodynamic parameters about methylene blue adsorption onto natural Zeolite. *Chemical Engineering Journal*, 145: 496-504.
- Juan, C.M., Rigoberto, G. and Lihana, G.** (2010). Removal of Mn, Fe, Ni and Cu ions from wastewater using cow bone charcoal. *Open access materials*, **3**: 452-466.
- Larsson, B.K., Sahlberg, G.P., Erikson, A.T. and Busk, L.A.** (1983). Polycyclic Aromatic hydrocarbons in Grilled food. *Journal of Agriculture and Food Chemistry*, **31**: 869-873.

- Mohammadine El, H.** (2012). Kinetic and thermodynamic studies on the adsorption behavior of Rhodamine B dye onto animal bone meal. *Journal of Chemical Engineering and Material Science*, **3**: 38 – 44.
- Mohammed, R.M. and Aazam, E.** (2013). Synthesis and characterization of pt-Zno-hydroxyapatite nanoparticles for photocatalytic degradation of benzene under visible light. *Desalination and water treatment*, **28**: 764-488.
- Nounnah A., Lacout J.L. and Savariault, J.M.** (1992) Localization of cadmium in cadmium containing hydroxyl and flourapatites. *Journal of Alloys Compound*, **2**: 14-18.
- Pankay, G. and Sanjee, V.C.** (2012). Adsorption of fluorine from drinking water on magnesium substituted hydroxyapatite. International conference on future environment and energy ICREE vol. 28. ACSIT Press, Singapore.
- Saeid, Z., Esmail, S. and Iman M.** (2013). Removal of Nickel from aqueous solution by nano hydroxyapatite derived from Persian Gulf corals. *Canadian Chemical transactions*, **3**: 173-190.
- Seyed, M. K., Seyed, H. F. and Saber, H.** (2012). Laboratory scale Bioremediation Experiment on Diesel and Polycyclic Aromatic Hydrocarbons contaminated soils. *Global Journal of research in Automotive Engineering*, **72**: 78-85.
- Shyamsundar, A.C.** (2009). Use of hydroxyapatite derived from catfish bones for remediating uranium contaminated groundwater M.Sc. Dissertation Auburn University, Alabama. Pg. 16-17.
- Tarabi, T., Tavakkoli, H., Zargaran, P. and Beiknejad, D.** (2012). Fabrication of perovskite type oxide BaPbO₃ Nanoparticles and their efficiency in photodegradation of methylene blue. *South African Journal of Chemistry*, **65**: 239-244.
- WHO** (1998). Polycyclic hydrocarbon in Guideline for drinking-water quality. 2nd Ed. Vol 2. Health criteria and other supporting information, geieva world health organization. Pp. 123-152.
- Yazdanbakhsh, M., Tavakkoli, H. and Hosseiln, S. M.** (2011). Characterization and evaluation catalytic efficiency of nanopowders in removal of reactive blue from aqueous solution. 281: 388-395.
- Yuan, S. Y., Chang, J. S., Yeh, J. H and Chang, B.** (2010). Biodegradation of phenanthrene in river sediment. *Chemosphere*, **43**: 273-278.