JASEM ISSN 1119-8362

Full-text Available Online at www.ajol.info and www.bioline.org.br/ja

J. Appl. Sci. Environ. Manage. *Feb.* 2017
Vol. 21 (1) 40-46

Remediation of Aqueous Solution of Cypermethrin and Chlorpyriphos Using Derived Adsorbent from *Jatropha* Curcas

*[1]OKEOLA, FO; [2]ODEBUNMI, EO; [1]NWOSU, FO; [1]ABU, TO; [1]IDIAGBONYA, OS; [3]AMOLOYE, MA; [2]ONIFADE, FT; [4]ABDULMUMMEEN, AG

[1]Industrial Chemistry Department, University of Ilorin, Ilorin, Nigeria
[2]Chemistry Department, University of Ilorin, Ilorin, Nigeria
[3]Chemical Engineering Department, University of Ilorin, Ilorin, Nigeria
[4]Chemistry Department, Federal University of Technology Minna, Nigeria
** Email: okeola.of@unilorin.edu.ng; okeolaf@yahoo.com*
Phone Number: +2348058749768, +2348038626501

ABSTRACT: The study focused on assessment of removal of cypermethrin and chloropyriphos in aqueous solution using activated carbon made from *Jatropha Curcas*. Batch adsorption experiments were carried out under different conditions of parameters such as pH, contact time, adsorbent dosage, and initial concentration of the adsorbate on pesticide adsorption. The adsorption data were described by Langmuir and Freundlich adsorption model. Adsorption capacity of 92.73% and 92.26% of chloropyriphos and cypermetrin respectively were removed by 2g of the adsorbent per 50 $cm^3$of initial concentration of 0.78 mg/l and 1.50 mg/l chloropyriphos and cypermetrin respectively .This was achieved at 90 min of the contact time and at optimum pH of 6.3.The study demonstrates that the activated carbon made from *Jatropha Curcas* can be effective in the adsorption of these two pesticides from water bodies. Equilibrium experiment results show that adsorption isotherms of cypermethrin and fit better to Freundlich adsorption isotherm while chloropyriphos fit better on the Langmuir adsorption isotherm

http://dx.doi.org/10.4314/jasem.v21i1.5

Key words: remediation, pesticides, *Jatropha Curcas,* cypermethrin, chloropyriphos, Langmuir and Freundlich equation

Safety in our environment has been the focus of the day. A major factors constituting to enormous threat to environment is pesticides pollution. Pesticides are artificially synthesized, toxic bio accumulative agents. Chemical pesticides are frequently applied in agricultural activities to ensure good harvest (Chang *et al*, 2011) The ongoing and uncontrolled use of pesticide to fight pest and improve agricultural production constitutes a risk for water quality (Mirjana *et al*, 2010). The pesticides have been detected by monitoring surface and underground waters. According to European Union Directives and Regulations for drinking water hygiene, the maximum allowed concentration of total pesticides is 0.5µg dm^{-3} (Mirjana *et al*, 2010). The problem of chemical pesticides in the environment is a social issue as the contaminant were frequently detected in the different water sources, rivers and soil. The leaching runs off from agricultural forest land & even residential places. The toxicity of pesticide and their degradation products is making these chemical substances a potential hazard (Salman *et al*. 2010).

Chloropyriphos (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate) is a common organophosphorus insecticide, widely used active ingredient for the protection of important agricultural crops such as corn, citrus, peanuts, etc and also effective in controlling a variety of insects including worms, cockroaches, flies, termites, fire ant and lice. On the other hand Cypermethrin is a pyrethroid pesticide and is used in the control of a wide range of insects on crops like vegetables, cereals and maize (USEPA, 2002).Conventional waste water technologies for treating pesticides wastewater and industrial effluents include chemicals, biological and physical treatments such as coagulation and flocculation,ozonation, electrochemical processes, nano filtration, and adsorption(Okeola *et.al,*2014; The following conventional methods were used for removal of some pesticides in wastewaters Fenton with coagulation (Chen et al, 2007), photo catalysis and electro-Fenton , combined ultrasound and Fenton (Ma et al, 2010), Oxidants and photolysis , biological degradation (Singh et al, 2008) and adsorption (Ignatowicz , 2009). However, adsorption process is one of the most widely applied techniques for pollutant removal. Adsorption plays a significant role in the environmental pollution control The common adsorbents include activated carbon molecular sieves polymetric adsorbents and some other low cost material.Among numerous clean-up techniques, adsorption technique with activated carbon from agricultural material or waste is ecofriendly . Such sources include bamboo, coconut shell,chestnut shells (Memon et al, 2007) and snail shell (Udeozor and Evbuomwan 2014). Adsorbents derived from *jatropha curcas* has been used effectively for various

**Correspondence author Email: okeolaf@yahoo.com; okeola.of@unilorin.edu.ng*

adsorptions, Raw treatment jatropha *curcas* was applied for adsorption of aqueous Cu (II) ion adsorption (Jain *et al* 2008), activated carbon processed from the shell of this crop has been used for adsorption of methylene blue (Okeola *et al* 2010), adsorption of Congo red (Okeola *et al* 2014), Removal of Fe (II) ion (Okeola and Odebunmi 2011).

Therefore this work is to determine the feasibility of application of the activated carbon from jatropha *curcas* shell for the adsorption of the pesticides cypermethrin and Chloropyriphos Thus reducing or removing them from aqueous environment.

MATERIALS AND METHODS

Adsorbate and adsorbent: The adsorbent employed is the already produced activated carbon from *jatropha curcas* shell. This has been used for effective adsorption of methylene blue and acetic acid (organic solutes) and potassium permanganate (inorganic solute).Chloropyriphos and cypermehtrin were procured from an agrochemical plaza along Ilorin,Kwara state, Nigeria. A 100mg/L solution of Cypermethrin pesticide was prepared by taking 1ml of the stock solution 100 g/L into 1000ml standard flask. Subsequent solutions of lower concentration were made by serial dilution.

Batch equilibrium studies: Batch adsorption experiments were carried out using a series of erlenmeyer flasks. The experiments were conducted to investigate the effect of pH contact time,initial pesticide concentration and adsorbent dosage. All the adsorption experiments were carried out at room temperature (30 ± 2^{o}C). The initial pH was adjusted with 0.1M HCl or 0.1M NaOH. Time course experiments were investigated by shaking the sorption mixture of (adsorbent and adsorbate) at various predetermined interval and conditions. The mixtures left were filtered and the filtrate analysed for the adsorbate concentration, blank solutions without adsorbent were also shaken and the concentrations determined. This was used as initial concentration. The concentrations of pesticide in the solution before and after adsorption were determined using a double beam UV-Vis spectrophotometer (Shimadzu DU 730) at its maximum wavelength of 300 nm and 375 nm for Chloropyriphos and cypermethrin respectively. Each batch of the experiment were duplicated under identical conditions and the results obtained from their means. In the determination of adsorption capacity of solute intake per unit mass of activated carbon (q_e, mg/g) was calculated using adsorption system mass balance as shown in equation (i)

$$q_e = \frac{V\,(C_i - C_f)}{w} \quad \text{.. (i),}$$

Where v = volume of solution (L)
w = amount of dry adsorbent/ substrate (g)
c_i = initial concentration (mg/l) and
c_f = final concentration (g)
The percentage of dye uptake (% uptake) was also calculated in some cases using the equation (ii);

$$\% \text{ uptake} = \frac{c_i - c_f}{c_i}\, x100 \quad \text{...................................(ii)}$$

Determination of Effect of adsorbent dosage on chlorpyriphos and cypermetrin: The effect of adsorbent dosage on adsorption of chlorpyriphos and cypermetrin was studied using initial concentration of 0.78 mg/l and 1.50mg/l respectively for different amount of the adsorbent (0.1, 0.2, 0.5, 1.0, 1.5, 2.0, 3.0) g that were separately weighed into different sample bottles. A 50ml of the same concentration of each of the pesticide solution was added into each sample bottles containing the adsorbent.

Determination of Effect of contact time on chlorpyriphos and cypermetrin: Contact time is an important factor in the efficient solute adsorption. The effect of contact time on the adsorption of each pesticide from aqueous solution on this activated was tested by taking 2.0 g activated carbon sample with 50 ml of 0.78 mg/l and 1.50 mg/l of chlorpyriphos and cypermetrin respectively in 250 ml flask. This was shaken on mechanical shaker at various time intervals between 15-105 mins. The clear solution was analysed for the residual pesticide concentration.

Determination of Effect of pH on chlorpyriphos and cypermetrin: The pH of the solution is an important controlling parameter in the adsorption process. The effect of pH on the equilibrium sorption of each pesticide was investigated by employing an initial concentration of chlorpyriphos and cypermetrin, 0.78 mg/l and 1.50 mg/l respectively and 0.2 g of activated carbon (TSC) in 50 ml of solution. The suspensions were shaken for 100 min and the amount of pesticide adsorbed determined. The experiment was repeated for pH 2.2-7.5.

Determination of Effect of initial concentration on chlorpyriphos and cypermetrin: The effect of initial concentration of chloropyriphos and cypermethrin concentration on adsorption was investigated. The experiments were carried out at a fixed dose of activated carbon (0.2 g), temperature 30^{o}C, pH 6.3 and different initial concentration of pesticide, range of 1.5 – 1.8 mg/l.

Evaluation of Adsorption Isotherm of chlorpyriphos and cypermetrin: The capacity of the adsorption isotherm is fundamental, and plays an important role in the determination of the maximum capacity of adsorption. It also provides a panorama of the course taken by the system under study in a concise form, indicating how efficiently an adsorbent will adsorb and allows an estimate of the economic viability of the adsorbent commercial applications for the specific solute. In order to adapt for the considered system, an adequate model that can produce the experimental results obtained, equations of Langmuir and Freundlich, have been considered. The two models have been the most widely used isotherm equation. Construction of Adsorption Isotherm was carried out from the batch adsorption experiment of effect of initial concentration by adding 0.2 g fixed dose of activated carbon temperature 30^{o}C, pH 6.3 and different initial concentration of pesticide, range of 1.5 – 1.8 mg/l.

Freundlich Adsorption Isotherm: The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface assumes that different sites with several adsorption energies are involved. Freundlich adsorption isotherm is the relationship between the amounts of solute adsorbed per unit mass of adsorbent, q_e, and the concentration of the solute at equilibrium, C_e. This isotherm can be described as in equation (iii)

$$log\ q_e = log K_f + \frac{1}{n} log C_e \qquad \text{(iii)}$$

Where q_e (mg/g) is the adsorption capacity at equilibrium, C_e (mg/L) is the equilibrium concentration of adsorbate in solution and K_f (mg/g) and n are the Freundlich physical constants,both are the indicator of the adsorption capacity and adsorption intensity respectively. (Ma *et al* 2010).

Langmuir Adsorption Isotherm: The Langmuir model is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. (Kumar and Gayathri 2009 ; Okeola and Odebunmi ,2010) The Langmuir isotherm is given in equation (iv)

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m \mathrm{K_L}}\frac{1}{Ce} \qquad \text{(iv)}$$

Where q_m (mg/g) and KL (L/g) are the Langmuir constants representing the maximum monolayer adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively.

RESULTS AND DISCUSSION

Effect of adsorbent dosage on adsorption of pesticides: In the studies the adsorption percent (%) of the respective pesticides was found to vary with different mass samples. From data presented in Table1,it shows that the suitable mass of activated carbon is (2g).The adsorption percent 92.73% and 92.26% for chloropyriphos and cypermetrin respectively was observed. A similar result was observed for the removal of carbofuran and chloropyriphos from aqueous solution using walnut shells (Memon et al 2007)

Table 1 Percentage adsorption of cypermethrin and chlorpyrophos at different mass of adsorbent

Adsorbate	Mass of adsorbent (g)	Co (mg/l)	Ce (mg/l)	X(mg/l)	% Adsorption
Cypermethrin	0.1	1.5	1.129	0.371	24.74
	0.2	1.5	0.728	0.772	51.46
	0.5	1.5	0.574	0.926	61.75
	1.0	1.5	0.437	1.063	70.86
	1.5	1.5	0.257	1.243	82.86
	2.0	1.5	0.116	1.384	92.26
	3.0	1.5	0.116	1.384	92.26
Chloropyrophos	0.1	0.78	0.672	0.108	15.11
	0.2	0.78	0.651	0.129	52.31
	0.5	0.78	0.544	0.236	55.75
	1.0	0.78	0.145	0.635	71.97
	1.5	0.78	0.061	0.719	89.78
	2.0	0.78	0.057	0.723	92.73
	3.0	0.78	0.057	0.723	92.73

pH = 6.3,time 1.5hr temp. 30^{o}C

Effect of contact time on adsorption of chlorpyriphos and cypermetrin: The influence of contact time on adsorption capacity of chlorpyriphos and cypermetrin is shown in table 2. The results clearly show that the adsorption of chlorpyriphos and cypermetrin increases with time until reaching a nearly saturation level. Rate of uptake of each pesticide is higher at the beginning which may be due availability of a large number of active sites on the adsorbent.As the sites become exhausted the uptake rate depends on transportation from outside to inside the adsorbent particles (Udeozor and Evbuomwan 2014) However, the time of saturation totally equals with chlorpyrifos and cypermetrin.The observation obviosly,shows the specific time of saturation of 90 mins for chlorpyrifos and cypermetrin with adsorption capacity of 92.29% and 92.78% respectively.

Table 2. Contact time factor on adsorption capacity and percentage adsorption of cypermethrin and chlorpyrophos

Adsorbate	Time	Co (mg/l)	Ce(mg/l)	X(mg/l)	Qe(mg/g)	% Adsorption
Cypermethrin	15	1.5	1.213	0.287	7.170	19.12
	30	1.5	0.674	0.827	20.663	55.1
	45	1.5	0.444	1.056	26.396	70.39
	60.0	1.5	0.278	1.222	30.544	81.45
	75	1.5	0.119	1.381	34.519	92.05
	90.0	1.5	0.116	1.384	34.609	92.29
	105.0	1.5	0.116	1.384	34.609	92.29
Chloropyriphos	15	0.78	0.672	0.108	2.711	13.9
	30	0.78	0.651	0.129	3.231	16.57
	45	0.78	0.544	0.236	5.899	30.25
	60.0	0.78	0.145	0.635	15.877	81.42
	75	0.78	0.061	0.719	17.983	92.22
	90.0	0.78	0.057	0.723	18.067	92.78
	105.0	0.78	0.057	0.723	18.067	92.78

Adsorbent dosage 2g/50ml pH 6.3 temp. 30^{o}C

Effect of pH on adsorption of chlorpyrifos and cypermetrin: The pH of the solution is an important controlling parameter in the adsorption process.The effect of pH on the adsorption uptake percent (%) of chlorpyrifos and cypermetrin is shown in table 3. From these data it is obvious that the percent adsorption gradually increases by increasing the pH till reaching maximum uptake at pH of 6.3. The adsorption percent of the each pesticide show similar trend. Meanwhile, the adsorption is low below pH 4.0 and increases rapidly at pH 5.6 getting to maximum at pH 6.3. At this pH of 6.3, 92.57% and 92.25% of chloropyriphos and cypermetrin respectively were adsorbed. At higher pH the pesticides start degrading. The trend of the results is seen in the removal of carbofuran and chloropyriphos from wastewater using walnut shell (Memon *et al* 2007)

Table 3. Effect of pH on adsorption capacity and percentage adsorption of cypermethrin and chlorpyrophos

Adsorbate	pH	Co (mg/l)	Ce(mg/l)	X(mg/l)	Qe(mg/g)	% Adsorption
Cypermethrin	2.2	1.5	1.360	0.140	3.499	9.33
	3.1	1.5	0.972	0.528	13.193	35.18
	4.1	1.5	0.529	0.971	24.285	64.76
	5.6	1.5	0.158	1.342	33.544	89.45
	6.3	1.5	0.116	1.384	34.594	92.25
	7.1	1.5	0.149	1.351	33.776	90.07
	7.5	1.5	0.245	1.255	31.365	83.64
Chloropyriphos	2.2	0.78	0.672	0.108	2.711	11.17
	3.1	0.78	0.651	0.129	3.231	46.87
	4.1	0.78	0.544	0.236	5.899	62.73
	5.6	0.78	0.145	0.635	15.877	88.52
	6.3	0.78	0.061	0.719	17.983	92.57
	7.1	0.78	0.057	0.723	18.067	89.76
	7.5	0.78	0.057	0.723	18.067	84.41

Adsorbent dosage 2g/50m temp. 30^{o}C

Effect of initial concentration on adsorption: The effect of initial pestide chloropyriphos and cypermethrin concentration in the range of 1.5 – 1.8 mg/l on adsorption was investigated and is shown in table 4. It is evident that the percentage pesticide removal increased with the increase in initial concentration of the pesticide. The initial pesticide concentration provides the necessary driving force to overcome the resistances to the mass transfer of pesticide between the aqueous phase and the solid phase. The driving force was observed to be greater in cypermethrin in which q_e (amount of adsorption per unit mass of adsorbent) of 87.5mg/g at initial concentration of 8.0 mg/l from 7.5mg/g at initial concentration of 1.5 mg/l. In chlorpyrifos q_e (amount of adsorption per unit mass of adsorbent) of 37.5mg/g at initial concentration of 7.0 mg/l from 5.0mg/g at initial concentration of 1.5 mg/l.

Isotherm Modelling: The adsorption isotherm data for the pesticide adsorption were as prepared in table 4. The graphical representations of these models are presented in figure1 for Langmuir and figure 2 for Freundlich isotherm respectively. Each of the pesticide adsorbed per gram, (q_e) and respective equilibrium concentration (Ce) for each initial concentration of the pesticide was prepared. The plot of 1/q_e against the 1/Ce on shows straight lines as displayed in figs. 1. This linear relationship is an indication that the adsorption process fit in and can be described by a Langmuir type isotherm. The fitting to Langmuir shows that the adsorption occurs mainly through the formation of a single monolayer of adsorbed molecules.Chloropyriphos adsorption fit better on Langmuir type isotherm

On the other hand, the plot of Log q_e against the Log Ce on shows straight lines as displayed in figs. 2 for cypermethrin and chlorpyrophos respectively this linear relationship is an indication that the adsorption process also fit in and can be described by a Freundlich isotherm. Cypermethrin adsorption was of course observed to fit better on Freundlich type isotherm

The isotherm equation is applied to describe the data in a quantitative way. (Okeola and Odebunmi, 2010). The isotherm parameters and correlation coefficient R^2 values are tabulated in table 6.When the value of correlation co - efficient, R^2 is nearer to 1, the respective experimental data tend to fits better to the respective equation. The values of n (from Freundlich equation) greater than unity, suggesting favourable adsorption .The result of q_m (from Langmuir equation) shows an higher adsorption of cypermethrin under the same adsorption factor (Chang *et al* 2011)

Table 4: Effect of initial concentration on adsorption and Adsorption isotherm Data

Adsorbate	Co (mg/l)	Ce(mg/l)	X(mg/l)	q_e (mg/g)	Log Ce	Log q_e	1/ q_e	1/Ce
Cypermethrin	1.5	1.2	0.3	7.5	0.079	0.875	0.133	0.833
	2.5	1.9	0.6	15.0	0.279	1.176	0.067	0.526
	3.5	2.4	1.1	27.5	0.380	1.439	0.036	0.416
	4.0	2.6	1.4	35.0	0.415	1.544	0.028	0.384
	6.0	3.9	2.1	52.5	0.591	1.720	0.019	0.256
	8.0	4.5	3.5	87.5	0.653	1.942	0.011	0.222
Chloropyriphos	1.5	1.3	0.2	5.0	0.114	0.699	0.200	0.769
	2.0	1.7	0.3	7.5	0.230	0.875	0.133	0.588
	3.2	2.6	0.6	15.0	0.415	1.176	0.067	0.385
	4.0	3.0	1.0	25.0	0.477	1.398	0.040	0.333
	6.0	4.8	1.2	30.0	0.681	1.477	0.033	0.208
	7.0	5.5	1.5	37.5	0.740	1.574	0.027	0.181

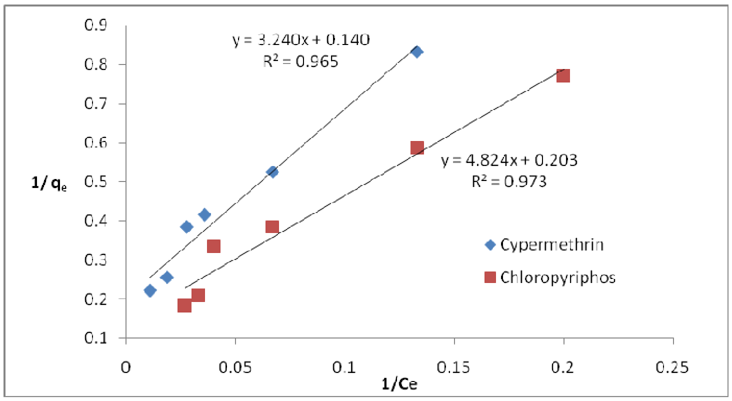

Fig 1: Langmuir adsorption of isotherm of cypermethrin and chloropyriphos adsorption

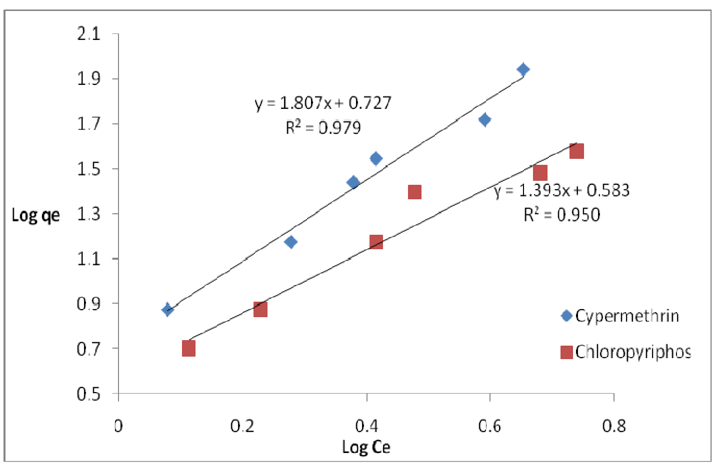

Fig 2: Freundlich adsorption of isotherm of cypermethrin and chloropyriphos adsorption

Table 5: Isotherm constants for cypermethrin and chloropyrophos adsorption

Pesticide	Freundlich		Langmuir	
cypermethrin	R^2	0.979	R^2	0.973
	K_f	9.53	K_L	0.454
	n	5.33	q_m	7.14
chloropyrophos	R^2	0.950	R^2	0.965
	K_f	8.91	K_L	0.974
	n	3.83	q_m	4.93

Conclusion: In this study the feasibility of application of the activated carbon from *jatropha curcas* shell for the adsorption of cypermethrin and Chloropyriphos adsorption was established.The adsorption depends on pH,contact time, mass of the sample and initial concentration of the pesticide. The adsorption process of cypermethrin and Chloropyriphos fits better on Freundlich and Langmuir isotherms respectively.

REFERENCES

Abdessalem, AK; Bellakhal, N; Dachraoui M; Oturan MA (2010). "Treatment of a mixture of three pesticides by photo- and electro-Fenton processes". *Desalination*, 250, 450-455 492.

Chang, K; Lin, J;Chen S (2011). "Adsorption Studies on the Removal of Pesticides (Carbofuran) using Activated Carbon from Rice Straw Agricultural Waste", *World Academy of science, Engineering and Technology,* Vol:5, 317-320.

Chen, S; Sun, DZ;. Chung, JS (2007. Treatment of pesticide wastewater by moving-bed biofilm reactor combined with Fenton-coagulation pretreatment, *J Hazard Mater*, 144 577-584.

Ignatoweiz, T; Toweel, G (2009)."Selection of sorbent for removing pesticides during water treatment". *J. Hazard Mater.* 169. 953-957.

Ma, YF; Sung, FT; JG; Lin BM (2010). Degradation of carbofuran in aqueous solution by ultrasound and Fenton processes: Effect of system parameters and kinetic study, *J. Hazard Mater*, 178 320-325.

Manuel Fernando, RF; Pereira Samanta, JMO; Soares Jose, LR; Figureueiredo A (2003). *Carbon,* 41, 811

Memon, GZ; Bhanger, MI; Akhtar, KT (2007) The removal efficiency of chestnut shells for selected pesticides from aqueous solutions*, J Colloid Interf Sci,* 315 33-40.

Mirjana, BN;Rada. DP; Mila, DL. (2010) "Removal of organochlorine pesticides from water using virgin and regenerated granular activated carbon", *J. Serb. Chem. Soc.* 75 (4) 565-573.

Jain, N; Josh, HH; Dutta, S.C; Kuma, RS; Panthak, H (2008). Biosorptrion of Copper from Waste Water using jatrophas seed coat, *J. of Scientific and Industrial Research* ,vol. 67154-160

Okeola, OF; Odebunmi EO; Bakare OF, (2014): "Equilibrium and Kinetics Studies of Adsorption of Congo red by Activated Carbon prepared from *Thevetia peruvianna* shell", J. of Raw Material Research

Okeola, FO; Odebunm,i EO (2010). "Comparison of Freundlich and Langmuir Isotherms for Adsorption of Methylene Blue by Agrowaste Derived Activated Carbon", *Advances in Natural and Applied Science*, 4(3), 281-288.

Okeola, OF; Odebunmi EO; Ameen OM; Adebayo GB (2011). "Adsorption of Iron (III) ion Aqueous Solution Using *Jatrophacurcas* Seed Coat Activated Carbon", *Proceedings of the 34th Annual International Conference of the Chemical Society of Nigeria,*

Salman, JM; Hammeed BH (2010). Removal of insecticide carboforan from aquoeous solutions by banana stalk activated carbon *J. Harzard Mater,*176, 814-819

Singh, DK; Rao, SD; and Kaate, HK (2008). Biodegradation and bioremediation of pesticide in soil: concept, method and recent developments, *Indian J Microbiol*, 48 35-40.

Udeozor, SO; Evbuomwan, BO (2014). The effectiveness of snail shell as adsorbent for the treatment of waste water from beverage industries using H_3PO_4 as activating agent, *J of Engieering,* Vol. 04, ISSN (p): 2278-8719

USEPA, U.S. Environmental protection Agency (2002), Revised Preliminary Human Health Risks Assessment for Atrazine Office of Pesticide Programs. Washington