IAA Journal of Biological Sciences 8(1):216-227,2022. ISSN: 2636-7254

Adsorption of Chlorpheniramine from Deionized and Spiked Pharmaceutical Liquid Waste Using Surface Functionalized Activated Carbon from Mango Kernel Seed

[1]Iloh, E. O., [2]Onyema-iloh, O. B., [3]Udeozo, P. I., and [4]Chime, C. C.

1-Pure and Industrial Chemistry, Chukwuemeka Odumegwu Ojukwu University, Uli Campus.
2-Chemical pathology, Nnamdi Azikiwe University Teaching Hospital, Nnewi.
3-Industrial Chemistry, Enugu State University of Science and Technology, Enugu.
4-Industrial Chemistry, Enugu State University of Science and Technology, Enugu.
Corresponding author:Iloh EO. Mobile number: 08065033697. E- mail address: emmanuelonyemai@yahoo.com

ABSTRACT

The adverse effects of some pharmaceutical drugs like chlorpheniramine (CHL), discharged into the environment either through industrial effluents, as unused drugs or expired drugs on humans, animals, aquatic life and environment at large remains a serious public health problem. In this study, surface modified Activated Carbon (AC) from mango kernel seed were prepared and the experiment designed for optimization.The ACs were oxidized with HNO_3 toproduce oxidized activated carbons (OAC) that were surface functionalized using ethylene diamine to producebasic surfaces (BAC) and ethylamine to produce hydrophobic carbonaceous surfaces (HAC).The adsorption of chlorpheniramineon these carbons were investigated at different initial pH, contact time, drug concentration and temperature. Drug adsorption depends mainly on solution pH and the adsorbent surfacenature, and initial pH 7 was found optimal for the removal of CHL. Equilibrium adsorption was reachedfaster on HAC and OAC than on BAC with kinetic adsorption data following well pseudo second order model much better than pseudo first order and intra-particle diffusion. Equilibrium adsorption data follow well the Langmuir model than the Freundlich model. The CHL uptake follows the order: HAC > OAC > BAC for mango kernel seed. Thermodynamic parameters showedthat drug adsorption is spontaneous and endothermic, with values less than 40kJmol^{-1} indicating physisorption processes domination.The adsorption capacity, q_e and %Adsorbed with time, of CHL from the spiked Pharmaceutical Liquid Waste (PLW), of the different carbons follow similar order to that from deionized water. For carbons of mango kernel seed on CHL from both deionized water and spiked PLW, the trend is: HAC > OAC > BAC. CHL adsorption from spiked Pharmaceutical Liquid Waste (PLW), showedslightly less capacity than that from deionized water but the same trend in the percentage adsorbed by the different carbons as in the deionized water and the different percentage adsorbed showed significant difference having $P<0.05$.
Keywords: pharmaceutical drugs, chlorpheniramine, quatic life and drug adsorption.

INTRODUCTION

A pharmaceutical medicinal product also referred to as a medicine or medication can be generally defined as any chemical substance or product intended for use in the medical diagnosis, cure, treatment, or prevention of diseases. They are an important element of the medical practice and their beneficial effects (and side-effects) on human and veterinary health are widely acknowledged. However, the area where we lack a global view is understanding what happens when these medicinal products are discharged into the environment, either through industrial effluents, consumption or as unused or expired products.

Chlorpheniramine (CHP) is an antihistamine used to treat the symptoms of allergic conditions such as allergic rhinitis (hay fever).Activated carbon, also called activated charcoal, is a form of carbon processed to have small, low-volume pores that increase the surface area available for adsorption or chemical reactions [1].

MATERIALS AND METHODS

All chemicals used were of analytical grade. Pure sample ofCHP was supplied by Sigma Aldrich. 25 g of clean dry seeds were charred in a carbon steel tube (internal diameter 5.1 cm and length 61 cm) that was heated in a tube furnace (GSL-1100X-110V, MTI Corporation, USA) under nitrogen atmosphere at 500°C for 2 hours. The chars were impregnated in saturated KOH solution in a weight ratio of 1:3.The mixtures were left in the oven (Hobersal Mon X B2-125 furnace, Hobersal, Spain) overnight at 120°C before being transferred to the tube furnace described above. The temperature was raised from room temperature to 550°C in a heating rate of ~8.6°C/min and was kept at 550°C for 1 hour under nitrogen for activation. Activated Carbon (AC) produced was washed thoroughly with deionized water to remove residual alkalinity. To keep the acidic functional groups on the carbon in H-form, AC was washed with 0.1M HCl followed by deionized water until no acidity was detected in wash water. AC of MKS was left to dry at 120°C until constant weight was obtained. After cooling in a desiccator and grinding, a size range between two sieves of 1.19 mm and 0.25 mm was selected for characterization.AC surfaces was heated with concentrated HNO_3 (1 g AC: 10 mL acid) at 80°C to almost dryness to produce Oxidized Activated Carbons (OAC), that was washed thoroughly until no acidity was detected in wash water. OAC was dried at 120°C until constant weight was achieved. OAC surface was functionalized to produce Basic Activated Carbons (BAC) as follows; 15 g of dry OAC was allowed to react with 25 % thionyl chloride in toluene (100 mL) under reflux for 6 hours at 70°C. During this stage, surface carboxylic groups were converted to acetyl chloride groups. The carbon was left to dry in the oven at 85°C for 2 hours and the carbon product was allowed to react with 100 mL 0.75 M 1,2-diaminoethane (ethylene diamine) at 90°C under reflux for 24 hours. By the end of the reaction, nitrogen-containing functional groups were immobilized on the carbon surface via amide coupling. For the preparation of hydrophobic activated carbons (HAC), 15 g of dry OAC was allowed to react with 50 % thionyl chloride in toluene under reflux for 2 hours at 70°C. The product was allowed to cool and the solvents were dried using rotary evaporator. After evaporation, the product was immediately mixed with 100 mL of ethylamine and the mixture was kept at 90°C for 2 hours under reflux. By the end of the functionalization steps for both types of surface functionalized carbons (BAC and HAC), the carbons were purified via Soxhlet extraction using 150 mL of acetone for 6 hours followed by washing with deionized water. Further washing using 2M HCl was carried out to remove residual amines from carbon surface. Finally, the carbons were thoroughly washed with deionized water to remove residual acid. The carbons were allowed to dry at 70°C in an oven under vacuum until constant weight was reached. Surface functionalization using EDA produced BAC of MKS. For hydrophobic carbons, surface modification using EA produced HAC of MKS. TheActivated Carbons (AC) was characterized by determining their moisture content, ash content, pore volume, density, and surface area. In addition, Scanning Electron Microscopy SEM, and Fourier Transform Infra-Red FTIR spectroscopy were performed on the AC to determine themorphological structures and functional groups present respectively.

Moisture Content: A portion (2g) of the sample was carefully measured into a pre weighed beaker (w_1) and the weight of the beaker and sample was noted (w_2). The

sample was carefully transferred to a laboratory oven set at 105°C and allowed to stand for 2hours. The sample was transferred to a desiccator and allowed to cool.

$$moisture\ content\ \% \left(\frac{w_2 - w_3}{w_2 - w_1}\right) \times 100$$

W_1 = weight of empty beaker W_2 = weight of empty beaker + wet sample W_3 = weight of empty beaker + dry sample

Ash content: A portion (2g) of sample was carefully weighed into a preweighed Crucible (w_1) and the weight of Crucible and sample was noted as w_2. The Crucible was transferred to a muffle furnace set at 600°C for 2hours.The Crucible was transferred to a desiccator and allowed to cool and weight noted (w_3).

$$Ash\ content\ \% \left(\frac{w_2 - w_3}{w_2 - w_1}\right) \times 100$$

W_1 = weight of empty crucible
W_2 = weight of empty crucible + wet sample
W_3 = weight of empty crucible + ash sample

Pore volume: A portion (2g) of sample was immersed in 50ml of water and boiled for 1 hour. The contents was filtered through a pre-weighed filter paper and dried in a laboratory oven set at 80°C.

$$Pore\ volume = \frac{change\ in\ weight}{density\ of\ water}$$

Bulk density: A portion (20g) of sample was carefully transferred into a dry 100ml measuring cylinder and the volume noted.

$$Density = \left(\frac{w_2 - w_1}{V}\right)$$

W_1 = weight of empty flask
W_2 = weight of empty flask + sample

The ground adsorbent will be sieved and a particle size of 400µm will be used in the whole experiment.

Preparations of Stock Solution of Chlorpheniramine:

All applied chemicals were of analytical reagent grade purchased from Sigma Aldrich while all the experiments were conducted using double-distilled deionized water.

Chlorpheniramine:Stock solution containing 50mg/L chlorpheniramine in maleate form, was prepared by dissolving 50mg of chlorpheniramine in deionized water in 1000ml volumetric flask.Adsorption experiments involving temperature, concentration, pH, and contact time variations will be carried out after serial dilution of standard solutions.

Drug analysis: High performance liquid chromatography (HPLC) equipped with diode array detector (Agilent technologies, 1260 Infinity Series, USA) was used for the analysis of Chlorpheniramine, at λmax 260 nm. The drug wasseparated using C18 analytical column and a mobile phase consisting ofmethanol and 20mm ammonium format buffer (pH 4.8) in a gradient elution mode with a flow rate of 45 µL/min and column temperature of 40 °C. Calibration standards of the three drug (1–20 mg/L) was prepared and standard curves were obtained by linear regression of the mean values of peak areas. Retention time for Chlorpheniraminewas found to be 2. For Chlorpheniramine, the linear rangewas found to be between 1–20 mg/L (R2: 0.9995). Accuracy of the method of analysis shows more than 98.2% recovery for both drugs [2].

Sorption Studies: The effect of **initial pH** on Chlorpheniramineadsorption was carried out by mixing 0.06 g of each of the carbons OAC, HAC and BAC, with 25 mL of drug (50 mg/L) solution in a glass vial. The initial pH was pre-adjusted to be between 3–11 using 0.1M NaOH and/or 0.1M HCl prior to carbon mixing. After carbon mixing, the solution was kept under mechanical agitation until the equilibrium was reached at 25 °C. The final pH was recorded and residual drug concentration was analyzed. Initial pH 7.0 was found optimal for Chlorpheniramine adsorption and was selected as initial pH for the kinetic and equilibrium studies. The effects of **pH** (3 to 11), **contact time** (30 to 180 min), **adsorbent dose** (0.1 to 0.5g) and **concentrations of the drugs** (50 to 250mg/L) were investigated. In each case the quantities adsorbed and percentages removed by the adsorbent were calculated using the equation:

qe = (Co – Ce)V/m
qt = (Co – Ce)V/m
%rem = (Co – Ce)100/Co

Kinetic Experiment: The kinetic experiment of the drug adsorption was studied by mixing 0.1g of each of the carbons from mango kernel seed (OAC, HAC and BAC) with

50 mL (50mg/L) at initial pH 7.0. The adsorption mixtures were kept at 25°C under mechanical agitation for 180mins during which the equilibrium was reached. At different time intervals, samples were separated for analysis. The filtrates obtained were then analyzed for chlorpheniramine concentrations. Results obtained were analyzed using Pseudo first-order, Pseudo second-order and Intra-particle diffusion kinetic models.

Pseudo-first order; $In(q_e - q_t) = Inq_e - k_1t$

Where:

q_t = the amount of drug adsorbed at any time t in mg/g

q_e = the amount of drug adsorbed at equilibrium time in mg/g

k_1 = pseudo first order rate constant in min^{-1}

Then a plot of $In(q_e - q_t)$ against t gives a negative slope, -k1 with intercept, Inq_e.

Pseudo-second order; $t/q_t = 1/k_2q_e^2 + t/q_e$

Where:

t = time in minutes

k_2 = second order rate constant in $gmg^{-1}min^{-1}$

q_t = amount adsorbed at a given time t in mg/g

A plot of t/q_t against t enables the calculation of q_e from the slope and the rate constant k_2 is then evaluated from the intercept.

Intra-particle diffusion

$qt = kit^{0.5} + C$

ki = intra-particle diffusion rate constant

C = intercept related to the thickness of the boundary layer

Equilibrium Experiment: For the equilibrium studies, 0.06 g of carbon was mixed with 25 mL of drug solutions at different concentrations (5–50 mg/L) at initial pH 7.0 and 25 °C under mechanical agitation. After the equilibrium, residual drugs each were separated and analyzed. The filtrates obtained were then analyzed for chlorpheniramine concentrations. Results obtained were analyzed using Langmuir and Freundlich isotherm models.

Langmuir: Ce/qe = 1/qmKL + Ce/qm

Freundlich: Inqe = Inkf + 1/nInCe

Where qe is the amount of drug adsorbed (mg/g); Ce is the equilibrium concentration of the drugs (mg/L); qm is the monolayer adsorption capacity (mg/g); KL is the Langmuir constant (L/mg); Kf (mg) is the Fleundlich constant; n is the empirical parameter which is related to the sorption intensity.

Thermodynamic Experiment: Adsorption of Chlorpheniramine from the stock solutions were investigated over the temperature range of 25°C, 35°C and 45°C. 40ml of Chlorpheniramine was drawn from each stock solution. This was made up to 1000ml to produce 0.002mg/ml of Chlorpheniramine. 100ml of the prepared solution was put into a beaker. 0.06g of the adsorbents each were added to the beakers and the mixtures stirred for even distribution. The beakers were placed in a thermostat water bath set at temperature of 25^0C and allowed to stand in the bath for an hour and after which, samples were drawn from them and filtered for analysis. These were repeated at temperatures of 35°C and 45°C.

Determination of the percentage adsorption of Chlorpheniramine present in the selected spiked Pharmaceutical Liquid Waste (PLW):

Several samples of Pharmaceutical Liquid Waste (PLW) were collected from the effluents of Gauze Pharmaceutical and Juhel Pharmaceutica companies, both in Awka, Anambra state of Nigeria, in a working week day. PLWsamples were kept in ice during transport and were filtered usingmembrane filter (0.45 μm pore size). PLW filtrate samples were mixedtogether in equal volumes making a representative sample. For the adsorptionof Chlorpheniraminefrom spiked PLW, samples of the stock solutionof Chlorpheniramine was spiked with the filtered PLW to achieve the rangeof initial concentrations as in the study of equilibrium adsorption fromdeionized water mentioned above [Syeda et al, 2019]. 0.06 g each of the carbons (OAC, HAC, BAC) prepared from mango kernel seed were mixed with25 mL of spiked drug solutions and was left at 25 °C under mechanicalagitation at 30, 60, 90, 120, 150, and 180 minutes. After equilibrium was obtained, samples of supernatant were separated and analyzed.

RESULTS

Table 1: The physical characteristics of Mango Kernel Seed Activated Carbon

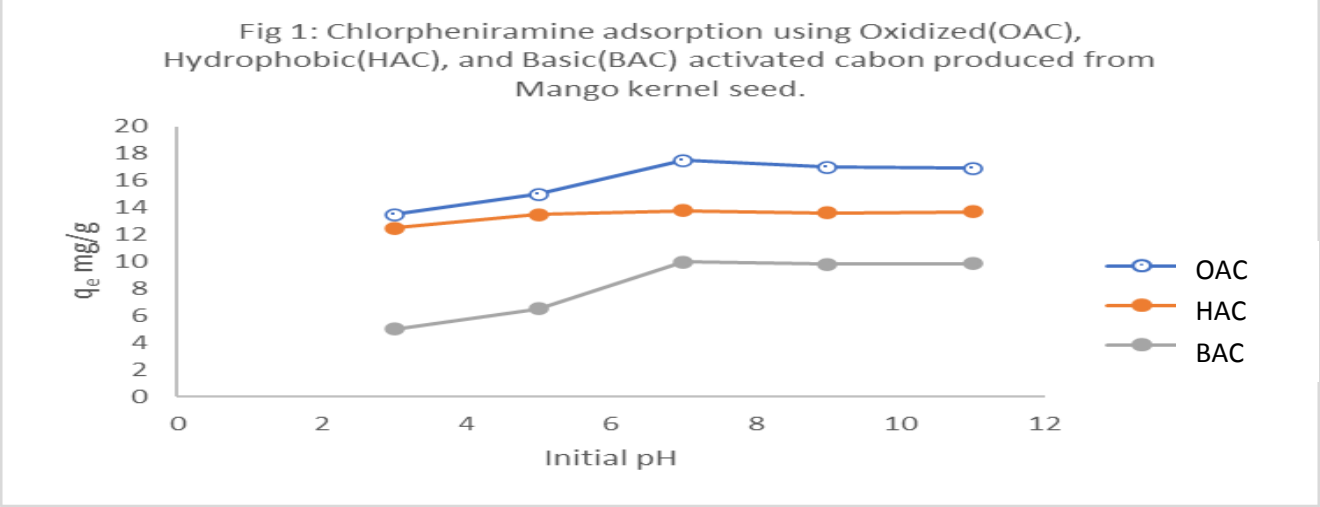
Parameter	AC(mango Karnel)
Moisture content %	8.20
Ash content %	0.90
Pore volume cm^3	0.58
Density gcm^{-3}	1.43
Surface area m^2g^{-1}	490.5

From Table 1, BET surface area of the adsorbent, MKSAC, was found to be 490 $m^2 g^{-1}$ which indicates MKSAC to be a very good adsorbent for efficient adsorption of pollutants from pharmaceutical liquid waste .The other physical properties like bulk density, porosity, average pore size of prepared activated carbon are given in Table 1 which may affect the adsorption capacity.

Effect of pH on drug adsorption

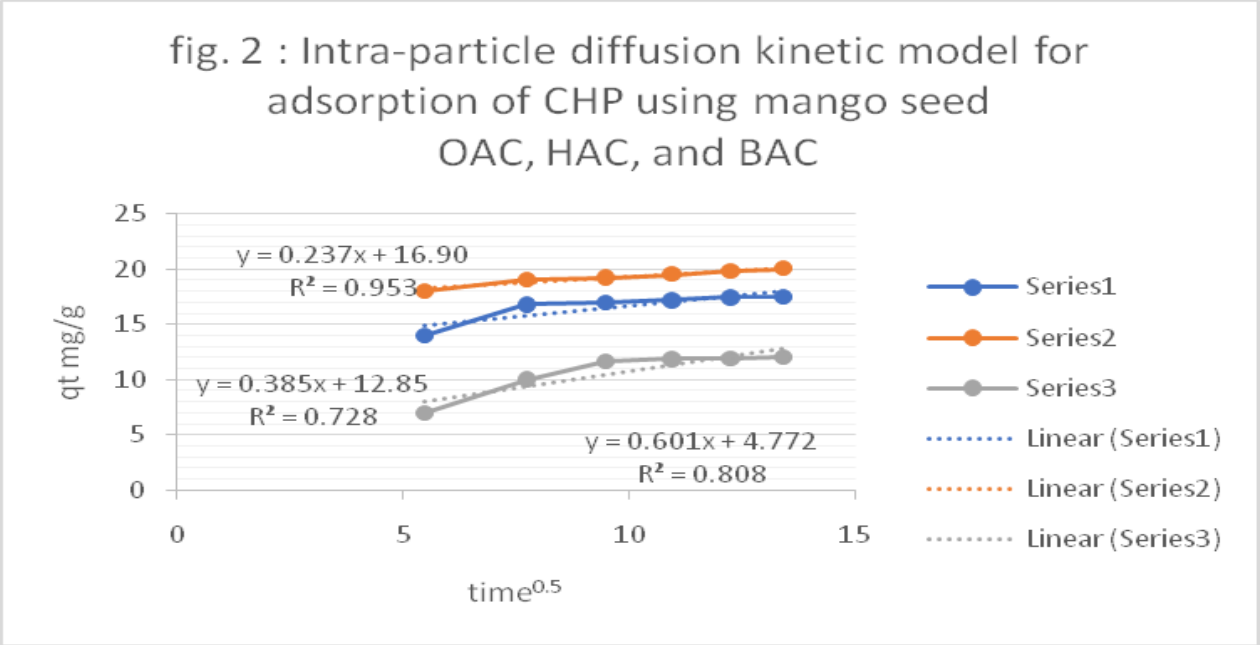
The pH effect on Chlorpheniramine (CHP) adsorption using OAC, HAC and BAC of mango kernel seedare presented in Fig. 1. CHP adsorptionon all the modified activated carbon of the materials above appears almost the same. Showing optimal adsorption at pH 7 in each case. OAC of mango seed possesses high pore volume (1.88cm^3) with less extent of carboxylic groups [El-Shafey et al, 2016] indicating that CHP adsorption on OAC takes place mostly via van der Waals interaction forces. Based on the pH range of the modified carbon, OAC is negatively charged and CHP is positively charged (on the tertiary amine group), thus, an extent of electrostatic attraction takes place between positively charged CHP and negatively charged OAC showing a maximum at initial pH 7.

For HAC and BAC, CHP shows almost same trend of adsorption as the pH approaches 7. Hydrophobic interactions between immobilized ethyl chains on HAC and hydrophobic parts of CHP molecule are expected to dominate. BAC shows the lowest uptake of CHP. Both CHP and BAC surface remain positively charged leading possibly to electrostatic repulsion and less CHP adsorption.



Effect of Contact time/Kinetic on drug adsorption

Adsorption of CHP was found fast reaching equilibrium in 120–150min for OAC, HAC and BAC. CHPuptake varies almost linearly with the half power of time in the early stages of its adsorption. kd for CHPdiffusion on BAC of all the adsorbents, show high values indicating faster diffusion mostly due to the electrostatic attraction between opposing charges of the CHP and BAC surfaces, but low for OAC and HAC fig.



As presented in Table 2, R^2 values are higher for pseudo second order model than for pseudo first order model indicating better fittingto pseudo second order model. This indicates that drug adsorption depends on both the adsorbate and the adsorbent, and suggests a mechanism of sharing or exchange of electrons between the carbon surface and the drug molecules [3]. Even the qe theorical for second order shows strong acceptance to these adsorptions.

Adsorption isotherm study

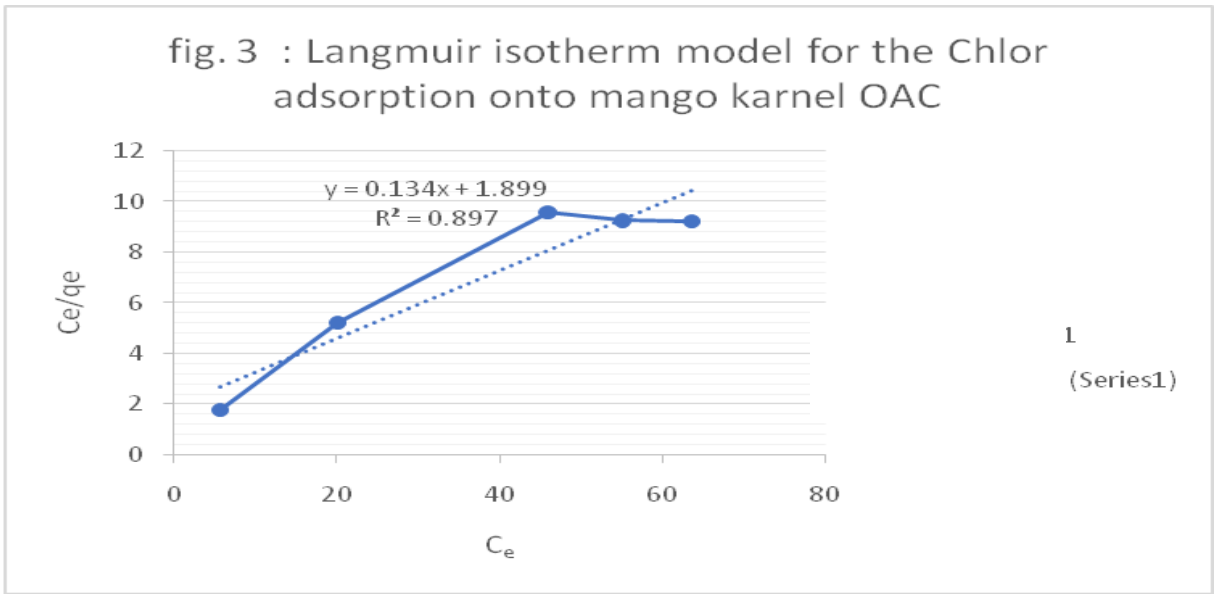
Table 2: Kinetic parameters for the adsorption of CHP on mango seed OAC, HAC, and BAC

Kinetic model	Mango seed AC	parameters				
Pseudo first-order model		slope	Intercept	R^2	K_1	q_e(theo)
$\ln(q_e-q_t)=\ln q_e-k_1 t$	OAC	-0.0311	2.0039	0.9283	0.0311	7.41793
	HAC	-0.0177	1.223	0.9583	0.0177	3.397365
	BAC	-0.0345	2.5552	0.9686	0.0345	12.87387
Pseudo second-order model					k_2	
$t/q_t = 1/k_2 q_e^2 + t/q_e$	OAC	0.0547	0.3974	0.9995	0.007529	18.28154
	HAC	0.0489	0.235	0.9998	0.010175	20.4499
	BAC	0.0722	1.7211	0.9937	0.003029	13.85042

Table 3: Adsorption isotherm parameter for Chlorpheniramine removal using mango karnel seed OAC, HAC, BAC

Activated	Langmuir				Freundlich						
Carbon AC	q_m	k_L	R_L	R^2	1/n	N	R^2	Lan slope	Lang Inte	Freu slope	Freu Inte/Kf
OAC	7.462687	0.070545	0.150521	0.897	0.2804	3.566334	0.8501	0.134	1.8995	0.2804	0.6254
HAC	7.955449	0.096028	0.115178	0.9613	0.2375	4.210526	0.9331	0.1257	1.309	0.2375	0.9304
BAC	4.374453	0.107198	0.104429	0.9543	0.1956	5.112474	0.8707	0.2286	2.1325	0.1956	0.5048

Two isotherm models which are Langmuir and Fleundlich were used for the treatment of adsorption data. Although Fleundlich have good fittings, the Langmuir had the best fittings with R^2 values of 0.897, 0.9613 and 0.9543 for OAC, HAC and BAC of mango kernel seed respectively as against Fruendlich R^2 of 0.8501, 0.9331 and 0.8707 for OAC, HAC and BAC of mango kernel seed respectively in the adsorption of Chlorpheniramine. Also the q_m values are very close to the experimental values. The fitness of the adsorption data into the Langmuir isotherm model is an indication that monolayer coverage of chlorpheniraminetook place on the homogeneous surface of all the activated carbon samples. From the dimensionless separation constant, R_L, the adsorption is favourable, being that R_L values are less than 1 and greater than 0(Kanga et al 2019). Nevertheless, the value of 1/n from the Freundlich isotherm model, is below 1 in all the adsorptions, showing that the adsorption process is normal adsorption, indicating a favourable sorption process [4].



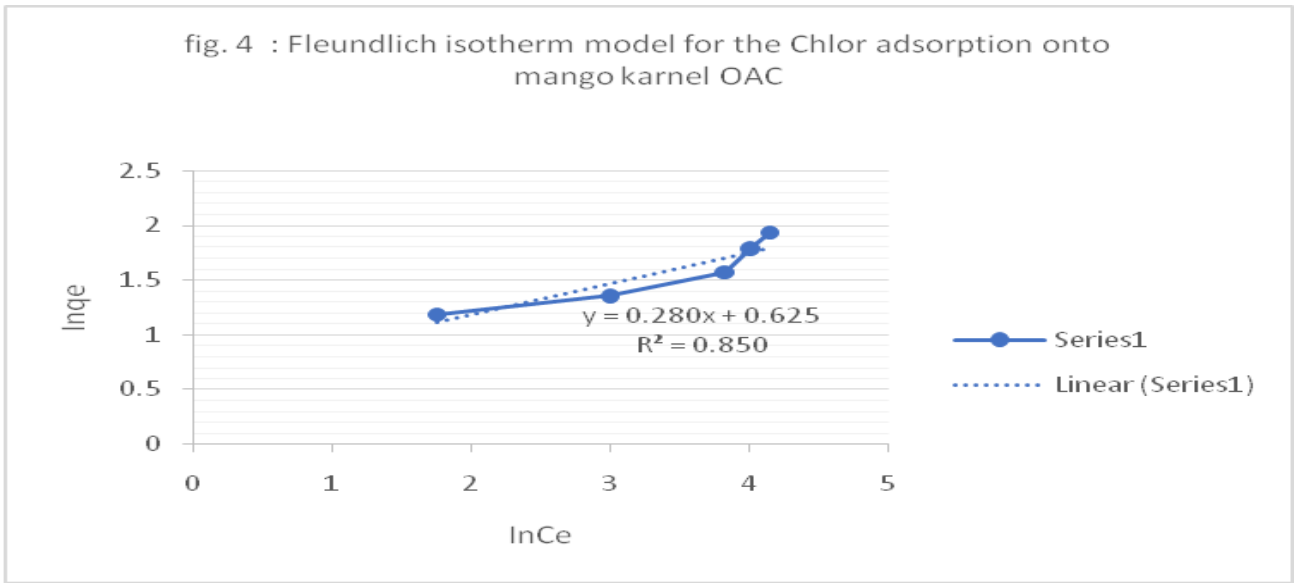


fig. 4 : Fleundlich isotherm model for the Chlor adsorption onto mango karnel OAC
lnqe
lnCe
y = 0.280x + 0.625
R² = 0.850
Series1
Linear (Series1)
2.5
2
1.5
1
0.5
0
0
1
2
3
4
5

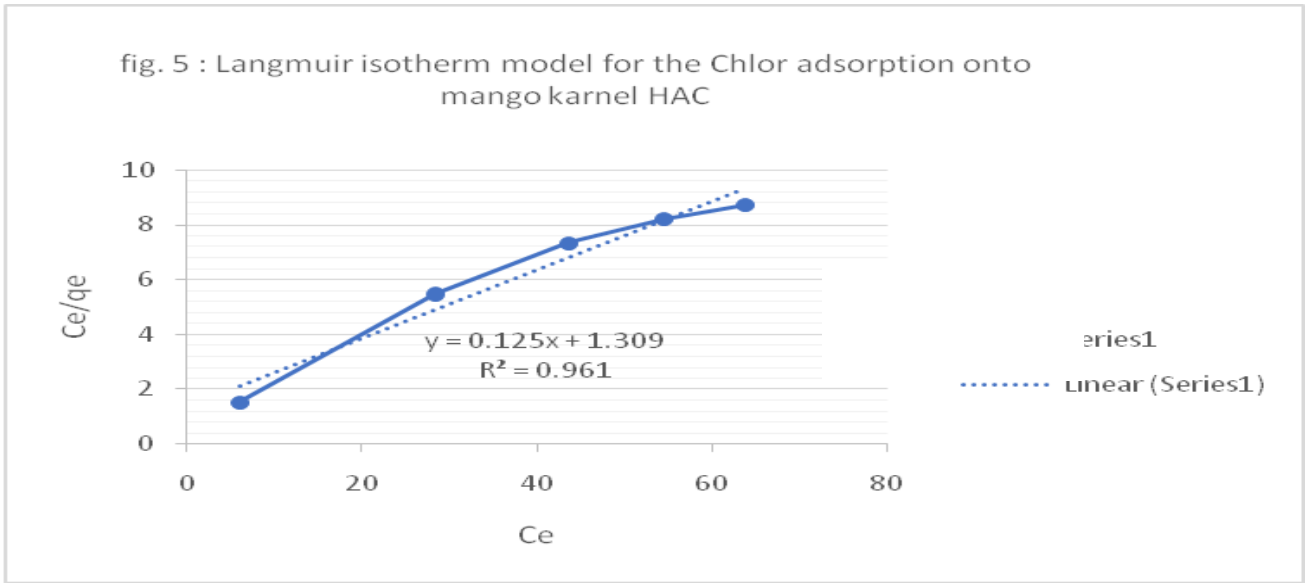


fig. 5 : Langmuir isotherm model for the Chlor adsorption onto mango karnel HAC
Ce/qe
Ce
y = 0.125x + 1.309
R² = 0.961
eries1
Linear (Series1)
10
8
6
4
2
0
0
20
40
60
80

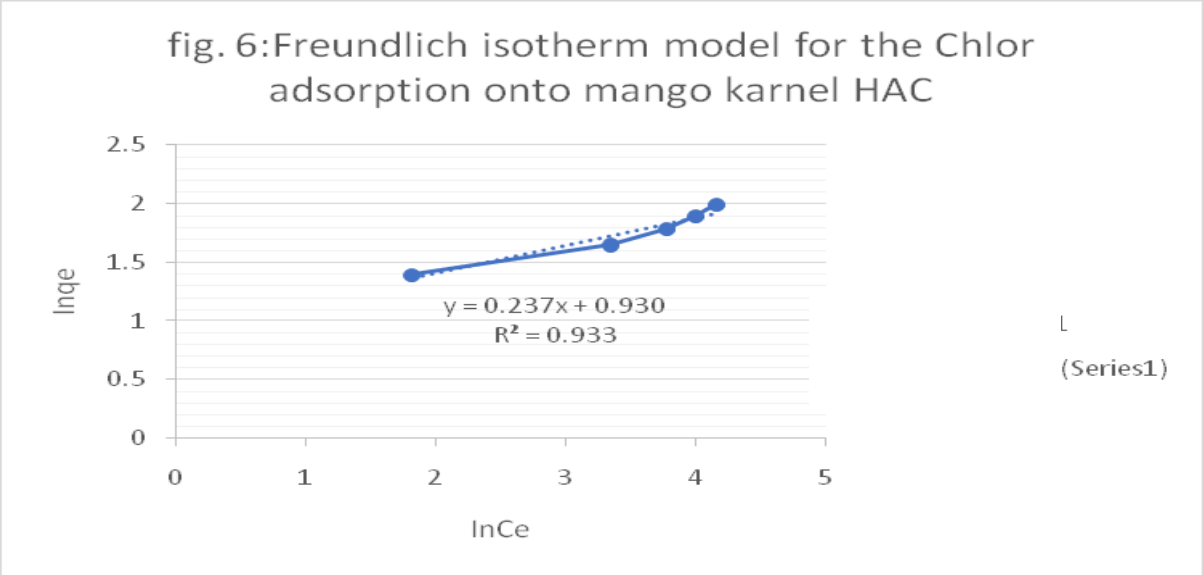


fig. 6:Freundlich isotherm model for the Chlor adsorption onto mango karnel HAC
lnqe
2.5
2
1.5
1
0.5
0
y = 0.237x + 0.930
R² = 0.933
0
1
2
3
4
5
lnCe
L
(Series1)

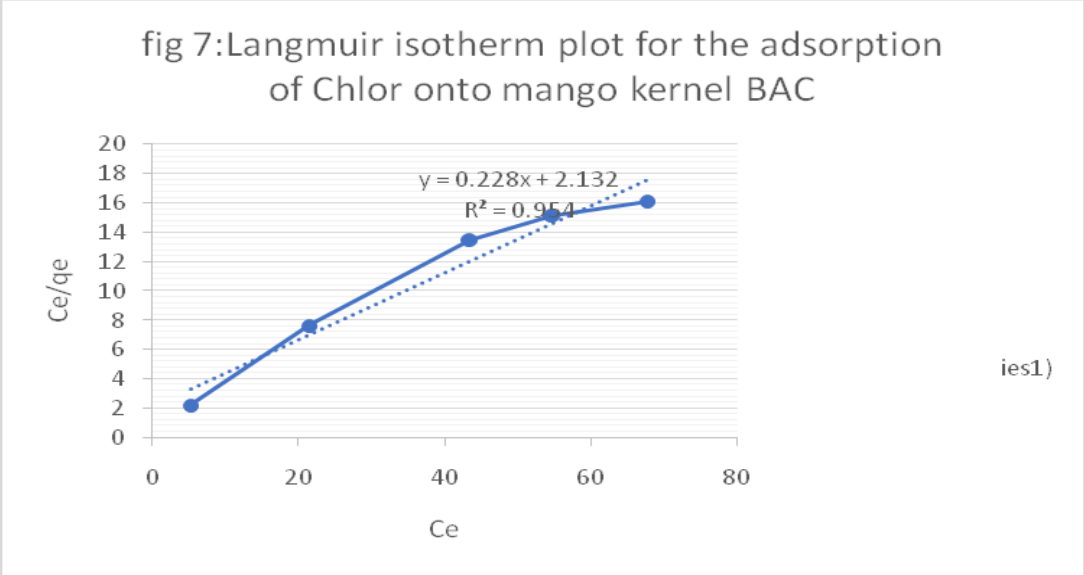
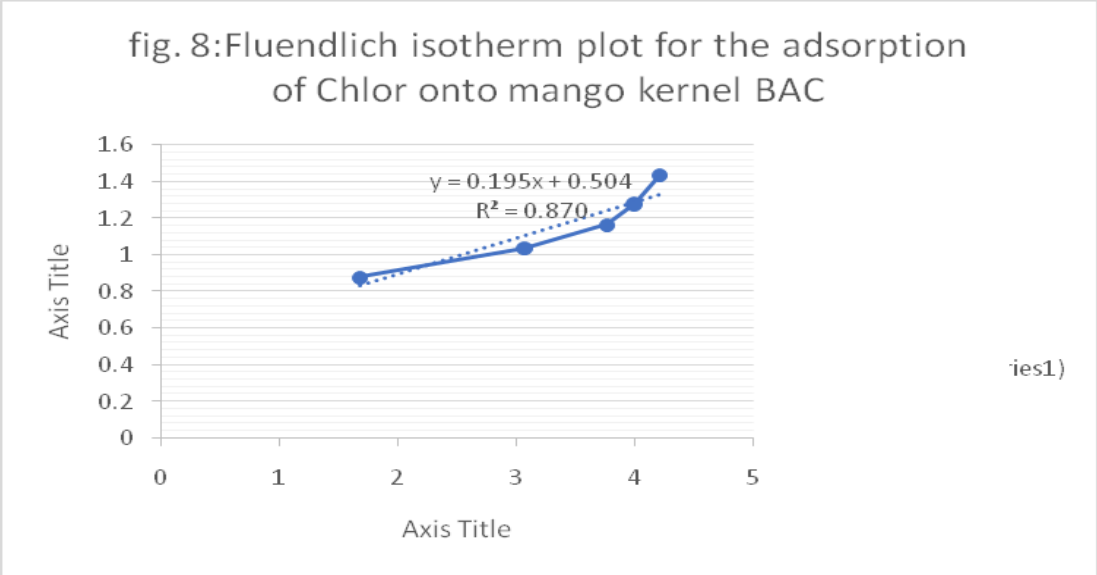


fig 7:Langmuir isotherm plot for the adsorption of Chlor onto mango kernel BAC
Ce/qe
20
18
16
14
12
10
8
6
4
2
0
y = 0.228x + 2.132
R² = 0.954
0
20
40
60
80
Ce
ies1)



Thermodynamic study

Table 4 : Thermodynamic parameters for chlor adsorption using mango karnel seed OAC, HAC, and BAC

Temp ^{0}C	Temp K	1/Temp	Ce	Qe	Kc	In Kc	ΔG(J/mol)	ΔH(J/mol	ΔS(J/molK)	Slope	Intercept
25	298	0.003356	62.8	138.788	2.21	0.792993	-1964.7	9298.378	37.72228	-1118.4	4.5372
35	308	0.003247	58.6	142.398	2.43	0.887891	-2273.63				
45	318	0.003145	52.3	146.44	2.8	1.029619	-2722.16				
25	298	0.003356	67.8	285.438	4.21	1.437463	-3561.42	2805.227	21.38444	-337.41	2.5721
35	308	0.003247	63.5	279.4	4.4	1.481605	-3793.96				
45	318	0.003145	58.4	263.968	4.52	1.508512	-3988.28				
25	298	0.003356	63.6	532.332	8.37	2.124654	-5263.98	21051.05	88.67712	-2532	10.666
35	308	0.003247	60.6	765.984	12.64	2.536866	-6496.18				
45	318	0.003145	58.4	831.616	14.24	2.656055	-7022.22				

The negative ΔG values in Table 4, for the adsorption of CHP using each of the adsorbent from mango kernel seed showed that drug adsorption is spontaneous and thermodynamically favorable [5]. ΔG^{o} for the drug adsorptions using the OAC of the adsorbent material show less values than that of HAC and BAC, indicating that less driving force is required for adsorption using OAC when compared with HAC and BAC of the mango kernel seed used. The positive values of ΔH for the CHP adsorption show that adsorption is endothermic with values<40 kJ/mol indicating physisorption processes domination (chemisorption, ΔH^{o}>40 kJ/mol) [6]. The positive values of ΔS^{o} show an increase in randomness at the solid-solution interface during the adsorption process of the drugs on all the three adsorbents [7].

Percentage adsorption from spiked Pharmaceutical Liquid Waste (PLW)

Table 5: %adsorption of Chlorpheniramine from deionized water and pharm. effluents using OAC, HAC, and BAC prepared with mango seed.

time		**qe (Deionized)**			**% Removal (Deionized)**			**qe (Effluent)**			
time	sqrt (t)	$qe_{(OAC)}$	qe HAC	qe BAC	$\%_{(OAC)}$	%HAC	%BAC	HAC	BAC	qe(OAC)	qe
30	5.477226	14	18	7	56	72	28	0.30429	0.782461	13.6	
60	7.745967	16.8	19	10	67.2	76	40	0.407682	0.774597	15.2	
90	9.486833	17	19.2	11.6	68	76.8	46.4	0.494106	0.81783	16.4	
120	10.95445	17.2	19.5	11.84	68.8	78	47.36	0.561767	0.925207	16.8	
150	12.24745	17.45	19.8	11.9	69.8	79.2	47.6	0.618558	1.029197	17.25	
180	13.41641	17.5	17.5	17.5	70	70	70	0.766652	0.766652	17.35	

A plot of the percentage adsorption with time of Chlorpheniramineon the carbons of Mango kernel seedfrom spiked PLW at 25 ˚C are shown in figure5 above. The adsorption data show a gradual increase in the percentage adsorbed with time. This is in agreement with that obtained from the drugs in deionized water as can be seen in table 5. The adsorption capacity, q_e and %Adsorbed with time, from the spiked PLW of the different carbons follow similar order to that of Chlorpheniraminefrom deionized water. For carbons of mango kernel seed on chlorpheniramine, from both deionized water and spiked PLW, the trends is: HAC > OAC > BAC. This could be due to the expected domination of the hydrophobic interactions between immobilized ethyl chains of HAC and hydrophobic parts of Chlorpheniramine molecule.BAC show the lowest uptake of CHL. This could be because, at the pH of the deionized and spiked PLW when the adsorption was done, both the drug and BAC surfaces remain positively charged leading possibly to electrostatic repulsion and less CHL adsorptions. Meanwhile it is expected that at higher pH 7-11, adsorption may increase as the drugs become less protonated while the BAC become deprotonated and thereby decreasing the extent of electrostatic repulsion and allowing probably an extent of H-bonding between the deprotonated amine groups on both CHL and BAC surfaces. However, there were less uptake from spiked PLW than from deionized water. Such decrease in drug uptake from spiked PLW is probably because of the competition of dissolved organic substances, available in spiked PLW, with Chlorpheniraminemolecules for adsorption sites on the adsorbents.

CONCLUSION

Activated carbon prepared from mango kernel seedpossesses high surface area and limited surface functional groups. Oxidized activated carbon possesses acidic surface properties with much low surface area than activated carbon. Surface functionalization of OAC to produce basic and hydrophobic activated carbons (BAC and HAC) were largely successful with a further decrease in their surface area. Chlorpheniramineinteract differently with the carbons under investigation depending on the nature of carbon surface. Adsorption forces involved in Chlorpheniramineadsorption include hydrophobic bonding, electrostatic interaction, H-bonding and van der Waals forces. Despite possessing a very low surface area (by nitrogen adsorption), HAC shows the best performance in Chlorpheniramineremoval in terms of kinetics, equilibrium isotherm and thermodynamic. The current study showed that functionalized surfaces can play betterrole in the removal of Chlorpheniramine, from aqueous solution than activated carbon with high surface area. OAC with a high content of -COOH shows better drug removal through electrostatic attraction for Chlorpheniramine. HAC shows the highest adsorption capacity for Chlorpheniramine because of dominating hydrophobic interaction forces. BAC shows lower adsorption capacity for Chlorpheniramine and this can be related to surface crowdedness and H-bonding among the amine groups on the surface. From literature, Activated Carbon (unoxidized) possesses high surface area and well-developed porous structure with dominating van der Waals forces. However, it shows the slowest process of drug uptake compared with the other carbons. OAC and other functionalized activated carbons show good capability of drug removalfrom spiked PLW. Surface functionalization of activated carbon shows a promising solution for pharmaceuticals removal from deionized water as well as pharmaceutical liquid waste.

REFERENCES

1. El-Shafey, E.I., Syeda N. F. Ali, Saleh Al-Busafi, Haider A. J. Al-Lawati. (2016). Preparation and characterization of surface functionalized activated carbons from date palm leaflets and application for methylene blue removal. *Journal of Environmental Chemical Engineering,* 4(3), 2713-2724. ISSN 2213-3437. doi:10.1016/j.jece.2016.05.015.
2. El-Shafey, E., Al-Lawati, H., Al-Sumri, A. S. (2012). Ciprofloxacin adsorption from aqueous solution onto chemically prepared carbon from date palm leaflets, *Journal of Environmental Sciences*, Volume 24, Issue 9,1579-1586,doi.org/10.1016/S1001-0742(11)60949-2.
3. Syeda, N. F. Ali, E. I. El-Shafey, Saleh Al-Busafi, Haider A. J. Al-Lawati (2019). Adsorption of chlorpheniramine and ibuprofen on surface functionalized activated carbons from deionized water and spiked hospital wastewater. *Journal of Environmental Chemical Engineering*. 7:2213-3437.
4. Soo, Yuchoong; Chada, Nagaraju; Beckner, Matthew; Romanos, Jimmy; Burress, Jacob; Pfeifer, Peter (2013). "Adsorbed Methane Film Properties in Nanoporous Carbon Monoliths". *Bulletin of the American Physical Society*. **58** (1): M38.001. Bibcode:2013APS..MARM38001S.