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Evaluation of isotherm parameters for adsorption of Chlorpheniramine (CHP), Ibuprofen (IBU) and Glipizide (GLI) using OAC, HAC and BAC of mango kernel seed.

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ABSTRACT

Some pharmaceutical drug residues have been found in water bodies, soil and air. Large concentration of these drugs in the environment could cause several diseases to man, animals and even plants. Therefore, efficient removal system of these drugs is paramount. Adsorption isotherm parameters for adsorption of Chlorpheniramine (CHP), Ibuprofen (IBU) and Glipizide (GLI) using OAC, HAC and BAC of mango kernel seed was examined in this study. Activated carbons (ACs), Oxidized activated carbons (OAC), hydrophobic activated carbons (HAC) and basic activated carbons (BAC) prepared from mango kernel seed were employed in this study. ACs were prepared from mango kernel seed (MKSAC), through KOH activation. The ACs were oxidized with HNO_3 to produce OACs that were surface functionalized using ethylene diamine to produce BACs and ethylamine to produce HACs. The adsorption isotherm parameters were comparatively determined. From our result, equilibrium adsorption was reached faster 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 CHP uptake follows the order: HAC > OAC > BAC whereas the adsorption of IBU and GLI follow the order: OAC > HAC > BAC for mango kernel seed. OAC, HAC and BAC of mango kernel seed showed good potential for Chlorpheniramine, Ibuprofen and Glipizide removal from pharmaceutical liquid waste.

Keywords: Chlorpherinamine, Glipizide, Ibuprofen, Freundlich model, Langmuir model and Adsorption isotherm.

INTRODUCTION

Some pharmaceutical drug residues have been found in water bodies, soil and air. Large concentration of these drugs in the environment could cause several diseases to man, animals and even plants. Chlorpherinamine is an antihistamine used to treat the symptoms of allergic disorders [1]. There are reports of Chlorpheniramine posing dangerous effects to man when its residues are discharged into the environment. Chlorpheniramine generates reactive oxygen species in excess amount that could overwhelm the body's internal defense system. This could lead to various diseases with the liver and heart as major target organs [2]. Ibuprofen belongs to the nonsteroidal anti-inflammatory drug (NSAID) class of drugs. It is used to treat pain, fever, and inflammation. It can also be used to treat inflammatory diseases like rheumatoid arthritis [3]. The toxic effects of ibuprofen to aquatic animals are well-documented [4-8]. Glipizide is a member of class of drugs called sulfonylureas. Glipizide enhances the release of insulin by the pancreas. Thus, it is used in the treatment of Diabetes mellitus [9]. Unwarranted efflux of Glipizide contributes to environmental pollution with adverse effects ranging from hyponatremia, hypoglycemia, allergy, low blood cell counts,

and liver cirrhosis [9]. Due to the outlined adverse effects of indiscriminate removal system of these drugs, it is crucial to adsorb these drugs from pharmaceutical effluents using surface functionalized activated carbon so as to avert the harmful effects of the drug residues in the environment. Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or solid-dissolved gas or liquid to a surface [10].Adsorption occurs in a variety of physical, biological, chemical, and natural systems. It is frequently used in industrial settings for things like water filtration, heterogeneous catalysts, activated charcoal, capturing and using waste heat to create cold water for air conditioning and other process needs (adsorption chillers), synthetic resins, and increasing the storage capacity of carbons made from carbides [11]. During the sorption processes of adsorption, ion exchange, and chromatography, certain adsorbates move from the fluid phase to the surface of insoluble, rigid particles that are suspended in a vessel or packed into a column. Adsorption is a result of surface energy, just like surface tension. In a bulk material, other atoms in the material fill all of the ionic, covalent, or metallic bonding gaps left by the constituent atoms. Adsorbate can be attracted to atoms on the surface of the adsorbent because they are partially surrounded by other adsorbent atoms. The specifics of the species involved will determine the type of bonding, but the adsorption process is typically categorised as either physisorption (characterised by weak van der Waals forces) or chemisorption (characterised by covalent bonding). It might also happen as a result of electrostatic attraction [12].

Isotherms describe the amount of adsorbate on the adsorbent as a function of pressure (for gas phase solutes) or concentration (for liquid phase solutes) at constant temperature. To enable comparison of various materials, the quantity adsorbed is almost always normalized by the adsorbent's mass. Different isotherm models have been stipulated but the commonest two are Freundlich and Langmuir models [13]. In 1906, Freundlich and Kuster published the first formula for a mathematical fit to an isotherm, which is purely empirical and applies to gaseous adsorbates: $x/m=kp1/n$

Where x is the mass of adsorbate that has been adsorbed, m is the mass of the adsorbent, p is the pressure of the adsorbate (which can be changed to concentration if studying a solution rather than a gas), and k and n are empirical constants for each pair of adsorbent and adsorbate at a specific temperature. Because x/m has an asymptotic maximum as pressure increases without bound, the function is insufficient at very high pressure. The constants k and n change with temperature in order to account for the empirical finding that the quantity adsorbed rises more slowly and higher pressures are needed to saturate the surface. In 1918, Irving Langmuir became the first person to derive an adsorption isotherm with a scientific foundation [14]. Gases that are adsorbed on solid surfaces are covered by the model. It was derived using statistical thermodynamics and is a semi-empirical isotherm with a kinetic basis. Because of how easily it can fit a variety of adsorption data and how easily it can be used, it is the most widely used isotherm equation. Langmuir isotherm is frequently used in surface kinetics (often referred to as Langmuir-Hinshelwood kinetics) and thermodynamics models of adsorption. Mango is an edible fruit produced by *Mangifera indica*. It originated in the Myanmar, Bangladesh, and northeastern part of India. At present, mango has spread across the globe including Nigeria. Mangos belongs to the family Anacardiaceae's genus *Mangifera* [15]. The seed embryos of mango varieties can either be monoembryonic or polyembryonic. Mango seeds are contained in the fruit and are usually disposed after consumption of the fruit or can be used by industries after processing for various purposes [16]. Surface functionalization can introduce other some adsorption forces such as H-bonding, electrostatic interaction, and hydrophobic bonding. An activated carbon surface can be tailored to utilize such powerful adsorption forces via chemical modification. In the present study, we examined adsorption isotherm parameters for adsorption of Chlorpheniramine, Ibuprofen and Glipizide. Activated

carbons (ACs), Oxidized activated carbons (OAC), hydrophobic activated carbons (HAC) and basic activated carbons (BAC) prepared from mango kernel seed were employed in this study.

MATERIALS AND METHODS

Materials

All chemicals used were of analytical grade. Mango kernel seeds (MKS) were collected from Orji village, Amokwe in Udi Local Government area, Enugu State, Nigeria. They were identified by a taxonomist in Botany Department of Nnamdi Azikiwe University, Awka. They were washed thoroughly with distilled water to remove dirt, sun dried for about a week and then ground to a fine powder.

METHODS

Preparation of Activated carbon (AC)

Clean dry seeds (25g) were charred differently 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 a nitrogen atmosphere at 500 oC for 2 hours. In a weight ratio of 1:3, the chars were impregnated with saturated KOH solution. 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. The temperature was raised from room temperature to 550°C at a heating rate of ~8.6°C/min and was kept at 550°C for 1 hour under nitrogen for activation. The ACs produced were washed thoroughly with deionized water to remove residual alkalinity. To keep the acidic functional groups on the carbon in H-form, ACs were washed with 0.1M HCl followed by deionized water until no acidity was detected in the wash water. All the ACs of MKS, APS, and VTS were dried at 120°C until they reached a constant weight. After cooling in a desiccator and grinding, a size range of each between two sieves of 1.19 mm and 0.25 mm was selected for characterization.

Surface modification of activated carbon AC

AC surfaces were heated with concentrated HNO_3 (1 g AC: 10 mL acid) at 80°C to almost dryness to produce Oxidized Activated Carbons (OACs), that were washed thoroughly until no acidity was detected in the wash water. OACs were dried at 120°C until a constant weight was achieved. The surfaces of OACs were functionalized to produce Basic Activated Carbons (BACs) by reacting 15 g of dry OAC 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 of 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 (HACs), 15 g of dry OAC each 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 a 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. At the end of the functionalization steps for both types of surface functionalized carbons (BACs and HACs), 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 the 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 a constant weight was reached. Surface functionalization using EDA produced Basic Activated Carbon-Mango Kernel Seed (BAC-MKS) of MKS. For hydrophobic carbons, surface modification using EA produced Hydrophobic Activated Carbon (HAC-MKS) of MKS.

Preparations of Stock Solutions of Chlorpheniramine, Glipizide, and Ibuprofen

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

Chlorpheniramine: A stock solution containing 50mg/L chlorpheniramine in maleate form, was prepared by dissolving 50mg of chlorpheniramine in deionized water in a 1000mL volumetric flask.

Glipizide: An initialdiluent was prepared through a mixture of water, acetonitrile, and methanol (3:1:1) and a mobile phase consisting of acetonitrile: 0.01M potassium di-hydrogen phosphate buffer (pH 3.5) in a ratio of 35:65, which was degassed by sonification.

A stock solution containing 50mg/L glipizide was prepared by accurately weighing about 50mg of glipizide and transferring the same into a 1000mL volumetric flask. Adding 50mL of diluent and keeping it in an ultrasonic bath until it dissolved completely. Make it up to the mark with the mobile phase and mix.

Ibuprofen: In a 1000mL volumetric flask, a stock solution containing 50mg/L ibuprofen was prepared by dissolving 50mg of ibuprofen in some 20% methanol to achieve complete solubility with deionized water. 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 a diode array detector (Agilent technologies, 1260 Infinity Series, USA) was used for the analysis of chlorpheniramine, ibuprofen, and Glipizide, at λmax 260 nm. The drugs were separated using a C18 analytical column and a mobile phase consisting of methanol and 20mm ammonium format buffer (pH 4.8) in a gradient elution mode with a flow rate of 45 μL/min and a column temperature of 40 °C. Calibration standards of the three drugs (1–20 mg/L) were prepared and standard curves were obtained by linear regression of the mean values of peak areas. Retention times for Chlorpheniramine, Ibuprofen, and Glipizide were found to be 2, 6.5, and 7 minutes, respectively. For chlorpheniramine, the linear range was found to be between 1–20 mg/L (R2: 0.9995). For Ibuprofen, the linear range was found to be between 1–20 mg/L (R2: 0.9996). For Glipizide, the linear range was found to be between 1–20 mg/L (R2: 0.9994). The accuracy of the method of analysis shows more than 98.2% recovery for both drugs [17].

Sorption Studies

The effect of initial pH on chlorpheniramine, ibuprofen, and glipizide adsorption was carried out by mixing 0.06 g of each of the carbons, OACs, HACs, and BACs, with 25 mL of drug (50 mg/L) solution in a glass vial. The initial pH was pre-adjusted to be between 3–11 for chlorpheniramine and 5–11 for Ibuprofen and Glipizide using 0.1M NaOH and/or 0.1M HCl prior to carbon mixing. After carbon mixing, the solution was kept under mechanical agitation until equilibrium was reached at 25 °C. The final pH was recorded and the residual drug concentration was analyzed. Initial pH 7.0 was found optimal for chlorpheniramine, ibuprofen, and glipizide adsorption and was selected as the 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:

$$qe = (Co - Ce)V/m \quad (i)$$

$$qt = (Co - Ce)V/m \quad (ii)$$

$$\%rem = (Co - Ce)100/Co \quad (iii)$$

Kinetic Experiment

The kinetic experiment of each of the drugs' adsorption was studied by mixing 0.1g of carbons from mango kernel seed (OACs, HACs, and BACs) with 50 mL (50mg/L) at an initial pH of 7.0. The adsorption mixtures were kept at 25°C under mechanical agitation for 180 min, during which the equilibrium was reached. At different time intervals, samples were separated for analysis. The filtrate obtained was then analyzed for chlorpheniramine, ibuprofen, and glipizide concentrations. Results obtained were analyzed using pseudo first-order, pseudo second-order and Intra-particle diffusion kinetic models.

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

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; $t/q_t = 1/k_2q_e^2 + t/q_e$ (v)

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

$qt = kit^{0.5} + C$ (vi)

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 filtrate obtained was then analyzed for chlorpheniramine, glipizide, and ibuprofen concentrations. Results obtained were analyzed using Langmuir and Freundlich isotherm models.

Langmuir: $Ce/qe = 1/qmKL + Ce/qm$ (vii)

Freundlich: $Inqe = Inkf + 1/nInCe$ (viii)

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.

RESULTS AND DISCUSSION

Adsorption isotherm parameters for adsorption of Chlorpheniramine (CHP), Ibuprofen (IBU) and Glipizide (GLI) using OAC, HAC and BAC of mango kernel seed.

Table 1: Adsorption isotherm parameter for CHP removal using mango kernel seed OAC, HAC, BAC

Activated Carbon AC	Langmuir				Freundlich						
	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

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Table 2: Adsorption isotherm parameter for IBU removal using mango Kernel seed OAC, HAC, BAC

Activated Carbon AC	Langmuir				Freundlich							
	q_m	k_L	R_L	R^2	k_f	1/n	N	R^2	Lan slope	Lang Inte	Freu slope	Freu Inte
OAC	8.097166	0.092976	0.11851	0.9663	2.696892	0.2206	4.533092	0.9033	0.1235	1.3283	0.2206	0.9921
HAC	9.891197	0.062573	0.166503	0.9486	2.504277	0.2727	3.667033	0.9052	0.1011	1.6157	0.2727	0.918
BAC	8.361204	0.040787	0.234578	0.876	1.391664	0.348	2.873563	0.8521	0.1196	2.9323	0.348	0.3305

Table 3: Adsorption isotherm parameter for GLI removal using mango kernel seed OAC, HAC, BAC

Activated Carbon AC	Langmuir				Freundlich							
	q_m	k_L	R_L	R^2	k_f	1/n	N	R^2	Lan slope	Lang Inte	Freu slope	Freu Inte
OAC	7.830854	0.284981	0.042019	0.9869	4.436652	0.1255	7.968127	0.88	0.1277	0.4481	0.1255	1.4899
HAC	10.26694	0.144532	0.079602	0.975	3.64188	0.2332	4.288165	0.9562	0.0974	0.6739	0.2332	1.2925
BAC	8.561644	0.145745	0.078991	0.9682	3.80532	0.1699	5.885815	0.8355	0.1168	0.8014	0.1699	1.3364

Two isotherm models, which are Langmuir and Fleundlich, were used for the treatment of adsorption data. Although Fleundlich had 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 R2 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 chlorpheniramine, ibuprofen, and glipizide took 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 zero [18]. 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 [19].

REFERENCES

1. Gray, Shelly L.; Anderson, Melissa L.; Dublin, Sascha; Hanlon, Joseph T.; Hubbard, Rebecca; Walker, Rod; Yu, Onchee; Crane, Paul K.; Larson, Eric B. "Cumulative Use of Strong Anticholinergics and Incident Dementia: A Prospective Cohort Study". *JAMA Intern. Med.,* 2015: **175** (3):401–7. .
2. Sherifa, S. Hamed, Sherine Abdel Salam, Manal F. El-Khadragy, Wafa A. AL-Megrin, Zeinab K. Hassan and Esraa M. Shuker. Chlorpheniramine Maleate Induced Cardiotoxicity, Hepatotoxicity and Antioxidant Gene Expression Changes in Male Wistar Rats. *International Journal of Pharmacology*, 2020; **16**: 351-366.
3. British National Formulary. Pharmaceutical Press, London, 67th Revised edition March 7, 2014.
4. Mohd Zanuri, N. B., Bentley, M. G. and Caldwell, G. S. Assessing the impact of diclofenac, ibuprofen and sildenafil citrate (Viagra®) on the fertilisation biology of broadcast spawning marine invertebrates. *Mar. Environ. Res.,* 2017; 127: 126-136
5. Di Nica, V., Villa, S. and Finizio, A. Toxicity of individual pharmaceuticals and their mixtures to Aliivibrio fischeri: Experimental results for single compounds and considerations of their mechanisms of action and potential acute effects on aquatic organisms. *Environ. Toxicol. Chem.,* 2017; 36 (3): 807-814.
6. Ding T, M. Yang, J. Zhang, B. Yang, K. Lin, J. Li, J. Gan. Toxicity, degradation and metabolic fate of ibuprofen on freshwater diatom Navicula sp. *J. Hazard Mater*, 2017; 330: 127-134.
7. Geiger, E., Hornek-Gausterer, R. and Saçan, M.T. Single and mixture toxicity of pharmaceuticals and chlorophenols to freshwater algae Chlorella vulgaris. *Ecotoxicol. Environ. Saf.*, 2016; 129: 189-198
8. Grzesiuk, M., Wacker, A., Spijkerman, E. Photosynthetic sensitivity of phytoplankton to commonly used pharmaceuticals and its dependence on cellular phosphorus status. *Ecotoxicology*, 2016; 25: 697-707.
9. Klein-Schwartz, W., Gina, L. and Isbister, G. K. Treatment of sulfonylurea and insulin overdose. *British journal of clinical pharmacology,* 2016; **81**(3):496-504.
10. Glossary of MHRA terms – P. *U.K.* Medicines and Healthcare products Regulatory Agency. Retrieved 2008.
11. Czelej, K., Cwieka, K., Colmenares, J. C. and Kurzydlowski, K. J. "Insight on the Interaction of Methanol-Selective Oxidation Intermediates with Au-or/and Pd-Containing Monometallic and Bimetallic Core@Shell Catalysts". Langmuir, 2016; **32** (30): 7493-7502. doi:10.1021/acs.langmuir.6b01906. PMID 273 73791.

12. Ferrari, L., Kaufmann, J., Winnefeld, F. and Plank, J. "Interaction of cement model systems with superplasticizers investigated by atomic force microscopy, zeta potential, and adsorption measurements". *J. Colloid Interface Sci,* 2010;.**347** (1): 1524. Bibcode:2010JCIS..347...15F. doi:10.1016/j.jcis.2010.03.005. PMID 20356605.
13. Foo, K. Y.and Hameed, B. H. "Insights into the modeling of adsorption isotherm systems". *Chemical Engineering Journal,* 2010; **156** (1):2–10. doi:10.1016/j.cej.2009.09.013. ISSN 1385-8947. S2CID 11760738.
14. Czepirski, L., Balys, M. R. and Komorowska-Czepirska, E. "Some generalization of Langmuir adsorption isotherm". Internet Journal of Chemistry, 2000; **3**(14): 1099-8292.
15. Fowomola, M.A. Some Nutrients and Antinutrients Contents of Mango (Magnifera indica) Seed. *African Journal of Food Science*, 2010; 4: 472-476.
16. Puravankara, D., Boghra, V. and Sharma, R. S. Effect of antioxidant principles isolated from mango (*Mangifera indica* L) seed kernels on oxidative stability of buffalo ghee (butter-fat). *Journal of Science of food and Agriculture*, 2000; **80** (4): 522-526.
17. Syeda, N. F., El-Shafey, E. A. B. and Haider, S. A. Adsorption of chlorpheniramine and ibuprofen on surface functionalized activated carbons from deionized water and spiked hospital wastewater. *Journal of Environmental Chemical Engineering*, 2018; **7**(1): 102860. 10.1016/j.jece.2018.102860.
18. Kanga, L. H. B., Siebert, S. C., Sheikh, M. and Legaspi, J. C. Pesticide Residues in Conventionally and Organically Managed Apiaries in South and North Florida. *Curr Inves Agri Curr Res,* **7**(3)-2019. CIACR.MS.ID.000262.DOI:10.32474/CIACR.2019.07.000262.
19. Goldberg, S. Equations and Models Describing Adsorption Processes in Soils. *Soil Science Society of America, Madison*, 2005.