IAA Journal of Scientific Research 10(1):9-16, 2023. ISSN: 2736-7319

Percentage adsorption of Glipizide (GLI) from deionized water and sPLW using OAC, HAC, and BAC prepared with velvet tamarind shell.

Iloh Emmanuel Onyema
Department of Pure and Industrial Chemistry, Chukwuemeka Odumegwu Ojukwu University Anambra State, Nigeria.
Email :emmanuelonyemai@yahoo.com and eo.iloh@coou.edu.ng

ABSTRACT

The search for effective pharmaceutical drugs disposal system has been an expeditious research endeavor. Some of the adverse effects of improper pharmaceutical drugs disposal include abdominal gout, acute kidney failure, sexual dysfunction, dry throat, a drop in the number of aquatic animals, and pollution of the soil and water. Glipizide (GLI) belongs to the group of medications known as sulfonylureas. GLI triggers the body's natural insulin to be released, lowering blood sugar levels and hence used in the management of Diabetes mellitus. GLI is one of the drugs whose release into the environment could pose deleterious effect to man, aquatic lives and soil. This study was therefore designed to evaluate percentage adsorption of GLI from deionized water and spiked Pharmaceutical Liquid Waste (sPLW) using oxidized activated carbons (OAC), hydrophobic activated carbons (HAC) and basic activated carbons (BAC) prepared from velvet tamarind shell. Activated carbons (ACs) were prepared from velvet tamarind shell (VTSAC), 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 capacity, qe and percentage adsorbed with time, from the sPLW and deionized water were comparatively determined. The adsorption capacity, qe and % adsorbed with time, from the sPLW of the different carbons follow similar order to that of Glipizide, from deionized water. Drug adsorption from sPLW showed slightly less capacity than that from deionized water but the same trend in the percentage adsorbed by the different carbons as in the deionized water. Such decrease in drug uptake from sPLW is probably because of the competition of dissolved organic substances available in sPLW with GLI molecules, for adsorption sites on the adsorbents. OAC, HAC and BAC showed good capability for drug removal from sPLW. In conclusion, OAC, HAC, BAC prepared with velvet tamarind shell displayed commendable percentage adsorption of GLI from deionized water and sPLW and so could be explored for removal of GLI from pharmaceutical industries.

Keywords: Glipizide, deionized water, drug adsorption, spiked Pharmaceutical Liquid Waste, Surface functionalization.

INTRODUCTION

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or solid-dissolved gas or liquid to a surface [1].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 [2]. 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. The German physicist Heinrich Kayser first used the term "adsorption" in 1881[3]. During adsorption from solutions, adsorbed molecules are those that are resistant to

washing with the same solvent medium. Thus, the washing circumstances can alter the measurement outcomes, especially when the interaction energy is low [4]. Glipizide is one of the commonly produced drugs in the pharmaceutical industries whose effluent into the environment can lead to environmental pollution. Glipizide (GLI) belongs to the group of medications known as sulfonylureas. GLI triggers the body's natural insulin to be released, lowering blood sugar levels and hence used in the management of Diabetes mellitus [5]. GLI is one of the drugs whose release into the environment could pose deleterious effect to man, aquatic lives and soil.

Over the past few decades, there has been a lot of interest in the development of effective and multifunctional activated carbon for the adsorption of pharmaceutical drugs. A serious public health concern continues to be the unfavourable effects of some pharmaceutical drugs that are released into the environment, whether through industrial effluents, as unused or expired drugs, or in other ways, on people, animals, aquatic life, and the environment at large [6]. According to Ternes, 1998 [7], 32 drugs were identified in the effluents of German municipal wastewater treatment plants with a maximum concentration of ibuprofen (IBU) 3.4 μg/L and 0.53 μg/L in the effluent of sewage treatment plants and river streams, respectively. In another study, in Portugal, 78 drugs were identified in hospital effluents, 50 out of which were found at low concentrations in the effluents of wastewater treatment plants. In that study, the maximum concentration of Ibuprofen in hospital effluents was found to vary from one hospital to another: university hospital (5.82 μg/L), general hospital (11.33 μg/L), paediatric hospital (38.15 μg/L) and maternity hospital (16.63 μg/L). However, after the treatment in a wastewater treatment plant, the maximum Ibuprofen concentration was found to be 0.37 μg/L [8]. According to Syeda *et al.* [9], 0.29 μg/L of chlorpheniramine (CP) was detected in hospital waste water (HWW) effluent from a hospital in Muscat. In a related study by Al-Odaini *et al.* [10], CP was not detected and this was attributed to the high extent of its metabolism in the human body. Gautam *et al.* [11] found that some HWW parts stay in the environment for a long time, and some of these are genotoxic. Although their concentrations in surface and wastewater are low (ng/L to μg/L), pharmaceuticals can cause adverse effects such as feminization of male fish, aquatic toxicity, generation of anti-resistant bacteria and biological imbalance in the aquatic ecosystem [12, 13]. Mutations in the genetic coding function are related to genotoxic substances and have been accused of causing cancers in the last few decades. Alabi *et al.* [14] reported the genotoxic effects of HWW on mice. Research efforts have continued to improve and diversify the carbon surface functionality via different treatment methods to enable activated carbon to efficiently remove specific pollutants from wastewater [15]. Surface modification of activated carbon has been carried out chemically, physically, and biologically after preparation [16, 17].Generally, London dispersion forces or van der Waals adsorption forces dominate the adsorption processes of non-modified activated carbon for the removal of organic compounds from aqueous solutions [18]. Surface functionalization can introduce other dominating 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. This study was therefore designed to evaluate percentage adsorption of GLI from deionized water and spiked Pharmaceutical Liquid Waste (sPLW) using oxidized activated carbons (OAC), hydrophobic activated carbons (HAC) and basic activated carbons (BAC) prepared from velvet tamarind shell.

MATERIALS AND METHODS

Materials

All chemicals used were of analytical grade. Velvet Tamarind shell (VTS) 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 are 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 oC 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-Velvet Tamarind Shell (BAC-VTS). For hydrophobic carbons, surface modification using EA produced Hydrophobic Activated Carbon (HAC-VTS) of VTS.

Preparations of Stock Solutions of Glipizide

An initial diluent 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.

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 Glipizide, at λmax 260 nm. The Glipizide was 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 Glipizide were found to be 7 minutes. The linear range of Glipizide 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 [19].

Determination of the percentage adsorption of Glipizide 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 Pharmaceutical companies, both in Awka, Anambra state of Nigeria, in a working week day. PLW samples were kept in ice during transport and were filtered using membrane filter (0.45 µm pore size). PLW filtrate samples were mixed together in equal volumes making a representative sample. For the adsorption of Glipizide from spiked PLW, samples of the stock solution of Glipizide were spiked with the filtered PLW to achieve the range of initial concentrations as in the study of equilibrium adsorption from deionized water mentioned above [19]. 0.06 g each of the carbons (OACs, HACs, BACs) prepared from velvet tamarind shell, were mixed with 25 mL of spiked drug solutions and was left at 25 °C under mechanical agitation at 30, 60, 90, 120, 150, and 180 minutes. After equilibrium was obtained, samples of supernatant were separated and analyzed.

RESULTS AND DISCUSSION

Table 1: Percentage adsorption of GLI from deionized water and sPLW using OAC, HAC, and BAC prepared with velvet tamarind shell.

Time		qe (Deionized)			% Removal (Deionized)			qe (Effluent)			% Removal (Effluent)		
Time	sqrt (t)	qe $_{(OAC)}$	qe HAC	qe BAC	$\%_{(OAC)}$	%HAC	%BAC	qe(OAC)	qe(HAC	qe(BAC)	%OAC	%HAC	%BAC
30	5.477226	21.6	10.5	12.4	86.4	42	49.6	21.24	10.38	11.8	84.96	41.52	47.2
60	7.745967	22	11.6	13.5	88	46.4	54	21.64	11.48	13	86.56	45.92	52
90	9.486833	22.7	12	14.1	90.8	48	56.4	22.3	11.86	13.6	89.2	47.44	54.4
120	10.95445	23.5	12.9	14.9	94	51.6	59.6	22.9	12.68	14.6	91.6	50.72	58.4
150	12.24745	23.64	13.2	14.96	94.56	52.8	59.84	23.4	12.94	14.78	93.6	51.76	59.12
180	13.41641	23.78	13.45	15	95.12	53.8	60	23.58	13.36	14.86	94.32	53.44	59.44

Fig.1: %Adsorbed of GLI from Deionized water using velvet tamarind shell OAC, HAC and BAC

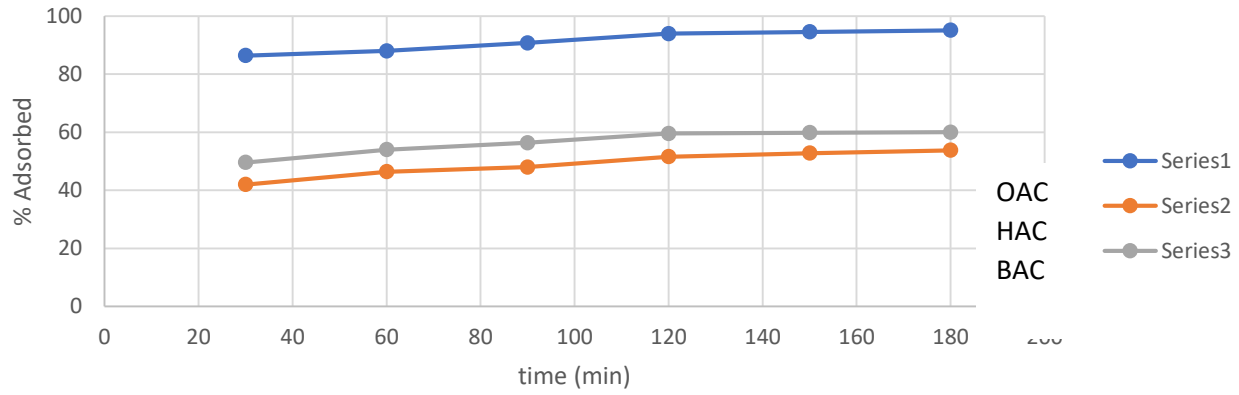
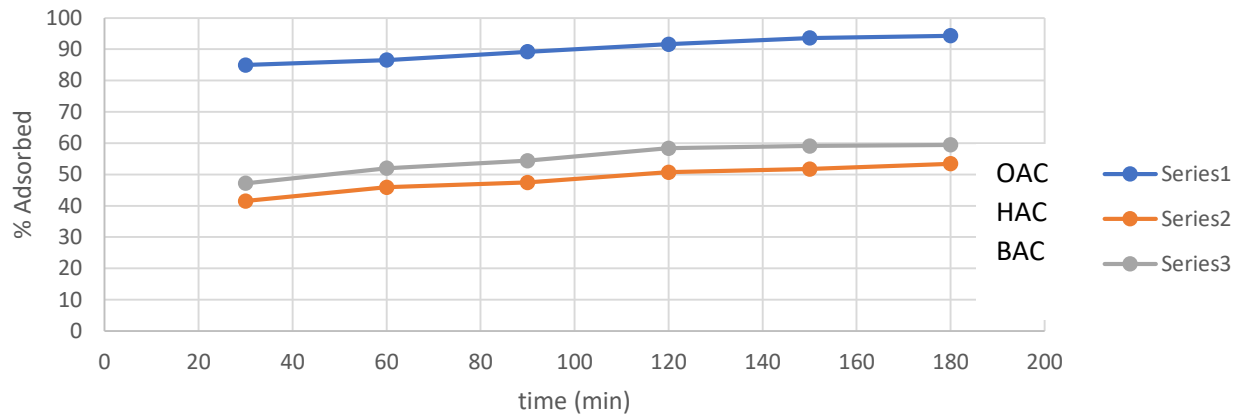


Fig.2: %Adsorbed of GLI from sPLW using velvet tamarind shell OAC, HAC and BAC



A plot of the percentage adsorption with time of glipizide (GLI) on the carbons velvet tamarind shell, from spiked PLW at 25 ˚C is shown in the figures 1-2 above. The adsorption data showed 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 the Table 1 above. The adsorption capacity, qe, and % Adsorbed with time, from the spiked PLW of the different carbons, follow a similar order to that, from deionized water. For carbons of velvet tamarind shell on Glipizide, from both deionized water and spiked PLW, the trends are: OAC > HAC > BAC. It is pertinent to note that velvet tamarind shell activated carbon has high porosity compared to the other carbons. BACs showed the lowest uptake of GLI. This could be because, at the pH of the deionized and spiked PLW when the adsorption was done, both the GLI and BACs surfaces remained positively charged, leading possibly to electrostatic repulsion and hence fewer GLI adsorptions. However, it is expected that at higher pH 7-11, adsorption may

increase as the GLI become less protonated while the BAC becomes deprotonated, thereby decreasing the extent of electrostatic repulsion and probably allowing an extent of H-bonding between the deprotonated amine groups on both GLI and BAC surfaces. Futher, there was less uptake from spiked PLW than from deionized water. Such a decrease in drug uptake from spiked PLW is probably because of the competition of dissolved organic substances, available in spiked PLW, with Glipizide molecules for adsorption sites on the adsorbents.

CONCLUSION

OAC, HAC, BAC prepared with velvet tamarind shell displayed commendable percentage adsorption of GLI from deionized water and sPLW and so could be explored for removal of GLI from pharmaceutical industries.

REFERENCES

1. Glossary of MHRA terms – P. *U.K.* Medicines and Healthcare products Regulatory Agency. Retrieved 2008.
2. 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 BimetallicCore@Shell Catalysts". Langmuir, 2016; **32** (30): 7493-7502. doi:10.1021/acs.langmuir.6b01906. PMID 27373791.
3. Heinrich, K.. "Über die Verdichtung von Gasen an Oberflächen in ihrer Abhängigkeit von Druck und Temperatur". *Annalen der Physik und Chemie,* 1881; **248** (4): 526–537.
4. Glossary of atmospheric chemistry terms (Recommendations 1990). Pure and Applied Chemistry. Vol. 62. 1990. p. 2167. doi:10.1351/goldbook.A00155. ISBN 978-0-9678550-9-7.
5. 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.
6. Crocq, M. A. "Alcohol, nicotine, caffeine, and mental disorders". *Dialogues Clin. Neurosci.* 2003; **5** (2): 175–185.
7. Ternes, T. A. Occurrence of drugs in German sewage treatment plants and rivers Dedicated to Professor Dr. Klaus Haberer on the occasion of his 70th birthday. *Water Research*, 1998; (**32**)11: 3245-3260.
8. Santos, M. J. B., Ludke, M. C. M. M., Ludke, J. V., Torres, T. R., Lopes, L. S. and Brito, M. S. Chemical composition and metabolizable energy values of alternative ingredients for broilers. *Ciênc. Anim. Bras.,* 2013; **14** (1): 32-40.
9. 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.
10. Al-Odaini, N. A., Zakaria, M. P., Yaziz, M. I., Surif, S. and Abdulghani, M. The occurrence of human pharmaceuticals in wastewater effluents and surface water of Langat River and its tributaries, Malaysia, *International Journal of Environmental Analytical Chemistry,* 2013; **93**(3): 245-264, DOI: 10.1080/03067319.2011.592949.
11. Gautam, R., Bassi, A.S. & Yanful, E.K. A review of biodegradation of synthetic plastic and foams. *Appl Biochem Biotechnol* , 2007 ;**141**: 85–108. https://doi.org/10.1007/s12010-007-9212-6.
12. Sim, W. J., Lee, J. W., Lee, E. S., Shin, S. K., Hwang, S. R. and Oh, J. E. Occurrence and distribution of pharmaceuticals in wastewater from households, livestock farms,

hospitals and pharmaceutical manufactures. *Chemosphere*, 2011; **82** (2):179-86. doi: 10.1016/j.chemosphere.2010.10.026. Epub 2010 Oct 30. PMID: 21040946.

13. El-Shafey, E.I., Syeda N.F. Ali, Saleh Al-Busafi, Haider A.J. Al-Lawati. Preparation and characterization of surface functionalized activated carbons from date palm leaflets and application for methylene blue removal. *Journal of Environmental Chemical Engineering*, 2016; **4**(3), 2713-2724.
14. Alabi, O. A., Olowu, J., Anaba, R. C. and Shokunbi, O. S. Bacteriology and Genotoxicity Assessment of a University Wastewater. *European Journal of Experimental Biology*, 2012; **2** (1):187-193.
15. Monser, L, and Darghouth, F. Simultaneous LC determination of paracetamol and related compounds in pharmaceutical formulations using a carbon-based column. *J Pharm Biomed Anal.*, 2002; **27**(6):851-60. doi: 10.1016/s0731-7085(01)00515-5. PMID: 11836048.
16. Rivera-Utrilla, J. and Sanchez-Polo, M. "The role of dispersive and electrostatic interactions in the aqueous phase adsorption of naphthalenesulphonic acids on ozone-treated activated carbons". Carbon, 2002; **40**(14): 2685–2691.
17. Shafeeyan, M. S., Daud, W.M.A.W., Houshmand, A, et al. A review on surface modification of activated carbon for carbon dioxide adsorption. *Journal of Analytical and Applied Pyrolysis*, 2010; **89**(2): 143–151.
18. Smith, M. and Farah, M. "Are prescription stimulants "smart pills"? The epidemiology and cognitive neuroscience of prescription stimulant use by normalhealthyindividuals". *Psychol . Bull.,* 2011; **137** (5): 717–41.
19. Syeda, N.F. Ali, E.I. El-Shafey, Saleh Al-Busafi, Haider A.J. Al-Lawati. Adsorption of chlorpheniramine and ibuprofen on surface functionalized activated carbons from deionized water and spiked hospital wastewater. *Journal of Environmental Chemical Engineering*, 2019; 7:2213-3437.