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Removal of Pharmaceutical Residues from Wastewater using Activated Carbon from Rice Husks

P. Kahara[1*], A. Gachanja[1], J. Kiptoo[1] and G. Nyaga[1]

[1]Chemistry Department, Jomo Kenyatta University of Agriculture and Technology, P.O Box 62, 000-00200, Nairobi, Kenya.

Authors' contributions

This work was carried out in collaboration among all the authors. Author PMK designed the study, wrote the protocol and the first draft of the manuscript. Authors AG, JKK and GN reviewed the experimental design and all drafts of the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

The presence of pharmaceutical residues in discharges that end up in rivers is a growing concern for the disruption of aquatic ecosystems and human health. The risk of exposure to these medical wastes becomes greater because they are not biodegradable even after sewage treatment. This study aimed to remove trimethoprim (antibiotic), paracetamol (painkiller), and nevirapine (anti-retroviral) from wastewater using activated carbon made from rice husks, an agricultural waste that was investigated as a potential adsorbent. The instrument used for analysis was a liquid chromatography-tandem mass spectrometer (LC-MS/MS). The powdered carbon of rice husks was carbonated at a temperature of 500^{o}C and then activated by phosphoric acid to increase its porosity. After activation, it was successfully characterized by the use of Scanning electron microscopy which showed irregular cavities with open fine pores. Fourier transform infrared showed different functional groups which determined adsorbent- adsorbate interactions while X-ray diffraction revealed amorphous particle arrangement. The effects of the adsorbent dose, contact time, pH, and initial drug concentration were studied. Freundlich and Langmuir's isotherms were used in the evaluation of adsorption phenomena. Thus, obtained results showed that rice husks activated carbon is an effective adsorbent.

**Corresponding author: E-mail: pekta7219@gmail.com;*

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1. INTRODUCTION

In recent years, the number of pharmaceutical products has increased tremendously. This is in response to an increase in population which has led to an increase in demand for pharmaceuticals. These pharmaceutical compounds are a source of increasing environmental pollution concern in that they are likely to be transported into the water system [1]. A pharmaceutical can be defined as any substance or a mixture of substances used in the diagnosis, treatment, or prevention of a disease, disorder, or abnormal physical state, or its symptoms in human beings or animals [2].

Pharmaceuticals are known to contain many different active ingredients. These ingredients are released into rivers, lakes, and oceans. The concentrations of medical residues in the environment have been found in low concentrations but when exposed to aquatic organisms such as fish, they cause endocrine malfunctions and possible antibiotic resistance in bacteria. Estrogens are known to cause gene mutations in fish [3]. Some of the effects on the endocrine system are low sperm count, breast and testicular cancer. However all evidence of direct adverse effects on human health is weak and inconclusive [4].

Considering the way pharmaceuticals are being used in the world today, their concentrations in the environment have almost reached toxicological significant levels. There are various ways of evaluating the environmental levels of a drug. One approach is based on factors such as consumption rate, metabolism, and excretion of the drugs, but it is a difficult process to estimate the national drug consumption of any one country as the consumption of over the counter drugs cannot be easily tracked as that of the prescription drugs [5].

The other problem in the evaluation of effects of a drug is that sometimes when the drug is ingested, it undergoes biochemical transformations which produce metabolites and other degradation products which could show either the same or modified activity as the unchanged parent compound thus evaluation may fail to show the true environmental load [6,5]. To deal with the problem of pharmaceutical residues in water, it is important to deal with the environmental threat by its source, sometimes advanced technologies such as ozonation and nanofiltration can be used but in developing countries, such methods are deemed to be expensive. The use of adsorbents such as activated carbon is a cheaper alternative and it shows potential to be effective regarding removal of these pharmaceutical products [7].

Most people get access to untreated wastewater through the disposal of the drugs directly into the water, throwing expired and unused drugs into the toilets, broken sewer pipes, and blocked manholes [8]. Another important pathway for pharmaceutical release in the terrestrial and aquatic environment is through leakage from pharmaceutical factories and application of animal manure and bio-solids containing excreted drug residues to agricultural land as fertilizer which finally leach to the ground and surface water [9]. They can also be introduced to agricultural land through irrigation using wastewater [10].

Activated carbon has been proposed to be an adsorbent for the removal of pharmaceuticals from water due to its unique physical-chemical properties such as porosity and large specific surface area in addition to the availability and maturity of adsorption technology [11]. Generally, activated carbon is applied at the polishing step for the removal of refractory compounds and precursors of disinfection by-products in water treatment [12]. Activated carbon is carbon produced from carbonaceous source materials such as nutshells, peat, wood, coir, lignite, coal, petroleum pitch, and maize cob. It can be produced by either physical or chemical activation. During activation, the raw material is impregnated with certain chemicals. The chemical is typically an acid, strong base or a salt. Chemical activation is always better than physical activation due to the lower temperatures, less time, and it is cheaper. The goal of this present study was to prepare activated carbon an adsorbent with large surface area, regular pores, and high adsorption capacity for removal of the selected pharmaceuticals from waste water systems.

2. MATERIALS AND METHODS

2.1 Sampling and Sample Pre-treatment

Rice husks a variety known as pishori basmati was collected from nice rice millers in Mwea,

Kirinyaga County Kenya (0.6897° S, 37.3400° E). Mwea irrigation scheme is the country's leading rice producer, covering over 26,000 acres, with farmers largely growing pishori, a fragrant basmati rice variety. The rice husks were washed with distilled water to remove all the adhering particles which may act as impurities. It was then dried at 110°C for 8 hours. It was ground and sieved to a particle size of 1 -2 mm, carbonated at a temperature of 500^{o}C, and activated with phosphoric acid. Batch experiments were done using distilled water spiked with the three drugs [13].

2.2 Instrumentation

All samples were analyzed using Liquid Chromatography with tandem mass spectrometry model micromass Quattro ultima with agilent 1100 HPLC (LC-MS/MS) while characterization of activated rice husks was done through scanning electron microscopy (SEM), Fourier transform infrared (FTIR), and X-ray diffractometer (XRD).

2.3 Carbonization and Chemical Activation of Rice Husks

Two hundred grams (200 g) of rice husks were carbonized at 500^{0}C in a muffle furnace (Advatec-KL-420 Japan) for 2 hours and then impregnated with 1dm^{3} of 3 Molar H_3PO_4, at 80^{0}C for 3 hours. It was then cleaned with distilled water until its pH becomes 7. The sample was then dried at 100^{0}C for 2 hours.

2.4 Characterization of Rice Husks Derived Activated Carbon

The surface morphology of activated carbon was analyzed using scanning electron microscopy (SEM, OPTO-EDU A63 7081 MODEL). Functional groups were determined using the Fourier Transform Infrared spectrophotometer (FTIR, 8000 SHIMATZU.JAPAN) operating between 400 and 2000 cm^{-1} using the KBr pellet method. The degree of crystallinity or amorphous nature of rice husks activated carbon was determined at the department of geology and mining in Nairobi using a Bruker D8 AXS X-ray diffractometer manufactured in Japan [14].

2.5 Batch Equilibrium Studies

After the activation, rice husks powder was applied in the adsorption of paracetamol, trimethoprim, and nevirapine. The parameters determined; effect of pH, contact time, adsorbent dosage and initial drug concentration, were based on a methodology developed by [15].

2.6 Data Analysis

Data from adsorption experiments were fitted to Langmuir and Freundlich isotherms models. Correlation coefficients r^2 and Chi-Square tests were used to determine the best fit for each model. ANOVA was also used [16].

3. RESULTS AND DISCUSSION

3.1 Characterization of Rice Husks Activated Carbon

The activated carbon of rice husks was characterized for identification of surface functional groups by use of FT-IR, Surface morphology using SEM, and its amorphous nature using XRD.

3.2 Functional Group Analysis

FT-IR 8000 Shimadzu model was used to identify the functional groups. It was operating between ranges of 500 – 4000cm^{-1}. KBr pellet method was used in the ratio of sample: KBr 1:10 pellets were obtained by pressing the mixture in a vacuum. Strong spectral bands were observed at 1396.4 cm^{-1}, 1598.9 cm$^{-1,}$ and 3340.5 cm^{-1} as shown in Fig. 1. The strong band at 3340.5cm^{-1}canbe attributed to hydroxyl (O-H) functional groups stretching vibrations inclusive of hydroxyl groups bonded to polymeric structures of rice husk or hydrogen-bonded to chemisorbed water. Another strong band at 1598.9 cm^{-1} corresponds to stretching vibrations of the carbonyl (C=0) groups while the band at 1396.4 cm^{-1} corresponds to C-H rocking vibrations. In addition to the major peaks, other distinctive peaks were shown at 2924 cm^{-1}, 1205 cm$^{-1,}$ and 1089 cm^{-1} respectively. The peak at 2924 cm^{-1} corresponds to~CH_3/ ~CH_2 deformation or C–H stretching of aliphatic carbon. Peak 1205 cm^{-1} is a result of carboxylic/aromatic skeletal, whereas peaks near 1089 cm^{-1} are related to C-O stretching vibrations of bonds present in phenol, esters, or ether group [17].

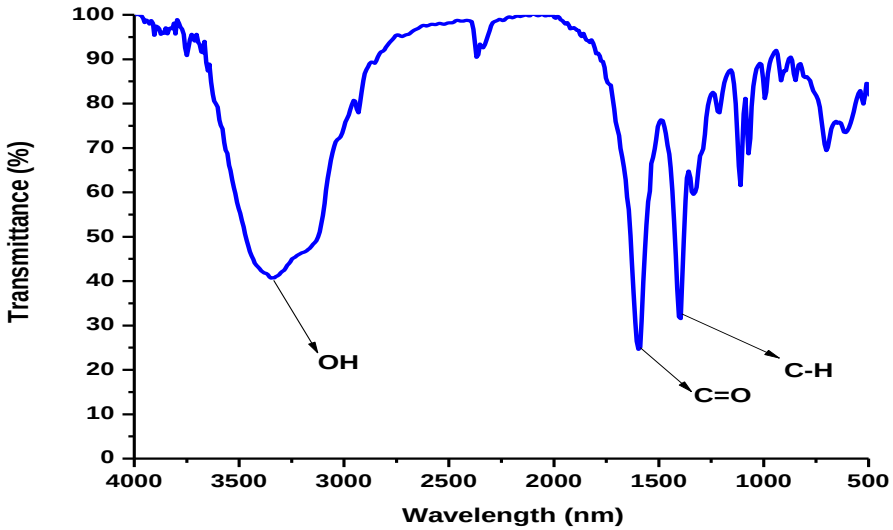

Fig. 1. FT-IR spectrum of rice husks activated carbon carbonated at 500^{0}C

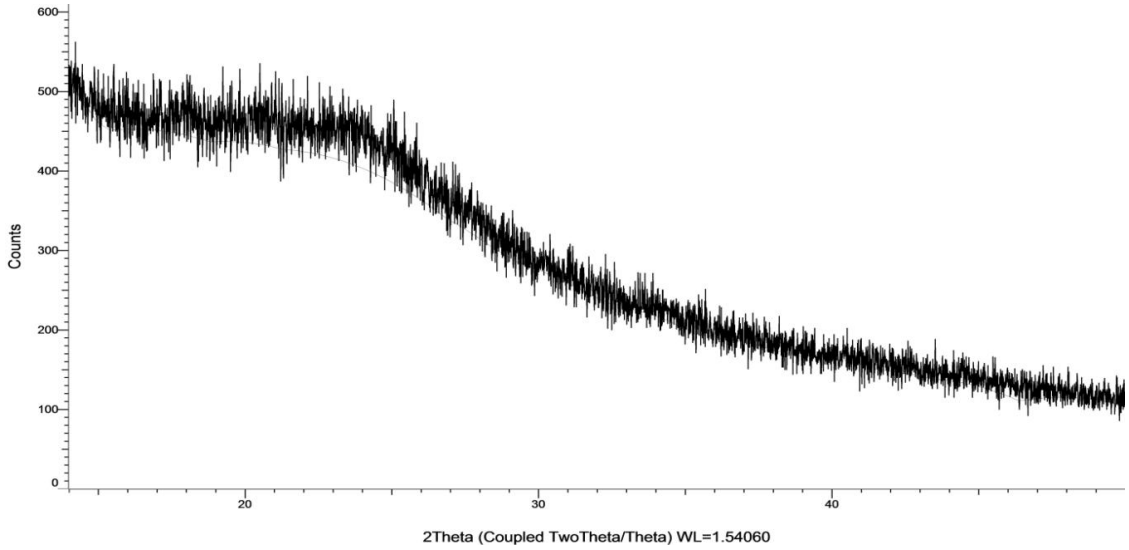

Fig. 2. X-ray Diffraction of rice husks activated carbon

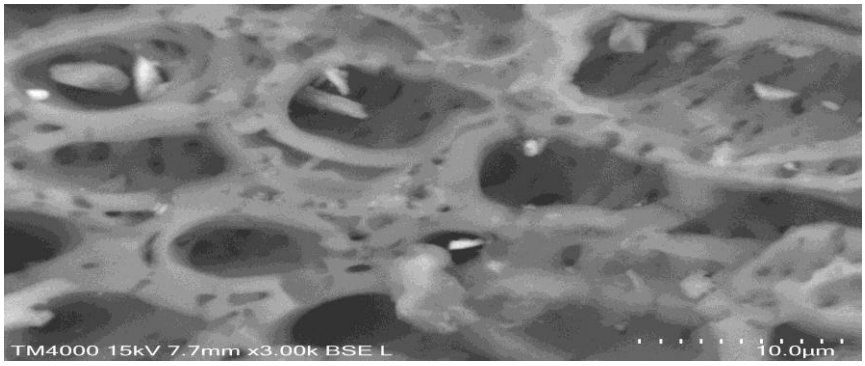

Fig. 3a. SEM micrograph of the rice husks before activation

3.3 X-ray Diffraction analysis (XRD) of Rice Husks Activated Carbon

This was done using a Bruker D8 X-ray diffractometer using Cu-kd radiation source and scan mode 2θ= 5°-90°. The diffraction pattern is represented by Fig. 2. It showed a broad diffused peak centered at 2Theta = 22.87° indicating that the activated carbon from rice husks is amorphous [18,19].

3.4 Surface Morphology Analysis of Rice Husks Activated Carbon

SEM micrographs of the rice husks before activation, Fig. 3a contained cavities but after activation with phosphoric acid Fig. 3b, the porosity seems to improve and the cavities become sharper and irregular. Activation removes the hemicellulose fibers thus increasing the pore size [10].The textural structures of rice husks activated carbon is made up of well-developed graphite layers with spaces in between carbon layer planes forming an interconnected network of pores, which in the long run accommodate adsorbate molecules. Fig. 3c, 3d, and 3e respectively represent SEM micrographs of activated carbon after adsorption. Before sorption, the surface morphology of activated carbon had uneven cavities and irregular open pores, but upon adsorption (drugs) the pores become regular and smoother. While working on adsorption of 4-chlorophenol from aqueous solution using activated carbon synthesized from Aloe Vera green wastes, [20] reported similar micrographs after SEM characterization. Herewith, surface chemistry is governed by small amounts of heteroatoms such as oxygen, hydrogen, nitrogen, phosphorus, and sulfur incorporated or bonded at edges of aromatic sheets within the carbon matrix resulting in heterocyclic ring systems.

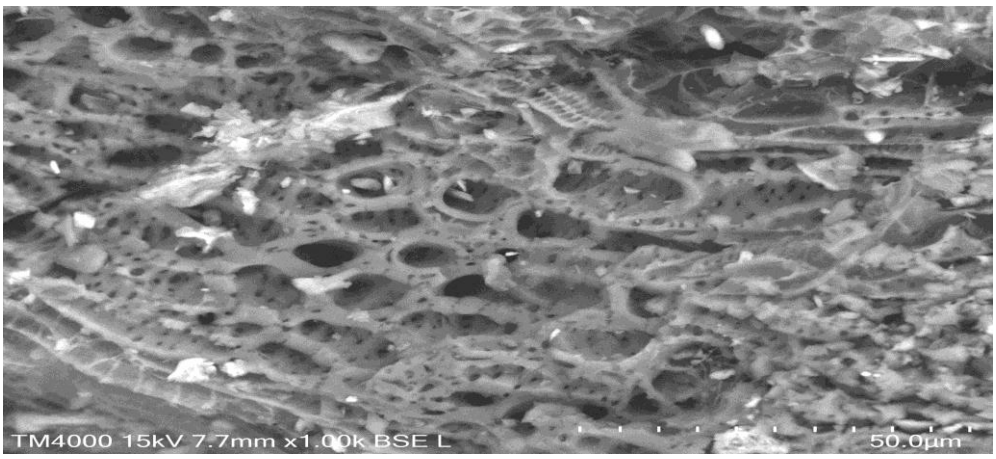

Fig. 3b. SEM micrograph of activated carbon before adsorption

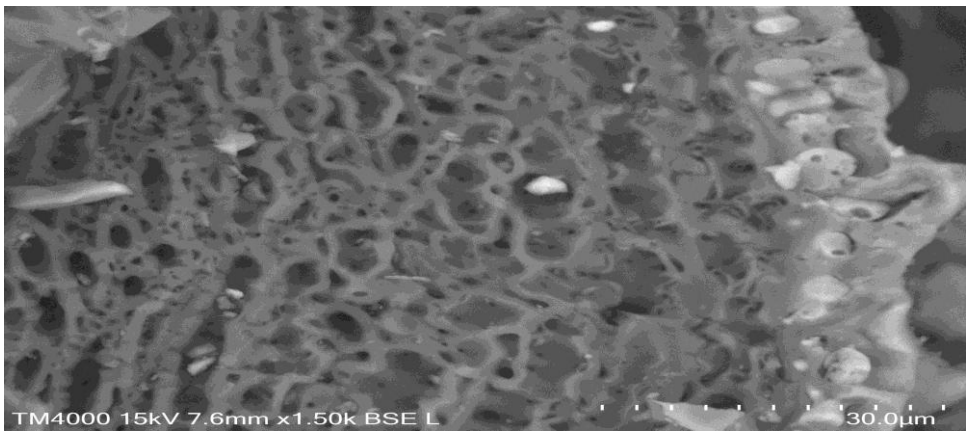

Fig. 3c. SEM micrograph of activated carbon after adsorption of nevirapine

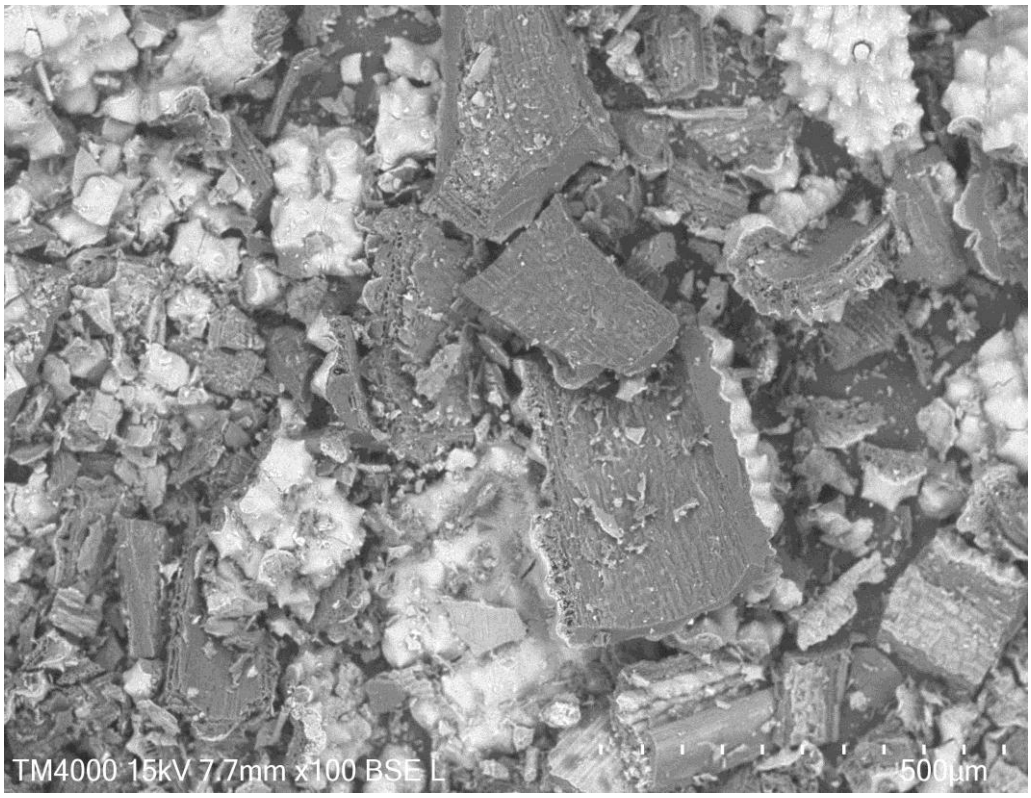

Fig. 3d. SEM micrograph of activated carbon after adsorption of trimethoprim

Fig. 3e. SEM micrograph of activated carbon after adsorption of paracetamol

3.5 Batch Equilibrium Studies

The prepared adsorbent was used to remove selected pharmaceuticals under different parameters that are; effect on contact time, effect on initial drug concentration, effect on pH, and effect on adsorbent dosage**.**

3.6 Measurement of Concentrations

Concentrations were determined using LC-MS/MS where the conditions were; eluent A: 30% water with 0.1% formic acid, eluent B: 70% methanol with 0.1% formic acid, and column: C18 5µm (2.1 mm×50mm) flow rate 0.45µl / min, retention time 7 minutes and the injection volume was 10 µl at a temperature of 40^{o}C. Isocratic elution was applied.

The percentage removal was calculated using the equation:

$$\% \text{ Removal} = \frac{\text{Ci}-\text{Ce}}{\text{Ci}} * 100 \quad 1$$

Where “Ci” is the initial concentration of the pharmaceutical while “Ce” is the equilibrium concentration.

The amount of pharmaceutical adsorbed at equilibrium qe (mg g-1) was calculated according to the equation

$$\text{qe} = \left(\frac{\text{Ci}-\text{Ce}}{\text{M}}\right) \text{V} \quad 2$$

Where “V” is volume used and “m” is the mass of the adsorbent

3.7 Effect of Initial Drug Concentration

It was observed that the adsorption of the three drugs decreased with an increase in initial concentrations of the three drugs. The higher initial adsorption can be attributed to the availability of more sites on the activated carbon than the solute molecules in the solution. At higher concentrations, the pharmaceutical molecules are more than the sites available. Initially, the percentage removal of the three drugs increased with an increase in initial drug concentration up to a maximum of 88% trimethoprim, 82 % paracetamol, and 70% nevirapine. In another study, the percentage of lead removal was reported to be 90.08% for 100 mg/l of initial concentration, but the value changed to 70.35% for an initial concentration of 1000 mg/l [21]. Fig. 4a represents the effect of initial drug concentration for the three drugs under study.

3.8 Effect of pH

The pH of a solution is known to affect the surface charge of the adsorbent which would, in turn, affect the adsorbent– adsorbate interactions. The electrical interactions taking place on the solid surface play an important role in adsorption kinetics. Though pH did not seem to have a significant effect on adsorption of trimethoprim (TMP), paracetamol (PARA) was adsorbed more on the acidic range while (NEV) nevirapine adsorption was higher at a pH of 7 [22] found adsorption of ibuprofen which is similar to paracetamol also increasing in acidic media. However, [23] reported that the removal of paracetamol was not affected by ph. While working on batch sorption dynamics, kinetics and equilibrium studies of Cr(vi), Ni(ii), and Cu(ii) from aqueous phase using *Syzygium cumini* leaves powder, [24] reported adsorption of Cu ions also increasing at acidic pH range. Working on desorption and theoretical study of propranolol hydrochloride drug on chitosan and cellulose acetate surfaces, [25] reported a case where pH was increased, the amount of adsorption of the drug on all adsorbents also increased. The trend was consistent between pH 3-7. Further increase of pH beyond 7 generally resulted in a decrease in the adsorption of the drug. The effect of pH is summarized in Fig. 4b.

3.9 Effect of Contact Time

It was found that there was an increase in the percentage removal of the three drugs as time increased until equilibrium was achieved. The three drugs required 15 minutes for maximum absorption to take place. The initial increase in adsorption of all three drugs was due to the presence of many pores on the adsorbent but adsorption became constant when the pores became saturated. Trimethoprim had maximum adsorption in 12 minutes, paracetamol in 14 minutes while nevirapine took 15 minutes to reach equilibrium. Nevirapine took the highest time because it was the largest molecule. While working on adsorption of copper (II) ions from aqueous solution using bottom ash of expired drugs incineration, [26] also reported a time frame of 15 minutes for equilibrium to be achieved. The results for the effect of contact time are shown in Fig. 4c.

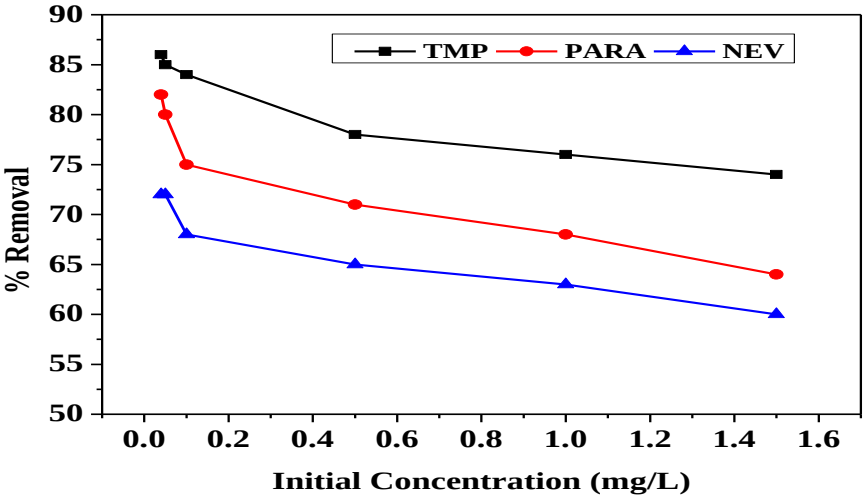

Fig. 4a. Effect of initial drug concentration on adsorption of trimethoprim, paracetamol, and nevirapine

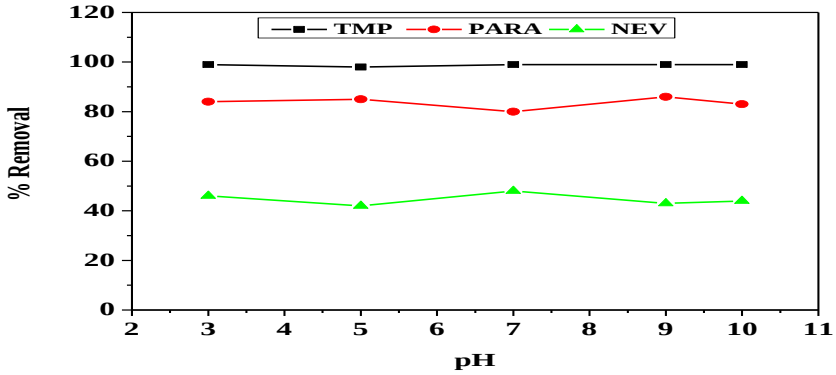

Fig. 4b. Effect of pH on adsorption of trimethoprim, paracetamol, and nevirapine

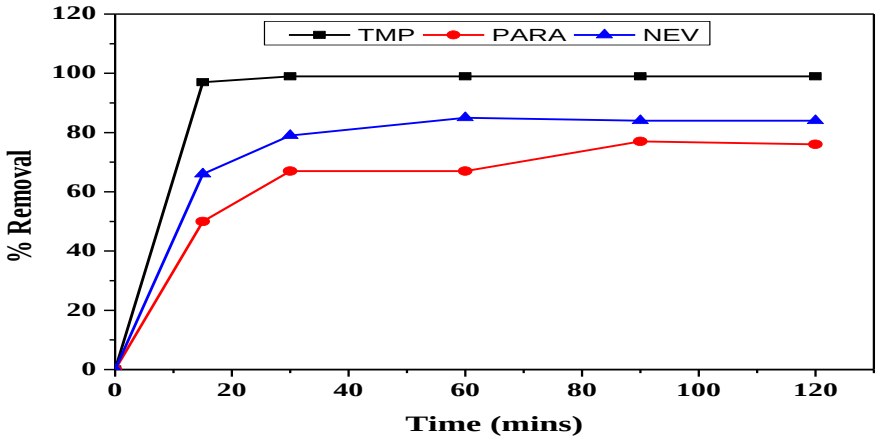

Fig. 4c. Effect of contact time on adsorption of trimethoprim, paracetamol, and nevirapine

3.10 Effect of Adsorbent Dosage

Adsorbent dosage was done using masses ranging from 0.0125g to 0.2g. Different masses of activated carbon showed varied adsorption abilities for trimethoprim, paracetamol, and nevirapine. The trend was that, for the three drugs, percentage removal increased with an increase in the mass of adsorbent until equilibrium was attained. Similar results have been reported where the percentage removal initially increased sharply with an increase in adsorbent dosage, but beyond a value of 25 g/L, the percentage removal reached an almost constant value [21]. This is attributed to increasing in the number of adsorption sites due to an increase in surface area as the mass increases. The decrease in removal at equilibrium can be attributed to aggregation and overlapping of the activated carbon resulting in a decrease in effective surface area for the adsorbent [24]. The positive correlation between adsorbent dose and pharmaceutical removal can be related to an increase in adsorbent surface area and the availability of more adsorption sites [23]. Further increase in adsorbent dose did not alter the percentage removal. This is due to the binding of almost all pharmaceutical molecules to the adsorbent surface and the establishment of equilibrium between the molecules on the adsorbent and in the solution [27]. It was also noted that the loading capacity (amount of drug-loaded per unit weight of the adsorbent) gradually decreased due to oversaturation of the pores. Effects of adsorbent dosage on the three drugs are represented in Fig. 4d.

3.11 Adsorption Isotherms

Adsorption is described through functions that connect the amount of adsorbate and adsorbent which are referred to as isotherms. For optimization of the design of sorption systems for the removal of chemical substances from water, isotherm models are usually employed. This is important in availing information on the physicochemical information required in explaining the mechanism of adsorption [28]. The distributions of chemical components between the liquid and solid phase are widely explained by isotherm models such as Langmuir and Freundlich. The Langmuir isotherm model explains that the maximum adsorption is proportional to the saturated monolayer of solute molecules on the surface of the adsorbent. When a particular site is saturated, no further sorption takes place and that indicates that the surface has achieved maximum adsorption. From the experimental data for adsorption of nevirapine, trimethoprim, and paracetamol, the r^2 values for the Freundlich model were 0.977, 0.994, and 0.977 while the Langmuir adsorption model was 0.9996, 0.9994, and 0.9831 respectively as summarized in Table 2. Both the Freundlich and Langmuir adsorption plots gave a good fit which meant that the adsorption of the pharmaceuticals by the rice husks charcoal obeyed both the Freundlich and Langmuir models.

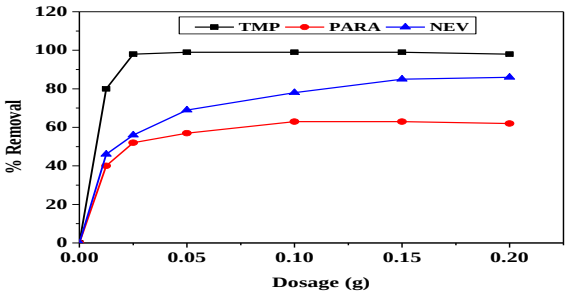

Fig. 4d. Effect of adsorbent dosage on adsorption of trimethoprim, paracetamol, and nevirapine

Table 1. Langmuir and Freundlich isotherm parameters for adsorption of paracetamol (PARA), trimethoprim (TMP), and nevirapine (NEV)

	Langmuir			Freundlich			
	b	**$Q_m$mg/g**	**r^2**	**K_F**	**1/n**	**n**	**r^2**
PARA	42.958	1.880335	0.99962	2.0219	0.11377	8.789663	0.97705
TMP	-372.704	1.765194	0.99938	2.2206	0.0634	15.77287	0.99434
NEV	1.399993	2.582111	0.98314	1.5147	0.50406	1.983891	0.97705

Table 2. Kinetic parameters for the removal of trimethoprim, paracetamol, and nevirapine

	pseudo-first-order			pseudo-second-order		
	k_1	r^2	qe	k_2	r^2	qe
TMP	$5.65x10^{-3}$	0.8166	1.3611	-1.64811	0.93205	$7.1866x10^{-2}$
PARA	$66.997x10^{-1}$	0.69744	1.3831	-2.51833	0.9769	$8.786x10^{-2}$
NEV	$8.00066x10^{-3}$	0.88686	3.2302	-1.63112	0.95215	$7.9758x10^{-2}$

3.12 Adsorption Kinetic Studies

Evaluation of the adsorption kinetics of pharmaceuticals, dyes, and metal ions in water has been done by application of various kinetic models. In this study, the mechanism of adsorption was investigated using characteristic constants of adsorption determined from Lagergren's pseudo-first-order, pseudo-second-order kinetic rate equation, and intra-particle diffusion model. Constants of pseudo-first-order, pseudo-second-order, were determined from the slope and intercept of the linear plot between log (qe - qt) versus t and t/qt versus t, respectively Table 2 below shows the kinetic parameters for the removal of trimethoprim, paracetamol, and nevirapine using activated carbon of rice husks.

From the data, the pseudo-second-order model recordedr^{2}values which were closer to unity compared to the pseudo-first-order model which was unfavorable, hence, did not adjust to experimental data [29,30,31].

4. CONCLUSION

Rice husks activated carbon which is an agricultural waste is an excellent adsorbent that can be used in the removal of paracetamol, trimethoprim, and nevirapine from water systems. Before adsorption studies, characterization of the adsorbent was done. FT-IR analysis showed strong peaks at 3340 cm^{-1} which corresponded to hydroxyl group vibrations and at 1596 cm^{-1} which was due to carbonyl group bending vibrations while the peak at 1396 cm^{-1} showed C=C bending vibrations. XRD analysis depicted the adsorbent as amorphous containing disordered particles while SEM analysis revealed the adsorbent as highly porous with a lot of cavities which were improved by phosphoric acid activation. Batch equilibrium studies revealed that removal of the three pharmaceuticals increased with increasing contact time, adsorbent dosage, and decreasing initial drug concentration. The pH did not seem to have a significant effect on the adsorption of trimethoprim but paracetamol adsorption increased in the acidic range while nevirapine had maximum adsorption at pH 7. The results indicated that the data fitted well in both Freundlich and Langmuir's isotherms. Adsorption kinetics showed that the pseudo-second-order model recorded r^2 values which were closer to unity as compared to the pseudo-first-order model hence the data favored pseudo-second-order kinetics.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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