



Comparative Assessment of the Efficiency of Rice Husk Biochar and Conventional Water Treatment Method to Remove Chlorpyrifos from Pesticide Polluted Water

Aderonke A. Okoya¹, Oyeyemi S. Adegbaju^{1*}, Oyindamola E. Akinola¹,
Abimbola B. Akinyele¹ and Omotayo S. Amuda²

¹Institute of Ecology and Environmental Studies, Obafemi Awolowo University, Ile Ife, Nigeria.

²Ladoke Akintola University of Technology, Ogbomoso, Nigeria.

Authors' contributions

This work was carried out in collaboration among all authors. Author AAO designed the study and wrote the protocol. Author Oyeyemi S. Adegbaju wrote the first draft of the manuscript and performed the statistical analysis. Authors OEA and ABA managed the analyses of the study. Author Omotayo S. Amuda managed the literature search. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/CJAST/2020/v39i230491

Editor(s):

(1) Dr. M. Abdullah Al. Mamun, Department of Soil Science, Faculty of Agriculture, Hajee Mohammad Danesh Science and Technology University, Dinajpur-5200, Bangladesh and Collaborative Professor, Kanazawa University, Japan.

Reviewers:

(1) James Burke, University of Arkansas, USA.

(2) Byron Baron, University of Malta, Malta.

Complete Peer review History: <http://www.sdiarticle4.com/review-history/54205>

Original Research Article

Received 05 December 2019

Accepted 11 February 2020

Published 20 February 2020

ABSTRACT

Nigeria is currently the largest rice producing country in Africa. High volumes of waste such as rice husk are inevitable with high production. Also pesticides used to rid of pests, diseases and improve crop yield find their ways into available surface water that serves domestic purpose. This study therefore determined the efficiency of conventional water treatment procedure for pesticide/pesticide residue removal and evaluated the performance of rice husk-based biochar as adsorbent to remove chlorpyrifos from domestic water supply with a view to manage solid waste (rice husk) for treating pesticide polluted water. Batch adsorption studies were carried out to assess the adsorption efficiency of rice husk biochar (RHB) for chlorpyrifos pesticide removal from surface water. Adsorbent dosage, initial concentration, contact time and dosage were optimized during

*Corresponding author: E-mail: yemiadegbaju@yahoo.com;

simulation experiment. RHB and commercial activated carbon (CAC) were used for the removal of chlorpyrifos from surface water sample using the optimum condition from the simulation experiment after which the concentrations were determined using Gas Chromatography with Mass Spectrometry detector. Both Langmuir and Freundlich adsorption isotherms were investigated. RHB gave percentage moisture (5.27±0.94), carbon yield (39.44±0.47), ash (41.96±0.96), fixed carbon (35.24±0.55), volatile matter (35.67±1.01 mg/g), Iodine number (85.57±0.81), surface area (97.20 m²/g), pH (7.90±0.14) and Electrical conductivity (298.8±1.14). Of the elements present in the char, Carbon has the highest percentage of 59.14%. Best adsorption conditions for RHB in this study were 2.8 mg/L initial concentration; 0.8 g of adsorbent dosage; pH of 5 and contact time of 30 min. The data fitted Freundlich than Langmuir model (R^2 0.996 and 0.8315 respectively). Percentage removal of chlorpyrifos for CAC and RHB was 93.7±3.96 and 94.5±5.23 respectively for the surface water sample. Results concluded that RHB was efficient for removal of chlorpyrifos present in water and could be used as alternative for CAC in water treatments.

Keywords: Rice husk; biochar; adsorption; pesticide; surface water.

1. INTRODUCTION

Rice (*Oryza Sativa*) is a staple food in Nigeria and other parts of the world. Nigeria is currently the largest rice producing country in Africa. This is as the result of conscientious efforts by the current administration to place more emphasis on agrarian production. With the available literature, annual rice production in Nigeria has increased from 5.5 million tons in 2015 to 5.8 million tons in 2017 [1]. In 2015, the consumption rate now is 7.9 million tons and the production rate has increased to 5.8 tons per annum. The increase was as a result of the Central Bank of Nigeria (CBN)'s Anchor Borrowers Program with a total of 12 million rice producers and four million hectares of FADAMA rice land [2]. Also, through the Anchor Borrowers Program Rice farming in the country has received a boost from the local central bank through that avails loans and distributes requisite tools to farmers to boost production. One of the consequences of rice production activities is the generation of high volumes of waste [3]. The main solid waste generated in this process includes: straw, husk, ash, bran and broken rice, whose disposal can be problematic since it occupies large spaces, and when poorly managed can pose environmental and health risks for the populace. According to Udemezue and Osegbue [1], each ton of processed paddy rice generates 200 kg of rice husk.

Pesticides, which are mostly used by agriculturists to get rid of pests, diseases and to improve crop yield find their ways into the available surface water that serves domestic purpose for humans. Surface runoff, mismanagement of pesticides containers, spray drift and equipment washing are some of the

major routes through which pesticides find their ways into water bodies. Most of these pesticides are harmful to humans at minute concentration, and tends to remain in water body over a significant period of time. Pesticide contained distinctive classes, for example, insecticides, fungicides, herbicides and rodenticides. Chlorpyrifos is an organophosphate pesticide introduced in 1965 by Dow Chemical Company. It has other trade name such as Brodan, Detmol UA, Dowco 179, Dursban, Eradex, Lorsban, Piridane, Stipend which kills various pests in which insects and worms are inclusive [4]. It is used on crops, animals, and building [4].

Water serves as an essential resource for advancement. In 2015, Target 10 of Objective 7 of the Millenium Development Goals (MDGs) was built up with the intension to decrease the extent of individuals living without access to quality drinking water. Legitimate fundamental sanitation issues of water supply in urban center (especially in developing nations) as detailed by [5], is a problem which is being addressed in MDGs and is significantly caused due to high populace development rate, absence of monetary assets, and suitable infrastructure. Numerous hazardous compounds have turned into a major toxin of surface water these days, a portion of these toxins include untreated and partially treated industrial effluents as well as agricultural run-off and a significant number of these contaminants are not effectively targeted for treatment by conventional water treatment approach. The majority of the water treatment plants especially in developing nations make use of basic techniques for water treatment, for example, coagulation-flocculation process which does not provide adequate purification. There are several methods by which pesticides can be

removed from drinking water which include photo-catalytic degradation, combined photo-Fenton and biological oxidation, advance oxidation process, nanofiltration, ozonation and adsorption [6].

Adsorption processes have been studied intensively using a significant range of adsorption materials and the results of which have made it most encouraging techniques as a result of their low-cost, simplicity of activity and efficiency for the removal of low concentrations of organic and inorganic micropollutants including pesticides. As of late, some agricultural waste items, biomass, and different solid substances have been produced into biochar as alternative cheap adsorbents to remove pesticides [7,8]. However, there was paucity of information on the use of rice husk despite increase in production of rice in Nigeria. Therefore, this study employed the use of rice husk which is produced in large quantities as waste from rice milling and agro-based biomass industry as renewable precursor for preparation of rice husk biochar (RHB) for chlorpyrifos removal.

2. MATERIALS AND METHODS

2.1 Structure of the Adsorbate

Chlorpyrifos ($C_9H_{11}Cl_3NO_3PS$) was obtained from an agrochemical store and used as an adsorbate. De-ionized water was used to prepare the stock solution.

2.2 Preparation and Characterization of Rice Husk Biochar

The rice husk was collected from a local mill as a by-product of rice production. The rice husk was washed, sun dried, and milled. Rice husk biochar was produced from slow pyrolysis of the dried rice husk at 700°C for 1 hour 30 mins using a muffle furnace (EK18/18 ESSEN, Germany). The RHB obtained was washed with 0.1M HCL and subsequently with distilled water till neutral pH was achieved, it was then oven-dried at 110°C till constant weight. Afterwards, gently ground using mortar and pestle, and homogenized to pass through sieve of 100µm and kept inside a plastic container for further use. The elemental composition of biochar sample was determined based on the dry combustion method using Bruanner-Emmett-Teller (BET) CHNS/O Elemental Analyzer (VARIO EL III, Elementar, Germany). The surface morphology of the

biochar was determined using Scanning Electron Microscope (SEM) and also the structural chemical functional groups in the biochar were determined using the Fourier Transform Infrared technique (SHIMADZU-FTIR-8400S).

2.3 Batch Adsorption Experiments

Batch adsorption studies were carried out in a set of conical flasks of 250 mL capacity where 50 mL of chlorpyrifos solution (2.8 mg/L) were put in each flask and RHB was introduced as adsorbent. Parameters such as adsorbent dosage, contact time, pH and initial concentration were optimized. The mixture was shaken on a rotary shaker (CELTECH KJ-201BD) at 120 osc/min. All samples were filtered prior to analysis in order to minimize interference of the carbon fines with the analysis. Each batch of the experiment was replicated under identical conditions. The filtrate was then extracted, concentrated and analyzed for residual chlorpyrifos after the contact period have been reached using Gas chromatography coupled with Mass Spectrophotometer (GC-MS). The percentage of pesticides adsorbed per unit mass of the adsorbent was calculated by using the following percentage balance equation. The procedure was repeated using the optimized conditions with simulation experiments for the inlet field surface water.

$$q_e = \frac{(c_o - c_e)V}{w} \quad [9]$$

where C_o and C_e are the pesticide concentration measured before and after adsorption (mg/L), V is the volume of aqueous solution (L) and W is dry weight of the adsorbent (g).

$$Adsorption(\%) = \frac{(c_i - c_e)}{c_i} \times 100 \quad [10]$$

Where:

C_i is the initial concentration before adsorption (mg/L).

C_e is the final concentration of Chlorpyrifos solution (mg/L) in the filtrate after adsorption.

2.4 Extraction of Chlorpyrifos

Each filtrate from the batch adsorption and 10 ml solvent (ethyl acetate) were mixed in a 250 ml capacity separating funnel (DURAN, Germany)

and was shaken by mixing well for about 10 min and then were allowed to stand for 10 – 15 min for clear separation [11]. The organic solvent layer was collected in a test tube. The aqueous layer was re-extracted by adding another 10 ml of ethyl acetate using a similar procedure. The organic solvent layers were added together and 2 g of anhydrous sodium sulphate (Merck, Germany) was added to remove the residual water. The collected extract was then concentrated to dryness under reduced temperature using a water bath (HH-W420 Thermostatic water cabinet). The concentrates were then reconstituted with ethyl acetate to a 1.5 ml in GC-MS vials for analysis [12].

2.5 Gas Chromatographic Analysis

The reconstituted organic solvent in 1.5 ml GC-MS vial was placed in the port of GC-MS Agilent 7890 series equipped with a Mass Spectrometry Detector (GC-MS) and ChemStation software (This was used for the identification and integration of peaks of the analytes). The column consisted of a DB-5 fused silica capillary column (30 m length × 250 µm × 0.25 µm film thickness). The column temperature was programmed from 60°C for 1 min and increase at the rate of 10°C/min to 200°C, held for 0 min and then continued at a rate of 5°C/min to 250°C, held for 4 min [13], in other to enhance good resolution at different boiling points. The oven temperature was 300°C. The injection was done on a splitless injector at 300°C and the purge activation time was 30s. The carrier gas was Helium at 44.854 cm.sec⁻¹. The run time was 30 minutes.

2.6 Sampling and Physicochemical Analysis of Water Samples

The 2.5 L size Amber bottles used for water sampling was pre-cleaned following the standard procedure for organic contaminant sampling [14-16]. The bottles were allowed to air dried for about 24hours and the mouth part were wrapped with aluminum foil to prevent further contamination till the time of sampling. Water samples were collected from two sampling points (the raw water stage and disinfection stage) in triplicate from water treatment plant. Parameters such as Temperature, Electrical conductivity, and pH of the water samples were determined in-situ. The water samples were properly labelled, acidified with concentrated H₂SO₄ and put in ice boxes and then transferred to the laboratory immediately for further analysis. The water samples were characterized for the presence of

chlorpyrifos residue in the raw and disinfected water to determine the efficiency of the treatment plant to remove chlorpyrifos [12]. Other physicochemical parameters such as Total dissolved solids, Total suspended solids, Alkalinity, Total Organic Carbon, Total Hardness, Nitrates, Nitrites, Chloride, Sulphates and Chemical Oxygen Demand, of the water were determined following the standard procedures by [17].

2.7 Adsorption Isotherm

Equilibrium models and sorption isotherms were used to explore how an adsorbate interacts with an adsorbent. Common equilibrium models used to describe isotherms of pesticide sorption on biochars include Langmuir and Freundlich which are applied in this study.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Parameter of Rice Husk and Its Biochar

The physicochemical characteristics of rice husk and its biochar are shown in Table 1.

3.2 Elemental Composition of the RHB

The result as shown in Table 2 shows that carbon has the highest percentage of all the elements present. Also, nitrogen, hydrogen and oxygen content was as low as 0.89%, 2.06% and 35.58% separately as a result of the high pyrolytic temperature (700°C) [18]. As reported by Kim, et al. [19] that nitrogen distribution in the biochars varied with biomass material and however not affected by biochar formation temperature.

3.3 Determination of the Functional Groups in RHB

The Fourier Transform Infra-Red (FTIR) spectra of rice husk biochar is presented in Fig. 1, the figure also highlights the major stretching frequencies of the surface functional group present in rice husk biochar. The Fourier Transform Infra-Red (FTIR) analysis affirms the presence of O-H as shown by the stretching frequency at 3410.26 cm⁻¹. 2891.39 cm⁻¹ and 1440.87cm⁻¹ peak was due to –CH₃ and =CH₂ bonding extending recurrence while the extending recurrence at 808.49 cm⁻¹ was because of =CH₂ bonding. The band at 1695.49 cm⁻¹ may be credited to ketonic and aldehydic

C=O extending frequencies. Additionally, the band at 1099.46 cm^{-1} was ascribed to -C-O-H extending and -OH distortion, while band at 557.45 cm^{-1} was due to metal-halogen bond.

3.4 SEM Image of Rice Husk Biochar

The SEM image as revealed in Fig. 2a and 2b shows that rice husk biochar appears in ridges, of which are firmly interlocked with each other and are marked with prominent pores [20].

3.4.1 Effect of adsorbent dosage

The results Fig. 3 demonstrated that increasing the mass of the biochar from 0.2 to 0.8 g increased the percentage of chlorpyrifos removal from 50.88 to 98.39%, this could be ascribed to the increased in number of available adsorption sites as the solid mass increases in solution. Similar adsorption studies using biochar and different adsorbent for pesticide removal have reported a similar effect [9,21].

Table 1. Physicochemical analysis of rice husk and its biochar

Parameter	Unit	Rice husk	Rice husk biochar
pH	-	-	7.90±0.14
Electrical Conductivity	($\mu\text{S}/\text{cm}$)	-	298.8±1.14
Ash	(%)	41.96±0.96	-
Yield	(%)	-	39.44±0.47
Fixed Carbon	(%)	35.24±0.55	-
Moisture Content	(%)	5.27±0.94	-
Volatile Content	(%)	35.67±1.01	-
Braunauer-Emett-Teller (BET) Surface area	(m^2/g)	-	97.20
Total pore volume	(m^2/g)	-	0.038
Micro pore volume	(m^2/g)	-	0.0044
Iodine Number	(mg/g)	-	85.57±0.81

Table 2. Elemental composition of rice husk biochar

Element	Percentage composition
Carbon	59.14%
Hydrogen	35.58%
Nitrogen	2.06%
Oxygen	0.89%
Sulphur	2.06%

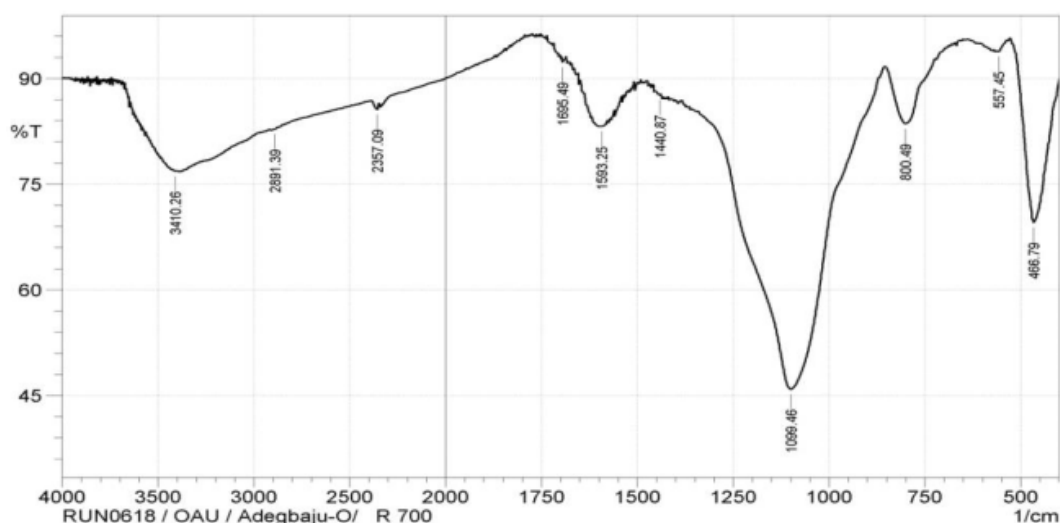


Fig. 1. FTIR image of rice husk biochar

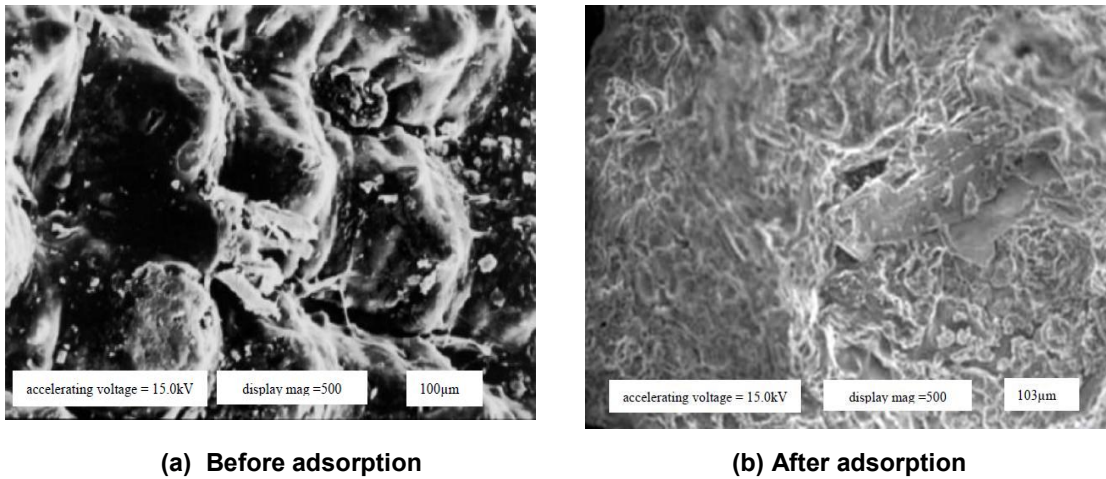


Fig. 2. SEM image of rice husk biochar

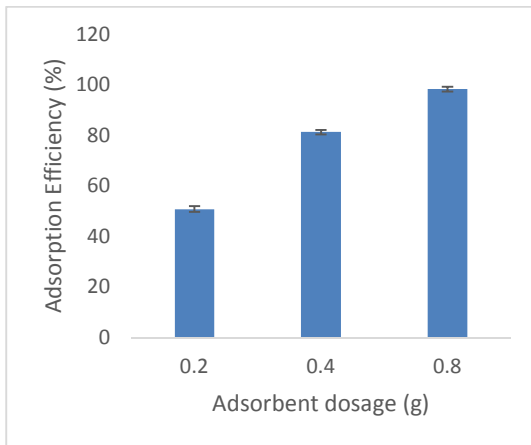


Fig. 3. Effect of adsorbent dosage on chlorpyrifos adsorption

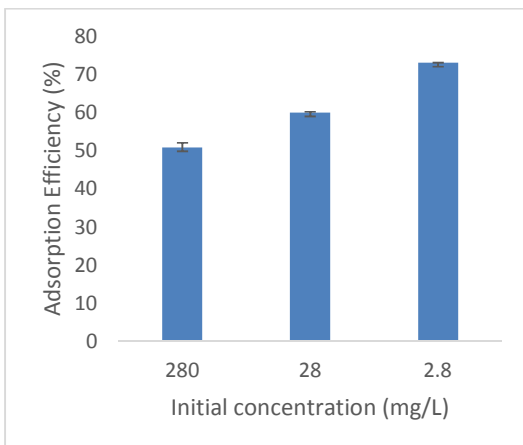


Fig. 4. Effect of initial concentration on chlorpyrifos adsorption

3.4.2 Effect of initial concentration

Fig. 4 demonstrates the adsorption efficiency of chlorpyrifos onto rice husk biochar. It was observed that adsorption efficiency increases with decrease in initial concentration of chlorpyrifos in solution. This result is in agreement with earlier studies of Thuy, et al. and Memon, et al. [9,22]. The lowest adsorption efficiency was recorded at 280 mg/L while the highest adsorption efficiency was obtained at 2.8 mg/L. This may be deduced that at low sorbate ion/sorbent ratio, sorbate ion sorption involves the higher energy sites. As the sorbate ion/sorbent ion increases, the higher energy sites are saturated and sorption begins on lower energy site, bringing about a reduction in percent sorption [23].

3.4.3 Effect of contact time

Fig. 5 demonstrates the effect of contact time on adsorption of chlorpyrifos. Effect of shaking time on percentage sorption of chlorpyrifos onto rice husk biochar was considered over a agitating time of 30 – 90 min, while other parameters were kept constant, at 120 osc/min shaking speed, for 50 ml of 280 mg/L of chlorpyrifos solution. Percent sorption increased with the increase of shaking time. The equilibrium was set up at 30 min. This might be because of the initial availability of large number of vacant sites for adsorption, later the adsorption limit tailed off because of the saturation of vacant sites. The dynamic increment in adsorption and consequently the attainment of equilibrium adsorption maybe due to limited mass transfer of Chlorpyrifos molecules from the bulk solution to the outside surface of the adsorbent [24,25].

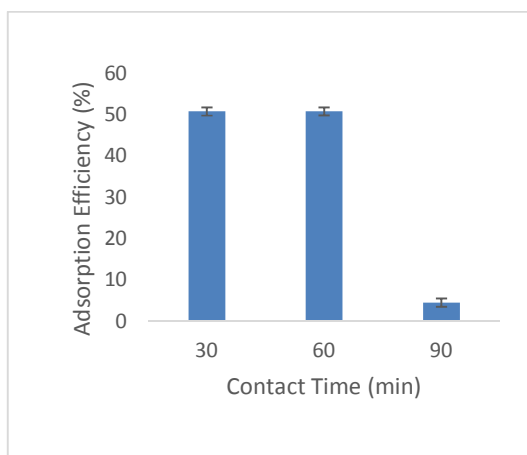


Fig. 5. Effect of contact time on chlorpyrifos adsorption

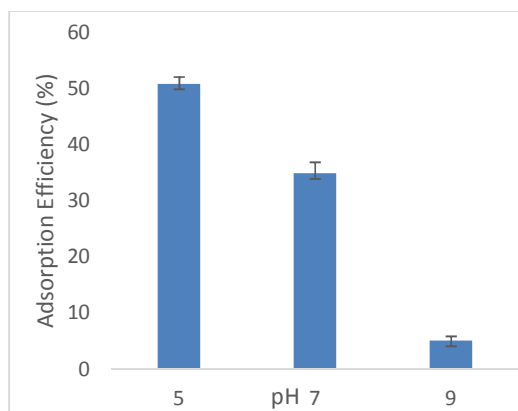


Fig. 6. Effect of pH on adsorption of chlorpyrifos

3.4.4 Effect of pH

Percentage sorption decreased with an increase in the pH of the solution from 5 to 9 as shown in Fig. 6. Adsorption as a function of pH was performed at known concentration, adsorbent doses and contact time. It was seen that best efficiency was at pH of 5 (acidic). At low pH value, the surface of the sorbent would be surrounded by the hydroxonium ions, which may enhance the sorbate interaction with binding sites of the sorbent by greater attractive forces and thus increase its take-up on polar sorbent [26]. The possible binding sites in the cells of rice husk biochar maybe dissociated at different pH values according to their dissociation constants and subsequently may participate in surface complexation. In this manner, pH assumes an

important role in the sorption onto surface of sorbent.

3.5 Physicochemical Analysis of Raw Water Sample

Table 3 presents the result of GC-MS analysis of raw and disinfected water; it was observed that chlorpyrifos is available in the raw water sample at a concentration of 5.29 µg/L. This might be because of direct run-off, leaching, careless disposal of empty pesticide container, equipment washing and so on, though, in disinfected water chlorpyrifos was below detection limit, the removal perhaps depends on the change in suspended and colloidal organic matter concentration that is accomplished after coagulant addition and flocculation after pre-oxidizing it with chlorine [27] because adding a coagulant causes agglomeration of suspended solids and colloids. This implies that the methods of coagulation and flocculation is effective in the treatment plant. Natural micropollutants, for example, pesticides may adsorb to these agglomerated particles. Likewise, chlorination process used in the majority of drinking water treatment plants ensures the removal of a significant number of the pesticides that may be available in natural water [28]. Also in the table, the percentage removal of pesticides with activated carbon and rice husk biochar in raw water sample confirms that the substances (e.g., natural organic matter) present in river water surface interact with the adsorbents and reduced the adsorbents' surface area available for adsorption [29] contrast with conventional water treatment technique.

3.6 Adsorption Isotherm

The sorption performance of rice husk biochar was evaluated through determination of sorption isotherm of Chlorpyrifos. Fig. 7a shows the plot of $\frac{c_e}{q_e}$ against c_e (Langmuir isotherm) and Fig. 7b shows the plot of $\ln q_e$ against $\ln C_e$ (Freundlich isotherm). Langmuir and Freundlich constants for the adsorption of Chlorpyrifos are presented in Table 4. Values of q_m and K_a are determined from the slope and intercepts of the plots of $\frac{c_e}{q_e}$ against c_e while the values of K_f and $\frac{1}{n}$ are obtained from the intercept and slope of the graph between $\ln q_e$ against $\ln C_e$.

Table 3. Physicochemical analysis of raw and disinfected water sample

S/N	Parameters	Units	Raw water before adsorption	Raw water after adsorption	Disinfected water
1	Temperature	°C	25.95±0.07	26.00±0.04	26.25±0.07
2	pH	-	6.30±0.00	6.92±0.01	6.90±0.14
3	Conductivity	µS/cm	110.85±0.25	98.41±1.63	303.5±12.02
4	Turbidity	NTU	8.58±0.12	4.28±0.23	0.94±0.59
5	Total Dissolved Solids	mg/L	128.50±0.71	113.98±0.15	144.5±0.71
6	Total Suspended Solids	mg/L	2.73±0.28	2.25±0.39	1.38±0.02
7	Alkalinity	mg/L	65.67±0.94	59.96±0.09	54.81±0.12
8	Total Organic Carbon	mg/L	6.70±1.15	3.71±0.40	5.40±0.047
9	Total Hardness	mg/L CaCO ₃	66.84±9.90	51.05±0.78	32.81±0.89
10	COD	mg/L	18.84±0.09	16.12±0.01	2.24±0.014
11	NO ₃ ⁻	mg/L	1.27±0.03	0.64±0.15	0.87±0.02
12	NO ₂ ⁻	mg/L	0.015±0.007	0±0.00	0±0.00
13	SO ₄ ²⁻	mg/L	4.64±0.02	3.51±0.07	0.5±0.71
14	Cl ⁻	mg/L	19.00±2.60	9.61±0.23	19.50±0.04
15	Chlorpyrifos with RHB (GC-MS)	µg/L	5.29±0.00	0.33±0.21	-
16	Chlorpyrifos with CAC (GC-MS)	µg/L	5.29±0.00	0.29±0.28	-
17	Chlorpyrifos (GC-MS)	µg/L	-	-	BDL

BDL: Below Detection Limit

In accordance with the results given in Table 4, the results of students' t-test of the adsorption of chlorpyrifos using rice husk biochar and commercial activated carbon shows that there is no statistical significance difference between the two adsorbents (rice husk biochar and commercial activated carbon). The analysis shows a sig. (2-Tailed) value of 0.537 which is greater than the probability level of 0.05. The removal efficiency of low initial chlorpyrifos concentration (5.29 µg/L) is nearly the same for rice husk biochar (93.7%) and industrially available activated carbon (94.5%). This demonstrates that at low initial chlorpyrifos concentration, the surface area and available sorption sites were relatively high in the two adsorbents. Therefore, it can be concluded that the structure of the pores of rice husk biochar is appropriate for adsorption of Chlorpyrifos as commercial activated carbon.

The parameters of Langmuir and Freundlich for the adsorption capacity of chlorpyrifos pesticide

onto rice husk biochar are obtained as described below in Table 5. The isotherm obtained using these parameters is presented in Fig. 7, together with experimental data points [30]. The Freundlich had the correlation coefficients (R^2) always >0.95, which shows the suitability of experimental isotherm data. The value of K_f (0.63) determines the adsorption capacity of an adsorbent at equilibrium concentration in a solution [31]. A higher K_f value corresponds to a higher adsorption capacity.

According to the K_f values in Table 5, the adsorption capacities of the pesticide studied are high for chlorpyrifos. Because adsorption of pesticides depends on their physicochemical properties [29], a more hydrophobic compound has a higher adsorption capacity and thus a higher removal efficiency [29]. This was confirmed in the experiment as the chlorpyrifos is slightly soluble in water.

Table 4. Adsorption efficiency of rice husk biochar and activated carbon on raw water sample

Contaminant	Adsorbent	Adsorption efficiency
Chlorpyrifos	RHB	93.7±3.96
	CAC	94.5±5.23

**Confidence level = 0.05; *Sig. value = 0.537

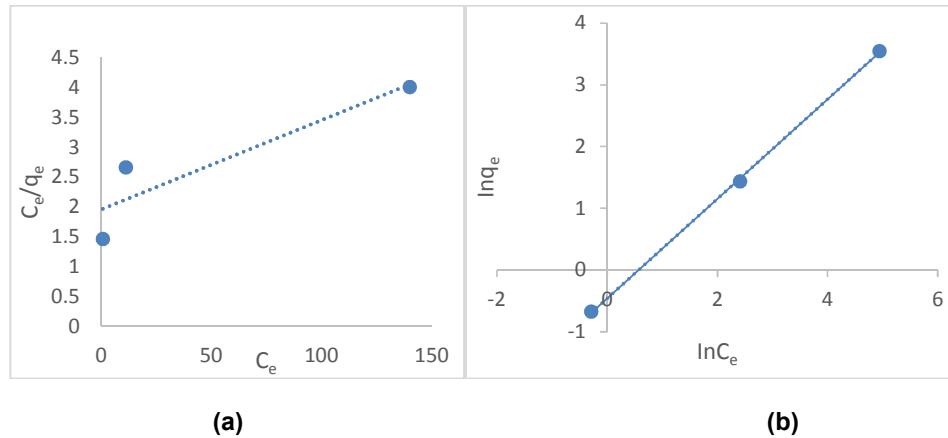


Fig. 7. Langmuir and freundlich adsorption isotherm for the adsorption of chlorpyrifos by rice husk biochar

Table 5. Langmuir and freundlich constants for the adsorption of chlorpyrifos using rice husk biochar

Adsorbent	Langmuir constants			Freundlich constants		
	q_m (mg / g)	K_a (L / mg)	R^2L	K_f (mg / g(L / mg)) $^{1/n}$	$1/n$	R^2F
RHB	19.61	0.026	0.8315	0.63	0.8066	0.9996

**R² = correlation coefficient*

The slope ($1/n$) value in Freundlich gives room for the assessment the adsorption intensity of a given substance from water phase of adsorbent [31]. The value of $1/n$ is known as the heterogeneous factor and ranges between 0 and 1 [30]; the more heterogeneous the surface, the closer $1/n$ is to 0 [32]. The slope ($1/n$) values for the three chlorpyrifos concentrations were <1 suggesting nonlinear adsorption isotherms. A slope <1 which are characterized by a decrease in the adsorption at higher aqueous concentration of compounds, thus, sorption of chlorpyrifos pesticide on rice husk biochar was concentration dependent [33]. This type of adsorption isotherms is observed when the molecules are sorbed in a flat position, not suffering a strong competition from the water molecule, which explains that rice husk biochar has a high affinity for Chlorpyrifos at low concentration and there is no competition from the solvent for adsorption site [30].

Both Langmuir and Freundlich isotherm have correlation coefficient (R^2), which are calculated from the graphs in Table 5, falls within $0 < R^2 < 1$ and both isotherms adequately describe the

experimental data of the adsorption of chlorpyrifos, Freundlich isotherm had a better fitting than Langmuir isotherm for the adsorbent (rice husk biochar). This is because the correlation coefficients of Freundlich isotherm R^2F is higher correlation coefficients of Langmuir isotherm (R^2L).

4. CONCLUSION

Best adsorption conditions for rice husk biochar in this study were 2.8 mg/L initial concentration; 0.8 g of adsorbent dosage; pH of 5 and contact time of 30 min. Rice husk biochar demonstrates a quantifiable adsorption for chlorpyrifos that is practically identical to activated carbon. This study demonstrated that agricultural wastes, for example, rice husk instead of constituting nuisance to the environment could be handled to fill in as less expensive, non-hazardous alternative adsorbent to the commercially expensive available activated carbon for treating consumable water for town supply.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our

area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

ACKNOWLEDGEMENT

The author acknowledged with gratitude SwWECh Laboratory, Institute of Ecology and Environmental Studies, Obafemi Awolowo University, Ile – Ife, Nigeria where most of the field and laboratory analyses were carried out.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Udemezue J, Osegbue E. Theories and models of agricultural development. *Ann. Rev. Res.* 2018;1(5):1-4.
2. Coker A, Akogun E, Adebayo C, Mohammed U. Assessment of implementation modalities of the anchor borrowers' programme in Nigeria. *Agro-Science.* 2018;17(1):44-52.
3. Nakhshiniev B, Biddinika MK, Gonzales HB, et al. Evaluation of hydrothermal treatment in enhancing rice straw compost stability and maturity. *Bioresource Technology.* 2014;151:306–313.
4. Rathod AL, Garg R. Chlorpyrifos poisoning and its implications in human fatal cases: A forensic perspective with reference to Indian scenario. *Journal of Forensic and Legal Medicine.* 2017;47:29-34.
5. Van der Bruggen B, Borghgraef K, Vinckier C. Causes of water supply problems in urbanised regions in developing countries. *Water Resources Management.* 2010;24(9):1885-1902.
6. Alves AADA, Ruiz GLDO, Nonato TCM, Pelissari C, Dervanoski A, Sens, ML. Combined microfiltration and adsorption process applied to public water supply treatment: Water quality influence on pesticides removal. *Environmental Technology.* 2019;1-11.
7. Amuda O, Ibrahim A. Industrial wastewater treatment using natural material as adsorbent. *African Journal of Biotechnology.* 2006;5(16).
8. Karakoyun N, Kubilay S, Aktas N, Turhan O, Kasimoglu M, Yilmaz S, Sahiner N. Hydrogel–biochar composites for effective organic contaminant removal from aqueous media. *Desalination.* 2011;280(1-3):319-325.
9. Thuy PT, Anh NV, Van der Bruggen B. Evaluation of two low-cost–high-performance adsorbent materials in the waste-to-product approach for the removal of pesticides from drinking water. *CLEAN – Soil, Air, Water.* 2012;40(3):246-253.
10. Murat Kili CK, Ozge Cepeligullar, Ayse E. Putun. Adsorption of heavy metals ions from aqueous solutions, by biochar a by-product of pyrolysis. *Applied Surface Science.* 2013;283:856-862.
11. Okoya AA, Ogunfowokan AO, Asubiojo OI, Torto N. Organochlorine pesticide residues in sediments and waters from cocoa producing areas of Ondo State, Southwestern Nigeria. *ISRN Soil Science;* 2013.
12. Hossain M, Chowdhury MAZ, Pramanik MK, Rahman M, Fakhruddin A, Alam MK. Determination of selected pesticides in water samples adjacent to agricultural fields and removal of organophosphorus insecticide chlorpyrifos using soil bacterial isolates. *Applied Water Science.* 2015;5(2):171-179.
13. Tu C, Zone WFT. Analysis of organophosphorus pesticides with Agilent 6820 gas chromatograph/nitrogen phosphorus detector. Agilent Technologies Publication; 2004.
14. Hunt DTE, Wilson AL, Wilson A. The chemical analysis of water: General principles and techniques: Royal Society of Chemistry. 1986;2.
15. Apha A. Wef (American public health association, American water works association and water environment federation). Standard methods for the examination of water and wastewater. 1998;19.
16. Apha A. Wef. Standard methods for the examination of water and wastewater. 2012;22.
17. Ademoroti C. Standard methods for water and effluents analysis. Ibadan: Foludex Press Ltd. 1996;3.
18. Ahmad M, Lee SS, Dou X, Mohan D, Sung JK, Yang JE, Ok YS. Effects of pyrolysis

- temperature on soybean stover-and peanut shell-derived biochar properties and tce adsorption in water. *Bioresource technology*. 2012;118:536-544.
19. Kim WK, Shim T, Kim YS, Hyun S, Ryu C, Park YK, Jung J. Characterization of cadmium removal from aqueous solution by biochar produced from a giant miscanthus at different pyrolytic temperatures. *Bioresource Technology*. 2013;138:266-270.
 20. Park BD, Wi SG, Lee KH, Singh AP, Yoon TH, Kim YS. Characterization of anatomical features and silica distribution in rice husk using microscopic and micro-analytical techniques. *Biomass and Bioenergy*. 2003;25(3):319-327.
 21. Zheng W, Guo M, Chow T, Bennett DN, Rajagopalan N. Sorption properties of greenwaste biochar for two triazine pesticides. *Journal of Hazardous Materials*. 2010;181(1):121-126.
 22. Memon GZ, Bhangar M, Akhtar M. The removal efficiency of chestnut shells for selected pesticides from aqueous solutions. *Journal of Colloid and Interface Science*. 2007;315(1):33-40.
 23. Sivaraj R, Namasivayam C, Kadirvelu K. Orange peel as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solutions. *Waste Management*. 2001;21(1):105-110.
 24. Wang S, Wu H. Environmental-benign utilisation of fly ash as low-cost adsorbents. *Journal of Hazardous Materials*. 2006;136(3):482-501.
 25. Onundi YB, Mamun A, Al Khatib M, Al Saadi M, Suleyman A. Heavy metals removal from synthetic wastewater by a novel nano-size composite adsorbent. *International Journal of Environmental Science & Technology*. 2011;8(4):799-806.
 26. Rengaraj S, Moon SH, Sivabalan R, Arabindoo B, Murugesan V. Agricultural solid waste for the removal of organics: Adsorption of phenol from water and wastewater by palm seed coat activated carbon. *Waste Management*. 2002;22(5):543-548.
 27. Ballard BAMA. Estimating the removal of anthropogenic organic chemicals from raw water by coagulation flocculation. *Journal of Environmental Engineering*. 2005;131:108-118.
 28. Ormad M, Miguel N, Claver A, Matesanz J, Ovelleiro J. Pesticides removal in the process of drinking water production. *Chemosphere*. 2008;71(1):97-106.
 29. Thuy PT, Moons K, Van Dijk J, Viet Anh N, Van der Bruggen B. To what extent are pesticides removed from surface water during coagulation–flocculation? *Water and Environment Journal*. 2008;22(3):217-223.
 30. Ayranci E, Hoda N. Adsorption kinetics and isotherms of pesticides onto activated carbon-cloth. *Chemosphere*. 2005;60(11):1600-1607.
 31. Ignatowicz K. Selection of sorbent for removing pesticides during water treatment. *Journal of Hazardous Materials*. 2009;169(1-3):953-957.
 32. Al Duri B. Adsorption modelling and mass transfer Use of adsorbents for removal of pollutants from wastewaters: CRC Press, New York. 1996;133-173.
 33. Giles C, MacEwan T, Nakhwa S, Smith D. Studies in adsorption. A system of classification of solution adsorption isotherms and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *Journal of the Chemical Society*. 1960;3973-3993.

© 2020 Okoya et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:

The peer review history for this paper can be accessed here:
<http://www.sdiarticle4.com/review-history/54205>