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Full Length Research Article

RICE HUSK AS BIOSORBENT FOR THE ADSORPTION OF METHYLENE BLUE

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ABSTRACT
The ability of rice husk (RH) to adsorb methylene blue (MB) from aqueous solutions has been studied at different initial dye concentrations (10, 20, 30, 40, and 50 mg/L), contact time (10 to 120 mins), pH (2–10) and adsorbent dosage (0.05, 0.1, 0.15, 0.20 and 0.25 g). The MB percentage removal was found to increase with increase in three adsorption parameters studied. Adsorption data were modeled using Langmuir and Freundlich adsorption isotherms with the Freundlich model being the best fit and pseudo-second-order model was the best order that described the kinetics of the MB adsorption process.

Keywords: Adsorption, Isotherms, Kinetics, Methylene blue, Rice husk

INTRODUCTION
Rapid developments in industrialization relative to the world increase in human population over the last few decades have resulted in to serious environmental pollution. Because of that, considerable attention was given to recovery, recycle and reuse of waste water due to the rapid increase in demand of water globally (Adetokun *et al.,* 2019; Chaudhry *et al.,* 2016; Das *et al.,* 2014; Gao *et al.,* 2018; Garba *et al.,* 2019a; Garba *et al.,* 2019b).
The textile industry plays a key role in the growth of the economy of many countries in the world. Dyes are one of the primary raw materials used in the industries. Over the last few years, consumption of synthetic dyes, particularly azo groups by textile industries have increased significantly. Synthetic dyes are the most widely used dyes and survey through the literature revealed approximately 700,000 tons of synthetic dyes are produced annually and over 70% of these dyes are consumed by textile, food, cosmetics and paint industries (Muhammad *et al.,* 2019; Zango & Imam, 2018). These dyes offers ease of applications, stability and low-cost in comparison to natural dyes (Garba *et al.,* 2015b; Garba *et al.,* 2015c; Zango *et al.,* 2017). Among the classes of synthetic dyes, basic dyes are considered as one of the most widely used (Ahmad, 2009; Garba *et al.,* 2015a). The main area of their application is in acrylic and modacrylic fibers in which they give very good fastness to light and to washing. They are sometimes used on cotton, wool but a mordant must be applied to the material. They exhibited a moderate fastness to cotton and poor fastness to wool. They are characterized by the presence amino group in their structures. They are mostly discharge inform of industrial effluents into the environment, where they caused severe toxic effects to human beings, plants and aquatic organisms. The effluents containing dyes are intensively colored and cause serious pollution to our environment. When discharged in to the various water bodies, basic dyes can cause significant problems to living organisms as they interfere with the metabolism and their possessed carcinogenic and mutagenic effects (Jaleel *et al.,* 2010; Zhao & Liu, 2008)
Water pollution is a serious threat to the developing countries as a result of irrational discharging of effluents from the textile. Effluents released without any treatment get their way into nearby aquatic environment and thus posing water pollution challenge to several countries. It was reported that wastewater discharged from textile, printing, leather, plastics and cosmetics industries usually contains about 10-20 % of dyes. Vast majority of these dyes are difficult to treat by conventional degradation methods (Shamsipur & Rajabi, 2014). Novel alternatives are required to address this issue. However, although a wide variety of research is going on how to remove the dyes from the waste water by using numerous low-cost materials. Some of the materials themselves cause serious harm to aquatic life and the fact that most of the dyes possesses complex aromatic structures which make them resist biodegradation (Gonga, 2005). Among the various traditional water treatment methods employed for the removal of dyes and other contaminants present in wastewater, Adsorption is considered as the most promising and popular technique (Abechi, 2018; Garba *et al.,* 2019c; Zango *et al.,* 2016), widely applied for the removal of various contaminants . Agricultural waste materials function as a good precursor and/or act as biosorbents for the removal of contaminants from wastewater such as heavy metals, dyes, pigments and large varieties of organic pollutants (Banerjee & Chattopadhyaya, 2017). Various adsorbents obtained from agricultural waste materials such corn stalk (Muhammad *et al.,* 2019), *canarium schweinfurthii* seed shell (Garba *et al.,* 2019a), modified plantain peels (Garba *et al.,* 2016b), banana peels (Dahiru *et al.,* 2018), coconut shell (Imam & Zango, 2018), *prosopis africana seed hulls* (Garba & Afidah, 2016; Garba & Afidah, 2014), defatted papaya seed (Garba *et al.,* 2016a), *borassus aethiopum* shells (Garba *et al.,* 2014), groundnut shell (Zango and Imam, 2018), among others have been reported for the removal dyes and other organic pollutants from wastewater. Rice husk is one another important agricultural waste product, representing about 20 % of the whole rice product, on weight basis of the whole rice. With agricultural waste residues offering best alternatives as a result of their low-cost and most importantly high adsorption efficiency, this work is therefore aimed at employing the use of rice husk (RH) obtained from agricultural waste for the adsorption of methylene blue (MB) dye.

MATERIALS AND METHODS
RH was obtained from Dawanau Market in Kano State, Nigeria in February 2017. MB dye was purchased from Sigma Aldrich (USA). The sulfuric acid, hydrochloric acid and sodium hydroxide

were obtained from Sinopharm Chemical Reagent Co. Ltd., China. All reagents used in this work is are of analytical grade and high purity. Distilled water was used throughout the work.

Adsorbent preparation
The adsorbent use in this study (RH) is a by – product of local rice milling industry, an undesirable agriculture mass residue is obtained from Dawanau, the largest market of agricultural products in Kano state Nigeria. Initially, all the unwanted particles were hand-picked from the rice husk before it was subjected to wash thoroughly with tap water. It was then air dried for a period of one week. It is then grinded into powder using mortar and pestle to powder form. It was then sieved to remove large particles, leaving only the fine particles. It was then washed with distilled water several times until all yellow color cause by lignin was completely removed. It was finally subjected to air drying for a period of 3 days.

Adsorbate
The dye stock solution (1000 mg/L) was prepared by dissolving 1g of MB in 1L distilled water. All reagents used in this work were of analytical grade. To prepare various solutions at desired concentrations from the stock solution, distilled water was used for the necessary dilutions. MB concentrations were analyzed by measuring the absorbance values before and after each experiment with a (UV–Vis) spectrophotometer (Japan) at the wavelength of 664 nm.

Batch adsorption experiment
In a typical experiment, 25 mL of 50 mg/L dye solutions was transferred into a conical flask and 0.05 g of adsorbent was stirred together until equilibrium was attained. About 2 mL of the solution was immediately transferred to the cuvette and the absorbance of the MB dye was recorded at different time intervals using a UV-visible spectrophotometer. All the experiments were conducted at room temperature and repeated 3 times to ensure accuracy of the obtained data. The removal efficiency (%),of the MB dye adsorbed at different time intervals (q_t, mg/g), and at equilibrium (q_e, mg/g) were calculated using the following equations:

$$\text{Percentage Removal } (\% R) = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

$$q_t = \frac{(C_o - C_t)V}{w} \quad (2)$$

$$q_e = \frac{(C_o - C_e)V}{w} \quad (3)$$

Where C_o, C_t and C_e represents initial, time and equilibrium concentrations of MB (mg/L), respectively and W is the weight of adsorbent (g) while V is the solution volume (L).

Effect of contact time
This experiment was done to determine the optimum equilibrium time of the adsorption. The experiment was carried out at different mixing time ranging from 20 to 140 minutes. The adsorbent dose used was 0.05 g; other factors were fixed.

Effect of adsorbent dose
This was carried out with different adsorbent dosages. The dose of adsorbent was varied from 0.05 to 0.25 g with 50 mL of dye solution. Samples were shaken with a fixed time interval, filtered and analyzed.

Effect of pH
To determine the optimum pH conditions for the adsorption of MB, the effect of pH was observed over the entire pH range (2 -10) with optimum contact time and adsorbent dosage which result from previous experiments with fixed other factors. The pH was adjusted using 0.1 M HCl and 0.1 M NaOH solutions.

Adsorption isotherms and kinetic models
The equilibrium experimental data were analyzed using Langmuir and Freundlich adsorption isotherm models. The mathematical expression for Langmuir isotherm is described as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot Q_a^0} + \frac{C_e}{Q_a^0} \quad (4)$$

The expression for the Freundlich isotherm model is:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

Where Q_a^0 (mg/g) and K_L (L/mg) are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The values of Q_a^0 and K_L can be determined from the linear plot $\frac{C_e}{q_e}$ versus C_e. K_F is the constant that stands for the adsorption capacity related to bond strength. While $\frac{1}{n}$ is constant indicating adsorption intensity. K_F and n were determined from the linear plot of $\log q_e$ versus $\log C_e$.
Batch kinetic experimental data for the adsorption of MB onto RH were analyzed by pseudo-first-order, pseudo-second-order.
The pseudo-first-order kinetic equation is expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

Where, q_e and q_t (mg/g) are the amounts of the dye adsorbed on RH at equilibrium and time t (min) respectively. While k_1 (min) is the adsorption rate constant.
For the pseudo-second-order model, the equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

Where k_2 is the rate constant for pseudo-second-order adsorption model.

RESULTS AND DISCUSSION

Effect of contact time
Figure 1 explains the effect of contact time at initial dye concentration of 50 mg/L, adsorbent dose of 0.05g. It is clear that the extent of adsorption is rapid in the initial stages (20 mins). However, the MB adsorption decreases with increasing contact time and becomes slow till saturation is reached. The final concentration of MB did not change after 120 min. This show that equilibrium time occurs at 120 min. It is due to saturation of active sites which do not allow further adsorption to take place. Similar results for were also reported by (Hameed et al., 2007).

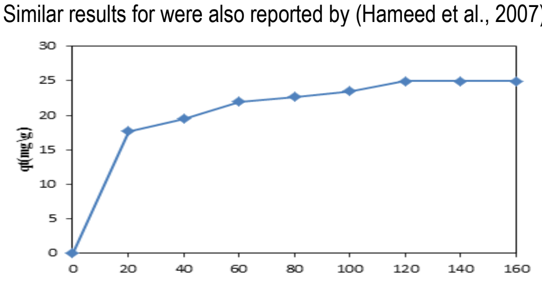

Fig. 1: Effect of contact time for adsorption of MB dye onto RH

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Effect of adsorbent dosage

The effect of adsorbent dosage is illustrated in figure 2. It was found that the amount of dye adsorbed at equilibrium (q_e) decreased from 24.93 mg/g to 4.98 mg/g as the adsorbent dosage increased from 0.05 to 0.25 g with initial dye concentration of 50 mg/L. This is due to increase in adsorbent dosage attributed to increase in surface area and availability of more adsorption sites. On the other hand, the adsorption sites remained unsaturated. Similar observations were reported elsewhere (Malik *et al.,* 2007; Yener *et al.,* 2008).

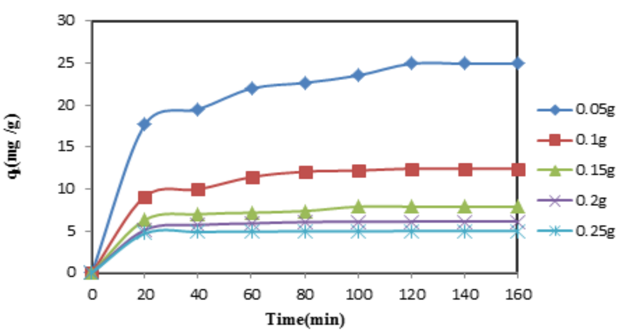

Fig. 2: Effect of adsorbent dosage for adsorption of methylene blue onto RH at initial concentration of 50 mg/L

Effect of initial dye concentration

Figure 3 shows the effect of changing MB dye concentration. About 100 % removal was observed when smaller concentrations of 10 mg/L and 20 mg/L were used with an adsorbent dosage of 0.05 g. However, reduction in the percentage removal was observed with dye concentrations of 40 mg/L and 50 mg/L to 95 % and 93 % removals were reported respectively. Higher removals at lower concentrations could be related to the ratio of dye molecules to the adsorption sites availability. At lower concentrations, the dyes have higher affinity to the adsorption sites (Banerjee & Chattopadhyaya, 2017).

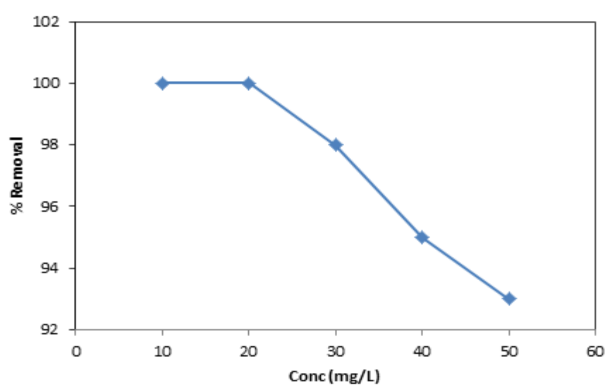

Fig. 3: Effect of initial dye concentration on adsorption capacity of methylene blue onto rice husk (0.05 g adsorbent dose**)**

Effect of solution pH

The effect of solution pH on the removal of MB using RH adsorbent is depicted in figure 4. At lower pH values, low removal was observed which was due to the high concentration of H^+ ions that resulted in repulsion and hence cause the reduced biosorption (Saeed & Sharif, 2010). However, at higher pH values, maximum removal was observed. The reason for increased in removal efficiency at alkaline pH is due to the availability of more negatively charged surface which caused decrease in repulsion between the positively charged dye molecule and the biosorbent.

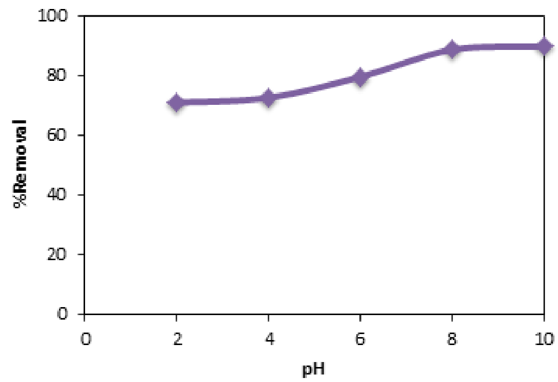

Fig. 4: Adsorption of methylene blue onto RH as a function of solution pH at initial concentration of 50 mg/L and adsorbent dosage of 0.05g.

Adsorption isotherm models

In this study, the equilibrium data for MB adsorption onto RH were modeled with the Langmuir and Freundlich models. The Langmuir isotherm model denotes monolayer biosorption while Freundlich isotherm model explain biosorption onto a heterogeneous surface. Freundlich model was fitted more by the adsorption data based on higher coefficient of correlation (R^2) value of 0.905 whereas Langmuir model has R^2 of 0.620 (Table 1). Also the Freundlich isotherm value ($\frac{1}{n}$), is a measure of the adsorption intensity on the surface of the biosorbent which is heterogeneous in nature. It indicated the easy uptake of MB dye. A value of $\frac{1}{n}$ value below one indicates a normal Freundlich isotherm whereas above one indicates cooperative adsorption (Hameed, 2007).

Table 1: Adsorption isotherm parameters

Langmuir parameters		Freundlich parameters	
Q_a^0 (mg/g)	13.50	K_F (mg^{1-n}/g L^n)	5.50
K_L (L/mg)	0.074	$\frac{1}{n}$	0.58
R^2	0.62	R^2	0.91

Kinetics of adsorption

The kinetics of MB and adsorption onto RH were analyzed using pseudo first-order and pseudo second-order kinetic models. The linear pseudo-first-order and pseudo-second order were shown in equation 6 and 7. The results of fitting experimental data with the pseudo first-order and pseudo second-order models for adsorption of MB on RH are presented in Table 2. As can be seen, there was an inconsistent trend in the R^2 values obtained for the pseudo-first-order model with poor or no good agreement between experimental ($q_{e\ exp}$) and the calculated ($q_{e\ cal}$) values obtained. This shows poor fitting of the MB kinetic adsorption data with pseudo first-order model. However, the closeness of obtained R^2 values to 1 indicated that the kinetic adsorption data obeyed pseudo-second-order model. A good agreement between $q_{e\ exp}$ and $q_{e\ cal}$ values further confirmed the validity of pseudo-second-order claim as the best model in describing the kinetics data of MB adsorption onto RH.

Table 2: Pseudo-first-order and pseudo-second-order constants for MB adsorption onto RH

Kinetic Models	Model parameters			
Pseudo-first-order	R^2	$q_{e\ exp}$ (mg/g)	$q_{e\ cal}$ (mg/g)	k_1 (1/mins)
	0.984	24.93	10.44	0.432
Pseudo-second-order	R^2	$q_{e\ exp}$ (mg/g)	$q_{e\ cal}$ (mg/g)	k_2 (g/mg mins)
	0.995	12.83	27.7	0.00065

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