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Comparative Study of Adsorption of Congo Red on Wheat Husk and Rice Husk

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Wheat husk, Rice husk, dye, adsorption isotherms, Langmuir constant

ABSTRACT

In this comparative study, Congo red dye was removed by utilizing wheat husk and rice husk as a biosorbent. The effects of adsorbent size, adsorbent dose, contact time, adsorbate concentration, pH, stirring rate, and temperature were assessed by batch adsorption experiments. The results have been verified based on Langmuir adsorption isotherm model. Optimal adsorption was observed at a dose of 0.5 g for wheat husk and 1.0 g for rice husk. Rice husk reached the adsorption equilibrium in 30 minutes, while wheat husk required 60 minutes. The percentage of dye removal increased with higher initial dye concentrations and was highest at pH 5 for both adsorbents, but rice husk consistently showed superior adsorption across all pH levels. Stirring rates of 100 rpm yielded the highest adsorption for both adsorbents, with higher stirring rates decreasing adsorption efficiency. Room temperature was optimal for adsorption, while higher temperatures reduced adsorption performance. The monolayer adsorption capacity calculated from Langmuir isotherm was 0.984 (WH) and 0.989 (RH) at 30°C. The study showed that rice husk proved to be the best adsorbent for the removal of congo red dye from aqueous solution as compared to wheat husk when all the parameters of adsorbent were studied.

1. INTRODUCTION

The first pollutant identified in wastewater are dyes, discharged as wastes from various industries such as paper, plastics, leather, pharmaceuticals, food, cosmetics, dyestuffs, and textiles. Even at deficient concentrations, these dyes in water are highly visible and unwanted (Jain and Sikarwar, 2006). The degraded by-products of organic dyes, particularly synthetic azo dyes, harm the environment due to the presence of toxic aromatic amine compounds dyes, harm the environment due to the presence of toxic aromatic amine compounds (Khedr *et al.*, 2009). Azo dyes are a significant class of

synthetic organic pigments with widespread global manufacturing and diverse applications. The toxicity and carcinogenic properties of these dyes and their precursors are threat to environmental (Xu and Ding, 2022). Moreover, the intricate aromatic structure of many dyes makes them challenging to degrade. This persistence of dyes in the waste water effect the ecosystem of aquatic life and contributes to public health issues, including allergic dermatitis, skin irritation, cancer, and mutations (Gong *et al.*, 2007; Alau *et al.*, 2010). Therefore, the removal of dyes is important from wastewater to prevent ongoing environmental pollution. Various methods,

whether used individually or in combination, are employed to remove these dyes. Recently, adsorption using a variety of agro-waste materials such as rice husk, wheat husk, plant leaves, and peels of fruits like orange, lemon, watermelon, banana, and peanut has been utilized on a laboratory scale to eliminate dyes from water (Kanmaz *et al.*, 2020; Rehman *et al.*, 2020; Uddin *et al.*, 2021).

Adsorbents prove to be cost-effective, efficient, eco-friendly, and simple to manage. Pakistan is recognized as the fourth largest producer of rice globally and is also known for its wheat production. Hence, there is a vast amount of waste materials generated from rice and wheat husks. This waste generated can serve as a key adsorbent for removing dyes found in different industrial wastewaters (Junaid *et al.*, 2014).

Congo red, also known as CR, is a type of benzidine-based azo dye chosen for the research due to its intricate chemical composition, strong solubility in water, and its enduring presence in the environment after being released. Congo red is prevalent in the waste discharged from industries like paper, printing textile, leather, etc., and during dyeing processes; approximately 15% of it is released into wastewater (Chatterjee *et al.*, 2010).

The research project aims to assess the adsorption properties of rice and wheat husk on aqueous solutions of methylene congo red (CR) as synthetic dye wastewater, which is readily available and cost-effective. Research conducted in batch mode with agitation is crucial for producing equilibrium and kinetic data, which can be used to assess the effective pore diffusivity of the adsorbate.

2. METHODOLOGY

All chemicals from Merk and Fluka were used for experimentation. All the apparatus used were autoclaved as well. The rice and wheat

husk were obtained from indigenous resources of Pakistan.

2.1 Preparation of Standard Dye Solution

For the stock solution of congo red dye (CR) (60910), 1gm of dye in ethanol was dissolved and volume was made up to mark with 1000ml of distilled water to make the concentration 1000ppm. For batch study, different concentrations were prepared by serial dilution (Hameed *et al.*, 2007) ranging from 5 to 25ppm, optical density was determined at wavelength 497nm. A calibration curve was obtained.

2.2 Preparation of Adsorbent

Two types of adsorbents were used for comparative study of adsorption for congo red, like:

- Wheat husk
- Rice husk

The wheat husk & rice husk was obtained from a market as solid waste and was used for sorption experiments without any treatment. The wheat husk & rice husk was sieved repeatedly.

2.3 Adsorption Experiments

The absorption experiments were conducted under normal temperature conditions. The pH of the solution was changed within the range 4 to 8 using acidic or alkaline solutions. A specified quantity of adsorbent was introduced into the sample and left to sit for one hour. Next, the mixture underwent filtration, and the concentration of the dye was determined using a spectro UV/VIS double beam UVD = 3500, with a λ_{max} of 497nm. The impact of different factors on the speed of the adsorption process was studied by changing the size of the adsorbent particles (20-80), the quantity of adsorbent (0.5-2.5gm), the duration (15 min-90 min), the speed of stirring (100-500rpm), the temperature (30-70°C), and the optimal pH



level (4-8). The constant volume of solution (V) remained at 35mL.

The equation for determining the Quantity of dye adsorbed, q_e , was as follows:

$$q_e = V (C_o - C) / M$$

q_e represents the equilibrium dye adsorption capacity in milligrams per gram, V is the volume of the dye solution in liters, C_o denotes the initial dye concentration in milligrams per liter, C indicates the dye concentration at any given time in milligrams per liter, and M stands for the dosage of the adsorbent in grams.

3. RESULTS

3.1 Effect of adsorbent size (mesh):

The effect of particle size on the adsorption of congo red was studied with different mesh sizes of WH and RH. The results obtained are presented in Fig. 1 and in Table 1. Adsorption yield decreased with increasing adsorbent size. The results showed that rice and wheat husk had maximum adsorption capacity at 20-40 mesh size. The comparative study exhibited a maximum effect of particle size on the %age adsorption of dye $RH > WH$.

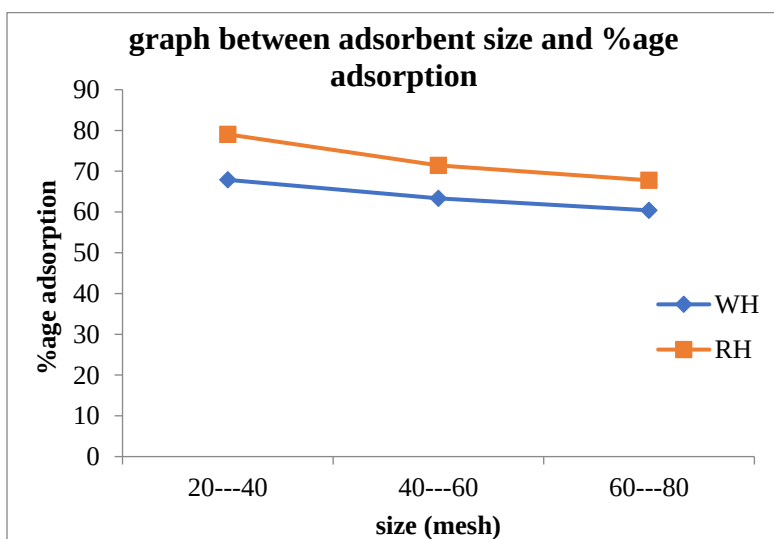


Figure 1. Effect of adsorbent particle size (mesh) on % adsorption

3.2 Effect of Adsorbent Dose

The change in the adsorbent dose effected the the adsorption capacity of congo red. It was studied with taking different adsorbent amount in the range of 0.5 – 2.5 g. The results obtained were preset in Fig 2 and Table 1. The %age adsorption increased at low adsorbent amounts 0.5 g for WH and 1.0g for RH, as more adsorption sites were available. The other behavior could be considered as the particles being such as accumulation, leading to an increased dose of adsorbent. The relative study

revealed that the effect of the adsorbent concentration on the %age adsorption of dye was maximum in $RH > WH$.

3.3 Effect of Contact Time

To evaluate the consequence of contact time on the adsorption process, the %age of Congo red adsorption was examined as a function of contact duration from 15 to 90 minutes. The outcomes are shown in Table 1 and Figure 3. The adsorbate was absorbed quickly, according to the adsorption characteristic. Furthermore, a greater number of surface sites that are



available for adsorption but that become harder to occupy over time may be the cause of the quick adsorption at the beginning stage. The contact time for WH and RH were observed to be 60 minutes and 30 minutes respectively. The study displayed that the effect of contact time on the adsorption %age was maximum in RH > WH.

3.4 Effect of Initial Dye Concentration

The effect of the initial dye concentration on the dye adsorption capacity was investigated in the concentration range of 5–25 ppm at pH (4–8) of the medium. The results in Figure 4 shows the increase in percentage adsorption with an increase in the initial dye concentration for

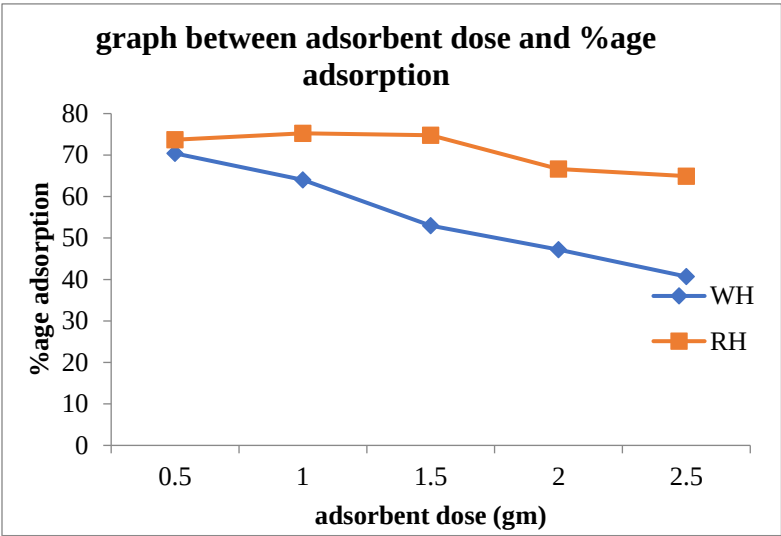


Figure 2. Effect of adsorbent dose (gm) on % adsorption

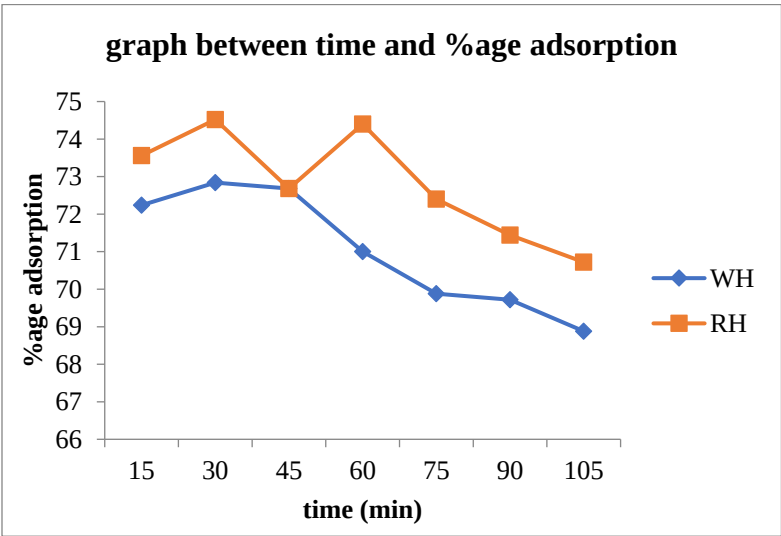


Figure 3. Effect of time (min) on % adsorption

both wheat husk (WH) and rice husk (RH). This could be due to an increase in the concentration gradient, an increase in the number of available active sites, or an increase in the dye's initial concentration. It also showed differences in the dye's capacity for adsorption. The study presented the effect of initial dye concentration on the adsorption %age RH > WH.

3.5 Effect of pH

The pH was the main element controlling the process of the adsorption. The percentage of congo red adsorption was examined in response to pH in the pH range of 4 to 8. The data obtained is pictorially displayed in Fig. 5. The amount of dye adsorbed decreases as pH

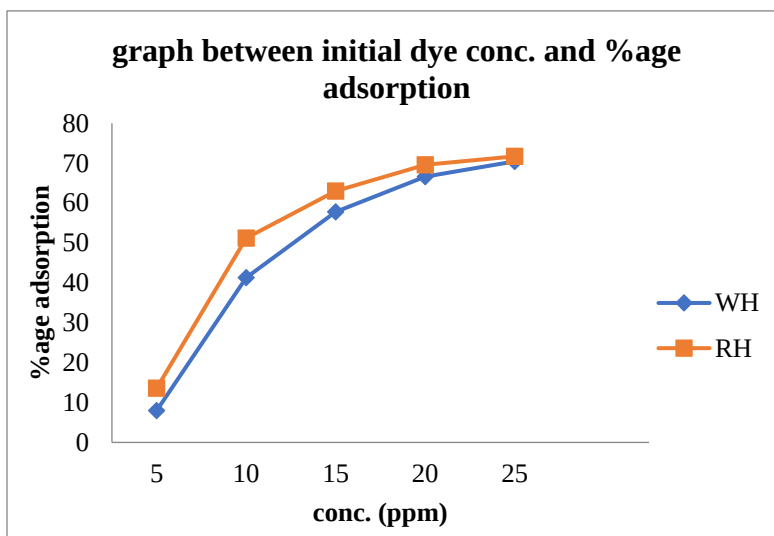


Figure 4. Effect of initial dye concentration (ppm) on % adsorption

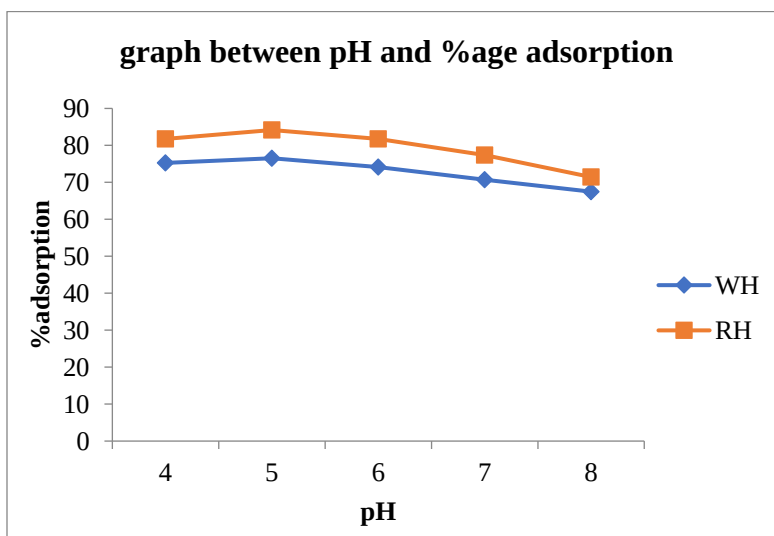


Figure 5. Effect of pH on % adsorption



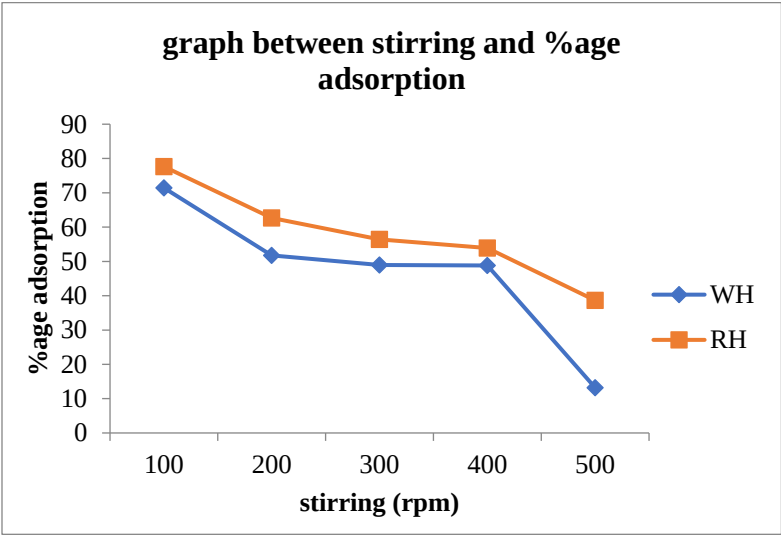


Figure 6. Effect of stirring rate on % adsorption

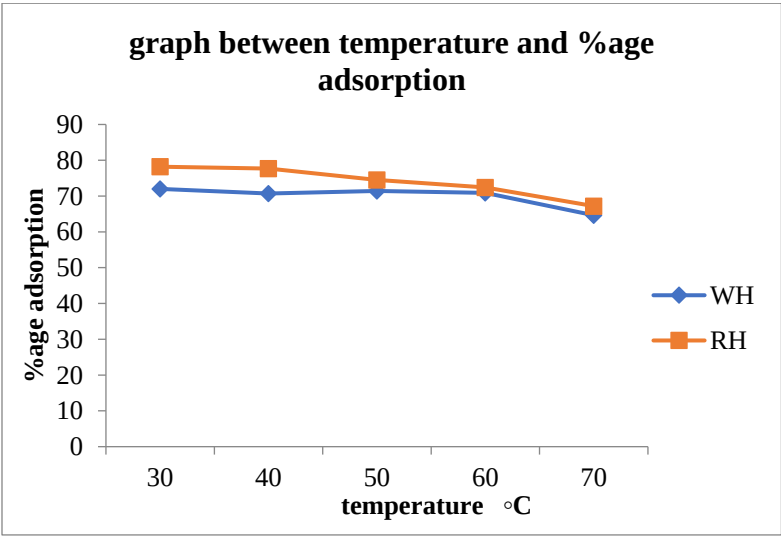


Figure 7. The effect of temperature on adsorption %

rises for WH and RH, whereas the percentage of adsorption increases at pH "5". The study presented the effect of pH on the adsorption %age of dye maximum in RH > WH.

3.6 Effect of Stirring Rate

Five different stirring speeds (ranging from

100 to 500 rpm) were utilized to examine the impact of speed variations on the adsorption. Fig. 6 illustrates the sorption kinetics of the adsorbent graphically. The dye absorbed most well for WH and RH at a modest stirring speed of 100 rpm. Following its reduction, there was no more rise in adsorption because all binding

sites had been occupied and no more could be found.

3.7 Effect of Temperature

Temperature is also helpful to determine the adsorption capacity. The impact of temperature on congo red dye was examined for adsorption capacity, ranging temperatures from 30 to 70 °C. The acquired results are shown in Fig. 7. The dye absorbed best at 30 °C (room temperature) for WH and RH. The molecules travel more quickly at high temperatures,

giving dye anions and the adsorbent material less time to interact. For sorption at high temperatures, the plant material is also denatured.

The process of adsorption along with the interaction between adsorbents and adsorbates were explained by adsorption isotherms. Finding the best association between the batch equilibrium data is crucial for the analysis and design of the adsorption system. The adsorption equilibrium data are most commonly described by the Langmuir model.

Table 1. Langmuir adsorption isotherm

Langmuir adsorption isotherm					
Husk	Intercept	Qmax (mg congo red/1g husk)	Slope	b (dm ³ /g)	R ²
WH	0.5174	1.93	8.39	0.062	0.9846
RH	0.0983	10.17	7.63	0.013	0.9894

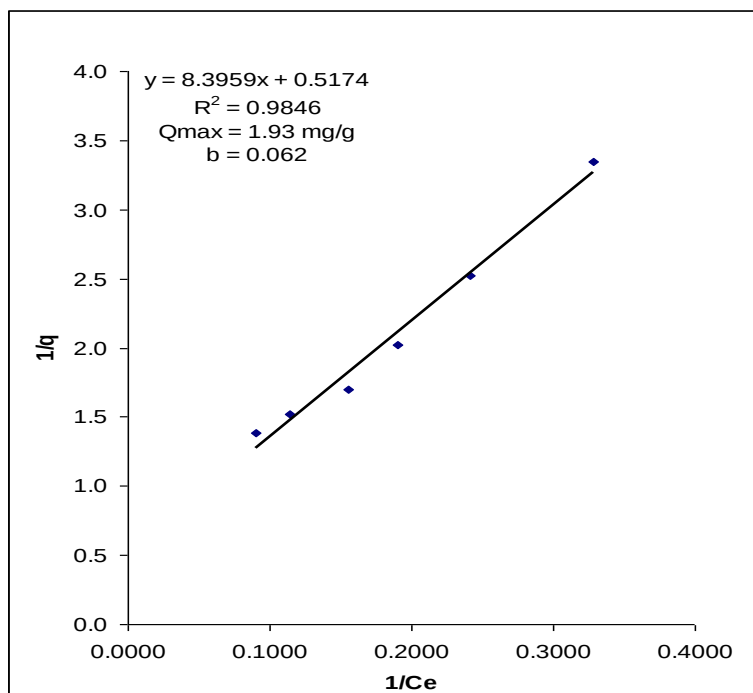


Figure 8. Langmuir isotherm for Wheat Husk



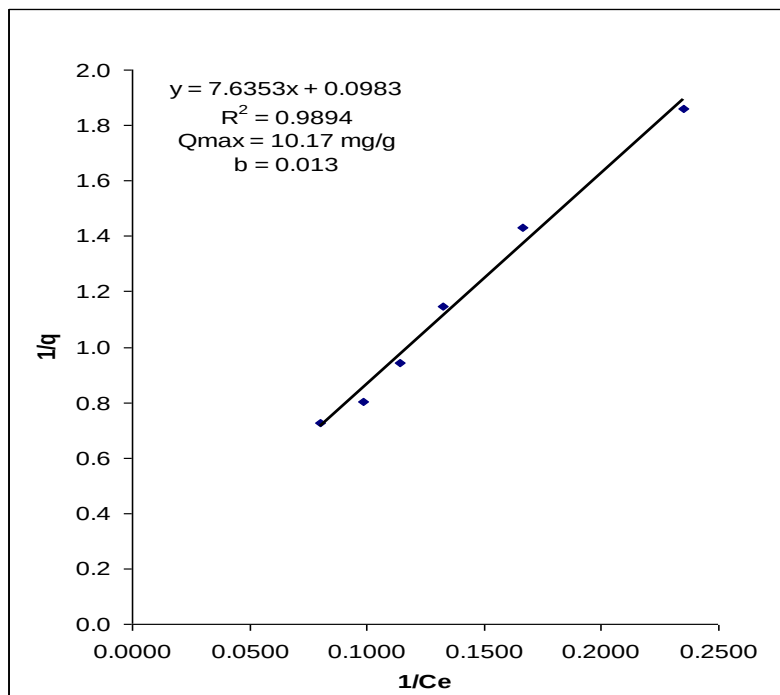


Figure 9. Langmuir isotherm for Rice Husk

This model was used in the current investigation to examine the adsorption isotherm. A well-known adsorption isotherms model, Langmuir, has also been used to analyze the experimental data (Eq. 1).

$$1/q = 1/b Q_{\max} C_e + 1/q_{\max} \quad \text{Eq.1}$$

$Q_{\max}$ is called Langmuir monolayer adsorption capacity, the value is 1.93 mg of dye gram of WH and 10.17 mg of dye gram of RH. Extreme adsorption capacity in case of RH indicating the enhanced active sites of rice husk are accessible for the dye. “b” is Langmuir isotherm constant is 0.062 dm³/g WH and 0.013 dm³/g RH. The value of R^2 shows a correlation or linear relationship. More that value is near 1 more linear relation there is. R^2 value indicates the type of Langmuir isotherm, $R^2 = 0$ means irreversible, $R^2 = 0 - 1$ means favorable for adsorption. $R^2 = 1$ means linear and $R^2 > 1$ means unfavorable value of $R^2 =$

0.984 (WH) and 0.989 (RH) given in the table for Langmuir isotherm of dye indicate favorable adsorption for WH and RH. The outcomes of Langmuir isotherm are given in Fig. 8 and 9.

4. DISCUSSION

The influence of particle sizing on congo red adsorption was dealt using mesh sizes differences in WH and RH. Larger the adsorbent size, lesser is its adsorption (Musthofa *et al.*, 2023). This study also examined the impact of varying adsorbent doses on congo red adsorption capacity. It is proved from experiments that adsorption capacity increased at low doses but decreased due to aggregation and unsaturated sites (Adegoke and Bello, 2015). Such aggregation would lead to a decrease in the total surface area of the adsorbent (Wong *et al.*, 2013). The



decrease in the absorption capacity was because some of the absorption sites remained unsaturated during the absorption process (Younas *et al.*, 2021). It is also found that surface sites facilitate adsorption, but solute repulsion makes it difficult. The maximum contact time for dye adsorption increased with increasing dye incorporation (Zare *et al.*, 2015). It takes a long time to reach equilibrium because the solute in the bulk and solid phase undergo repulsion (Amuda *et al.*, 2014). The variance may result from desorption occurring simultaneously with adsorption (Abechi *et al.*, 2006). The study found that the initial concentration of dye in wheat and rice husk in concentration range of 5-25 ppm at pH (4-8) of the medium, increases with the initial concentration, possibly due to more active sites and concentration gradient driving force (Akar *et al.*, 2009; Ahmad *et al.*, 2015). WH and RH both show an increasing trend of dye adsorption at pH '5', but this adsorption begins to decrease with further increase of pH due to diminishing electrostatic force. This may be due to a fading of the electrostatic forces of attraction between the negatively charged adsorbate and adsorbent, which eventually causes the percentage of adsorption to drop (Nithya *et al.*, 2021). The study examined the impact of stirring speed on Congo red adsorption (Azlan *et al.*, 2009), using five speeds (100-500 rpm). Results showed that low stirring speed was optimal for WH and RH dye adsorption, with no further increase after decreasing. Temperature also significantly impacts adsorption of Congo red, with best adsorption at 30°C (Room Temperature) for WH and RH. High temperature leads to faster molecules and less interaction time for dye anions and plant material. Also the plant material is denatured for sorption at high temperature (Kheddo *et al.*, 2020). Adsorption isotherms describe the adsorption process and interaction between adsorbates and adsorbents. The Langmuir model is commonly used to describe equilibrium data for adsorption

systems analysis. This study applied the Langmuir model to study adsorption isotherms. The maximum adsorption capacity for rice husk dye is 1.93 mg, while the Langmuir isotherm constant is 0.062 dm³/g WH and 0.013 dm³/g RH. The R² value indicates the type of Langmuir isotherm, with values near 1 indicating linear relationships (Wekoye *et al.*, 2020).

5. CONCLUSION

It is concluded from the above discussion that wheat husk and rice husk can successfully be applied as biosorbents to introduce an inexpensive environmentally friendly system for the removal of dyes in aqueous media. The relative study displayed that rice husk was found to be the best adsorbent for the removal of congo red dye from aqueous environments as compared to wheat husk.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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