

## A COMPARATIVE STUDY OF THE ADSORPTION OF CONGO RED DYE ON RICE HUSK, RICE HUSK CHAR AND CHEMICALLY MODIFIED RICE HUSK CHAR FROM AQUEOUS MEDIA

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**ABSTRACT.** Desirable cost and removal effectiveness of the adsorbents can be obtained by the use and modification of agricultural waste products. Therefore, in this study rice husk (RH), rice husk char (RHC) and chemically modified rice husk char (CMRHC) were prepared and used as adsorbents for the removal of Congo Red dye from aqueous media under different experimental conditions. It was observed that the adsorption of Congo Red dye was not only affected with the types of adsorbents used but also with other experimental variables such as time, adsorbent dose, dye concentration, pH and temperature. Thermodynamics study indicated that the adsorption of Congo Red dye on the three adsorbents is spontaneous and exothermic process. Kinetics data showed that the adsorption of Congo Red dye on these adsorbents follow pseudo-second order model better than the pseudo-first order model. Equilibrium adsorption data were tested with Langmuir, Freundlich, and Temkin adsorption isotherm models. It was observed that the equilibrium data of RH and RHC were found best fit to the Langmuir adsorption isotherm model whereas that of CMRHC was best fit to the Freundlich and Temkin models. CMRHC showed better efficiency compared to both RH and RHC.

**KEY WORDS:** Rice husk char, Thermo-chemical modification, Adsorption, Thermodynamics, Isotherms

### INTRODUCTION

Nowadays high quantity of dye effluents are discharged into the aquatic environment due to very high speed of industrial growth in many countries. Approximately 15% of the dyes are lost during the dyeing processes which are discharged to water [1]. Dyes are used in many industries, like food, leather, plastics, mineral processing, paper, rubber, cosmetics, pharmaceutical, and textile [2]. The colored effluents which are discharged into water cause environmental pollution with harmful effects on aquatic life [3]. Most of the dyes are stable to degradation by any chemical or biological means. They are also stable to oxidizing agents and sunlight; they prevent the penetration of sunlight and hence disturb the ecological balance [4]. The discharged dye-waste water to the aquatic environment is highly problematic and mutagenic to the aquatic life and human [5]. Various methods including chemical-coagulation, ozonation, activated carbon adsorption, biological treatment and catalytic reduction are used to control the dye-waste effluents [6-8]. Congo Red dye is an anionic, diazo, water soluble direct dye having maximum absorption at 520 nm; this is mostly used in textile, paper, printing, leather and plastic industries and causes irritation to eyes and skin as its main side effects [9]. Recently an attempt was made for the removal of Congo Red dye by adsorption approach while using *Solanum tuberosum* (potato) peels and *Pisum sativum* (pea) peels as adsorbents [9].

Rice husk is agriculture by product of the rice processing industry. It is an important agricultural residue. It consists of about 20% of the whole rice mass [10]. About 500 million tones rice is produced in developing countries and the total rice husk available in these countries is approximately 100 million tones. The rice husks are used for the manufacturing of blocks used in civil construction as penal and is also used as energy sources for boilers in the rice industries [10]. However, the available rice husk is too much to be used locally and hence have

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caused disposal problems. Rice husk has granular structure; it is chemically stable and locally available at low cost [10]. That is why it has been chosen as adsorbent material for the adsorption of dye from aqueous media. Rice husk consists of 32.24% cellulose, 21.34% hemicellulose, 21.44% lignin, 1.82% extractives, 8.11% water and 15.05% mineral ash. The mineral ash is 94.5–96.34% SiO<sub>2</sub> [11, 12]. Recently modified rice husk was used for the removal of pollutants from aqueous media. Tartaric acid has been used for the modification of rice husk adsorbent that was used for the removal of copper and lead. The effect of various parameters like initial adsorbate concentration, pH, particle size and temperature was also studied. It was reported that modification of RH can be useful for the removal of copper and lead from water [13].

Keeping in view the toxic/side effects of dyes on living things, it is important to remove them from aqueous media. Removal of dyes by adsorption is one of the major efficient and cheaper techniques to control water pollution. Similarly, the cost and removal capacity of adsorbents is mainly responsible for effectiveness of the adsorption techniques. Consequently, agricultural waste materials such as Rice Husk have gained our attention for the removal of Congo Red because of its low price and a good expected efficiency. It was also expected that the adsorption efficiency and choice of the adsorbents could be enhanced by thermo-chemical modification and activation of rice husk. Therefore, in the present study three different rice husk (RH) based adsorbents namely rice husk (RH), rice husk char (RHC) and chemically modified rice husk char (CMRHC) were prepared and used as adsorbents for the removal of Congo Red dye from water under different experimental variables. Comparative adsorption efficiency of these adsorbents under varying experimental parameters such types of adsorbent, dye/adsorbent ratio, temperature, time and pH of the medium is also discussed.

## EXPERIMENTAL

### *Materials and methods*

The source material, rice husk, was collected from the rice processing mills of the local area of district Mardan, Pakistan. The textile dye (Congo Red) was obtained from the Merck/Sigma Aldrich. The analytical grade chemicals (NaOH, HCl, KOH, etc.) were used without further purification. Doubly distilled water was used for the preparation of stock and working solutions of dyes and Pyrex glass vessels were employed for solution storage and carrying out reactions.

### *Preparation of rice husk (RH) adsorbent*

A 100 g of the RH (rice husk), obtained from the rice processing mill was dispersed in doubly distilled water and agitated with magnetic stirrer for one hour to remove the water soluble contents. The dispersed solid was separated from liquid and the residue was washed with 1 M HCl solution through agitation with magnetic stirrer for 30 min. The resulting dispersion was filtered to separate solid from liquid, the solid obtained was dispersed in 0.5 M NaOH solution and agitated with magnetic stirrer for 30 min at room temperature. The dispersed solid was separated from solution and the residue was washed with sufficient amount of distilled water. After washing the product was dried in electric oven at 60 °C for four hours and then grinded to fine powder form and sieved to separate the large particles from the fine particles. The fine particles obtained were used as adsorbent.

### *Preparation of rice husk char (RHC) adsorbent*

The rice husk char (RHC) was prepared from the source material by using thermal activation procedure. For this purpose a known amount (e.g. 100 g) of the rice husk were kept in furnace at

around 350 °C for about one hour. The blackish type product was obtained, known as the rice husk char (RHC) that was used as adsorbent for the adsorption of dyes from aqueous media.

#### *Preparation of chemically modified rice husk char (CMRHC) adsorbent*

About 50 g of RHC was dispersed in 100 mL of KOH solution (1 M) and was kept on at 80 °C for 6 hours under continuous stirring. A dried paste obtained was grinded and kept in furnace at 450 °C for one hour. The as prepared product was grinded to powder form and was used as adsorbent for the removal of dye from aqueous media. This product was named as “chemically modified rice husk char” (CMRHC).

#### *Adsorption experiment*

A 1000 mg/L stock solution of Congo Red dye was used for the preparation of different dilute solutions. To investigate the optimum time 0.5 g of the adsorbent was taken in a conical flask followed by the addition of 15 mL of 80 mg/L of dye solution. Five sets of experiments were performed at stirring time of 10, 20, 30, 40 and 50 min. Each time the flask was placed on magnetic stirrer at 30 °C at speed of 250 rpm. On the completion of the stirring time each of the suspension was filtered and the absorbance of filtrate was determined by using UV-Vis spectrophotometer (UV 1800 UV-Vis spectrophotometer Shimadzu). The change in concentration of the dye was investigated using a standard calibration curve or by using Beer-Lambert law. Optimization of dye concentration, adsorbent dose, temperature and pH were determined by varying the corresponding parameter and keeping the other parameters constants. The percent dye removal/adsorption and adsorption capacity was calculated by using the equations [14]:

$$\% \text{Removal} = [(C_o - C_f) / C_o] \times 100 \quad (1)$$

$$q_e = [(C_o - C_f)V] / m \quad (2)$$

where,  $q_e$  = adsorption capacity (mg/g),  $V$  = volume of metal ion solution in liters,  $C_o$  and  $C_f$  is the initial and final/equilibrium dye concentration (mg/L), respectively and  $m$  = adsorbent dose (g). The effect of various parameters such as initial dye concentration, adsorbent dose, time, temperature and pH was elaborated effectively.

## RESULTS AND DISCUSSION

#### *Effect of contact time*

Effect of contact time on the removal of Congo Red dye on RH, RHC and CMRHC adsorbents was studied in the range of 10-50 min. The adsorption experiments were performed using 15 mL of dye solution whose concentration was 80 mg/L containing 0.5 g of each adsorbent at pH 7 with agitation speed 250 rpm at room temperature. Analysis indicated that the rate of adsorption was high in the first 10 min, thereafter the rate of adsorption decreased gradually and remained constant when equilibrium was established. Each of the three adsorbents RH, RHC and CMRHC could remove 81.3%, 84.4% and 96.6% of the dye respectively from aqueous solution in 20 min after that it was noted that there was no significant change in the concentration of dye in the solution. This indicated that chemical modification of the rice husk char enhances its surface activation and hence increase the adsorption efficiency to a maximum level.

### Effect of adsorbent dose

Variation of adsorbent dose can affect the adsorption of Congo Red dye on the RH, RHC and CMRHC adsorbents. The percentage removal of dye at different adsorbent dose is shown in the Figure 1. Higher percentage of dye removal with the increase of adsorbent dose can be attributed to the availability of more binding sites for the adsorption of dye. After certain adsorbent dose, the percentage removal of dye remains constant and further addition of adsorbent dose do not affect the adsorption of dye on the surface of adsorbent which suggests that the maximum adsorption takes place and the concentration of adsorbate reduces to its minimum level [15]. The experimental results showed that 0.5 g of the adsorbent was sufficient for the maximum adsorption of the dye whose concentration is 80 mg/L and volume is 15 mL. Further addition of the adsorbent provides more adsorption sites for the adsorption whereas the dye molecules are almost completely adsorbed by the adsorbent hence thereafter no more dye is adsorbed as indicated in the Figure 1. This figure also indicates that at constant adsorbent dose the adsorption efficiency of CMRHC is greater than the other two adsorbents.

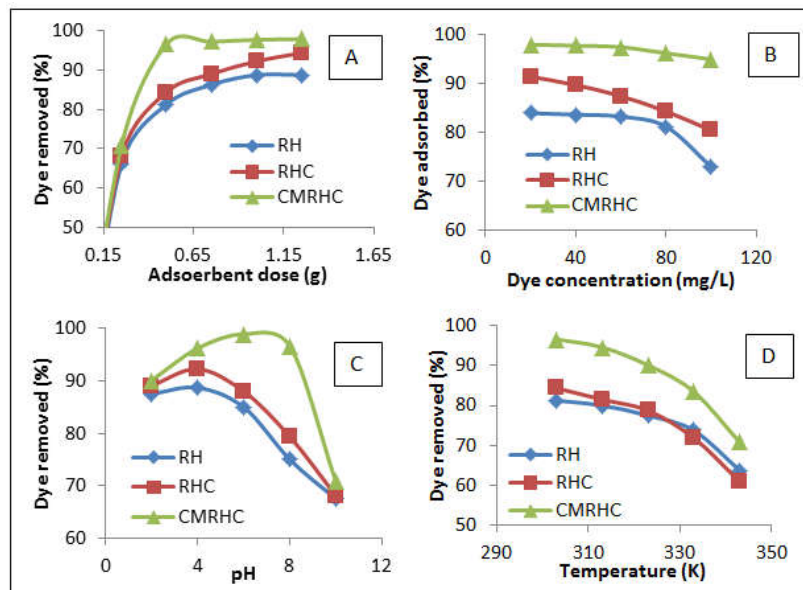


Figure 1. Effect of (a) adsorbent dose, (b) dye concentration, (c) pH, and (d) temperature on the adsorption of Congo Red dye on RH, RHC and CMRHC at experimental conditions: initial dye conc. 80 mg/L, pH = 7, adsorbent dose = 0.5 g and volume of the dye solution = 15 mL.

### Effect of dye concentration

The dye removal from aqueous media on RH, RHC and CMRHC adsorbents at different initial dye concentrations (20-100 mg/L) is shown in the Figure 1. Analysis of percentage removal of dye versus different initial dye concentrations showed that the percentage adsorption decreased with increase in initial dye concentration, but the uptake capacity increased with increase in initial dye concentration. At lower concentrations of dye, the numbers of dye molecules which

are available in the solution are less as compared to the available sites on the adsorbent. However, at higher concentrations the available sites for adsorption become fewer which decrease the percentage removal of dye. Hence, the percentage removal of dye from aqueous media depends on the initial dye concentration. The maximum removal of Congo Red dye was achieved at 20 mg/L of the dye solution on RH, RHC and CMRHC adsorbents were 84%, 92% and 98%, respectively as shown in the Figure 1. Comparative analysis of the three adsorbents indicated that CMRHC has greater adsorption capacity (more than 90%) even at high concentration of dye in the aqueous media. These results also indicated that thermal modification of rice husk enhanced its adsorption properties which could be further increased by chemical modification to its maximum.

#### *Effect of pH*

The pH plays an important role in the adsorption of Congo Red dye on the adsorbents because it influences the surface polarity of the adsorbents, ionic mobility and degree of ionization of the pollutants (Congo Red dye) [16]. It is a known fact that when pH of solution greater than  $pH_{pzc}$ , the adsorbents surface gets negative charge and favors the uptake of cationic dye while at pH of solution less than  $pH_{pzc}$ , the adsorbent surface acquires positive charge and then adsorbs the anionic dye (Congo Red) easily [9, 13, 16]. Under neutral condition the surface of the adsorbents is almost neutral. As Congo Red is anionic dye, hence, the adsorption of Congo Red dye on these rice husk based adsorbents is preferred at pH less than  $pH_{pzc}$  of adsorbents, i.e. at neutral and or acidic pH of solution. These three adsorbents have different uptake ability at different solution temperatures; it is due to difference in their surface polarity in response to pH of the medium. Maximum adsorption of Congo Red dye on the surface of RH and RHC was investigated as 88.7% and 92.3%, respectively at pH 4, whereas CMRHC could remove 98.9% of the dye at pH 6 as indicated in Figure 1. This suggests that the chemically modified rice husk char has greater adsorption capacity in almost neutral media. Its surface polarity and active sites could be blocked by high concentration of  $H^+$  or  $OH^-$  ions hence the adsorption efficiency decreases at very high or very low pH value. On the other hand the adsorption capacity of RH and RHC is higher in acidic media as compared to the neutral media which suggests that the active sites and surface polarity of these adsorbents are increased in acidic media that enhances the adsorption of dye. Comparative analysis of the three adsorbents indicated that CMRHC is more efficient adsorbent even in the neutral media. It could almost completely remove the dye from aqueous media at pH 6. To simplify more the adsorption mechanism in the present case it can be concluded that a decrease in the adsorption at higher pH reflect that electrostatic repulsion may occur between the anionic Congo Red dye and negatively charged adsorbent surface under alkaline pH conditions. While under acidic pH (lower pH), concentration of  $H^+$  ion increases and also the adsorbent surface acquires positive charge. Under this condition attractive forces may occur between anionic dye molecule and the positively charged adsorbent surface. At lower pH which causes maximum removal of dye. Furthermore, excess amount of negatively charged hydroxyl ions may also compete with dye molecules for adsorbent sites under higher pH condition (basic pH) and so decrease the adsorption effectiveness of Congo Red on adsorbents used.

#### *Effect of temperature*

The effect of temperature on the adsorption of Congo Red dye on RH, RHC and CMRHC adsorbents is shown in the Figure 1. The adsorption of dye on the three adsorbents was studied at five different temperatures (303, 313, 323, 333 and  $343 \pm 3$  K). It was investigated that the adsorption of Congo Red on RH, RHC and CMRHC adsorbents decreases with the increase in temperature which inferred that the process is exothermic this indicates that all the three

adsorbents used are mostly of the same chemical nature. However, at a given temperature the CMRHC has more efficiency of adsorption for the dye molecules which suggests for its modified surface that have more active sites than the other two adsorbents. The exothermic nature of the adsorption process is also supported by the negative value of  $\Delta H$  given in Table 1.

#### *Thermodynamic studies*

Temperature is an important entity in the adsorption studies because it helps to determine basic thermodynamic parameters like  $\Delta H$  (enthalpy change),  $\Delta S$  (entropy change) and  $\Delta G$  (Gibbs free energy change). The thermodynamic properties of the adsorption of Congo Red on RH, RHC and CMRHC adsorbents could be explained on the basis of Gibbs free energy, which could be calculated by using the following equation [17].

$$\Delta G = -RT \ln K \quad (3)$$

where R is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ), T is the temperature in Kelvin and K is the equilibrium constant which is given by;

$$K = C_{\text{ads}}/C_e \quad (4)$$

In equation 4,  $C_{\text{ads}}$  is the concentration of dye adsorbed on the adsorbent and  $C_e$  is the equilibrium dye concentration. The relationship between free energy and temperature is given by the following equation [18];

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

The plots of  $\Delta G$  versus T are shown in the Figure 2. The values of  $\Delta S$  and  $\Delta H$  can be determined from the slope and intercept respectively. The thermodynamic parameters are given the Table 1. The negative value of  $\Delta H$  indicates that the adsorption of Congo Red dye on RH, RHC and CMRHC-adsorbents is exothermic process which is supported by the decrease in the % adsorption of dye with rise in temperature as shown in the Figure 1. Furthermore, the range of heat evolved ( $-\Delta H$ ) for physical adsorption is 2.1 to 20.9 kJ/mol and that for chemical adsorption is generally 80 to 200 kJ/mol [19]. From Table 1, the values of heat evolved ( $-\Delta H$ ) for RH, RHC and CMRHC are 19.61 kJ/mol, 25.74 kJ/mol and 47.77 kJ/mol, respectively, which indicated that the adsorption of Congo Red on the surface of RH is physical process whereas that on the surface of RHC and CMRHC is physicochemical. The comparative high value of the ( $-\Delta H$ ) for CMRHC than the other two adsorbents reveals for its chemical nature of adsorption along with physio-sorption. The  $\Delta S$  determine the degree of disorderliness of the system. The negative values of  $\Delta G$  reveal that the adsorption process is feasible and spontaneous.

Table 1 indicated that the values of  $\Delta S$  for the adsorbents are negative for all the three adsorbents which inferred that the randomness of adsorbents at the adsorbent/adsorbate interface is decreased during the sorption process. In other words it means that the dye molecules have more freedom and hence the randomness in the bulk of solution compared to their attachment at the surface of adsorbent. It further indicates that the adsorbed molecules become more localized at the solid/water interface compared to their de-localized Brownian movement in the bulk of solution. Comparative analysis indicated that the value of  $-\Delta S$  for CMRHC is higher than that of the other two adsorbents which infers for its less randomness behavior at the adsorbent/adsorbate interface as compare to RH and RHC. Table 1 also showed that the value of  $-\Delta H$  is greater for CMRHC than that of the other two adsorbents which suggests that adsorption at surface of CMRHC is more spontaneous and exothermic than RH and RHC. The thermodynamic parameters further reflect that the spontaneity of the adsorption process is dominated by the negative values of  $\Delta H$  rather than the values of  $\Delta S$ ; hence, the process is said to be enthalpy driven spontaneous process.

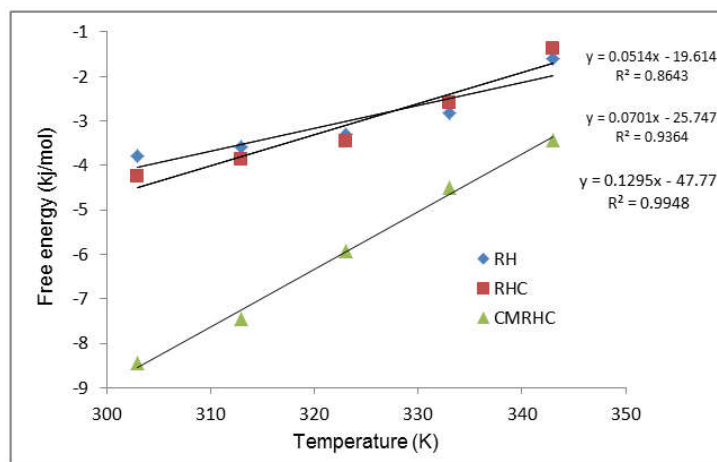


Figure 2. Plots of free energy versus temperature for the adsorption of Congo Red dye on RH, RHC and CMRHC.

Table 1. Thermodynamic parameters for adsorption of Congo Red dye on RH, RHC and CMRHC.

Temperature (K)	$\Delta G$ (kJ/mol)			Values of (K)			$\Delta H$ (kJ/mol)	$\Delta S$ (J/mol.K)
	RH	RHC	CMRHC	RH	RHC	CMRHC		
303	-3.779	-4.248	-8.431	4.33	5.40	28.4	-19.61 (RH)	-51 (RH)
313	-3.591	-3.855	-7.451	4.00	4.40	17.5	-25.74 (RHC)	-70 (RHC)
323	-3.303	-3.454	-5.930	3.44	3.62	9.10		
333	-2.823	-2.591	-4.489	2.80	2.55	5.06	-47.77 (CMRHC)	-129 (CMRHC)
343	-1.594	-1.375	-3.438	1.75	1.62	3.33		

#### Kinetics of dye removal

The kinetics of dye removal was investigated by pseudo-kinetics models [20, 21]. The rate of dye removal is given as;

$$dx/dt = -KC^n \quad (6)$$

where  $C$  is the concentration of dye,  $n$  is order of interaction between dye and adsorbent material,  $k_1$  is the rate constant and  $t$  is the operating time. The pseudo-first order reaction model is given as [20, 21];

$$\ln(C_t/C_o) = -k_1 t \quad (7)$$

where  $C_o$  = initial concentration of dye before adsorption,  $C_t$  = concentrations at time  $t$  during adsorption process. Figure 3 indicates the plot of  $\ln(C_t/C_o)$  versus  $t$ . The rate constant  $k_1$  (1/min) was determined from the slope of the plot. The pseudo-second order reaction model is given as [20, 21];

$$[1/C_t - 1/C_o] = k_2 t \quad (8)$$

Figure 3 shows the plots of  $[1/C_t - 1/C_o]$  versus  $t$ . The rate constants  $k_2$  (L/(mg.min)) are determined from the slope of the plots. By fitting the linear regression of both the kinetics model, the rate constants ( $k_1$  and  $k_2$ ) are determined. The values of rate constants ( $k_1$  and  $k_2$ ) and

their  $R^2$  for the adsorption of Congo Red dye on RH, RHC and CMRHC are given in the Table 2. The  $R^2$  values for pseudo-first order model are less than that of pseudo-second order model which indicated that the kinetics data follows the pseudo-second order model better than pseudo-first order model [21, 22].

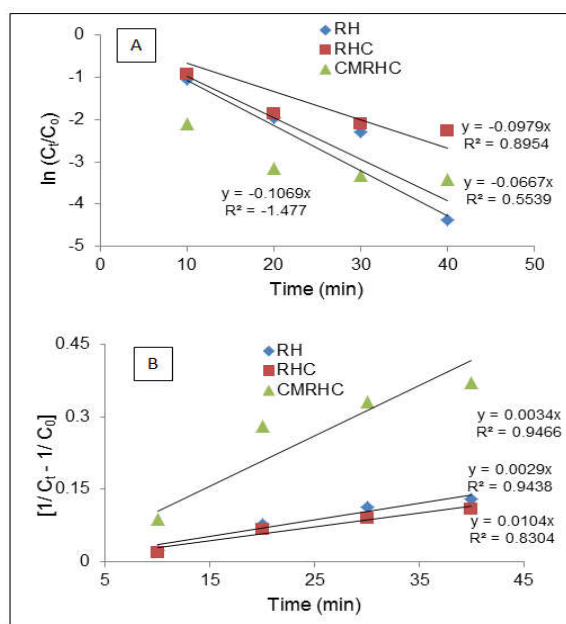


Figure 3. Kinetics models (a. Pseudo-first order and b. Pseudo-second order) for the adsorption of Congo red dye on RH, RHC and CMRHC at  $C_0 = 80$  mg/L.

Table 2. The values of rate constants ( $k_1$  and  $k_2$ ) and their  $R^2$  for the adsorption of Congo Red dye on RH, RHC and CMRHC at initial concentration = 80 mg/L.

Adsorbent	Pseudo-first order		Pseudo-second order	
	$k_1/(\text{min}^{-1})$	$R^2$	$k_2/L.(\text{mg.min})^{-1}$	$R^2$
RH	-0.097	0.895	0.003	0.946
RHC	-0.066	0.555	0.002	0.943
CMRHC	-0.106	-1.47	0.010	0.830

#### Adsorption isotherm models

The development of various adsorption isotherms such as Langmuir adsorption isotherm, Freundlich adsorption isotherm, Temkin adsorption isotherm and D-R isotherms for the adsorption of Congo Red is too much important; as these can give fruitful information about the interaction of dye and adsorbents for optimization of adsorption process from both academic and applied point of views. The equilibrium adsorption isotherms also play an important role in calculating the adsorption capacity of dye molecules and detecting the nature of its adsorption onto rice husk based adsorbents [23].



*Langmuir adsorption isotherm model*

Langmuir adsorption isotherm refers to homogeneous adsorption, in which all the active sites of adsorbent have equal affinity for the adsorbate molecules and hence the sorption activation energy and enthalpies of each adsorbent molecule remains constant. The linear form of the Langmuir adsorption isotherm is given as [23];

$$C_e/q_e = C_e/q_m + 1 / Kq_m \quad (9)$$

where,  $C_e$  is the equilibrium concentration of adsorbate in the solution ( $\text{mg. L}^{-1}$ ),  $q_e$  is the amount of adsorbate adsorbed on the adsorbent at equilibrium ( $\text{mg. g}^{-1}$ );  $q_m$  is the monolayer adsorption capacity ( $\text{mg. g}^{-1}$ ) and  $K$  is the Langmuir adsorption equilibrium constant ( $\text{L. mg}^{-1}$ ), which is related to the energy of adsorption. The Langmuir constants  $q_m$  and  $K$  could be determined from the intercept and the slope of the straight line obtained by plotting  $C_e/q_e$  versus  $C_e$  (Figure 4) [24, 25].

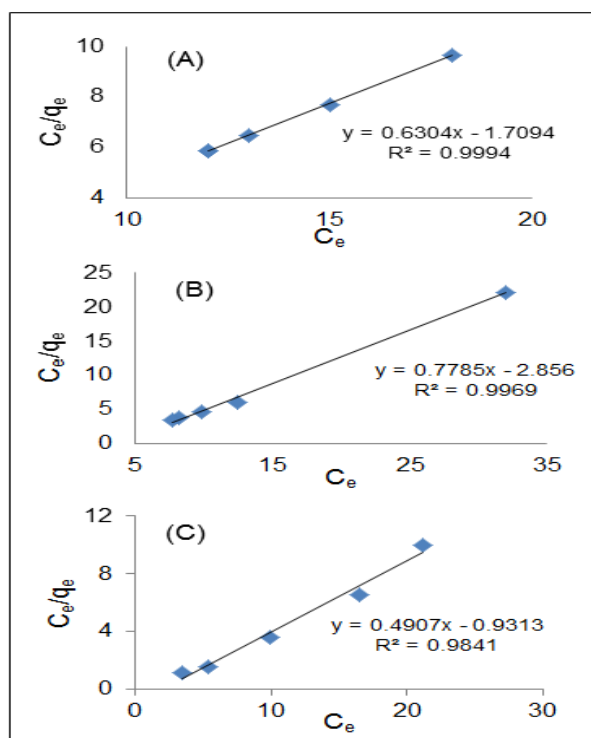


Figure 4. Langmuir adsorption isotherms for the adsorption of Congo red on (A) RH, (B) RHC and (C) CMRHC.

*Freundlich isotherm model*

Freundlich isotherm model is developed to describe the non-ideal, reversible and multilayer adsorption [26]. This empirical model refers to the heterogeneous surface of adsorbent [27]. The linear form of Freundlich isotherm is represented by the following equation;

$$\log q_e = \log K_F + 1/n \log C_e \quad (10)$$

where  $q_e$  is the quantity of dye adsorbed at equilibrium (mg/g).  $C_e$  is the concentration of adsorbate at equilibrium (mg/L).  $K_F$  and  $n$  are Freundlich constants related to adsorption capacity and adsorption intensity of the adsorbent, respectively. The Freundlich isotherm constants are calculated from the plot of  $\log q_e$  versus  $\log C_e$  as shown in Figure 5 [28].

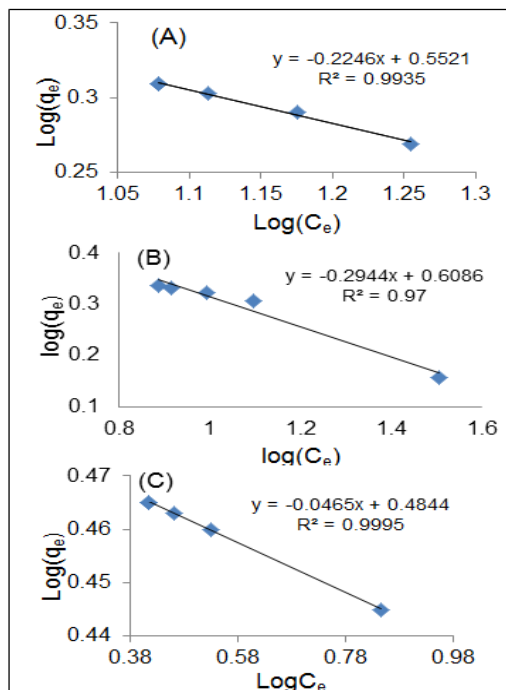


Figure 5. Freundlich adsorption isotherms for the adsorption of Congo red on (A) RH, (B) RHC and (C) CMRHC.

#### The Temkin adsorption isotherm model

The Temkin adsorption model indicates the effect of adsorbent-adsorbate interactions on adsorption process. The model also suggests that the heat of adsorption of all the molecules in the layer decreases linearly with coverage. The linear form of Temkin equation is given as [29];

$$q_e = B \ln K_{TK} + B \ln C_e \quad (11)$$

or,

$$q_e = 2.303B \log K_{TK} + 2.303B \log C_e \quad (12)$$

where  $B = RT/b$ , is the Temkin constant related to the heat of adsorption and  $K_{TK}$  is the Temkin isotherm binding constant (L/mg) related to maximum binding energy [30]. The values of these constants were calculated from the slope and intercept obtained from plot of  $q_e$  versus  $\text{Log } C_e$  (Figure 6). Table 3 indicated that the heat of adsorption and binding energy are greater for the adsorption of Congo Red dye on CMRHC than that of RHC and RH which argues that CMRHC

is more efficient adsorbent than the other two in the removal of Congo Red dye from aqueous media.

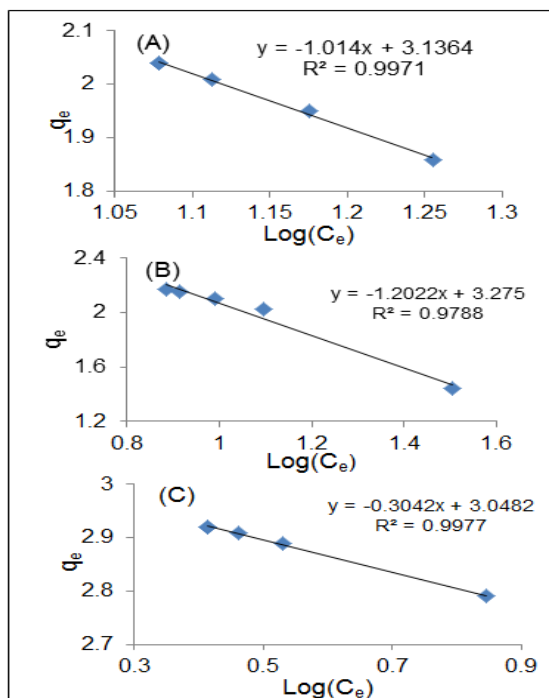


Figure 6. Temkin adsorption isotherms for the adsorption of Congo red on (A) RH, (B) RHC and (C) CMRHC.

Table 3. Parameters in Langmuir, Freundlich and Temkin adsorption isotherm models.

Adsorbent	Parameters in Langmuir adsorption model			Parameters in Freundlich adsorption model			Parameters in Temkin adsorption model		
	$q_m$ (mg/g)	$K_L$ (L/mg)	$R^2$	$n$	$K_F$ (L/mg)	$R^2$	$b$ (J/mol)	$K_{KT}$ (L/g)	$R^2$
RH	1.58	-0.37	0.999	1.81	0.597	0.993	-5721	$6.6 \times 10^{-4}$	0.997
RHC	1.28	-0.27	0.996	1.64	0.508	0.970	-4826	$1.17 \times 10^{-4}$	0.978
CMRHC	2.04	-0.52	0.984	2.06	0.899	0.999	-19082	$8.02 \times 10^{-2}$	0.997

In all these cases of adsorption isotherms study, the experimental data were fitted to the Langmuir, Freundlich and Temkin isotherm model. The values of regression coefficient/constant ( $R^2$ ) are listed in Table 3.  $R^2$  values for RH and RHC adsorbents in Langmuir isotherm model are greater than that of Freundlich and Temkin which suggests for monolayer coverage and finite number of adsorption sites of uniform adsorption energies. However, the  $R^2$  values for CMRHC in the Freundlich and Temkin isotherm models are greater than that of Langmuir model. It reveals the multilayer adsorption with the assumption of heterogeneous surface in which the energy varies as a function of the surface coverage. Hence, it is concluded that adsorption of Congo Red dye on RH and RHC is best fit to Langmuir model whereas that on CMRHC is best fit to Freundlich and Temkin models. Moreover, it is obvious

from Table 3 that the value of Freundlich constants 'n' is greater for CMRHC than the other two adsorbents which infers for its more heterogeneous surface and multilayer formation [31, 32].

### CONCLUSION

Rice husk (RH), rice husk char (RHC) and chemically modified rice husk char (CMRHC) are the adsorbents almost of the same chemical nature but their surfaces are slightly different from each other. These three adsorbents were used for the adsorption of Congo Red dye under different experimental conditions. The adsorption efficiency was prominently affected on changing the experimental conditions. Comparative adsorption studies showed that maximum adsorption of Congo Red dye at pH 4 on the surface of RH and RHC were investigated as 88.7% and 92.3%, respectively, whereas CMRHC could remove 98.9% of the dye at pH 6. This shows that CMRHC has greater adsorption efficiency for Congo red dye than the RH and RHC due to its surface polarity and greater number of active sites. It could remove 98.9% of Congo Red dye from aqueous media at pH = 6, this infers that it is more efficient than the other two adsorbents. Thermodynamic studies revealed that the adsorption process is spontaneous and exothermic for all the three adsorbents as the values of  $\Delta G$  and  $\Delta H$  are negative. However the adsorption process on the surface of CMRHC is more spontaneous, feasible and exothermic due to large values of  $\Delta G$  and  $\Delta H$  as compare to the other two adsorbents. The negative values of  $\Delta S$  infer that the randomness decreases at the adsorbent/adsorbate interface during the adsorption process. The kinetics studies indicated that the adsorption of Congo Red dye on these adsorbents follow pseudo-second order model better than pseudo-first order model. The equilibrium data for the adsorption of dye on these adsorbents was tested with various adsorption isotherms such as Langmuir, Freundlich, and Temkin models. It was observed that the equilibrium data follow all the three isotherms. The data is best fit to the Langmuir adsorption isotherm model for RH and RHC which indicated that these adsorbents possess homogeneous surfaces with uniform active sites. However, the data is best fit to Freundlich and Temkin models for CMRHC which indicates that it possesses heterogeneous surface with non-uniform adsorption sites and multilayer formation. Comparative study inferred that the adsorption efficiency of CMRHC for Congo Red dye is higher than that of RH and RHC.

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