



Improvement of the Adsorption Efficiency of Rice Husk Ash for Crystal Violet Dye Removal from Aqueous Medium

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Abstract

Rice husk ash (RHA) product was chemically modified and utilized for the adsorption of toxic dye from water. The textile dye (crystal violet) was removed from aqueous media using Rice Husk Ash (RHA) and Chemically Modified Rice Husk Ash (CMRHA) as adsorbents. The effects of stirring time, dye concentration, adsorbent dose, pH and temperature on the adsorption capacity were studied. The chemical modification of RHA enhanced the absorption efficiency from 88.9% to 99.1% at pH 6 and room temperature by using 2g/L of adsorbents. Thermodynamics study indicated that the process is exothermic and spontaneous. The kinetics study indicated that the adsorption process for the two adsorbents best fitted to the pseudo-second order kinetics model. The equilibrium data were tested with Langmuir, Freundlich, and Temkin equations. It was investigated that data best fitted to the Langmuir and Temkin models, which indicated for chemisorptions process and heterogeneous surface of the adsorbents.

Keywords: Rice husk; Chemical modification; Adsorption; Crystal violet dye; Isotherms.

1. Introduction

Effluents from dyeing industries cause pollution in aquatic environment as they are colored suspended organic particles [1]. Dyes which are discharged to water could affect the photosynthesis in the aquatic environment [2, 3]. Dyes are mutagenic and cause cancer, they are not biodegradable [2, 4]. Dyes could be classified as anionic, cationic, and non-ionic dyes [5]. Acidic (anionic) dyes are generally the organic sulfonic acid, sodium salts are the commercially available forms of acidic salts which are stable in water. They are generally used with fiber types like polyamides, wool, acrylic, silk, polypropylene, cotton, polyesters, etc.[6]. Various methods are utilized for the removal of dyes from aqueous media. These methods

include precipitation technique, membrane filtration, electrochemical, coagulation, chemical oxidation, ion exchange, and adsorption [6, 7]. Adsorption is one of the techniques used for the removal of dyes from aqueous media [8]. Different types of cheaper, effective, and selective adsorbents were developed for the removal of dye from aqueous media; these include orange peel [9], rice husk [10], banana pith [11], clay [12], powdered activated sludge [13], neem's leaf powder [14], activated carbon [15] and Zeolite [16].

Adsorption technique is interesting and applicable technique for the purification of water. The use of low-cost adsorbents for the water treatment is one of the effective and affordable methods. Removal of dye from dilute solutions is a difficult task that could only

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be achieved by the process of adsorption [17]. Crystal violet dye (hexamethyl pararosaniline chloride) is one of the cationic dyes. It is used in many industries like paper-making, food, cosmetic, and textile processing industries [18, 19].

Herein, a research investigation was performed to prepare and develop an efficient and effective adsorbent for the treatment of wastewater especially for the removal of textile dyes from aqueous media. Such efficient adsorbents receive the expectations in research academic and industries. It is believed that the use of such adsorbents remove the toxic dyes from aqueous media almost completely. It was expected that the adsorption efficiency of the adsorbents could be improved by chemical modification and activation. For this purpose, the low cost locally available rice husk ash (RHA) was used as adsorbent for the removal of crystal violet dye. Additionally, this adsorbent was chemically modified which made it more efficient. The chemically modified Rice Husk Ash (CMRHA) could remove the crystal violet dye from aqueous media almost completely.

2. 2. Experimental

2.1. Materials

The Rice Husk was collected from local rice processing plants in Mardan Pakistan district. Crystal violet dye was purchased from Sigma Aldrich with purity (98%). Other chemical reagents (NaOH, HCl, and KOH) were purchased from Alfa Aesar and used without any further purification (99% purity). Deionized water was used for solution preparation. Pyrex glass vessels were used for solution storage and reactions and the tube furnace was used for adsorbent preparation.

2.2. Methods

2.2.1. Preparation and activation of the adsorbents

Preparation of Rice Husk (RHA) adsorbent

The Rice Husk raw materials were washed with distilled water, acidic, and basic solutions to eliminate the soluble materials. After full washing, the product was dried at ambient temperature, and then burned in furnace at 600 °C to produce ashes. 30 g of the ashes were kept in the tube furnace at 600 °C for one hour). The obtained product (Rice Husk Ash (RHA)) is white powder color. This product was used as adsorbent for the adsorption of crystal violet dye from aqueous media.

Preparation of Chemically Modified Rice Husk Ash (CMRHA) adsorbent

20 g of RHA were dispersed in 100 mL of 1M KOH solution and held for 10 hours on magnetic stirrer at 80 °C. A dried product was grinded and held in furnace for one hour at 700 °C. The collected sample was grinded to powder. The obtained product (Chemically Modified Rice Husk Ash (CMRHA)) was used as adsorbent to extract dye from aqueous media.

2.2.2. Adsorption Experiment

A 1000 mg/L Crystal Violet dye stock solution was used for the preparation of various dilute solutions. 10 g/L of the adsorbent was taken in a conical flask to determine the optimal time. Five tests were conducted at stirring time (10, 20, 30, 40, and 50 min) with stirrer speed at 250 rpm. Upon completion of the stirring time, each suspension was filtered. The intensity of the filtrate absorption was calculated using UV-Vis spectrophotometer (UV 1800 UV-Vis Shimadzu). Dye concentration change was investigated using a normal calibration curve or using Beer-Lambert law. Optimization of dye concentration, adsorbent dose, temperature and pH was determined by modifying the corresponding parameter and maintaining constant parameters.

3. Results and discussion

3.1. Effect of adsorbent dose

The effect of adsorbent dose on the adsorption of crystal violet dye on the RHA and CMRHA was investigated. The percentage adsorption of dye at different adsorbent dose is represented in Fig.1a. It is notified that high percentage of dye was removed from aqueous solution with the increment of adsorbent dose, which give indication about the increment of the adsorbent binding sites for dye adsorption. Following such adsorbent dosages, the percentage adsorption of dye remains stable, and further adsorption did not influence the removal of dye from the liquid solution, which shows the actual adsorption of dye on the adsorbent surface and the minimum concentration of dye in the solution [20]. The results indicated that 10g/L of the adsorbent was enough for the maximum removal of the dye with concentration is 100 mg/L. Additionally, the figure indicates that at constant adsorbent dose, the adsorption efficiency of CMRHA is greater than RHA.

3.2. Effect of dye concentration

The adsorption of dye from aqueous solution on RHA or CMRHA at different initial concentration of dye (20-100 mg/L) is represented in Fig.1b, which indicated that the percentage of dye adsorption decreased with increase in initial concentration; however, the amount of dye adsorbed per gram of adsorbent increased. At low dye concentrations, the numbers of available sites on the adsorbent are higher than the dye molecules, which almost completely adsorbed the dye molecules. However, at higher initial concentrations of dye the available sites on the adsorbent surface for adsorption are not enough for the dye molecules, which decreases the percentage adsorption of dye. Hence, the initial dye concentration could affect dye removal from aqueous media. The maximum adsorption of crystal violet dye was obtained at 20 mg/L of the dye solution. Fig.1b showed that the adsorption capacity of the dye was (92% and 98.5%) for RHA and CMRHA, respectively. Comparative study of the two adsorbents indicated that CMRHA has greater adsorption capacity (more than 96%) even at high initial concentration. Hence, the chemical modification of RHA enhanced its adsorption capacity for the removal crystal violet dye from aqueous media.

3.3. Effect of pH

The pH could also affect the adsorption of crystal violet dye on the adsorbents because it has influence on the adsorbent surface polarity, ionic mobility and degree of ionization of the adsorbate [21]. As shown in Fig.1c, the maximum adsorption of crystal violet dye on RHA and CMRHA was investigated as 88.9% and 99.1%, respectively at pH 6. This indicates that the chemically modified Rice Husk Ash has greater adsorption capacity than RHA. It could almost completely remove the crystal violet dye from aqueous media at pH = 6.

3.4. Effect of temperature

Temperature plays an important role in the adsorption of crystal violet dye on RHA and CMRHA-adsorbents. The adsorption of dye on the two adsorbents was investigated at five different temperatures (303, 313, 323, 333 and 343 K with ± 3 K possible error). It was notified that the adsorption of crystal violet dye on RHA and CMRHA-adsorbents decreases with the increase in temperature as shown in Fig.1d. The figure indicated that adsorption of dye on the surface of CMRHA decreases gradually and

slowly with the increase in temperature, whereas that on the surface of RHA indicates a high decrease with rise in temperature. The adsorption process on both the adsorbents is exothermic in nature. However, the adsorption efficiency of CMRHA is higher than that of RHA at a given temperature. Furthermore, CMRHA could remove more than 85% dye from aqueous media even at 340 K, which indicating about its modified surface and high adsorption efficiency.

3.5. Effect of contact time

The Effect of contact time on the adsorption of crystal violet dye on RHA and CMRHA was studied in the range of 10-50 min. The experiments were conducted using 20 mL of dye solution whose initial concentration was 100 mg/L containing 10 g/L of the adsorbent at pH 6 with stirring speed of 250 rpm at 303 K. It was investigated that the rate of dye removal was high in the first 10 minutes and then decreased gradually. It was notified that the rate of adsorption remained constant after 20 minutes agitation (Figure is not shown here). Results indicated that in 20 minutes stirring time, RHA could remove 85.4% the crystal violet dye from aqueous solution whereas the chemical modification of the adsorbent enhanced its adsorption capacity to 98%.

3.6. Thermodynamic Studies

The thermodynamic properties of the adsorption of crystal violet dye on RHA and CMRHA could be explained on the basis of Gibbs free energy, which could be calculated by using the following equation [22];

$$\Delta G = -RT \ln K \quad (1)$$

Where (R) is the universal gas constant (8.314 J mol⁻¹ K⁻¹), (T) is the temperature in Kelvin and (K) is the equilibrium constant which is given by;

$$K = C_{ads}/C_e \quad (2)$$

(C_{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 [23].

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

The plots of ΔG versus temperature are shown in Fig.2. The values of ΔS and ΔH can be determined from the slope and intercept respectively. The thermodynamic parameters are represented in Table 1. The negative value of ΔH indicates that the adsorption of crystal violet dye on RHA and CMRHA is

exothermic process. The ΔS determine the degree of disorderliness of the system. The negative values of ΔG reveal that the adsorption of crystal violet dye on RHA and CMRHA is feasible and spontaneous. Table 1 showed that the values of ΔS for both the adsorbents are negative which inferred that the randomness decreased at the adsorbent/adsorbate interface during the sorption process. Comparative analysis indicated that the value of ΔS for CMRHA is higher than that of RHA, which inferred for more stable and localized dye molecules on the surface of chemically modified adsorbent. Table 1 also showed that the negative value of ΔH for CMRHA is greater than that of RHA, which reveals for it's more spontaneous and exothermic adsorption process.

3.7. Kinetics of dye removal

Kinetic studies determine the rate and mechanism of adsorption process. The pseudo-first order model is concerned with the physical force between the particles of adsorbent and adsorbate. This model also

assumes that the rate of adsorption is proportional to the vacant sites of adsorbent surface. The nonlinear form of this model is given as [24, 25];

$$dq_t/dt = k_1 (q_e - q_t) \quad (4)$$

The rate is constant when (q_e) and (q_t) are the dye adsorbed per unit mass of the adsorbent at equilibrium and time (t) and (K_1) . Integration of Eq. (4), we obtain the linear form of Eq. (5) in boundary conditions $q = 0$ in $t = 0$, and $q = q_t$ in $t = t$.

$$\log (q_e - q_t) = \log q_e - K_1 t / 2.303 \quad (5)$$

The constant reaction rate K_1 can be calculated from the slope of the $\log (q_e - q_t)$ vs t . The chemical absorption of metal ions on the adsorbent surface was described by the kinetic equation of the pseudo-second order. Its nonlinear form is shown as equation (6) [26, 27].

$$dq_t/dt = k_2 (q_e - q_t)^2 \quad (6)$$

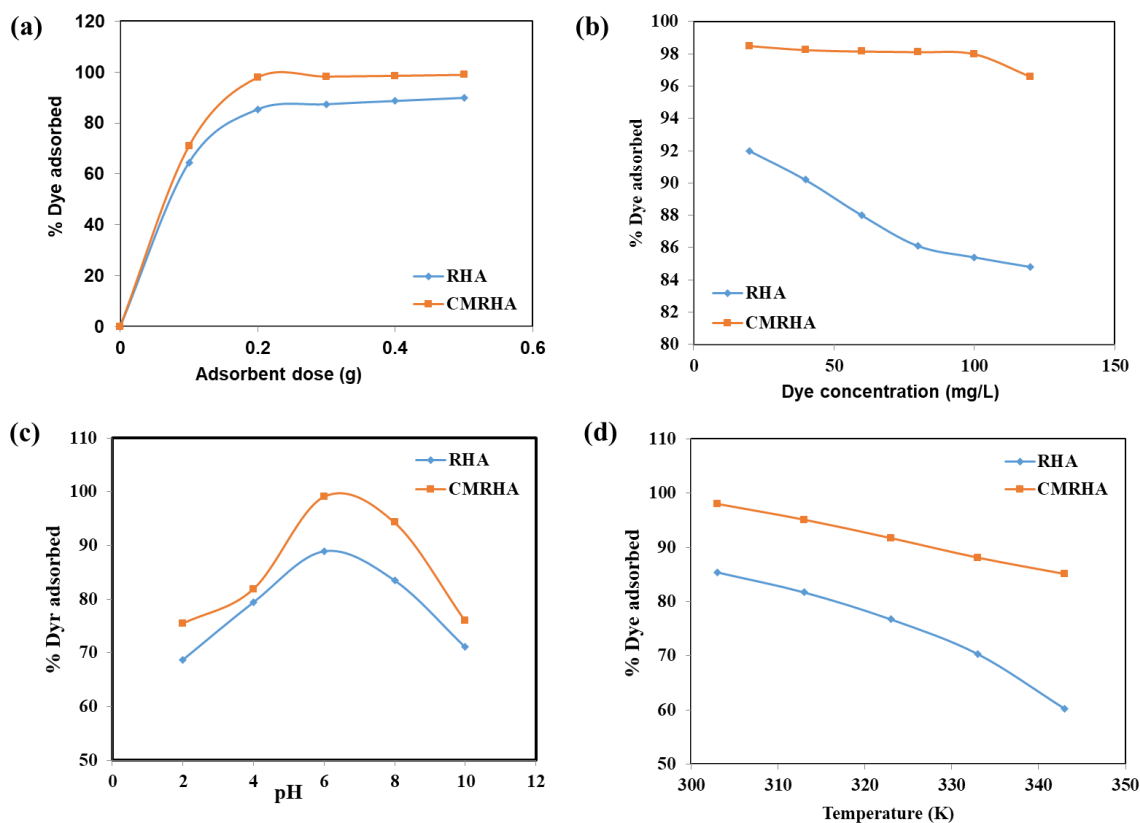


Fig. 1. Effect of (a) adsorbent dose, (b) dye concentration, (c) pH, and (d) temperature on the adsorption of crystal violet dye on RHA and CMRHA; experimental conditions: initial dye conc. 100mg/l, pH = 6, adsorbent dose = 10g/L.

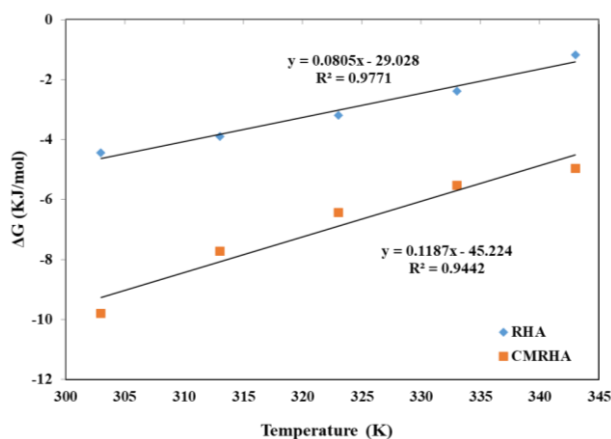


Fig. 2. Plots of Free Energy vs Temperature for the adsorption of crystal violet dye on RHA and CMRHA.

Table 1. Thermodynamic adsorption parameters for crystal violet on RHA and CMRHA.

Temperature (K)	ΔG (kJ/mol)		Values of (K)		ΔH (kJ/mol)	ΔS j/mol/k
	RHA	CMRHA	RHA	CMRHA		
303	-4.448	-9.799	5.849	49.0	-29.02 (RHA)	-80 (RHA)
313	-3.893	-7.728	4.464	19.4		
323	-3.198	-6.445	3.291	11.04	-45.22 (CMRHA)	-118 (CMRHA)
333	-2.383	-5.537	2.367	7.40		
343	-1.177	-4.961	1.512	5.71		

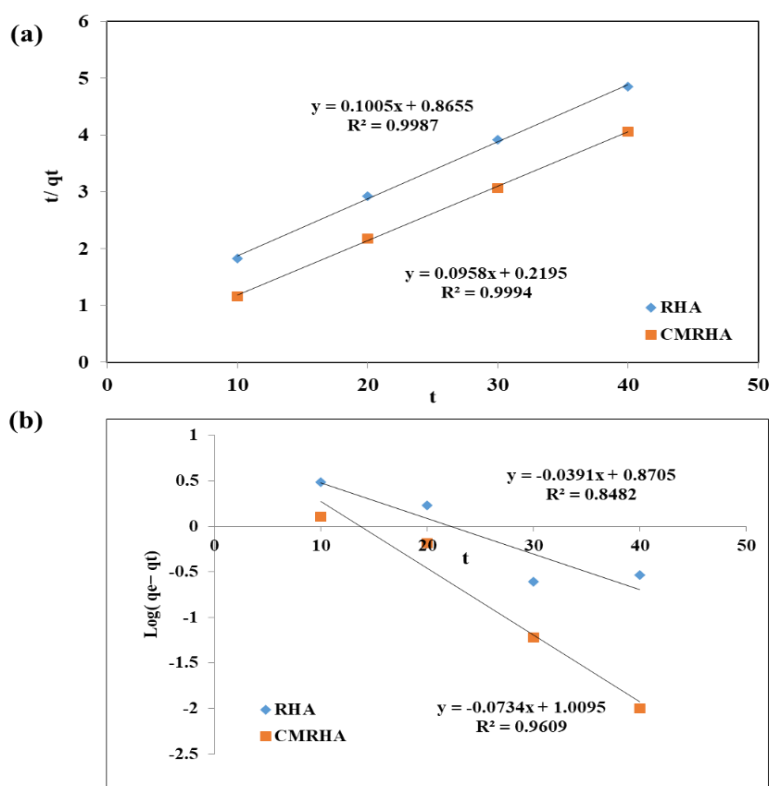


Fig. 3. Kinetics Models (a. Pseudo-First Order and b. Pseudo-Second Order) for the adsorption of crystal violet dye on RHA and CMRHA at $C_0 = 100$ mg/L.

Integration of this equation at the boundary conditions gives its linear form.

$$t/q_t = t/q_e + 1/k_2 q_e^2 \quad (7)$$

The values of (K_2) and (q_e) are determined from the slope and intercept of the plot of t/q_t versus t respectively. Fig. 3 shows the plots of pseudo-first and pseudo-second order reactions respectively. By fitting the linear regression of both the kinetics model, the rate constants (K_1 & K_2) are determined.

The values of rate constants (K_1 & K_2), q_e and their R^2 for the adsorption of crystal violet dye on RHA and CMRHA 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 suggested that the kinetics data follows the pseudo-second order model better than pseudo-first order model. Furthermore, the calculated value for q_e from pseudo-second order kinetics model is in close agreement with the experimental one, which infers for its best fitness to the kinetics data. The pseudo-second order kinetic model assumed that the rate limiting factor is chemisorption in the process of adsorption. Hence, the adsorption of Crystal violet dye on both RHA and CMRHA should be a chemical process [28].

3.8. Adsorption Isotherm Model

3.8.1 Langmuir adsorption isotherm model

Fig.4 displays the Langmuir, Freundlich, and Temkin adsorption models of Crystal violet dye on RHA and CMRHA adsorbents. The homogeneous adsorption mechanism is explained by the Langmuir adsorption isotherm. Its linear form given as;

$$C_e/q_e = C_e/q_m + 1 / Kq_m \quad (8)$$

Where (C_e) is the equilibrium concentration of Crystal violet dye in the solution (mg L^{-1}) (q_e) is the adsorption capacity (mg.g^{-1}); q_m is the monolayer adsorption capacity (mg.g^{-1}) and K is the Where (C_e) is the equilibrium of the crystalline violet dye in solution (mg L^{-1}) (q_e) the adsorbent capacity (mg.g^{-1}); q_m is the monolayer capacity of the adsorption (mg.g^{-1}) and K is the constant of the adsorption of the Langmuir equilibrium (L.mg^{-1}). From the intercept and slope, the Langmuir constants q_m and K could be

calculated by plotting C_e / q_e against C_e as shown in Fig.4.a, b) [29, 30].

3.8.2. Freundlich adsorption isotherm model

Freundlich isotherm model refers to reversible and multilayer adsorption [31]. This empirical model explains the heterogeneous surface of adsorbent [32]. Its linear form is given as;

$$\log q_e = \log K_F + 1/n \log C_e \quad (9)$$

Where (q_e) is the equilibrium adsorption capacity (mg / g). (C_e) is the equilibrium adsorbate concentration (mg / L). (k_f) and (n) Freundlich constants, related to the adsorbent's adsorption capability and adsorption strength, respectively. The values of these constants are determined from the $\log q_e$ vs $\log C_e$ plot (Annadurai et al. 2002) as shown in (Fig.4.c,d.) All these models were fitted with experimental results. Table 3 lists the values of regression coefficient / constant (R^2). In the Langmuir isotherm model the R^2 values for RHA and CMRHA adsorbents are similar to 1, which indicates monolayer coverage as well as chemisorption. The R^2 value for the Temkin model is also high for adsorbents that indicate its heterogeneous surfaces. [33].

3.8.3. The Temkin adsorption isotherm model

The Temkin model refers to a linear decrease in the heat of the adsorption of all molecules in the depth of the layer. The linear shape of Temkin is given as [33];

$$q_e = B \ln K_{TK} + B \ln C_e \quad (10a)$$

or

$$q_e = 2.303B \log K_{TK} + 2.303B \log C_e \quad (10b)$$

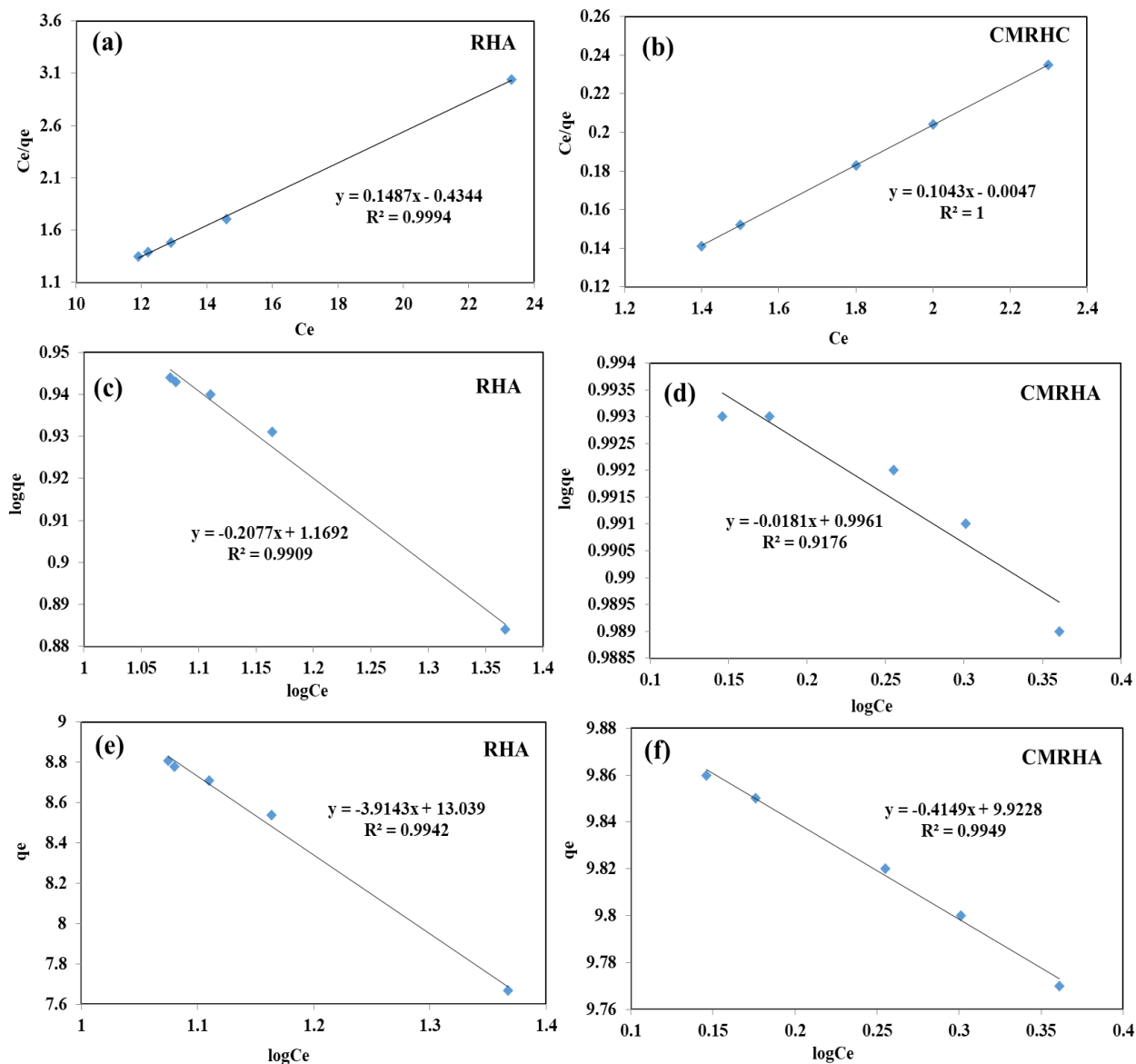
Where ($B = RT / b$) is the Temkin heat adsorption constant and (K_{TK}) is the Temkin isotherm binding constant (L / mg) associated with the maximum binding energy. Values (B) and (K_{TK}) can be determined from the slope and the Intercept of the plot of q_e versus $\text{Log} C_e$ (Fig.4.e,f). Table 3 showed that the heat of the adsorption and binding energy for the adsorption of Crystal violet dye on CMRHA is higher than that of RHA for CMRHA's efficiencies in the removal of crystal violet dye from aqueous media.

Table 2. The values of rate constants (K_1 & K_2) and their R^2 for the adsorption of crystal violet on RHA and CMRHA at initial concentration =100 mg/L.

Adsorbent	Pseudo-first order			Pseudo-second order		
	k_1 (min^{-1})	R^2	q_e (mg/g)	$k_2/\text{L}.$ ($\text{mg.min})^{-1}$	R^2	q_e (mg/g)
RHA	0.0169	0.848	7.413	0.0115	0.998	10.0
CMRHA	0.0316	0.960	10.2	0.0434	0.999	10.25

Table 3. Calculated parameters from Langmuir, Freundlich and Temkin adsorption isotherm models.

Adsorbent	Parameters in Langmuir model			Parameters in Freundlich model			Parameters in Temkin adsorption model		
	q_m	K_L	R^2	n	K_F	R^2	b (j/mol)	K_{KT} (L/g)	R^2
RHA	6.75	-0.341	0.999	-4.83	14.57	0.990	-1482.7	4.65×10^{-4}	0.994
CMRHA	9.61	-26.01	1.00	-55.5	9.908	0.917	-14073.4	8.26×10^{-25}	0.994

**Fig. 4.** The adsorption of crystal violet dye: Langmuir adsorption isotherm on (a) RHA and (b) CMRHA; Freundlich adsorption isotherms on (c) RHA and (d) CMRHA; Temkin adsorption isotherms on (e) RHA and (f) CMRHA.

4. Conclusion

Crystal violet dye adsorption was examined with RHA and chemically adjusted RHA. The experimental variables have a significant influence on the adsorption of dye on both adsorbents. At pH 6, the maximum adsorbent capacity was investigated for

both adsorbents and it was proposed that both adsorbents have almost the same chemical nature. However, at this pH the CMRHA, remove the crystal violet dye from aqueous media almost completely (99.1%), which infers for its enhanced adsorption properties for the dye. Thermodynamics study indicated that adsorption of crystal violet dye on the

two adsorbents is exothermic and spontaneous process. The negative values of ΔS for both the adsorbents suggests for their decrease randomness at the adsorbent/adsorbate interface during the adsorption process. However, the negative value of ΔS for CMRHA is higher than that of RHA, which indicated that randomness at the adsorbent/adsorbate interface for CMRHA is comparatively low in other words it can be stated as the dye molecules are more localized on the surface of chemically modified adsorbent. High negative value of ΔH for CMRHA inferred for its spontaneous and exothermic process. The kinetics data for both the adsorbents follow the pseudo-second order kinetics model, which revealed for chemisorptions of crystal violet dye on these adsorbents. The equilibrium data was analysed with isothermal adsorption models Langmuir, Freundlich and Temkin. All three isothermic models are followed, which is better adapted to the Langmuir model. R^2 values for both RHA and CMRHA in Langmuir model are closer to 1 which suggests for their chemisorptions nature. The value of R^2 for Temkin model is also high (>0.99) for both the adsorbents which infers for their heterogeneous surfaces. Hence, it is concluded that both RHA and CMRHA have almost the same chemical nature. Additionally, the adsorption properties of CMRHA are enhanced to its maximum for the removal of crystal violet dye from aqueous media.

Conflict of Interest

The authors declare that they have no conflict of interest.

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