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Full Length Research Paper

Application of chitosan padded rice and wheat husk for the removal of reactive dye from aqueous solution

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Industrial waste especially textile effluents contain many harmful ingredients, which cause environmental problems. In the present study, the removal of reactive red 195 dye was carried out using chitosan padded wheat husk (CWH) and rice husk (CRH) adsorbents. Chitosan was prepared in the laboratory from chitin which was obtained from crab shells by adopting reported method. The removal of dye was carried out by batch adsorption method under the optimized conditions of amount of adsorbent, stay time, temperature and dye concentration. Spectrophotometric technique was adopted for the measurement of concentration of dye before and after adsorption. Adsorption data was fitted in Freundlich and Dubinin-Radushkevich adsorption isotherm equations. The values of the corresponding constants were evaluated from the slope and intercept of their respective plots. Thermodynamic parameters such as free energy (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o) of the system were also calculated by using distribution coefficient K_D. From the percent removal data, it was concluded that chitosan-rice husk (CRH) and chitosan- wheat husk (CWH) systems showed about 83 and 79% removal tendency respectively. Chitosan itself act as a good adsorbent and its derivative with rice and wheat husk (mainly cellulose) show high removal tendency and may be used as low cost biosorbents for the removal of pollutants from the industrial effluent.

Key words: Adsorption, reactive red 195 dye, chitosan, rice husk, wheat husk.

INTRODUCTION

Dyeing industries produces highly colored toxic wastes. Synthetic dyes are extensively used for textile dyeing process and are also employed as additive in petroleum products. Approximately 10,000 different dyes and pigments are used industrially, and over 0.7 million tonnes of synthetic dyes are produced worldwide annually. It is estimated that about 10 to 15% of these dyes were lost in the effluent during dyeing process (Garg et al., 2003; Young and Yu, 1997). Most of the dyes are toxic to aquatic life. The reactive dyes waste is harmful for marine life due to its limited biodegradability in an aerobic environment. Many reactive azo dyes are used in paper, textile, rubber, plastic, leather, food stuff, cosmetics and pharmaceuticals industries (Reed et al., 1998). The effluents of these industries contain large amount of dye content, which on mixing with water bodies causes severe problems such as increasing the chemical oxygen demand (COD) and reducing the light penetration and visibility, which poses adverse effects on marine life (Murray and Parsons, 2004).

The agricultural waste rice husk was used as adsorbent in several studies for dye removal (Safa and Bhatti, 2011). Similarly indigocarmine was removed from the industrial effluent by using rice husk as adsorbent (Jain et al., 2010). Similarly, several metal ions were also removed by using coconut shell husk (Abdulrasaq and Basiru, 2010).

Usually, dyes have complex aromatic structure, so they are more stable, and difficult to biodegrade. Degradation of dyes is a typically slow process. Various physical and chemical methods were used for the purification of waste water like coagulation, flocculation, oxidation, ozonation, membrane separation, ultra chemical filtration, chemical

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treatment, etc (Brown and Hamburger, 1987; Shu et al., 1994; Shu and Huang, 1995; Gurses et al., 2006; Allègre et al., 2006; Pagga and Taeger, 1994; Santhy and Selvapathy, 2006; Robinson et al., 2002).

The adsorption processes were found to be more efficient method for the removal of dyes and metal pollutants from wastewater. It also provides an alternative way for the physical treatment of effluent, especially if the adsorbent is inexpensive and readily available. The various types of natural adsorbent materials such as activated carbon, bagass, fly ash (Gupta and Ali, 2001), wool fiber (Perineu and Molinier, 1983), fertilizer waste (Shrivastava and Tyagi, 1995), shale oil ash (Al-Qodah, 2000), rice husk (Srinivasan et al,. 1988), fruit stones (Gharaibeh et al,. 1998), red mud (Gupta et al,. 2001) , used tea leaves (Hameed, 2009), montmorillonite clay powder (Monvisade and Siriphannon, 2009), and algea (Aksu and Tezer, 2005) were utilized to remove dyes and colorants from waste water. It is now recognized that adsorption using low-cost adsorbents is an effective and economic method for the treatment of wastewater.

Nowadays much attention is paid to the elaboration of technologies with the use of natural and effective sorbents, including chitin. The chitin is characterized by its high adsorption tendency. It is the second most abundant polysaccharide on the earth crust next to cellulose, and is composed of poly-2-acetamido-2-deoxy-D-glucose. It is a main component in the shells of crustaceans, shrimps, crabs and lobsters. It is a well known derivative of chitin and the major difference is the degree of deacetylation (DAC) in chitosan, which is same as relative amount availability of free amines (Higazya et al., 2010). It has high chelating ability in comparison with other natural polymers (Debbaudt et al., 2004).

Chitosan can also be used in water processing as a part of a filtration process. It causes the fine sediment particles to bind together, and they are subsequently removed with the sediments (Juang and Shiau, 2000). The heavy metals, minerals, phosphorus and oils can be removed from the waste water by using chitosan and its combination with bentonite, gelatin, silica gel, or other fining agents. The chitosan-rice husk (CRH) and wheat husk (CWH) padded forms were applied for the removal of reactive red 195 from the waste water by adsorption method.

The present study aimed to determine the most beneficial method of chitosan preparation and its padded species. In this respect, the adsorption capacity of rice husk and wheat husk was enhanced by padding with chitosan, which would provide a high removal efficiency of dyes.

MATERIALS AND METHODS

Collection of crab shells

Crabs were collected from Arabian Sea near Karachi, Pakistan. The crab shells were separated from the flesh. These shells were washed, oven dried and then they were subjected to crushing, grinding and sieving to obtain 100 µm mesh size.

Preparation of chitin from crab shell

The chitin was prepared from the crab shells via a described method (Yen et al., 2009) by adopting the following pattern. After grinding and sieving, crab shells were subjected to demineralization by treating with 1 N HCl and deproteinization by treating with 5% NaOH solution followed by washing till neutralization. In order to decolourize, they were treated with 1% $KMnO_4$ for 1 h followed by treating with 1% oxalic acid solution for 1 h. The contents were washed till neutralization and then oven dried to obtain pure chitin.

Preparation of chitosan from chitin

The prepared chitin was treated with 40% NaOH solution and the content was heated till boiling for 2 h and then they were filtered and washed with distilled water till neutral pH. Finally, the chitosan was obtained.

Preparation of chitosan padded rice and wheat husk adsorbents

From the agricultural fields of district Multan Pakistan, rice and wheat husk were collected. They were washed with distilled water in order to remove impurities and ground. The padded form of rice and wheat husk was prepared with chitosan in the ratio of 6:1 w/w. it was dissolved in 2% acetic acid solution with continuous stirring for 12 h. Then, content was filtered and oven dried to get padded form of rice and wheat husk and placed in electric oven (J-FM 3, JISICO) at 65 ± 2°C for 3 h for activation in order to remove the physisorbed species.

Adsorbate

The reactive red 195 dye was used as adsorbate. Its various molar concentrations were prepared (1×10^{-5} to 5×10^{-4} mol/dm^3) by using deionized water. The dye concentration was recorded by using UV-Visible Spectrophotmeter (T-80 UV/ VIS Spectro-photometer, PG Instrument Ltd, UK.). The structure of reactive red 195 is shown in Figure 1.

Adsorption process

Adsorption experiments were preceded under the optimized conditions.

Optimization of amount of adsorbent

In order to find out the effect of amount of adsorbent at which maximum adsorption occurs, a test experiment was performed. For this purpose, 50 ml of 1×10^{-5} M solution of reactive red 195 dye was taken in a conical flask with different amount of adsorbent ranging from 0.1 to 1.2 g and placed in the shaking incubator (JISICO) for 30 min at 150 rpm. After specific time period, the content was filtered and the concentration noted down. The results are shown in Figures 2 and 3.

Optimization of stay time

The effect of stay time for the adsorption of dye was also

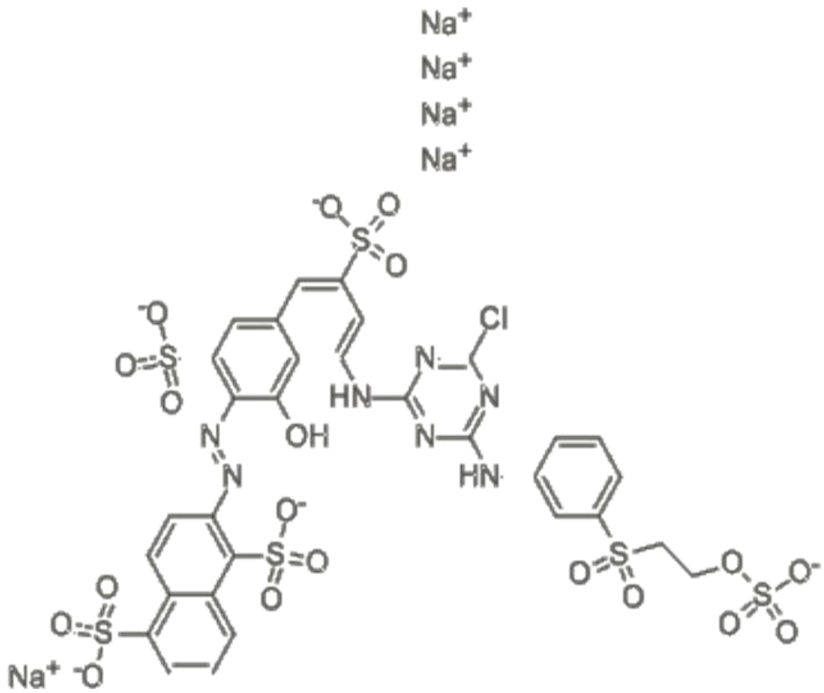

Figure 1. Structure of reactive red 195 dye.

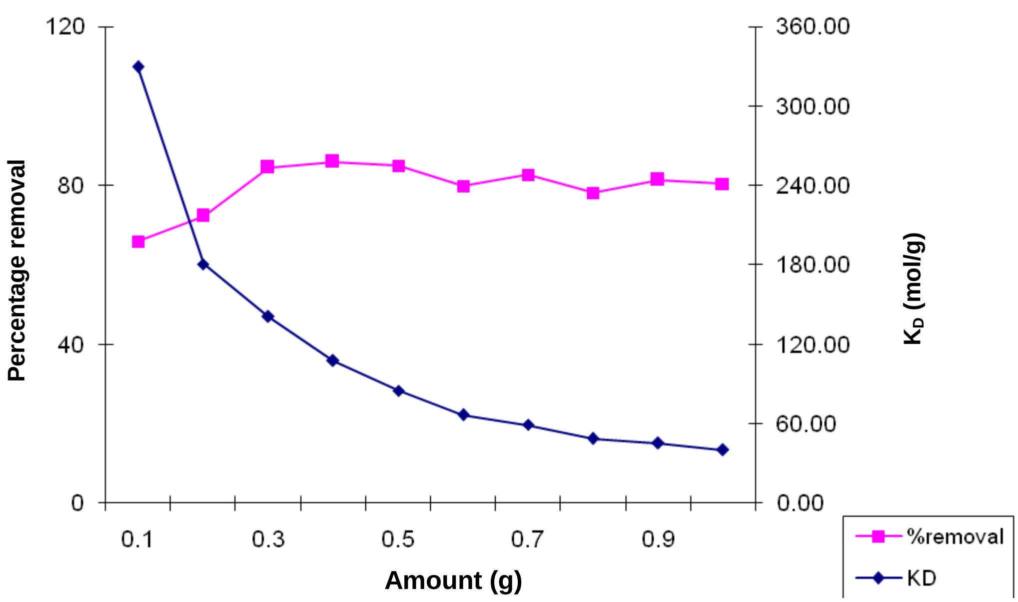

Figure 2. Optimization of stay time plots of chitosan-rice husk (CRH) system and reactive red 195 (RR195).

determined. 50 ml of 1 × 10^{-5} M reactive red 195 dye was taken in a number of conical flasks and the optimum amount of adsorbent. The content was placed in shaking incubator at various time periods varying from 5 to 60 min with the interval of 5 min. After specific time, the content of each flask was drawn, filtered and then subjected to measure the concentration.

Adsorption isotherms

The concentrations of dye solutions (2 × 10^{-5}, 4 × 10^{-5}, 6 × 10^{-5}, 8 × 10^{-5}, 1 × 10^{-4}, 2 × 10^{-4}, 3 × 10^{-4}, 4 × 10^{-4} and 5 × 10^{-4} M) were prepared and employed for adsorption by using optimum amount of adsorbent, stay time and temperatures varied from 303 to 328 ± 5

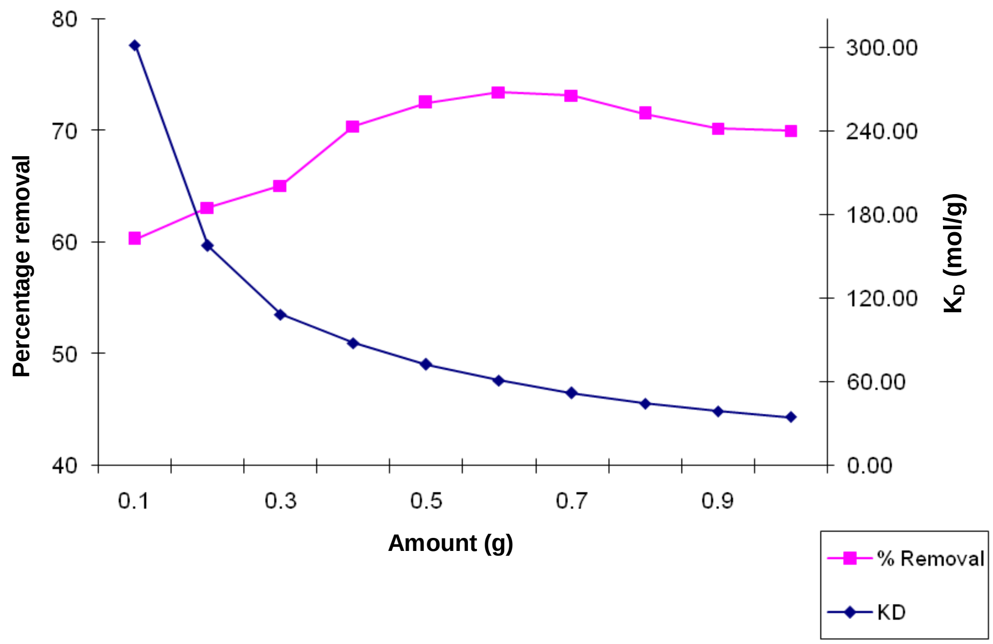

Figure 3. Optimization of stay time plots of chitosan-wheat husk (CWH) system and reactive red 195 (RR195).

K. After the specific time period, the solutions were filtered by using Whatman 42 filter paper and analyzed using UV-Visible spectrophotometer (Tahir et al., 2010).

RESULTS AND DISCUSSION

Adsorption of reactive red 195 (RR 195) dye, was studied on chitosan padded with rice (CRH) and wheat husk (CWH) which were used as adsorbent. The surface of both adsorbents is homogenous, having the mesh size about 100 µm and its surface is covered with adsorbed film containing oxygen and other impurities both of which were physically and chemically adsorbed. The adsorbate forms a stable bond with the surface of the adsorbent (Sabrina and Hasmah, 2008).

Effect of the amount of adsorbent

The effect of amount of adsorbent for the adsorption of reactive red 195 (RR 195) dye was studied. The adsorption of dye increased as the amount of padded chitosan-RH increased up to 0.4 g and then decreased. Similarly, for Chitosan-WH system, the optimum amount of adsorbent was found to be 0.6 g at 1.0×10^{-5} M dye solution as shown in Figures 2 and 3. The K_D values were calculated using the expression:

$$K_D = C_1 / C_2 \quad (1)$$

Where, C_1 is the adsorbed amount of dye per gram of the adsorbent; and C_2 is the concentration of dye per ml of the dye solution. The values of K_D decreased with increase in the amount of adsorbent.

Effect of the stay time

The results show that removal tendency of dye increased with increase in the stay time, and reached the maximum value at 40 min for CRH system and 35 min for CWH system, after which they started decreasing. When the adsorption equilibrium reached a constant value, % removal was attained. The results are shown in Figures 4 and 5.

Adsorption isotherms

Several theories of adsorption isotherm were applied to evaluate the feasibility of adsorption process. By employing Freundlich and Dubinin-Radushkevich (D-R) adsorption isotherm, the values of respective constants were determined.

Freundlich isotherm

The Freundlich isotherm is applied to find out the feasibility of adsorption process by using the equation:

$$\log X/m = \log K + 1/n \log C_e \quad (2)$$

Where, X/m is the amount adsorbed per unit mass of the

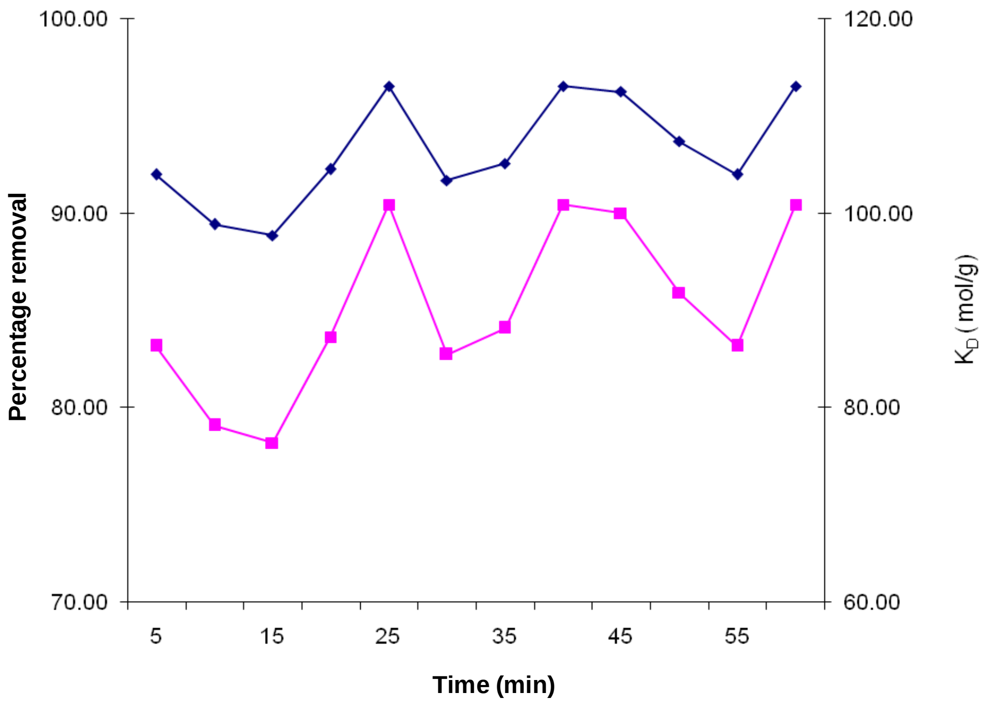

Figure 4. Optimization of amount of adsorbent chitosan-rice husk (CRH) system and reactive red 195 (RR195).

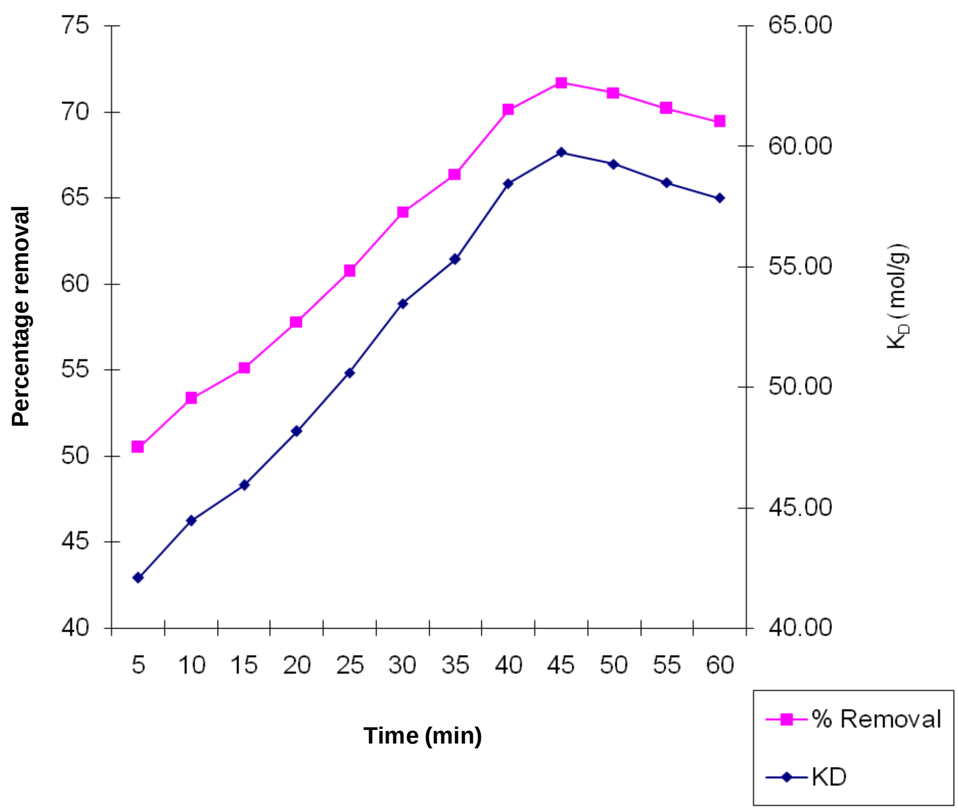

Figure 5. Optimization of amount of adsorbent chitosan-wheat husk (CWH) system and reactive red 195 (RR195).

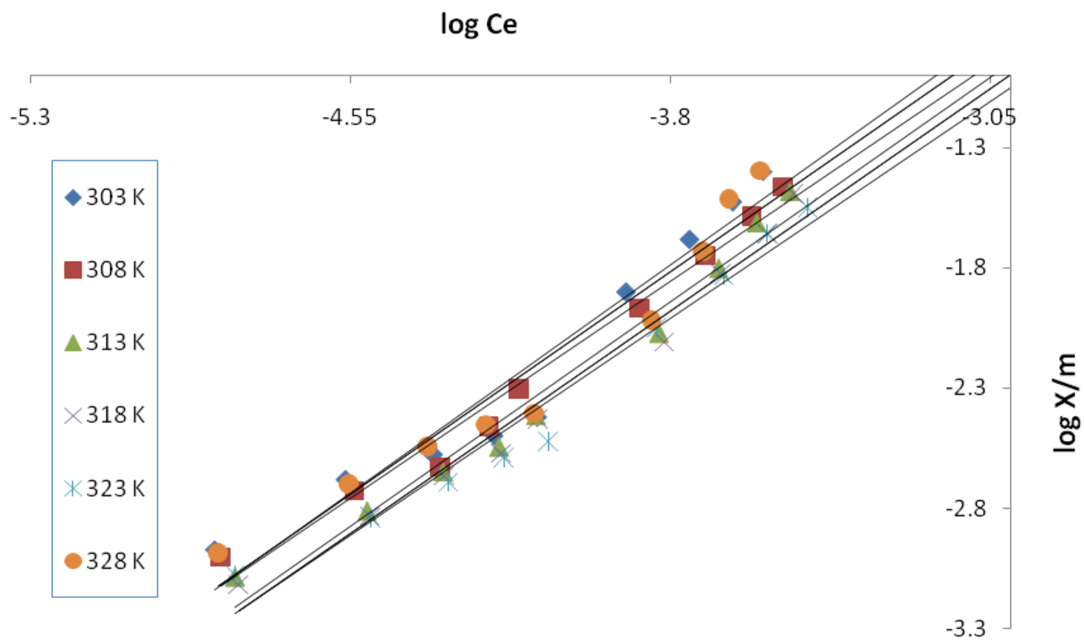

Figure 6. Freundlich plot for reactive red 195 (RR-195) on chitosan-wheat husk derivative (CWH).

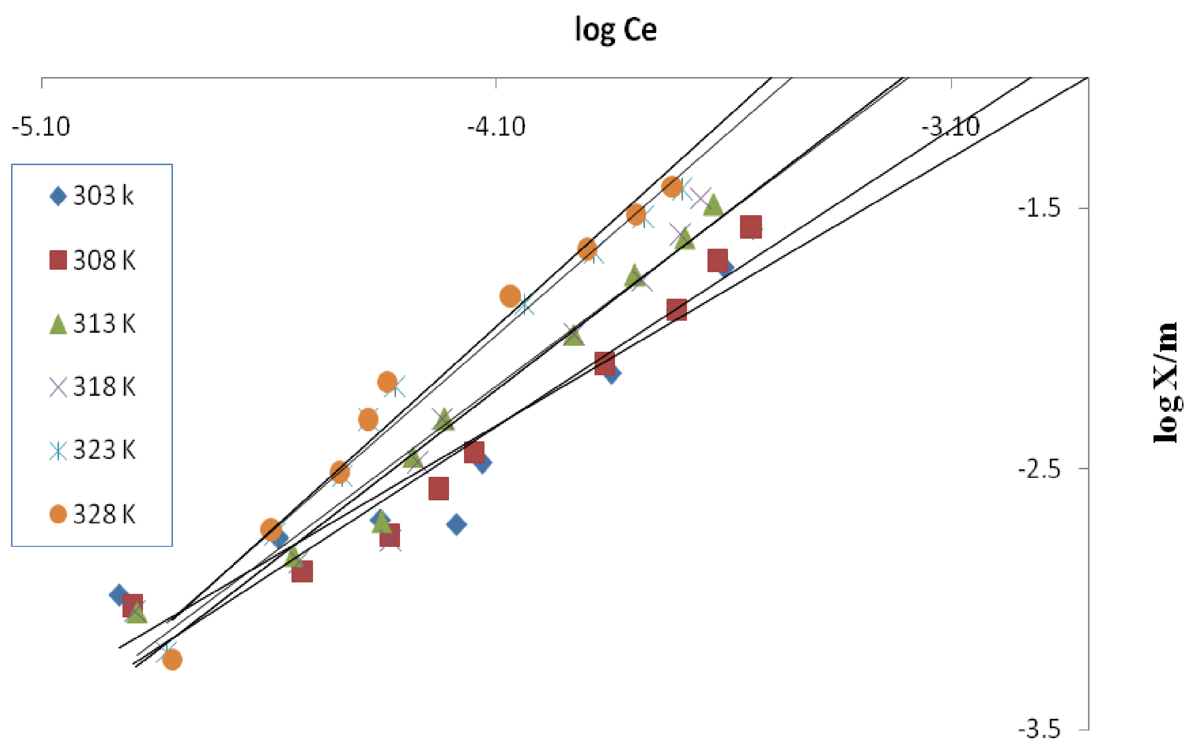

Figure 7. Freundlich isotherm plots of chitosan-rice husk (CRH) system and reactive red 195 (RR195).

adsorbent, C_e is the equilibrium concentration while 1/n and K are the constants. Figures 6 and 7 show the Freundlich isotherm at the temperatures (303 to 328 K). The values of K and n were calculated from the slopes and intercepts of their respective plots, as shown in Table 1. The value of K relates the degree of adsorption, which

Table 1. Freundlich parameters for reactive red 195 dye (RR-195) on Chitosan-rice husk (CR) and chitosan-wheat husk (CW).

Adsorbent	Temperature (K)	K (10^{-2})	n
Chitosan-rice husk derivative	303	7.76	0.97
	313	15.2	0.76
	318	20.4	0.75
	328	34.4	0.63
Chitosan-wheat husk	303	10.2	0.79
	313	6.03	0.80
	318	4.99	0.82
	328	7.33	0.81

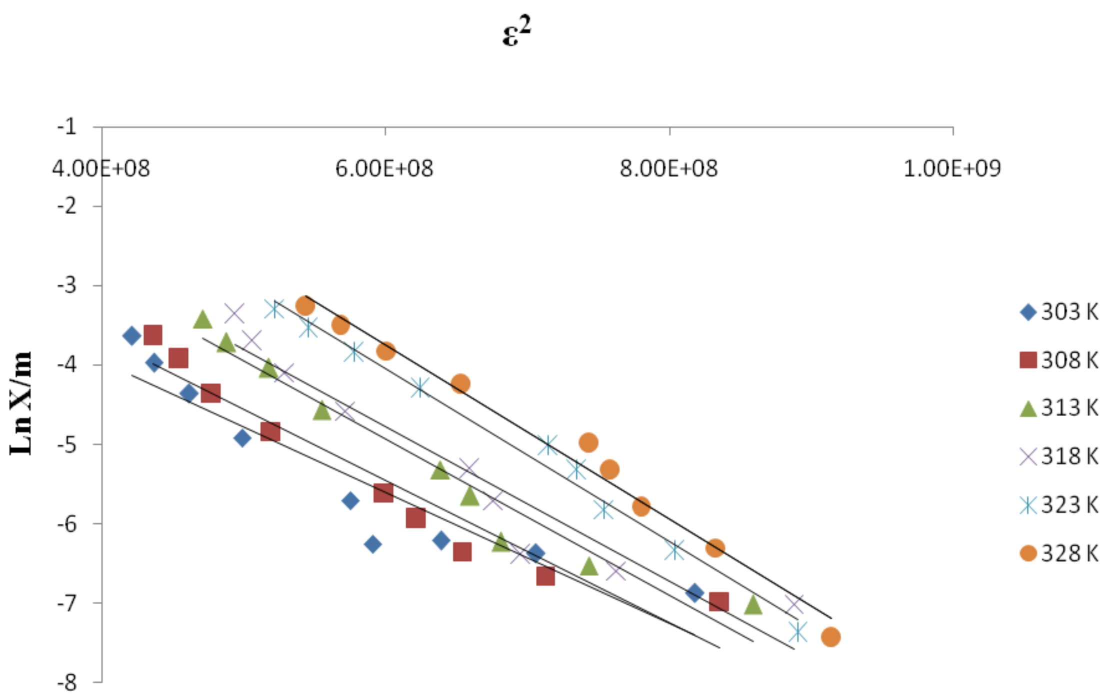

Figure 8. D-R isotherm plots of chitosan-wheat husk (CWH) system and reactive red 195 (RR195).

increased with the rise in temperature for CRH system and decreased for CWH system.

Dubinin-Radushkevich (D-R) isotherm

The Dubinin-Radushkevich (D-R) isotherm equation was also applied which is shown as:

$$\ln X/m = \ln Xm - K\varepsilon^2 \quad (3)$$

$$\varepsilon = RT\ln(1 + 1/Ce) \quad (4)$$

Where, X_m is the monolayer capacity of adsorbent, K is a constant related to the adsorption energy, ε is adsorption potential, R is a gas constant and T is the temperature while other constants have usual meaning as explained earlier. The D-R Plots are shown in Figures 8 and 9, and the values of constants X_m and K were calculated from the intercept and slopes of their respective plots, and the mean free energy of sorption (E_s) was calculated from K using the following equation:

$$E_s = (-2K)^{-1/2} \quad (5)$$

The values of sorption free energy E_s for CRH system decrease with the increase in temperature indicating less adsorption tendency at higher temperatures while in reactive red 195-CWH system, the E_s values increase

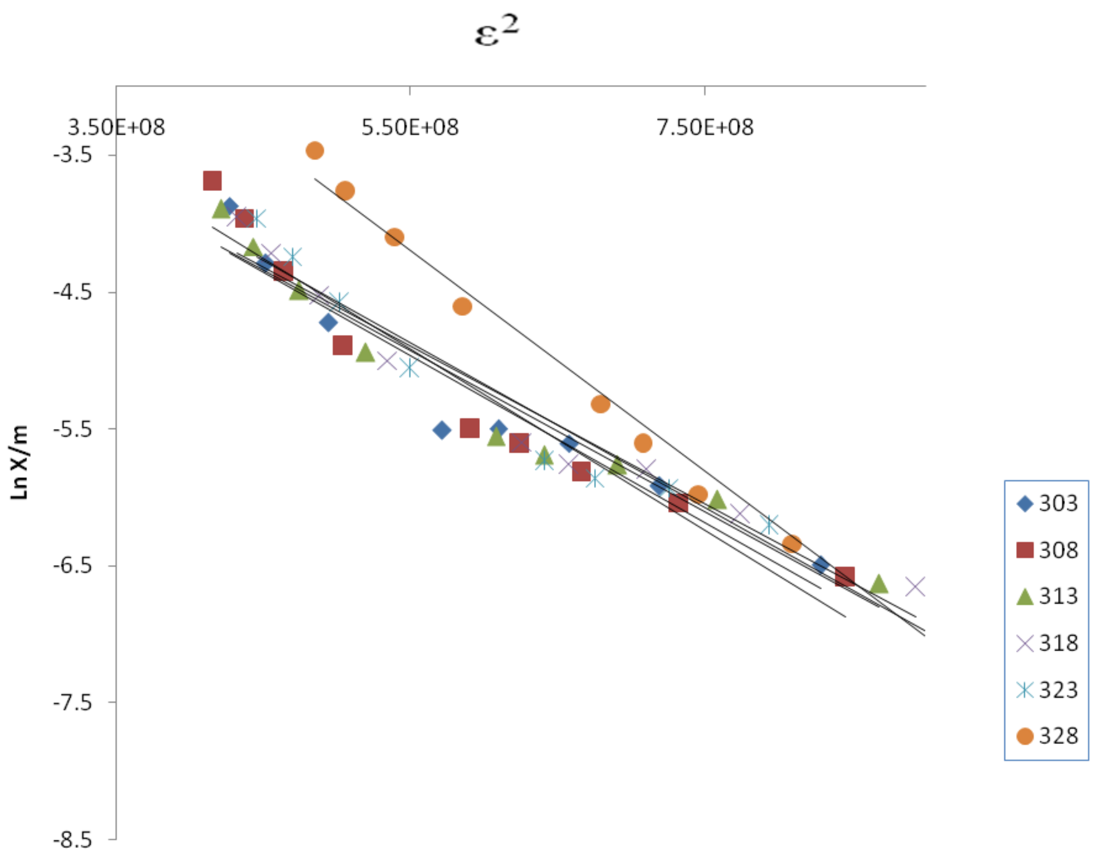

Figure 9. D-R isotherm plots of chitosan-rice husk (CRH) system and reactive red 195 (RR195).

Table 2. D-R parameters for reactive red 195 dye (RR-195) adsorption on chitosan-rice husk (CR) and chitosan-wheat husk (CW).

Adsorbent	Temperature (K)	Es (J/mol) (10^{-3})	Xm (10)
Chitosan-rice husk	303	7.78	5.270
	313	7.12	0.269
	318	7.15	0.296
	328	6.75	1.680
Chitosan-wheat husk	303	7.22	0.154
	313	7.23	0.165
	318	7.37	0.148
	328	7.66	0.193

with the increase in temperature. The results are summarized in Table 2.

Thermodynamic parameters

The thermodynamic study plays an important role in understanding the nature of adsorption. The thermo-dynamics parameters such as free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°), were evaluated using the following equations:

$$\text{Ln } k = \Delta S°/R - \Delta H°/RT \quad (6)$$

$$\Delta G° = \Delta H° - T\,\Delta S° \quad (7)$$

The values of ΔH° and ΔS° were calculated from the slope and intercept of the linear variation of Ln K with the

Table 3. Thermodynamic parameters for reactive red 195 dye (RR-195) adsorption on chitosan-rice husk (CR) and chitosan-wheat husk (CW).

Adsorbent	Conc. of dye (M) (10^5)	ΔH (kJ/mol) (10)	ΔS (J/mol)	ΔG (kJ/mol) (× 10)			
				303 K	313 K	318 K	328 K
Chitosan-rice husk	2.0	1.26	0.93	-1.56	-1.65	-1.70	-1.79
	6.0	1.18	0.91	-1.57	-1.66	-1.71	-1.80
	10	2.47	1.30	-1.47	-1.60	-1.67	-1.80
	20	2.50	1.31	-1.47	-1.60	-1.67	-1.80
	40	2.30	1.23	-1.43	-1.55	-1.61	-1.74
Chitosan-wheat husk	2.0	1.20	0.86	-1.39	-1.48	-1.52	-1.61
	6.0	0.67	0.70	-1.45	-1.53	-1.56	-1.63
	10	0.58	0.68	-1.49	-1.56	-1.59	-1.66
	20	0.42	0.64	-1.51	-1.57	-1.60	-1.67
	40	0.58	0.68	-1.48	-1.55	-1.59	-1.65

reciprocal of temperature (1/T). The values of thermodynamic parameters are shown in Table 3.

The results show that values of ΔG° were negative at different temperatures showing spontaneous behavior of adsorption process. The values of ΔH° were positive for both systems, showing the endothermic nature of the system. The values of ΔS° show random behavior.

The comparative removal studies were also carried out at different temperatures. The adsorption on CWH and CRH systems showed about 80% removal of reactive red 195 dye at 313 K.

Conclusion

From the present study, animal and agricultural waste can be utilized as low cost adsorbent. The animal waste was obtained from the Arabian Sea while agricultural waste was collected from fields. The recycling of waste and regeneration of adsorbing materials is a low cost way to save the environment and eco-system.

Chitosan was synthesized from the chitin of crab shells which acts as an effective adsorbent. Rice and wheat husk padding with chitosan, enhances the adsorption capacity of husk materials.

By employing adsorption method, about 80% removal of reactive dye was achieved. The reactive dyes are main pollutant of textile effluents. They can be effectively removed by batch adsorption method. The present model system can be implemented on industrial scale for the treatment and purification of industrial wastes.

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