A Comparative Study for Adsorptive Removal of Remazol Red R and Remazol Black B from Aqueous Solution by ZnO

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Abstract

Adsorptive removal of remazol red R (RRR) and remazol black B (RBB) from aqueous solution has been investigated by using ZnO as an adsorbent. Time for adsorption equilibrium, kinetics of adsorption at different initial concentrations of dyes and adsorption isotherms at different temperatures have been studied. Adsorption capacity increased with increasing initial dye concentration. The pseudo first-order and pseudo second-order kinetics were used to describe kinetic data and the rate constants were evaluated. Experimental data fits better in the pseudo second-order kinetic model than in the pseudo first-order kinetic model for both the dyes. Langmuir and Freundlich isotherm models were applied to describe the adsorption of RRR and RBB onto ZnO powders. Langmuir isotherm model provided a better correlation for the experimental data in comparison to the Freundlich isotherm model. Adsorption of both RRR and RBB on ZnO are physical in nature and increases with decreasing temperature. The equilibrium adsorption capacity decreases from 3.43 mg/g at 20 °C to 2.36 mg/g at 40 °C for RRR whereas that in the case of RBB changes from 0.77 mg/g at 30 °C to 0.75 mg/g at 40 °C. Adsorption of RRR on ZnO was found to be three times higher than the adsorption of RBB at a particular temperature. A model for adsorption of both the dyes has been proposed.

I. Introduction

Textile, leather, pulp and paper, food and plastics industries have been using dyes extensively. These dyes are classified as acid and reactive dyes, cationic and anionic dyes etc[1-3]. Among different types of dyes reactive dyes are most commonly used. Reactive dyes differ from all other classes of dyes in the way that they form covalent bond to the textile fibers. Characteristic bright color, simple method of application and low consumption of energy are the main reasons for extensive use of reactive dyes in the textile industries[4,5]. For several organisms reactive dyes are very toxic. Once released to the aquasphere reactive dyes possess a great threat to aquatic life. They block out the sunlight, hence reduce photosynthesis which cause the decrease in concentration of dissolved oxygen[6,7]. Moreover, dyes have carcinogenic and mutagenic effects on human and other life forms[8,9]. Azo compounds remazol red R (RRR) and remazol black B (RBB) (Fig. 1) both are reactive dyes and are frequently used in textile industries. Hence textile industry effluents contain these toxic reactive dyes until properly treated.

There are various techniques for removing reactive dyes from aqueous solution. Among them reverse osmosis, chemical coagulation, trickling filter, activated sludge and photodegradation techniques have been investigated extensively[10-13]. Adsorption is another effective method for dye removal from aqueous solution. During adsorption, dye molecules dissolved in aqueous solution get attached to the surface of the adsorbents[14,15]. The possibility of using chitin[16,17], activated carbon[18,19], silica[12], peat[20,21] and others[22-28] as adsorbent has already been studied. Zinc oxide powders have been used as semi-conductors, photocatalyst, non-linear optical materials etc. Zinc oxide powders can also act as an effective adsorbent[29,30]. In this work, zinc oxide was employed as an adsorbent for removal of RRR and RBB from aqueous solution. The dyes were chosen because one of the dye (RRR) has one longer chain with anionic ($-OSO_3^-$) group, whereas the other, RBB has two such chains. Adsorption capacity, kinetic and isothermal parameters were evaluated and compared.
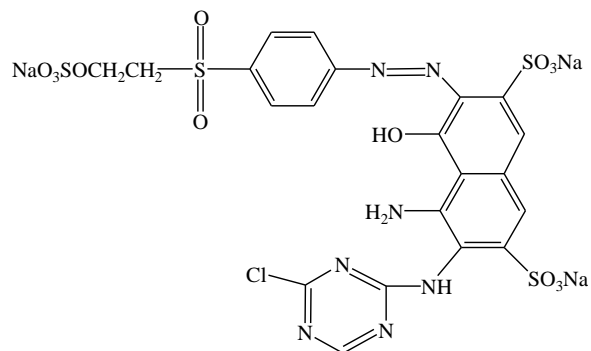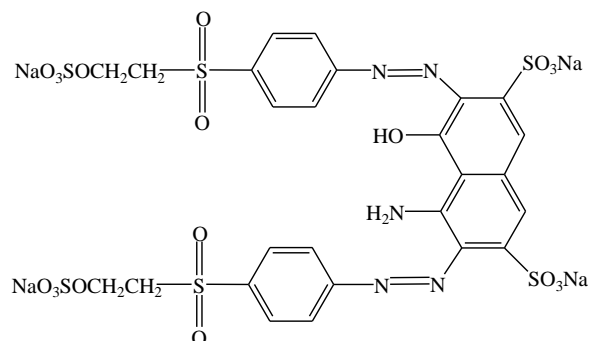

Fig.1. (a) Remazol red R (RRR)

Fig. 1. (b) Remazol black B (RBB)

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II. Experimental

Materials and techniques

The adsorbent ZnO was obtained from Merck, Germany and was used as purchased. Commercial grade RRR and RBB dyes were purchased from Dyestar, Germany and was used without further purification. UV-visible spectra of both RRR and RBB were recorded on a Shimadzu UV-1650 spectrophotometer. SWB-20, HAAKE thermostatic shaker was used for shaking at 200 rpm and a laboratory centrifuged machine (Digisystem, DSC-N158A) was used to centrifuge (3000 rpm) the dye solution after adsorption.

Adsorption proces

The wavelengths of maximum absorbance, λ_{max} were determined from the absorption spectra and λ_{max} were found 516 and 594 nm for RRR and RBB respectively.

In order to estimate equilibrium time of adsorption of RRR and RBB, experiments were performed in well stopper reagent bottles containing 30.0 mL of the dye solutions. A fixed amount of ZnO was added to the dye solution. The reagent bottles were shaken in a thermostatic shaker at 30 °C. The reagent bottles were successively withdrawn after a definite time interval and 10.0 mL of supernatant liquid from each bottle was centrifuged and the UV-visible spectra were recorded to determine the change in concentration of the dye solutions.

For kinetic data a series of reagent bottles with dye solutions and fixed amount of ZnO were stirred at 30 °C and the changes in concentration were monitored after 5, 15, 30, 45, 60, 75 and 90 min during the adsorption process. The adsorption isotherm for each dye was studied through the batch method in which concentrations varied from 1.0×10^{-5} mol L^{-1} to 1.0×10^{-4} mol L^{-1} for RRR and 1×10^{-5} mol L^{-1} to 5×10^{-5} mol L^{-1} for RBB. Adsorption isotherm was studied at three different temperatures, 20 °C, 30 °C and 40 °C .

The amount adsorbed was determined from difference between the initial concentration (C_o) in aqueous solution and the concentration of unadsorbed dye that found after centrifugation. Adsorption isotherm was obtained by plotting q_t vs C_e, where q_t is the amount of adsorbed (in mg) per gram of adsorbent, ZnO at time t, C_e is the equilibrium concentration of dye. The value of qt was obtained using the following relation.

$$q_t = \frac{(C_0 - C_e)VM}{Z} \times 1000$$

Where, V = Volume (L) of the solution in each bottle

M = Molecular weight of the dye (g mol^{-1})

Z = Amount of ZnO (g)

III. Results and Discussion

Estimation of equilibrium time

In the process of adsorption, dye molecules diffused through the boundary layer into the porous structure of the adsorbent. Adsorption of RRR and RBB on ZnO at 30 °C were studied by varying the initial concentration of dyes. Higher initial concentration of dyes results in higher adsorption capacity of the adsorbent[29]. Maximum 3.29 mg/g of RRR was adsorbed for 10×10^{-5} mol L^{-1} of RRR while 0.77 mg/g was the maximum adsorption capacity for 5×10^{-5} mol L^{-1} of RBB. For all the experiments, dye concentrations were decreased with time and after a certain time, the concentration of dye became steady. At this point rate of adsorption become equal to the rate of desorption of dye molecules. Time required to reach this equilibrium condition was same irrespective of the initial concentration of the dye solution. Approximately 60 minutes and 70 minutes were required to reach the equilibrium for the adsorption of RRR (Fig.2) and RBB (Fig.3), respectively. These results prove that ZnO is an effective adsorbent because bioadsorbents take much longer time to reach adsorption equilibrium[26,28].
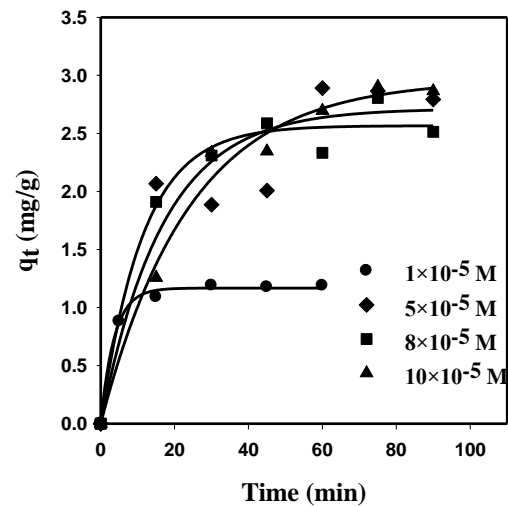

Fig. 2. Estimation of equilibrium time for adsorption of different initial concentrations of RRR on 0.2 g / 30.0 mL ZnO at pH 5.83.
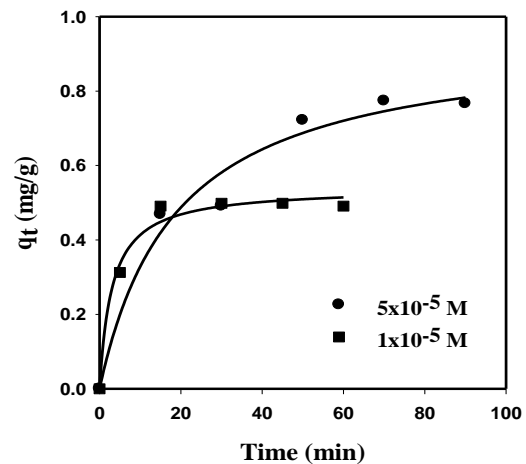

Fig. 3. Estimation of equilibrium time for adsorption of different initial concentrations of RBB on 0.4 g / 30.0 mL ZnO at pH 5.83.

Kinetics of adsorption of RRR and RBB on ZnO

There are numerous kinetic models proposed to elucidate the mechanism of dye adsorption. In this work two different kinetic models, Lagergren pseudo-first order and Ritchie pseudo-second order kinetic models, were used.

Lagergren pseudo-first order model[31,32] is expressed as follows:

$$\log(q_e - q_t) = \log q_e - k_1 t \qquad (1)$$

According to the pseudo-second order model[33], the dye adsorption kinetics can be described as

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

Where, q_t is the amount of dye adsorbed (mg/g) at times t, q_e is the maximum adsorption capacity (mg/g) for both pseudo-first order and pseudo-second order adsorption, k_1 and k_2 are the pseudo-first order (min^{-1}) and pseudo-second order (g mg^{-1} min^{-1}) rate constants, respectively. The values of pseudo-first order and pseudo-second order rate constants for adsorption of RRR (Fig. 4a and Fig. 4b) and RBB (Fig. 5a and Fig. 5b) are calculated and recorded in Table. 1. The correlation coefficients (R_2^2 for pseudo-first order model and R_2^2 for pseudo-second order model) show that pseudo-second order model fits the experimental data better than the pseudo-first order model for bothRRR and RBB. In other words, adsorption of RRR and RBB on ZnO follows pseudo-second order kinetic model. Several research groups have found that adsorption of dye molecules on bioadsorbent or ZnO surface follows pseudo-second order kinetic model[27-30] and our findings agrees well.

Table. 1. Kinetic parameters of pseudo first-order and pseudo second-order model for adsorption of RRR and RBB on ZnO.

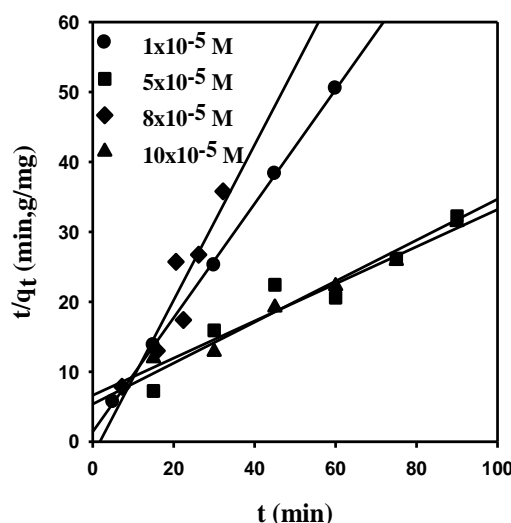| Dye	$C_o \times 10^5$ /mol L^{-1}	Pseudo-first order model		Pseudo-second order model	
		k_1 /min^{-1}	R_1^2	k_2 /g mg^{-1}min^{-1}	R_2^2
RRR	1.0	0.104	0.603	0.474	0.999
	5.0	0.048	0.598	0.160	0.914
	8.0	0.028	0.565	0.060	0.976
	10.0	0.021	0.901	0.010	0.977
RBB	1.0	0.030	0.900	1.126	0.997
	5.0	0.076	0.496	0.053	0.967

Fig. 4. (b) Pseudo second-order kinetic model for adsorption of RRR on 0.2 g / 30 mL ZnO at pH 5.83.
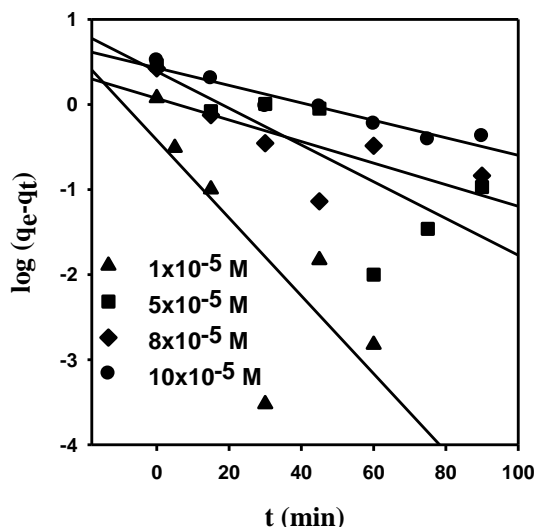

Fig. 4. (a) Pseudo first-order kinetic model for adsorption of RRR on 0.2 g / 30 mL ZnO at pH 5.83.
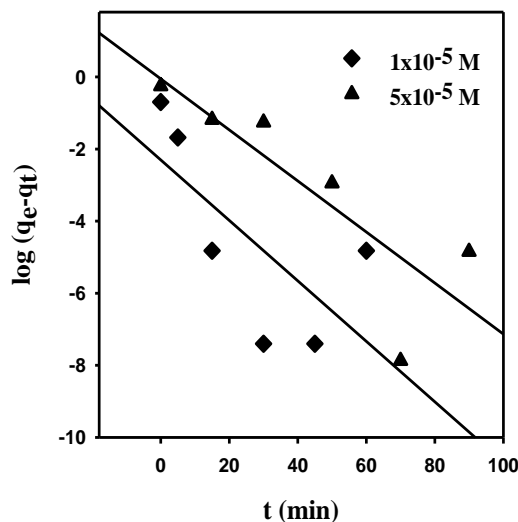

Fig. 5. (a) Pseudo first-order kinetic model for adsorption of RBB on 0.4 g / 30 mL ZnO at pH 5.83.
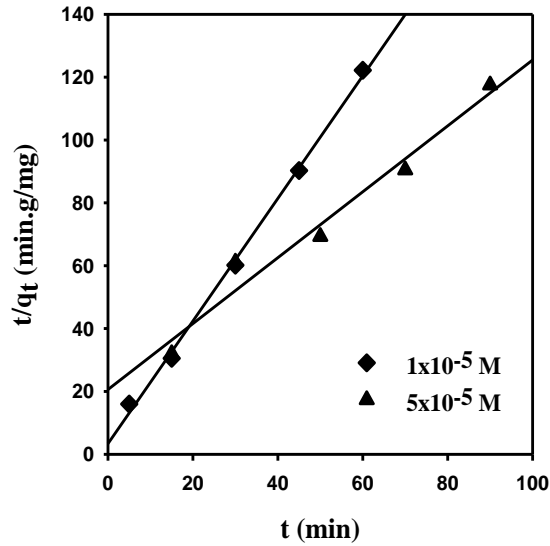
Fig. 5. (b). Pseudo second-order kinetic model for adsorption of RBB on 0.4 g / 30 mL ZnO at pH 5.83.

Adsorption Isotherm

In designing of an adsorption system, the adsorption isotherms are of fundamental importance. In the present work, adsorption of 10×10^{-5} mol L^{-1} of RRR on zinc oxides was studied at three different temperatures and that of 5×10^{-5} mol L^{-1} of RBB was studied at two temperatures. Amount of dye absorbed decreases with the increase of temperature (Fig. 6 and Fig. 7) which suggest that both RRR and RBB undergo physical adsorption at the surface of ZnO. Maximum adsorption capacity of RRR was 3.43 mg/g at 20 °C and that of RBB was 0.77 mg/g at 30 °C.
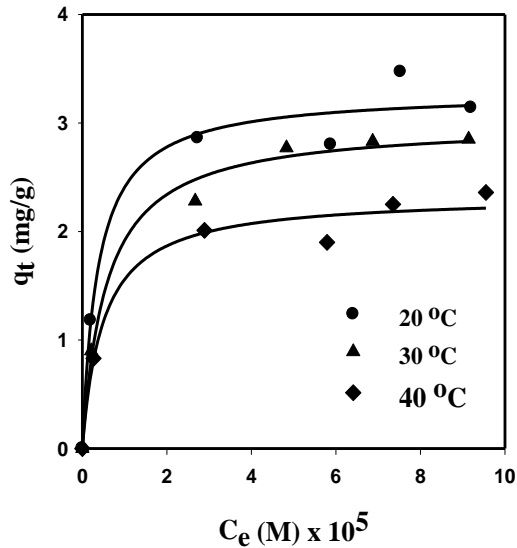

Fig. 6. Adsorption isotherms of RRR on 0.2 g / 30 mL ZnO at three different temperatures.
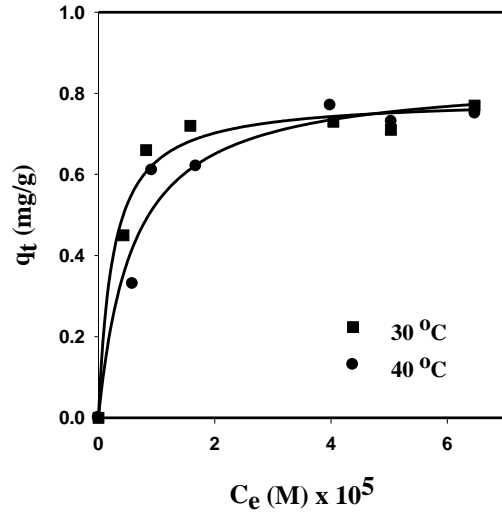

Fig. 7. Adsorption isotherms of RBB on 0.4 g/30 mL ZnO at two different temperatures.

The experimental equilibrium adsorption data were analyzed using the Freundlich[31] and the Langmuir[34] isotherm models. The linear form of these two isotherms are expressed by the following equations.

Freundlich isotherm:

$$\log q_t = \log K_F + \frac{1}{n}\log C_e \tag{3}$$

Langmuir isotherm:

$$\frac{1}{q_t} = \frac{1}{q_e} + \frac{1}{K_L q_e}\frac{1}{C_e} \tag{4}$$

Where, K_F parameter is relative to the adsorption capacity and n is a measure of adsorption intensity. The Langmuir constant, K_L is relative to energy ofadsorption and q_e is the maximum value of adsorption capacity. The values of K_F, n, K_L, q_e are calculated and recorded in Table. 2 along with the values of regression coefficients for Langmuir isotherm (R_L^2) and Freundlich isotherm (R_F^2).
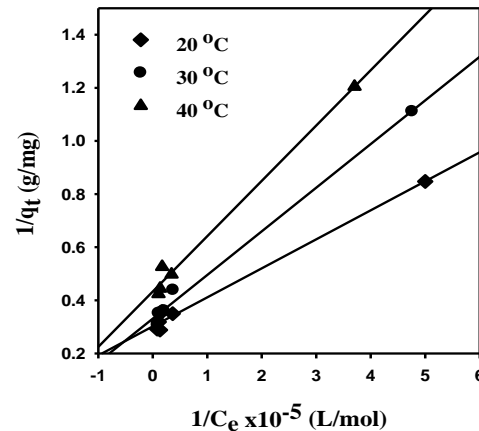

Fig. 8. (a) Langmuir isotherms for adsorption of RRR on ZnO at different temperatures.
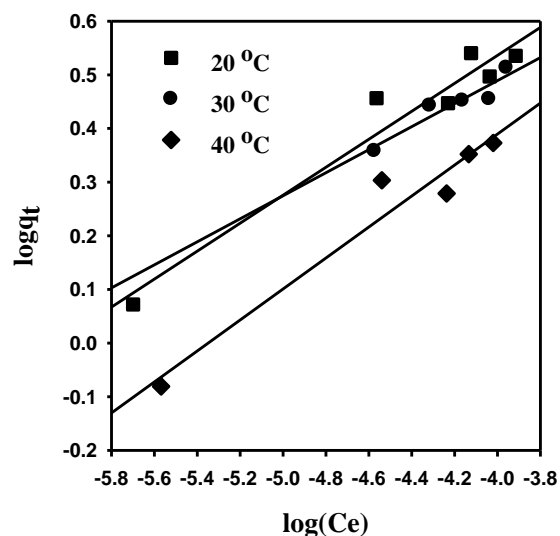
Fig. 8. (b) Freundlich isotherms for adsorption of RRR on ZnO at different temperatures.

Table. 2. Characteristic parameters of adsorption process of RRR and RBB on ZnO.

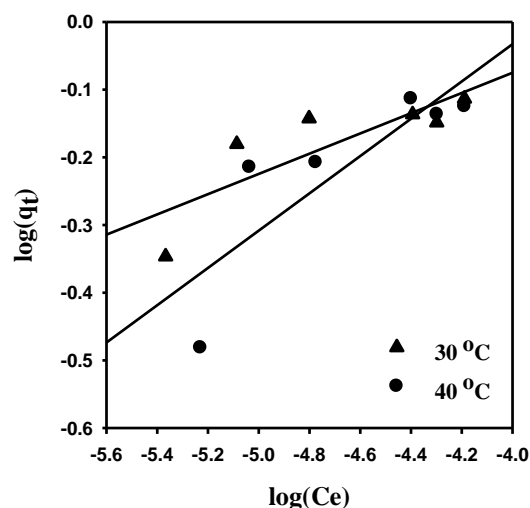| Dye	Temperature / °C	Freundlich isotherm			Langmuir isotherm		
		K_F	n	R_F^2	$q_e/mg\ g^{-1}$	$K_L x10^{-5}/L\ mol^{-1}$	R_L^2
RRR	20	37.84	3.846	0.945	3.311	2.77	0.989
	30	61.09	3.135	0.979	3.021	2.02	0.992
	40	35.08	3.472	0.949	2.039	2.08	0.989
RBB	30	3.33	6.711	0.685	0.814	3.21	0.893
	40	11.72	3.636	0.714	0.941	1.08	0.834

Fig. 9. (b) Freundlich isotherms for adsorption of RBB on ZnO at different temperatures.

The values of correlation coefficients (R^2) for the two models (Table. 2) suggest that the experimental data for both RRR and RBB were more suitable to the Langmuir model than to the Freundlich model. K. Ada et al also found that Langmuir model as a better fit to the adsorption of remazol brilliant blue R[29].

Proposed model for adsorption of RRR and RBB on ZnO.

Adsorption of RRR on ZnO is approximately three times higher than that of RBB.At 30 °C temperature, 3.26 mg RRR was adsorbed per gram of ZnO while amount adsorbed of RBB was 0.77 mg/g (Fig. 10). Again at 40 °C, amount adsorbed of RRR was 2.36 mg/g while that of RBB was 0.75 mg/g (Fig. 11).
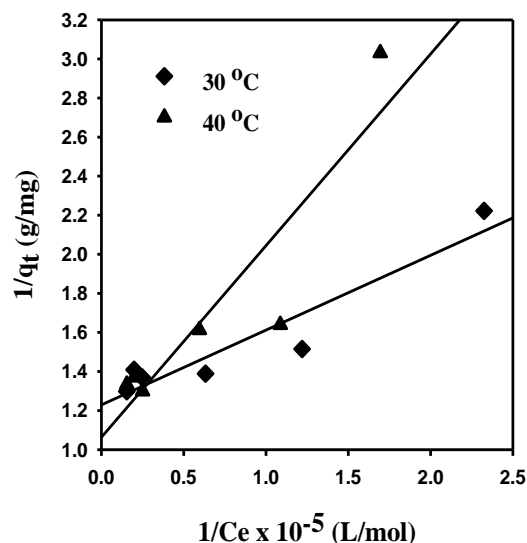

Fig. 9. (a) Langmuir isotherms for adsorption of RBB on ZnO at different temperatures.
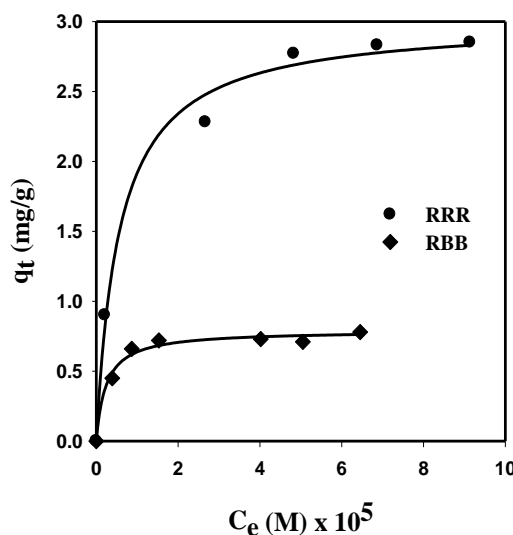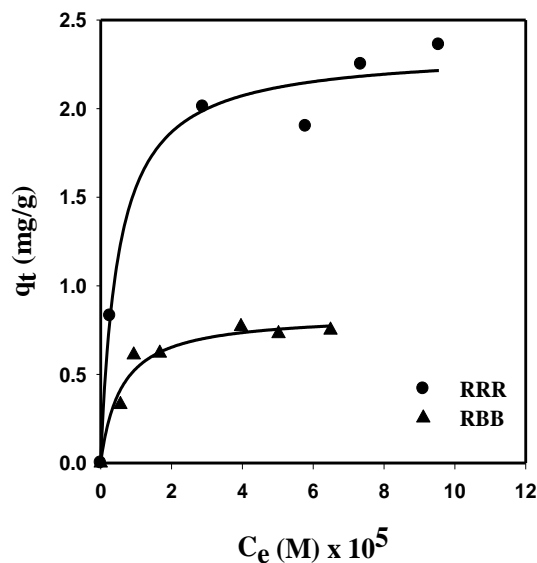

Fig. 10. Adsorption isotherm of RRR and RBB at 30° C.

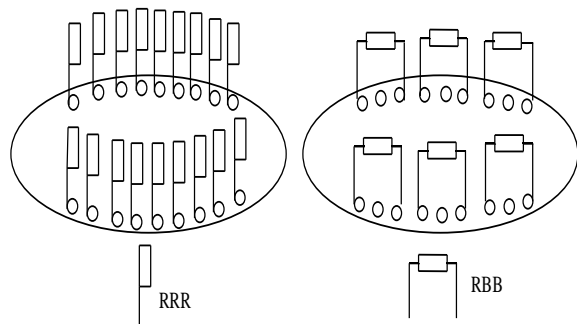**Fig. 11.** Adsorption isotherm of RRR and RBB at 40° C.

Fig. 12. Schematic representation of the adsorption of RRR and RBB on the active sites of ZnO surface.

From the molecular structures (Fig.1a and Fig.1b), we see that RRR has one tail ($C_6H_5CH_2CH_2OSO_3-$)whereas RBB has two tails ($C_6H_5CH_2CH_2OSO_3-$). It is likely that these tails of dye molecules are adsorbed on the active sites of the adsorbent during adsorption. RBB uses its two tails to attach with two active sites of ZnO surface, i.e. it adsorbs horizontally. However because of length of the main skeleton, it left one active site as blank (Fig. 12). Thus it is expected that three active sites are used to take up one RBB molecules. On the other hand, RRR uses its one tail to attach with only one active site of ZnO surface and adsorbs vertically. Every active sites on the ZnO surface can take up one RRR molecule. Hence, for a given number of active sites on ZnO surface, RRR molecules shows three times higher adsorption than the RBB molecules.

IV. Conclusion

The adsorption behavior of RRR and RBB on the ZnO powders in aqueous solution was investigated. Two different kinetic models were used to interpret the results obtained from different concentrations range between 1.0×10^{-5} mol L^{-1} and 10.0×10^{-5} mol L^{-1} for RRR and 1.0×10^{-5} mol L^{-1} to 5×10^{-5} mol L^{-1} for RBB. With the increase of

initial concentration, adsortion capacity of the dyes increses. It was found that the adsorption of both RRR and RBB follow pseudo second-order kinetic model. Adsorption of RRR and RBB on ZnO was carried out at different temperatures between 20 ^{o}C and 40 ^{o}C. Langmuir isotherm model provides better fit compared to the Freundlich isotherm. The amount of dye adsorbed on ZnO decreases with increasing temperature. This results indicate that the interactions between adsorbate and adsorbent were physical in nature. Maximum RRR uptake was found to be 3.43 mg/g at 20 ^{o}C for 10.0×10^{-5} mol L^{-1} RRR solution and maximum RBB uptake (0.77 mg/g) was observed at 30 ^{o}C for 5.0×10^{-5} mol L^{-1} RBB solution. Adsorption capacity of RRR was almost three times higher than that of RBB on ZnO powders due to structural differences. The results suggest that ZnO can be used as an effective adsorbent material for the removal of RRR and RBB from wastewater.

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