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Study Of The Adsorption Kinetics And Thermodynamic For The Removal Of Congo Red From Aqueous Solution Using Powdered Eggshell

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Abstract : The effect of temperature on Congo Red (CR) removal using powdered eggshell has been studied. From experiment it can be seen that the CR removal using powdered eggshell increased with increasing temperature. The adsorption kinetic data of CR on powdered eggshell was well described by a pseudo-second-order model, with the kinetic constants in the range of 0.093 – 0.108 g mg^{-1} min^{-1}. From both the intra-particle diffusion and Boyd kinetic models indicated that the CR adsorption process may be controlled by the intra-particle diffusion. Thermodynamic parameters data indicated that the CR sorption process was non-spontaneous and endothermic under the experimental conditions, with the Gibbs free energy (ΔG^o) in the range of 2.33-0.93 kJ mol^{-1}, enthalpy (ΔH^o) and entropy (ΔS^o) of 7.21 kJ mol^{-1} and 17.55 J mol^{-1}, respectively and the activation energy was 14.98 kJ mol^{-1}.
Keywords: adsorption, Congo Red, eggshell, kinetic, thermodynamic.

1. Introduction

The treatment of effluent containing dyestuff poses considerable problems in the wastewater industry. It is well known that textile industries, pulp mills and dyestuff manufacturing discharge highly colored wastewaters which have provoked serious environmental concerns all over the world.

The high stability and toxicity are the major problem in the treatment of wastewater containing dyes. Due to the biological and chemical stability of dyestuffs in a number of conventional water treatment methods, adsorption is considered as an attractive and favorable alternate for the removal of dyes and other chemicals from wastewater streams due to have high efficiency, simple operation, no harmful by-product, easy recovery and reuse adsorbent[1-7].

Congo Red (CR) is a benzidine based azo dye and it was selected in this study as a model anionic dye because of its complex chemical structure, high solubility in aqueous solution and its persistence, once it is discharged into natural environment[6].

In our previous work, we showed that the eggshell powdered could remove of CR from aqueous solution; in which percentage of removal depend on agitation time, pH and dosage of powdered eggshell[8].

In the present study, it was aimed to study the removal of CR compound at various temperatures. In addition, the adsorption mechanism through various adsorption kinetics models as pseudo-first-order, pseudo-second-order, intra-particle diffusion and Boyd models were investigated.

2. Materials and Methods

2.1. Materials

Chicken eggshells collected from Balubur traditional market Bandung, Indonesia were washed with distilled water, air-dried, ground into powder with particle sizes of 150 µm and stored in desiccators. The characteristic of this eggshell can be shown at our work previously [9,10]. For adsorption studies lignosulfonate obtained from Aldrich was used as adsorbate. Water used was generated from distillation system. All materials were used without further purification.

2.2. Methods

2.2.1. Sorption studies

Adsorption experiments were carried out in 100 mL flasks immersed in a thermostated rotary shaker (ORBITEK, Chennai, India) at 25 ^{o}C, 45 ^{o}C, 65 ^{o}C and 85 ^{o}C for 5, 10, 15, 30, 45, 60, 75 and 90 minutes. Chicken eggshell samples of 20 g were mixed with 50 mL CR of 20 mg/L. At the end of each adsorption period, the suspension was centrifuged. The concentrations of CR in the supernatant solutions after and before adsorption were determined spectrophotometrically, at 495.7 nm using a UV-vis spectrophotometer (Hitachi, model U-3210, Tokyo).

2.2.2. Kinetic study

The kinetic study was investigated by varying the temperature of experiments (25, 45, 65 and 85 ^{o}C) which other conditions were held constant at pH 7, particle size of 150 µm, dye concentration of 20 mg/L and adsorbent dosage of 20 g. The experimental data were calculated to determine the kinetic and mechanism by using the pseudo-first-order, pseudo-second-order, intra-particle diffusion and Boyd models.

3. Results and Discussion

3.1. Effect of temperature and agitation time on CR adsorption

The effect of temperature on CR adsorption onto eggshell at vary agitation time is shown in Figure 1. It can be seen that a rapid initial uptake of CR takes place at the beginning agitation time and thereafter, the adsorption increases gradually with increasing agitation time and reaches equilibrium after 20 minutes.

As shown in Figure 1, the amount of CR removal using eggshell powdered increases with the increasing of temperature. This arises from the increase in the mobility of dye molecule with increasing temperature [11,12] and more molecules across the external boundary layer and the internal pores of the adsorbent particles. Furthermore, increasing temperature may produce a swelling effect within the internal structure of adsorbent, penetrating the large dye molecule further [2,12-14].

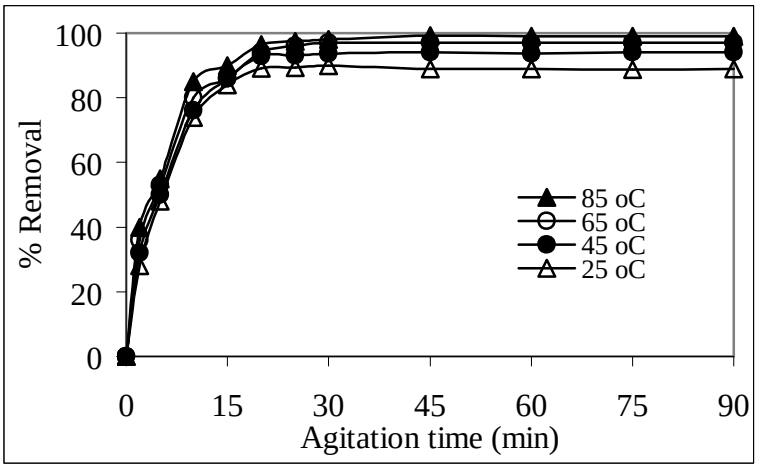

Fig. 1. Effect of temperature on CR removal using powdered eggshell.

3.2. Adsorption kinetics

In order to examine the controlling mechanism of CR adsorption process such as mass transfer and chemical reaction, the pseudo-first-order adsorption, the pseudo-second-order adsorption, the intra-particle diffusion and Boyd models were used to test the experimental data.

The pseudo-first-order rate expression of Lagergren (1898) is generally described by the following equation [1-5,7,10,12,15-20]:

$$\log(q_e - q_t) = \log q_e - k/2.303.\ t \qquad (1)$$

where q_e and q_t are the amounts of organic compounds, (mg/g) adsorbed on sorbents at equilibrium, and at time t, respectively and k is the rate constant (min^{-1}). The rate k was obtained from slope of the linear plots of log ($q_e - q_t$) against t. The plots of log ($q_e - q_t$) against t at different temperature is shown in Figure 2 and its parameter are listed in Table 1. It was observed that the first-order kinetic model did not adequately fit the experimental values. Also from Table 1, it is indicated that the values of the correlation coefficients are not high for the different dye concentration. Furthermore, a large difference of equilibrium adsorption capacity (q_e) between the experiment and calculation was observed, indicating a poor pseudo first-order fit to the experimental data.

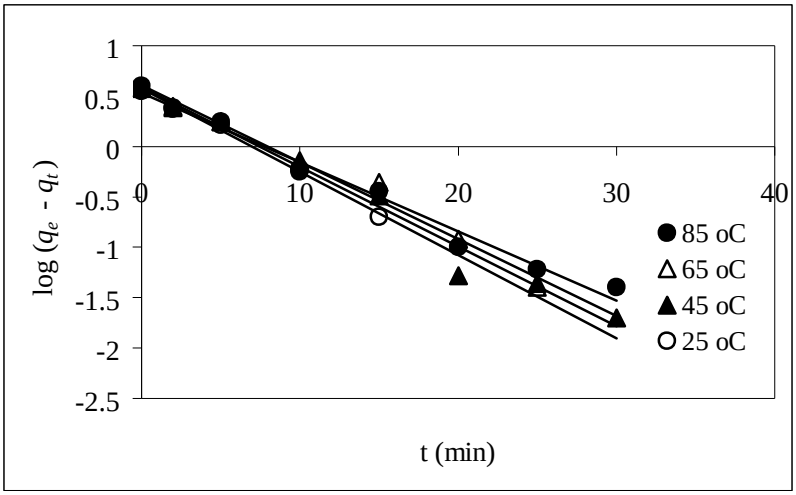

Fig. 2. Pseudo-first-order plots for adsorption of CR onto powdered eggshell.

Table 1. The pseudo-first-order and second-order kinetic parameters for CR adsorption using eggshell powder.

Temperature ^oC)	Pseudo-first-order			Pseudo-second-order			
	k_1 (min^{-1})	*qe*, cal (mg/g)	R^2	k_2 (g mg^{-1} min^{-1})	*qe*, cal (mg/g)	R^2	*qe*, exp (mg/g)
25	0.190	3.768	0.994	0.093	3.897	0.998	3.86
45	0.182	3.886	0.979	0.127	3.912	0.998	3.92
65	0.175	4.045	0.985	0.161	4.034	0.999	4.03
85	0.158	3.398	0.984	0.258	4.098	0.999	4.08

The kinetic data were further analyzed using pseudo second-order kinetics model. This model is based on the assumption the sorption follows second order chemisorption. It is assumed that the sorption capacity is proportional to the number of active sites occupied on the adsorbent, then the kinetic rate law can be written as follows [1-5,7,10,12,15-20]:

$$t/q_t = 1/k.q_e^2 + t/q_e \quad (2)$$

where q_e and q_t are the amounts of organic compounds, (mg/g) adsorbed on adsorbents at equilibrium, and at time t, respectively and k is the rate constant (g/mg.min^{-1}). If second-order kinetics is applicable, the plot of t/q_t against t of Eq. (2) should give a linear relationship from which the constants q_e and k can be determined. The plots of t/q_t against t at different temperature can be seen at Figure 3 and correlation coefficients, R^2, and the pseudo-second-order parameters i.e. k_2, q_e,exp and q_e,calc, are given in Table 1. From this figure we can see that the pseudo-second-order rate equation for sorption of CR onto eggshell agreed well with the data.

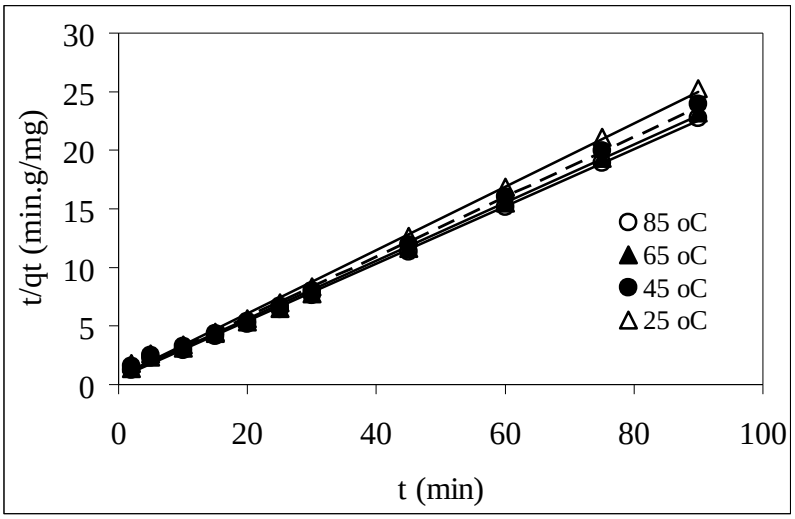

Fig. 3. Pseudo-second-order plots for adsorption of CR onto powdered eggshell.

At all studied temperatures, the straight lines with extremely high correlation coefficients (>0.99) were obtained. In addition, the calculated q_e values also agree with the experimental data in the case of pseudo-second-order kinetics (Table 1). These suggest that the adsorption data are well represented by pseudo second order kinetics and the supports the assumption that the rate-limiting step of CR onto powdered eggshell may be chemical sorption or chemisorption. From Table 1, the values of the rate constant k_2 increase with increasing temperature. The reason for this behavior can be attributed to the increase in the mobility of dye molecule with increasing temperature and consequently higher diffusion rates are obtained. Similar phenomena are observed in the adsorption of CR on activated carbon prepared from coir pith [19].

The kinetic data can also be analyzed by intra particle diffusion kinetics model, formulated as [7,12,15-18,20]:

$$q_t = k.t^{0.5} + c \quad (3)$$

where k and c are intra-particle diffusion rate constant (mg/g.min$^{0.5}$) and a constant, respectively. The k is the slope of straight-line portions of plot of q_t vs. $t^{0.5}$. These plots generally have a dual nature i.e. an initial curved portion and a final linear portion. The first linear region is related to the instantaneous adsorption stage (k_{d1}) that represents boundary layer diffusion effects. The second linear (k_{d2}) is a relatively slow adsorption region. This stage is a result of intra-particle diffusion effects [3,7,10-12,15,17,18,20], which is the rate-limiting step. Extrapolating the linear portion of the plot yields the intercept (c) is proportional to the extent of boundary layer thickness [3,7,10,12,15,16,18,20].

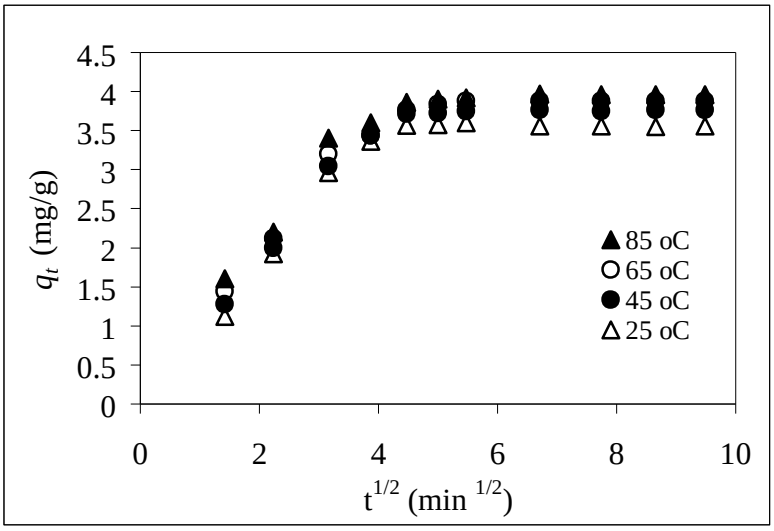

Fig. 4. Intra-particle diffusion plots for adsorption of CR onto powdered eggshell.

Figure 4 shows intra-particle diffusion plot at different temperature and values k_i, C and correlation coefficient are shown in Table 2. Since the second linier of plot of qt versus $t^{1/2}$ does not pass through the origin, the intra-particle diffusion is not the only rate controlling step during the gradual adsorption stage, and boundary layer diffusion and intra particle diffusion take place simultaneously during the gradual adsorption stage [11,20].

Table 2. Parameters of the intra-particle diffusion model for CR adsorption using eggshell powder.

Temp. (^{o}C)	k_{d1}	C_1	R_1^2	k_{d2}	C_2	R_2^2
25	0.940	-.0170	0.988	-0.009	3.638	0.604
45	0.911	0.007	0.988	0.003	3.733	0.219
65	0.864	0.253	0.971	-	3.880	-
85	0.876	0.361	0.960	0.008	3.894	0.420

From Table 2 it can be seen that the thickness of the boundary layer (C) for the adsorption of CR on powdered eggshell increased with increasing temperature. This suggests that the effect of boundary layer diffusion for the adsorption of CR on powdered eggshell probably became more important at higher temperature because of the greater random motion associated with the increased thermal energy [20].

Furthermore, the thickness of the boundary layer in the second stage (C_2) is larger than that of the first stage (C_1) (Table 2). Consequently the values of the intra-particle diffusion rates k_{d2} are smaller than the film diffusion rates k_{d1} [7,10,15]. That gives prediction that the CR adsorption process may be controlled by the intra-particle diffusion [7,10,15].

To determine the actual process involved in the dye sorption process, the kinetic data as obtained by the batch method were further analyzed using the Boyd model given by [7,10]:

$$B_t = - 0{,}4977 - \ln (1 - F) \quad (4)$$

F represents the fraction of solute adsorbed at any time, t (h), which is calculated as follows:

$$F = q_t / q_\alpha \quad (5)$$

where, q_α represents the amount sorbed (mg/g) at infinite time. The calculated B_t values were plotted against time t (h). The linearity of the plots can be used to identify control of sorption rate process, whether film diffusion or intra-particle diffusion [7,21]. The Boyd linear plots (Figure 5) with high correlation coefficients R^2 (>0.90) indicate that intra-particle diffusion mainly governs the CR adsorption process.

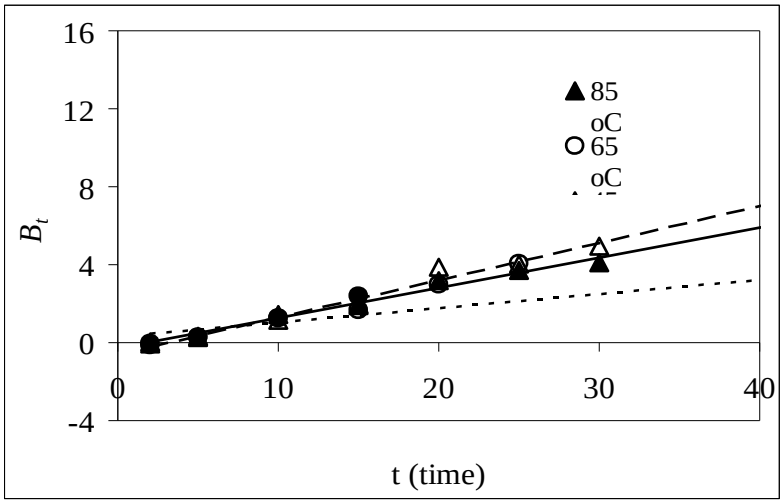

Fig. 5. Boyd plots for adsorption of CR onto powdered eggshell.

3.2. Thermodynamic parameters

The thermodynamic parameters (ΔH^o, ΔS^o and ΔG^o) for CR sorption on powdered eggshell are calculated from the temperature dependent sorption isotherms. The value enthalpy (ΔH^o) and entropy (ΔS^o) can be calculated from slope and intercept of the plot of ln K_L vs 1/T [1,3,4,7,12,19,20]:

$$\ln K_L = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{R.T} \quad (6)$$

The Gibbs free energy change (ΔG^o) is calculated as:

$$\Delta G^o = \Delta H^o - T.\ \Delta S^o \quad (7)$$

Where R (8.314 J/mol K) is the gas constant, T (K) absolute temperature and K_L (L/mg) is the Langmuir isotherm constant.

The values of parameters obtained from equation 6 and 7 are given in Table 3. A positive value of the standard enthalpy change indicates that the adsorption of CR on powdered eggshell takes place by an endothermic process. Generally, the magnitude of the ΔH^o value lies in the range of 2.1 – 20.9 kJ/mol and 80 – 200 kJ/mol for physical and chemical adsorption, respectively [1,20]. The value of ΔH^o for the present study is 7.21 kJ/mol (Table 3), indicating that CR adsorption on powdered eggshell is likely a physical process.

Table 3. Thermodynamic parameters of CR adsorption process at different temperature.

Temperature (°C)	K_L (L/mg)	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (J/mol)	E_a (kJ/mol)
25	0.444	2.33	7.21	17.55	14.98
45	0.541	1.63			
65	0.632	1.28			
85	0.717	0.93			

The positive values of Gibbs free energy (ΔG^o) indicate the non-spontaneous nature of adsorption. The value of ΔG^o become more negative with the increase of temperature, which indicates that the reaction is more favorable at high temperatures. The positive value of entropy change (ΔS^o) implies some structural changes during the sorption process, which leads to an increase in the randomness at the solid-solution system [1,4,12,19,20].

The Arrhenuis equation has been applied to measure the activation energy (E_a) of adsorption, which represents the minimum energy that reactants must have for the reaction to proceed, as shown by equation [4,12,20]:

$$\ln k = \ln A - \frac{E_a}{R.T} \quad (8)$$

where E_a is the activation energy (kJ/mol), A the Arrhenius factor, R the gas constant (8.314 J/mol K) and T is the absolute temperature (K). When ln k is plotted versus 1/T, a straight line with slope $-E_a$/R is obtained (Figure 6).

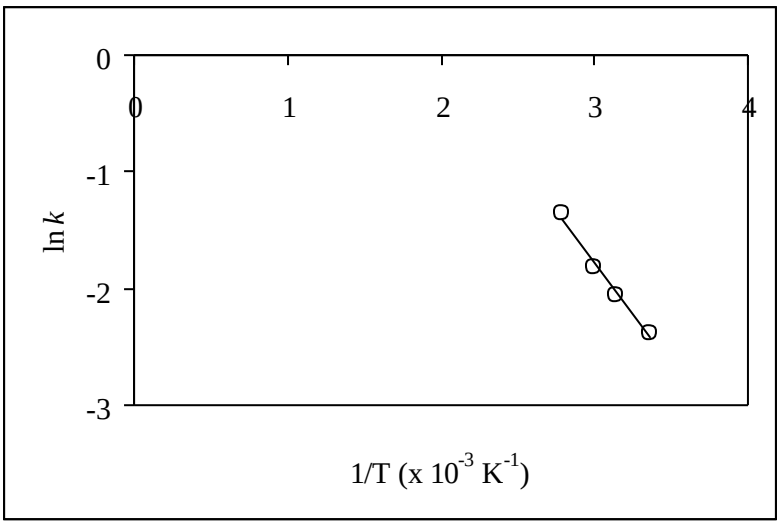

Fig. 6. Arrhenius plots for adsorption of CR onto powdered eggshell.

The magnitude of activation energy gives an idea about the type of adsorption, which is mainly physical or chemical. The physisorption processes usually have activation energies in the range of 0-40 kJ/mol, while higher activation energies (40-800 kJ/mol) suggest chemisorption [4,12]. The obtained value of activation energy (14.98 kJ/mol) in Table 3 confirms that the adsorption of CR onto eggshell is physisorption.

Conclusions

The result from this work showed that the temperature has an important role in the adsorption of CR dye onto powdered eggshell. The kinetic experimental data properly correlated with the pseudo-second-order kinetic model with a rate constant in the range of 0.093 – 0.108 g mg^{-1} min^{-1}, while both the intra-particle diffusion and Boyd kinetic models indicated that the CR adsorption process may be controlled by the intra-particle diffusion. Thermodynamic parameters data indicated that the CR sorption process was non-spontaneous and endothermic under the experimental conditions, with the Gibbs free energy (ΔG^o) in the range of 2.33-0.93 kJ mol^{-1}, enthalpy (ΔH^o) and entropy (ΔS^o) of 7.21 kJ mol^{-1} and 17.55 J mol^{-1}, respectively and the activation energy was 14.98 kJ mol^{-1}.

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