



Kinetic and Equilibrium Studies on the Adsorption of Reactive Black 5 Dye by Cross-linked Chitosan/Oil Palm Ash Composite Beads

Masitah Hasan
Bassim H. Hameed
A.Latif Ahmad

ABSTRACT

In this study, the potential of cross-linked chitosan/oil palm ash composite beads (CLCOPA) in the removal of synthetic anionic dye reactive black 5 from aqueous solutions was investigated. Experiment was conducted in a batch system at initial dye concentration of 50-500 mg/L and temperature of 30°C. Equilibrium isotherm models, Langmuir and Freundlich were employed to describe the adsorption capacity of dye solutions. The adsorption capacity was found to be 357.1 mg/g. The result of this analyses showed the adsorption of reactive black 5 can be successfully described by Langmuir and Freundlich equilibrium isotherm model. The adsorption kinetics of reactive black 5 onto CLCOPA were also studied to characterize of the surface complexation reaction. A pseudo-second-order mechanism has been developed to predict the rate constant of the adsorption, the equilibrium capacity and initial adsorption rate with the effect of initial concentration.

Keywords: Adsorption isotherm, Cross-linked chitosan/palm ash composite beads, Kinetic model, Reactive black 5 dye

Introduction

Over the last few decades, society has become increasingly sensitive towards the protection of the environment. Due to this problem, global nowadays has concern about the potential adverse effects to the chemical industry on the environment, although the response in some parts of the world has been much faster and more intense than in others. The colour manufacturing industry represents a relatively small part of the overall chemical industry.

Dyes and pigments are highly visible material. Thus even minor release into the environment may cause the appearance of colour, for example in open waters, which attracts the critical attention of public and local authorities. There is thus the requirement on industry to minimise environmental release of colour, even in cases where a small but visible release might be considered as toxicologically rather innocuous. A major source of release of colour into the environment is associated with the incomplete exhaustion of dyes onto textile fibre from an aqueous dyeing process and the need to reduce the amount of residual dye in textile effluent has thus become a major concern in recent years.

An alternative approach to addressing the problem of colour in textile dyeing effluent has involved the development of effluent treatment methods to remove colour. These method inevitably add to the cost of the overall process and some present the complication associated with the possible toxicity of degradation products.

Adsorption process has been a prominent method of treating aqueous effluent in industrial processes (Benkli et al., 2005) for a variety of separation and purification purposes. This technique is also found to be highly efficient for the removal of colour in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances (Garg et al., 2004). Therefore, adsorption using activated carbon is currently of great interest for removal of dyes and pigments.

Activated carbon has been the most popular and widely used adsorbent in wastewater treatment applications throughout the world. This is due to its high adsorption capacity, high

surface area, microporous structure, and high degree of surface reactivity (Ozcan et al., 2004). In spite of its prolific use, activated carbon remains an expensive material since the higher the quality of activated carbon, the greater it costs. Therefore, this situation makes it no longer attractive to be widely used in small-scale industries because of cost inefficiency. Due to the problems mentioned previously, research interest into the production of alternative adsorbent to replace the costly activated carbon has intensified in recent years. Today, attention has been focused on the low-cost adsorbents as alternative adsorbent materials. Fytianos et al., (2002) investigated the removal of dyes on three low-cost adsorbents, fly ash, bentonite, bleaching earth and also on activated carbon. A large number of low-cost adsorbents have been treated for dyes removal. The successful removal using low cost adsorbents has been carried out by several researchers (Mall et al., 1996 and Bailey et al., 1999). Armagan et al., (2004) have studied the adsorption of reactive azo dyes on zeolite and modified zeolite. Besides that, waste materials from seafood processing industry such as chitosan (Sakkayawong et al., 2005) was used to adsorb anionic dyes. Natural materials such as rice husk, sawdust and palm kernels also occupy a position in the production of inexpensive adsorbents (Davila-Jimenez et al., 2005).

Recently, chitosan that is used as an adsorbent has drawn attentions due to its high contents of amino and hydroxy functional groups showing high potentials of the adsorption of dyes (Uzun et al., 2004), metal ions (Wu et al., 2000) and proteins (Zeng et al., 1998). Chitosan is the deacetylated form of chitin, which is linear polymer of acetylamino-D-glucose. Other useful features of chitosan include its abundance, non-toxicity, hydro-philicity, biocompatibility, biodegradability and anti-bacterial property (Ravi Kumar, 2000). Moreover, the adsorption of reactive dyes (Reactive Red 189, Reactive Red 222, Reactive Yellow 2 and Reactive Black 5), basic dyes (methylene blue), and acidic dyes (Acid Orange 51, Acid Green 25) in natural solutions using chitosan shows large adsorption capacities (Uzun et al., 2004 and Yoshida et al., 1991). Although chitosan shows better adsorption ability in the bead form than in the flake form due to its higher specific surface area (Wu et al., 2000), the weak mechanical property (highly swollen in water) and low specific gravity of the beads make them inconvenient for practical use in column mode adsorption.

The palm oil industry is one of the most important agricultural industries in Malaysia. Oil palm ash, a waste material from oil palm industries, cause a disposal problem. However, oil palm ash has received attention for its unique combination of physical and chemical properties (high oxide contents). Zainuddin et al., (2005) reported that the palm ash contents a very high oxide (SiO_2 40.0%: Al_2O_3 6.1%: Fe_2O_3 2.5%) which give its structure the credibility as a good adsorbent. Moreover, Ahmad et al., 2006 reported that the oil palm ash showed very high adsorption capacity to remove direct dye.

Materials and Methods

Chitosan and Activated Palm Ash

The dried oil palm ash (OPA) was sieved through a stack of U.S. standard sieves, and the fine particle size of $63\mu\text{m}$ are used. Then, OPA were washed with deionized water until neutral. Fifty grams of OPA were activated by refluxing with 250ml of 1 mol L^{-1} H_2SO_4 at 80°C in a round-bottom flask for 4 hours. The slurry was air-cooled and filtered with a glass fiber. The filter cake was repeatedly washed with deionized water until the filtrate is neutral. It is then dried in an oven at 110°C before use.

The Reactive Black (RB5) dye used in this work was obtained from Sigma-Aldrich, Malaysia and used without further purification. The aqueous solution was prepared by dissolving solutes in deionized water to the required concentrations without any pH adjustment. The wavelength of maximum absorbance (λ_{max}) for RB5 was 597 nm.

Cross-linked Chitosan /Oil Palm Ash Composite Beads

Chitosan flake (1g) was dissolved in 1 mol L⁻¹ acetic acid (100ml) and mixed with activated oil palm ash (1g) and were agitated for 1 hour. Then the viscous solution is sprayed dropwise through a syringe, at a constant rate, into neutralization solution containing 15% NaOH and 95% ethanol in a volume ratio of 4:1. They are left in the solution for one day. The formed composite beads were washed with deionized water until solution become neutral and then stored in distilled water. Epichlorohydrin (ECH) purchased from Sigma-Aldrich was used as cross-linking agent in this study and used without further purification. The procedure for cross-linking was same as reported previously (Chiou and Chuang, 2006). Basically, the cross-linking bath agent contained 50 cm³ of 1N sodium hydroxide solution and chemical cross-linking reagent ECH were mixed and shaken for 6 h at 50 °C with water bath. The molar ratio of cross-linking reagent/chitosan was 0.5. The cross-linking composite beads were filtered out, washed with deionized water and stored in distilled water. Then, the beads were dried in a freeze dryer for 6 h before used as an adsorbent

Experimental Procedures

Adsorption isotherm was performed in a set of 43 Erlenmeyer flasks (250mL), where solutions of dye (100mL) with different initial concentrations (50-500 mg/L) are placed. An equal masses of 0.2g of particle size (2-3mm) composite bead (adsorbent) are added to dye solution, and the mixture are then kept in an isothermal shaker (30°C ± 0.1) for 48 hours to reach equilibrium. A similar procedure is followed for another set of Erlenmeyer flask containing the same dye concentration without adsorbent to be used as a blank. The flasks are then removed from the shaker, and the final concentrations of dyes in the solution was measured at 597nm, using UV-Visible spectrophotometer (Shimadzu UV/Vis1601 Spectrophotometer, Japan). The amount of adsorption at equilibrium time t , q_e (mg/g), is calculated by:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_t (mg/L) are the liquid-phase concentrations of dye at initial and any time t , respectively. V is the volume of the solution (L), and W is the mass of dry adsorbent used (g).

The procedures of kinetic experiments are basically identical to those of equilibrium tests. The aqueous samples are taken at present time intervals, and the concentrations of dye are similarly measured.

The amount of adsorption at time t , q_t (mg/g), is calculated by:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

where C_0 and C_t (mg/L) are the liquid-phase concentrations of dye at initial and any time t , respectively. V is the volume of the solution (L), and W is the mass of dry adsorbent used (g).

Results and discussions

Effect of Initial Dye Concentration and Contact Time

The effect of initial concentration and contact time on dyes adsorption by cross-linked chitosan/oil palm ash composite beads was studied at different initial RB 5 concentrations ranging from 50 – 500 mg/L as shown in Figure 1. This parameter was studied at temperature 30 °C and without any pH adjustment (pH = 6.2). As can be seen from Figure 1, the amount of the adsorbed dyes at low initial concentration (50-200 mg/L) achieve adsorption equilibrium in about 4 hours, reaches a constant value beyond which no more is removed from solution. While at high initial dye concentration (300-500 mg/L), the time necessary to reaches equilibrium was about 24 hours. However, the experimental data were measured at 48 hours to make sure that full equilibrium was attained. It was observed that the uptake of dyes increase with time. These curves indicate the

possible monolayer coverage of dye on both the surface of dye on and the surface of cross-linked chitosan/oil palm ash composite beads. The uptake of dyes faster because the RB5 dye structure contains two azo chromophore, which is a disazo dye. The negative charge on the sulfonic reactive group on molecular structure of RB5 should repel that of a cationic adsorbent that strongly adsorbed by electrostatic interaction. Cicek *et al.*, (2007) reported that equilibrium time required for the adsorption of reactive blue 19, reactive red 195 and reactive yellow 145 dye by wheat bran was almost 5 hours while Osama *et al.*, (2007) found the time taken to reach equilibrium for adsorption of reactive black 5 on sunflower seed shells was about 3 ½ hours. The adsorption process is considered high because most of adsorbate species adsorbed within a short contact time (4 hours). This indicates that initial dye concentrations and contact time played an important role on the adsorption of RB5 dye on the cross-linked chitosan/oil palm ash composite beads.

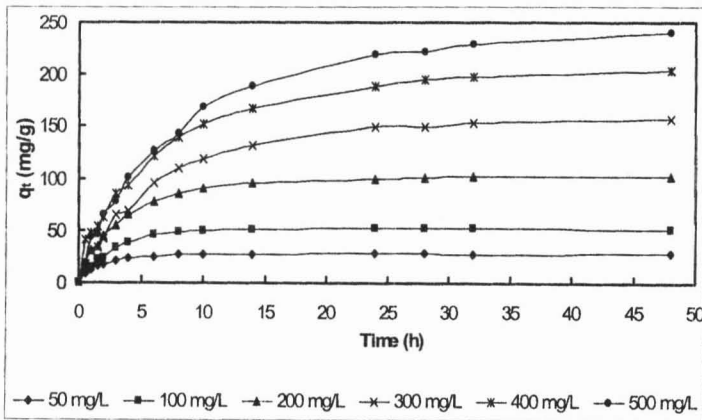


Figure 1: Effect of Initial Concentration and Contact Time on the Uptake of RB 5 on Cross-linked Chitosan/Oil palm Ash Composite Adsorbent. (W=0.2g, pH= 6.2, Temperature= 30°C)

Adsorption Isotherms

The adsorption isotherm are the most important information to indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. Isotherm equations such as the Langmuir and Freundlich were used to describe the equilibrium characteristics of adsorption and to optimize the design of an adsorption system for the adsorption of adsorbates. The equilibrium data for adsorption of RB5 dye on cross-linked chitosan/oil palm ash composite beads were studied at temperature 30°C. Figure 2 shows the equilibrium adsorption of RB5 at pH 6.2, 30 °C, on the cross-linked chitosan/palm ash composite beads.

Langmuir Isotherm

Langmuir's isotherm model suggests that uptake occurs on homogeneous surface by monolayer sorption without sorption interaction between sorbed molecules. The model assumes uniform energies of adsorption onto surface and no transmigration of adsorbate in the plane of the surface.

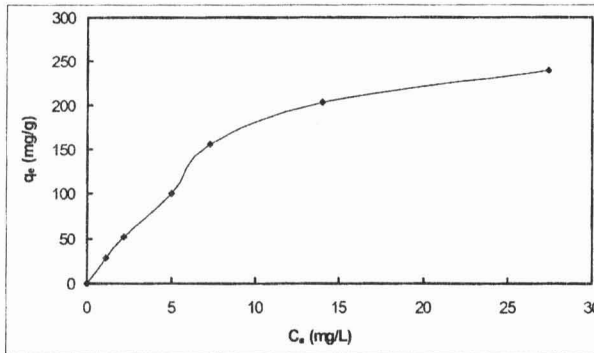


Figure 2: Equilibrium Adsorption Isotherm for the Adsorption of RB5 Dye Cross-linked Chitosan/Palm Ash Composite Bead at Different Initial Dye Concentration.

The well-known expression of the Langmuir model is given by Eq (1) (Langmuir, 1918):

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \tag{1}$$

Equation (1) can be written in a variety of linear forms in order to determine the model parameters. The following three linear form of the Langmuir isotherm model are equivalent, but one may be preferred to the others for a particular situation, depending on the range and spread of data to be described. The linear form of Langmuir isotherm equation is represented by the following equations:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{2}$$

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{b Q_0 C_e} \tag{3}$$

$$q_e = Q_0 - \frac{q_e}{b C_e} \tag{4}$$

where q_e is amount adsorbed at equilibrium time (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L). The constant Q_0 signifies the maximum adsorption capacity (monolayer capacity)(mg/g) and b is related with the energy of the adsorption (L/mg). The constants value of Langmuir model, Q_0 and b , are calculated from slope and intercept of the plot of experimental data C_e/q_e versus C_e or $1/q_e$ versus $1/C_e$ or q_e versus q_e/C_e . Figure 3 show the linear plot of C_e/q_e versus C_e . Table 1 indicates that the computed maximum adsorption capacity Q (357.1 mg/g) of RB5 on the cross-linked chitosan/palm ash composite beads. Based on the correlation coefficient (R^2) shown in Table 1, the adsorption isotherm with cross-linked chitosan/oil palm ash composite beads can be well described by Langmuir and Freundlich isotherm model.

Furthermore, the effect of the isotherm shape was considered with a view to predict whether an adsorption system were favourable or unfavourable. Therefore, the essential characteristics of the Langmuir isotherm which is used to determine whether adsorption is favourable in terms of R_L , a dimensionless constant referred to as the separation factor, which is defined as

$$R_L = \frac{1}{1 + b C_0}$$

The value of R_L indicated the shape of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$). Table 1 show the calculated separation factor, R_L at different initial dye concentrations (50 – 500 mg/L) for RB5 dye on cross-linked chitosan/oil palm ash composite beads at temperature 30°C. The fact that the R_L value for the adsorption of RB 5 dye onto cross-linked chitosan/ oil palm ash composite bead was 0.023 show that the adsorption process was favourable in all range initial concentration dyes studies.

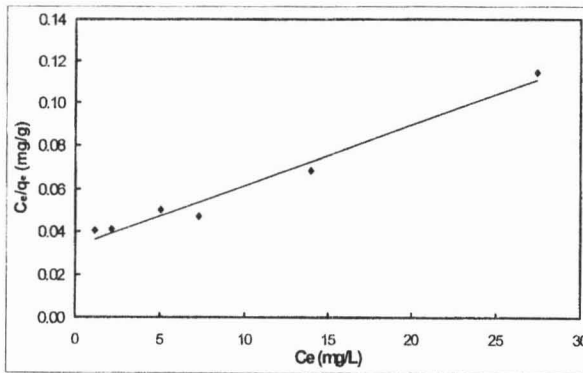


Figure 3: Langmuir Isotherm of RB 5 at Different Initial Dye Concentrations on Cross-linked Chitosan/Palm Ash Composite Beads.

Freundlich Isotherm

The Freundlich equation has been widely used and is applicable for isothermal adsorption. This is a special case for heterogeneous surface energies in which term, b , in the Langmuir equation varies as a function of surface coverage, q_e , strictly due to variations in heat of adsorption. The Freundlich equation has the general form (Freundlich, 1926):

$$q_e = K_F C_e^{1/n} \quad (2.6)$$

The Freundlich equation basically empirical but is often useful as a means for data description. Data are usually fitted to the linear form of the equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2.7)$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbent (mg/L), and K_F and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. When $\ln q_e$ is plotted against $\ln C_e$, (Figure 4) a straight line with slope $1/n$ and intercept $\ln K_F$ is obtained. The intercept of line, $\ln K_F$, is roughly an indicator of the adsorption capacity and the slope, $1/n$, is an indicator of adsorption intensity (Weber, 1967). The slope $1/n$, ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. The values of n lie at 1.14 which represents good sorption potential of the sorbent for which $1 < n < 10$. The high magnitude of K_F values of Freundlich model showed easy uptake of dyes from aqueous medium on the cross-linked chitosan/oil palm ash composite beads.

The applicability of both Langmuir and Freundlich isotherms to the RB5 dye implied that the cross-linked chitosan/oil palm ash composite beads might exhibit monolayer adsorption and heterogeneous surface conditions. Similar results were observed for the adsorption of Reactive blue MR onto modified silk cotton hull waste (Thangamani et al., 2007).

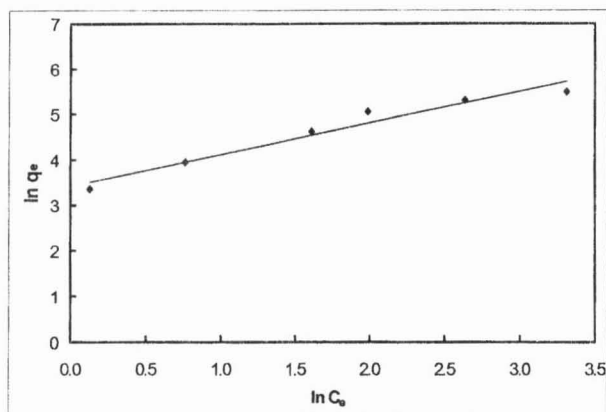


Figure 4: Freundlich Isotherm of RB 5 at Different Initial Dye Concentrations on Cross-linked Chitosan/Palm Ash Composite Bead.

Table 1: Langmuir and Freundlich Isotherm Constants for Adsorption of RB 5 on Cross-linked Chitosan/Palm Ash Composite Beads.

Langmuir isotherm				Freundlich isotherm		
Q_0 (mg/g)	b (1/mg)	R^2	R_L	n	K_F (mg/g)(L/mg) ^{1/n}	R^2
357.1	0.08	0.97	0.023	1.44	30.57	0.96

Adsorption Kinetics

Pseudo-First-Order Kinetic Model

The first-order rate expression of Lagergren and Svenska, (1989) based on solid capacity is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2.14}$$

where q_e and q_t are the amount adsorbed at equilibrium and at time t , respectively (mg/g), and k_1 is the rate constant of first-order adsorption (1/min). After integration and applying boundary conditions, $t = 0$ to $t = t$ and $q = 0$ to $q = q$, integrated form of Eq. (2.14) becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{2.15}$$

The slopes and intercepts of plots of $\log(q_e - q_t)$ vs. t (Figure 5) were used to determine the first order rate constant, k_1 . In many cases the first order equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption processes (McKay and Ho, 1999a)

Pseudo-Second-Order Kinetic Model

Based on adsorption equilibrium capacity, the second-order kinetic model (Ho and McKay 1998, 2000) is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2.16}$$

where k_2 is the rate constant of pseudo second-order adsorption (g/mg min), q_e and q_t are the amounts of adsorbed at equilibrium and at time t , respectively. Integrating equation (2.16) and

applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, gives

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (2.17)$$

Rearranged Eq. (2.17) to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2.18)$$

and, the initial sorption rate, h (mg/g min) at $t \rightarrow 0$ is defined as

$$h = k_2 q_e^2 \quad (2.19)$$

Herein, the initial adsorption rate is $h = k_2 q_e^2$. From equation (2.19), the values of k_2 and q_e can be obtained from the intercept and slope of the plot of (t/q_t) vs. t and there is no need to know any parameter beforehand. It is more likely to predict the behavior over the whole range of adsorption and is in agreement with chemical sorption being the rate-controlling step (McKay and Ho, 1999).

Based on table 2, the magnitude of correlation coefficients, $R^2 > 0.95$ for pseudo-first order compared to pseudo-second order. Therefore, it can be concluded that adsorption of RB5 dye systems obey the pseudo-first order kinetic model. Moreover, the calculated q_e values agree very well with experimental data in the case of pseudo-first order kinetics. These results suggest that the dye sorption is first-order model, based on the assumption that the rate limiting step may be chemisorption. Similar results were reported in the adsorption of dye RR222 on composite beads using chitosan and activated clay (Chang and Juang., 2004). Besides that, similar phenomenon are also observed in adsorption of dye RY2 and RB5 on chitosan (Chiou and Li, 2002).

Table 2: Comparison of Pseudo First-order and Pseudo Second-order Adsorption Rate Constants, Calculated q_e and Experimental q_t Values for Different Initial Dye Concentrations.

Initial dye concentration (mg/L)	Pseudo-first order kinetic model				Pseudo-second order kinetic model		
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1 1/hr	R^2	$q_{e,cal}$ (mg/g)	k_2 (g/mg.hr)	R^2
50	28.42	22.89	0.376	0.98	29.94	0.034	0.98
100	52.37	54.20	0.369	1.00	61.35	0.007	0.89
200	100.22	91.66	0.235	1.00	101.01	0.005	0.91
300	156.10	150.56	0.148	0.99	142.86	0.002	0.77
400	202.99	182.47	0.133	0.98	156.25	0.003	0.88
500	239.79	226.73	0.112	0.98	188.68	0.002	0.79

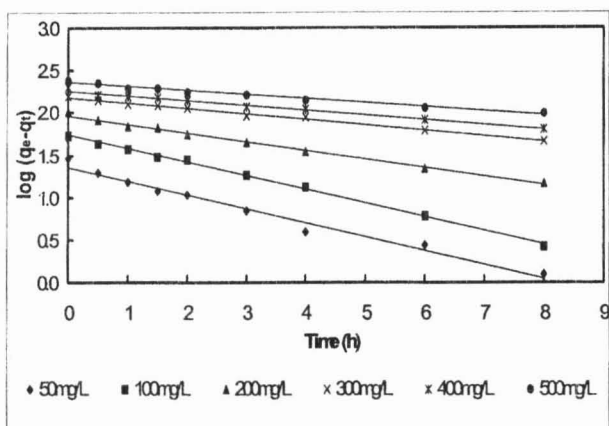


Figure 5: Pseudo-first Order Kinetic Model for Adsorption of RB 5 at Different Initial Dye Concentrations

Conclusions

The cross-linked chitosan/oil palm ash composite beads have a considerable potential as low-cost and highly efficient adsorbent for the removal of reactive dyes from wastewaters using batch adsorption systems. RB5 dye fitted well with the Langmuir and Freundlich isotherm model. The applicability of both Langmuir and Freundlich isotherm to the dye implied that the adsorbent might exhibit monolayer adsorption and heterogeneous surface conditions. Adsorption kinetics followed the pseudo second-order mechanism, which was the model that provided the best correlation with the experimental data.

Acknowledgement

The authors acknowledge the research grant provided by University Sains Malaysia, under short term grant and Universiti Malaysia Perlis (FRGS grant) that has resulted in this article.

References

- Armagan, B., Turan, M., Celik, M.S., (2004). Equilibrium studies on the adsorption of reactive azo dyes into zeolite. *Desalination*, 170, p. 33–39.
- Bailey, S.E., Olin, T.J., Bricka, R.M., Adrian, D.D., (1999). A review of potentially low cost sorbents for heavy metals. *Water Resources*, 33, p. 2469–2479.
- Benkli, Y.E., Can, M.F., Turan, M., Celik, M.S., (2005). Modification of organo-zeolite surface for the removal of reactive azo dyes in fixed-bed reactors. *Water Resources*, 39, p. 487–493.
- Chiou, M. S., Li, H. Y. (2003). Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads. *Chemosphere*, 50, p. 1095–1105.
- Cicek, F., Ozer, D., Ozer, A., Ozer, A., (2007). Low cost removal of reactive dyes using wheat bran. *Journal of Hazardous Materials*, 146, p. 408–416.
- Dávila-Jiménez, M.M., Elizalde-González M.P., Peláez-CidA.A., (2005). Adsorption interaction

- between natural adsorbents and textile dyes in aqueous solution. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 254, p. 107-114.
- Freundlich, H., (1906). Adsorption in solution. *Phys. Chem. Soc*, 40. p. 1361-1368
- Fytianos, K., Voudrias, E., Kokkalis, E., (2000). Sorption-desorption behavior of 2,4-dichlorophenol by marine sediments. *Chemosphere*, 40. p. 3-6.
- Garg, V.K., Amita, M., Kumar, R., Gupta, R., (2004a). Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste. *Dyes Pigments*, 63, p. 243-250.
- Ho, Y.S., McKay, G., (2000). The kinetics of sorption of divalent metal ions onto sphagnum Moss peat. *Water Resources*, 34, p. 735-742.
- Ho, Y.S., McKay, G., (1998). A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents. *Process Saf. Environ. Prot.*, 74 (B4), p. 332-340.
- Lagergren, S., (1898). Zur theorie der sogenannten adsorption geloster stoffe. *Kungliga Svenska Vetenskapsakademiens. Handlingar*, Band, 24 (4), p. 1-39.
- Langmuir, I., (1918). The adsorption of gases on plane surface of glass, mica and platinum. *Journal American Chemical Society*, 40 (9), p. 1361-1403.
- Mall, I.D., Upadhyay, S.N., Sharma, Y.C., (1996). A review on economical treatment of wastewaters, effluents by adsorption. *International Journal Environmental Studies*, 51, p. 77-124.
- McKay G, Ho Y.S., (1999). Pseudo-second-order model for sorption processes. *Process Biochemistry*, 34, Pp. 451-65.
- Osma, J.F., Saravia, V., Toca-Herrera, J. S., Couto, S.R., (2007). Sunflower seed shells: A novel and effective low-cost adsorbent for the removal of the diazo dye Reactive Black 5 from aqueous solutions. *Journal of Hazardous Material*, 147, p 900-905.
- Ozcan, A.S., Erdem, B., Ozcan, A., (2004). Adsorption of Acid Blue 193 from aqueous solutions onto Na-bentonite and DTMA-bentonite. *Journal of Colloid and Interface Science*, 280, p. 44-54.
- Ravi Kumar, M.V.V., (2000). A review of chitin and chitosan applications. *Reaction Function Polymers*, 46, p. 1-27
- Sakkayawong, N., Thiravetyan, P., Nakbanpote, W., (2005). Adsorption mechanism of synthetic reactive dye wastewater by chitosan. *Journal of Colloid and Interface Science*, 286, p. 36-42.
- Thangamani, K.S., Sathishkumar, M., Sameena, Y., Vennilamani, N., Kadirvelu, K., Pattabhi S., Yun S.E., (2007). Utilization of modified silk cotton hull waste as an adsorbent for the removal of textile dye (reactive blue MR) from aqueous solution *Bioresources Technology*, 98, p. 1265-1269.
- Uzun, I., Guzel, F., (2004). Kinetics and thermodynamics of the adsorption of the adsorption of some dyestuffs and p-nitrophenol by chitosan and MCM-chitosan from aqueous solution. *Journal of Colloid and Interface Science*, 274, p. 398-412.
- Weber, Jr., (1967). *Physicochemical Processes for Water Quality Control*. John Wiley & Sons

Inc., New York. p. 1972

Wu, F.C., Tseng, R.L., Juang, R.S., (2000). Comparative adsorption of metal and dye on flake-and bead- types of chitosans prepared from fishery waste. *Journal of Hazardous Materials*, 73, p. 63-75.

Yoshida, H., Fukuda, S., Okamoto, A., Kataoka, T., (1991). Recovery of direct dye and acid dye by adsorption on chitosan fiber-equilibria. *Water Science Technology*, 23, p. 1667-1676.

Zainuddin, N.F., Lee, K.T., Kamaruddin, A.H., Bhatia, S., Mohamed, A.R., (2005). Study of adsorbent prepared from oil palm ash (OPA) for the flue gas desulfurization, *Separation and Purification Technology*, 45, p. 50-60.

Zeng, X., Ruckenstein, E., (1998). Cross-linked macroporous chitosan anion-exchange membranes for protein separations. *Journal Membrane Science*, 148, p. 195-205.

MASITAH HASAN, School of Environmental Engineering, Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 3, 02600 Jejawi, Perlis.

BASSIM H. HAMEED & A. LATIF AHMAD, School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang.