Journal of Applied Sciences

ISSN 1812-5654

Journal of Applied Sciences 11 (13): 2292-2298, 2011
ISSN 1812-5654 / DOI: 10.3923/jas.2011.2292.2298

Low Cost Removal of Reactive Orange 16 Dye using Cross-linked Chitosan/oil Palm Ash Composite Beads

[1]H. Masitah, [1]H.H. Bassim, [2]A.A. Latif, [3]M. Zulfakar, [1]I. Naimah and [1]M.Z.M. Salwa
[1]School of Environmental Engineering, Universiti Malaysia Perlis,
Kompleks Pusat Pengajian Jejawi, 302600 Jejawi, Perlis, Malaysia
[2]School of Chemical Engineering, Engineering Campus, University Science Malaysia,
14300 Nibong Tebal, Penang, Malaysia
[3]School of Bioprocess Engineering, Universiti Malaysia Perlis,
Kompleks Pusat Pengajian Jejawi, 302600 Jejawi, Perlis, Malaysia

Abstract: In this study, the adsorption of Reactive Orange 16 (RO16) onto cross-linked chitosan/oil palm ash composite beads (CC/OPA) was studied in batch mode operation with respect to temperature and initial dye concentration. The adsorption of RO16 onto cross-linked chitosan/oil palm ash composite beads increased with increasing temperature (30-50°C) and initial dye concentration (50-500 mg L^{-1}). The Langmuir and Freundlich isotherms models were used to describe the isotherm data; of which the Freundlich model described the isotherm data with high correlation coefficients. The monolayer coverage capacities of cross-linked chitosan/oil palm ash composite beads of RO16 dye was obtained 303.1, 434.8 and 588.2 mg g^{-1} at temperature 30, 40 and 50°C, respectively. It was observed that the reactive orange 16 dye adsorption capacity of cross-linked chitosan/oil palm ash composite beads increased in the order 30>40>50°C. The pseudo-first-order and pseudo-second-order were applied to the experimental data and it was found that results of correlation coefficients, the adsorption kinetics obey a pseudo-first-order.

Key words: Reactive orange 16, cross-linked chitosan/oil palm ash composite bead, adsorption isotherm

INTRODUCTION

The major problems concerning environmental pollutants are removing color from water and wastewater industrial activities. Dyes are released into wastewaters from various industrial units, mainly from the dye manufacturing and textiles and other fabric finishing (Janos *et al*., 2003). Most dyes are non-biodegradible in nature which are stable to light and oxidation. Therefore, the degradation of dyes in wastewater either traditional chemical or biological process has not been very effective (Metivier-Pignon *et al*., 2003; Orthman *et al*., 2003; Waranusantigul *et al*., 2003).

Reactive dyes are most problematic compounds among others dyes in textile wastewater. Reactive dyes are highly water-soluble and estimated that 10 to 20% of reactive dyes remains in the wastewater during the production process of these dyes (Koprivanac *et al*., 2000) and nearly 50% of reactive dyes may lost to the effluent during dyeing processes of cellulose fibers (Netpradit *et al*., 2004). Reactive dye wastewater has limited biodegradability in an aerobic environment and many azo dyes under anaerobic conditions decompose into potentially carcinogenic aromatic amines (Netpradit *et al*., 2003; Panswad and Luangdilok, 2000).

Adsorption process has been found becoming a prominent method of treating aqueous effluent in industrial processes for a variety of separation and purification purpose (Benkli *et al*., 2005). This technique 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. In spite of its prolific use, activated carbon remains an expensive material since higher the quality of activated carbon, the greater in cost. This has led to the search for cheaper substitutes. Today, attention has been focused on the low-cost adsorbents as alternative adsorbent materials such as oil palm ash (Ahmad *et al*., 2006). This ash is produced after combustion of oil palm fiber and shell as boiler fuel to produce steam for palm oil mill consumption. This solid

---

Corresponding Author: H. Masitah, School of Environmental Engineering, Universiti Malaysia Perlis,
Kompleks Pusat Pengajian Jejawi, 302600 Jejawi, Perlis, Malaysia

waste is highly abundant in Malaysia which is one of the largest palm-oil exporters in the world. Malaysia thus generates huge loads of palm ash each year. The oil palm ash showed very high adsorption capacity to remove direct dye (Ahmad *et al*., 2006).

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 (Ilhan and Fuat, 2004), metal ions (Feng *et al*., 2000) and proteins (Zeng and Ruckenstein, 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 (Kumar, 2000). Moreover, the adsorption of reactive dyes, basic dyes and acidic dyes in natural solutions using chitosan shows large adsorption capacities (Ilhan and Fuat, 2004; Yoshida *et al*., 1991).

Many textile wastewaters are highly acid. In acid aqueous solutions, the amino groups of chitosan are much easier to be cationized and they adsorb the dye anions strongly by electrostatic attraction (Kumar, 2000). However, chitosan formed gels below pH 5.5 and could not be evaluated. This problem limits the use of chitosan as adsorbent for dye removal, as this compound is highly soluble in such environments. This has led to prepare cross-linked chitosan adsorbent which is necessary to stabilize the prepared adsorbent in acid medium as well as to grant the material the mechanical strength necessary for the adsorption studies in dynamic systems. Yoshida *et al.* (1993) used Denacol EX841 as a cross-linking reagent and obtained a high adsorption capacity (1200-1700 g kg^{-1}) of Orange II (AO7) on the cross-linked chitosan fibers in acid solutions of pH 3.0 and 4.0. Chiou and Li (2003) prepared cross-linked chitosan by Epichlorohydrin (ECH) and exhibited a high adsorption capacity (1802-1840 g kg^{-1}) of reactive dye (RR189) on the cross-linked chitosan beads in acid aqueous solutions at 30°C, pH 3.0.

The aim of this study was to investigate the adsorption of reactive orange (RO16) dye onto cross-linked chitosan/oil palm ash composite beads which is a low-cost adsorbent for the removal of dye.

MATERIALS AND METHODS

Adsorbate reactive orange 16: The Reactive Orange (RO16) dye used in this study was obtained from Sigma-Aldrich, Malaysia and used without further purification. The aqueous solution was prepared by dissolving solute in deionized water to the required concentrations without any pH adjustment. The wavelength of maximum absorbance (λ_{max}) for RO16 was 494 nm.

Chitosan and oil palm ash: The chitosan flake derived from deacetylated lobster shell wastes are supplied by Hunza Pharmaceutical Sdn Bhd., Nibong Tebal, Malaysia. The chitosan flake were washed three times with deionized water and dried at 50°C in an oven before use. The Oil Palm Ash (OPA) was provided by United Oil Palm Mill, Penang, Malaysia. It was sieved through a stack of U.S. standard sieves and the fine particle size of 63 μm was used. Then, OPA was washed with deionized water until neutral and oven dried at 110°C overnight. Fifty grams of OPA are activated by refluxing with 250 mL of 1 mol L^{-1} H_2SO_4 at 80°C in a round-bottom flask for 4 h. 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 was then dried in an oven at 110°C before use.

Preparation of chitosan/oil palm ash composite beads: Chitosan flake (1 g) is dissolved in 1 mol L^{-1} acetic acid (100 mL) and mixed with activated oil palm ash (1 g) and are agitated for 1 h. 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 were left in the solution for one day (Chang and Juang, 2004). The formed composite beads were ashed with deionized water until solution become neutral and then stored in distilled water.

Preparation of cross-linked chitosan/oil palm ash composite beads: Epichlorohydrin (ECH) purchased from Sigma-Aldrich was used as cross-linking agent in this study. The procedure for cross-linking was same as reported previously (Chiou and Li, 2003). Basically, wet non-cross-linked chitosan/oil palm ash composite beads (0.1 g dry basis of chitosan) and 50 cm^3 of 1N sodium hydroxide solution were poured together in a 500 cm^3 flask. ECH was added into the above solution 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 chitosan/oil palm ash composite beads (CC/OPA) were filtered out, washed with deionized water and stored in distilled water. Then, the beads (2-3 mm) were dried in a freeze dryer for 6 h before used as an adsorbent.

Batch equilibrium studies: Adsorption isotherms were performed in a set of 43 Erlenmeyer flasks (250 mL) where solutions of dye (100 mL) with different initial concentrations (50-500 mg L^{-1}) were place in these flasks. The original pH of the solutions was used which was around 6. Equal masses of 0.2 g of particle size (2-3 mm) CC/OPA (adsorbent) were added to dye solutions and the mixtures were then kept in an isothermal shaker (30°C±0.1) for 48 h to reach equilibrium. A similar procedure was followed for another set of Erlenmeyer flask containing the same dye concentration without adsorbent to be used as a blank. The flasks were then removed from the shaker and the final concentration of dye in the solution was measured at 494 nm, using UV-Visible spectrophotometer (Shimadzu UV/Vis1601 Spectrophotometer, Japan). The amount of adsorption at equilibrium time t, q_e (mg g^{-1}), is calculated by:

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

where, C_0 and C_t (mg L^{-1}) 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).

Experimental conditions consisted of 0.2 g adsorbent, 100 mL of 200 mg L^{-1} RO16 solution, temperature equal to 30°C and contact time 48 h. The effect of temperature (at 30, 40 and 50°C) on the adsorption of RO16 by CC/OPA was studied at pH 6.0, 0.2 g adsorbent and initial RO16 concentration of 50-500 mg L^{-1} for 48 h.

Batch kinetic studies: The procedures of kinetic experiments are basically identical to those of equilibrium tests. The aqueous samples were taken at present time intervals and the concentrations of dye were similarly measured. The amount of adsorption at time t, q_t (mg g^{-1}), is calculated by:

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

where, C_0 and C_t (mg L^{-1}) 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 DISCUSSION

Effect of initial dye concentration: The adsorption of dye by CC/OPA was studied at different initial RO16 concentrations ranging from 50 to 500 mg L^{-1}. Figure 1 shows the result for effect of initial dye concentration on adsorption of RO16 onto CC/OPA at pH 6. As can be seen from Fig. 1, the amount of the adsorbed dye at low initial concentration (50-200 mg L^{-1}) achieve adsorption equilibrium in about 4 h, at some point in time, reaches a constant value beyond which no more is removed from solution. While at high initial dye concentration (300-500 mg L^{-1}), the time necessary to reaches equilibrium was about 24 h. However, the experimental data were measured at 48 h to make sure that full equilibrium was attained. The adsorption capacity at equilibrium increases from 39.9 to 401.7 mg g^{-1}, with increase in the initial dye concentration from 50 to 500 mg L^{-1}. Similar trend was observed for the amount of adsorbed dyes of RO16 at 40 and 50°C, respectively. An increase in initial dye concentration leads to increase in the adsorption capacity of dye on CC/OPA. This indicates that initial dye concentrations played an important role in the adsorption of RO16 on the CC/OPA. A similar phenomenon was observed for the adsorption of reactive blue 15 dye from an aqueous solution on cross-linked chitosan beads (Chiou and Chuang, 2006). 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 h while Osama *et al.* (2007) found the time taken to reach equilibrium for adsorption of reactive black 5 on sunflower seed shells was about 3½ h. The adsorption process is considered high because most of adsorbate species adsorbed within a short contact time (4 h).

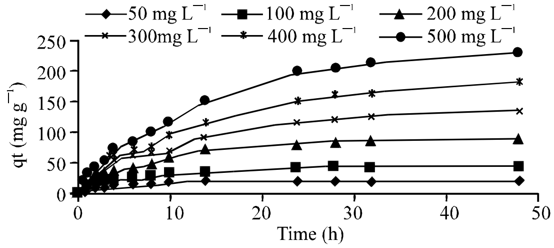

Fig. 1: Effect of initial concentration on the adsorption of RO16 on CC/OPA at pH 6, 30°C.

Effect of temperature: A study of the temperature dependence of adsorption process gives valuable information about the enthalpy during adsorption. The effect of temperature on the adsorption isotherm was studied by carrying out a series of isotherms at 30, 40 and 50°C (Figure not shown). At temperature 50°C, more dye strongly adsorbed by the CC/OPA and thus induced a higher Q_0 value (Table 1). This process was endothermic, where increasing the temperature increases the value of Q_0. Results indicate that the adsorption capacity of CC/OPA for adsorption RO16 increase with increasing temperature which is typical for the adsorption of most organics from their solutions. The effect of temperature is fairly common and increasing the temperature increases

Table 1: Langmuir and Freundlich isotherm model constants and correlation coefficients for adsorption of RO16 onto CC/OPA

Isotherms	Temperature (°C)	b ($L\ mg^{-1}$)	Q_0 ($mg\ g^{-1}$)	R_L	R^2
Langmuir	30	0.05	303.0	0.058	0.94
	40	0.04	434.8	0.086	0.87
	50	0.02	588.2	0.123	0.73
Isotherms	Temperature (°C)	K_F ($mg\ g^{-1}$) $/(L\ mg^{-1})^{1/n}$		n	R^2
Freundlich	30	21.67		1.60	0.99
	40	17.71		1.28	0.95
	50	15.12		1.17	0.96

the mobility of the dye molecule. Similar result was also obtained for the adsorption of reactive blue 19, reactive red 195 and reactive yellow 135 dyes onto wheat bran for temperature studied range between 20 to 50°C (Cicek *et al*., 2007).

Adsorption isotherm: The adsorption isotherm are the most important information for indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves. Various isotherm equations like those Langmuir and Freundlich were used to describe the equilibrium characteristics of adsorption. The linear form of Langmuir isotherm is expressed as:

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

where, q_e is amount of dye adsorbed per unit weight of adsorbent ($mg\ g^{-1}$), C_e is the equilibrium concentration of dye in solution ($mg\ L^{-1}$). The constant Q_0 signifies the adsorption capacity ($mg\ g^{-1}$) and b is related with the energy of the adsoprtion ($L\ mg^{-1}$). A plot of C_e/q_e versus C_e (Figure not shown). yields a straight line with slope $1/Q_0$ and intercept $1/Q_0b$. Table 1 lists that the computed maximum adsorption capacity Q_0 of RO16 onto the CC/OPA at different temperatures.

The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L given by (Hall *et al*., 1996):

$$R_L=\frac{1}{1+bC_o} \tag{4}$$

where, b is the Langmuir constant and C_0 the highest initial dye concentration ($mg\ L^{-1}$). According to the value of R_L, the isotherm shape may be interpreted as follows $R_L>1.0$ (Unfavourable), R_L = 1.0 (Linear), $0<R_L<$\1.0 (Favourable) and R_L = 0 (Irreversible). Value of R_L calculated at 30, 40 and 50°C were in range between 0 and 1 which indicate that the adsorption is favourable at operation conditions studied.

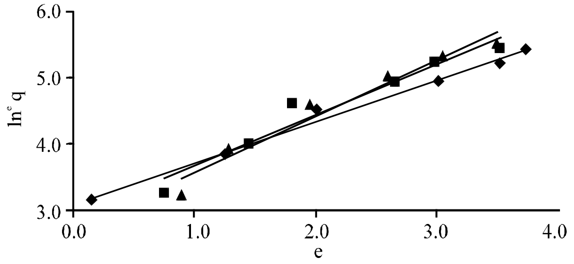

Fig. 2: Freundlich adsorption isotherm of RO16 cross-linked chitosan/oil palm ash composite beads at different temperatures

The Freundlich isotherm (Freundlich, 1906) is an empirical equation based on a heterogeneous surface. A linear form of the Freundlich expression will yield the constants K_F and n Hence:

$$\ln q_e=\ln K_F+\frac{1}{n}\ln C_e \tag{5}$$

Therefore, a plot of ln q_e versus ln C_e (Figure not shown) enables the constant K_F and exponent n to be determined. K_F can be defined as adsorption of distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for an equilibrium concentration. 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. These values together with the correlation coefficient are presented in Table 1. Based on the correlation coefficient (R^2) shown in Table 1, the adsorption isotherm with CC/OPA can be described by Freundlich equation. Also, the Freundlich equation yields a better fit of the experimental data than Langmuir equation (Fig. 2). In principle, the Freundlich equation is an empirical approach for adsorbent with very uneven adsorbing surface and is applicable to the adsorption of single solutes within a fixed range of concentration.

Adsorption kinetics: In order to investigate the mechanism of adsorption, the pseudo-first-order and pseudo-second-order equations were used to test the experimental data of initial concentration. The Lagergren (1898) rate equation which is the first rate equation developed for sorption in liquid/solid systems, is based on solid capacity. The pseudo-first-order equation is represented as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{6}$$

where, q_e and q_t are the amounts of dye adsorbed on adsorbent at equilibrium and at time t, respectively (mg g^{-1}). The slope and intercept of plot of log(q_e-q_t) versus t were used to determine the pseudo-first-order rate constant k_1(1/h).

The pseudo-second-order kinetic model (Ho, 1995; Ho and McKay, 1999a) expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \tag{7}$$

where, k_2 (g/mg h) is the rate constant of pseudo-second-order adsorption. If pseudo-second-order kinetics is applicable, the plot t/q_t versus t shows a linear relationship. There is no need to know any parameter beforehand and q_e and k_2 can be determined from the slope and intercept of the plot (Figure not shown). Also, it is more likely to predict the behavior over the whole the range of adsorption and is in agreement with chemical sorption being the rate-controlling step (Ho and McKay, 1999b) which may involve valency forces through sharing or exchange of electrons between dye anions and adsorbent.

The correlation coefficient of the pseudo-first-kinetic model for the linear plots are more than 0.95, thus suggesting that kinetic adsorption can be described by the pseudo-first-order rate equation. The values of the parameters k_1, k_2 were also calculated and summarized in Table 2. The magnitude of the correlation coefficients, R^2>0.9 for pseudo-first order kinetic model, compared to pseudo-second-order for RO16 dye at all temperature studies (30, 40 and 50°C). Therefore, it can be concluded that adsorption of RO16 dye systems obey the pseudo-first-order kinetic model.

Adsorption thermodynamic: In order to evaluate the thermodynamic parameters for adsorption of RO16 on CC/OPA, the adsorption studies were carried out at different temperatures 30, 40 and 50°C. The adsorption standard free energy changes (ΔG^0) can be calculated according to:

$$\Delta G^{O} = -RT\ln K_C \tag{8}$$

$$K_C = \frac{q_e}{C_e} \tag{9}$$

where, R is the universal gas constant (8.314 J mol^{-1} k), q_e is the amount of dye (mg) adsorbed on the adsorbent per liter of the solution at equilibrium, C_e is the equilibrium concentration (mg L^{-1}) of the dye in the solution and T is the temperature in Kelvin. The average standard enthalpy change (ΔH^0) is obtained from Van't Hoff equation:

$$\ln Kc = \frac{\Delta S^{O}}{R} + \frac{\Delta H^{O}}{RT} \tag{10}$$

where, Kc is the equilibrium constant. T is the solution temperature (K) and R is the gas constant. ΔH^0 and ΔS^0 were calculated from the slope and intercept of plot of ln K_C versus 1/T. The results are given in Table 3.

The results show that the enthalpy of adsorption ΔH^0 for RO16 was 6.78 kJ mol^{-} . A positive standard enthalpy change (ΔH^0) suggests that the interaction of RO16 adsorbed by CC/OPA is endothermic which is supported by the increasing adsorption of RO16 with the increase in temperature while a negative adsorption standard free energy change (ΔG^0) and a positive standard entropy change (ΔS^0) indicate that the adsorption reaction is a spontaneous process (Niwas *et al*., 2000) and more favorable at high temperature. Generally, the absolute magnitude of the change in free energy for physical adsorption is smaller than that of chemisorption. The former ranges from -20 to 0 kJ mol^{-1} and the latter ranges from-80 to-400 kJ mol^{-1} (Jaycock and Parfitt, 1981). When the temperature increased from 30 to 50°C, ΔG^0 was increase from -5.59 to-6.57 kJ mol^{-1}. This could be considered as physical adsorption and more favorable at high temperature.

The pseudo-second-order rate constant of dye adsorption is expressed as a function of temperature by the Arrhenius type relationship:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \tag{11}$$

where, E_a is the Arrhenius activation energy of sorption, representing the minimum energy that reactants must have for the reaction to proceed, A is Arrhenius factor, R is gas constant and T is the solution temperature. When ln k_2 is plotted versus 1/T (Figure not shown) a straight line with slope-E_a/R is obtained. The chemisorption or physisorption mechanisms are often an important indicator to describe the type of interaction between dye molecule and adsorbent. The physisorption processes usually have energies in the range of 4 to 40 kJ mol^{-1}, while higher activation energies (40-400 kJ mol^{-1}) suggest chemisorption (Nollet *et al*., 2003). The value of E_a was 2.24 kJ mol^{-1} L and indicates that process was physisorption mechanism.

Table 2: Kinetic parameters of RO16 adsorbed onto CC/OPA at different initial concentrations

		Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
C_0 (mg L^{-1})	$q_{e,\,exp}$ (mg g^{-1})	$q_{e,\,cal}$ (mg g^{-1})	k_1 1/h	R^2	$q_{e,\,cal}$ (mg g^{-1})	k_2 (g mg^{-1} h)	R^2
50	23.02	18.61	0.15	0.95	23.58	0.016	0.88
100	45.33	37.61	0.10	0.96	38.17	0.012	0.95
200	90.43	82.24	0.10	0.97	76.34	0.004	0.87
300	136.93	126.36	0.08	0.96	147.06	0.001	0.84
400	183.78	167.73	0.06	0.95	128.21	0.002	0.86
500	227.82	216.32	0.07	0.99	172.41	0.001	0.82

Table 3: Thermodynamic parameters for the adsorption of RO16 on CC/OPA

			ΔG^0 (kJ mol^{-1} L)		
E_a (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1})	303 K	313 K	323 K
2.24	6.78	41.07	-5.59	-6.22	-6.57

CONCLUSION

This study confirmed that cross-linked chitosan/oil palm ash composite beads were an excellent adsorbent for removal of reactive orange 16 dye from aqueous solution. The maximum adsorption observed at pH 6 for cross-linked chitosan/oil palm ash composite beads. A decrease in the pH of solutions leads to a significant increase in the adsorption capacity of dye RO16 on the adsorbent. Langmuir and Freundlich isotherm equation were used to describe the adsorption of RO16 onto CC/OPA. Freundlich showed better correlation coefficient than the other models at all temperatures studied. The prepared adsorbent exhibits a high adsorption capacity to remove RO16, whose adsorption maximum monolayer adsorption capacity is greater than 300 mg g^{-1} at pH 6 and 30°C. It was found that the pseudo-second-order equation was better in describing the adsorption kinetics of reactive orange 16 on CC/OPA. The data obtained from adsorption isotherms at different temperatures were used to calculate thermodynamic quantities such as ΔG^0, ΔH^0 and ΔS^0 of adsorption. The results indicate that RO16 adsorption onto CC/OPA is spontaneous and physical in nature.

ACKNOWLEDGMENT

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

REFERENCES

Ahmad, A.A., B.H. Hameed and N. Aziz, 2006. Adsorption of direct dye on palm ash: Kinetic and equilibrium modeling. J. Hazard. Mater., 141: 70-76.

Benkli, Y.E., M.F. Can, M. Turan and M.S. Celik, 2005. Modification of organo-zeolite surface for the removal of reactive azo dyes in fixed-bed reactors. Water Res., 39: 487-493.

Chang, M.Y. and R.S. Juang, 2004. Adsorption of tannic acid, humic acid and dyes from water using the composite of chitosan and activated clay. J. Colloid Interface Sci., 278: 18-25.

Chiou, M.S. and G.S. Chuang, 2006. Competitive adsorption of dye metanil yellow in acidic solutions on chemically cross-linked chitosan beads. Chemosphere, 62: 731-740.

Chiou, M.S. and H.Y. Li, 2003. Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads. Chemosphere, 50: 1095-1105.

Cicek, F., D. Ozer, A. Ozer, A. Ozer, 2007. Low cost removal of reactive dyes using wheat bran. J. Hazard. Mater., 146: 408-416.

Feng, C.W., L.T. Ru and S.J. Ruey, 2000. Comparative adsorption of metal and dye on flake and bead-types of chitosans prepared from fishery wastes. J. Hazard Mater., 73: 63-75.

Freundlich, H.M.F., 1906. Uber die adsorption in lusungen. Z. Phys. Chem., 57: 385-470.

Garg, V.K., M. Amita, R. Kumar and R. Gupta, 2004. Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: A timber industry waste. Dyes Pigments, 63: 243-250.

Hall, K.R., L.C. Eagleton, A. Acrivos and T. Vermeulen, 1966. Pore and solid diffusion kinetics in fixed bed adsorption under constant-pattern condition. Ind. Eng. Chem. Fundam., 5: 212-223.

Ho, Y.S. and G. McKay, 1999a. Pseudo-second order model for sorption processes. Process Biochem., 34: 451-465.

Ho, Y.S. and G. McKay, 1999b. The sorption of lead (II) ions on peat. Water Res., 33: 578-584.

Ho, Y.S., 1995. Adsorption of heavy metals from waste streams by peat. Ph.D. Thesis, The University of Birmingham, Birmingham, UK.

Ilhan, U. and G. Fuat, 2004. Kinetics and thermodynamics of the adsorption of some dyestuffs and p-nitrophenol by chitosan and MCM-chitosan from aqueous solution. J. Colloid Interface Sci., 274: 398-412.

Janos, P., H. Buchtova and M. Ryznarova, 2003. Sorption of dyes from aqueous solutions onto fly ash. Water Res., 37: 4938-4944.

Jaycock, M.J. and G.D. Parfitt, 1981. Chemistry of Interfaces. Ellis Horwood Publishing Co., Winchester, London, UK., ISBN-13: 9780470270134, pp: 279.

Koprivanac, N., A.L. Bozic and S. Papic, 2000. Cleaner production processes in the synthesis of blue anthraquinone reactive dyes. Dyes Pigm., 44: 33-40.

Kumar, M.N.V.R., 2000. A review of chitin and chitosan applications. React. Funct. Polym., 46: 1-27.

Lagergren, S., 1898. Zur theorie der sogenannten adsorption geloster stoffe. K Sven Vetenskapsakad Handl, 24: 1-39.

Métivier-Pignon, H., C. Faur-Brasquet and P.L. Cloirec, 2003. Adsorption of dyes onto activated carbon cloths: Approach of adsorption mechanisms and coupling of ACC with ultrafiltration to treat coloured wastewaters. Sep. Purif. Technol., 31: 3-11.

Netpradit, S., P. Thiravetyan and S. Towprayoon, 2003. Application of waste metal hydroxide sludge for adsorption of azo reactive dyes. Water Res., 37: 763-772.

Netpradit, S., P. Thiravetyan and S. Towprayoon, 2004. Adsorption of three azo reactive dyes by metal hydroxide sludge: Effect of temperatuire, pH and electrolytes. J. Colloid Interface Sci., 270: 255-261.

Niwas, R., U. Gupta, A.A. Khan and K.G. Varshney, 2000. The adsorption of phosphamidon on the surface of styrene supported zirconium (IV) tungstophosphate: A thermodynamic study. Colloid Surf. A: Physicochem. Eng. Asp., 164: 115-119.

Nollet, H., M. Roels, P. Lutgen, P. van der Meeren and W. Verstraete, 2003. Removal of PCBs from wastewater using fly ash. Chemosphere, 53: 655-665.

Orthman, J., H.Y. Zhu and G.Q. Lu, 2003. Use of anion clay hydrotalcite to remove coloured organics from aqueous solutions. Sep. Purif. Technol., 31: 53-59.

Osama, J.F., V. Saravia, J.L. Toca-Herrera and S.R. Couto, 2007. Sunflower seed shells: A novel and effective low-cost adsorbent for the removal of the diazo dye reactive black 5 from aqueous solutions. J. Hazard. Mater., 147: 900-905.

Panswad, T. and W. Luangdilok, 2000. Decolorization of reactive dyes with different molecular structures under different environmental conditions. Water Res., 34: 4177-4184.

Waranusantigul, P., P. Pokethitiyook, M. Kruatrachue and E.S. Upatham, 2003. Kinetics of basic dye (methylene blue) biosorption by giant duckweed (*Spirodela polyrrhiza*). Environ. Pollut., 125: 385-392.

Yoshida, H., S. Fukuda, A. Okamato and T. Kataoka, 1991. Recovery of direct dye and acid dye by adsorption on chitosan fiber-equilibria. Water Sci. Technol., 23: 1667-1676.

Yoshida, H., A. Okamoto and T. Kataoka, 1993. Adsorption of acid dye on cross-linked chitosan fibers: Equilibria. Chem. Eng. Sci., 48: 2267-2272.

Zeng, X. and E. Ruckenstein, 1998. Cross-linked macroporous chitosan anion-exchange membranes for protein separations. J. Membr. Sci., 148: 195-205.