International Journal of Physical Sciences Vol. 5(5), pp. 582-595, May 2010
Available online at http://www.academicjournals.org/IJPS
ISSN 1992 - 1950 © 2010 Academic Journals

Full Length Research Paper

Equilibrium studies and kinetics mechanism for the removal of basic and reactive dyes in both single and binary systems using EDTA modified rice husk

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Accepted 25 February, 2010

The potential of using ethylenediamine tetraacetic acid modified rice husk (ERH) to remove different types of dyes, namely basic and reactive dyes were studied. Sorption characteristic of ERH showed that it was pH dependent. The kinetics of sorption for both dyes was rapid within the first 60 min regardless of its initial concentration. Using the pseudo-second order kinetics model, the predicted uptakes of Methylene Blue (MB) and Reactive Orange 16 (RO16) agreed closely with experimental values obtained. Three isotherm models were used to fit with equilibrium data, namely Langmuir, Freundlich and BET models. It was found that the equilibrium fitted well in Freundlich isotherm with higher regression coefficient value, R^2. Thermodynamic parameters showed that the sorption of process of MB and RO16 are exothermic and endothermic, respectively. Decrease in sorbent particle size led to an increase in the sorption of dyes. The study revealed that ERH is suitable to use as a single sorbent to remove both MB and RO16 in all systems.

Key words: EDTA modified rice husk, adsorption, binary mixture system, methylene blue, reactive orange 16.

INTRODUCTION

Colour is considered as the first pollutant to be identified in wastewater and it is mostly caused by the effluents discharged from dyeing industries such as paper, rubber, cosmetics, textile and plastics. Approximately 10,000 different dyes and pigments are used for industries and over 7×10^5 tons of these dyes are annually produced worldwide (Mane et al., 2007). Majority of dyes are visually detected even at the concentration of less than 1 mg/l. In addition, some dyes or their metabolites are either toxic or mutagenic and carcinogenic (Pavan et al., 2007). Thus, the discharge of dyes into water has severe environmental impact and therefore the removal of dyes from wastewater has becomes a challenging and perplexing problem.

In order to overcome this problem, various physicochemical and biological techniques have been studied extensively. Nevertheless, adsorption of dye effluents onto activated carbon has been considered as the most efficient method for the removal of various dyes. However, due to the high generation cost of activated carbon (Tsai et al., 2007), many low-cost adsorbents

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Abbreviations: ERH, Ethylenediamine tetraacetic acid modified rice husk; **EDTA,** ethylenediamine tetraacetic acid; **MB,** methylene blue; **NRH,** natural rice husk.

prepared from native agricultural by-products had been investigated as an alternative adsorbent, such as peanut hull, tea dust leaves, rice hull, wood products, coir pith and sugarcane baggase (Kadirvelu et al., 2003; Ong et al., 2009a; Ong et al., 2009b).

In this present study, rice husk was chosen as the local low-cost adsorbent since more than 350,000 metric tonnes of rice husks are produced annually as a result of paddy cultivation (Annual Report of Bernas Sdn Bhd, 2008). Rice husk in its natural state contains a high proportion of cellulose (32.34%), hemicellulose (21.34%), lignin (21.44%) and mineral ash (15.05%) (Wan Ngah et al., 2007; Marshall et al., 1993) and this cellulosic surface will becomes partially negatively charged when immersed in water and hence, produce columbic interaction with cationic species in water (Kumar, 2006; Laszlo, 1994; McKay et al., 1987).

Various modifications on rice husk have been reported in order to enhance their sorption capacities for metal ions, dye and other pollutants (Wong et al., 2003; Lakshmi et al., 2009; Ong et al., 2009a; Gong et al., 2008; Mane et al., 2007). Most of the studies indicated that the modified adsorbents are efficient in binding either the cationic or anionic species but not both. However, a mixture of different types of dyes is usually found in the industrial effluents. Therefore, there is a need to have adsorbents capable of removing different types of dyes either singly or simultaneously. In our continued effort to use low-cost materials for the removal of organic pollutants, we have investigated the performance of ethylenediamine tetraacetic acid (EDTA) modified rice husk as a sorbent for basic and reactive dyes in both single and binary systems.

MATERIALS AND METHODS

Sorbent

The rice husk was collected from a local rice mill. It was washed thoroughly with water and then sun dried. The dried rice husk was ground to size of 1 mm using a grinder and labelled as natural rice husk (NRH). The modification with EDTA was attempted by varying temperature (60 - 90°C) and the ratio of EDTA to rice husk (0.0125 - 0.125:1). Based on its sorption of all dye systems, it was found that the optimum conditions for the modification of rice husk were by treating 8 g of grinded rice husk with 0.5 g of EDTA and soaked in 300 ml of 1.0 M sodium hydroxide (NaOH) for 3 h at 70°C. The treated rice husk was filtered and washed with excess water and dried in an oven at 60°C and the material was labeled as ERH.

Batch studies

Batch studies were conducted using 0.1 g of sorbent in 20ml of 25 mg/l dye solution and were shaken at 150 rpm for 4 h. The supernatant was analyzed for its dye concentration using double beam UV-vis spectrophotometer (Perkin Elmer Lambda 35) with the maximum absorption wavelength of 664 and 494 nm for MB and RO16, respectively. All experiments were conducted in duplicates and the results stated are the means. Controls without sorbent were simultaneously carried out to ascertain that sorption was due to sorbent and not the wall of the centrifuge tube. The percentage of dye uptake was calculated using the following equation:

$$\%Uptake = \frac{C_i - C_t}{C_i} \times 100\% \qquad (1)$$

where C_i is the initial concentration and C_t the concentrations at time t.

The effect of pH on the sorption capacity of sorbent was studied by equilibrating the sorption mixture from pH 2 to 10 by adding dilute HCl or NaOH solution. Time course experiments were carried out by shaking the sorption mixture at various predetermined intervals (5 - 420 min) and analyzing the dye content at the end of the contact time. Three isotherm models were employed to study the sorption isotherm, namely Langmuir isotherm, Freundlich isotherm and BET model (Brunauer, Emmet and Teller). The isotherms results were obtained by equilibrating dye solutions at different initial concentrations ranged from 5 to 150 mg/l.

The effect of temperature on the sorption of dye solutions was studied in the temperature range of 30 to 70°C at the natural pH of the dye solution. The effect of agitation rate on the dye removal was carried out by varying the agitation rate from 50 to 200 rpm. The experiment on the effect of sorbent dosage on dye sorption was performed using sorbent concentrations of 0.05 – 0.2 g. As for the effect of particle size, it was studied by sieving the sorbent into four different size ranges, 150 - 300, 300 - 600, 600-800 and > 800 micron.

Sorbates

MB and RO16 were used in this study as sorbates. The structures of dyes are shown in Figure 1. A stock solution of 1000 mg/l was prepared for both MB and RO16 and it was diluted to a suitable initial concentration for further analysis. The binary mixture system was obtained through the mixing of MB and RO16.

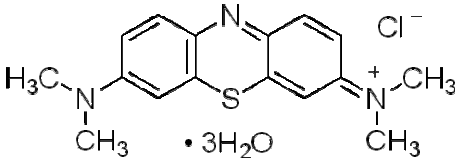
RESULTS AND DISCUSSION

Comparative studies

A comparative study of sorption of MB and RO16 in both single and binary dye solutions was carried out by using NRH and ERH as sorbents as shown in Figure 2. The results showed that MB was adsorbed by NRH effectively, with 90.3 and 90.8% in both single and binary systems, respectively. Rice husk in its natural state consists of high proportion of cellulose and the cellulosic surface that would become negatively charged when immersed in water (Kumar, 2006; Laszlo, 1994; McKay et al., 1987). Therefore, when the dye molecule of MB dissociates into a positively charged species, an electrostatic interaction formed between the surface of NRH and MB dye molecule. However, the percentage uptake of RO16 by NRH was relatively low and this may due to the coulombic repulsion between the anionic dye molecules and the negatively charged surface groups of NRH (Ong et al., 2007; Lee et al 2008).

After modification, ERH showed its sorption capability for different charged dyes, in either single or binary dye

Methylene blue



Reactive orange 16

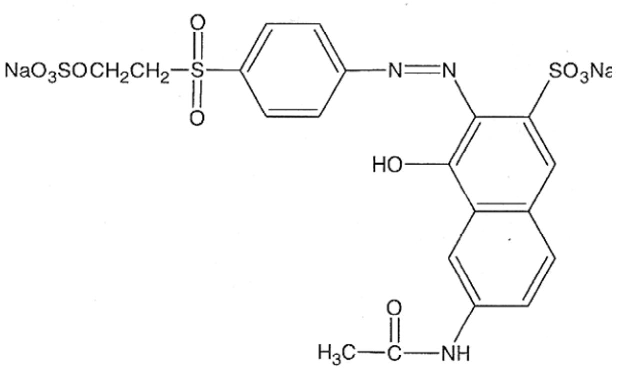


Figure 1. Structures of MB and RO16.

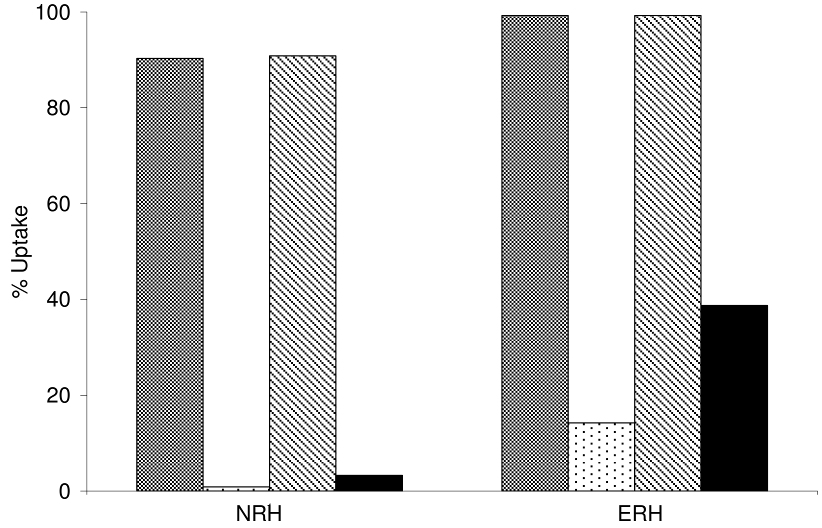


Figure 2. Comparative uptake between NRH and ERH. ▩, ░, ▧, ■ - single MB, single RO16, binary MB and binary RO16

solutions. The high affinity of ERH for both MB and RO16 is probably due to the presence of carboxyl and amine groups introduced from the EDTA modification. The negatively charged carboxyl group is likely to be responsible for the adsorption of positively charged MB whereas the negatively charged RO16 is attracted to the

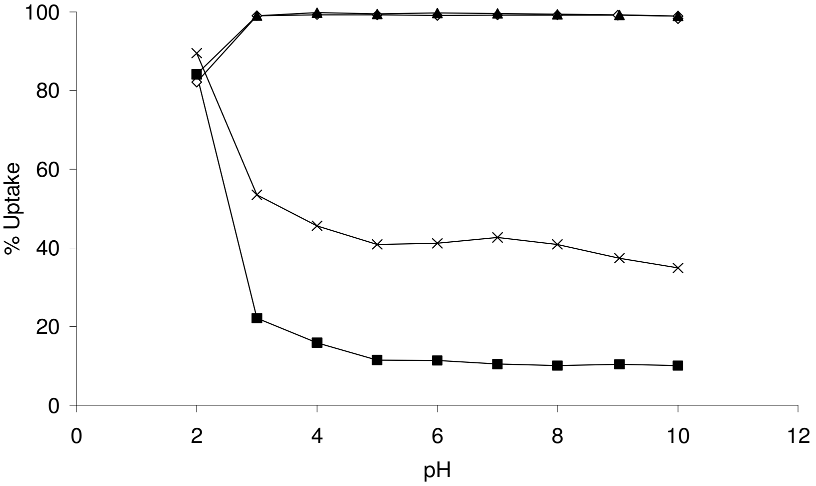


Figure 3. Effect of pH. ◊, ■, ▲, × - single MB, single RO16, binary MB and binary RO16.

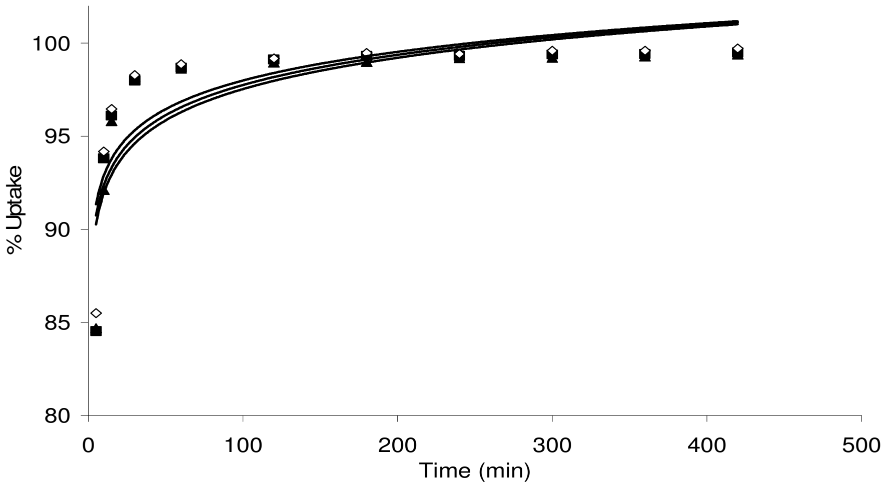


Figure 4. Effect of initial concentration and contact time. ◊, ■, ▲ - 15, 20 and 25 mg/l.

protonated amine group.

Effect of pH

The pH value of the solution is an important process controlling parameter in the adsorption study since it determines the surface charged of sorbent. Figure 3 shows that uptake of RO16 decreased from 84.2 to 10.1% with the increase in pH from 2 to 10. As the pH of the system increases, this lead to the deprotonation of surface groups and the presence of excess OH^-, results in the electrostatic repulsion between the anionic dye and negatively charged sites. Similar behaviour was obtained in binary dye solutions. The reversed trend was observed in the removal of MB where the percentage of uptake was more favourable in high pH. At low pH, the surface of the sorbent was surrounded by hydronium ions (H^+), which prevented the MB dye molecules from approaching the binding sites. With increasing pH, the carboxyl groups are predominantly deprotonated, resulting in sorption sites that were available for binding with MB.

Effect of initial concentration and sorption kinetics

The rate of sorption of single MB by ERH as a function of initial concentrations is shown in Figure 4. Similar plots were also obtained for single RO16, binary MB and Binary RO16. The uptake rate was rapid in the first 60

Table 1. Sorption capacities and correlation coefficients based on pseudo-first and pseudo-second kinetics.

Dye	Initial Concentration	Pseudo-first order		Pseudo-second order		Experimental sorption capacities (mg/g)
		Sorption capacities (mg/g)	R^2	Sorption capacities (mg/g)	R^2	
MB-Single	15	7.153	0.327	2.994	1.000	2.991
	20	16.226	0.321	3.986	1.000	3.980
	25	25.305	0.338	4.975	1.000	4.969
RO16-Single	15	9.899	0.851	0.327	0.993	0.307
	20	9.756	0.910	0.567	0.989	0.558
	25	9.774	0.877	0.684	0.986	0.658
MB-Binary	15	7.309	0.439	2.994	1.000	2.988
	20	16.259	0377	3.986	1.000	3.982
	25	25.345	0.444	4.967	1.000	4.958
RO16-Binary	15	9.337	0.744	0.901	0.999	0.889
	20	9.367	0.849	1.039	0.998	1.013
	25	8.543	0.820	1.832	0.999	1.829

min followed by a slower process. The fast uptake at the beginning may be attributed to the rapid attachment of the dye molecules to the surface of the sorbent and the following slower sorption to intraparticle diffusion (Amin, 2008). The initial rapid phase may also be due to the increased number of vacant sites available at the initial stage, consequently exist an increase in driving force of the concentration gradient between adsorbate in solution and adsorbate in the adsorbent (Ju et al ., 2008; Kavitha and Namasivayam, 2007).

With increasing initial concentration of dye solutions, the percent uptake of MB and RO16 in single and binary systems decreased. This indicates the saturation and quick exhaustion of the binding sites on the sorbent as the number of dye molecules per unit volume increased. At low initial concentration, dye molecules are adsorbed on a specific binding site, however, when the concentration increases, there exist reductions in immediate solute adsorption due to the lack of available binding sites (Amin, 2008).

In order to explore the potential rate-controlling steps involved in the sorption of MB and RO16 onto ERH, both pseudo-first and pseudo-second kinetics models have been used to fit experimental data at various dye concentrations. The pseudo-first order (Lagergren, 1898) and pseudo-second equations (Ho and McKay, 1999) are expressed as in equations (2) and (3), respectively.

$$\log(q_e - q_t) = \log qe - {k_1 t}/{2.303} \quad (2)$$

$$t/q_t = 1/h + t/q_e \quad (3)$$

where q_e = the amount of dyes sorbed at equilibrium (mg/g), q_t = the amount of dyes sorbed at time *t* (mg/g), k_1 = the rate constant of pseudo-first order sorption (1/min), h = $(k_2 q_e^2)$ = the initial sorption rate (mg/g min) and k_2 = the rate constant of pseudo-second order kinetics (g/ mg min).

The various sorption capacities and correlation coefficients based on pseudo-first and pseudo-second order kinetics were summarized in Table 1. For all the systems studied, good correlation coefficients are obtained ($R^2 \approx 1$) by fitting the experimental data to pseudo-second order kinetics rather than that of pseudo-first order kinetic model. Besides, the equilibrium sorption capacities calculated from based on pseudo-second order kinetic model agreed well with those obtained experimentally. Therefore, the sorption is more favourably by pseudo-second order kinetic model which is based on the assumption that the rate limiting step may be chemisorption involving valency forces through sharing or exchange of electron between sorbent and sorbate (Ho and McKay, 1999).

Table 2. Empirical parameters for predicted q_e, k and h from C_o.

Dyes	A_q (g/mg)	B_q (g/L)	A_k (mg min/g)	B_k (mg^2min/g L)	A_h (gmin/mg)	B_h (gmin/L)
MB-Single	0.000	5.014	5.596	-56.727	0.031	2.636
MB-Binary	0.000	5.027	2.423	39.498	-0.448	14.822
RO16-Single	-1.066	60.333	55.685	-655.980	-84.524	3277.900
RO16-Binary	-0.168	19.930	25.400	-257.650	1.813	129.920

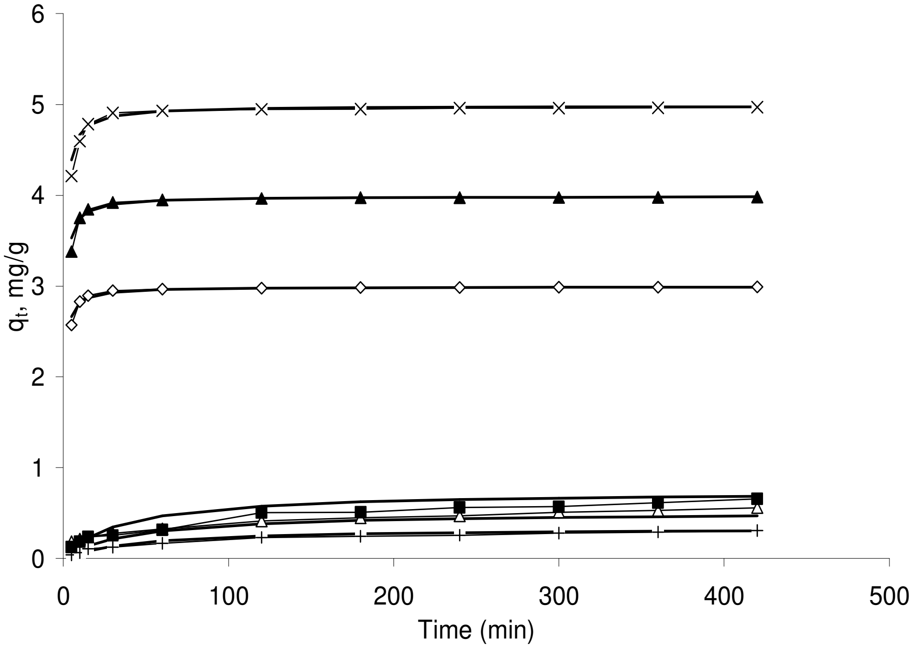


Figure 5. Comparison between the measured and pseudo-second order modelled time profiles for MB and RO16 from single dye solutions. ◊, ▲, × - 15, 20 and 25 mg/l of MB (experimental); +, Δ, ■ – 15, 20 and 25 mg/l of RO16 (experimental); line – theoretical.

According to Ho and McKay (2000), the values of q_e, k_2 and h against C_o in the corresponding linear plots of the pseudo-second order equation can be regressed to obtain expressions for these values in terms of initial concentration (Table 2). These parameters can be expressed as a function of C_o for MB and RO16 on ERH as follows:

$$q_e = \frac{C_o}{A_q C_o + B_q} \tag{4}$$

$$k_2 = \frac{C_o}{A_k C_o + B_k} \tag{5}$$

$$h = \frac{C_o}{A_h C_o + B_h} \tag{6}$$

where A_q, B_q, A_k, B_k, A_h, B_h are constant for the respective equations. The theoretical model derived for MB and RO16 at concentrations of 15 - 25 mg/l was applied to the uptake of both dyes and the result was compared to the experimental values as shown in Figure 5. For the uptake of MB, it is apparent that the theoretical curve generated based on the model agreed well with the experimental data but a slight deviation was observed for RO16.

Effect of agitation rate

The variation of dyes uptake with agitation rate is shown in Figures 6 and 7. Uptake of RO16 is independent of agitation rate; this is probably associated with the rapid uptake of the dye. The minimal effect of agitation rate on the dye sorption by sorbent indicated also that external mass is not the sole rate-limiting factor in a well agitated system. However, uptake of MB increased with increasing agitation rate. Increasing agitation rate decreases the film resistance to mass transfer surrounding the sorbent particles thus increasing sorption

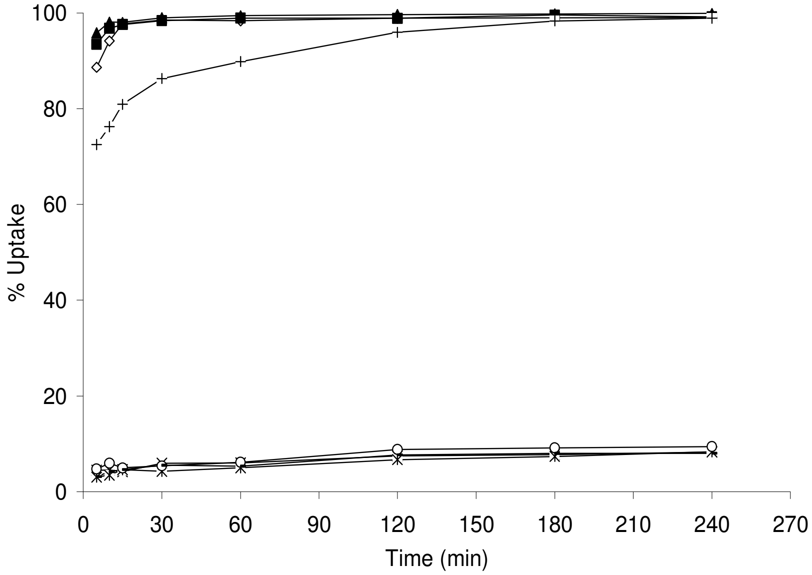


Figure 6. Effect of agitation rate. +, ◊, ■, ▲ - 50, 100, 150 and 200 rpm for single MB; -, ×, *, ○ – 50, 100, 150 and 200 rpm for single RO16.

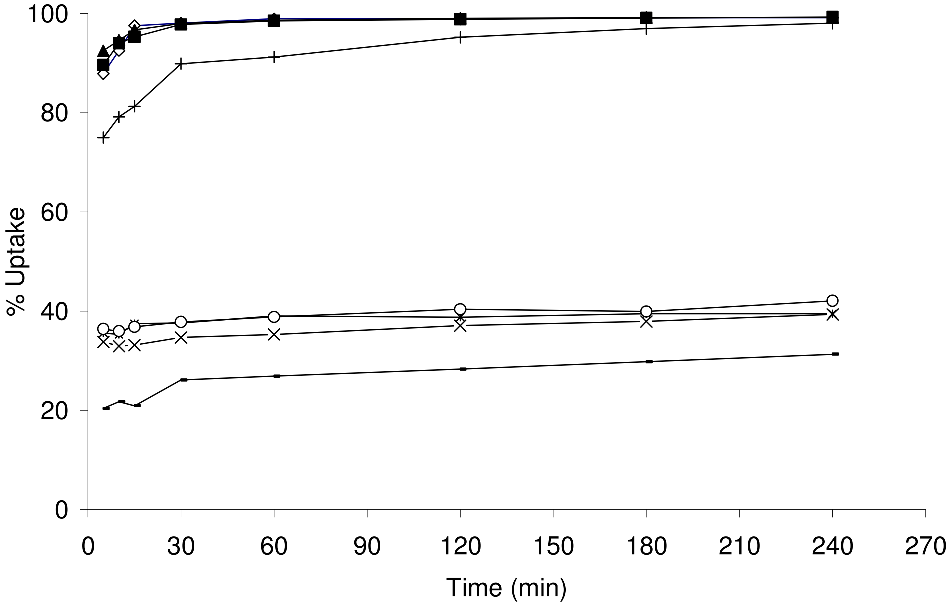


Figure 7. Effect of agitation rate. +, ◊, ■, ▲ - 50, 100, 150 and 200 rpm for binary MB; -, ×, *, ○ – 50, 100, 150 and 200 rpm for binary RO16.

of dye molecules. Similar behaviour was observed in the binary dye solutions.

Intraparticle diffusion

In order to study the mechanism of adsorption process, intraparticle diffusion was studied. Weber and Moris model was used and the equation is shown as below:

$$K_p = q_t / \sqrt{t} \tag{7}$$

Where K_p is an intraparticle diffusion coefficient (mg/g min$^{0.5}$) which can be obtained from the slope of the plot q_t versus $\sqrt{t}$ presented in Figure 8. q_t is the amount of MB or RO16 adsorbed by ERH at time t.

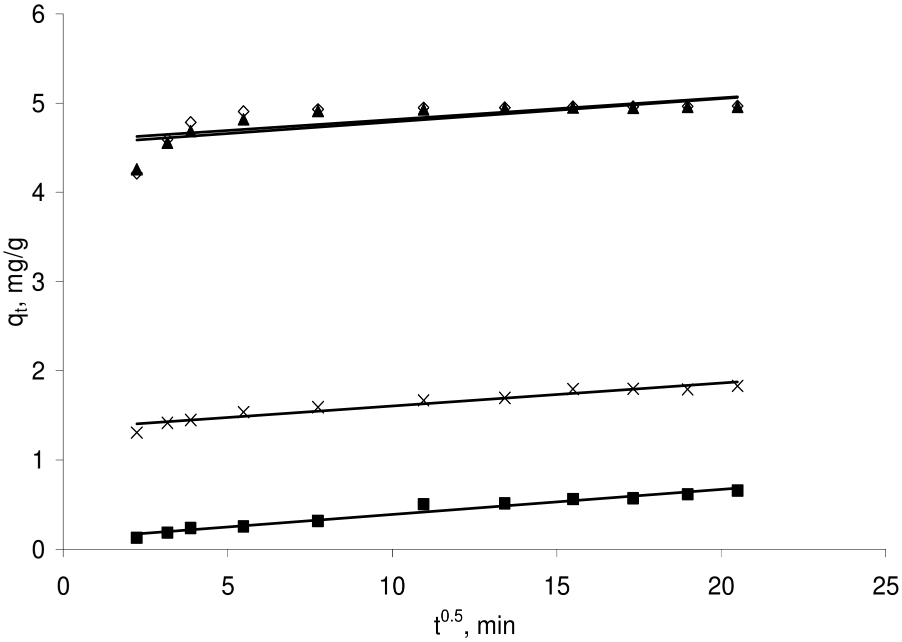


Figure 8. Intraparticle diffusion. ◊, ■, ▲, × - single MB, single RO16, binary MB and binary RO16.

As referred to Figure 8, there are two portions which suggest that two processes are involve, the surface sorption and intraparticle diffusion. Initial curve portion is attributed to boundary layer effect while the second linear portion is due to the intrapaticle diffusion (Arivoli et al., 2007). Deviation of the plot from the origin indicates that intraparticle diffusion is not the only rate-limiting mechanism.

Sorption isotherm

The sorption of dyes by ERH is a function of the equilibrium dye concentration in solution at constant pH and temperature. Various models have been used to describe the equation state between the two phases composing the adsorption system. These include Langmuir, Freundlich and Brunauer- Emmet- Teller isotherm models. Various assumptions are made depending on the choice of model. The sorption data in the present study was applied to both Langmuir and Freundlich isotherm models. The linearised Langmuir model is written as:

$$\frac{C_e}{N_e} = \frac{1}{N^* b} + \frac{C_e}{N^*} \qquad (8)$$

whereas the linear form of Freundlich can be represented as:

$$\log N_e = \frac{\log C_e}{n} + \log K_f \qquad (9)$$

where C_e = equilibrium concentration of the dye solution (mg/L), N_e = amount of dye sorbed at equilibrium (mg/g), N* = maximum sorption capacity (mg/g), *b* = constant related to the energy of the sorbent (l/mg), n = Freundlich constant for intensity and K_f = Freundlich constant for sorption capacity.

As for the essential characteristic of Langmuir isotherm, it can be expressed in terms of dimensionless separation parameter, R_L, which is indicative of the isotherm shape that predicts whether an adsorption system favourable or unfavourable (El-Ashtoukhy et al., 2007) as shown in Table 3. R_L is defined as follow:

$$R_L = \frac{1}{1 + K_a C_o} \qquad (10)$$

where C_o is the initial concentration of dye solution and K_a is the Langmuir constant. When R_L value is in between 0 and 1 then it is favourable, > 1 is unfavourable, = 1 is linear and = 0 is irreversible.

By comparing the regression coefficient, R^2 between Langmuir and Freundlich isotherms, the equilibrium data was well presented in Freundlich isotherm since the R^2 values ranging from 0.9721 to 0.9946 for all the systems

Table 3. The values of R_L for MB and RO16 dye solutions.

Dye solutions	Initial concentration, C_o (mg/L)	R_L
MB-Single	25	0.064
	30	0.054
	50	0.033
	70	0.024
	90	0.019
	150	0.011
MB-Binary	5	0.364
	10	0.222
	15	0.160
	24	0.106
	30	0.086
	35	0.076
RO16-Single	50	0.775
	70	0.772
	80	0.683
	100	0.633
	120	0.589
	150	0.535
RO16-Binary	10	0.929
	15	0.898
	25	0.840
	30	0.814
	35	0.789
	40	0.767

Table 4. Langmuir, Freundlich and BET constants for the adsorption of MB and RO16 in single and binary systems.

Dyes	Langmuir			Freundlich			BET	
	N* (mg/g)	B (l/mg)	R^2	K_f	n	R^2	x_m (mg/g)	R^2
MB-Single	46.30	0.589	0.947	82.737	1.406	0.995	46.29	0.947
MB-Binary	49.51	0.313	0.5709	11.625	1.172	0.979	47.61	0.642
RO16-Single	7.68	0.006	0.9203	0.110	1.422	0.975	7.41	0.209
RO16-Binary	17.24	0.008	0.6812	0.178	1.180	0.972	16.86	0.598

under study. As a result, it can be said that the overall adsorption of all dyes in this study are preferably to obey Freundlich isotherm in which adsorption is based on heterogeneous surface. The maximum adsorption capacities for MB and RO16 in binary system were 49.51 and 17.24 mg/g, respectively as compared to 46.30 and 7.68 mg/g for MB and RO16 in single dye solutions. The constant value for Langmuir, Freundlich and BET are summarized in Table 4.

Effect of temperature

Figure 9 shows the effect of temperature in the sorption of MB and RO16 from single and binary dye solutions. A rise in temperature decreases the percentage uptake of MB from 99.3 to 95.8%, indicating that the sorption process was exdothermic. This effect can be explained by assuming that at higher temperature, the total energy of the sorbate molecules was increased and consequently their escaping tendency was also increased. Similar observations were reported in the adsorption of Cu and Pb ions (Wong et al., 2003) and MB (Hamdaoui and Chiha, 2007). On the other hand, sorption of RO16 on ERH was more favourable at higher temperature. This is probably due to the fact that at higher temperature, an increase in free volume occurred and leading to an increment in the mobility of the solute. Alternatively, the enlargement of the pore sizes of the adsorbent particle at elevated temperatures can also be beneficial towards the dye sorption. Guo et al. (2003) suggested that adsorption increased with temperature is probably due to the increase of intraparticle diffusion rate of the sorbate into the interior sites of the sorbent since diffusion is an

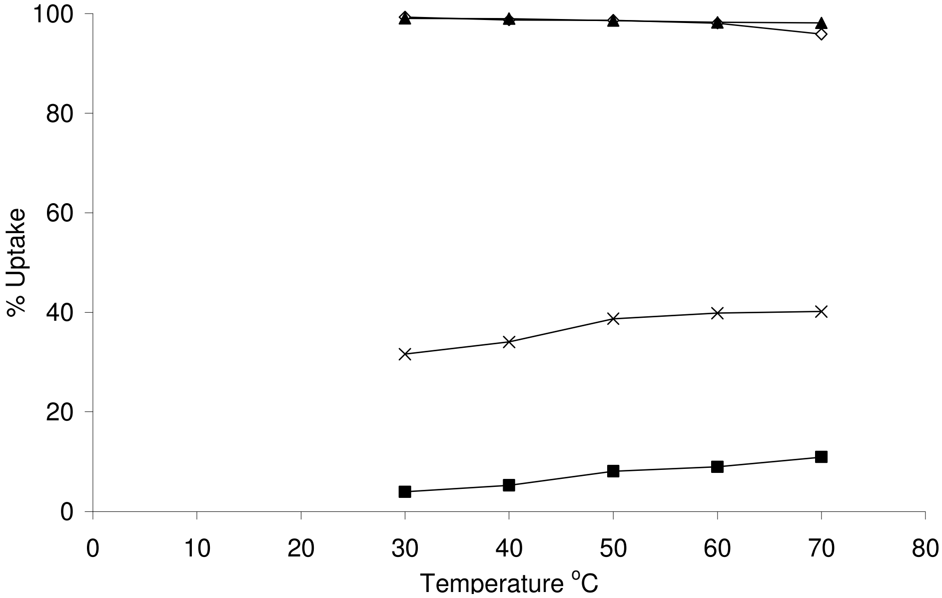


Figure 9. Effect of temperature ◊, ■, ▲, × - single MB, single RO16, binary MB and binary RO16.

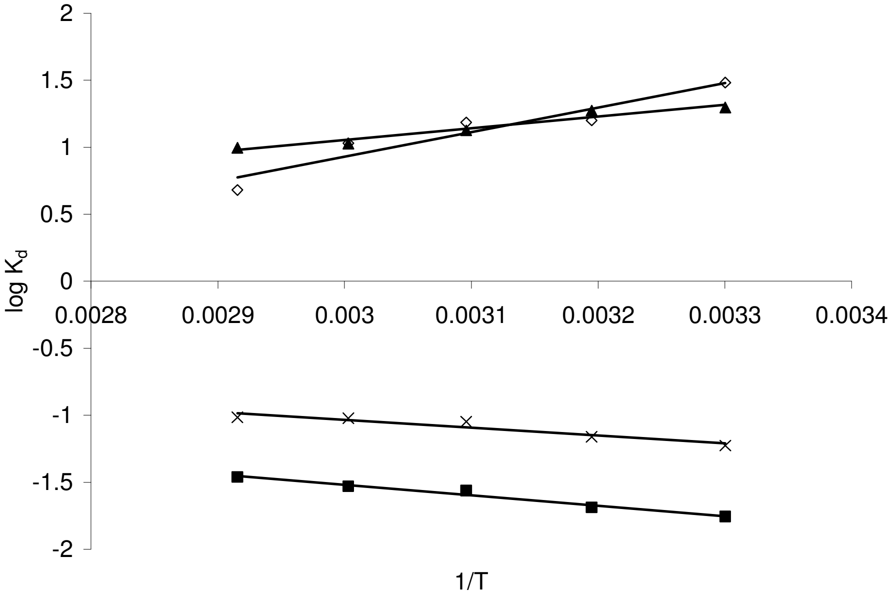


Figure 10. Van't Hoff plot. ◊, ■, ▲, × - single MB, single RO16, binary MB and binary RO16.

endothermic reaction.

The dependence of dye sorption on temperature can be further confirmed by the van't Hoff plots (Figure 10) based on the equation below:

$$\log K_d = \frac{\Delta S^o}{2.303 R} - \frac{\Delta H^o}{2.303 RT} \tag{11}$$

where K_d = distribution coefficient defined as N_e/C_e (l/g), N_e = the amount of dye sorbed at equilibrium (mg/g), C_e = equilibrium concentration (mg/l), T = absolute temperature (K), R = gas constant (8.3145 J/mol K), ΔS^o = entropy change (J/mol K), ΔH^o = enthalpy change (J/mol).

The values of ΔS^o and ΔH^o are presented in Table 5. It was found that, the negative value of enthalpy in the adsorption of MB indicates the exothermic nature of adsorption whereas the positive value of enthalpy indicates that the adsorption of RO16 is an endothermic

Table 5. Thermodynamic parameters for the adsorption of MB and RO16 in single and binary dye solutions.

Dye solutions	ΔH^o, the enthalpy change (kJ/mol)	ΔS^o is the entropy change (J/mol)
MB-Single	- 16.83 kJ/mol	30.32 J/mol
MB-Binary	- 35.06 kJ/mol	87.40 J/mol
RO16-Single	14.95 kJ/mol	15.76 J/mol
RO16-Binary	11.25 kJ/mol	13.94 J/mol

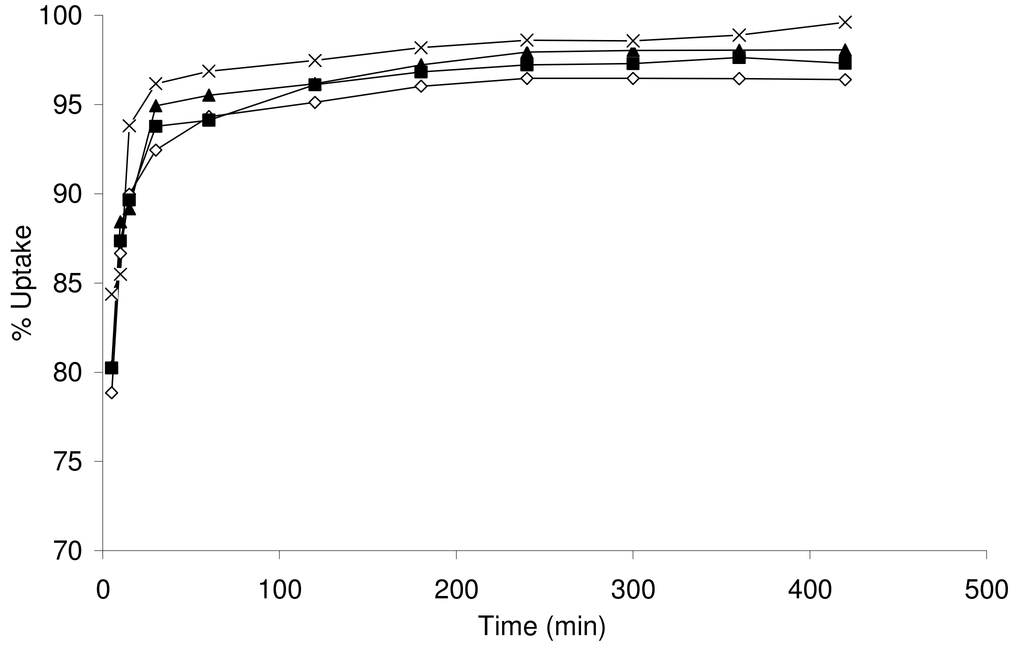


Figure 11. Effect of particle size. ◊, ■, ▲, × - > 800 micron, 800 - 600, 600 - 300 and 300 - 150 micron for single MB.

reaction. The positive value of ΔS^o_{total} indicating an increase in disorder and randomness at the solid solution interface of dye molecule with sorbent (Arivoli et al., 2007) which is attributed to the structural changes during the adsorption of MB and RO16 in single and binary dye solutions.

Effect of particle size

The experimental results obtained from a series of contact time studies for the sorption of RO16 in both single and binary dye solution onto ERH by three different size ranges are presented in Figures 12 and 14. The results indicated that the dye uptake increased with decreasing particle size. In the case of MB, Figures 11 and 13 showed that the uptake was lying close to each other and this may be due to the high affinity of ERH towards MB dye molecules. The percentage uptake at equilibrium was increased by 3.23 and 3.30% for single and binary systems, respectively. This suggests that surface activity and surface area of the sorbent plays an important role in the sorption of dye molecules. Furthermore, smaller particle sizes move faster in dye solution compared to larger particles and thus results in faster and higher rate of sorption. Similar results were observed in the removal of Astrazon Yellow 7GL by wheat bran where the amount of dye adsorbed increased from 5.20 to 6.30 mg/g for a decrease in particle size from 846 to 354 µm (Sulak et al., 2007).

Effect of sorbent dosage

The effect of sorbent dosage on sorption of MB and RO16 in single and binary systems is shown in Table 6. For RO16, it followed the usual pattern of increasing uptake as the sorbent concentration increased. This corresponds to an increase in active sites for sorption. Levelling off in the case of MB uptake can be explained in terms of depletion of dye in solution and accumulation of dye molecules on the surface of substrate giving rise to

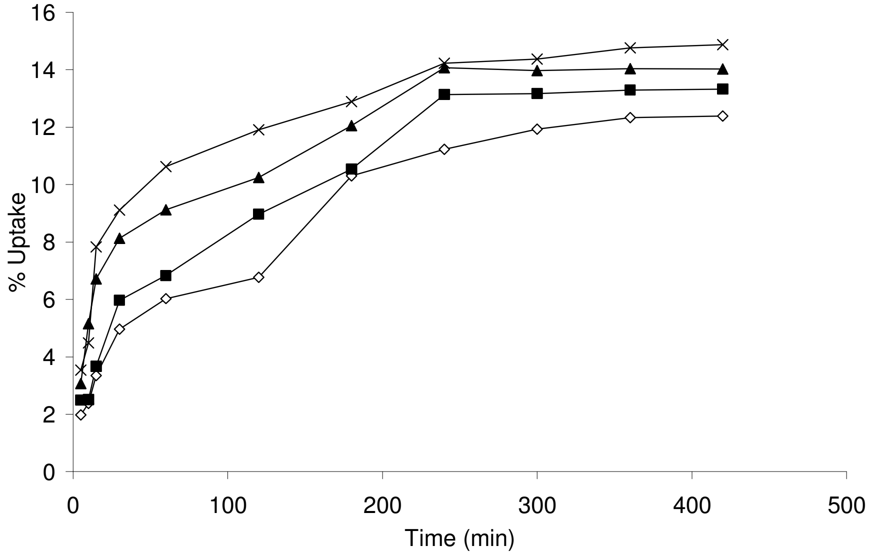


Figure 12. Effect of particle size. ◊, ■, ▲, × - > 800 micron, 800 - 600 micron, 600 - 300 and 300 - 150 micron for single RO16.

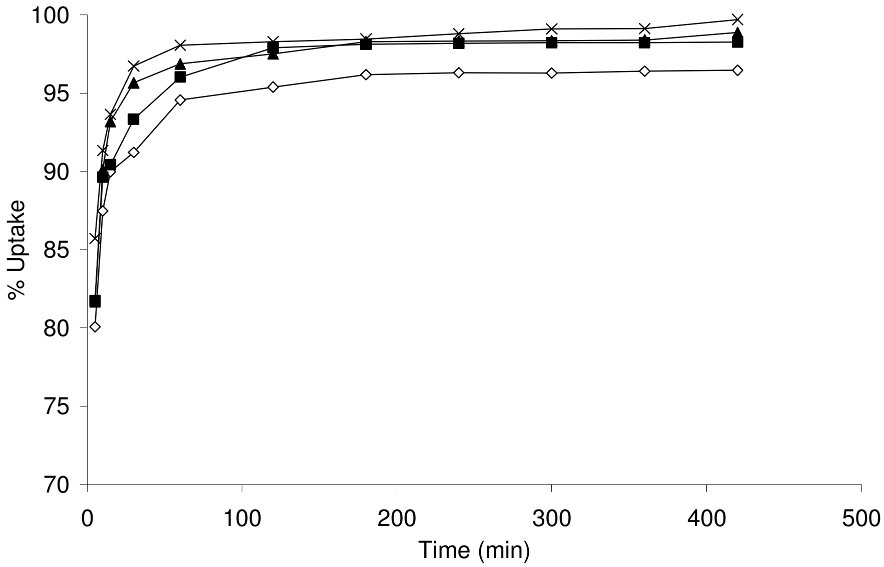


Figure 13. Effect of particle size. ◊, ■, ▲, × - >800, 800 - 600, 600 - 300 and 300 - 150 micron for binary MB.

hindering the rest of dye to diffuse inside the substrate matrix. Such a study is useful for establishing the optimum amount of ERH required in the removal of dyes.

Conclusion

The present study shows that EDTA modified rice husk (ERH) was capable to act as a single sorbent to remove both MB and RO16 dyes in single and binary systems. The percent removal of MB and RO16 was greatly depended on pH. The optimum pH for the removal of MB was found to be in the range of pH 4 to pH 9 whereas for the removal of RO16 was at pH 2. Moreover, the removal efficiency of both dyes also depended on the initial concentration and contact time. As initial concentration of dye solution increased, the percentage uptake of MB and RO16 decreased. With an increasing contact time, the percentage uptake of dye in all systems increased. An increasing trend was observed for the removal of dye in

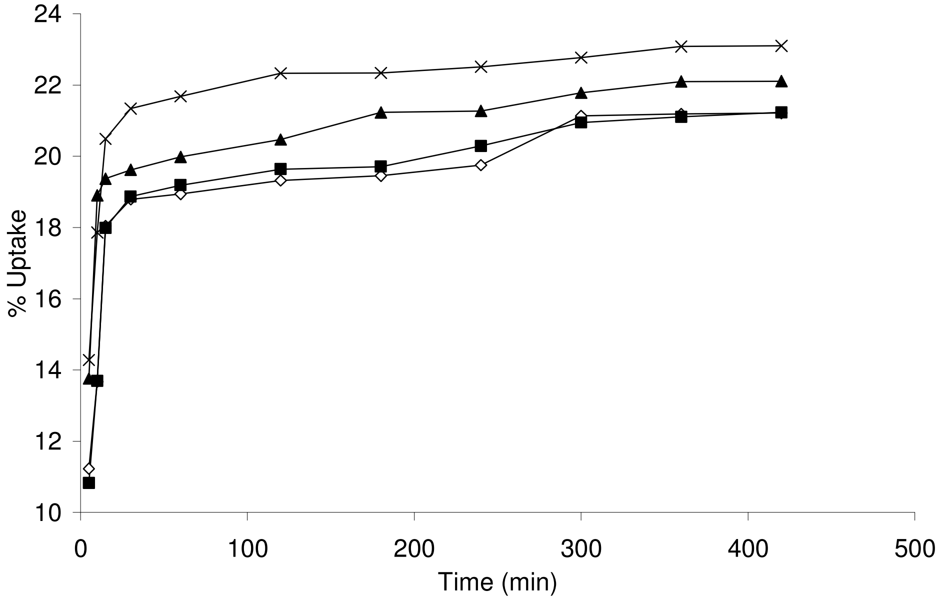


Figure 14. Effect of particle size. ◊, ■, ▲, × - > 800, 800 - 600, 600 - 300 and 300 - 150 micron for binary RO16.

Table 6. Effect of sorbent dosage.

Dye Sorbent dosage (g)	% Uptake (MB-Single)	% Uptake (RO16-Single)	% Uptake (MB-Binary)	% Uptake (RO16-Binary)
0.05	97.96	5.98	97.99	23.35
0.10	98.89	12.30	99.05	25.94
0.15	98.96	17.19	98.69	28.50
0.20	99.25	22.17	99.30	32.23

both single and binary systems when the sorbent dosage as well as the agitation rate increased. As for the effect of temperature, the removal of MB decreased with increasing temperature, however, an opposite trend was observed for the removal of RO16. Particle size of sorbent seem to have apparent effect on the adsorption of MB and RO16 in single and binary systems, that is, decreased particle size causes an increase in the percent removal of dye. The adsorption data was well fitted to Freundlich isotherm and pseudo-second order model in both sorption isotherm and kinetic studies, respectively. A significant increase in the percentage uptake of RO16 was observed in binary system as compared to single which indicates that there is a synergistic effect between the adsorbed dye molecules.

ACKNOWLEDGEMENTS

Financial support from the International Foundation of Science, Stockholm, Sweden and the Organisation for the Prohibition of Chemical Weapons, The Hague, The Netherlands via grant no. W/4368-1 as well as the lab facilities provided by Universiti Tunku Abdul Rahman (UTAR) are acknowledged.

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