



Dyes and Pigments 74 (2007) 446-453



# Low cost removal of disperse dyes from aqueous solution using palm ash

M. Hasnain Isa <sup>a,\*</sup>, Lee Siew Lang <sup>b</sup>, Faridah A.H. Asaari <sup>a</sup>, Hamidi A. Aziz <sup>a</sup>, N. Azam Ramli <sup>a</sup>, Jaya Paul A. Dhas <sup>c</sup>

<sup>a</sup> School of Civil Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia <sup>b</sup> Infineon Technologies (Kulim) Sdn. Bhd., Krystal Point II, I-4-20/21, Lebuh Bukit Kechil 6, Bayan Lepas, Penang, Malaysia <sup>c</sup> PENFABRIC, Penfabric Mill 4 (Head Office), Prai Free Industrial Zone 1, 13600 Prai, Penang, Malaysia

Received 12 November 2005; received in revised form 16 December 2005; accepted 27 February 2006 Available online 27 April 2006

#### **Abstract**

Palm oil and textile industries are important contributors to Malaysia's economic growth. However, these industries also generate various pollutants of the environment. This research explores the possibility of using a low cost adsorbent i.e. ash produced from palm oil factory, for the removal of dyes from aqueous solution. For the treatment to be truly low cost, not only should the adsorbent be easily and cheaply available in abundance but it should also require minimal or no pre-treatment, for expensive pre-treatment procedures would add to the overall treatment cost. Two commercial dyes i.e. disperse blue and disperse red were used. The study incorporates both batch as well as continuous flow experiments. The effects of different system variables, viz., pH, initial dye concentration and agitation time were studied in the batch tests. Acidic pH was found to favour dye removal. The optimum pH and agitation time for the removal of the two dyes were 2 and 60 min, respectively. Both Langmuir and Freundlich isotherms could be used to describe the adsorption of the dyes, with the former yielding somewhat better fits. The experimental data fitted well to the pseudo-second-order kinetic model with  $R^2 > 0.98$  for all concentrations (50–250 mg/l) tested. Column plugging was the main problem encountered due to the fine particle size of the ash. Pelletisation of ash using calcium oxide and calcium sulphate was not successful. For industrial application, pelletisation will have cost implications and may not be recommended. Ash may be better used in its natural form in batch process.

Keywords: Disperse dyes; Colour; Adsorption; Isotherms; Kinetics; Palm ash

#### 1. Introduction

Many industries such as textile, leather tanning, paper and pulp and food consume dyes extensively. Among them, textile industry ranks first in the usage of dyes for colouration of fibre [1]. Colour can cause hazards to the environment due to the presence of a large number of contaminants like toxic organic residues, acids, bases and inorganic contaminants. Some of the dyes are carcinogenic and mutagenic because they were formerly made by hazardous chemicals such as benzidine,

metals, etc. [2]. The discharge of coloured wastes into the receiving water bodies not only affects their aesthetic nature but also interferes with the transmission of sunlight and therefore reduces the photosynthetic activity [3]. This disturbs the natural equilibrium by affecting the aquatic life and food chain.

Due to the chemical stability of the dye components, conventional wastewater treatment technologies are often ineffective for handling wastewater containing synthetic textile dyes [4]. Considerable research has been done on colour removal from industrial effluents to decrease their impact on the environment. These technologies include adsorption onto inorganic or organic matrices, decolourisation by photo-catalysis or photo-oxidation processes, microbiological decomposition, chemical oxidation, ozonation and coagulation.

<sup>\*</sup> Corresponding author. Tel.: +604 599 6217; fax: +604 594 1009. *E-mail addresses:* mhisa@eng.usm.my, hasnain\_isa@yahoo.co.uk (M. Hasnain Isa).

Adsorption onto activated carbon has been proven to be an effective process for dye removal, but it is an expensive process. Consequently, numerous low cost alternatives have been proposed including peanut hulls [5], waste coir pith [3,6], corncob and barley husk [7], Indian Rosewood sawdust [8] and pine sawdust [9]. For an adsorption procedure to be truly low cost, not only should the adsorbent be easily and cheaply available in abundance but it should also require minimal or no pre-treatment, for expensive pre-treatment procedures would add to the overall treatment cost. An adsorbent requiring no pre-treatment was sought from oil palm due to its abundance in Malaysia. After oil extraction, large amounts of solid wastes i.e. empty fruit bunches (EFBs), shell and palm fibre are left behind. The EFBs are usually spread over estate ground as mulch whereas the shell and fibre can be used as boiler fuel supplement. A huge amount of ash is also produced in the oil extraction process. Isa et al. [10] have demonstrated the potential use of palm ash as an adsorbent. Their study, however, focussed on iron removal.

The purpose of this study was to evaluate the suitability of using palm ash for the adsorption of disperse dyes. The effects of pH, initial dye concentration and agitation time on the adsorption of disperse dyes onto ash were investigated. The Langmuir and Freundlich isotherm models were tested for their applicability. The experimental data were analyzed using the pseudo-first-order and second-order adsorption kinetic models and kinetic constants were evaluated.

### 2. Materials and methods

# 2.1. Ash and dyes

The boiler ash used as adsorbent in this study was collected from a local palm oil mill in Penang, Malaysia. It was used directly in the experiment without any pre-treatment. Two dyes viz., disperse blue and disperse red, were used in this study. Their commercial names are Begacron Blue BBLS 200% and Miketon Polyester Scarlet RCS, respectively.

An accurately weighed quantity of each dye was dissolved in distilled water to prepare the desired concentrations of dye solutions. For each dye type, the absorbance was read in the range of visible wavelengths (340–825 nm) using a spectrophotometer (Nova 60). The optimum absorbance wavelength was found to be 665 nm for disperse blue and 500 nm for disperse red. The absorbance at the optimum wavelengths was plotted against the corresponding concentrations of each dye to generate standard curves for use in the determination of dye concentrations after treatment.

# 2.2. Batch studies

Batch adsorption experiments were carried out by agitating 500 mg of the ash with 100 ml of dye solutions of desired concentrations and pH at room temperature using an orbital shaker operating at 200 rpm. Prior to the measurement of colour, the dye solutions were filtered through Whatman (no. 1) filter paper to exclude the adsorbent particles. Dye

concentrations were measured at the wavelengths corresponding to their maximum absorbance using a spectrophotometer (Nova 60).

The effect of pH was studied by adjusting the pH of dye solutions using 1 N  $H_2SO_4$  or 1 N NaOH solution. pH was measured using a pH meter. The effect of initial dye concentrations was carried out by shaking 100 ml dye solutions of desired concentrations (50, 100, 150, 200 and 250 mg/l) with 500 mg of the adsorbent. All the samples were adjusted to the optimum pH prior to the addition of the adsorbent. The samples were withdrawn from the shaker at pre-determined time intervals (5, 10, 20, 30, 60, 90, 120, 180, 240, 300 and 360 min). The amount of dye adsorbed onto the adsorbent,  $q_e$  (mg/g), was calculated by a mass—balance relationship:

$$q_{\rm e} = (C_0 - C_{\rm e}) \frac{V}{W} \tag{1}$$

where  $C_0$  and  $C_e$  are the initial and equilibrium state dye concentrations (mg/l), V is the volume of the solution (l) and W is the mass of the adsorbent used (g).

#### 2.3. Continuous flow studies

The continuous flow studies were conducted using disperse blue only. The methods tried are described in the following sections.

#### 2.3.1. Up-flow column test with ash as medium

The ash was filled in a glass column of height 20 cm and internal diameter (ID) 1 cm. Glass wool and wire mesh were fitted at the inlet and outlet of the column as supporting medium and to prevent the loss of the adsorbent particles. Distilled water was run through the column for cleaning prior to the experiment. Synthetic (coloured) wastewater was pumped through the column at the desired flow rate. To avoid channelling, the dye solution at the desired concentration was loaded to the column in an up-flow mode. The outlet tube directed the effluent to a measuring cylinder to measure the volume of the effluent collected at different times. The concentration of the dye solution in the effluent was monitored by collecting 5 ml of the effluent for analysis.

# 2.3.2. Up-flow column test with mixture of ash and inert sand as medium

The glass column (1 cm ID, 20 cm height) was clamped vertically and a layer of glass wool and wire mesh was inserted at the bottom. The space above the glass wool was filled with a 1:4 (w/w) mixture of ash and inert sand. Another layer of glass wool was placed on the top. The column medium was rinsed with distilled water to remove impurities before commencing the dye flow. The operation of the column and the analysis followed the description given in Section 2.3.1.

## 2.3.3. Pelletisation of ash

To increase the particle size and porosity of the column medium (ash), water hydration process [11] was adopted to

produce adsorbent pellets. A fixed amount of CaO (7.5 g) was added to 100 ml of distilled water at 70 °C. Simultaneously, 15 g of ash and 7.5 g CaSO<sub>4</sub> were added to the slurry. The slurry was heated up to 95 °C and was maintained at that temperature using a hot plate for 2 h. The water level was always monitored and maintained. The resulting slurry was then filtered and dried at 200 °C for 2 h to produce a dry powder type adsorbent. To pelletise the adsorbent, the powder was subjected to a pressure of 3 tonnes.

#### 3. Results and discussion

#### 3.1. Batch studies

#### 3.1.1. Effect of pH

pH plays an important role in the adsorption process; particularly on the adsorption capacity. The influence of pH on adsorption of the two dyes is shown in Fig. 1. For both the dyes the maximum removal (about 99%) was achieved at pH 2. As the pH was increased from 2 to 5 the removal of disperse blue and disperse red decreased to 5% and 19%, respectively. Thereafter, the percent removal remained low up to pH 12. Thus the optimum pH for further studies was adopted as 2 for both the dyes.

The results show that acidic pH was favourable for the adsorption of the two dyes. In the study by Ozacar and Sengil [2], the optimum pH for the adsorption of disperse dyes onto the calcined alunite also occurred at acidic condition. Solution's pH would affect both surface binding sites of adsorbents and aqueous chemistry [9]. In acidic condition, the positive charge dominates the surface of the adsorbent. Thus, a significantly high electrostatic attraction exists between the positively charged surface of the adsorbent and negatively charged dye species [12]. This attractive force increases the adsorption chances of dye species onto the surface of the adsorbents. As the pH of the system increases, the surface of the adsorbent tends to become negatively charged, which does not favour the adsorption of disperse dyes due to electrostatic repulsion. At the same time, the presence of excess OH<sup>-</sup>

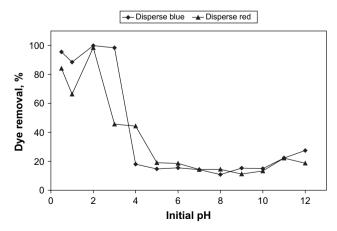


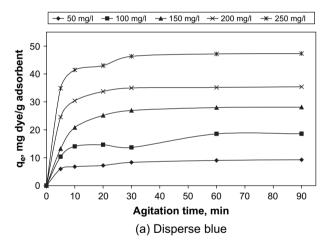
Fig. 1. Effect of pH on disperse dye removal by ash. (Adsorbent dosage, 500 mg per 100 ml; agitation time, 3 h; dye concentration, 50 mg/l.)

ions in alkaline pH will compete with the dye anions for the adsorption sites [12].

Low aqueous solubility of disperse dyes as reported by Ramakrishna and Viraraghavan [13] will result in a higher affinity for solid surfaces than for water. Disperse dyes are hydrophobic. As the solubility of disperse dyes in the aqueous solution is low, they have a tendency to accumulate at the surface of adsorbents [2]. Thus, the adsorption capacity will increase if the solubility of the dyes is low.

#### 3.1.2. Effect of initial dye concentration and agitation time

Fig. 2 shows the effect of dye concentration and agitation time on dye removal. The equilibrium time was found to be 60 min for both the dyes. The amount of dye adsorbed per unit weight of adsorbent increased with the increase in initial dye concentration. For disperse blue and dispersed red the amount of dye adsorbed increased from 9.0 to 47.2 mg dye/g adsorbent and from 10.5 to 48.6 mg dye/g adsorbent, respectively, when the initial dye concentration was increased from 50 mg/l to 250 mg/l. As other variables such as adsorbent dosage, pH and agitation speed were the same for different experimental runs, the dye concentration affected the diffusion



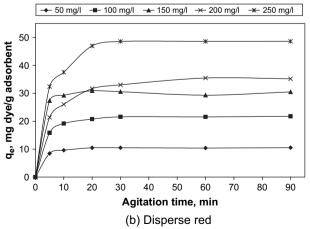


Fig. 2. Effect of initial dye concentration and agitation time on dye removal. (Adsorbent dosage, 500 mg per 100 ml; initial pH 2; agitation speed, 200 rpm; dye concentrations, 50 mg/l, 100 mg/l, 150 mg/l, 200 mg/l, 250 mg/l.)

of dye molecules through the solution to the surface of the adsorbent. Higher concentration resulted in higher driving force of the concentration gradient. This driving force accelerated the diffusion of dyes from the solution into the adsorbent [9].

It is clear that the efficiency of dye removal depends on the initial dye concentration. The amount of dye adsorbed increased with increase in dye concentration and remained nearly constant after the equilibrium time. A similar trend was reported for the adsorption of dyes such as malachite green onto treated sawdust [1], methylene blue onto treated Indian Rosewood sawdust [8], metal complex dyes onto pine sawdust [9], Congo Red onto coir pith [12] and Direct Red 12 onto biogas residual slurry [14].

#### 3.1.3. Adsorption isotherms

Two commonly used isotherms i.e. Langmuir and Freundlich were tested. The Langmuir isotherm and its linear form are represented by the following equations:

$$q_{\rm e} = \frac{bQ_0C_{\rm e}}{1 + bC_{\rm e}} \tag{2}$$

$$\frac{1}{q_{\rm e}} = \left[ \frac{1}{bQ_0} \right] \frac{1}{C_{\rm e}} + \frac{1}{Q_0} \tag{3}$$

where  $q_e$  is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g),  $Q_0$  denotes the adsorption capacity (mg/g), b indicates the energy of adsorption (l/mg) and  $C_e$  is the equilibrium concentration of the adsorbate in solution (mg/l).

The Freundlich isotherm and its linear form are represented by the following equations:

$$q_{\rm e} = K_{\rm f} C_{\rm e}^{1/n} \tag{4}$$

$$\ln q_{\rm e} = \ln K_{\rm f} + \frac{1}{n} \ln C_{\rm e} \tag{5}$$

where  $K_f$  is the Freundlich capacity factor and 1/n is the Freundlich intensity parameter.

Plots of the linear forms of Langmuir and Freundlich equations for the two disperse dyes yielded coefficients as shown in Table 1. Both the Langmuir and Freundlich isotherms were found to fit well to the experimental data, with the former being slightly better as indicated by the higher  $R^2$  values. The applicability of these isotherms suggests monolayer coverage of the dye on the surface of the ash. The characteristics of the Langmuir isotherm can be expressed

by a dimensionless constant, the equilibrium parameter  $R_L$  [3], which is defined by:

$$R_{\rm L} = \frac{1}{(1 + bC_0)} \tag{6}$$

where b is the Langmuir constant and  $C_0$  is the initial dye concentration (mg/l). The value of  $R_{\rm L}$  indicates whether the isotherm is unfavourable ( $R_{\rm L} > 1$ ), linear ( $R_{\rm L} = 1$ ), favourable ( $0 < R_{\rm L} < 1$ ) or irreversible ( $R_{\rm L} = 0$ ) [2]. From the b values (Table 1) and the range of dye concentrations (50–250 mg/l) tested, it follows that  $R_{\rm L}$  lies between 0 and 1 i.e. the adsorption is favourable.

The Freundlich equation describes heterogeneous systems and reversible adsorption; and is not limited to the formation of a complete monolayer. It can be seen from Table 1 that the correlation coefficients for Freundlich isotherms are only slightly less than those obtained for the Langmuir expression. Thus, Freundlich isotherm cannot be totally rejected in the equilibrium studies.

The Freundlich intensity parameter, 1/n, indicates the deviation of the adsorption isotherm from linearity. If n = 1, the adsorption is linear i.e. the adsorption sites are homogeneous and there is no interaction between the adsorbed species. If 1/n < 1, the adsorption is favourable; the adsorption capacity increases and new adsorption sites appear. If 1/n > 1, the adsorption is unfavourable; the adsorption bonds become weak and the adsorption capacity decreases. The values of 1/n for disperse blue and disperse red being less than 1 (Table 1) indicate favourable adsorption. The Langmuir and Freundlich expressions for disperse blue and disperse red removal by ash can be represented as below:

Langmuir equation,

Disperse blue : 
$$q_e = \frac{624.9C_e}{1 + 12.625C_e}$$
 (7)

Disperse red : 
$$q_e = \frac{23.8C_e}{1 + 0.3872C_e}$$
 (8)

Freundlich equation,

Disperse blue : 
$$q_e = 64.5C_e^{0.4493}$$
 (9)

Disperse red: 
$$q_e = 17.7C_e^{0.3863}$$
 (10)

# 3.1.4. Adsorption kinetics

Kinetic modelling was examined to investigate the mechanism of adsorption and the potential rate-controlling processes

Table 1 Langmuir and Freundlich isotherm constants and correlation coefficients

Dye	Langmuir isotherm coefficients			Freundlich isotherm coefficients			
	$\overline{Q_0}$	b	$R^2$	$K_{ m f}$	1/n	$R^2$	
Disperse blue	49.50	12.6250	0.9489	64.54	0.4493	0.9320	
Disperse red	61.35	0.3872	0.9546	17.67	0.3863	0.8253	

such as mass transfer and chemical reaction. The pseudo-firstorder and pseudo-second-order kinetic models were used to analyse the adsorption kinetics of the disperse dyes. The two kinetic models and their linear forms are as follows:

Pseudo-first-order model,

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k_1(q_\mathrm{e} - q) \tag{11}$$

$$\ln(q_e - q) = \ln q_e - k_1 t \tag{12}$$

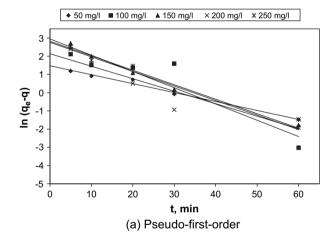
Pseudo-second-order model,

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k_2 (q_\mathrm{e} - q)^2 \tag{13}$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{14}$$

where  $q_e$  and q are the amounts of dye adsorbed (mg/g) at equilibrium and at time t, respectively.

Figs. 3 and 4 show the linear plots of the pseudo-first-order and pseudo-second-order models for disperse blue and disperse red, respectively. Table 2 shows the values of  $k_1$ ,  $k_2$ ,  $q_{\rm e}$  and  $R^2$  for the models. The results show good agreement of the experimental data with the pseudo-second-order model compared to the pseudo-first-order model for both the dyes.



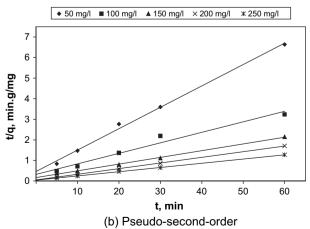
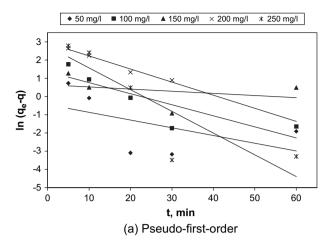


Fig. 3. Plots of kinetic models for disperse blue adsorption on ash.



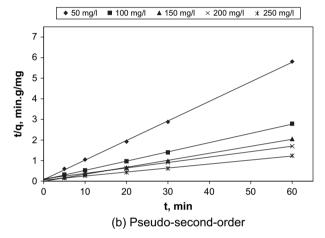


Fig. 4. Plots of kinetic models for disperse red adsorption on ash.

As can be seen from Table 2, the correlation coefficients for the second-order kinetic model were greater than 0.98 for all cases. And the calculated  $q_{\rm e}$  values also agreed well with the experimental data. It can therefore be inferred that both the dye adsorption systems followed the pseudo-second-order kinetic model, for which the rate-limiting step may be chemisorption [2,15,16]. A similar phenomenon was observed in the adsorption of reactive blue 114, reactive yellow 64 and reactive red 124 onto calcined alunite [2], Congo Red onto coir pith [12], reactive red 222, reactive yellow 145 and reactive blue 222 onto swollen chitosan beads [15], reactive red 189 onto chemical cross-linked chitosan beads [16] and acid blue 193 onto Na-bentonite and DTMA-bentonite [17].

## 3.2. Continuous flow studies

# 3.2.1. Up-flow column test with ash as medium

The test was conducted with an influent dye (disperse blue) concentration of 1000 mg/l. The removal efficiency of the dye in the column test was very encouraging. The leakage of dye in the effluent was barely detectable. However, operation of the column filled with ash was difficult consequent of the excessive head loss and reduction in flow velocity due to the fine particle size of the ash. Throughout the experiment, frequent

Table 2 Parameter values<sup>a</sup> of pseudo-first-order and pseudo-second-order models

Dye type and initial	$q_{\rm e,exp}~({\rm mg/g})$	Pseudo-first-order model			Pseudo-second-order model		
concentration (mg/l)		$k_1  (\text{min}^{-1})$	q <sub>e,cal</sub> (mg/g)	$R^2$	k <sub>2</sub> (g/mg min)	q <sub>e,cal</sub> (mg/g)	$R^2$
Disperse blue							
50	9.27	0.0491	4.37	0.9867	0.0220	9.72	0.9986
100	18.59	0.0891	18.96	0.8521	0.0075	19.88	0.9882
150	28.12	0.0794	16.76	0.9839	0.0076	29.76	0.9988
200	35.41	0.0684	8.42	0.8360	0.0158	36.23	0.9998
250	47.33	0.0799	15.83	0.9762	0.0158	48.08	0.9995
Disperse red							
50	10.47	0.0424	0.64	0.2740	0.1123	10.55	0.9998
100	21.71	0.0608	3.92	0.7273	0.0311	22.08	0.9999
150	30.90	0.0117	1.90	0.1036	0.0895	30.40	0.9990
200	35.40	0.0719	19.01	0.9763	0.0077	36.76	0.9995
250	48.68	0.1193	16.16	0.7414	0.0091	50.25	0.9992

 $q_{e,exp} = \text{Experimental value}, q_{e,cal} = \text{calculated value (from model)}.$ 

adjustments needed to be made to the variable speed pump because of the increased resistance to flow in the column with time due to the ash fines. A constant flow rate of 0.5 ml/min could be maintained at the beginning (up to about 90 min) of the run, thereafter column plugging started and reached a critical level (after about 260 min of operation) at which the flow rate was reduced to only 0.08 ml/min although the pump was running at its maximum speed. The run had to be terminated before a complete breakthrough curve was obtained.

Maintaining a constant flow rate is important because it determines the residence time in the column and thus the time of contact between the adsorbate and the adsorbent [18]. When the flow rate and velocity through the bed decrease, there is more time for adsorption on each layer [19]. But long contact times are not practicable in industrial applications because higher equipment costs would be required.

# 3.2.2. Up-flow column test with a mixture of ash and inert sand as medium

To overcome the problems associated with high head loss due to fine ash particles, the column test procedure adopted by Agyei et al. [20] was followed. Inert sand was mixed with ash to improve the bed porosity. Before the inert sand was put to use, a batch test was carried out to check its adsorption capacity for the disperse dye. It was found that the difference in disperse blue concentration before and after the test was 10%. It was therefore concluded that the sand might be regarded as inert with respect to dye adsorption. Ash was mixed with sand in the ratio of 1:4 (w/w) and the mixture was used for the column test. Fig. 5 shows the plot of the ratio of effluent dye concentration to the initial dye concentration (1000 mg/l) versus the cumulative volume of the effluent. A complete breakthrough curve was almost achieved with the ash and inert sand mixture. From Fig. 5, the breakthrough volume was found to be about 35 ml when the effluent dye concentration was 5% of the initial concentration. The highest effluent dye concentration was about 90% of the initial concentration when the cumulative volume reached 58 ml.

The flow rate reduced after the column was operated for about 90 min (Fig. 6). This may be due to the high head

loss that occurred when the ash formed a layer at the top of the inert sand bed. At the beginning of the run, the mixture of ash and inert sand was not stratified. The flow was able to pass through the bed without high pressure loss. But after the initial rinsing with distilled water and continued column operation, the inert sand with higher density started to settle down at the bottom of the column whereas the ash with lower density tended to suspend. The ash gradually built up a layer above the inert sand and the resistance to flow progressively increased. Finally, the medium in the column was stratified into two distinct layers i.e. ash and inert sand. The resistance to flow increased as it passed through the layer of ash. The residence time of the dye solution in the column increased due to the slow flow rate. The effluent became clearer after the flow rate was reduced (Fig. 5) and again the complete breakthrough curve could not to be established by using this method either.

# 3.2.3. Pelletisation of ash

Previous column test results showed that the low density and small particle size of the ash resulted in high resistance to flow and prolonged residence time in the column. These operational difficulties will limit the application of the ash as an

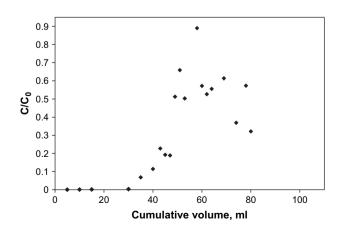


Fig. 5. Ratio of the effluent dye concentration to initial dye concentration ( $C/C_0$ ) versus cumulative volume of dye solution for up-flow column test with a mixture of ash and inert sand in the ratio of 1:4 as medium.

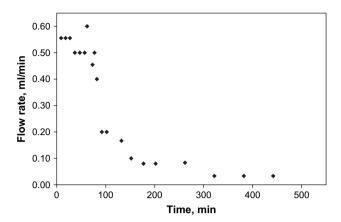


Fig. 6. Flow rate versus time for the up-flow column test with a mixture of ash and inert sand in the ratio of 1:4 as medium.

adsorbent. To study the efficacy of adsorption by ash in continuous flow, pelletisation following the procedure described earlier was tried.

This method was used successfully to develop pellet type adsorbent from power plant fly ash [11]. However, in the present case the process failed to develop the ash pellets. Only a very small part of the powder mixture of ash, CaO and CaSO<sub>4</sub> was bound. The strength of the pellet was very weak. It would be crushed to powder easily. The failure of the pelletisation process may be due to several reasons. The chemical constituents in the power plant fly ash may be different from the organic ash used in this study. Thus, the chemical reactions between the adsorbents and chemical binders were not the same. Thus, CaO and CaSO<sub>4</sub> may not have been suitable binders in this study. Several other chemical binders under different reaction conditions have been used in pellet production, such as kaolin and starch to bind rice hull ash [21] and sugarcane molasses, sugar beet molasses, corn syrup and coal tar to bind sugarcane bagasse, rice hulls and rice straw [22].

The conditions such as the ratio of binders to the adsorbent, the period of hydration, the drying temperature and the compression force play an important role in the pelletisation process. It appears that the procedure [11] adopted in this study could not provide optimum conditions for the pelletisation of oil palm ash. Detail physical and chemical studies of the ash are required to select a suitable chemical binder. Further studies will also be required for the pelletised adsorbent because the adsorbent's characteristics may change due to the add-in chemical binders and the chemical reactions. The efficacy of the pelletised adsorbent will have to be determined through a new set of batch studies and compared with the original adsorbent's adsorption capacity. The pelletisation process, however, will have additional cost implications and affect the status of ash as an economical adsorbent.

#### 4. Conclusions

In the laboratory-scale studies conducted, palm ash was capable of adsorbing disperse blue and disperse red dyes effectively from aqueous solutions. The adsorption capacity of the ash for the dye removal was found to be affected by the solution's pH, with lower pH favouring adsorption. This was attributed to the presence of excess positive charge on its surface. Over 99% removal was achieved for both the dyes at pH 2. The required low pH will have an impact on the operating cost in real practice, but the adsorbent (ash) itself is virtually free. An analysis of the economy of ash application as adsorbent will have to take into consideration both these factors. The amount of disperse dyes adsorbed increased with the increase in contact time and initial dye concentrations. The equilibrium time for both the dyes was 60 min. Adsorption of the disperse dyes could be described by both the Langmuir and Freundlich isotherms, with the former yielding somewhat better fits. The adsorption kinetics followed the pseudosecond-order model indicating that chemisorption was the rate-controlling step in the adsorption of the dyes.

The major difficulty encountered in the continuous flow studies was column plugging because of the fine particle size of ash. Different arrangements of the column media were tried, in vain, to achieve a constant dye solution flow rate through the column. The breakthrough curve could not be obtained due to excessive head loss and continuous reduction in flow rate. Thus, ash was considered unsuitable for continuous flow applications. An attempt to convert the ash into pellet also failed and the mixture of ash, calcium oxide and calcium sulphate remained in powder form after compression.

Ash is an unwanted by-product of the palm oil industry and its pre-treatment is not desirable especially from the view point of economy. The difficulties encountered in running the column tests and the high treatment efficiencies obtained in the batch tests suggest that ash may be better used in its natural form in batch process.

# Acknowledgement

The authors acknowledge the research grant provided by Universiti Sains Malaysia, Penang that has resulted in this article.

#### References

- Garg VK, Gupta R, Yadav AB, Kumar R. Dye removal from aqueous solution by adsorption on treated sawdust. Bioresource Technology 2003;89:121-4.
- [2] Ozacar M, Sengil AI. Adsorption of reactive dyes on calcined alunite from aqueous solutions. Journal of Hazardous Materials 2003; 98:211-24.
- [3] Namasivayam C, Radhika R, Suba S. Uptake of dyes by a promising locally available agricultural solid waste: coir pith. Waste Management 2001;21:381-7.
- [4] Forgacs E, Cserhati T, Oros G. Removal of synthetic dyes from wastewaters: a review. Environment International 2004;30:953-71.
- [5] Ernst WR. Adsorption of textile dyes from aqueous solution by activated carbon from peanut hulls. USA: Georgia Institute of Technology; 1979.
- [6] Namasivayam C, Kumar MD, Selvi K, Begun RA, Vanathi T, Yamuna RT. Waste coir pith — a potential biomass for the treatment of dyeing wastewaters. Biomass and Bioenergy 2001;21:477–83.

- [7] Robinson T, Chandran B, Nigam P. Removal of dyes from an artificial textile dye effluent by two agricultural waste residues, corncob and barley husk. Environment International 2002;28:29–33.
- [8] Garg VK, Amita M, Kumar R, Gupta R. Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste. Dyes and Pigments 2004;63:243-50.
- [9] Ozacar M, Sengil AI. Adsorption of metal complex dyes from aqueous solutions by pine sawdust. Bioresource Technology 2005;96:791–5.
- [10] Isa MH, Al-Madhoun WA, Aziz HA, Asaari FAH, Sabiani NHM. Fe removal by adsorption using ash from palm oil factory, Third national civil engineering conference (AWAM 2004). Penang, Malaysia: Universiti Sains Malaysia; 2004.
- [11] Lee KT. Flue gas desulfurization studies using absorbent prepared from coal fly ash. PhD thesis, School of Chemical Engineering, Universiti Sains Malaysia, Penang, Malaysia; 2004.
- [12] Namasivayam C, Kavitha D. Removal of Congo Red from water by adsorption on activated carbon prepared from coir pith, an agricultural solid waste. Dyes and Pigments 2002;54:47-58.
- [13] Ramakrishna KR, Viraraghavan T. Use of slag for dye removal. Waste Management 1997;17:483—8.
- [14] Namasivayam C, Yamuna RT. Adsorption of direct red 12B by biogas residual slurry: equilibrium and rate processes. Environmental Pollution 1995;89:1-7.

- [15] Wu FC, Tseng RL, Juang RS. Enhanced abilities of highly swollen chitosan beads for color removal and tyrosinase immobilization. Journal of Hazardous Materials 2001;B81:167-77.
- [16] Chiou MS, Li HY. Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads. Chemosphere 2003;50: 1095–105.
- [17] Ozcan AS, Erdem B, Ozcan A. Adsorption of acid blue 193 from aqueous solutions onto Na-bentonite and DTMA-bentonite. Journal of Colloid and Interface Science 2004;280:44—54.
- [18] Benefield LD, Judkins JF, Weand BL. Process chemistry for water and wastewater treatment. USA: Prentice Hall, Inc.; 1988.
- [19] Droste LR. Theory and practice of water and wastewater treatment. USA: John Wiley & Sons Inc.; 1997.
- [20] Agyei NM, Strydom CA, Potgieter JH. The removal of phosphate ions from aqueous solution by fly ash, slag, ordinary Portland cement and related blends. Cement and Concrete Research 2002;32:1889–97.
- [21] Chou KS, Tsai JC, Lo CT. The adsorption of Congo Red and vacuum pump oil by rice hull ash. Bioresource Technology 2001;78:217–9.
- [22] Ahmedna M, Marshall WE, Rao RM. Granular activated carbons from agricultural by-products: preparation, properties, and application in cane sugar refining. Available from World Wide Web: <a href="http://www. Isuagcenter.com/communications/paths\_bak/lae869carbons.pdf">http://www. Isuagcenter.com/communications/paths\_bak/lae869carbons.pdf</a>; 2000 [online] [accessed 31st March 2005].