Adsorption of reactive dyes using shale oil ash in fixed beds

Z. Al-Qodah and W. Lafi

ABSTRACT

A series of batch and dynamic column experiments were carried out for adsorbing reactive dyes present in textile mill effluents under different conditions. Jordanian shale oil ash, produced by burning oil shale at 800°C, was used to adsorb these dyes in a fixed bed adsorber. The bed depth service time (BDST) model was applied to illustrate the bed performance. The experimental and predicted results are compared for various operating conditions. The effects of feed flow rate, inlet concentration, adsorbent article diameter and temperature on the bed service time and performance are considered. It was found that the rate at which the breakthrough point is achieved increases with increasing temperature and inlet concentration, and decreases as the particle size increases. The results indicate that a bed of 0.20 m in height and 0.025 m in diameter is adequate for full development of the adsorption zones in all experiments. The spent adsorbent was easily regenerated by burning at 600°C. The results obtained indicate that shale oil ash has potential as an adsorbent and could be easily used in continuous processes. In addition, the BDST model gave reasonable results in predicting the bed performance using the relationships proposed by previous researchers or proposed in this study.

Key words | adsorption of acid reactive dyes, breakthrough curves, dynamic adsorption, fixed-bed adsorbers, industrial wastewater treatment

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INTRODUCTION

The presence of colored compounds such as dyes in industrial wastewater has been of great concern because these compounds usually have many adverse effects on the treatment processes. These materials impede light penetration in the treatment pans, thus upsetting the biological treatment processes within the treatment plant. In addition, these dyes are toxic in nature and increase the BOD, thus reducing the dissolved oxygen concentration. They may also cause direct destruction or inhibition of the activated sludge catalytic capabilities (Asfour *et al*. 1985). Therefore, a treatment process is required to remove or reduce the concentration of dyes in the industrial effluents before they undergo biological treatment.

Adsorption beds are widely used for purification of industrial streams and are gaining prominence as treatment processes. These beds usually produce good quality effluents containing low concentrations of dissolved organic materials, such as dyes, thus meeting environmental restrictions (Mckay & Allen 1983; Mckay *et al*. 1984). It is well known that activated carbon is the most effective and widely used adsorbent for removing aqueous pollutants. It was successfully used in fixed bed adsorbers for the treatment of textile effluents (Walker & Weatherley 1997). However, there is growing interest in using low cost, commercially available materials for the adsorption of dyes. A wide variety of materials are being used as low cost alternatives to activated carbon (Gupta *et al*. 1997; Al-Qodah 2000).

In a previous study shale oil ash (SOA), developed after the direct combustion of the shale oil, was used as an adsorbent for reactive dyes (Al-Qodah 2000). Equilibrium uptake and sorption dynamics showed that SOA has good

potential as a cheap and efficient adsorbent for reactive dyes found in textile processing wastewater. Because the adsorption isotherms do not give accurate scale-up data in fixed bed systems, lab scale studies are essential for industrial-scale design (Gupta 1998). For this reason, this study is directed to investigate the practical applicability of SOA by employing this adsorbent in continuous fixed bed operations. In this study the effect of some process variables, i.e. solution flow rate, bed height, initial adsorbate concentration and temperature on the performance of a fixed bed packed with shale oil ash as an adsorbent will be studied.

MATHEMATICAL MODELING

Modeling of continuous adsorption systems is challenging, because the general dynamics of a fixed bed process are rather complex (Yu & Wang 1989). These systems usually show strong non-linearities in the adsorption isotherms, significant mass transfer resistance between the fluid phase and the solid phase, and the presence of dispersion in the fluid phase (Kaczmarski *et al.* 1995).

Generally, there are three steps in developing a mathematical model for the description or prediction of the adsorption dynamics. The first step is to provide a representation of the equilibrium behavior via a convenient isotherm model. The second step is to characterize the associated rate phenomena according to the relative importance of the mass transport resistance of the adsorbate. The final step is to apply the thermodynamic principle of mass continuity or conservation of mass for each component of interest within each phase in the adsorber.

While the first two steps were the subject of a previous study (Al-Qodah 2000) in which the adsorption kinetics of reactive dyes onto shale oil ash were investigated, this paper deals with the third step. According to the previous study, the experimental isotherm and kinetic data were excellently fitted with the Langmuir isotherm model and the two-resistance film and homogeneous solid phase diffusion model, respectively.

One of the most critical aspects of the design of a fixed bed adsorber involves characterization of the effluent concentration profile as a function of time of operation. This profile, commonly referred to as the breakthrough curve, represents the specific combination of equilibrium and rate factors that control the adsorption process. Most of the models for the design of fixed bed adsorbers are based on the mathematical analysis and prediction of the shape of breakthrough curves. One of these models is the bed depth service time (BDST) model, which has been reported as a simplified approach because it offers a rapid prediction of the adsorber performance (Mckay & Bino 1990; Walker & Weatherley 1997). This model deals with the movement of the adsorption zone through the bed. A simple form of the model proposed by Hutchins (1973) is represented by the following linear equation:

$$t = sZ + c \tag{1}$$

where the slope $s = N_o/C_o F$ and the intercept $c = 1/LC_o \ln C_o/C_b - 1$.

At 50% breakthrough, or the time at which the value of the exit concentration of the dye equals half its inlet concentration, i.e. $C_b = C_o/2$ then t is called as $t_{0.5}$, and as a consequence Equation 1 becomes as the following:

$$t_{0.5} = cZ \tag{2}$$

Consequently, a plot of BDST at 50% breakthrough against bed height should be a straight line passing through the origin.

Hutchins (1973) proposed the following two equations to evaluate the effect of changing the initial adsorbate concentration, C_o, on the slope and the intercept of the line, respectively:

$$s_2 = s_1 \left(\frac{C_1}{C_2} \right) \tag{3}$$

$$c_2 = c_1 \left(\frac{C_1}{C_2} \right) \frac{\ln \frac{C_2}{C_b} - 1}{\ln \frac{C_1}{C_b} - 1} \tag{4}$$

where s_1 and s_2 are the two slopes of the BDST lines of two different initial concentrations C_1 and C_2, respectively.

Mckay & Bino (1990) proposed the following expression to evaluate the effect of changing the adsorbate flow rate on the slope of Equation 4 and reported that the intercept in that equation remains the same:

$$s_2 = s_1(F_1/F_2) \qquad (5)$$

where s_1 and s_2 are the slopes of the BDST lines at F_1 and F_2, respectively.

Based on preliminary experimental results it was found that the adsorption of reactive dyes onto shale oil ash is an endothermic process in a temperature range from 20 to 50°C. This means that the adsorption capacity increases as temperature increases within this range. Based on the experimental results obtained in this study, the following proposed equation could describe the effect of changing the temperature on the slope of Equation 1:

$$s_2 = s_1(t_2/T_1)^n \qquad (6)$$

where s_1 and s_2 are the slopes of the BDST lines at T_1 and T_2, respectively, and n is a constant. The value of n was estimated from the experimental and BDST results. The applicability of the above equations will be tested in the present system of SOA as an adsorbent and the adsorbate of reactive dyes in a fixed bed.

MATERIALS AND METHODS

Analytical methods

Spectroscopic analysis was carried out using a PV 8700 visible spectrophotometer (Philips Scientific). Samples of the effluent dye solution of about 1 ml were diluted with distilled water if necessary, then the concentration was measured with 1.0 cm light path glass cells. The chemical composition of the ash was determined by X-ray fluorescence technique (Diano, USA). The material is first fluxed and formed into pellets. The X-ray analyzer reads the major 10 components of the sample. The density of the ash was determined using the specific gravity bottles, and its porosity was determined by the mercury porosimeter.

Table 1 │ Some properties of the reactive dyes used

Dye	Drim yellow-K4G	Drim blue-KBL	Drim red K4BL
Type	Azo dye	Anthraquanine dye	Azo dye
Wave length	420	620	530
pH	4.5 (acidic)	6.5 (acidic)	7.5 (basic)

The specific surface area of the ash was measured using a surface area analyzer (Core Lab., Agait, Canada).

Material preparation

The shale oil ash (SOA) used in this study was obtained from the Authority of Natural Resources, Jordan. Samples of this material were burned at 800°C for 4 h. The residual ash was cooled, then milled and sieved to several fractions. Three fractions of 302.5, 425 and 600 μm median diameter were used. The size intervals for the above fractions are 255–350, 350–500 and 500–700 μm, respectively. The studies were conducted with the ash of 300 μm unless stated otherwise.

The SOA was first mixed with warm distilled water and stirred for 30 min in order to remove the adhering impurities and to dissolve the soluble portion of the ash. The ash was then filtered and dried before using it in the continuous adsorption experiments.

The reactive dyes used in this study are listed in Table 1. These dyes were used as received from Jordan Spinning and Weaving Co. Ltd (JSWCO), Zarka, Jordan.

Column studies

The continuous experiments were carried out in a bench-scale fixed-bed reactor packed with shale oil ash. A schematic representation of the adsorption system is shown in Figure 1. It consists of a plexiglas column of 0.025 m internal diameter and 0.5 m height. The column is surrounded by a water jacket, which is connected to a thermostat (Grant Instruments, England) in order to
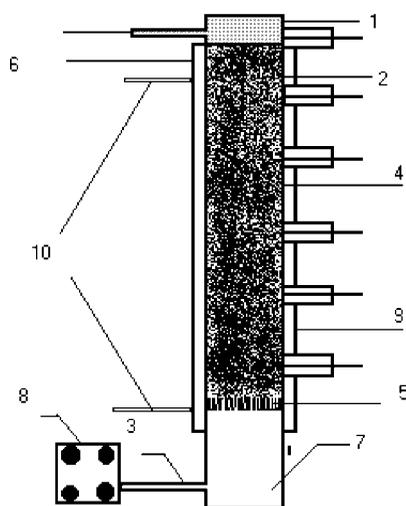
Figure 1 │ Schematic diagram of the continuous adsorber: 1 plexiglas column,
2 sampling port, 3 adsorber inlet, 4 shale oil ash particles, 5 supporting grid,
6 adsorber outlet, 7 polyethylene particles, 8 peristaltic pump, 9 water jacket,
10 thermostat.

maintain isothermal conditions in each experiment. A stainless steel grid of 0.15 mm pore diameter is mounted at the base of the column to support the adsorbent particles. The dye solution enters the bed through a distribution section of 0.07 m height packed with polyethylene particles of 1 mm diameter to ensure uniform liquid distribution in the bed. Six sampling ports closed with rubber seals are mounted and axially spaced at 0.05 m intervals on the column wall. A hypodermic needle was used to withdraw samples from the center of the bed through these ports at regular time intervals. Samples of the adsorbent were wetted for 20 h in distilled water then fed to the water-filled column as slurry in order to expel the gas pockets that are entrained within the adsorbent particles.

Aqueous solutions of the dyes were formulated in concentrations ranging from 50 to 250 mg dm^{-3}. These values are similar to the varying dye concentrations found in wastewater discharged from textile plants. The solutions were pumped to the bed in up-flow mode from a 20-dm^3 plexiglas tank using a variable speed peristaltic pump (Gallenkamp, England). A variable speed mixer (Stuart Scientific, England) was installed in the feed tank to ensure that the dye concentration is uniform.

Regeneration

At the end of each experiment, the spent adsorbent particles were withdrawn from the column to a tank and stirred with distilled water for 30 min. After filtration of the ash, it was transferred to an oven where it was dried at 110°C for 1 h and finally heated again to 600°C and kept at this temperature for 2 h. In this procedure the adsorptive capabilities of the ash are regenerated, as part of the adsorbed dye molecules are extracted by water and the remainder are burned in the oven.

RESULTS AND DISCUSSION

Characterization of the adsorbent material

The approximate chemical analysis of shale oil ash is as the following: 32% CaMg (CO$_3$)$_2$, 19% clay, 16% CaCO$_3$, 15% SiO$_2$, 10% NaAlSi$_3$O$_8$, 6% KAlSi$_3$O$_8$ and 1% FeS$_2$.

The bulk density of the ash particles is 1450 kg/m^3 and the porosity is about 0.42. The specific surface area of the fraction of 300 μm was about 100 m^2/g. The material is amorphous in nature and quite stable in water, salt solutions and weak acids. It was observed that the particles of the ash became brittle and tended to disintegrate after five to six cycles of adsorption and regeneration.

Adsorption isotherm

According to the results obtained in a previous study (Al-Qodah 2000), the isotherm data fit well to the Langmuir isotherm represented by Equation 7. The linear form of Langmuir can be represented by Equation 8:
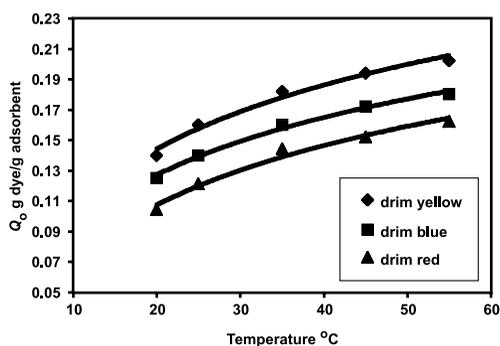
$$q_e = \frac{aC_e}{1 + bC_e} \tag{7}$$

$$\frac{1}{q_e} = \frac{1}{aC_e} + \frac{b}{a} \tag{8}$$

where a represents the ratio of the adsorption to desorption rates at equilibrium and a/b represents the adsorbed amount of dye to complete a monolayer cover on the adsorbent. The Langmuir isotherm parameters a and b were obtained by plotting the value $1/q_e$ versus $1/C_e$. After

Table 2 │ Values of the two isotherm parameters of shale oil ash (d_p=425 μm) with drim yellow, drim blue and drim red at 25°C

Parameter	a (ml/g)	b (ml/g)
Drim yellow	6,944	25,461
Drim blue	5,988	36,690
Drim red	3,152	26,040

Table 3 │ The thermodynamic parameters for the adsorption of reactive dyes with shale oil ash

Dye	Parameter ΔG^o (kJ/mole)	ΔH^o (kJ/mole)	ΔS^o (kJ/mole K)
Drim yellow	– 17.67	17.99	119.6
Drim blue	– 16.63	18.97	1119.4
Drim red	– 11.42	14.32	99.63

Figure 2 │ Effect of temperature on the Langmuir monolayer capacity of the adsorbent from three different dyes (C_0=200 mg/l, F=40 ml/min, D=0.425 mm).
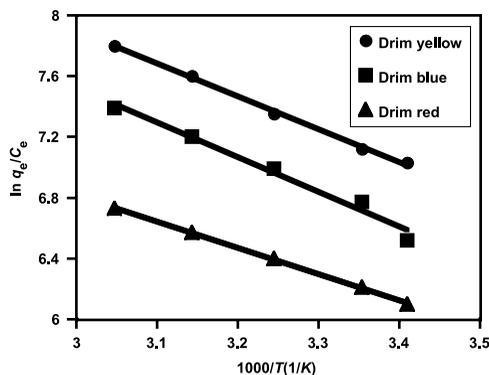
Figure 3 │ Van't Hoff plot for the adsorption of drim dyes with shale oil ash (C_0=200 mg/l, F=40 ml/min, D=0.425 mm).

fitting the data using the computer program "Origin", Equation 8 becomes as Equation 9:

$$\frac{1}{q_e} = \frac{0.1442}{C_e} + 4.395 \tag{9}$$

The value of R^2 for Equation 9 is 0.9957. Table 2 shows the values of the parameters of the Langmuir model at 25°C for the three dyes.

The ratio a/b in the Langmuir isotherm is defined as the maximum uptake, or Langmuir monolayer capacity Q_o. The effect of temperature on this ratio is shown in Figure 2. It is evident that Q_o increases as the temperature increases, thereby indicating that the adsorption of reactive dyes with shale oil ash is endothermic in nature. This behavior could be referred to as the changes in the size of the pores of the adsorbent particles as well as the increase in the number of active sites due to the breaking of some internal bonds near the edge of the particle at higher temperatures (Gupta 1998).

The change in standard Gibbs free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔSG^o) are shown in Table 3. These values were obtained using the Van't Hoff equation:

$$\Delta G^o = - RT \ln K \tag{10}$$

$$\ln K = \Delta S^o/R - \Delta H^o/RT \tag{11}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{12}$$

where K is the distribution coefficient defined as q_e divided by C_e. T is the absolute temperature. A plot of $\ln K$ versus $1/T$ produces a straight line as shown in Figure 3. The slope of this line is $-\Delta H^o/R$ and the intercept is $\Delta S^o/R$.

A negative value of ΔG^o indicates that the process of adsorption of reactive dyes with shale oil ash is spontaneous and confirms the feasibility of the process.
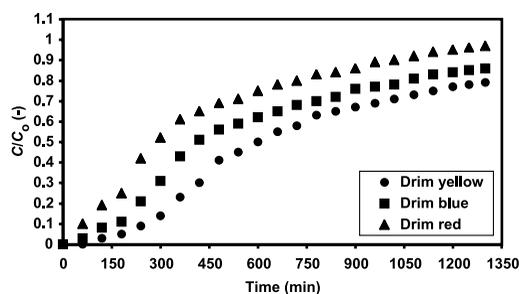
Figure 4 | Breakthrough curves for three different dyes at a height of 0.2 m (C_o=200 mg/l, F=40 ml/min, D=0.425 mm, T=25°C).

However, these values are relatively small, which is indicative of the diffusion-controlled process. In addition, the positive values of ΔS^o reflect the affinity of the ash material to the reactive dye molecules and suggest some structural changes in both the adsorbent and the adsorbate.

Column performance

The prediction of column breakthrough, or the shape of the adsorption wave front, which determines the operating life span of the bed, is considered as the most important criterion in the design of packed bed adsorbers (Walker & Weatherly 1997). The breakthrough point represents the ratio of the exit to the inlet concentration of the adsorbate. Generally, the value of this point is chosen for the process depending on the nature of the adsorbate. In the case of heavy metals the value of 20% is enough. If the exit adsorbate concentration reaches the breakthrough point this means that the bed is exhausted and needs regeneration. For a given adsorbent and a given adsorbate, many process variables affect bed breakthrough curves. These include the adsorbent bed height, adsorbate flow rate and temperature. The effect of these on the performance of a bed of shale oil ash in contact with reactive dyes is evaluated and discussed. The discussion includes a comparison between the experimental results and those predicted by the BDST model.

Figure 4 shows typical breakthrough curves for the adsorption of three different dyes from single solute solutions onto shale oil ash. The initial concentration of the

three dyes C_o was 200 mg/l, the bed height was 0.2 m and the flow rate was 40 ml/min. It can be estimated from Figure 4 that after 1300 min of continuous operation the concentrations of drim red, drim blue and drim yellow in the effluent were 150, 166 and 190 mg/l, respectively. In addition, Figure 4 shows the 50% breakthrough point of the three dyes, e.g. when the relative effluent concentration of drim yellow $C/C_o = 0.50$ the adsorption time is 580 minutes. The adsorbed quantity of drim yellow during this time could be calculated by collecting the effluent during these 580 minutes and measuring the dye concentration in it. The following equation then could be applied:

$$A = V_b(C_o - C) \tag{13}$$

This quantity A is then divided by the mass of the bed to obtain the loading capacity of the adsorbent at the 50% breakthrough point. This value for drim yellow was found to be 0.045 g dye/ g adsorbent. At this point, the adsorbed quantity is equivalent to 45% of that adsorbed in the batch experiments. The difference between the batch and continuous capacity could be attributed to the channeling of the flowing stream. This problem usually occurs in the fixed beds. In addition, the effective surface area of the packed particles in the fixed beds is usually lower than that in stirred tank vessels. This result indicates that the ash behaves as a good adsorbent of the three dyes. It appears in Figure 4 that the operation time t_o, needed for the dye to appear in the effluent, depends on the dye. The values of these times are 300, 250 and 200 min for drim yellow-K4G, drim blue-KBL and red K4BL, respectively. This indicates that a bed of 0.20 m in height and 0.025 m in diameter is adequate for full development of the adsorption zones in all experiments.

Effect of bed height

Figure 5 illustrates the effect of bed height on the adsorption process via breakthrough curves at four axial heights. It is evident in the plot that at certain bed heights the dimensionless concentration C/C_o increases with time. For example, at a bed height of 0.10 m, C/C_o increases
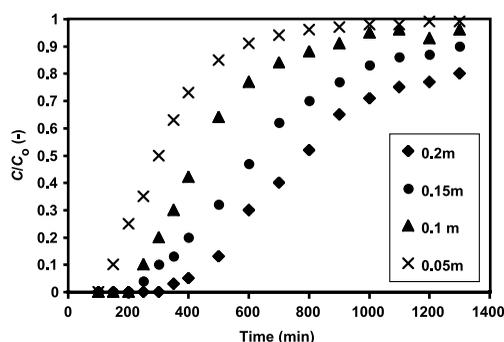
Figure 5 │ Effect of bed height on breakthrough curves (Drim yellow K4G, C_0=200 mg/l, F=40 ml/min, D=0.425 mm, T=25°C).

Figure 6 │ BDST at 50% breakthrough against bed height at different flow rates (Drim yellow K4G, C_0=200 mg/l, D=0.425 mm, T=25°C).

from zero to 0.95 during 1100 min of continuous operation. This increase is repeated at all axial positions in the bed. In addition, Figure 5 shows that the shapes of the breakthrough curves resemble to some extent the characteristic "S" shape profiles, although the shapes of the six profiles are not identical. This indicates the applicability of the model to the adsorption system. Furthermore, Figure 5 shows that the profiles are characterized by a relatively wide adsorption front, i.e. adsorption of the dye starts at the top of the bed before complete saturation of the adsorbent at the bottom of the bed. Notice, for example, that after 450 min from the beginning of the experiment the value of C/C_o at an axial position of 0.20 m is 0.10, while its value at an axial position of 0.05 m is 0.8. This phenomenon usually occurs in the adsorption of large molecules such as dyes. This behavior suggests that the adsorption of dyestuffs requires higher beds than those required for the adsorption of small molecules.

Figure 6 shows the plot of BDST at 50% breakthrough against the bed depth at different flow rates. Each point represents a BDST ($t_{0.5}$) at a different bed height. The solid lines represent the experimental and the dashed lines represent the predicted results. It is clear in Figure 6 that the slope of the BDST ($t_{0.5}$) and the breakthrough time decrease as the volumetric flow rate increases, owing to the decreased contact time between the dye molecules and the adsorbent particles. The following equation represents the BDST expression for drim yellow-K4G. It was obtained from the slope of the line in Figure 6 at a flow rate of 30 ml/min.
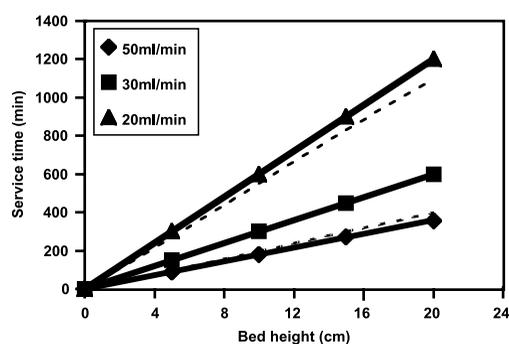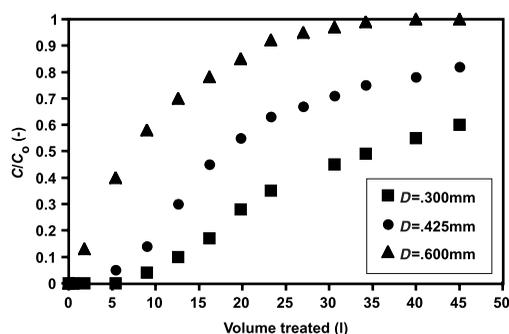

Figure 7 │ Effect of particle size on breakthrough curve at a bed height of 0.2 m (Drim yellow K4G, C_0=100 mg/l, F=30 ml/min, T=25°C).

$$t_{0.5} = 30\,Z \tag{14}$$

After developing a BDST equation from the continuous adsorption experiments at a certain flow rate, the expression for BDST at different flow rates could be obtained by using Equation 14. The adsorption capacity at complete exhaustion can be determined by multiplying the volume treated at $t_{0.5}$ by the dye concentration and dividing the resultant value on the adsorbent mass. In addition, the adsorbent capacity decreases as the adsorbate flow rate increases.

Effect of adsorbent particle size

Figure 7 shows the effect of adsorbent particle size on the breakthrough curves. It can be noticed that the values of the volume treated before the appearance of the dye in the effluent, V_o are 7.5, 4.2 and 1.8 l for average particle
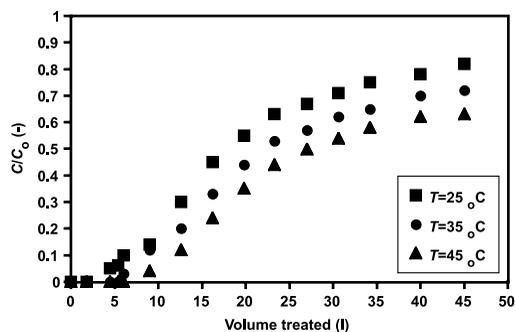
Figure 8 | Effect of temperature on breakthrough curve at a bed height of 0.2 m (Drim yellow K4G, C_0=200 mg/l, F=30 ml/min, D=0.425 mm).

Figure 9 | BDST at 50% breakthrough against bed height at three different temperatures (Drim yellow K4G, C_0=200 mg/l, D=0.425 mm).

diameters of 302.5, 425 and 600 μm, respectively. This means that the breakthrough time decreases as the particle size increases. This result indicates that in continuous adsorption the rate of adsorption and the adsorption capacity increase as the particle size decreases. This means that the relatively large particles need a longer time to reach the adsorption capacity of small particles. This behavior is attributed to the fact that the inter-particle surface area increases and the intra-particle pore depth decreases as the particle diameter decreases. In addition, the shape of the breakthrough curve in a relatively small particle system tends to take the standard "S" profile. These results agree with those of Walker & Weatherley (1997) for the adsorption of acid dyes on to granulated activated carbon, and they are consistent with the kinetic data obtained previously (Al-Qodah 2000).

Effect of temperature

Temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particles, owing to the decrease in the viscosity of the solution. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate.

The concentration profiles along the bed at three operating temperatures of 25, 35 and 45°C are shown in Figure 8. It is evident in Figure 8 that the values of the
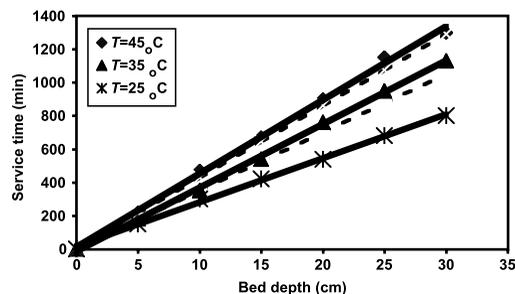
service time are 300, 350 and 420 min for temperatures of 25, 35 and 45°C respectively. This result indicates that the volume treated before the appearance of the dye in the effluent increases by more than 40% for an increase of 20°C in temperature. This temperature enhancement for the adsorption of reactive dyes onto shale oil ash agrees with the results of the kinetic study (Al-Qodah 2000) and suggests that hot wastewater effluents from textile mills could be treated with this ash directly, without waiting to be cooled.

The effect of temperature on the bed performance is described using the BDST model, where the bed depth versus service time at constant flow rate, initial dye concentration and particle size is plotted in Figure 9. The breakthrough point increases as the temperature increases. Consequently, the slope of the BDST increases. This means that beds operated at high temperatures operate for a longer time before exhaustion. In addition, the predicted BDST equations calculated from the slope of the 25°C line for the other two lines using Equation 8, which is proposed in this study, show good agreement when the value of n is 0.80. The correlation coefficient R^2 values calculated from the linearization of the experimental data are quite high, with values all above 0.96.

Effect of regeneration temperature

The cost of an adsorption system is highly dependent on the ability to regenerate the adsorbent. For shale oil ash, thermal regeneration by heating in an oven is possible without loss of adsorbent. This method is used in this
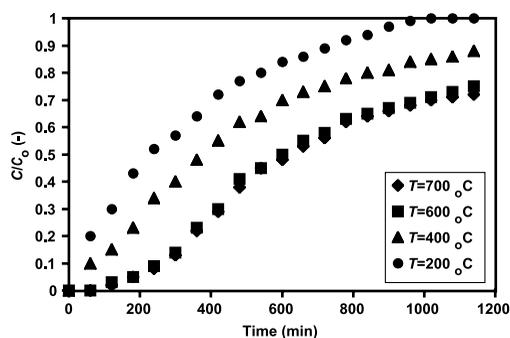
Figure 10 │ Effect of regeneration temperature on breakthrough curves (Drim yellow K4G, C_0=200 mg/l, F=30 ml/min, D=0.425 mm, T=25°C).

study after desorption of the majority of the dye by cold water as illustrated above.

Figure 10 shows the effect of regeneration temperature on the breakthrough curves. Four different temperatures of 200, 400, 600 and 700°C are used to regenerate the adsorbent. It could be seen that the service time of the regenerated bed increases as the regenerated temperature increases until it reaches 600°C. At temperatures beyond this value, i.e. 700°C, the service time does not increase as the temperature increases. This behavior could be explained by the effect of heat on the decomposition of the adsorbed dye molecules from the adsorbent surface and internal pores, which occurs at 600°C. This means that the ash is completely regenerated at 600°C, and further heating will not increase the adsorption capacity of the adsorbent.

Cost estimation

Shale oil ash is produced as a material from power plants using shale oil as feedstock. The final cost of this material including expenses for transport, chemicals and energy would not exceed $40 ton^{-1}. Further recovery of the dyes and regeneration of the adsorbent would minimize that cost. This cost is much lower than that of the cheapest variety of commercially available activated carbon which costs more than $1,000 ton^{-1}

CONCLUSIONS

Based upon the experimental and the predicted results in this investigation, the following conclusions can be drawn:

- The adsorption isotherm data show that the shale oil ash, developed as a waste product from shale oil processing, is an effective low cost adsorbent for the removal of reactive dyes from industrial wastewater.
- The adsorption process is spontaneous and the continuous adsorption capacity, N_o increases as temperature increases. This observation leads to the conclusion that this process is internal diffusion controlled.
- The adsorption of reactive dyes with shale oil ash is an endothermic process. Increasing the temperature increases the rate of this process.
- The breakthrough curves for the adsorption of reactive dyes onto shale oil ash indicate that the breakthrough time increases as the operating temperature increases.
- The BDST model represents a useful tool for studying the adsorber performance under different process conditions.
- Regeneration of the adsorbent by burning at 600°C produces a regenerated adsorbent that resembles the fresh ash in its adsorption capacity.

NOMENCLATURE

A adsorbed quantity of the dye during the breakthrough time, kg/m^3

a isotherm constant for Langmuir equation, m^3/kg solid

b isotherm constant for Langmuir equation, m^3/kg dye

C dye concentration in the collected volume at the breakthrough point, kg/m^3

C_b dye concentration in the bulk of the liquid phase, kg/m^3

C_{bf} breakthrough dye concentration, kg/m^3

C_o initial dye concentration, kg/m^3

C_e equilibrium dye concentration, kg/m^3

D particle diameter, m

d_p particle diameter

F feed flow rate, m^3/s

ΔG^o standard Gibbs free energy, kJ/mole

ΔH^o standard enthalpy, kJ/mole

L rate constant of adsorption, $mg^{-1}\ ml\ min^{-1}$

K distribution coefficient [q_e (mg dye/g adsorbent)]/[C_e mg dye/g solution)]

N_o adsorption capacity in BDST model, kg/m^3

Q^o batch adsorption capacity, kg dye/m^3 adsorbent

Q_o the maximum uptake, or Langmuir monolayer capacity, kg dye/kg solid

q_e equilibrium dye concentration in the particle, kg dye/kg adsorbent

S slope of BDST plot, min/m

ΔS^o standard entropy, kJ/mole

T temperature, °C

t_o time needed for the dye to appear in the effluent, min

$t_{0.5}$ time at which the outlet concentration of the dye equal half the inlet concentration, min

V volume of the liquid treated, m^3

V_b volume of the liquid treated at the breakthrough point, m^3

V_o volume of the liquid treated before the appearance of the dye in the effluent, m^3

Z bed height, m

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