

A TWO-STAGE BATCH SORPTION OPTIMIZED DESIGN FOR DYE REMOVAL TO MINIMIZE CONTACT TIME

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The sorption of Basic Blue 69 and Acid Blue 25 dyes onto biosorbents (wood and peat) in a batch adsorber has been studied. A model has been developed for the design of a two-stage batch adsorber. The model has been optimized with respect to contact time in order to minimize total contact time to achieve a fixed percentage of Basic Blue 69 and Acid Blue 25 dye removal.

Keywords: dye, batch sorption, optimization model.

INTRODUCTION

In recent years many cheap, widely-available materials have been identified as suitable adsorbents for the removal of colour from wastewaters. The sorption of various dyes on peat¹⁻³, onto pith^{4,5} and onto wood^{6,7} has been studied. However, only limited application of such data has been directed towards the design of adsorption treatment systems such as batch adsorber design^{8,9} or fixed bed adsorber design^{10,11}. Batch sorber design has mainly concentrated on reducing adsorbent costs, which is particularly relevant when expensive sorbent materials such as active carbon, silica, zeolites and resins are used. But for cheaper adsorbents minimizing the contact time for a fixed percentage of pollution removal using a fixed mass of adsorbent will result in being able to process more batches of polluted wastewater per day, thus enabling the required treatment plant items to be reduced in size, with a decrease in the plant capital cost.

The cost and performance of product/equipment/system or the mode of application are always of concern to control the process efficiency. Therefore the sorption capacity and required contact time are two of the most important parameters to understand in a sorption process. Equilibrium analysis is fundamental to evaluate the affinity or capacity of a sorbent. However, thermodynamic data can only predict the final state of a system from an initial nonequilibrium mode. It is therefore important to determine how sorption rates depend on the concentrations of sorbate in solution and how rates are affected by sorption capacity or by the character of sorbent in terms of kinetics. From the kinetics analysis, the solute uptake rate—which determines the residence time required for completion of the sorption reaction—may be analysed and established. This approach has been adopted and is presented in the present paper.

This paper studies the sorption of Basic Blue 69 (BB69) and Acid Blue 25 (AB25) dyes onto two biosorbents (wood and peat) and develops a two-stage batch adsorber design model. A design analysis method has been developed to predict the percentage of dye removal at various times of

contact for a fixed mass of adsorbent. The model enables the total contact time to be minimized to achieve a fixed percentage of BB69 and AB25 dye removal using a fixed mass of biosorbent material. This minimum contact time enables the minimum size of the batch sorption equipment to be specified and therefore minimize capital investment costs.

MATERIALS AND METHODS

The cheap, widely-available sorbents used in this study are sphagnum peat moss obtained from Northern Ireland, but widely available in most countries of the world, and wood particles from Northern Ireland of the soft spruce wood type.

Sorption of Basic Blue 69 Dye on Peat

Contact time

A 0.1 g sample of wood (500–710 μm) was added to each 50 ml volume of BB69 dye solution. The initial concentrations of BB69 dye solution tested were 50, 100, 200 and 500 mg dm^{-3} .

Equilibrium isotherms

To determine the BB69 removal capacities of the BB69/peat system, isotherm experiments were carried out and the data analysed using the Langmuir equation. Isotherms were determined for a peat particle size range of 500–710 μm , and the contact time given for each experiment was 8 hours. In each case, a set weight of peat (0.02–0.3 g) was added to a 50 ml volume of BB69 dye solution of initial concentration 200 mg dm^{-3} .

Sorption of Acid Blue 25 Dye on Peat

Contact time

A 0.5 g sample of wood (500–710 μm) was added to each 50 ml volume of AB25 dye solution. The initial concentrations of AB25 dye solution tested were 20, 50, 100 and 200 mg dm^{-3} .

Equilibrium isotherms

Isotherms were determined for a peat particle size range of 500–710 μm , and the contact time given for each experiment was 8 hours. In each case, a set weight of peat (0.05–0.8 g) was added to a 50 ml volume of AB25 dye solution of initial concentration 100 mg dm^{-3} .

Sorption of Basic Blue 69 Dye on Wood

Contact time

A 0.1 g sample of wood (500–710 μm) was added to each 50 ml volume of BB69 dye solution. The initial concentrations of BB69 dye solution tested were 50, 100 and 200 mg dm^{-3} .

Equilibrium isotherms

Isotherms were determined for a wood particle size range of 500–710 μm , and the contact time given for each experiment was 8 hours. In each case, a fixed weight of wood (0.05–0.8 g) was added to a 50 ml volume of BB69 dye solution of initial concentration 200 mg dm^{-3} .

Sorption of Acid Blue 25 Dye on Wood

Contact time

A 0.5 g sample of wood (500–710 μm) was added to each 50 ml volume of AB25 dye solution. The initial concentrations of AB25 dye solution tested were 20, 50, 100 and 200 mg dm^{-3} .

Equilibrium isotherms

Isotherms were determined for a wood particle size range of 500–710 μm , and the contact time given for each experiment was 8 hours. In each case, a fixed weight of wood (0.05–2 g) was added to a 50 ml volume of AB25 dye solution of initial concentration 100 mg dm^{-3} .

RESULTS AND DISCUSSION

Kinetic and Equilibrium Analysis

The kinetics of dye sorption onto peat have been studied using three models—intraparticle diffusion, Lagergren pseudo-first order and pseudo-second order kinetics¹². The model which provided the best correlation with experimental data was the pseudo-second order model and this has been used to analyse the experimental batch adsorber contact time data in the present paper.

The rate constant of the pseudo-second order chemical sorption process can be determined using the following equation:

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

where q_e is the amount of dye sorbed at equilibrium mg g^{-1} , q_t is the amount of dye sorbed at time t (mg g^{-1}) and k is the equilibrium rate constant for pseudo-second order sorption ($\text{g mg}^{-1} \text{min}^{-1}$).

A kinetic analysis of the sorption on peat and wood has been undertaken according to a pseudo-second equation for the dye/sorbents system. Figure 1 shows a plot of equation (2) for the sorption of BB69 using peat. The results demonstrate a highly significant linear relationship between BB69 sorbed, t/q_t , and t in these studies with

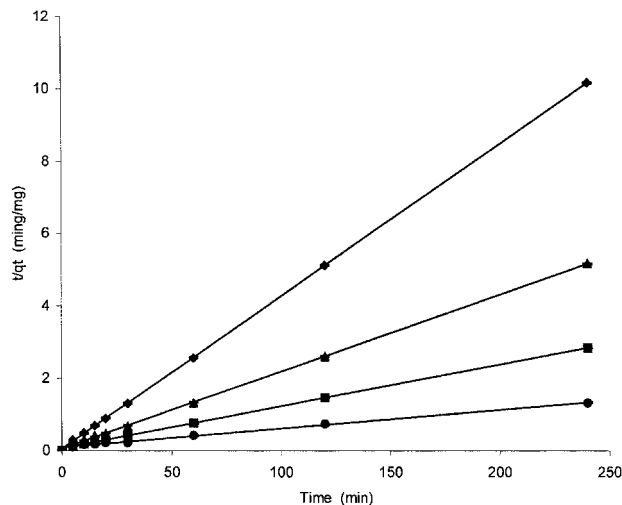


Figure 1. Pseudo-second order sorption kinetics of BB69 onto peat at various initial concentrations. \blacklozenge 50 mg dm^{-3} , BB69 peat—BB69/peat, second order model; \blacktriangle 100 mg dm^{-3} , BB69 peat—BB69/peat, second order model; \blacksquare 200 mg dm^{-3} , BB69/peat—BB69/peat, second order model; \bullet 500 mg dm^{-3} , BB69/peat—BB69/peat, second order model.

high correlation coefficients. The correlation coefficients r^2 , the pseudo-second order rate parameters k , initial sorption rate h , and sorption capacity q_e , are shown in Tables 1 to 4 for the sorption of BB69 onto peat and wood and AB25 onto peat and wood respectively.

To be consistent it is important that the kinetic model should satisfy the criteria of the equilibrium isotherm. The operating lines for batch adsorber contact systems can be plotted on the equilibrium isotherms, the equilibrium sorption capacity can be predicted from the isotherm and this equilibrium capacity, q_e mg dye g^{-1} adsorbent, can be compared with the theoretical q_e results evaluated from the kinetic models.

An isotherm study is significant in obtaining the equilibrium sorption capacity as the maximum capacity. The Langmuir isotherms for the sorption of BB69 dye and AB25 dye onto peat and wood are shown in Figures 2 and 3 respectively. The saturation equilibrium sorption

Table 1. Parameters for effect of initial concentration on the BB69/peat system.

C_0 mg dm^{-3}	r^2	k $\text{g mg}^{-1} \text{min}^{-1}$	h $\text{mg g}^{-1} \text{min}^{-1}$	q_e mg g^{-1}
50	1.000	2.95×10^{-2}	16.7	23.8
100	1.000	6.62×10^{-3}	14.8	47.2
200	1.000	1.84×10^{-3}	13.8	86.4
500	0.997	2.62×10^{-4}	9.94	95

Table 2. Parameters for effect of initial concentration on the BB69/peat system.

C_0 mg dm^{-3}	r^2	k $\text{g mg}^{-1} \text{min}^{-1}$	h $\text{mg g}^{-1} \text{min}^{-1}$	q_e mg g^{-1}
50	1.000	3.09×10^{-3}	1.80	24.1
100	0.997	1.14×10^{-3}	1.94	41.3
200	0.995	5.58×10^{-4}	2.16	62.2

Table 3. Parameters for effect of initial concentration on the AB25/peat system.

C_0 mg dm ⁻³	r^2	g mg ⁻¹ min ⁻¹	h mg g ⁻¹ min ⁻¹	q_{e-1} mg g ⁻¹
20	0.999	4.42×10^{-2}	0.152	1.85
50	0.999	1.10×10^{-2}	0.213	4.40
100	0.994	1.56×10^{-3}	0.0941	7.76
200	0.924	7.47×10^{-4}	0.121	12.7

Table 4. Parameters for effect of initial concentration on the AB25/wood system.

C_0 mg dm ⁻³	r^2	g mg ⁻¹ min ⁻¹	h mg g ⁻¹ min ⁻¹	q_{e-1} mg g ⁻¹
20	0.996	2.72×10^{-2}	2.76×10^{-2}	1.01
50	0.994	1.20×10^{-2}	6.53×10^{-2}	2.83
100	0.988	5.08×10^{-3}	9.76×10^{-2}	5.38
200	0.977	3.21×10^{-3}	0.182	7.53

capacity, calculated from the intercept and slope of the Langmuir equation, is 105 mg g⁻¹ peat for the BB69/peat sorption system, 12.7 mg g⁻¹ peat for the AB25/peat sorption system, 71.3 mg g⁻¹ wood for the BB69/wood sorption system, and the capacity of wood for AB25 is 16.0 mg g⁻¹.

The mass balance on the agitated batch adsorber shows the slope of the operating line, for two similar stages, to be $-L/S$. Since the initial dye concentration C_0 is specified then the operating line can be constructed on the isotherm diagram. This is shown on Figure 3 for three initial dye concentrations—20, 50 and 100 mg dm⁻³—for the sorption of AB25 dye on wood. In Figure 2, the operating lines are shown for three initial dye concentrations—50, 100 and 200 mg dm⁻³—of BB69 dye on wood. Knowing C_0 and $-L/S$; the operating lines are drawn and the experimental isotherm equilibrium capacity $q_{e,s}$ is determined. These values are compared with the theoretical predictions using equation (1) and are presented in Table 5.

The agreement between q_e and $q_{e,s}$ values is much greater

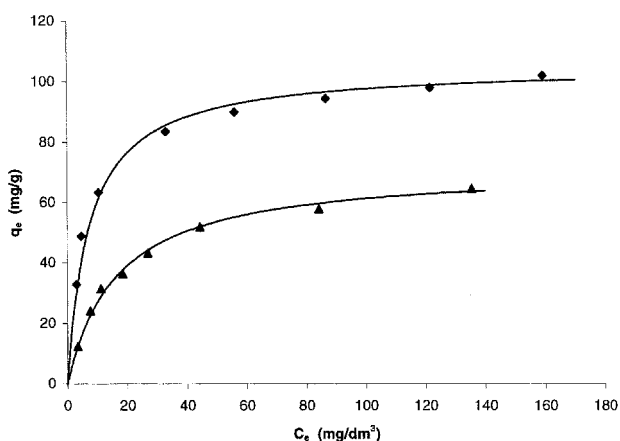


Figure 2. Langmuir isotherm of Basic Blue 69 onto peat and wood. ◆ BB69/peat, experimental data—BB69/peat, Langmuir equation; ▲ BB69/wood, experimental data—BB69/wood, Langmuir equation.

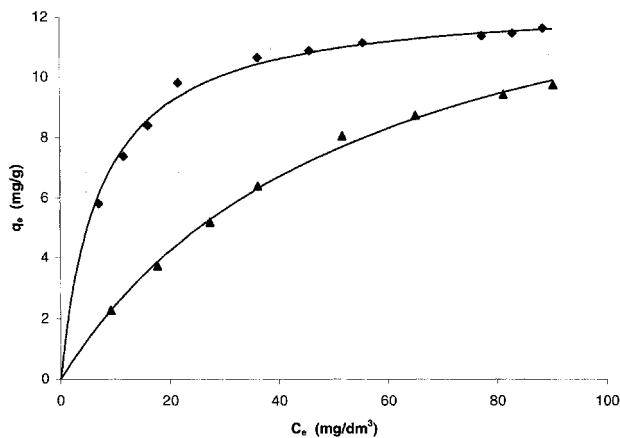


Figure 3. Langmuir isotherms of Acid Blue 25 onto peat and wood. ◆ AB25/peat, experimental data—AB25/peat, Langmuir equation; ▲ AB25/wood, experimental data—AB25/wood, Langmuir equation.

for the pseudo-second order model than for the pseudo-first order model.

Batch Adsorber Design Analysis

The application of the contact time model to the design and time optimization of batch sorbers is undertaken in this section. The basis of this model is now discussed.

The schematic diagram for a two-stage sorption system is shown in Figure 4. The solution to be treated contains L dm⁻³ solution and the dye concentration is reduced for each stage from C_{n-1} to C_n mg dm⁻³. The amount of sorbent added is S g with solid phase dye concentration on the peat q_0 mg g⁻¹. The dye concentration on the sorbent increases from q_0 to q_n mg g⁻¹ sorbent. The mass balance equation gives:

$$L(C_{n-1} - C_n) = S(q_n - q_0) \quad (2)$$

When fresh sorbents are used at each stage and the pseudo-second order rate expression is used to describe equilibrium in the two-stage sorption system, then the mass balance equation can be obtained by combining equations (1) and (2):

$$C_n = C_{n-1} - \frac{Skq_n^2 t}{L(1 + kq_n t)} \quad (3)$$

The total amount of dye removal can be calculated analytically as follows:

$$\sum_{n=1}^n (C_{n-1} - C_n) = \sum_{n=1}^n \frac{Skq_n^2 t}{L(1 + kq_n t)} \quad (4)$$

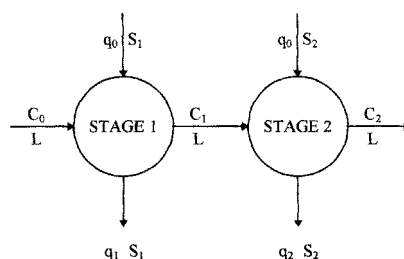


Figure 4. Schematic for two-stage countercurrent batch sorption.

Table 5. Comparison of experimental and kinetic model predicted equilibrium capacities.

Dye	Adsorbent	C_0 mg dm ⁻³	q_{e-1} mg g ⁻¹	$q_{e,s-1}$ mg g ⁻¹
BB69	Peat	50	23.8	24
BB69	Peat	100	47.2	48
BB69	Peat	200	86.4	85
BB69	Wood	50	24.1	24
BB69	Wood	100	41.3	40
BB69	Wood	200	62.2	61
AB25	Peat	20	1.85	1.9
AB25	Peat	50	4.40	4.6
AB25	Peat	100	7.76	8.1
AB25	Wood	20	1.01	1.3
AB25	Wood	50	2.83	3.2
AB25	Wood	100	4.88	6.0

Table 6. Empirical parameters for predicted q_e and k from C_0 .

	A_q	B_q	r^2	A_k	B_k	r^2
BB69/Peat	0.697	0.909	0.999	82.8	-2.03	0.999
BB69/Wood	1.69	0.685	0.994	0.371	-1.24	0.991
AB25/Peat	0.157	0.839	0.996	12.3	-1.86	0.976
AB25/Wood	0.0736	0.880	0.999	0.478	-0.958	0.990

The dye removal, R_n , in each stage can be evaluated from the equation as follows:

$$R_n = \frac{100(C_{n-1} - C_n)}{C_0} = \frac{100Skq_n^2 t}{LC_0(1 + kq_n t)} \quad (5)$$

The total removal of dye can be calculated analytically as follows:

$$\sum_{n=1}^n R_n = \frac{100St}{LC_0} \sum_{n=1}^n \frac{kq_n^2}{1 + kq_n t} \quad (6)$$

The corresponding linear plots of the values of q_e and k against initial dye concentration C_0 , were regressed to obtain expressions for these values in terms of the initial dye concentration. High correlation coefficients were obtained as shown in Table 6. Therefore it is useful for process design purposes if q_e and k can be expressed as a function of C_0 for sorption of dye onto peat and wood as follows:

$$q_e = A_q C_0^{B_q} \quad (7)$$

$$k = A_k C_0^{B_k} \quad (8)$$

Substituting the values of q_e and k from equations (7) and (8) into equations (5) and (6), the equations (5) and (6) can be represented as follows:

$$R_n = \frac{100S(A_k C_{n-1}^{B_k})(A_q(C_{n-1}^{B_q}))^2 t}{LC_0[1 + (A_k C_{n-1}^{B_k})(A_q C_{n-1}^{B_q})t]} \quad (9)$$

$$\sum_{n=1}^n R_n = \frac{100St}{LC_0} \sum_{n=1}^n \frac{(A_k C_{n-1}^{B_k})(A_q C_{n-1}^{B_q})^2}{[1 + (A_k C_{n-1}^{B_k})(A_q C_{n-1}^{B_q})t]} \quad (10)$$

Equations (9) and (10) can then be used for predicting the removal of dye at any given initial dye concentration and the reaction time for any multi-stage system.

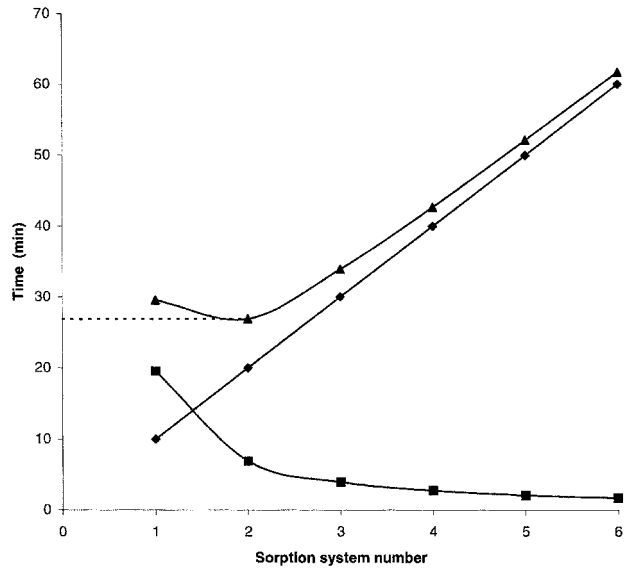


Figure 5. Comparison of 90% BB69 removal time of each stage in two-stage BB69/peat process. ◆ Stage 1, BB69/peat; ■ Stage 2, BB69/peat; ▲ 90% removal, BB69/peat.

In the case of a two-stage countercurrent batch sorption system, the design procedure is now outlined. For example, 5 m³ of solution is to be treated. The amount of sorbent added is 10 kg in each of the two stages and the BB69 initial concentration is 200 mg dm⁻³ in the first stage. A series of contact times from 10 minutes up to 220 minutes in 10-minute increments has been considered in stage one of a two-stage sorption system. Therefore, in Figures 5–12, each system number is based on a 10-minute contact time interval. In the first adsorber, for example, a system number 6 implies the first adsorber contact time; t_1 , is $6 \times 10 = 60$ minutes. Therefore, the contact time in the second adsorber; t_2 , is the time required, T minutes, to achieve a fixed total % dye removal minus the contact time in the first adsorber

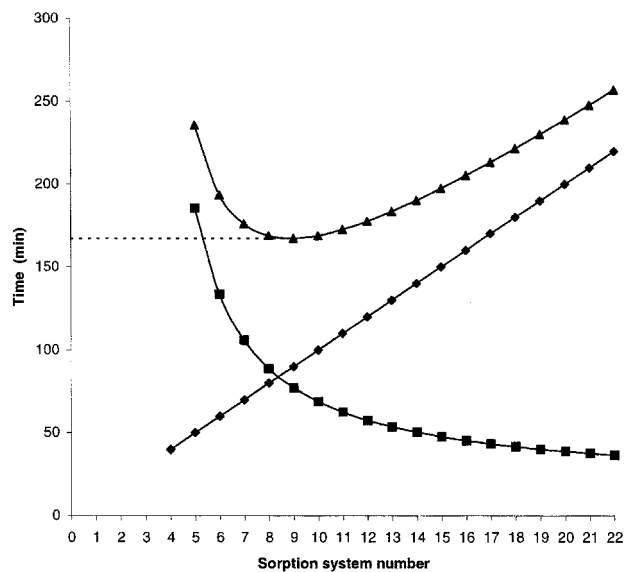


Figure 6. Comparison of 80% BB69 removal time of each stage in two-stage BB69/wood process. ◆ Stage 1, BB69/wood; ■ Stage 2, BB69/wood; ▲ 80% removal, BB69/wood.

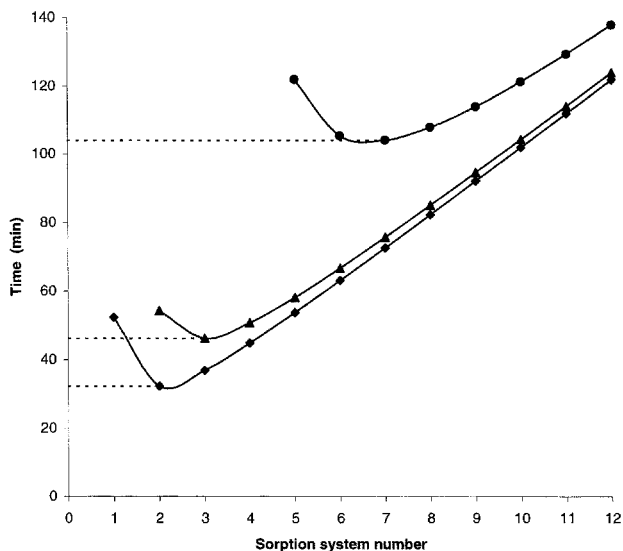


Figure 7. Minimum contact time for various percentage BB69 removal in a two-stage BB69/peat process. ◆ 93% removal, BB69/peat; ■ 96% removal, BB69/peat; ● 99% removal, BB69/peat.

stage t_1 .

$$T = t_1 + t_2 \quad (11)$$

For N systems, t_1 becomes $10N$ minutes, and

$$T = 10N + t_2 \quad (\text{for a fixed \% removal}) \quad (12)$$

The total contact time is calculated for each system number for a fixed percentage dye removal. The T values are plotted against system number, as shown in Figures 5–12, and the minimum contact time may be determined.

Figures 5 and 6 show a comparison of the time for 90% BB69 removal using peat and 80% BB69 removal using wood for each stage and the total reaction time of the two-stage countercurrent batch sorption process. Figures 7 and 8

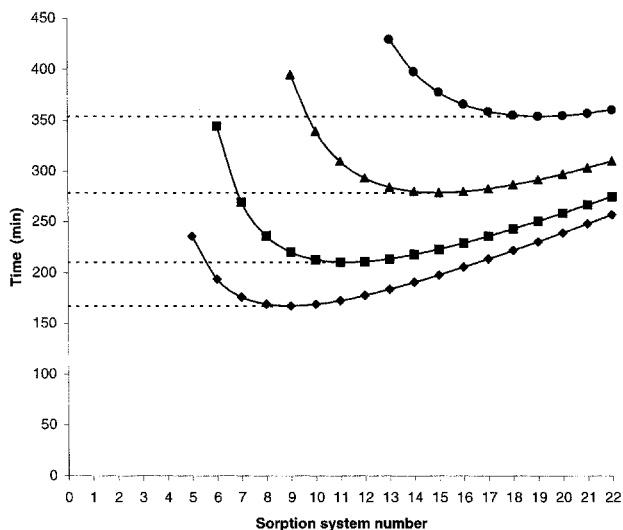


Figure 8. Minimum contact time for various percentage BB69 removal in a two-stage BB69/wood process. ◆ 80% removal, BB69/wood; ■ 83% removal, BB69/wood; ▲ 86% removal, BB69/wood; ● 88% removal, BB69/wood.

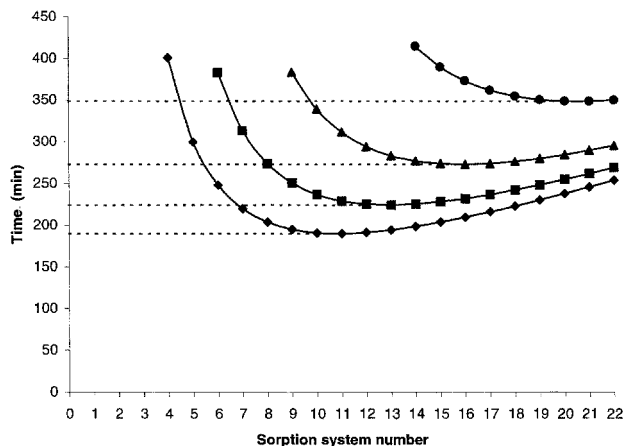


Figure 9. Minimum contact time for various percentage AB25 removal in a two-stage AB25/peat process. ◆ 80% removal, AB25/peat; ■ 83% removal, AB25/peat; ▲ 86% removal, AB25/peat; ● 89% removal, AB25/peat.

show the minimum contact time of the two stages in series for the two-stage sorption of BB69/peat and BB69/wood systems.

Figures 9 and 10 show a series of two-stage contacting systems. The minimum operating time for various percentages of AB25 removal in a two-stage process can be evaluated from equation (9). The AB25 solution to be treated, contains 5 m^3 solution, the amount of sorbent added is 50 kg in each of the two stages and the AB25 initial concentration is 100 mg dm^{-3} in the first stage. Figures 11 and 12 respectively show a comparison of the time for 80% AB25 removal using peat and 50% AB25 removal using wood for each stage and the total reaction time of the two-stage countercurrent batch sorption process. The minimum contact times for the various fixed percentages of dye removal are shown.

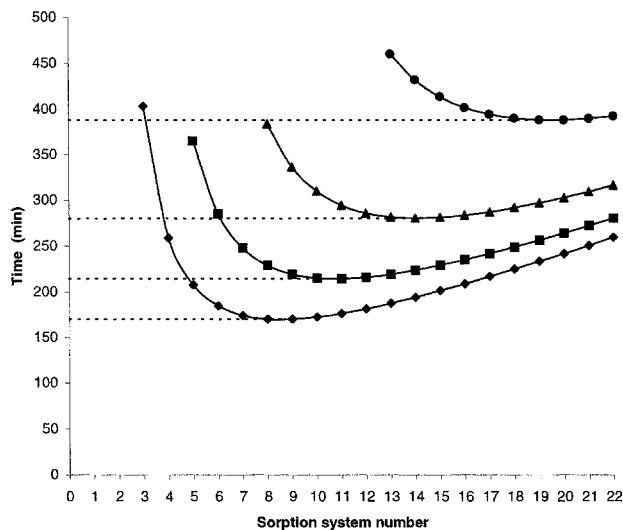


Figure 10. Minimum contact time for various percentage AB25 removal in a two-stage AB25/wood process. ◆ 50% removal, AB25/wood; ■ 53% removal, AB25/wood; ▲ 56% removal, AB25 wood; ● 59% removal, AB25/wood.

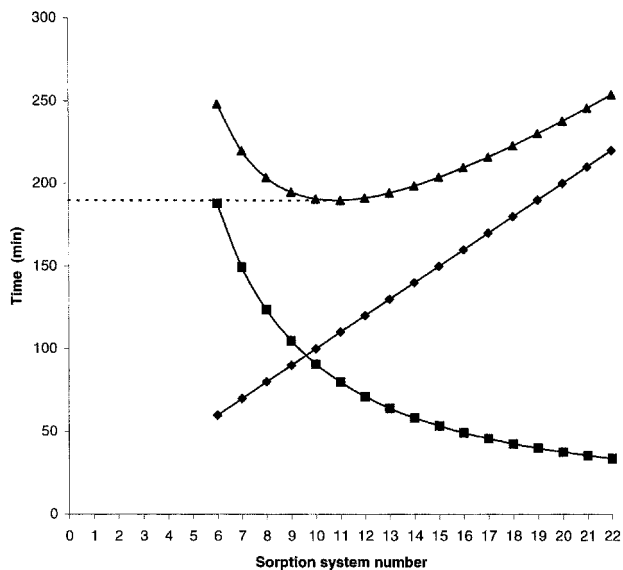


Figure 11. Comparison of 80% AB25 removal time of each stage in two-stage AB25/peat process. \blacklozenge Stage 1, AB25/peat; \blacksquare Stage 2, AB25/peat; \blacktriangle 80% removal, AB25/peat.

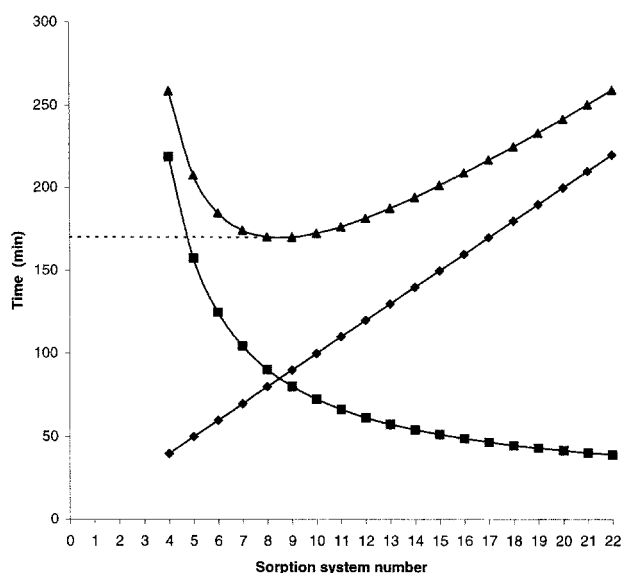


Figure 12. Comparison of 50% AB25 removal time of each stage in two-stage AB25/wood process. \blacklozenge Stage 1, AB25/wood; \blacksquare Stage 2, AB25/wood; \blacktriangle 50% removal, AB25/wood.

CONCLUSION

The method proposed in this paper enables the contact time in a two-stage batch adsorber to be minimized to achieve a fixed percentage of dye removal. The use of a two-stage adsorber enables the contact time to be reduced by more than 50% using the optimization procedure presented for dye removals of over 90%. In some cases, a single-stage batch adsorber cannot achieve the high levels of dye removal specified but these can be readily achieved using an optimized two-stage batch adsorber design.

NOMENCLATURE

A_k	empirical correlation constant in equation (7)
A_q	empirical correlation constant in equation (8)
B_k	correlative exponent in equation (7)
B_q	correlative exponent in equation (8)
C_o	initial liquid phase dye concentration, mg dm^{-3}
h	initial rate of adsorption, $\text{mg g}^{-1} \text{min}^{-1}$
k	pseudo-second order adsorption rate parameter, $\text{g mg}^{-1} \text{min}^{-1}$
L	volume of solution, dm^3
n	number of contact stages
N	system number = number of batch sorbers
q_e	equilibrium solid phase dye concentration, mg g^{-1}
q_0	initial equilibrium solid phase dye concentration, mg g^{-1}
r^2	linear regression correlation coefficient
R_n	percentage total dye removal
S	mass of adsorbent, g
t	system contact time, min
T	total contact time, min

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