

Solid diffusion control of the adsorption of basic dyes onto granular activated carbon and natural zeolite in fixed bed columns

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(Received 31 July 2000)

The adsorption of basic dyes from aqueous solutions onto granular activated carbon and natural zeolite was studied using a fixed bed column. The design procedures for fixed bed adsorption columns were investigated for two basic dyes Maxilon Goldgelb GL EC 400 % (MG-400) and Maxilon Schwarz FBL-01 300 % (MS-300). A computer program based on the solid diffusion control model has been developed. The model parameters: solid diffusion coefficient, D_S , axial dispersion coefficient, D_L and external mass transfer coefficient, k_f for all the investigated systems were estimated by means of a best fit approach.

Keywords: solid diffusion control, dye adsorption, granular activated carbon, natural zeolite, adsorption modelling.

INTRODUCTION

Colour removal from textile effluents has been the subject of great attention in the last few years, not only because of its toxicity but mainly due to its visibility.¹ Through hundreds of years, the scale of production and the nature of dyes has changed drastically, consequently the negative impact of dyes on the environment has increased.² Adsorption processes which produce good quality effluents that are low in concentration of dissolved organic compounds, such as dyes,^{3,4} are rapidly gaining importance as treatment processes.

Activated carbon is the most effective and widely used adsorbent for wastewater treatment,⁵ but it is expensive. Consequently, new materials, such as chitin,⁶ silica gel,⁷ wood,⁸ natural clay,⁹ bagasse pith,¹⁰ fibers and polymeric adsorbents,¹¹ are being studied. A very limited amount of information is available on the use of natural zeolites as a method for dye removal.^{12,13} A full description of low cost adsorbents for waste and wastewater treatment has been reviewed by Pollard *et al.*¹⁴

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The adsorbents are usually used in the fixed bed process because of the ease of operation. To design and operate a fixed bed adsorption process successfully, the column dynamics must be understood; that is the breakthrough curves under specific operating conditions must be predictable. A mathematical model of fixed bed adsorbents is very useful for the proper design and the determination of the optimal operating conditions for this equipment. Different models for the adsorption process of gaseous or liquid components have been proposed in the literature.¹⁵ The differences in the mathematical models of adsorption processes arise from the different representation of the equilibrium behaviour, the different expressions of the mass transfer inside and outside the adsorbent particle and from how the axial dispersion is taken into account in the material balance for the adsorbate in the fixed bed column. Also various numerical techniques have been developed for the solution of the fixed bed adsorbent models.

In most adsorption systems dyes-adsorbents, Langmuir,^{13,16} Freundlich⁹ and Redlich-Peterson¹⁰ isotherms have been applied to describe the equilibrium between liquid-solid phases.

Two intraparticle diffusion mechanisms are involved in the adsorption rate: (a) diffusion within the pore volume, known as pore diffusion, and (b) diffusion along the surface of the pores, known as surface diffusion.¹⁷ For different dye-adsorbent systems, some investigators applied the pore diffusion model with^{12,18} and without film resistance.⁹ McKay¹⁰ developed a homogeneous surface phase diffusion model to describe different systems of dyes on bagasse pith.

The homogeneous surface diffusion model was developed and analysed by several researchers.^{19,20} Models for the heterogeneous diffusion model have been developed that assume macropore and micropore diffusion occurring in series or in parallel.^{21,22} Yao and Tien^{23,24} presented two approximate expressions for the rate of solute uptake by spherical adsorbent pellets. They used these expressions for adsorption calculations of batch, continuous flow stirred tank and fixed bed systems. A full description of the mass transfer mechanisms for zeolite adsorption and ion exchange in wastewater treatment has been presented by Robinson *et al.*²⁵

The objective of this study focused on the understanding of the mechanisms of adsorption in fixed bed columns for single-component dye adsorption on granular activated carbon (GAC) and natural zeolite as adsorbents. The mathematical model is governed by a set of partial differential equations which were solved numerically using Speedup Software. The calculated results were compared with experimental data.

MATHEMATICAL MODEL

The dynamics of a fixed bed is described by a set of convection diffusion equations, coupled with source terms due to adsorption and diffusion inside the adsorbent particles. Prediction of the breakthrough curves is based on correctly formulating the mathematical model for a fixed bed adsorbent. The system considered here is an isothermal adsorption column packed with porous adsorbent (GAC or natural zeolite). At time zero, a step change in the concentration of an adsorbate was introduced to the flowing stream. The adsorption column was subjected to axial dispersion, external diffusion

film resistance, and solid diffusion resistance. The following assumptions were made in the analysis:

- Isothermal adsorption of a single component;
- Negligible concentration gradient in the radial direction;
- The Linear Driving Force (LDF) model was used for presenting the mass transfer into the pellets;
- Constant cross section and uniform properties of the adsorbent bed throughout the column.

Under the above assumptions, the governing equations and appropriate initial and boundary conditions can be written as follows:

$$v \frac{\partial c_b}{\partial z} + \frac{\partial c_b}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \frac{d}{dt} (\varepsilon_p \bar{c} + \bar{q}) = D_L \frac{\partial^2 c_b}{\partial z^2} \quad (1)$$

$$t = 0, c_b = 0 \quad (2)$$

$$z = 0, c_{in} = c_b - \frac{D_L}{v} \frac{\partial c_b}{\partial z} \quad (3)$$

$$z = L; \frac{\partial c_b}{\partial z} = 0 \quad (4)$$

By introducing the dimensionless coordinates

$$Y = \frac{z}{L}, \theta = \frac{tv}{L}$$

Eqs. (1–4) become

$$\frac{\partial c_b}{\partial Y} + \frac{\partial c_b}{\partial \theta} + \left(\frac{1-\varepsilon}{\varepsilon} \right) \frac{d}{d\theta} (\varepsilon_p \bar{c} + \bar{q}) = \frac{1}{Pe} \frac{\partial^2 c_b}{\partial Y^2} \quad (5)$$

$$\theta = 0; c_b = 0 \quad (6)$$

$$Y = 0; c_{in} = c_b - \frac{1}{Pe} \frac{\partial c_b}{\partial Y} \quad (7)$$

$$Y = 1; \frac{\partial c_b}{\partial Y} = 0 \quad (8)$$

where $Pe = \frac{Lv}{D_L}$ is the Peclet number.

The third part in Eqs. (1) or (5), the uptake rate expressed on the basis of unit adsorbent volume,²⁴ is given by

$$m = \frac{d}{dt} (\varepsilon_p \bar{c} + \bar{q}) \quad (9)$$

In terms of external mass transfer, m may be written as

$$m = \frac{3k_f}{R_p} (c_b - c_s) \quad (10)$$

The uptake rate in terms of the intraparticle diffusion can be obtained from the solution of the appropriate intraparticle diffusion equation. The uptake rate expression based on the linear driving force (LDF) model²³ for solid diffusion is

$$m = \frac{15D_s}{R_p^2} (q_s - \bar{q}) \quad (11)$$

q_s and c_s are the adsorbed phase and the fluid phase concentrations, respectively, at the fluid – pellet interface and they are in an equilibrium defined by the Langmuir equation

$$q_s = \frac{q_m K c_s}{1 + K c_s} \quad (12)$$

or

$$c_s = \frac{q_s}{q_m K - K q_s} \quad (13)$$

To eliminate the surface concentration from any equation involving the rate of mass transfer, because it cannot be measured by standard techniques, at the steady state, the rate of mass transfer of adsorbate from the bulk fluid to the external pellet surface (Eq. (10)) is equal to the net rate of solid diffusion, which is given by Eq. (11)

$$\frac{3k_f}{R_p} (c_b - c_s) = \frac{15D_s}{R_p^2} (q_s - \bar{q}) \quad (14)$$

Substituting Eq. (13) into Eq. (14), one obtains

$$Bi \left(c_b - \frac{q_s}{q_m K - K q_s} \right) = 5(q_s - \bar{q}) \quad (15)$$

where $Bi = \frac{k_f R_p}{D_s}$ is the Biot number.

Assuming

$$\frac{d}{dt} (\epsilon_p \bar{c} + \bar{q}) = \frac{15D_s}{R_p^2} (q_s - \bar{q}) \quad (16)$$

and taking into account that the pore accumulation term is generally small in comparison with the accumulation within the solid ($\epsilon_p \bar{c} \ll \bar{q}$), one obtains

$$\frac{d\bar{q}}{dt} = \frac{15D_s}{R_p^2} (q_s - \bar{q}) \quad (20)$$

The combination of Eqs. (20) and (15) in dimensionless form yields

$$\frac{d\bar{q}}{d\theta} = 3BiT \left(c_b - \frac{q_s}{q_m K - Kq_s} \right) \quad (21)$$

where $T = \frac{D_s L}{R_p^2 \nu}$

Differentiating Eq. (15) with respect to θ yields

$$\frac{dq_s}{d\theta} = \frac{\frac{d\bar{q}}{d\theta} + \frac{Bi}{5} \frac{dc_b}{d\theta}}{1 + \frac{Bi}{5} \frac{K}{(q_m K - Kq_s)^2}} \quad (22)$$

Substituting Eq. (21) into Eq. (22) gives

$$\frac{dq_s}{d\theta} = \frac{3BiT \left(c_b - \frac{q_s}{q_m K - Kq_s} \right) + \frac{Bi}{5} \frac{dc_b}{d\theta}}{1 + \frac{Bi}{5} \frac{K}{(q_m K - Kq_s)^2}} \quad (23)$$

Substituting Eq. (21) into Eq. (5) yields

$$\frac{\partial c_b}{\partial \theta} + \frac{\partial c_b}{\partial Y} + 3BiT \left(\frac{1-\varepsilon}{\varepsilon} \right) \left(c_b - \frac{q_s}{q_m K - q_s K} \right) = \frac{1}{Pe} \frac{\partial^2 c_b}{\partial Y^2} \quad (24)$$

In this paper a computer program based on the mathematical model described by Eqs. (23) and (24) with initial and boundary condition given by Eqs. (6–8) was developed using SPEEDUP software. The SPEEDUP language is capable of solving ordinary and partial differential equations and provides a choice of different integration routines. In this investigations the mathematical model was transformed into a set of first order ordinary differential equations using the finite difference method and the SUPERDAE algorithm.

EXPERIMENTAL

Materials

Adsorbates. Two basic dyes were used as adsorbates: Maxilon Goldgelb GL EC 400 % (MG-400) and Maxilon Schwarz FBL-01 300 % (MS-300). They were used as commercial salts without purification and were supplied by Ciba – Geigy, Germany.

Adsorbents. The natural zeolite type ZB was supplied by "Nemetali", Vranjska Banja, SR Yugoslavia. The mineralogical composition of the natural zeolite is 90 % clinoptilolite and the rest is mordenite and haylandrite. Prior to an experiment, the natural zeolite was dried at 300 °C for 48 h in order to remove any traces of moisture or other contaminants. The granular activated carbon (GAC) was supplied by "Miloje Zakić", Kruševac, SR Yugoslavia. Prior to an experiment the GAC was washed and dried at 100 °C for 24 h. Some of the properties of the adsorbents are listed in Table I.

TABLE I. Properties of the natural zeolite nad GAC

	Natural zeolite	GAC
Particle diameter/mm	1 – 3	1.15 – 1.35
Bed porosity	0.325	0.411
Particle density/g cm ⁻³	2.12	1.87
Bulk density/g cm ⁻³	1.43	1.0 – 1.2
Surface area/m ² g ⁻¹	20 – 40	950 – 1000

Analysis

The concentration of dyes were measured with Hach DR/2010 spectrophotometer at a wavelength corresponding to the maximum absorbance for each dye, 450 nm and 600 nm for MG-400 and MS-300, respectively. In accordance with the Lambert–Beer law, the absorbance was found to vary linearly with concentration and dilutions were undertaken when the absorbance exceeded 0.6.

Equilibrium isotherms

For the determination of adsorption isotherms, a constant adsorbent mass (0.5 g granular activated carbon and 2.0 g natural zeolite) and 0.1 dm³ of aqueous dye solution of known initial concentration were mechanically stirred in 0.5 dm³ flasks. The isotherms were obtained at 20 °C. The equilibrium for the investigated systems was established after 4 to 10 days.

Fixed bed experiments

The column tests were carried out in a glass column with an internal diameter of 1.5 cm and a height of 15 cm. Known weights of the (40 g of natural zeolite and 23 g of GAC) were randomly introduced into the column. The average temperature during the experiments was maintained at 20 °C. In an adsorption column test, an aqueous dye solution was fed to the bottom of the column by a peristaltic pump (AMEX Mastreflex), flowed through adsorbent bed and then exited from the top of the column. The column test conditions are summarized in Table II.

TABLE II. Experimental conditions of the fixed bed column test

Run	Dye	Adsorbent	Initial conc. c_0 /mg dm ⁻³	Flow rate F /cm ³ min ⁻¹
1	MS-300	GAC	50; 100; 200	40; 50; 65
2	MG-400	GAC	50; 100; 200	5; 35; 40
3	MS-300	Natural zeolite	50; 100; 200	2; 10; 25; 35; 50
4	MG-400	Natural zeolite	50; 100; 200	2; 8; 40

RESULTS AND DISCUSSION

Adsorption isotherms

The equilibrium isotherms for the investigated dyes onto GAC and natural zeolite as adsorbents at 20 °C are presented in Fig. 1 and Fig. 2, respectively.

All the adsorption isotherms display a non-linear dependence on the equilibrium concentration. The adsorption data for all the systems were fitted by Langmuir, Freundlich, Langmuir-Freundlich and Redlich-Peterson equations.¹³ The correlation between the experimental data and the theoretical models was very good in all the cases. The Langmuir adsorption isotherm was selected to be introduced in the fixed bed model.

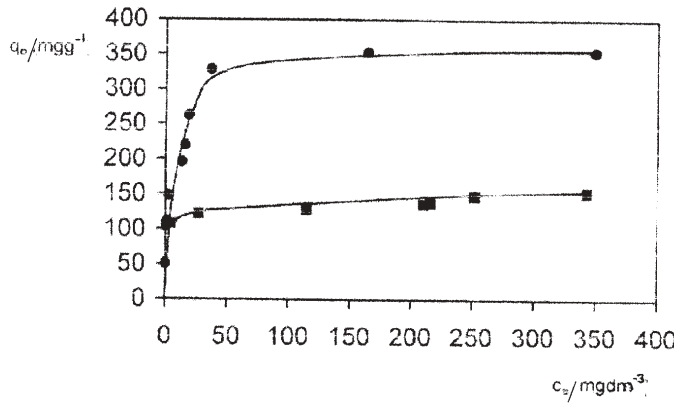


Fig. 1. Equilibrium adsorption isotherms of MG-400 (■) and MS-300 (●) on granular activated carbon, $T = 20\text{ }^\circ\text{C}$.

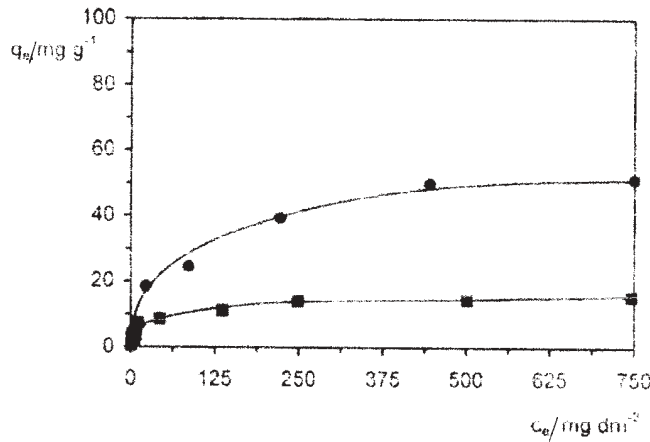


Fig. 2. Equilibrium adsorption isotherms of MG-400 (■) and MS-300 (●) on natural zeolite, $T = 20\text{ }^\circ\text{C}$.

Effect of the initial dye concentration on the breakthrough curves

The initial dye concentration of the effluent is important since a given mass of adsorbent can only adsorb a fixed amount of dye. Therefore, the more concentrated an effluent, the smaller is the volume of effluent that a fixed mass of adsorbent can purify. Several experiments were undertaken to study the effect of varying the initial dye concentration on the rate of dye removal from the solution. The breakthrough curves for the investigated systems are presented in Figs. 3 and 4.

The effect of the initial dye concentration in the inlet flow is one of the limitation factors and a main process parameter. Increasing the inlet dye concentration increases the slope of the breakthrough curve, reducing the volume treated before adsorbent regeneration. Increasing inlet dye concentration at constant flow rate decreases the throughput until breakthrough. This may be caused by saturation of the adsorbent more quickly with high dye concentrations, thereby decreasing the breakthrough time.

Wastewater treatment is limited by the breakthrough point or the dynamics of reaching that point. These systems have a small time delay with higher concentrations in the inlet, so the dye solutions have to be diluted before separation for better removal.

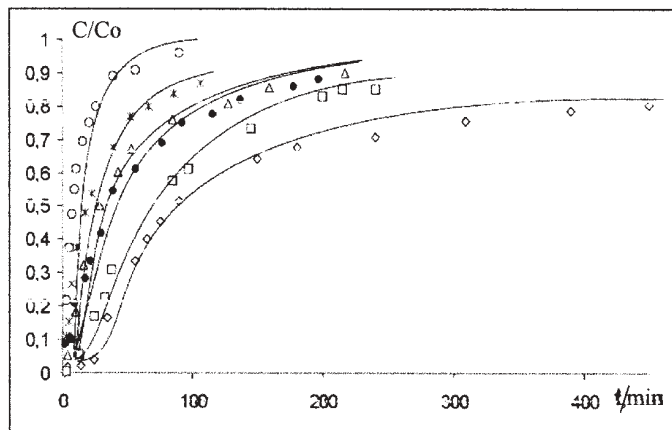


Fig. 3. Effect of the initial dye concentration c_0 , for the systems: MS-300 on GAC at $F = 65 \text{ cm}^3 \text{ min}^{-1}$: \diamond – 50 mg dm^{-3} , \square – 100 mg dm^{-3} , Δ – 200 mg dm^{-3} ; MS-300 on natural zeolite at $F = 35 \text{ cm}^3 \text{ min}^{-1}$: \bullet – 50 mg dm^{-3} , \times – 100 mg dm^{-3} , \circ – 200 mg dm^{-3} .

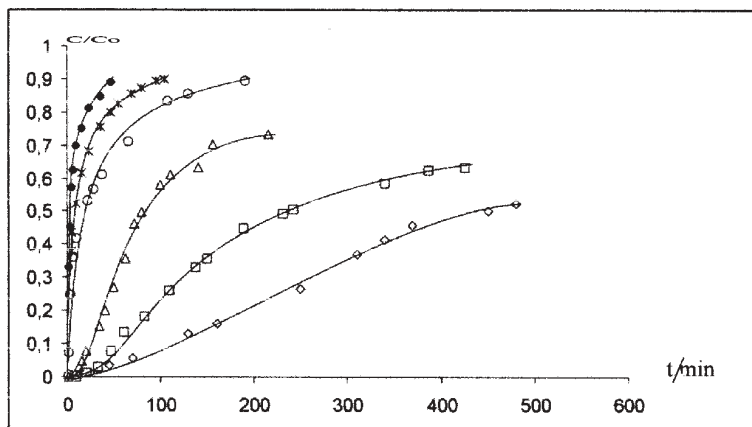


Fig. 4. Effect of the initial dye concentration c_0 , for the systems: MG-400 on GAC at $F = 40 \text{ cm}^3 \text{ min}^{-1}$: \diamond – 50 mg dm^{-3} , \square – 100 mg dm^{-3} , Δ – 200 mg dm^{-3} ; MG-400 on natural zeolite at $F = 40 \text{ cm}^3 \text{ min}^{-1}$: \circ – 50 mg dm^{-3} , \times – 100 mg dm^{-3} , \bullet – 200 mg dm^{-3} .

The estimated values of the model parameters: solid diffusion coefficient, D_s , axial dispersion coefficient, D_L and external mass transfer coefficient, k_f for all the investigated systems for different initial concentrations are presented in Table III.

TABLE III. Parameters in the mathematical model – effect of the initial dye concentration

$c_0/\text{mg dm}^{-3}$	MS300-GAC; $Q = 65 \text{ cm}^3 \text{ min}^{-1}$			MS300-natural zeolite; $Q = 65 \text{ cm}^3 \text{ min}^{-1}$		
	$D_s/\text{m}^2 \text{ s}^{-1}$	$D_L/\text{m}^2 \text{ s}^{-1}$	$k_f/\text{m s}^{-1}$	$D_s/\text{m}^2 \text{ s}^{-1}$	$D_L/\text{m}^2 \text{ s}^{-1}$	$k_f/\text{m s}^{-1}$
50	7.69×10^{-8}	3.71×10^{-1}	4.52×10^{-8}	7.69×10^{-8}	3.71×10^{-6}	4.52×10^{-8}
100	1.37×10^{-8}	6.90×10^{-6}	1.39×10^{-8}	1.39×10^{-9}	3.97×10^{-6}	5.55×10^{-8}
200	1.37×10^{-10}	6.90×10^{-6}	2.77×10^{-8}	2.22×10^{-8}	3.69×10^{-6}	2.55×10^{-6}
	MG400-GAC; $Q = 40 \text{ cm}^3 \text{ min}^{-1}$			MG400-natural zeolite; $Q = 40 \text{ cm}^3 \text{ min}^{-1}$		
	$D_s/\text{m}^2 \text{ s}^{-1}$	$D_L/\text{m}^2 \text{ s}^{-1}$	$k_f/\text{m s}^{-1}$	$D_s/\text{m}^2 \text{ s}^{-1}$	$D_L/\text{m}^2 \text{ s}^{-1}$	$k_f/\text{m s}^{-1}$
50	1.15×10^{-11}	4.24×10^{-6}	1.24×10^{-8}	7.77×10^{-9}	4.08×10^{-6}	1.93×10^{-5}
100	1.15×10^{-11}	4.24×10^{-6}	2.22×10^{-8}	4.27×10^{-8}	4.11×10^{-6}	1.39×10^{-5}
200	7.77×10^{-11}	4.24×10^{-6}	5.77×10^{-8}	4.05×10^{-8}	3.36×10^{-6}	3.58×10^{-5}

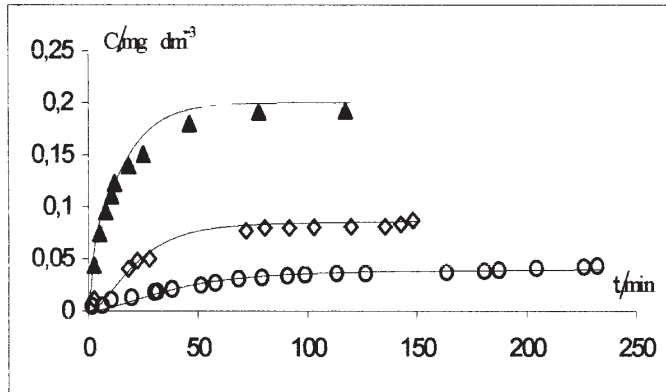


Fig. 5. Simulated breakthrough curves for the system: MS-300 on natural zeolite at $F = 35 \text{ cm}^3 \text{ min}^{-1}$: $\circ - c_0 = 50 \text{ mg dm}^{-3}$; $\blacktriangle - c_0 = 100 \text{ mg dm}^{-3}$; $\diamond - c_0 = 200 \text{ mg dm}^{-3}$.

It can be seen that the axial dispersion coefficient is almost constant with varying initial dye concentration. Thus, it was confirmed that the axial dispersion coefficient is insignificant not affecting either the shape or the lasting time of the breakthrough curves. Hence, in further simulation studies based on the SDC model, the axial dispersion term (Eq. (24)) might be ignored.

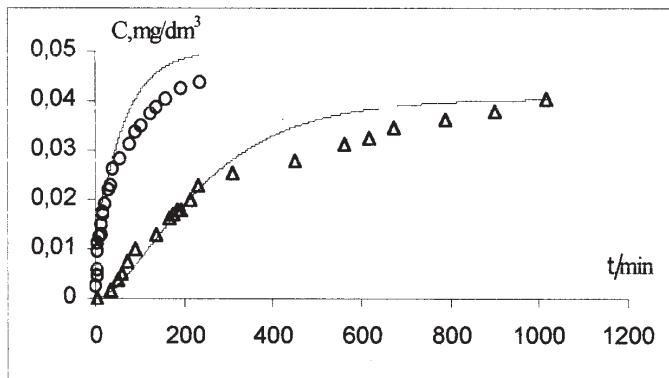


Fig. 6. Simulated breakthrough curves at $c_0 = 50 \text{ mg dm}^{-3}$ and $F = 50 \text{ cm}^3 \text{ min}^{-1}$: $\Delta - \text{MS-300 on GAC}$; $\circ - \text{MS-300 on natural zeolite}$.

Our experiments showed a dependence of D_s on the initial dye concentration. The concentration dependence of D_s is more pronounced for the less favourably adsorbed adsorbate (MG-400) than for the more favourably adsorbed one (MS-300). In order to obtain a better agreement between the theoretical and experimental data, it is necessary to introduce the D_s dependence on the concentration in the mathematical model.

The external mass transfer coefficient increases with increasing concentration and, at the same time, the k_f values are higher for the system basic dye – natural zeolite than for the system basic dye – GAC.

Some of the simulated breakthrough curves obtained from the solid diffusion control (SDC) model are presented in Figs. 5 and 6. The comparison of the simulated breakthrough

curves and the experimental data for adsorption of MS-300 onto natural zeolite for different initial dye concentrations is presented in Fig. 5. The correlation between the theoretical and the experimental data is good especially for lower values of the initial dye concentration. For higher initial dye concentration, the deviation from the experimental data is more obvious when the values of the effluent concentration are near the value of the initial concentration. At high dye concentrations it could be expected that pore diffusion from liquid filled pores within the particle starts to have an effect on the rate controlling mechanism.

The comparison of the simulated breakthrough curves and experimental data for adsorption of MS-300 onto GAC and natural zeolite is presented in Fig. 6. The slope of the breakthrough curve for the adsorption of the basic dye onto natural zeolite is bigger than for the adsorption of the same dye onto GAC. This leads to a decrease of the operation time which means that the saturation of the adsorbent is faster.

Effect of the volumetric flow rate on the breakthrough curves

In the design of a fixed bed adsorption column, the contact time is the most significant variable, and therefore the bed depth and the dye flow rate are the major design parameters. The effect of varying the volumetric flow rate was investigated for all the systems and the breakthrough curves are presented in Figs. 7 and 8.

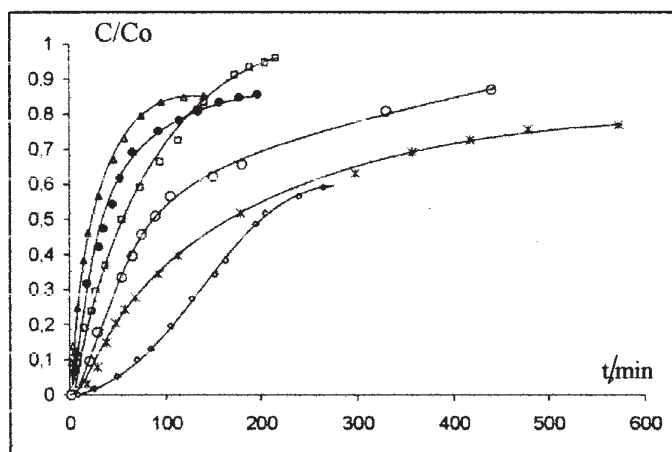


Fig. 7. Effect of the volumetric flow rate, F_1 for the systems: MS-300 on GAC at $c_0 = 50 \text{ mg cm}^{-3}$: \circ – $65 \text{ cm}^3 \text{ min}^{-1}$, \times – $50 \text{ cm}^3 \text{ min}^{-1}$; MS-300 on natural zeolite at $c_0 = 50 \text{ mg dm}^{-3}$: \diamond – $10 \text{ cm}^3 \text{ min}^{-1}$, \square – $25 \text{ cm}^3 \text{ min}^{-1}$, \bullet – $35 \text{ cm}^3 \text{ min}^{-1}$, Δ – $50 \text{ cm}^3 \text{ min}^{-1}$.

From Figs. 7 and 8 it is obvious that increasing the flow rate decreases the volume treated until breakthrough and, therefore, the service time of the bed. This is due to the decreased contact time between the dye and the adsorbent at higher flow rates. When the flow rate is smaller, equilibrium corresponding to batch experimental data could be reached, and the shape of the curves is more like the ideal breakthrough curve, or that the critical value of the outlet concentration is moved towards the theoretical value close to 90 % of the inlet concentration. For the same flow rate, the contact time is smaller for the systems dye–natural zeolite than for the systems dye–GAC.

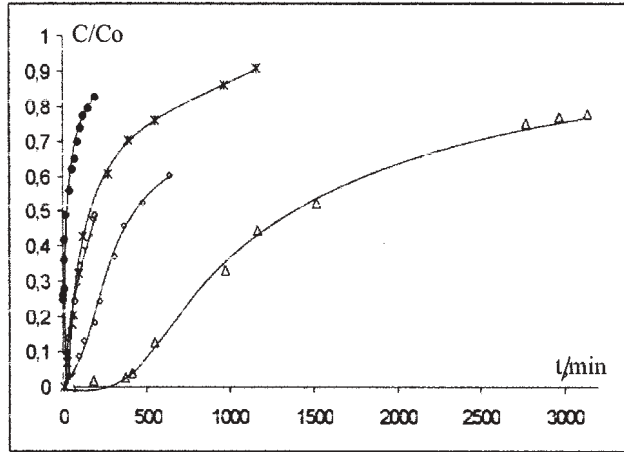


Fig. 8. Effect of the volumetric flow rate, F_1 for the systems: MG-400 on GAC at $c_0 = 50 \text{ mg dm}^{-3}$: $\diamond - 40 \text{ cm}^3 \text{ min}^{-1}$; $\circ - 100 \text{ cm}^3 \text{ min}^{-1}$; MG-400 on natural zeolite at $c_0 = 50 \text{ mg dm}^{-3}$: $\Delta - 2 \text{ cm} \text{ min}^{-1}$, $\times - 8 \text{ cm}^3 \text{ min}^{-1}$, $\bullet - 40 \text{ cm}^3 \text{ min}^{-1}$.

The estimated values of the model parameters obtained from the simulation study for different volumetric flow rates for the investigated systems are presented in Table IV.

TABLE IV. Parameters in the mathematical model – effect of the volumetric flow rate

$Q/\text{cm}^3 \text{ min}^{-1}$	MS300-GAC; $c_0 = 50 \text{ mg dm}^{-3}$			MS300-natural zeolite; $c_0 = 50 \text{ mg cm}^{-3}$			
	$D_s/\text{m}^2 \text{ s}^{-1}$	$D_L/\text{m}^2 \text{ s}^{-1}$	$k_f/\text{m s}^{-1}$	$Q/\text{cm}^3 \text{ min}^{-1}$	$D_s/\text{m}^2 \text{ s}^{-1}$	$D_L/\text{m}^2 \text{ s}^{-1}$	$k_f/\text{m s}^{-1}$
40	1.6×10^{-13}	4.24×10^{-6}	8.33×10^{-8}	25	1.43×10^{-5}	2.65×10^{-6}	2.76×10^{-7}
50	1.39×10^{-10}	5.30×10^{-6}	1.39×10^{-8}	35	7.691×10^{-8}	3.82×10^{-6}	4.52×10^{-8}
65	1.37×10^{-10}	6.88×10^{-6}	1.66×10^{-8}	50	1.39×10^{-8}	5.19×10^{-4}	3.30×10^{-5}
	MG400-GAC; $c_0 = 50 \text{ mg dm}^{-3}$			MG400-natural zeolite; $c_0 = 50 \text{ mg cm}^{-3}$			
40	1.15×10^{-11}	4.24×10^{-6}	1.24×10^{-8}	2	6.66×10^{-9}	2.12×10^{-7}	5.77×10^{-7}
50	1.97×10^{-10}	5.27×10^{-6}	1.95×10^{-5}	8	7.50×10^{-9}	8.00×10^{-7}	1.52×10^{-5}
65	7.77×10^{-11}	6.69×10^{-6}	1.68×10^{-5}	40	4.05×10^{-8}	3.36×10^{-6}	3.58×10^{-5}

The axial dispersion coefficient varies insignificantly with the flow rate in the range between 25 and $65 \text{ cm}^3 \text{ min}^{-1}$. The adsorption of MG-400 onto natural zeolite is the exception and the axial dispersion coefficient for this system increases with increasing flow rate. The solid diffusion coefficient and the external mass transfer coefficient depend on the flow rate but a general conclusion cannot be deduced.

CONCLUSIONS

The adsorption of basic dyes onto granular activated carbon and natural zeolite in a fixed bed column was studied. The experimental results showed that both the adsorbents removed the dyes effectively and the effect of changing the column operating variables, such as flow rate and initial dye concentration, were studied.

The solid diffusion control (SDC) model describing single solute adsorption in a fixed bed is based on the Linear Driving Force (LDF) kinetic model. The finite difference method was used for transforming the partial differential equation into a set of ordinary differential equations.

Generally, the agreement between the experimental and the simulated breakthrough curves appears to be satisfactory. However, some deviations were found between the predicted and the experimental data which reflect the fact that the assumptions of the model were not quite fulfilled for these experiments. This refers especially to the assumption of a constant solid diffusion coefficient. It is necessary to adjust the values of the solid diffusion coefficient, the axial dispersion coefficient and the external mass transfer coefficient to obtain satisfactory agreement between the simulated and the experimental breakthrough curves.

NOTATION

- Bi – Biot number
 c_b – bulk phase dye concentration, mg dm^{-3}
 c_s – liquid phase concentration in equilibrium with q_s on the surface, mg dm^{-3}
 c_{in} – inlet concentration, mg dm^{-3}
 \bar{c} – average liquid phase concentration, mg dm^{-3}
 D_L – axial dispersion coefficient, m^2s^{-1}
 D_s – solid diffusion coefficient, m^2s^{-1}
 k_f – mass transfer coefficient, m s^{-1}
 K – Langmuir isotherm parameter, $\text{dm}^{-3} \text{mg}^{-1}$
 L – column length, m
 m – uptake rate of adsorption, $\text{mg s}^{-1} \text{dm}^{-3}$
 \bar{q} – average adsorbed phase dye concentration, mg g^{-1}
 q_s – concentration on the surface of the pellets, mg g^{-1}
 q_m – Langmuir isotherm parameter, mg g^{-1}
 R_p – radius of the adsorbent pellets, m
 t – time, s
 v – interstitial velocity, m s^{-1}
 Pe – Peclet number
 Y – dimensionless axial coordinate
 z – axial coordinate, m
Greek letters:
 ε – bed porosity
 ε_p – porosity of an adsorbent pellet
 θ – dimensionless time variable

ИЗВОД

МОДЕЛ ДИФУЗИЈЕ У ЧВРСТОЈ ФАЗИ ЗА АДСОРПЦИЈУ БАЗНИХ БОЈА НА
 ГРАНУЛИРАНОМ АКТИВНОМ УГЉУ И ПРИРОДНОМ ЗЕОЛИТУ У КОЛОНИ СА
 ФИКСНИМ СЛОЈЕМ

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Истраживана је адсорпција базних боја из водених раствора на гранулираном активном угљу и природном зеолиту у колони са фиксним слојем. Студиран је про-

јектни поступак за адсорпцију две базне боје и to Maxilon Goldgelb GL EC 400 % (MG-400) и Maxilon Schwarz FBL-01 300 % (MS-300) у колони са фиксним слојем. На бази модела дифузије у чврстом израђен је компјутерски програм за симулацију. За све испитиване системе одређени су параметри модела: коефицијент дифузије у чврстом, D_s , коефицијент аксијалне дисперзије, D_L и коефицијент преноса масе у спољашњем филму k_f помоћу методе најбољег фита.

(Примљено 31. јула 2000)

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