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A. L. Cukierman & N. O. Lemcoff**

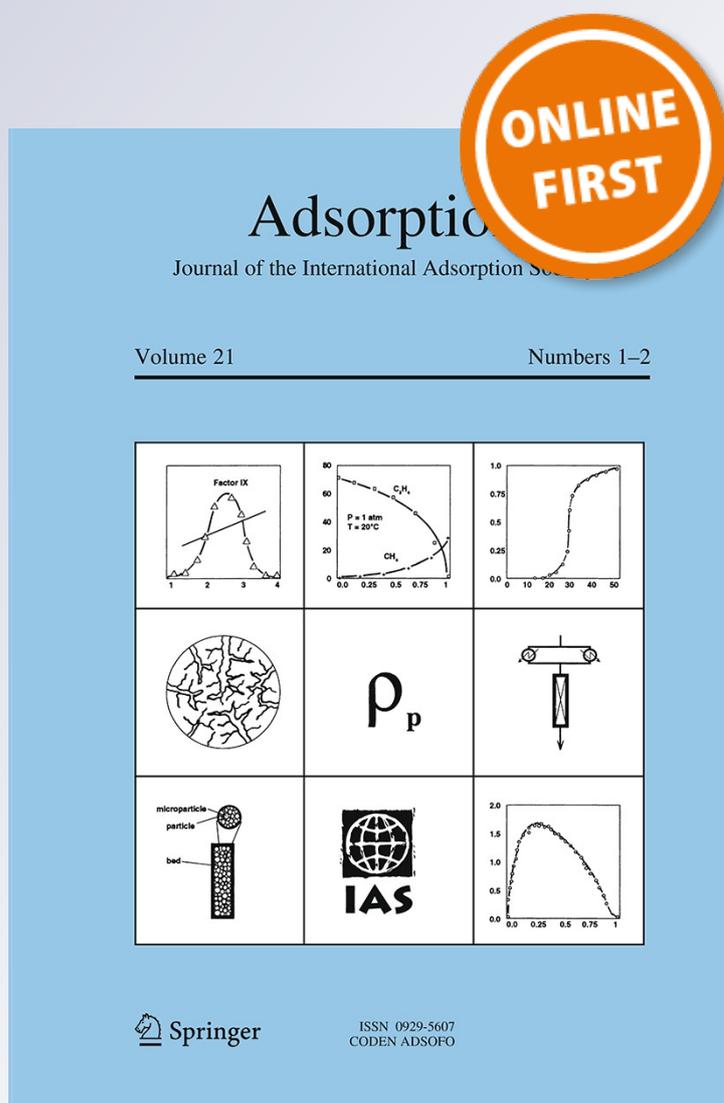
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Modeling the biosorption of basic dyes from binary mixtures

M. E. Fernandez · P. R. Bonelli · A. L. Cukierman ·
N. O. Lemcoff

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Abstract The biosorption of basic dyes, methylene blue and rhodamine B, from binary aqueous solutions onto cypress cone chips, was analyzed through mathematical modeling. This study aimed at introducing a novel model to predict the dynamic binary sorption of the dyes. It consisted of a modified Langmuir multicomponent isotherm coupled with a linear driving force model. Experimental data from recent studies using the untreated and alkaline-treated biosorbent was used to determine the model parameters, and the breakthrough predictions are in good agreement with the experimental results. Useful information on the effects of bed length and feed concentration on the breakthrough time and mass transfer length was obtained. This can guide the design and optimization of the biosorbent column.

Keywords Biosorption · Basic dyes · Dynamic studies · Modeling

1 Introduction

Industrial effluents are often contaminated and need to be processed before their discharge in bodies of water. One

group of contaminants are the dyes used in textile, paper and plastic industries. In particular, dyes used by the textile industry are mainly synthetic and derived from either coal tar or petroleum-based intermediates (US EPA 1997). Most dyes are classified either as acid or basic dyes, and its use depends on the substrate involved. Acid dyes contain sulfonic acid groups and are preferentially used with protein fibers. Basic dyes are cationic salts which can interact with the surface of the substrate, and are mainly used with wool, silk and some acrylic fibers (Pereira and Alves 2012).

Activated carbons are the traditional adsorbents used for dyes, but a large number of alternative low-cost adsorbents have also been reported in the literature (Gupta and Suhas 2009). Adsorption studies are usually carried out in batch systems, and both kinetic and equilibrium data for single and/or multicomponent mixtures is obtained. The experimental results are modeled using mainly Langmuir and Freundlich isotherms, multilayer models, and the ideal adsorption solution (IAS) theory (Walker and Weatherley 2000, Ozcan et al. 2004, Turabik 2008, Crini and Badot 2008, Noroozi and Sorial 2013). The kinetic uptake is represented in most cases by general rate models (pore diffusion, surface diffusion), linear driving force (LDF) model, and pseudo first and second order models (Ozcan et al. 2004, Crini and Badot 2008, Ho and McKay 1999, Xu et al. 2013).

Since the number of dyes used in industry is quite large, in order to develop and/or test adsorbents that can be used in the removal of these contaminants, probe molecules are normally used (Fernandez et al. 2012). Methylene blue (MB) and rhodamine B (RhB) are two of the basic or cationic dyes whose adsorption has been extensively studied. Eftekari et al. (2010) studied their competitive adsorption on a mesoporous adsorbent, while Jafari-zare and Habibi-yangjeh (2010) used a natural zeolite. Both their studies

M. E. Fernandez · P. R. Bonelli · A. L. Cukierman
Programa de Investigación y Desarrollo de Fuentes Alternativas
de Materias Primas y Energía-PINMATE, Departamento de
Industrias, Facultad de Ciencias Exactas y Naturales,
Universidad de Buenos Aires, Ciudad Universitaria,
Buenos Aires, Argentina

N. O. Lemcoff (✉)
Department of Engineering and Science, Rensselaer Polytechnic
Institute Hartford, 275 Windsor Street, Hartford, CT 06120,
USA
e-mail: lemcon@rpi.edu

showed that a pseudo second order kinetic model represents the uptake in single component systems, and a Langmuir isotherm represents adsorption equilibrium data in both single and binary component systems.

Adsorption of single components from liquid solutions has been successfully represented by both Langmuir and Freundlich isotherms (Sheindorf et al. 1981). However, when dealing with multi-component systems, the extended isotherms, used for adsorption from the gas phase, do not always accurately predict the system behavior. It is necessary to take into account additional interactions. Sheindorf et al. (1981, 1982) developed a Freundlich-type multicomponent isotherm to describe the adsorption in aqueous – solid systems, such as water pollutants on activated carbon. They assumed the individual components are well represented by the Freundlich isotherm, and that for each component an exponential distribution of adsorption energies exists. The multicomponent adsorption isotherm for component i in a k -component system is expressed as

$$q_i = b_i c_i \left(\sum_{j=1}^k a_{ij} c_j \right)^{n_i - 1} \quad (1)$$

where the parameters b_i and n_i are constants that depend on the temperature, and are determined from the single-component system data. The competition coefficients a_{ij} are determined from the multicomponent isotherm.

Ghaedi et al. (2013) studied the biosorption of two basic dyes (Methylene blue and Brilliant green) in single and binary mixtures, and analyzed the experimental results using both Langmuir and Freundlich adsorption isotherms. In order to predict the multicomponent system performance and account for the interactions between the dyes, they used a lumped capacity factor P_i . The P -factor is defined as the ratio between the monolayer capacities in single- and multi-solute systems (McKay and Al Duri 1987).

However, very few studies have dealt with the prediction of breakthrough curves and the design of biosorbents. Some of the difficulties arise from the need of a good model to represent the system behavior. Adsorption kinetics and equilibrium isotherms, external and internal mass transfer kinetics, and flow patterns in the biosorbent are the main phenomena that need to be considered in the development of an appropriate model.

Using experimental data previously reported (Fernandez et al. 2010, 2012), a model was developed in this work to predict the dynamic performance (breakthrough time and overshoot pattern) of biosorbents in the removal of binary mixtures of dyestuffs. Fernandez et al. (2010, 2012) studied the biosorption of MB and RhB from aqueous solutions using natural (PNAT) and modified (PKOH) cypress cone chips. Adsorption isotherms and breakthrough curves for single-dye systems were determined for each dye at its

optimal pH, namely pH 4 for RhB, and pH 7 for MB. On the other hand, both batch and dynamic studies were carried out for binary-dye solutions at the two pH values, and the competitive biosorption of the dyes was analyzed. For both biosorbents, the MB is more strongly adsorbed, and a roll-up effect was observed at pH 4. Although kinetic and breakthrough data was fit by available analytical solutions, there was no attempt to develop a model able to predict the system performance.

In this work, a Langmuir multicomponent isotherm, modified to account for the interaction of the components, and a LDF model were used to predict the sorption of the binary mixture. Model parameters were obtained from single component biosorption data and from batch and dynamic studies on natural and alkaline treated cypress cone chips. Numerical simulation studies of the sorption process were carried out using COMSOL Multiphysics, commercial computer simulation software (COMSOL 2015).

2 Mathematical model for multicomponent biosorption

2.1 Model equations

The mathematical model used to simulate the dynamic experiments assumed axial dispersion in a packed bed with a porous adsorbent. The rate of mass transfer to the solid particles is represented by the LDF model. The material balance equations can be expressed as (Ruthven et al. 1994)

$$\varepsilon \frac{\partial c_i}{\partial t} = -u \frac{\partial c_i}{\partial z} + \varepsilon D_z \frac{\partial^2 c_i}{\partial z^2} - \rho_b \frac{dq_i}{dt} \quad (2)$$

where c_i is the concentration of component i in the liquid phase (mol/m³), q_i is the amount of component i adsorbed on the biosorbent (mol/g), ε is the total bed void fraction, u is the superficial velocity (m/s), D_z is the axial diffusivity (m²/s), and ρ_b is the bulk density of the adsorbent (kg/m³). The adsorption rate can be represented by the LDF model (Xu et al. 2013, Qiu et al. 2009)

$$\frac{dq_i}{dt} = k_i (q_{eq,i} - q_i) \quad (3)$$

where k_i is the LDF constant (1/s), and $q_{eq,i}$ is the equilibrium amount of component i adsorbed on the biosorbent (mol/kg). This equation accounts both for the external and internal diffusional resistances.

To predict the adsorption equilibrium for component i , we introduce a modified multicomponent Langmuir isotherm

$$q_{eq,i} = m_i c_i / \left(1 + \sum_{j=1}^k a_{ij} K_j c_j \right) \quad (4)$$

where K_i is the adsorption equilibrium constant (m^3/mol), m_i is related to the monolayer adsorption capacity $q_{mL,i}$ through the equation $m_i = q_{mL,i} K_i$, and a_{ij} are the competition coefficients, which measure the interaction of the components in the binary system. Since these coefficients are the ratio between the adsorption coefficients in Langmuir isotherms, it can be shown that $a_{ij} = 1/a_{ji}$.

2.2 Model parameters

Fernandez et al. (2010, 2012) carried out dynamic biosorption studies for both single and binary solutions of MB and RhB on cypress cone chips at two pH values (pH 4 and pH 7). A summary of the experimental conditions is shown in Table 1.

The objective of this work is to model the binary adsorption equilibrium in liquid phase using an extended Langmuir equation, and accurately predict the performance of natural and modified cypress cone chips in the removal of MB and RhB from aqueous solutions at pH 4.

To predict the behavior of the binary system it is first necessary to determine the appropriate model parameters. It should be pointed out that the adsorption isotherms and single-dye dynamic studies done by Fernandez et al. (2010, 2012) were only carried out for one of the components at each pH.

The following are the assumptions made to model the binary system:

- The value of the Langmuir isotherm adsorption constants K_i were obtained from the single component batch biosorption studies (Fernandez et al. 2010, 2012).

Table 1 Breakthrough studies—experimental conditions

Bed diameter	0.016 m
Bed length	0.100 m
Adsorbent weight	6×10^{-3} kg
Average particle diameter	1.775×10^{-4} m
Bed porosity	0.37
Dye concentration	0.21 mol/m ³
Solution flow rate	11 mL/min (6.6×10^{-4} m ³ /h)
Temperature	20 °C

Table 2 Biosorption model parameters used in numerical simulation

	PNAT		PKOH	
	Methylene blue	Rhodamine B	Methylene blue	Rhodamine B
m_i (m ³ /kg)	39.54	6.20	46.36	4.91
K_i (m ³ /mol)	106.3	28.4	95.1	15.2
k_i (1/s)	2×10^{-4}	2×10^{-4}	2×10^{-4}	2×10^{-4}
a_{ij}	0.5	2	0.5	2

Since no adsorption data was available for the adsorption of methylene blue at pH 4, the adsorption constant at this pH was assumed to be the same as that for pH 7.

- The Langmuir monolayer adsorption capacity (-maximum adsorption capacity) $q_{mL,i}$ was obtained from the fitting of the model solution to the experimental single component dynamic studies data, and minimizing the difference between the measured and predicted capacities.
- The competition coefficients a_{ij} were derived from the binary dynamic studies, following the method proposed by Ghaedi et al. (2013). The auto-interaction coefficients a_{ii} are equal to 1.
- The LDF constant was obtained from the single component dynamic biosorption studies. A value of $k_i = 2 \times 10^{-4}$ 1/s was found to represent well the uptake data for both MB and RhB, and is in reasonable agreement with values observed in similar systems (Dogan et al. 2009). If the driving force model had been used in the batch kinetic studies reported by Fernandez et al. (2010, 2012), the corresponding kinetic constants would have been of the order of 10^{-3} 1/s. This represents about an order of magnitude higher than the values obtained in this work from the analysis of the single component dynamic biosorption studies. This difference can be attributed to the additional mass transfer effects that exist in the dynamic studies.
- The value of the axial diffusivity was obtained from the correlation given by Gunn (1987)

$$D_z = u d_p / Pe \tag{5}$$

where the Peclet number for the dynamic studies is $Pe = 0.436$, and d_p is the average particle diameter.

The values of the parameters used in the simulation of the dynamic binary-dye biosorption are summarized in Table 2.

The magnitude of the axial dispersion effect can be estimated from the parameter δ , defined as (Ruthven 1984)

$$\delta = \left(\frac{1 - \varepsilon}{\varepsilon} \right) \left(\frac{6k_i}{d_p} \right) \left(\frac{D_z}{u^2} \right) \tag{6}$$

It measures the relative importance of axial dispersion and mass transfer resistance. When the value of δ is less than 1, the flow pattern is close to plug flow and the mass

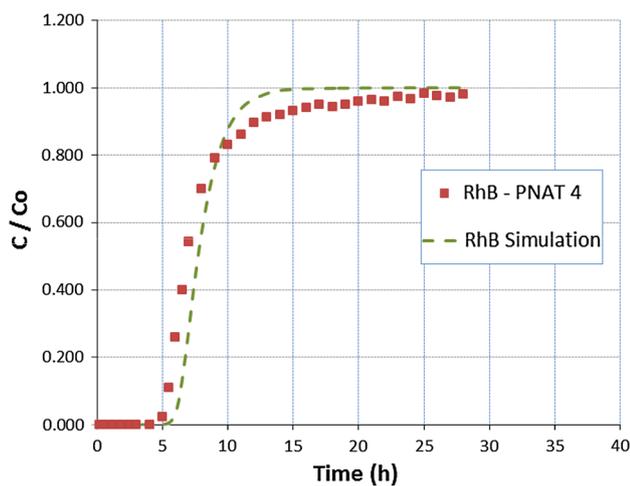


Fig. 1 Breakthrough curve for single solutions of rhodamine B on PNAT at pH 4 (Simulation vs. Experimental)

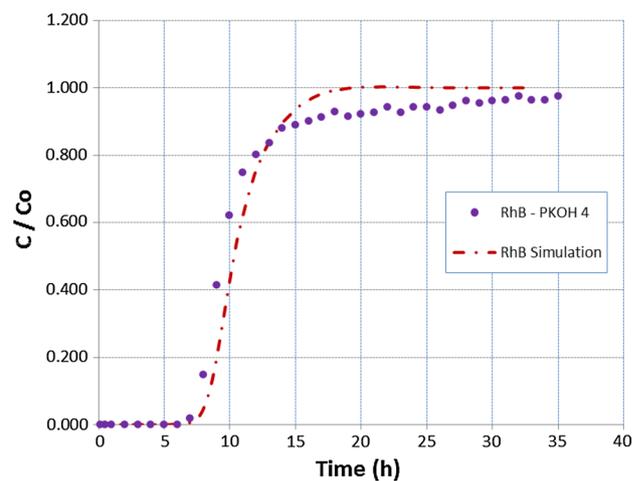


Fig. 2 Breakthrough curve for single solutions of rhodamine B on PKOH at pH 4 (Simulation vs. Experimental)

transfer resistance is high. As δ increases, the axial dispersion effect increases and the mass transfer resistance decreases. In this case, the value of δ is about 3.3, which suggests that both effects play some role in the dynamic studies.

The analysis of the single component isotherms indicates that the system is quite non-linear, with a value of $\beta = 1 - q_o/q_s$ smaller than 0.25 for all the cases studied. q_o represents the amount of dye adsorbed under equilibrium conditions at the feed concentration, while q_s represents the maximum amount at saturation.

3 Results and discussion

A comparison between the experimental results and model predictions for single solutions of RhB on PNAT and PKOH is shown in Figs. 1 and 2. The proposed model is a very good representation of the experimentally measured single component breakthrough curves, although it predicts a faster approach to the feed concentration for $C/C_o > 0.80$.

For the prediction of the behavior of the binary dynamic systems, the modified multicomponent Langmuir isotherm was used (Eq. 4). The only parameter values to be fitted are a_{ij} . Since there are two adsorbable components, and $a_{ij} = 1/a_{ji}$, there is only one degree of freedom. The remaining model parameters arise from the single component sorption data or from correlations. Model predictions and experimental results for both PNAT and PKOH are shown in Figs. 3, 4, 5, 6 for $a_{12} = 0.5$ ($a_{21} = 2$), and a good agreement is observed. Although for both biosorbents, the predicted roll-up effect is slightly greater than the measured values, with a maximum difference of about 15 %,

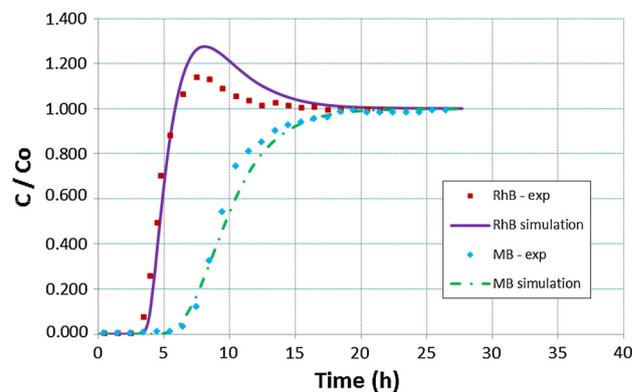


Fig. 3 Breakthrough curves for binary mixtures of methylene blue (MB) and rhodamine B (RhB) on PNAT at pH 4 (Simulation vs. Experimental)

the model predicts quite accurately the breakthrough times (Figs. 3, 5).

The breakthrough time for MB in PNAT is much shorter than that in PKOH, and the RhB roll-up effect is also smaller. The roll-up effect can be explained in terms of the relative ratios of both the maximum capacities of the dyes and of the adsorption constants. The ratios (m_i/m_j) and (K_i/K_j) between RhB and MB are both closer to 1 for the biosorption on PNAT than on PKOH. The maximum capacities ratios are 0.157 and 0.106 for PNAT and PKOH, respectively, while the adsorption constants ratios are 0.267 and 0.160 for PNAT and PKOH, respectively. It can be concluded that the dyes biosorption characteristics are more similar in the case of PNAT, and the competition for sites is less intense.

The effect of the bed length was studied for PNAT and PKOH at pH 4. The original bed length of 0.10 m was

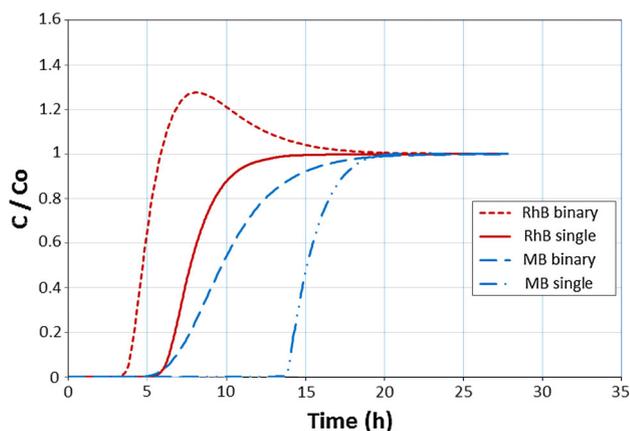


Fig. 4 Simulated breakthrough curves (single and binary) for methylene blue (MB) and rhodamine B (RhB) on PNAT at pH 4

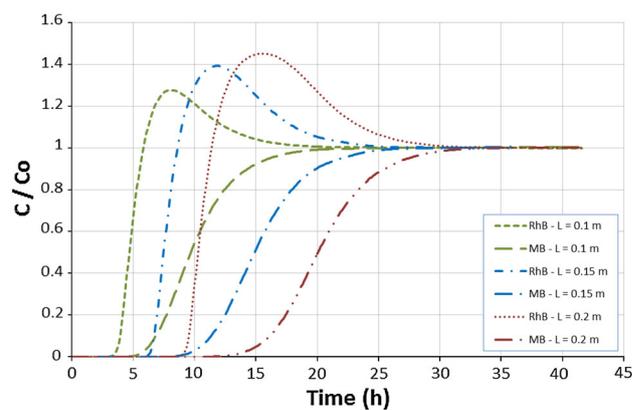


Fig. 7 Effect of adsorber length on the breakthrough curves for binary mixtures of methylene blue (MB) and rhodamine B (RhB) on PNAT at pH 4

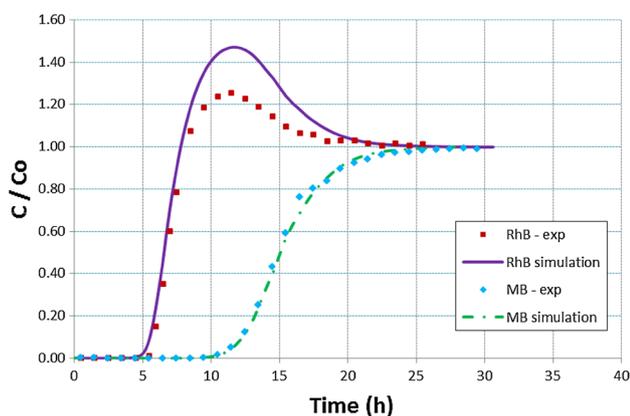


Fig. 5 Breakthrough curves for binary mixtures of methylene blue (MB) and rhodamine B (RhB) on PKOH at pH 4 (Simulation vs. Experimental)

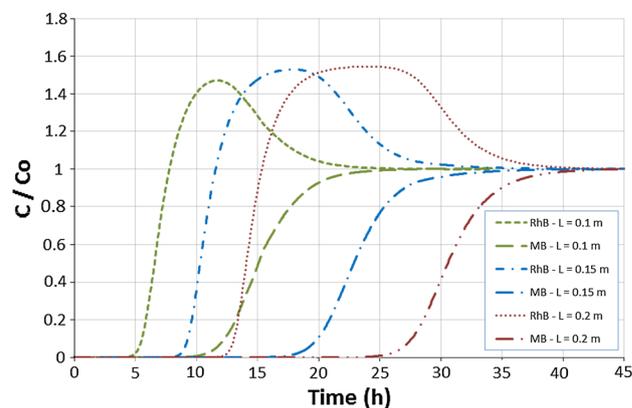


Fig. 8 Effect of adsorber length on the breakthrough curves for binary mixtures of methylene blue (MB) and rhodamine B (RhB) on PKOH at pH 4

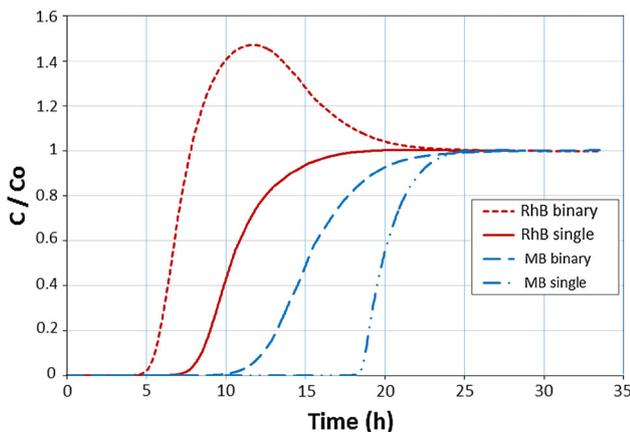


Fig. 6 Simulated breakthrough curves (single and binary) for methylene blue (MB) and rhodamine B (RhB) on PKOH at pH 4

increased to 0.15 and 0.20 m. The breakthrough curves for both adsorbed components show the approach to constant pattern behavior. In the case of the less strongly adsorbed

component (RhB), a relatively steep curve is observed during the initial breakthrough, but the roll-up shape changes significantly, especially for the modified biosorbent (Figs. 7, 8). Actually, the slope of the concentration front as it exits the bed does not change with the bed length.

The breakthrough times are shown in Fig. 9, and a nearly linear increase in t_b can be seen as the bed length increases. However, these lines do not go through the origin due to the entry effect, namely the development of the concentration profiles in the entry region of the column. The slopes of these lines, a measure of the effect of bed length, are much higher for MB as compared with RhB, and also for PKOH as compared with PNAT.

In the case of PNAT, in which the dyes biosorption characteristics are more similar, the maximum effluent concentration for RhB both increases and shifts in time, but the shape of the curve does not change significantly (Fig. 7). In the case of PKOH, the shape of the roll-up

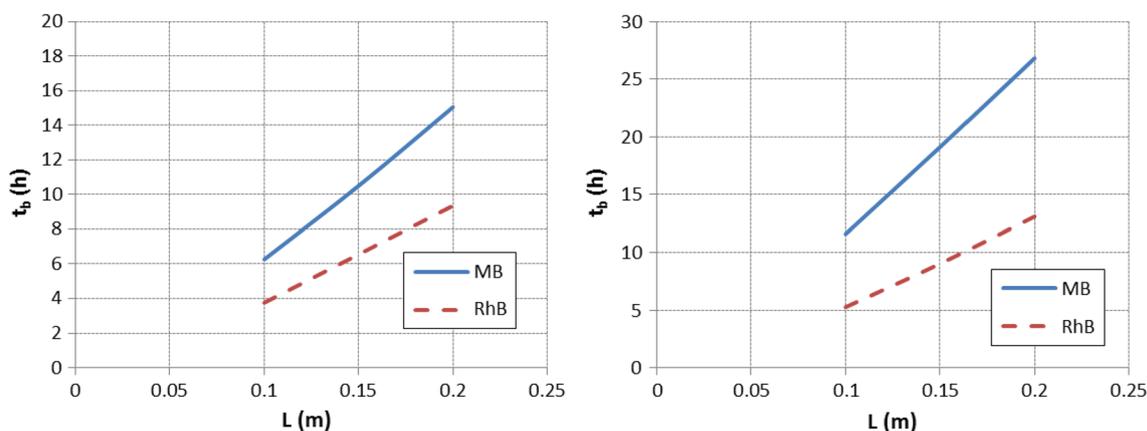


Fig. 9 Effect of adsorber length on the breakthrough time for binary mixtures of methylene blue (MB) and rhodamine B (RhB) on PNAT and PKOH at pH 4

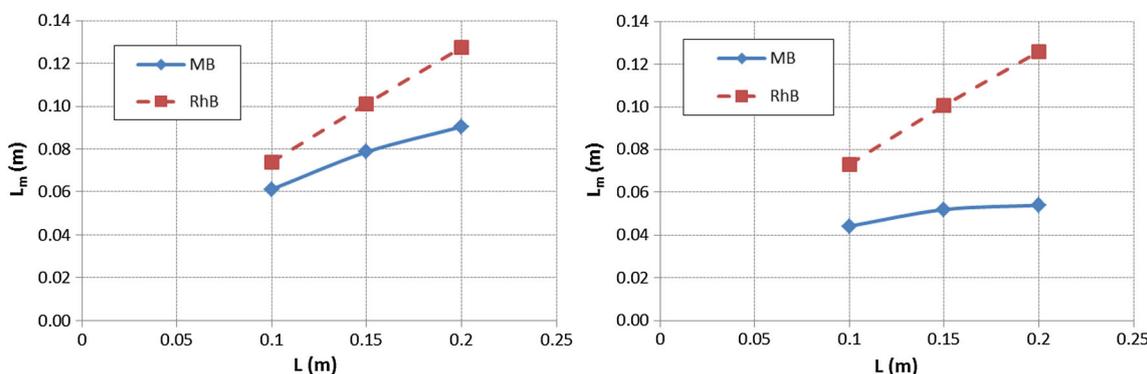


Fig. 10 Effect of adsorber length on the mass transfer length for binary mixtures of methylene blue (MB) and rhodamine B (RhB) on PNAT and PKOH at pH 4

curve for RhB changes and shows a widening plateau with only a slight increase in the maximum effluent concentration (Fig. 8).

The approach to constant pattern is better evaluated by analyzing the mass transfer length, L_m calculated as

$$L_m = L \times (1 - t_b/t_e) \tag{7}$$

where L is the bed length, and t_b and t_e are the breakthrough and exhaust times, respectively. For the more strongly adsorbed component, those are the times at which the exit dye concentration reaches 5 and 95 % of the feed concentration, respectively. Since the less strongly adsorbed component shows a roll-up, the exhaust time for rhodamine B is the time at which the exit concentration drops to 105 % of the feed concentration. The length of the mass transfer zones for the two biosorbents is shown in Fig. 10.

As the bed length increases, the more strongly adsorbed component shows a faster approach to constant pattern for the biosorbent with the steeper isotherm. On the other

hand, a broadening of the roll-up zone is seen for the less-adsorbed dye.

It can be seen that the approach to constant pattern behavior for methylene blue is faster on PKOH due to the steeper isotherm as compared with PNAT. On the other hand, the mass transfer zone for rhodamine B increases almost linearly with the bed length. It should be pointed out that the concentration profiles at the mid-point of the 0.2 m long bed, are about the same as those observed at the exit of the 0.1 m long bed.

The effect of feed concentration on the performance of the biosorbents was studied by increasing the value used in the original experiments by a factor of 2. The predicted breakthrough curves are depicted in Figs. 11 and 12. As the feed concentration is doubled, β ($=1 - q_o/q_s$) decreases from values below 0.25 to values below 0.14, indicating a high degree of non-linearity of the system. The breakthrough time is reduced in all cases by a factor greater than 2. For linear adsorption isotherms, an increase in the contaminants concentration does not significantly affect the breakthrough

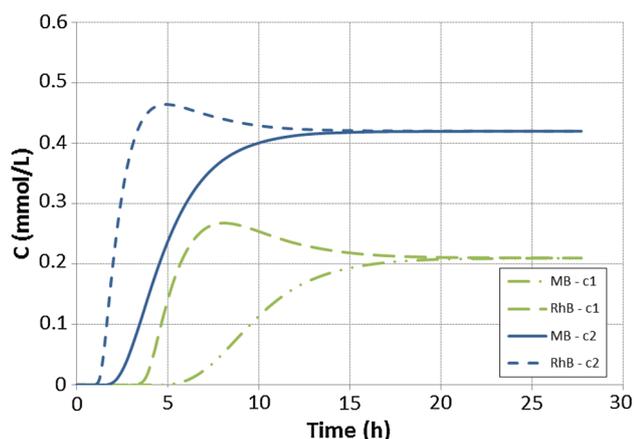


Fig. 11 Effect of feed concentration of biosorption of dyes on PNAT at pH 4

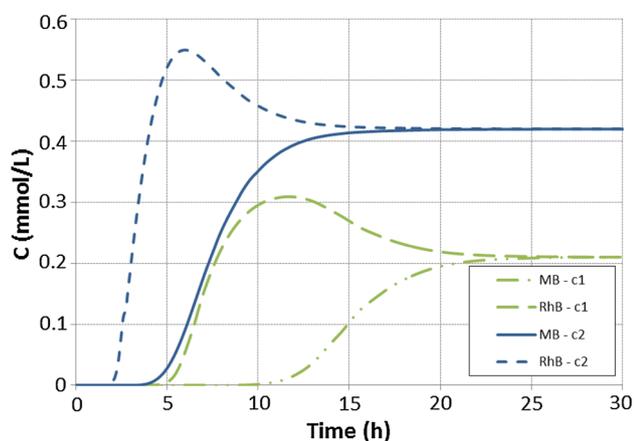


Fig. 12 Effect of feed concentration of biosorption of dyes on PKOH at pH 4

time, but for non-linear isotherms the reduction in the breakthrough time can be significant, as it is shown in this case. In particular, lowering the feed concentration may allow utilizing the biosorbent more efficiently. The model developed can be used to predict the system performance and design and optimize a biosorbent column.

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