

KINETIC STUDY OF BLUE M-EB DYE SORPTION ON ION EXCHANGE RESINS

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A kinetic study concerning the Blue M-EB reactive dye sorption from aqueous solutions on Purolite ion exchange resins of macroporous (A – 500) and gel (A – 400) type has been made. To establish the rate – controlling step, the time required for 50% sorption equilibrium ($t_{1/2}$), rate constant of the process (\bar{K}), diffusion coefficient and activation energy (E_a) for both resins have been calculated. On the basis of the calculated values it is obvious that sorption process is in the diffusion domain, rate-controlling step is the particle diffusion. This result is confirmed by the fact that reactive dye Blue M-EB sorption is in good agreement with shell-progressive model.

Keywords: exchange resins, dye removal, sorption, kinetic study, wastewaters, decontamination

Introduction

The decontamination of natural or wastewaters impurified with organic pollutants has become one of the needs of the day. The great diversity in chemical structure of the dyes as well as the variable concentrations of dyes and co-solutes, such as inorganic salts, sizing agents and surfactants in the effluents of dyehouse operations make impossible a general available method for removing textile dyes from waste water [1-3]. The several traditional wastewater treatment methods (biological processes, ozonation, coagulation, membrane filtration, etc.) are acceptable in decolorizing textile wastewaters with a satisfactorily cost-effectiveness [4].

Due to the polar nature of the their functional groups, most commonly-used dyes are relatively easy to remove by sorption on various materials: activated carbon [5], non ionic or ionic synthetic polymers [6,7], biomass-based exchangers [8], anionic clay minerals [9] and also adsorbents [10]. The dye binding potential of these materials is affected by physic-chemical characteristics of both sorbent and dye, there compatibility, as well as the operating conditions (particle size of granulated sorbent, pH, ionic strength, temperature, solution flow rate, etc.) [11].

The economic use of various sorbents in removing color from textile effluents, but also a better understanding of these processes in natural systems require informations on the kinetics of dye uptake.

The thermodynamic, kinetic characterization, the mechanism and determinant factors study of the sorption process of reactive dyes on Purolite ion exchangers are of major important stages in evaluation of these resins application in the recovery of wastewaters of textile industry.

This paper describes a study of Blue M-EB reactive dye sorption kinetics onto Purolite anion exchange resins. For this purpose, resin loading as a function of the contact time was monitored.

Experimental

The experiments were carried out using ion exchange resins purchased from Purolite International LTD (UK), their typical properties are listed in *Table 1*.

The reactive bifunctional monochlorotriazinic dye Blue M-EB (*Fig.1*) was used as a stock aqueous solution containing 0.4 g L⁻¹. The working solutions were prepared by appropriate dilution of the stock solution with doubly distilled water.

Table 1 Properties of Purolite resins used in kinetic measurements

Parameter	Type of Purolite resins	
	A - 400	A - 500
Matrix	polystyrene-divinylbenzene	polystyrene-divinylbenzene
Structure	gel	macroporous
Functional group	R - (CH ₃) ₃ N ⁺	R - (CH ₃) ₃ N ⁺
Ionic form	Cl ⁻	Cl ⁻
Mean particle diameter/mm	0.64 (± 0.03)	0.64 (± 0.03)
Capacity*/ meqg ⁻¹	3.72	3.93

* determined by pH-metric titration of resins dried at room temperature for 72 hours

Table 2 Sorption half times, $t_{1/2}$ at different concentrations and temperatures of Blue M - EB dye solution for the Purolite resins

C_0 / gL^{-1}	T / K	$t_{1/2} / \text{min}$	
		A - 400	A - 500
0.10	284.15	20	16
0.10	296.15	17	10
0.14	284.15	14	13
0.20	284.15	11	9

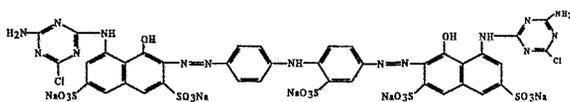


Fig. 1 Structure of reactive dye blue M-EB

The continuous kinetic experiments were performed by the "limited bath" technique. Weighed amounts of anionic resin (1g) were contacted with 250 mL solution containing known amounts of reactive dye, under constant vigorous stirring. The temperature of solutions was held constant (284.15 and 296.15 K) during the experiment with a thermostatic bath. After the predetermined time intervals, varying from 5 to 60 minutes, samples of 2mL supernatant were taken for measurements of dye content. Analysis of Blue M-EB dye was carried out by spectrophotometric method ($\lambda_{\text{max}} = 650 \text{ nm}$) with a HACH DR 200 UV-VIS spectrophotometer.

The extent of sorption was expressed by the fractional attainment of equilibrium, $F = \frac{q_t}{q_0}$ where, q_t is

the amount of sorbed dye per gram of resin at time t and q_0 is the amount of dye sorbed per gram of resin after 24 hours

Results and Discussion

In our previous work [12], the equilibrium sorption of reactive dye Blue M-EB onto Purolite anion exchange resins was studied. The low capacity of resins to remove Blue M-EB dye from industrial aqueous effluents has

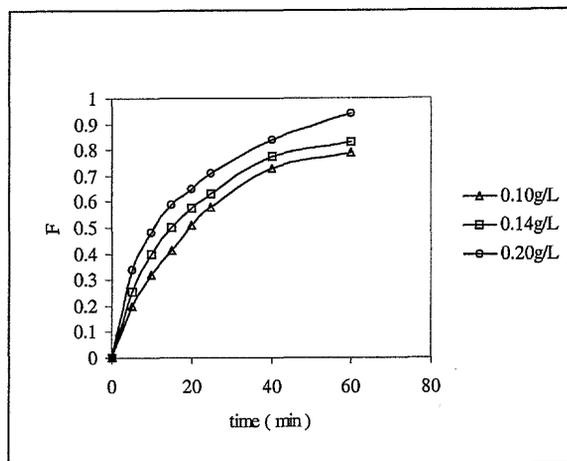


Fig. 2a Rate of sorption of Blue M-EB dye on Purolite A - 400 resin at different initial concentration. Temperature = 296.15K

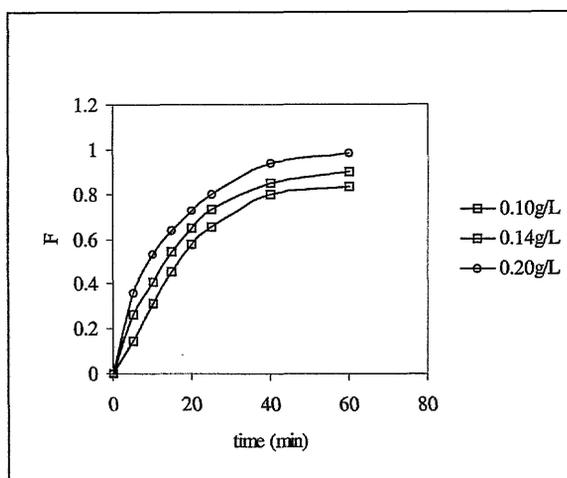


Fig. 2b Rate of sorption of Blue M-EB dye on Purolite A - 500 resin at different initial concentration. Temperature = 296.15K

been explained by the inability of large dye molecules to saturate exchange sites of the sorbent (the steric hindrance effect). By potentiometric titration of released chloride it was found that immobilization of the dye on the studied resins takes place by an ion-exchange mechanism, but also π - π interactions between the organic matrix of sorbent and condensed rings of the dye have a considerable importance. The stoichiometry of dye association with the anion exchange sites is a 1:1, such relationship is in good agreement with other workers [13].

In this paper the kinetics of Blue M-EB reactive dye sorption on Purolite anion exchange resins (A-400 and A-500) were studied with respect to the following variables: initial dye concentration, dye solution temperature and structure type of resin. Sorption rates were measured for same particle size fractions and for a constant high degree of agitation to minimize the film diffusional resistance.

The data, plotted as fractional attainment of equilibrium sorption (F) versus time (t), are reported in Figs. 2 and 3.

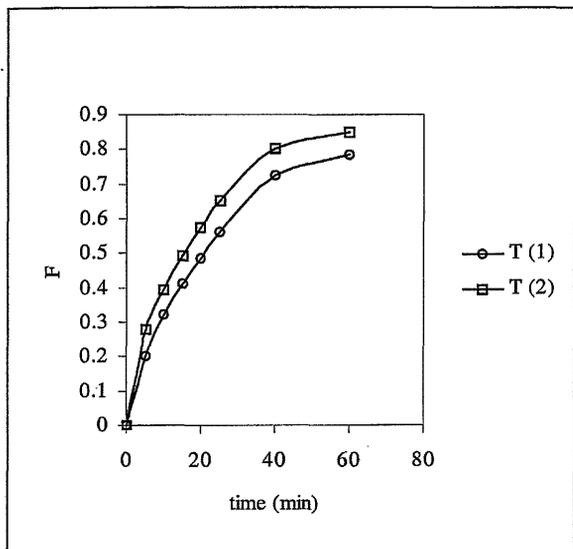


Fig. 3a Rate of sorption of Blue M-EB dye on Purolite A - 400 resin at different temperatures, T/K, at initial concentration $C_0 = 0.1 \text{ g L}^{-1}$

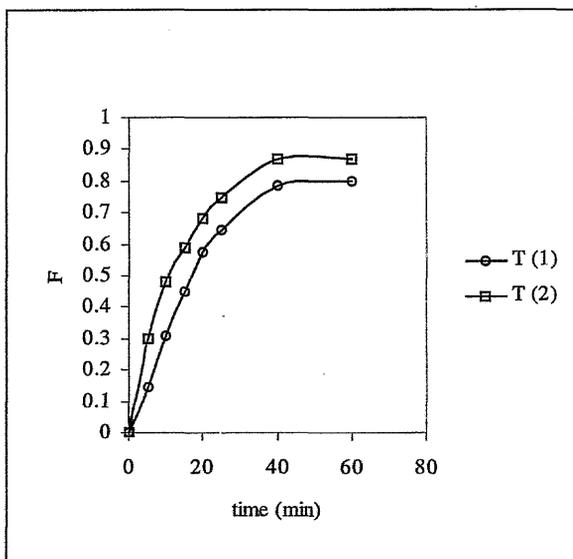


Fig. 3b Rate of sorption of Blue M-EB dye on Purolite A - 500 resin at different temperatures, T/K, at initial concentration $C_0 = 0.1 \text{ g L}^{-1}$

The influence of equilibrium parameters on the rate of sorption was quantitatively evaluated by means of sorption half-time ($t_{1/2}$) (Table 2).

It is seen that the initial dye concentration has a significant effect on sorption kinetics: increasing the dye concentration gradient between the solution and resins enhances sorption. Also, the increasing of dye solution temperature with $\sim 283\text{K}$ has a beneficent effect on the rate of sorption (and increase of 1.2 - 1.8 times), the results indicate that the process under investigation occurs in diffusion region.

In addition, due to the much greater accessibility of the sorption sites (the more open structure), the macroporous resin A-500 provides a better kinetic

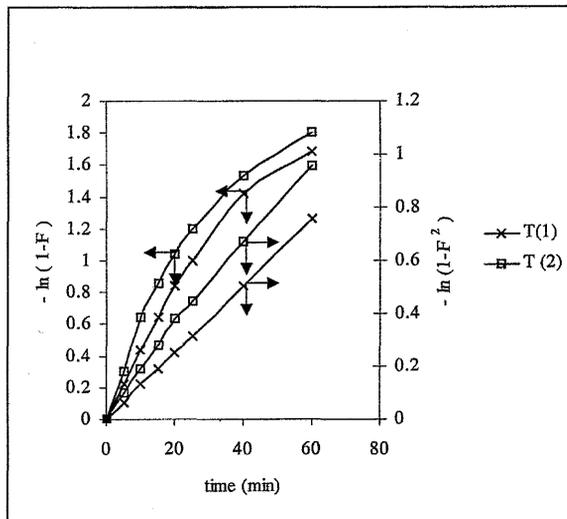


Fig. 4 Test of equations 1 and 2 for sorption of the Blue M - EB dye on Purolite A - 500 at $C_0 = 0.1 \text{ g L}^{-1}$ and $T_1 = 284.15\text{K}$; $T_2 = 296.15\text{K}$

properties toward dye ions than to the gel type resin A-400.

The ion sorption onto solid ion exchange resins must be considered as a liquid - solid phase reaction including the diffusion of ions from the solution to the resin surface, the diffusion of ions within the resin particle itself and chemical reaction between ions and functional groups [14]. The sorption kinetic is governed by the slowest of these processes. In most cases, the rate-determining step in the kinetics has been established to be diffusion through either the externally adherent liquid film or resin particle. Rate laws have been derived based on the Nernst - Planck equation for film and particle - diffusion controlled process [15].

If the liquid film diffusion controls the rate of process, the following expression can be used:

$$-\ln(1-F) = Kt \quad (1)$$

where $K = \frac{3DC}{r_0\delta C}$ is the kinetic coefficient or rate

constant / sec^{-1} , D is the diffusion coefficient in the film / cm^2s^{-1} , C and \bar{C} are concentration of the incoming ions in solution and in resin, respectively / mmol L^{-1} ; r_0 is the radius of sorbent particle/cm and δ is the diffusion film thickness /cm.

The rate equation for intraparticle diffusion control is given as:

$$-\ln(1-F^2) = \bar{K}t \quad (2)$$

where $\bar{K} = \frac{\bar{D}\pi^2}{r_0^2}$ is the kinetic coefficient / s^{-1} , \bar{D} is the

diffusion coefficient in the resin phase/ cm^2s^{-1} .

The sorption data of Blue M-EB dye onto both studied resins were analyzed by the rate equations for the liquid film and the particle diffusion models (Figs. 4 and 5).

Although the extremely low concentration of the dye in the initial solution suggests a liquid film diffusion

Table 3 Kinetic parameters and the energy of activation for sorption of Blue M-EB dye ($C_0 = 0.1 \text{ gL}^{-1}$) onto Purolite resins

Resin	T/K	\bar{K} / s^{-1}	$\bar{D} / \text{cm}^2 \text{s}^{-1}$	E_a / Jmol^{-1}
A - 400	284.15	5.33×10^{-5}	1.53×10^{-8}	36.25×10^3
A - 400	296.15	9.87×10^{-5}	2.83×10^{-8}	
A - 500	284.15	2.99×10^{-4}	8.36×10^{-8}	35.94×10^3
A - 500	296.15	5.37×10^{-4}	3.07×10^{-7}	

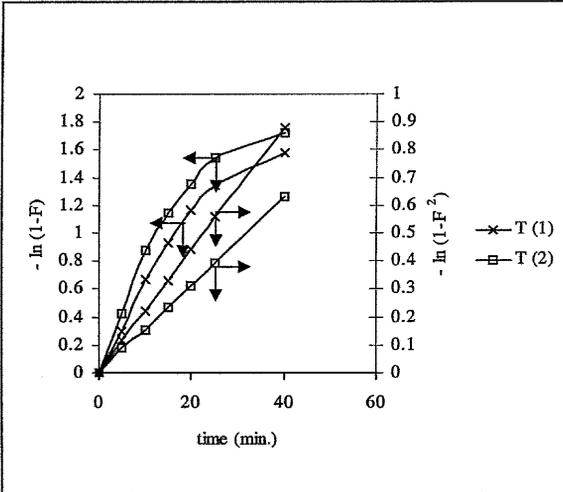


Fig. 5 Test of equations 1 and 2 for sorption of the Blue M-EB dye on Purolite A-500 at $C_0 = 0.1 \text{ g L}^{-1}$ and $T_1 = 284.15 \text{ K}$, $T_2 = 296.15 \text{ K}$

controlled model, a linear correlation between $-\ln(1-F)$ and time is observed only during the initial minutes. The linear regression analysis shows that the kinetics of dye sorption onto both studied resins fit the rate equation for the particle diffusion model (the correlation coefficients, $r = 0.9994 - 0.9997$).

The values of the sorption rate constants and of the diffusion coefficients in the resin phase calculated from the slope of the straight lines (Fig. 4 and 5), summarized in Table 3, show that the macroporous type resin A-500 is faster in reaching equilibrium. Also, an increase in temperature is favourable to increase the values of diffusion coefficients of Blue M-EB dye sorption with respect to ionites of both structures.

Taking into account the rate constants, \bar{K} , at two different temperatures, the activation energy, E_a , required for sorption process was calculated using Arrhenius equation:

$$\bar{K} = \bar{K}_0 \exp(-E_a/RT) \quad (3)$$

where E_a is the activation energy/ J mol^{-1} and R - gas constant = $8.3144 \text{ Jmol}^{-1} \text{ K}^{-1}$.

The values of activation energy (Table 3) have confirmed the diffusion nature of dye sorption.

To explain the dye concentration effect on the rate of sorption the "moving boundary" model of sorption kinetics has been considered [16]. This model assumes a

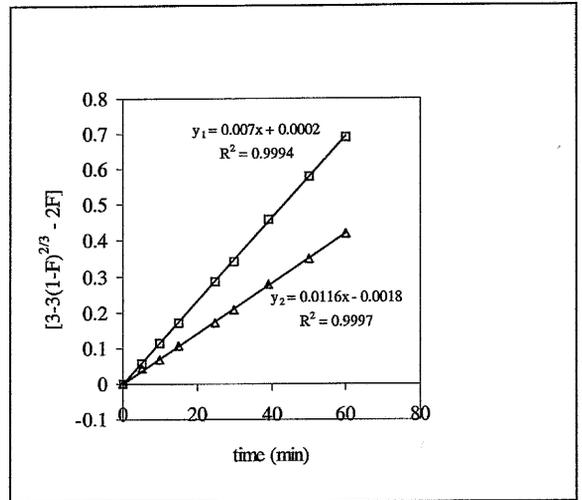


Fig. 6a Test of equation 5 for sorption of Blue M-EB dye on Purolite A-400 (\square) and A-500 (Δ) resins at $T_1 = 284.15 \text{ K}$

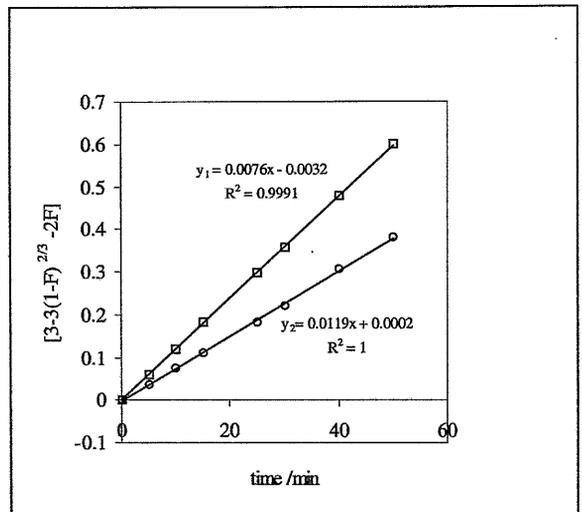


Fig. 6b Test of equation 5 for sorption of Blue M-EB dye on Purolite A-400 (\square) and A-500 (\circ) resins at $T_2 = 296.15 \text{ K}$

sharp boundary that separates a completely reacted shell from an unreacted core and that advances from the surface toward the center of the solid with the progression of sorption. The rate equation for the moving boundary model is given as:

$$[3 - 3(1-F)^{2/3} - 2F] = \bar{K}t \quad (4)$$

$\bar{K} = \frac{6\lambda\bar{D}C}{qr_0^2}$ is the kinetic coefficient $/\text{s}^{-1}$, λ - the molar distribution coefficient, q - the sorption capacity of the unreacted resin bead at equilibrium $/ \text{mmol L}^{-1}$.

In order to test the moving boundary model for dye sorption onto both Purolite resins, the plots of $[3 - 3(1-F)^{2/3} - 2F]$ versus time have been presented in Fig. 6.

Linearity of the plots obtained show the validity of the moving boundary model, yielding correlation coefficients in the 0.9997.

Conclusions

Research on the kinetics of Blue M-EB reactive dye sorption by using Purolite anion exchangers of both gel and macroporous structures has resulted in the conclusion that dye sorption is limited by intraparticle diffusion and follows moving – boundary behavior. The dependencies found : $\ln(1-F^2)$ vs, t and $[3 - 3(1-F)^{2/3} - 2F]$ vs, t proves this model.

Dye sorption using macroporous resin proceeds faster than with gel type resin.

The values of diffusion coefficients and activation energy of dye sorption on Purolite resins of both structures confirms that the process in investigation occurs in diffusion region.

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