KINETIC MODELING OF DYE SORPTION FROM AQUEOUS SOLUTIONS ONTO APPLE SEED POWDER

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Batch kinetic studies were carried out for the removal of Brilliant Red HE-3B and Methylene Blue dyes from aqueous media onto apple seed powder. The kinetic data were modeled using three well-known kinetic models: pseudo-first order (Lagergreen model), pseudo-second order (Ho model), and Elovich model, as well as two diffusion models: intraparticle diffusion model (Weber and Morris model) and film diffusion model (McKay model). In order to determine the best-fitting kinetic model, the coefficient of correlation, R^2, the Chi-square test, χ^2, and the residual root mean square errors were used for estimating the error of the investigated analysis methods. The sorption kinetics can be described well by the pseudo-second-order model, and the rate limiting step may be represented by both surface diffusion and intraparticle diffusion.

Keywords: apple seeds, Brilliant Red HE-3B dye, kinetic study, Methylene Blue dye, sorption

INTRODUCTION

Many industrial processes (dye and paper manufacturing, textile and leather finishing, dye-consuming industries) discharge colored wastewater into natural water resources. This can be considered one of the major causes of environmental pollution: directly, due to its appearance, or indirectly, through the degradation compounds together with a large amount of suspended matter. Over the time, many different methods of removing dyes from industrial effluents have been applied: from physical-chemical and chemical processes to biological ones.[1-6] The application of any method depends mainly on the structure of dyes, the composition of the effluent, and not least, it must consider the biodegradability of the dyes.[1,4]

Although various methods have been used for wastewater treatment, adsorption remains one of the most efficient and inexpensive methods, due to both operating conditions and equipment required for carrying it out, and the variety of adsorptive materials that can be used. These can be selected according to the environmental characteristics of the aqueous environment subjected to the adsorption process. Within the class of adsorptive materials, agricultural or industrial wastes (husks, seeds, straws, shells of different kinds of seeds, and other types of lignocellulosic materials) represent, under certain conditions, an interesting alternative, inexpensive and feasible to synthesize material.[1,4,7-15] The apple, one of the most used fruit, can be considered a complex mixture of antioxidants, phyto-nutrients, flavonoids (such as quercetin, epicatechin, and procyanidin B2) and polyphenolics, vitamin C and beta-carotene, B-complex vitamins (such as riboflavin, thiamin, and pyridoxine (vitamin B-6)) and minerals (like potassium, phosphorus, and calcium), distributed in all its parts (pulp, peel and seeds), making the exploitation of all these components important and necessary.

The aim of this paper is to study the sorption process kinetics and investigate the mechanism of Brilliant Red HE-3B and Methylene Blue dye sorption onto apple seed powder. Using batch kinetic experiments, the experimental data was processed in order to obtain valuable information

that would help identify the optimum operating conditions necessary in the study of real industrial effluents and further apply the adsorption procedure in industrial scale removal processes. For this purpose, the kinetic behavior of the considered systems was studied and characteristic sorption constants using the pseudo first-order, pseudo-second, intraparticle diffusion, and film diffusion models were determined and compared.

EXPERIMENTAL
Materials

The experiments were carried out using apple seeds as sorbent. This material is considered as waste and is produced during the processing of apple fruit in the food industry (soft drinks, flavours, sugar, marmalade or chips (dehydrated fruit slices), and jam), bakeries or catering agencies. For the experiments, seeds from different varieties of apples, which are available on the Romanian local market and generally used in the food industry or for individual consumption, were selected, such as Idared, Jonathan, Florina, Starkrimson and Golden Delicious. Our previous studies revealed that the apple seed composition includes amigdalin (B17
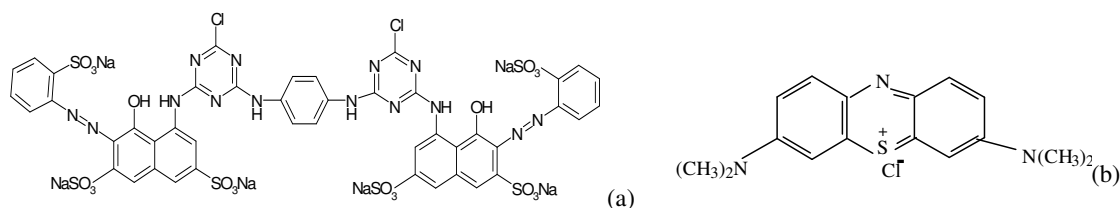
vitamin), linoleic acid (48-64%), oleic acid (24-42%), and palmitic acid (48-71%).[16] Also, the FT-IR spectra of apple seeds indicated numerous peaks allocated to different functional groups, some which are able to interact with molecular dye species (species like OH stretch in alcohols, phenols, C=O stretch in non-conjugated ketones and carboxyl groups, or in conjugated ketones).[17]

Sorbent preparation included collection, drying at 90 °C for 24 hours, crushing and sieving to get particles of 1-2 mm size.

Brilliant Red HE-3B (BRed), an anionic, bifunctional reactive dye (MW = 1463 g/mol, λ_{max} = 530 nm; Fig. 1a), and Methylene Blue (MB), a cationic, phenotiazine dye (MW = 319.85 g/mol, λ_{max} = 660 nm; Fig. 1b), were used. Stock solutions with concentrations of 500 mg/L of BRed dye and 320 mg/L of MB dye, respectively, were prepared from commercial dye salts. These are textile dyes used in chemical textile finishing, and their presence in the industry effluents not only affects aquatic aesthetics, but also can pollute the aquatic environment by decomposition processes, releasing toxic chemical compounds that affect organisms and microorganisms.

Figure 1: Chemical structure of Brilliant Red HE-3B dye (a) and Methylene Blue dye (b)

Kinetic sorption methodology

The kinetic studies aim to identify and interpret the influence of the contact time of phases on the process of sorption, and also to establish the sorption rate and the sorption controlling step. For this purpose, the 'limited bath' technique was used. Therefore, samples of around 0.25 g sorbent were added, under stirring, to 100 mL solution of dye with 100 mg/L initial BRed dye concentration, and 38.4 mg/L initial MB dye concentration, respectively, and were maintained at 25 °C. After different time periods (from 10 to 360 min), 0.5 mL volumes of supernatant were taken for the dye content determination. The UV-VIS spectrophotometric method was applied, respecting the conditions of Lambert Beer law, and using a UV-VIS Digital Spectrophotometer, S 104D/WPA.

The sorption capacity of the sorbent was evaluated by the amount of dye sorbed:

$$q = (C_0 - C_e) \cdot V/G \text{ (mg/g)} \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations of dye in solution (mg/L), G is the

amount of sorbent (g), and V is the volume of solution (L).

The extent of sorption was expressed by the fractional attainment of equilibrium, F:

$$F = q_t/q_e \tag{2}$$

where q_t and q_e (mg/g) are the amount of dye sorbed at time t and at equilibrium (24 h).

Error analysis

Even if the linear regression coefficient, R^2, is the most commonly used error function in many studies, in the literature, there are other complex analysis methods for error, such as average relative error, a hybrid error function, Marquardt's percent standard deviation, non-liner Chi-squared test, the sum of squares of the errors, standard deviation of relative errors, sum of the absolute errors, Spearman's correlation coefficient, which have been used to establish the most proper equation.[18-20] The Chi-square test, χ^2, and the residual root mean square errors, *RMSE*, were selected to be

used in this study. The standard equations are as follows:

$$\chi^2 = \sum_{i=1}^{N} \frac{\left(q_{e,exp} - q_{e,calc}\right)^2}{q_{e,calc}} \tag{3}$$

$$RMSE = \sqrt{\frac{1}{N-2} \sum_{i=1}^{N} \frac{\left(q_{e,exp} - q_{e,calc}\right)^2}{q_{e,calc}}} \tag{4}$$

where: $q_{e,exp}$ and $q_{e,calc}$ represent the experimental and calculated values of sorption capacity (mg/g), and N is the number of experimental data.

RESULTS AND DISCUSSION

Our previous studies[16,17] demonstrated that the considered sorption processes were endothermic and spontaneous processes ($\Delta G^0 < 0$ and $\Delta H^0 > 0$), and could be influenced by physical forces more than by chemical ones, depending on the operational parameters of the process, as well as by the structure of dyes. The values of the mean free energy (E) obtained from the Dubinin–Radushkevich model were in the range of 6-8 kj/mol (BRed) and 5-6 kj/mol (MB) for a sorbent dose of about 4 g/L, positively influenced by increasing temperature and applicable to moderate concentrations of dye in aqueous effluents. Sorption equilibrium was reached after 6 hours, and the best values of sorption capacity were obtained at a pH of 3 for BRed dye and of 6 for MB dye, because of their structure and the value of sorbent pH_{PZC} (5).

Taking into account these conclusions, our kinetic experiments were realized in an aqueous dye solution with $pH_{BRed} = 3$ and $pH_{MB} = 6$, and the working initial dye concentration corresponding to the saturation of available adsorption sites of the sorbent: $C_{0,BRed} = 100$ mg/L and $C_{0,MB} = 38.4$ mg/L.

Contact time of phases in sorption process

One of the most important operating parameters used to characterize, model and optimize the sorption process is the contact time of the liquid and solid phases. Studies on the influence of contact time on the amount of dye retained allow establishing the time to reach equilibrium, the time required to retain half of the dye – values that are then used in kinetic modeling.

The effect of phases contact time on the removal of Brilliant Red HE-3B reactive dye and Methylene Blue cationic dye by the apple seed powder is presented in Figure 2. As seen in Figure 2, the values of the fractional attainment of equilibrium rapidly increase with contact time, especially during the first 50 min, and after that the rate of sorption became slower for both dyes and the time period required for maximum removal was found to be up to 6 hours. However, the sorption half-times ($t_{1/2}$) were of no more than 10 min for BRed, and 15 min for MB.

Kinetic modeling

In order to design and model the sorption process, the kinetic parameters were determined. Also, they were used for selecting the most advantageous working conditions for a full-scale batch process.
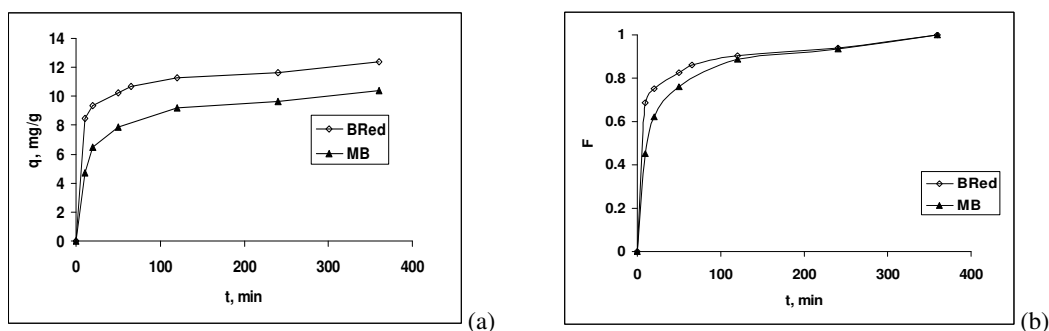

Figure 2: Effect of contact time in BRed and MB dyes sorption onto apple seed powder ($C_{0,BRed} = 100$ mg/L; $C_{0,MB} = 38.4$ mg/L; adsorbent dose = 2 g/L; $pH_{BRed} = 3$; $pH_{MB} = 6$; temperature = 25 °C)

It is well known that the sorption mechanism may involve three processes or their combination:[21,22] surface adsorption, chemical interaction and diffusion. The slowest of these processes determines the rate limiting step. In order to identify the kinetic order and the rate limiting step, the experimental data was processed using three of the most widely used adsorption

kinetic models in the literature:[13,21] the pseudo first-order model (Eq. 5), pseudo-second order model (Eq. 6) and Elovich model (Eq. 7). The pseudo first-order model (Lagergren) assumes that sorption is preceded by diffusion through the boundary layer, being usually expressed as:

$$\lg(q_e - q_t) = -\frac{k_1}{2.303}t + \lg q_e \qquad (5)$$

where q_e and q_t are the amounts of sorbed dye (mg/g) at equilibrium (24 h) and any time t (min), respectively, and k_1 is the Lagergren rate constant of the first-order sorption (min^{-1}).

The pseudo-second order model (Ho model) assumes that the sorption follows a second-order mechanism, and the rate limiting step may be chemical sorption, involving valence forces or covalent forces between sorbent and sorbate. The rate of the pseudo-second order reaction is expressed by the equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \cdot t \qquad (6)$$

where k_2 is the rate constant of second-order sorption (g/mg.min) and $h = q_e^2 . k_2$ can be regarded as the initial sorption rate (mg/ g.min) as t approaches zero.

The Elovich model is usually applied in the sorption system in which the sorbent surface is heterogeneous, which is the case of the studied powder of apple seeds:

$$q_t = \frac{\ln(\alpha \cdot \beta)}{\beta} + \frac{1}{\beta}\ln t \qquad (7)$$

where constant α is the initial sorption rate (mg/g min), and constant β refers to the extent of surface coverage, and activation energy for chemisorption (g/mg).

The kinetic parameters related to each model, calculated from the intercepts and slopes of the corresponding linear plots (Fig. 3), are presented in Table 1. The fitting of each model to the experimental data was estimated using the linear regression correlation coefficient, R^2, Chi-test and RMSE values.

The shape of the graphs from Figure 3 and the data from Table 1 allow the following conclusions regarding the kinetics of the studied sorption processes:

• The R^2, Chi-test and RMSE values suggested that the Lagergren model is not a good fit for modelling the kinetic data; also, the estimated values of q_e were not in very good agreement with the experimental ones. This model could only describe the initial stage of the sorption process when rapid sorption occurs.

• The linearity of the plots of t/q_t versus t, the range of values of the coefficient of correlation, R^2, Chi-test, and RMSE, as well as the correlation between experimental and calculated values of sorption capacity, q, indicate that sorption kinetics followed a pseudo-second order kinetic model and sorption may occur through chemical interactions.

• The graphical representation of Elovich model (Fig. 3b) suggested that the experimental data do not fit well with this model. It becomes clear that, to identify the rate limiting step, it is necessary to study the diffusion process.
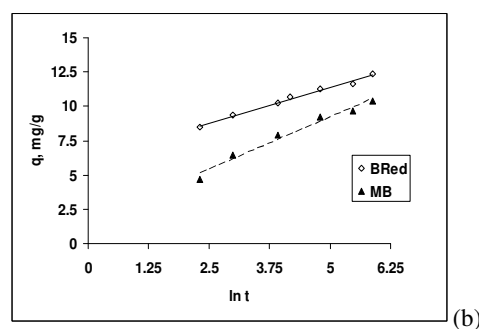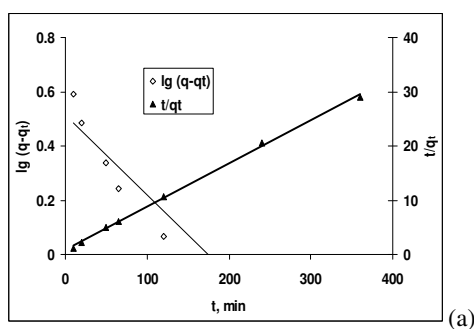

Figure 3: Applicability of the pseudo-first and pseudo-second order kinetic models (a) and Elovich model (b) in BRed and MB dyes sorption onto apple seed powder ($C_{0,Bred} = 100$ mg/L; $C_{0,MB} = 38.4$ mg/L; adsorbent dose = 2 g/L; pH$_{Bred}$ = 3; pH$_{MB}$ = 6; temperature = 25 °C)

Diffusion mechanism

The literature underlines that the sorption process of dyes onto solid materials is a multiphase process consisting of the following steps: (1) mass transfer of dye molecules from solution to the sorbent surface (film diffusion), (2) diffusion of the dye molecules inside the sorbent (pore diffusion or intraparticle diffusion) and (3)

sorption of organic molecules on active centers of sorbent by chemical interactions (ion exchange, complexation or chelatization), stronger, or by a weak physical interaction.[15,22-26]

Table 1
Kinetic parameters for BRed and MB dyes sorption onto apple seed powder

Dye / Kinetic model	BRed	MB
q_{exp}, mg/g	12.4	10.362
Pseudo-first-order kinetics		
k_1, 1/min	0.007 ± 0.0001	0.009 ± 0.0015
q_e, mg/g	3.26 ± 0.42	4.58 ± 0.9
R^2	0.9037	0.9147
RMSE	0.0581	0.0753
χ^2	0.0815	0.1065
Pseudo-second-order kinetics		
k_2, g/mg.min	0.008 ± 0.003	0.006 ± 0.001
q_e, mg/g	12.5 ± 0.22	10.64 ± 0.2
R^2	0.9981	0.9986
$t_{1/2}$, min	9.6	16
RMSE	0.9984	0.2646
χ^2	0.3096	0.1058
Elovich model		
α, mg/g.min	393.123	4.595
β, g/mg	0.9601	0.6644
R^2	0.991	0.9761

In order to determine more accurately the diffusion mechanism (film or intraparticle), the kinetic data were further processed using two models: the intraparticle diffusion model (Eq. 8), and film diffusion model (Eq. 9).[23,24]

The intraparticle diffusion model, proposed by Weber and Morris (where k_d is the rate constant for intraparticle diffusion, mg/g min$^{1/2}$; c is intercept to the y axis):

$$q_t = k_d t^{1/2} + c \qquad (8)$$

suggests that the intraparticle diffusion is involved in the sorption process if the plot q_t vs. $t^{1/2}$ (Fig. 4a, Table 2) is linear and is the rate limiting step if the line passes through the origin.

The film diffusion model, proposed by McKay (where k_f is the rate constant for film diffusion, min^{-1}; F is the fractional attainment):

$$\ln (1 - F) = k_f t \qquad (9)$$

specifies that the film diffusion is involved in the sorption process if the plot $ln(1-F)$ vs. t (Fig. 4b, Table 2) is linear, and is the rate limiting step if the line passes through the origin.
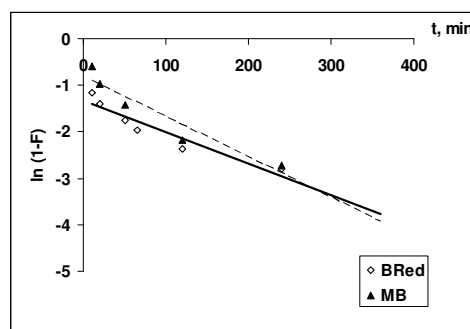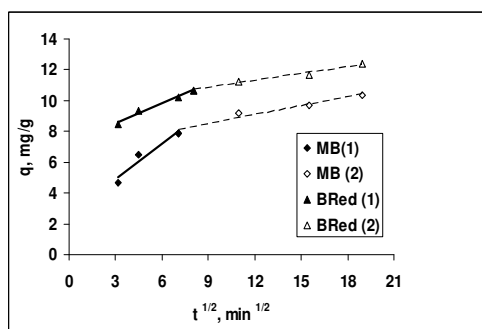

Figure 4: Applicability of intraparticle diffusion kinetic model (a) and film diffusion model (b) in the BRed and MB dyes sorption onto apple seed powder ($C_{0,Bred}$ = 100 mg/L; $C_{0,MB}$ = 38.4 mg/L; adsorbent dose = 2 g/L; pH_{Bred} = 3; pH_{MB} = 6; temperature = 25 °C)

Table 2
Diffusion data for BRed and MB dyes sorption onto apple seed powder

Dye / Kinetic model	BRed	MB
Intraparticle diffusion		
k_{d1}, mg/g.min$^{0.5}$	0.422 ± 0.04	0.774 ± 0.12
C_1	7.28 ± 0.24	2.55 ± 1.03
R^2	0.9819	0.9376
RMSE	0.1105	0.1498
χ^2	0.0059	0.0546
k_{d2}, mg/g.min$^{0.5}$	0.149 ± 0.02	0.2 ± 0.03
C_2	9.49 ± 0.25	6.69 ± 0.45
R^2	0.9723	0.9487
RMSE	0.05934	0.2013
χ^2	0.0037	0.0196

In Figure 4, the graphical representations are linear, but none passes through the origin, which leads to the conclusion that both diffusion mechanisms are involved in the sorption processes, and may be the rate determining step. Graphical representation of the amount of dyes sorbed by the apple seed powder *versus* $t^{1/2}$ (Fig. 4a) revealed two line segments for each dye. The first part is generally associated with film diffusion (or chemical reaction), and the following second linear part represents intraparticle diffusion into the porous structure of the sorbent.[15,25,26] The y-intercept of the two linear portions (*C* value, Table 2) is considered a measure of the thickness of the boundary layer; the larger the value of *C*, the greater is the boundary effect. Also, the value of the constant k_1 greater than that of k_2 corresponds to the initial process of sorption on the surface of sorbent particles. This process takes place very fast until reaching the saturation of the solid surface, followed by sorption of the dye molecules inside the porous sorbent particles, a process that takes place at a much smaller rate ($k_2 > k_1$). This behavior is in agreement with the results of other studies from the literature.[23-26]

CONCLUSION

The results of the present kinetic study on the sorption of BRed and MB dyes onto apple seed powder lead to the conclusion that the pseudo-second-order model describes well these two sorption processes. It was observed that the studied processes are complex, and both film diffusion and intraparticle diffusion contribute to the rate limiting steps.

The kinetic study confirms the results previously obtained by equilibrium and thermodynamic studies,[17] according to which the apple seeds can indeed be used as an effective sorbent for Brilliant Red HE-3B dye.

Also, the results of this investigation complete the data obtained from previous studies on sorption equilibrium[16,17] and provide the necessary informational support for future optimization of sorption processes, necessary for extending the study to sorption under dynamic conditions.

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