# KINETIC STUDY OF METHYLENE BLUE DYE SORPTION FROM LIQUID MEDIA ONTO LIGNIN

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**Abstract**

*There is a need for alternative technologies, which must be inexpensive, easy to be applied, requiring no special skills to operate and being locally available. For this point of view, sorption is one of the several techniques that have been successfully applied for dyes removal using a large variety of sorbents.*
*A special attention is focused on lingo-cellulosic materials, due to their fundamental characteristics, such as accessibility and low prices, mechanical resistance, high porosity and specific surface area, hydrophilic character that ensures a rapid sorption rate, tolerance to biological adsorbed solid layers, easy functionalization, possibility of be used in different forms and regimes (discontinuous and continuous processes). Lignin is one of these types of sorbents.*
*This paper continues our former studies concerning employment of lignin as sorbent for decolourization of textile wastewater. Kinetic studies were carried out in order to understand the sorption mechanism of cationic dye, Methylene Blue, onto lignin materials.*

**Keywords:** kinetic study, lignin, Methylene Blue dye, sorption.

## INTRODUCTION

The industrial wastewater treatment must be in consence with the viable procedures of the *production water management*: (*i*) minimi-zation of water use; (*ii*) the development of new processes and the optimization of existing or new ones with the aim of saving water, materials and energy, and (*iii*) the reuse and recycling of wastewater [1-2]. All industries discharge potential contami-nants into public sewerage systems or different emissars and have the obligation to report to the local water authority each exceeding of the maximum admissible concentration or hourly load.

To avoid the pollution of water resources it is necessary the individual or combined industrial wastewater treatment with municipal wastewater [2].

It has been reported by the scientific literature that the presence of coloured compounds (i.e. different dyes, etc.) in aqueous environments can reduce light penetration, thus affecting the photosynthetic process of aquatic plants. In addition to their visual effect (aesthetic impact on receiving waters), many synthetic dyes are toxic, mutagenic and carcinogenic [3].

Literature data present a large number of methods for dyes removal from dye-bearing effluents, such as membrane separation, flocculation, sonolysis, anaerobic biological treatments, oxidative destruction via UV/ozone treatment, photocata-lytic degradation, methods which have certain efficiency but their initial and operational costs are so great [4-6].

There is a need for alternative technologies, which must be inexpensive, easy to maintain,

requiring no special skills to operate and being locally available. For this point of view, sorption is one of the several techniques that have been successfully applied for dyes removal using a large variety of sorbents [7-9].

A special attention is focused on ligno-cellulosic materials, due to their fundamental characteristics, such as accessibility and low prices, mechanical resistance, high porosity and specific surface area, hydrophilic character that ensures a rapid sorption rate, tolerance to biological adsorbed solid layers, easy function-nalization, and possibility of be used in different forms and regimes (discontinuous and continuous processes). Lignin is one of these types of sorbents [10].

This paper continues our former studies concerning employment of lignin as sorbent for decolourization of textile wastewater [10-13]. Kinetic studies were carried out in order to understand the sorption mechanism of cationic dye, Methylene Blue, onto lignin materials.

## MATERIALS AND METHOD

*Materials*

Our experiments were carried out using industrial lignin that represents the main by-product of the pulp industry, and also can represent a product obtained from renewable resources. The experiments were carried out with alkali lignin $L_1$ (from Wheat straw 100-W-A) (offered by Granit Co.) with the main characteristics presented in Table 1 [14].

**Table 1.** The characteristics of industrial lignin

| **Characteristics** | **$L_1$ (100-W-A)** |
|---|---|
| Acid insoluble lignin, % | 90 |
| Acid soluble lignin, % | 1 |
| COOH, mmole/g | 3.8 |
| Aromatic-OH, mmole/g | 1.7-1.8 |
| OH/C9 groups, chemical method | 1.02 |
| Ash, % | 2.5 |
| pH (10% dispersion) | 2.7 |
| MW | 3510 |
| $S_{softening}$, $^0$C | 170 |
| Solubility in furfuryl alcohol, % | 88.5 |
| Solubility in aqueous alkali, pH 12, % | 98.5 |

The selected dye was used as commercial salt and is characterized in Table 2 and figure 1a. The working solutions were prepared by dilution to the desired concentrations.

**Table 2.** *Characteristics of the studied dye*

| C.I. | Type of dye | MW, g/mol | $\lambda_{max}$, nm | Concentration of the stock solution, mg/L |
|---|---|---|---|---|
| 2015 | cationic phenothiazine dye | 319.85 | 660 | 320 |

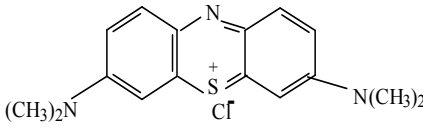



***Fig 1.*** *Chemical structure of Methylene Blue*

*Method*

Effect of the contact time on the sorption of this cationic dye onto lignin was determined by the "limited bath" technique. A sample of 0.1 g of sorbent was added under stirring to 25 mL of dye solution of 89.6 mg/L initial concentration (into the conical flask with 250 mL capacity) placed in a thermostatic assembly. The temperature of solutions was maintained at 5, 25 and 55$^0$C. After appropriate time intervals (10 - 400 min), volumes of supernatant were taken for spectro-photometric measure-ments of residual dye content using an UV-VIS SP-830 Plus spectrophotometer, Metertech Inc. Version 1.06. The amount of sorbed dye, *q* (mg dye/g lignin) was evaluated by equation:

$$q = \frac{(C_0 - C)\cdot V}{G} \qquad (1)$$

where $C_0$ and $C$ are the initial and residual dye concentration (mg/L), $G$ is the amount of lignin (g) and $V$ is the volume of solution (L).

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

$$F = \frac{q_t}{q} \qquad (2)$$

where $q_t$ and $q$ (mg/g) are the amounts of dye sorbed at time $t$ and at equilibrium (24 h), respectively.

## RESULTS AND DISCUSSION

*Establishing the rate limiting step of the sorption process*

The contact time between the two phases is an important factor for establishing of specific rate of the sorption process, and the limiting step of the sorption process rate. Due to the significant influence of temperature in the sorption process, the kinetic study was performed taking into consideration the temperature.

The effect of contact time vs. removal of Methylene Blue dye from aqueous solutions of 89.6 mg/L initial concentrations by sorption using lignin, at three different temperatures, is showed in Fig. 2.

For the appreciation of lignin efficiency as sorbent it was studying the sorption kinetic. For this it was applied three kinetic models from the scientific literature summarized in Table 3 [9, 15]. With their help it can be established the controlling mechanism of sorption process: chemical reaction, diffusion control or mass transfer [9, 15].

The kinetic parameters related to each model are calculated from the intercepts and slopes of the corresponding linear plots (Figure 3 a, b, c).

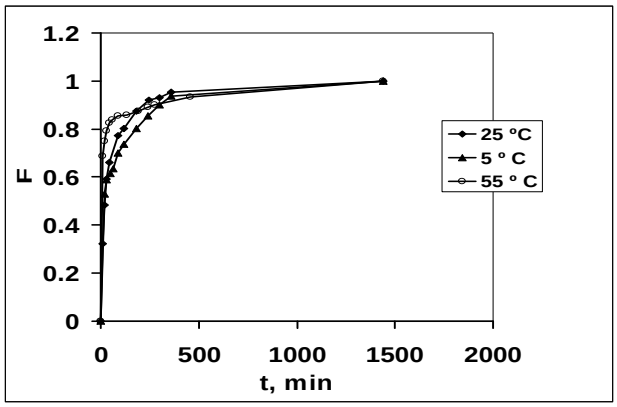



***Fig. 2.*** *The fractional attainment of equilibrium (F) versus time for sorption of Methylene Blue cationic dye onto lignin: T= 25°C; pH= 6; 4 g lignin /L, $C_0$ = 89.6 mg/L*

**Table 3.** The linear forms of the tested kinetic models for determination of controlling mechanism of Methylene Blue dye sorption onto lignin

| Kinetic model | Equation | Kinetic parameters |
|---|---|---|
| Pseudo-first order (Lagergren model) | $\lg(q_0 - q) = -\frac{k_1}{2.303}t + \lg q_0$ | $k_1$ – rate constant of pseudo-first order model sorption |
| Pseudo-second order (Ho model) | $\frac{t}{q} = \frac{1}{k_2 q_o^2} + \frac{1}{q_o}\cdot t$ | $k_2$ – rate constant of pseudo-second order model sorption $k_2 q_0^2 = h$ – initial sorption rate |
| Intraparticle diffusion (Webber and Morris model) | $q = k_p t^{0.5} + c$ | $k_p$ is the rate constant for intraparticle diffusion (mg/g.min$^{0.5}$) C - constant |

The characteristic parameters of kinetic models are summarized in Table 4. The results from this table show that the pseudo-first-order model is not suitable for modelling the sorption process of Methylene Blue dye onto lignin ($R^2$ values of the pseudo-second-order kinetic model are higher than in case of pseudo-first-order). Generally, the sorption of tested dye onto lignin follows a pseudo-second order rate equation, suggesting that the sorption process appears to be controlled by the chemical process. Some similar results are reported also in the studied scientific literature [16].

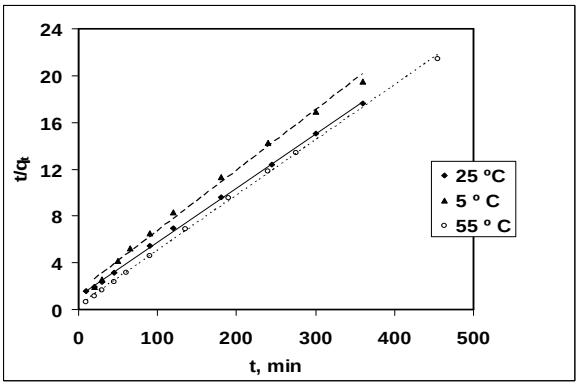



***Fig. 3a.*** *The applicability of the pseudo-first order kinetic model of dye sorption onto lignin: pH= 6; $C_0$= 89.6 mg/L; 4 g lignin/L*

Because neither of these two considered models can suggest the accuracy of the sorption mechanism, respectively if diffusion is involved in the sorption mechanism, the kinetic results were also analyzed by the intra-particle diffusion models. In this direction the scientific literature specifies that the sorption process generally is a combination of three steps: film diffusion, intra-particle or pore diffusion and sorption into sites. Since the last step is very rapidly the sorption must be controlled by the other steps [17].

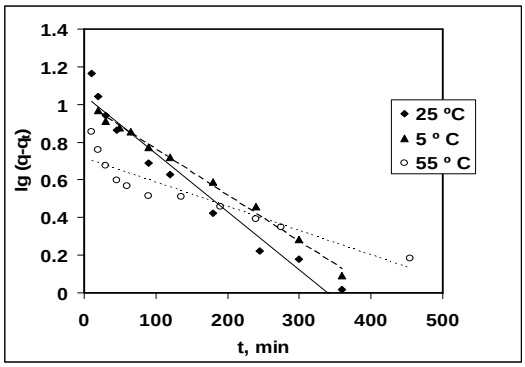



***Fig. 3b.*** *The applicability of the pseudo-second order kinetic model of dye sorption onto lignin: pH= 6; $C_0$= 89.6 mg/L; 4 g lignin/L*

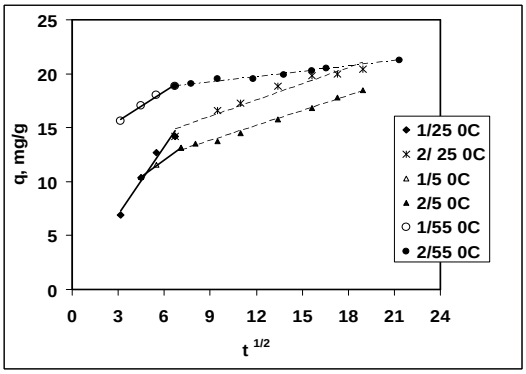



***Fig. 3c.*** *The applicability of the intra-particle diffusion kinetic model of dye sorption onto lignin: pH= 6; $C_0$= 89.6 mg/L; 4 g lignin/L*

**Table 4.** *The kinetics parameters of dyes sorption onto lignin*

| Kinetic model | Parameters | Temperature, K | | |
|---|---|---|---|---|
| | | 278 | 298 | 318 |
| Lagergren model | $k_1$ / min$^{-1}$ | 0.0055 | 0.0071 | 0.003 |
| | $q_0$/mg g$^{-1}$ | 10.176 | 11.69 | 5.169 |
| | $R^2$ | 0.9946 | 0.9607 | 0.8681 |
| Ho model | $k_2$/ g mg$^{-1}$.min$^{-1}$ | 0.00167 | 0.0019 | 0.0063 |
| | h / mg g$^{-1}$.min$^{-1}$ | 0.632 | 0.885 | 2.853 |
| | $q_0$/mg g$^{-1}$ | 19.455 | 21.64 | 21.28 |
| | $R^2$ | 0.9943 | 0.9994 | 0.9992 |
| Intra-particle diffusion model | $k_{p1}$/mg g$^{-1}$.min$^{-0.5}$ | 1.0374 | 2.0834 | 0.9083 |
| | $R_1^2$ | 0.9985 | 0.9703 | 0.9864 |
| | $k_{p2}$/mg g$^{-1}$.min$^{-0.5}$ | 0.4627 | 0.4988 | 0.1613 |
| | $R_2^2$ | 0.9928 | 0.9497 | 0.9838 |

So, diffusion is involved in the sorption process if the plot of $q_t$ vs. $t^{1/2}$ is linear. If the straight line passes through the origin, the intra-particle diffusion is the rate controlling step [16].

From figure 3c it can be observed two distinct phases in the plots $q_t$ vs. $t^{1/2}$: (*1*) first attributed to the diffusion of dye from solution to the external surface of sorbent and (*2*) the second phase indicating the intra-particle diffusion of dye molecule into the pores of lignin.

Because the value of $k_{p1}$ is higher than $k_{p2}$ it can be said that the rate limiting step in the studied sorption process is the intra-particle diffusion. Also, it can be observed that the plots do not pass through origin, that fact suggesting that the intra-particle diffusion is not the only rate limiting step and other kinetic models may control the rate of process. In this case it can conclude that the studied sorption process of cationic dye Methylene Blue onto lignin is a complex process where both intra-particle diffusion and surface sorption contributes to the rate limiting step.

Similar results were reported in literature for other sorption processes [15, 17].

*Evaluation of activation energy*

In order to re-confirm the type of Methylene Blue dye sorption process onto lignin established in other previous papers [13] it was estimated the magnitude of activation energy by using the Arrhenius equation (Eq. 3) [18].

$$k_2 = k_0 \exp\left(-\frac{E_a}{R \cdot T}\right) \qquad (3)$$

where: $k_2$ represents the rate constant of pseudo-second order model sorption; $k_0$ is the temperature independent factor; g/mg min; $E_a$ – the apparent activation energy of sorption, kJ/mol; $R$ – the gas constant, 8.314 j/mol K and $T$ – the absolute temperature, K.

The value of activation energy was determined from the slope of the Arrhenius linear equation plots of *ln* $k_2$ vs. *1/T* (Figure 4).

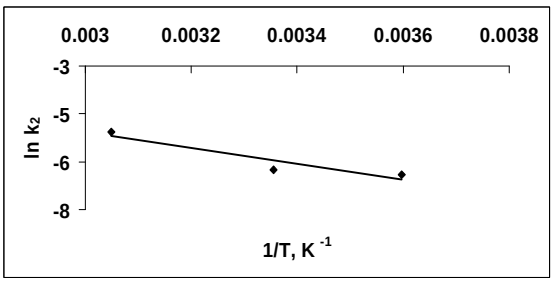



***Fig. 4.*** *The ln k plotted versus 1/T for the Methylene Blue dye sorption onto lignin: pH= 6; $C_0$= 89.6 mg/L; 4 g lignin/L*

The value of activation energy was found to be 20.7 kJ/mol. This obtained positive value of $E_a$ underlines the endothermic nature of sorption process that places this in the field of chemical sorption. This fact is in accordance with our previous conclusions of the Methylene Blue dye sorption onto lignin indicating that the adsorption is rather physical than chemi-sorptions [13].

## CONCLUSIONS

Kinetic studies were carried out to establish the favorable conditions for removal of Methylene Blue cationic dye onto lignin and also to describe the sorption mechanism. There were applied kinetic models from scientific literature (i.e. the pseudo-first order, pseudo-second order kinetic models, and also the intra-particle diffusion model). The best fitted kinetic data correspond to the pseudo-second order kinetic, indicating the chemisorption of cationic dye onto lignin.

The studied sorption process of cationic dye, Methylene Blue, onto lignin is a complex process where both intra-particle diffusion and surface sorption contributes to the rate limiting step. The confirmation of sorption type was performed also by calculation of the activation energy magnitude that was underlining the endothermic nature of sorption process placing it in the field of chemical sorption (i.e. $E_a$ = 20.7 kJ/mol).

The results of this study evidenced that the lignin may be an inexpensive and efficient sorbent for cationic textile dyes removal from aqueous media.

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