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REMOVAL OF METHYLENE BLUE AND METHYL BLUE FROM WASTEWATER BY ELECTROCHEMICAL DEGRADATION

Electrochemical degradation of such dyes as methylene blue (BM-ylene) and methyl blue (BM-yl) was investigated using UV-Vis spectrophotometry, in order to be removed from the solutions, leading to discoloration of wastewater obtained under simulated laboratory conditions. The electrochemical degradation in the presence of SO_4^{2-} ions, as well as in the presence of Cl^- ions were compared for the synthetic waters containing BM-ylene and BM-yl. The results showed that the fastest degradation and discoloration of the BM-yl solution containing Cl^- ions was achieved, with a high value for its color removal (CR) of 89.7% obtained after 10 min.

1. INTRODUCTION

Wastewater emerged from different industry branches contain various pollutants (organic matters, i.e. dyes, biologically active bacteria, suspended solid particles, dissolved salts). The treatment of these effluent type is important for natural waters protection. Organic matter is very difficult to be eliminated using conventional processes because of their substitution groups such as azo, nitro or sulpho group [1]. Conventional methods for wastewater treatment consist of different combinations of biological, physical and chemical processes [2, 3].

Structural classification of synthetic dyes may include: acidic, basic, azo, diazo, anthraquinone, sulphone, azine, metal complex or combinations of those types [4]. Most of them are resistant to biodegradation, thereby biological or enzymatic treatment processes have low efficiency [5]. Classical processes (adsorption, coagulation,

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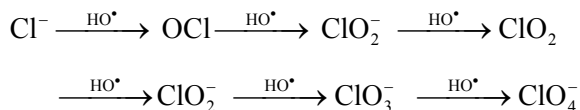
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incineration, membrane filtration) are often replaced with other methods. These may be alternative effective ways to remove dyes from wastewater [6, 7].

In the past years, chemical oxidation methods (with reagents such as ozone, hydrogen peroxide, ozone/UV, hydrogen peroxide/UV, Fenton's reagent) were used but a great problem is formation of byproducts causing additional costs for secondary treatment [8–10]. Many studies have demonstrated that complete mineralization can be obtained with high efficiency by electro-oxidation without additional chemicals.

The pseudo-first order reaction was examined for galvanostatic oxidation of eosin Y and orange II textile dyes on an indium tin oxide coated glass electrode [11]. Solution of anthraquinone dye, alizarin red S, was successfully decolorized and totally mineralized by anodic oxidation on boron doped diamond electrode in acidic media [12]. Solution of amaranth azo dye was totally decolorized (99–100% color removal) on activated carbon fiber but partial COD removal was observed (52% for electrooxidation and 62% for electroreduction) [13]. UV-Vis spectra of 80 mg·dm⁻³ Amaranth solution, before and after electrochemical oxidation on platinum electrode, confirmed that azo bond was destroyed in potential range of from -800 to -200 mV and from 600 to 1400 mV [14].

Indirect electrooxidation by electrogenerated species (active chlorine species, e.g. dissolved chlorine, hypochlorous acid and hypochlorite ions, chlorine dioxide, chlorate, perchlorate; ozone; OH radicals and hydrogen peroxide) is a particularly challenging tool for wastewater treatments. The stepwise oxidation may take place with OH radicals contribution, as shown below [15, 16]:



Direct and indirect electrochemical oxidation was compared for a synthetic solution containing methylene blue on boron doped diamond and TiRuO₂ oxide anode, respectively. This comparison showed that faster mineralization and discoloration of the solution was achieved by indirect electrolysis [17]. Second order reaction was observed for electrochemical oxidation of complex organic molecules of Reactive Red procion H-EXGL on Ti/Pt-Ir and Ti/Pd-O + Co₃O₄ [18].

Reactive Red 120, 141, 198, Reactive Blue 49, 19, Reactive Orange 16, Reactive Black 5, Reactive Yellow 84 and 15 were degraded in chlorine mediated electrochemical oxidation, on titanium based dimensionally stable anodes. The degradation rates of mixed dyes were dependent on temperature, current density, NaCl concentration and initial dye concentration. COD and TOC removals ranged from 39.5% to 82.8% and from 11.3 to 44.7%, respectively, after 120 min of electrolysis. Anthraquinonic dye showed a short electrolysis time and a high value of rate constant, reaching 0.28 min⁻¹, while diazo triazinic dye showed a high electrolysis time and

a small rate constant of 0.05 min^{-1} . The authors stated that triazine – diazo compounds need more time for complete discoloration than the monoazo or anthraquinone compounds. [19]. The addition in the simulated wastewater of a redox mediator, such as $\text{Co}^{2+/3+}$, enhanced the electrochemical degradation rate of bromophenol blue, indigo, Poly R-478, phenol red, methyl orange, fuchsine, methyl green, crystal violet. Nearly complete discoloration was achieved for bromophenol blue ($k = 0.198 \text{ min}^{-1}$) followed by methyl orange ($k = 0.096 \text{ min}^{-1}$) and methyl green ($k = 0.0072 \text{ min}^{-1}$), whereas phenol red was hardly decolorized (30% in 60 min, $k = 0.006 \text{ min}^{-1}$) [20]. Other studies revealed that Fenton's reagent is efficient to degrade different dyes, like: *p*-methyl red ($k = 0.42 \text{ min}^{-1}$), methyl orange ($k = 0.25 \text{ min}^{-1}$), methylene blue ($k = 0.041 \text{ min}^{-1}$), Congo red ($k = 0.055 \text{ min}^{-1}$), Drimaren yellow ($k = 0.139 \text{ min}^{-1}$) [21–24].

The aim of this study was to determine the discoloration degree (color removal) of methylene blue (BM-ylene) and methyl blue (BM-yl) from synthetic solutions containing SO_4^{2-} and Cl^- ions, in simulated laboratory conditions, using electrochemical degradation associated with UV-Vis spectrophotometry. Moreover, a kinetic model of degradation of dyes was proposed. Concentration of methylene blue and methyl blue used are within the limits found in polluted waters ($50\text{--}1000 \text{ mg/dm}^3$) [25] and in doses used in medicine (inherited or acute methemoglobinemia, $50\text{--}250 \text{ mg/day}$ for a lifetime; ifosfamid-induced neurotoxicity, $4 \times 50 \text{ mg/day}$; prevention of urinary tract infections in elderly patients, orally $3 \times 65 \text{ mg/day}$; Alzheimer's disease, $3 \times 60 \text{ mg/day}$; pediatric malaria, $2 \times 12 \text{ mg/kg}$ for 3 days) [26].

2. MATERIALS AND METHODS

UV-Vis spectrophotometry. BM-ylene and BM-yl, Sigma Aldrich products having the purity of analytical grade (assay $\geq 95\%$ calc. with respect to the dried substance) were used as dyes to prepare synthetic solutions, in order to determine their degradation degree. Their molecular structures are shown in Fig. 1.

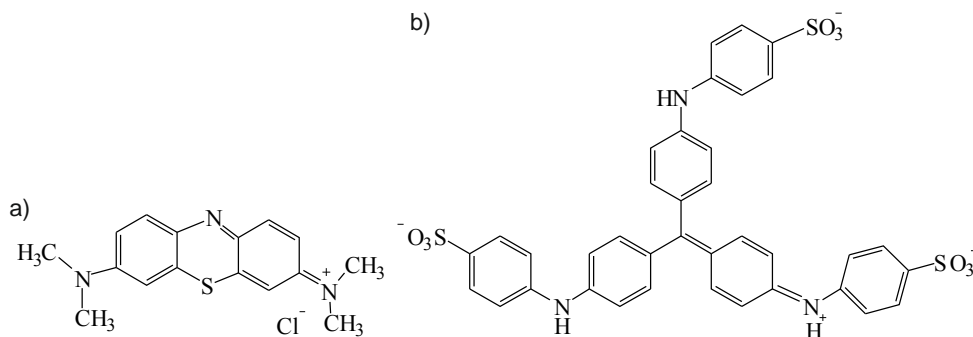


Fig. 1. Molecular structures of the dyes: a) methylene blue (BM-ylene), b) methyl blue (BM-yl)

In our experiments, we used the following solutions [25, 26]: 0.1 mol/dm³ Na₂SO₄ containing 21 mg/dm³ BM-ylene; 0.1 mol/dm³ Na₂SO₄ containing 52 mg/dm³ BM-yl; 0.1 mol/dm³ NaCl containing 21 mg/dm³ BM-ylene; 0.1 mol/dm³ NaCl containing 52 mg/dm³ BM-yl. Na₂SO₄ and NaCl with analytical grade were obtained from Merck. The solutions were analyzed by UV-Vis spectrophotometry, in order to determine the absorbances of solutions containing the above mentioned dyes.

The absorbances of the solutions were measured using the UV-Vis Varian Cary 40 spectrophotometer in the range of 450–850 nm for each sample, analysis report was obtained using the Cary Win software.

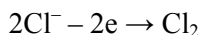
The UV-Vis spectra of the dye solution during the degradation process were recorded between 450 and 850 nm. The degrees of dye degradation at various reaction times: 20 min, 40 min, 60 min; 80 min, 100 min, 140 min and 180 min were determined by measuring the absorbances at $\lambda_{\max} = 662$ nm for BM-ylene and at 580 nm for BM-yl.

Electrochemical degradation. In the experiments, a standard electrochemical cell was used. The two electrodes, the anode and cathode were identical, made of platinum plates of the area of 1.0 cm². The electrolysis was carried out using a Keithley SourceMeter 2420 3A potentiostat/galvanostat, maintaining a constant current density of 25 mA/cm² for 180 min, at room temperature. Electrochemical discoloration of the solutions containing MB-yl and BM-ylene was achieved in dynamic conditions, the stirring rate being kept constant at 300 rpm, using a magnetic stirrer. The electrolysis cell during degradation contained: 0.1 mol/dm³ Na₂SO₄ with 21 mg/dm³ BM-ylene, or 0.1 mol/dm³ Na₂SO₄ with 52 mg/dm³ BM-yl, 100 cm³ each. Similar solutions of dyes were prepared in 100 cm³ of 0.1 mol/dm³ NaCl.

3. RESULTS AND DISCUSSION

3.1. UV-VIS SPECTROPHOMETRY

Figure 2 shows UV-Vis spectra of the dyes dissolved in solutions of 0.1 mol/dm³ Na₂SO₄, and 0.1 mol/dm³ NaCl BM-ylene has two absorption peaks, at 609 nm and 662 nm, corresponding to chromophore groups (Fig. 2a). The electrolyte solutions containing the dyes were electrolyzed in the presence of chloride ions to generate active species of chlorine, in order to catalyze their reaction of degradation. At sufficiently high concentration of chloride ions, formation and dissolution of chlorine occurs:



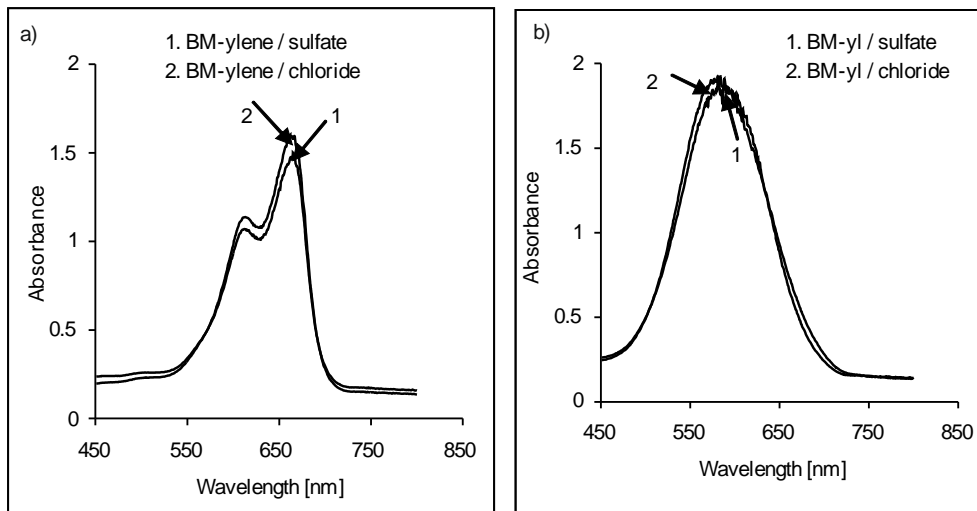


Fig. 2. UV-Vis absorption spectra of dyes: a) methylene blue (BM-ylyene), b) methyl blue (BM-yl)

In the visible range BM-yl absorption spectrum shows a single maximum centered around 580 nm (Fig. 2b), both in presence of SO_4^{2-} ions, as well as in the solution containing Cl^- ions.

3.2. ELECTROCHEMICAL DEGRADATION

Decomposition of the two dyes was performed under similar conditions. In both cases, their absorption spectra during decomposition both dyes during electrochemical degradation are similar in the presence of SO_4^{2-} and of Cl^- ions (Figs. 3, 4).

Based on Fig. 3, it can be observed that: (i) during electrochemical degradation of BM-ylyene in the presence of SO_4^{2-} ions, the absorption maximum does not shift; (ii) the absorbance slowly decreases over time, compared to absorbance in the presence of Cl^- ions; (iii) in the presence of chloride ions, BM-ylyene is completely degraded after 40 min, its absorption maxima being shifted from 609 nm to 620 nm, and from 662 nm to 674 nm, respectively. This indicates that, chloride ions may change the absorption characteristics of chromophores; (iv) during the electrochemical process, the oxidized forms of chlorine certainly appear, catalyzing the reaction of decomposition of BM-ylyene, leading to complete discoloration of the solution after 40 min (Fig. 3b), in contrast to the discoloration time in the presence of sulfate ions, exceeding 180 min (Fig. 3a). The electrochemical degradation processes of BM-yl, in the presence of sulfate and chloride ions are illustrated in Fig. 4. In this case, the degradation process is faster than that of BM-ylyene. In the presence of chloride ions, deg-

radiation is almost complete after 10 min (Fig. 4b) in contrast to its slow and easy controllable electrochemical degradation in the presence of sulfate ions (Fig. 4a).

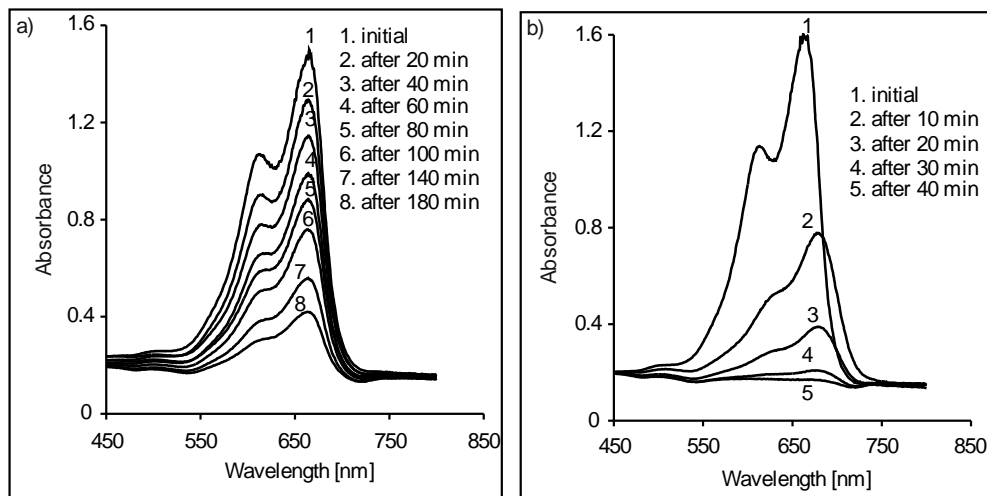


Fig. 3. UV-Vis spectrophotometric scans of degradation of methylene blue (BM-ylene) in the presence of SO_4^{2-} (a) and Cl^- (b) ions

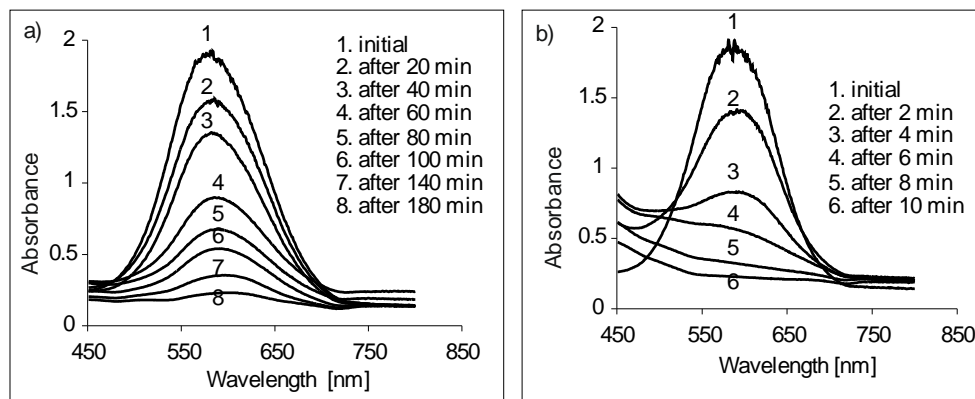


Fig. 4. UV-Vis spectrophotometric scans of decomposition of methyl blue (BM-yl) in the presence of sulfate (a) and chloride (b) ions

The degree of color removal CR , %, representing the degradation degree of the dyes solutions under electrochemical degradation was estimated from the equation

$$CR = \frac{A_0 - A}{A_0} \times 100 \quad (1)$$

where A_0 is the initial absorbance, A is the absorbance after time t .

In the presence of SO_4^{2-} ions, BM-yl is more susceptible to electrochemical process than BM-ylyene (Fig. 5). This is expressed by its maximum value $CR = 87.9\%$ with respect to the BM-ylyene discoloration degree $CR = 73.4\%$, both reached after 180 min (Table 1).

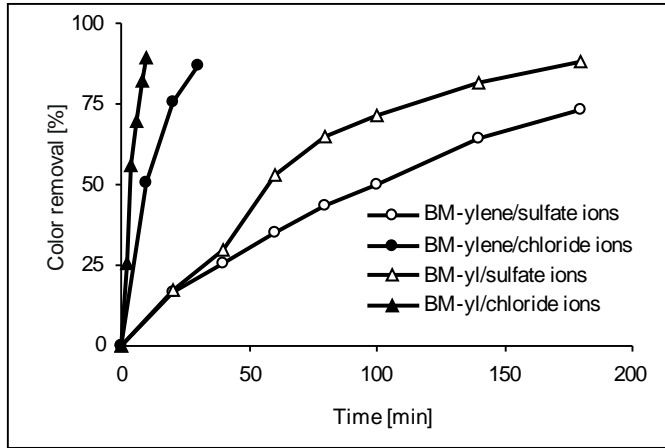


Fig. 5. Color removal (CR) of methylene blue (BM-ylyene) and methyl blue (BM-yl) solutions in the presence of sulfate and chloride ions

Also, for both dyes, electrochemical degradation, under the present experimental conditions is facilitated by chloride ions (Fig. 5). This is due to the fact that, the oxidized species of chlorine catalyze the decomposition reaction of dyes. On the other hand, BM-yl discoloration is much faster than that of BM-ylyene, its CR reaching a value of 89.7%, after 10 minutes, compared with BM-ylyene solution, whose fading occurs after 30 minutes, in proportion of 87.2% (cf. also Table 1).

3.3. KINETIC APPROACH

Usually reactions of decomposition of dyes occur in accordance with the first order reaction kinetics [19–24]:

$$-\frac{d[\text{dye}]}{dt} = k[\text{dye}] \quad (2)$$

After integration we have

$$\ln \frac{[\text{dye}]_0}{[\text{dye}]} = kt \quad (3)$$

and

$$[\text{dye}] = [\text{dye}]_0 e^{-kt} \quad (4)$$

where: $[\text{dye}]_0$ is the initial concentration of dye ($6.5 \cdot 10^{-5} \text{ mol/dm}^3$), $[\text{dye}]$ is its actual concentration, k – the rate constant (min^{-1}).

The absorbance is linear function of concentration of the dye degraded under simulated laboratory conditions. Thus, the time dependence of the absorbance in given experimental conditions for both studied dyes should follow the first order kinetics [27–29].

$$\ln \frac{A_0}{A} = kt \quad (5)$$

$$A = A_0 e^{-kt} \quad (6)$$

where A_0 and A represent the initial absorbance and absorbance after time t , respectively.

In accordance with the above, the experimental data obtained for both dyes were modeled to demonstrate that their degradation follows the first order reaction kinetics. Based on the time dependence of absorbance, the checking of first order reaction kinetics was performed as follows:

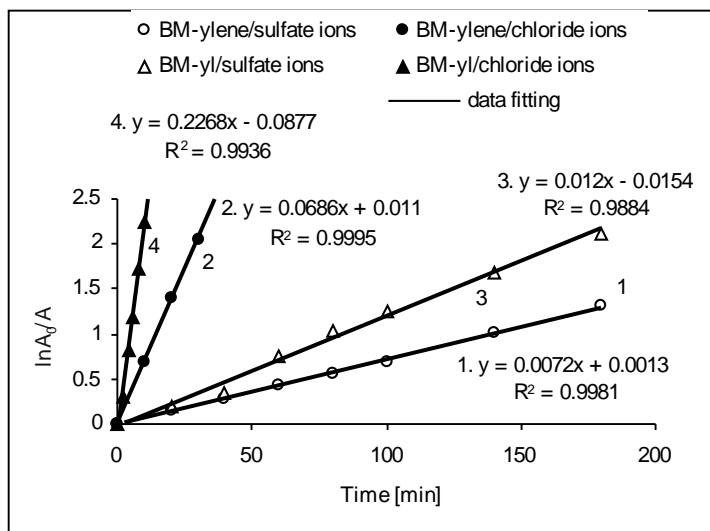


Fig. 6. The diagram of integrated rate law corresponding to the first order reaction kinetics obtained for BM-ylene and BM-yl degradation in aqueous medium in the presence of sulfate and chloride ions

By plotting $\ln A_0/A$ vs. time (Eq. (5)), a straight line passing through the origin with the slope dy/dx ($d[\ln A_0/A]/dt$) equal to the rate constant k was obtained (Fig. 6). The equations and deviation from linearity (R^2) are presented in the figure. The R^2 values are very close to unity, which indicates a strong adherence of the assumption of the first order reaction kinetics.

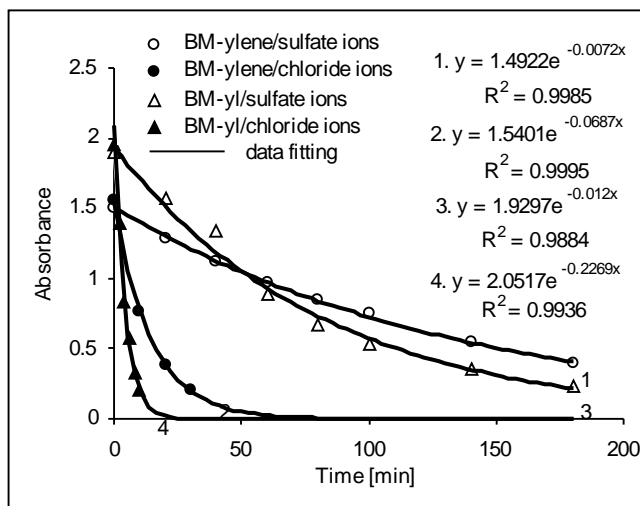


Fig. 7. Exponential time dependence of absorbance according to the first order reaction kinetics during electrochemical degradation of BM-ylene and BM-yl

Table 1

Color removal (CR) and rate constant (k) for BM-ylene and BM-yl degradation reaction obtained in presence of SO_4^{2-} of and Cl^- ions by fitting the experimental data using the first order reaction kinetics

Parameters	BM-ylene		BM-yl	
	SO_4^{2-}	Cl^-	SO_4^{2-}	Cl^-
Time [min]	180	30	180	10
A_0 experimental	1.5	1.56	1.9	1.96
A_0 by data fitting	1.49	1.54	1.93	2.05
A_t experimental	0.4	0.2	0.23	0.2
CR [%]	73.4	87.2	87.9	89.7
k [min^{-1}] from Eq. (5)	0.0072	0.0686	0.012	0.2268
k [min^{-1}] from Eq. (6)	0.0072	0.0687	0.012	0.2269

From these results, it can be concluded that the rate constants are higher in the presence of Cl^- ions in the solutions with respect to those determined in the presence

of SO_4^{2-} ions. However, in the presence of sulfate as well as chloride ions the rate constants of electrochemical degradation of BM-yl are higher than those of BM-ylene.

The first order reaction kinetics for degradation of BM-ylene and BM-yl dyes was also confirmed by the exponential decrease of their absorbance. Equations obtained for the two dyes are shown in Fig. 7, and the rate constants are expressed as exponents. From Figures 6 and 7, it can be concluded that, rate constants obtained by the two ways are in good agreement, confirming the first order reaction kinetics for decomposition reaction of both BM-ylene and BM-yl.

Results obtained by the simulation of experimental data using mathematical expressions of the first order reaction kinetics are given in Table 1. The initial values of absorbance obtained by fitting the experimental data according to the equations shown in Fig. 6 are very close to those obtained experimentally. Moreover, similar values of rate constants are observed.

4. CONCLUSIONS

Electrochemical degradations in the presence of SO_4^{2-} ions, as well as in the presence of Cl^- ions were compared for the synthetic solutions containing methylene blue (BM-ylene) and methyl blue (BM-yl) dyes using UV-Vis spectrophotometry. This comparison showed a faster degradation and discoloration of the BM-yl solution under indirect electrolysis.

For BM-ylene, the degradation degree associated with the color removal (*CR*) increases from 73.4% in the presence of SO_4^{2-} ions after 180 min, to 87.2%, in the presence of Cl^- ions after 30 min. For BM-yl, higher *CR* values were obtained such as: 87.9% in solution containing SO_4^{2-} ions after 180 min, and 89.7% in solution containing Cl^- ions after 10 min.

For both dyes, the first order reaction kinetics was verified using the equations referring to the linear relationship of $(\ln A_0/A)$ vs time, as well as the exponential decrease of the absorbance in time. The rate constants for BM-ylene degradation are lower than those obtained for BM-yl under the same simulated conditions, showing faster degradation of BM-yl, than that BM-ylene, both in Na_2SO_4 solution, as well as in NaCl solution.

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