

# Research Journal of Pharmaceutical, Biological and Chemical Sciences

## Studies on electrochemical degradation of the azo dye Methyl Orange by anodic oxidation.

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### ABSTRACT

The electrochemical oxidation of a synthetic wastewater containing Methyl Orange was investigated. A series of electrochemical degradation runs was performed in order to assess the effect of the following operating parameters on color removal: applied current (4–5 A), dye concentration (50–200 mg/L), pH (4–11), temperature (25–65 °C) and NaCl concentration (1.5–3.5 g/L). The complete decolorization was achieved in any experimental conditions indicating that the electrochemical oxidation is a suitable method for treatment of dye wastewaters. Performance was improved at operating conditions of 3.5 g/L NaCl concentration, pH 4, 25°C temperature and 5A current intensity. Degradation of the aromatic rings was demonstrated by the decrease of absorbance at UV region in UV–Vis spectra. The kinetic and energy consumption were also discussed.

**Keywords:** anodic oxidation, Methyl Orange, decolorization, wastewater treatment.

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## INTRODUCTION

Textile industries generate large amount of wastewaters highly charged with acid or basic dyes, salts and adjuvants. Many of the chemicals contained in these wastewaters are difficult to biodegrade and characterized by intense color and high chemical oxygen demand (COD) [1]. The presence of even very small amounts of dyes in water can cause a very visible color change [2], which affects not only the transparency of water and the aquatic life, but also raises environmental concerns [3]. Several conventional processes (physical, chemical and biological) have been investigated for the removal of dyes [4]. However, due to the large variability of the composition of textile wastewaters, most of these traditional methods are becoming ineffective [5].

Electrochemical oxidation has received a great deal of attention recently due to its promising advantages, such as high efficiency, versatility, ease of operation and environmental compatibility [7,8]. The organic and toxic pollutants can be destroyed by direct oxidation through electron transfer reactions on the anode surface, or indirect anodic process via the production of strong oxidants [8] such as hydroxyl radicals ( $\bullet\text{OH}$ ), which are non-selective and react rapidly with most organic compounds. The removal of contaminants may also be mediated by the electrogeneration of active chlorine ( $\text{Cl}_2$ ,  $\text{HClO}$ , and  $\text{OCl}^-$ ) [9]. The latter mechanism is responsible for the highest degradation rates attained using electrooxidation processes.

This study deals with the degradation of a model azo dye, methyl orange (MO), by anodic oxidation. Experiments were conducted under different operating conditions. The influence of various process parameters such as pH, applied current intensity, temperature and initial electrolyte and dye concentration on the efficiency of the process has been investigated. The performance of anodic oxidation was analyzed in terms of decolorization.

## MATERIALS AND METHODS

All the reagents used in this study are of analytical grade and used without further purification. NaCl was used as supporting electrolyte and the initial solution pH was adjusted with sulfuric acid or sodium hydroxide.

### Experimental setup

The experimental plant is schematically shown in Fig.2. All trials were performed in a stirred electrochemical reactor of 6 L capacity. The glass cell was surrounded by a double jacket for recirculation of thermostated water to maintain the solution temperature at a desired value using a ULTRATEMPS 2000 julabo F30 thermostat. A cylindrical platinized titanium (Ti/Pt) grid was used as anode and the cathode was a rod of same metal. The electrical energy for the system was drawn from a regulated power supply (EA-7015-050). The solution was constantly stirred at 300 rpm using a BIOBLOCK SCIENTIFIC stirrer.

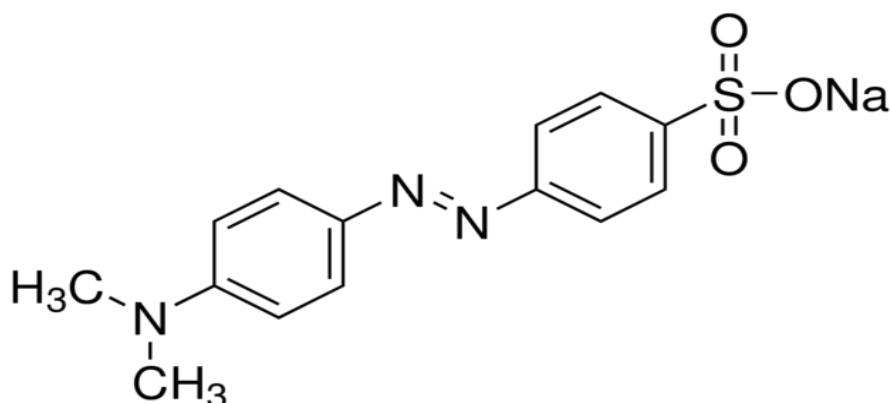


Fig. 1. Methyl Orange structure.

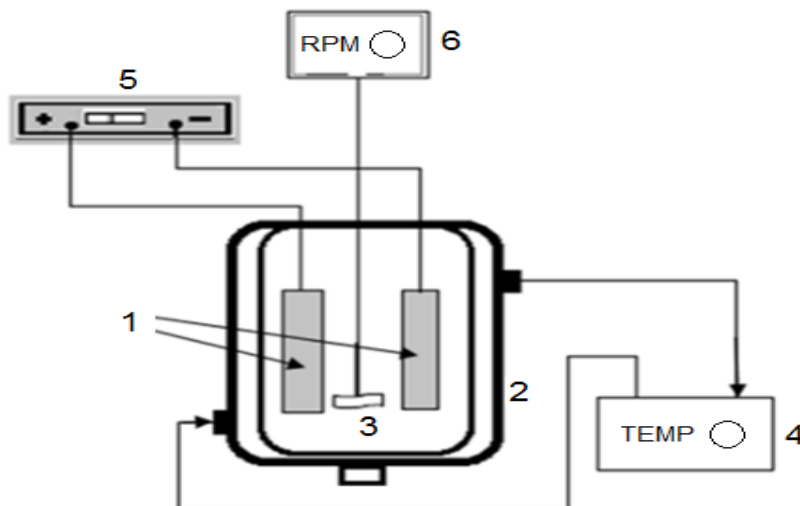


Fig.2. Experimental setup of electrochemical reactor (1– electrodes; 2 – electrochemical cell; 3 – impeller; 4–thermostat; 5– DC power source; 6 – stirrer).

### Analysis techniques

The solution pH was determined with a HACH pH-meter (Modèle Sension 7). The decolorization of MO solutions was monitored by measuring absorbance decrease at the maximum visible wavelength, using a UV 1201 Shimadzu spectrophotometer. The decolorization efficiency was calculated as follows:

$$\% \text{ decolorization} = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

Where  $A_0$  and  $A_t$  are the absorbance at initial time and time  $t$  at the characteristic  $\lambda_{\text{max}} = 460 \text{ nm}$ .

## RESULTS AND DISCUSSION

### Effect of initial pH

To investigate the effect of initial pH on the decolorization efficiency, experiments were performed at acidic (i.e. pH 4), neutral (i.e. pH 6.6) and alkaline (i.e. pH 10 and 11) conditions. Fig. 3 shows the variation of initial pH on the decolorization of MO during the electrochemical degradation.

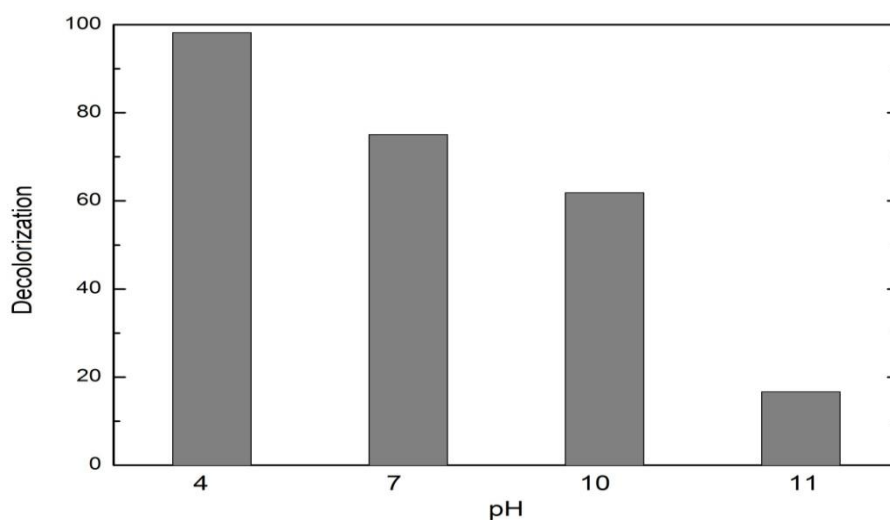
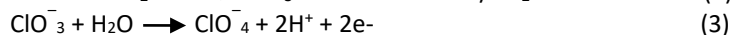
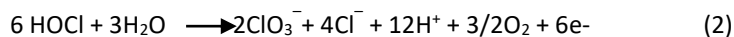


Fig. 3. Effect of initial pH on electrochemical degradation of MO (I: 5A, MO: 50 mg/L, T: 25 °C and NaCl: 2.5 g/L).

The results showed that the color removal decreased with increase in the initial pH of the solution. Degradation is clearly favored at acidic conditions where about 60% decolorization after 30 min of treatment; 76, 61, 16 % at pH 7, 10 and 11 respectively. This behavior can be explained by the decreased production of chlorine/hypochlorite, due to parasite reactions of chlorate or perchlorate as follow:



Another reason is that at lower pH, the chlorine is present in the solution in the form of hypochlorous acid. According to Szpyrkowicz et al. [10] extensive oxidation in acidic condition may be due to higher oxidation potential of hypochlorous acid rather than hypochlorite. Similar results were also obtained by A. Maljaei et al. [11].

### Effect of current intensity

Fig. 4 shows the evolution of the dye decolorization as a function of electrolysis time and current intensity (i.e. 4 and 5A). It is clear that, the rate of decolorization increases with electrolysis time.

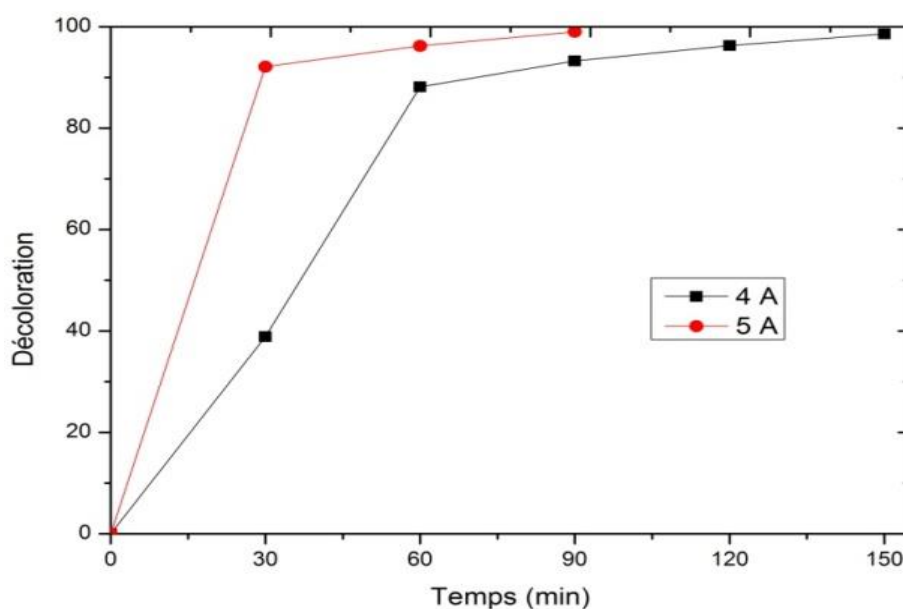


Fig. 4. Effect of applied current intensity on electrochemical degradation of MO (MO: 50 mg/L, T: 25 °C and NaCl: 2.5 g/L).

Furthermore, it can be ascertained from the figure that higher removal efficiencies were obtained at higher current intensities. D. Rajkumar et al. [12] attributed this to the increase of  $\text{Cl}_2$ , HOCl and  $\text{OCl}^-$  concentrations in the cell solution, which accelerate the removal of dye

Also, according to Szpyrkowicz et al. increasing the current intensity of the electrochemical cell follows production of more electrons, which eventually increase the rate of dye degradation[13].

### Effect of temperature

Fig.5 presents the rate of decolorization during the electrochemical oxidation at different reaction temperatures. Dye removals of 96%, 90% and 77% were obtained with the temperature values of 25, 50 and 60 °C, respectively at the end of 90 min of electrolysis. Degradation is clearly favored at ambient temperature, which is in good agreement with previous studies [16,17].

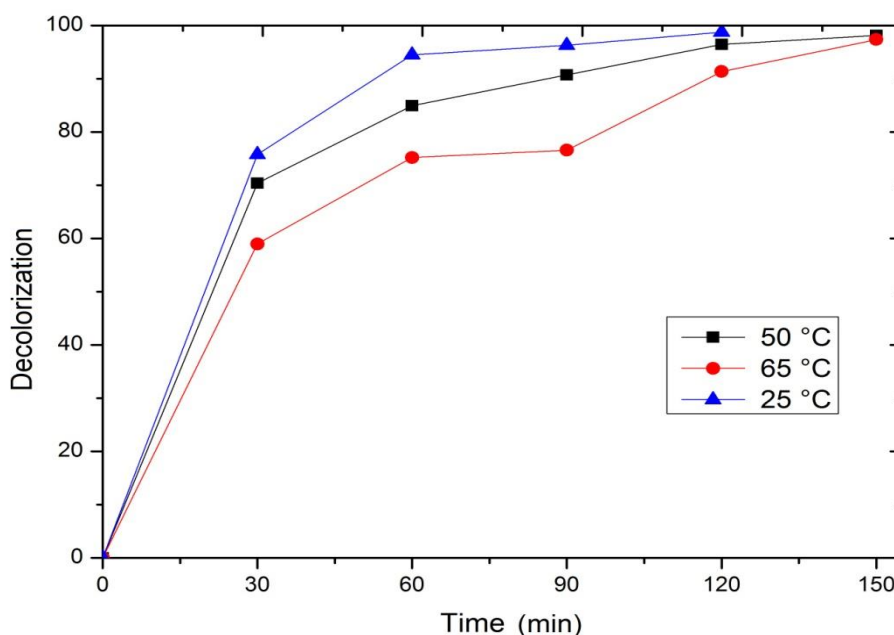


Fig. 5. Effect of temperature on electrochemical degradation of MO (I: 5A, MO: 50 mg/L, T: 25 °C and NaCl: 2.5 g/L).

Increased temperature leads to decreasing of removal efficiency, this behavior was attributed to a decrease of the rate of generation of chlorine/hypochlorite at high temperatures [12]. Another reason may be the less solubility of Cl<sub>2</sub> gas while increasing the temperature of the solution [16].

#### Effect of initial dye concentration

The effect of initial dye concentration on the electrochemical degradation was investigated for 50-200 mg/L solutions of pH 4 in the undivided tank reactor at 5A and 25 °C. Results are shown in Fig. 6.

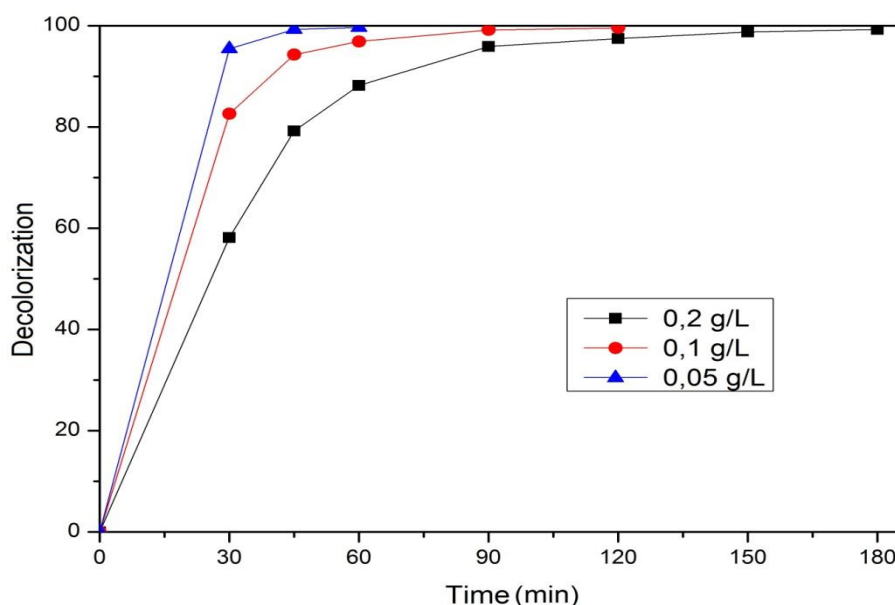


Fig. 6. Effect of initial dye concentration on electrochemical degradation of MO (I: 5A, T: 25 °C and NaCl: 2.5 g/L).

Complete removal of MO was reached for all initial dye concentrations. However the rate of decolorization decreased with increasing dye concentration, as expected. The time required for the total color removal is 40, 90 and 150 min, respectively, for 50, 100 and 200 mg/L dye concentration.

This may be explained by the fact that, at a given current intensity, the chlorine/hypochlorite is consumed rapidly by both MO molecule and intermediate compounds while increasing the initial dye concentration [17]. Similar results were also obtained earlier in other works [12,19].

**Effect of supporting electrolyte concentration**

Supporting electrolyte has an important effect on the electrochemical process[19]. Fig. 7 illustrates the effect of varying the electrolyte concentration on the MO color removal. Decolorization rate of 93 % was obtained after 30 min of electrolysis with the electrolyte concentration of 3.5 g/L, whereas it took 60 min to reach a decolorization rate of 81% with the electrolyte concentration of 1.5 g/L. The obtained results showed that dye degradation increased with the increasing of electrolyte concentration.

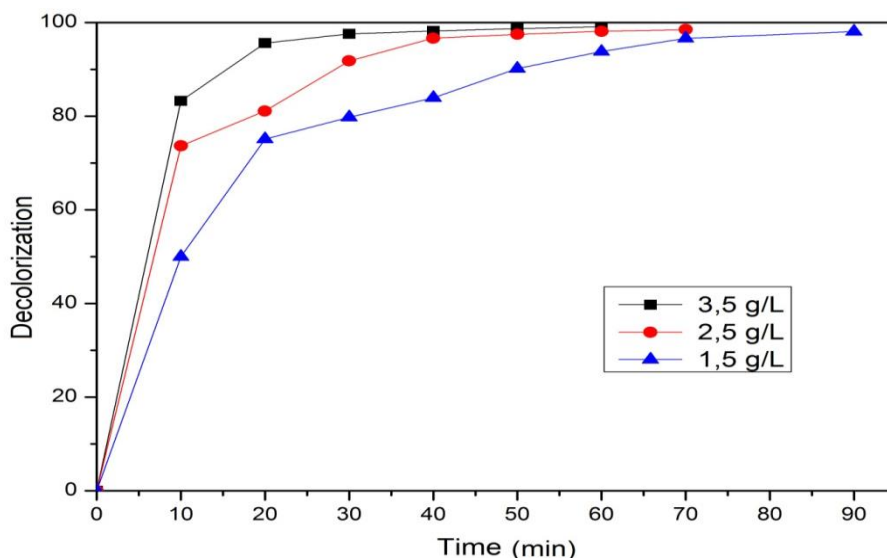


Fig. 7. Effect of electrolyte concentration on electrochemical degradation of MO (T: 25 °C, MO: 50 mg/L and I: 5 A).

This can be explained by the fact that Increasing Cl<sup>-</sup> concentrations enhances the formation of active chlorine species and the solution conductivity, hence improves the overall efficiency of the electrochemical degradation reaction [21,22].

Dye concentration decreases exponentially with time at each concentration of NaCl (Fig.8). The kinetics of disappearance of MO as shown in the inset of Fig. 8 can be represented by the following first-order mechanism:

$$\ln\left(\frac{C_0}{C}\right) = k t \tag{4}$$

Where C<sub>0</sub> is the initial dye concentration (g/L), C is the dye concentration at t (g/L), k is the apparent pseudo-first-order rate constant (min<sup>-1</sup>) and t is the decolorization time (min). The results are shown in Table 1. The decolorization reaction rate order at different electrolyte concentrations is as follows k<sub>1.5</sub> < k<sub>2.5</sub> < k<sub>3.5</sub>. Furthermore, the electrical energy consumption per unit volume was analyzed at different NaCl concentrations using the following equation:

$$\text{Energy consumption} = U.I.t/V \tag{5}$$

Where U is the mean applied voltage (V), I is the current (A), t is the treatment time (min) and V is the liquid volume (L).

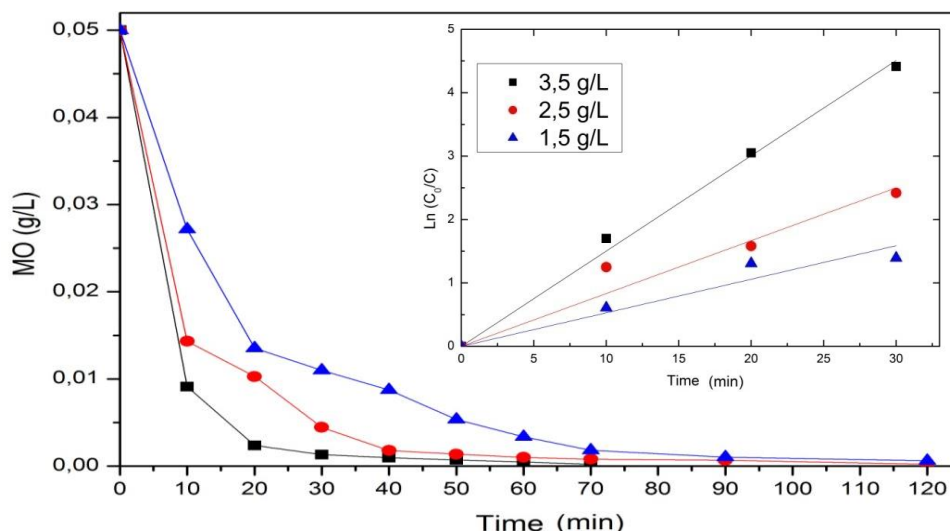


Fig . 8. MO concentration decay with electrolysis time at different NaCl concentrations (T: 25 °C, MO: 50 mg/L and I: 5 A). The inset graph illustrates the corresponding kinetic analysis assuming a pseudo first-order reaction for MO

Table 1. Kinetic constants for first order models of MO decolorization and energy consumption (T: 25 °C, MO: 50 mg/L and I: 5 A).

NaCl (g/L)	Color removal (>95 %)			
	Electrolysis Time (min)	Kinetic constants ( $10^{-2} \text{ min}^{-1}$ )	R <sup>2</sup>	Energy consumption (kWh/m <sup>3</sup> )
3,5	40	13,3	0,94	4,39
2,5	60	7,8	0,96	8,78
1,5	90	4,6	0,97	15,37

### UV-Vis spectra

Fig.9 presents the UV–visible absorption spectra of MO degradation by electrochemical oxidation. The peak observed at 460 nm was attributed to the azo structure of MO. It considerably decreased and finally disappeared after 60 min of electrolysis. The absorption band at 275 nm presented in the UV spectrum was assigned to the aromatic rings formed. It rises with the increase of electrolysis time until it reaches its maximum, and then diminishes.

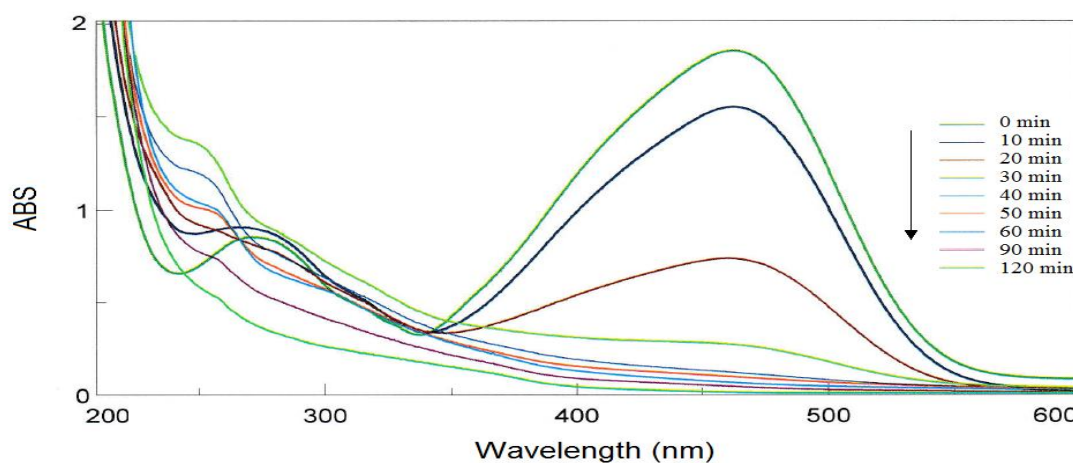


Fig. 9. UV–visible spectra of MO during the electrochemical degradation at different time intervals (I: 5A, MO: 50 mg/L, T: 25 °C and NaCl: 2.5 g/L).

These results indicate that the conjugated bonds of MO are destroyed and the aromatic rings are broken into small molecules [22,24].

### CONCLUSION

Anodic oxidation has been successfully applied to completely remove all the color from a synthetic wastewater containing MO. The effect of various operational parameters on the efficiency of decolorization was investigated. The results of this study revealed the following:

- ✓ Color removal increased with increasing current intensity and NaCl concentrations, while it was found to decrease with the increase in initial dye concentration.
- ✓ The best decolorization results can be achieved at ambient temperature.
- ✓ A faster degradation is found in acid solutions.
- ✓ Energy consumption measured during the electrolysis of MO dye largely depends on NaCl.

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