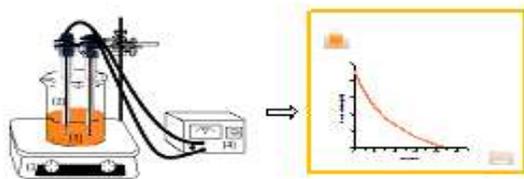


Electrochemical Oxidation Process to the Degradation of Aqueous Solution Dyes

Fadila Louafi¹, Ouarda Brahmia²

Abstract— In this study, the electrochemical decolourisation of Water textile dyes on Pt electrodes was assessed. The results demonstrate from one hand, a partial pollutant degradation reaching a maximum of 40 % in the case of Methyl orange in direct oxidation.



On the other hand, the electrochemical process with the cobalt redox mediator ($\text{Co}^{2+}/\text{Co}^{3+}$) is able to electrocatalyse efficiently dyes oxidation by shortening significantly the treatment time and enhancing clearly the dye decolourisation rate. Nearly complete decolourisation was achieved. The most striking results achieved with the cyclic voltammetry study demonstrate undoubtedly the product mineralisation. Electrochemical experiments were performed using the spectrophotometric method which is very convenient, easy and allows monitoring the spectral changes as well as the determination of the dye concentration during the process. The kinetics data shows first-order kinetics in the case of the indirect oxidation. A mechanism was advanced to explain the different phenomenon during the electrochemical process.

Keywords—Decolourisation, Textile Dyes, catalyst, Platinum, cobalt, Mediated electrochemical oxidation, mineralisation, cyclic voltammetry.

I. INTRODUCTION

Wastewaters originated from various industry such as textile contain various pollutants including a high content of organic matter and suspended masses and dissolved salts [1, 2]. Moreover, organic dyes used to dye cotton, acrylic, silk and wood are considered as widespread environmental pollutants. [3] In the case of textile industry, up to 50 % of the synthetic dyes with different structural varieties such as; azo, diazo, quinine imine, thiazole and others [4] are lost after the dyeing process and disposal out of the effluents [5]. Therefore, their elimination from wastewaters is an obligation to prevent the ecosystem destruction. Conventional wastewater treatment based on the biological process is not suitably enough to

remove recalcitrant dyes from effluents [6]. Physical and chemical methods used for eliminating dyes (i.e. adsorption, incineration, electrocoagulation, photocatalysis, ozonation and others) are reasonably effective but relatively cost [7, 8]. That's why; it's necessary to find an effective wastewater method capable of degrading toxic organic compounds from industrial effluents. As an alternative, the electrochemical oxidation process is a clean advanced oxidation technology because the main reagent; the electron, is a clean one [9]; it was applied successfully and proved to be convenient and fruitful to destruct bio-refractory organic compounds due to its high effectiveness and environment well-suited. In the electrochemical oxidation under room temperature and atmospheric pressure, generally, researchers focus their particular interest on the anode oxidation process than the cathode reduction. One alternative to efficiently remove color from solutions of structurally different dyes (methyl orange, phenol red, crystal violet, bromophenol blue, fuchsin, and poly R-478) is provided by Mediated Electrochemical Oxidation (MEO) with Co(III) [10]. In this context, we accomplish the MB [11], CR electrochemical degradation in the presence of $\text{Co}^{2+}/\text{Co}^{3+}$ selected as a redox mediator using Pt electrodes. Moreover, it is noteworthy the conductor behavior of MO, MG and CR that's why we achieved this study without a supporting electrolyte to test the feasibility of dyes electrochemical degradation. It should be noted as well that generally dyes are susceptible to undergo a photochemical degradation as they absorb in the visible part of the electromagnetic spectrum, that's why we have worked in the obscurity to avoid any probability of a possible photodegradation pathway. The aim of this work is to test the feasibility of the electrodegradation of MO, MG and CR in our particular conditions. The decolourisation rate has been evaluated with and without the redox mediator and the mechanism of the process was as well suggested in both direct and indirect oxidation.

II. EXPERIMENTAL SECTION

A. Materials

Methyl orange (MO), Congo red (CR) and Methyl green (MG) was purchased from Labosi (for analysis) and used without further purification. The cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) used as redox mediator was purchased from Biochem. Solutions were prepared using distilled water.

B. Methods summary

The electrochemical process was carried out using the spectrophotometric method to follow the dyes decolourization.

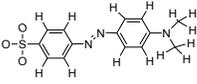
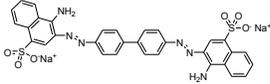
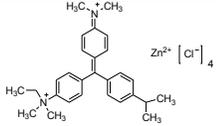
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The study was conducted on the aqueous solution of MO, CR and MG, under atmospheric pressure, at room temperature, and in the obscurity. Experiments were carried out in an electrochemical cell containing the amount of 25 ml of dyes for each experiment and using electrodes placed in the cell center with a distance of 2 cm separating them. The anode and cathode are Pt wire from Voltalab. The ratio electrode surface/volume of dye solution was 0.04 m². m⁻³ at laboratory scale. A constant voltage drop of 5 Volt was applied to the electrodes using Potentiostat (Alimentatore per elettroforsi el VI 16, Italy). The reaction vessel was placed on a magnetic stirrer for continuous stirring to ensure the solution homogeneity during the electrochemical process. The conductivity of the initial dyes solution was measured by a conduct-meter model (Inolab Cond 7110) and diverse chromophoric groups of highly unbiodegradable and recalcitrant characteristics were in table1. According to this conductor behavior, we choose to perform our experiments without any electrolytes and test the feasibility of Methyl orange, Congo red and Methyl green degradation in this condition. During the electrochemical process, after each treatment time, we transfer the solution to the UV-visible spectrophotometer (Jenway 6505) to record the absorption spectra of the dye solution and to measure the absorbance at the maximum absorbance using a matched pair of quartz flows cells (1 cm path length). The absorbance data were converted

to the concentration using Beer-Lambert equation (1). $A = \epsilon \cdot C \cdot L$ (1), where A and ϵ are respectively the absorbance and molar absorptivity coefficient values at the maximum absorbance wavelength of each dye, C is the dye concentration at time t, l is the light path length. The value of ϵ at maximum absorbance wavelength was deduced from the dyes calibration curve. The assays were done twice; the experimental error was below 3 %. The decolourisation rate of the dye was expressed as a percentage and calculated by the following equation (2); % dye decolourisation = $[(C_0 - C_t) / C_0] \times 100$ (2), where C₀ and C_t are the dye concentrations at time 0 and time t respectively. The concentration of the dye was calculated from the absorbance value at maximum absorbance wavelength using a calibration curve. Voltammetric experiments were carried out with a potentiostat model Gamry (USA). The working electrode was a platinum electrode and a reference electrode was a saturated calomel electrode (SCE). All potentials were reported vs. the SCE. A platinum electrode was used as the counter electrode. The scan rate was 100 mV/ s. The experiments were achieved using a cell of 20 ml, we purged the dissolved oxygen by nitrogen bubbling during 25 minutes and we used as 0.1 M of KCl as supporting electrolyte.

TABLE 1 : PRINCIPAL PARAMETERS OF USED DYES

Name	Methyl orange	Congo red	Methyl green
Class	Azo	Azo	Triphenylmethane
Formule brute	C ₁₄ H ₁₄ N ₃ O ₃ S	C ₃₂ H ₂₇ N ₆ Na ₂ O ₆ S ₂	C ₂₆ H ₃₃ Cl ₂ N ₃ , ZnCl ₂
Chemical Structure			
Molecular weight (g/mol)	696,663	696.66	594,80
λ_{max} (nm)	470	500	635
pH	8.39	8.79	7.34
Conductivity (\square S/cm)	110	210	110

III. RESULTS AND DISCUSSION

A. Direct monocomponent oxidation of MO, CR and MG

Decolourisation rate

To assess the feasibility of the electrochemical process conducted on a solutions dyes (45 \square M) at initial basic pH, we experimentally followed the decolourisation by measuring the dye absorbance at its absorption maximum as a function of the different electrochemical treatment time. The decolourisation expressed in terms of percentage was calculated according to equation (1). The obtained results are shown in figure (1).

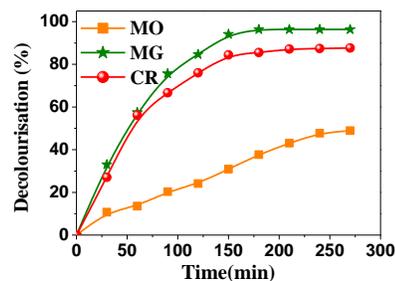


Fig. 1 : Decolourisation rate (%) of MO, CR and MG with respect to the treatment time.

We notice on the figure (1) a progressive increase of the dye decolourisation at 180 min for the CR and 180 min for the MG with a decolourisation rate > at 90 % ; the evolution of the decolourisation of MO up to 210 minutes which this last

reached a maximum of 47 %. For a treatment time of 250 minutes, the decolourisation percentage does not change; this leads us thinking about an inhibitory effect on the elimination of MO due probably for its aromatic structure

Electro-degradation kinetics

To better understand the pollutant behavior, we convert the absorbance to concentration and plotted the kinetics of the pollutant disappearance (figure 2).

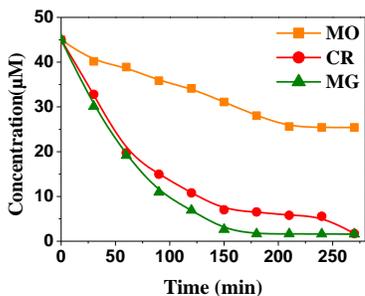
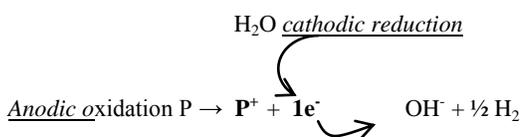


Fig. 2 : Direct electrochemical decolourisation of MG, CR and MO.

According to the plotted curve, it appears two different phases, the first one corresponds to a treatment time between 0 and 150 minutes, the elimination rate is rapid at the beginning of the reaction. During this time period, we can readily admit that the reaction proceeds most probably by a transfer of electrons. On one hand, the pollutant undergoes anodic oxidation since it is capable of giving electrons especially those of the lone doublets of sulfur and nitrogen atoms. On the other hand, we admit a cathodic reduction of water; this last lead to the formation of OH⁻ anions with the release of H₂ according to the reaction (1): 2 H₂O + 2 e⁻ → 2 OH⁻ + H₂ (1) We can summarize the mechanism of electro-degradation according to the following scheme (where P and P⁺ are respectively the pollutant and the oxidized pollutant).



Scheme 1: Mechanism of dyes direct oxidation

The second part of the curve is included between 210 and 250 minutes, we stopped at this end because the electro-degradation rate no longer changes. This strongly suggests that the intermediates formed during the reaction can compete with the pollutant itself and thus inhibit its elimination. We can generally accept that reactions consuming electrons can limit the dyes direct oxidation in solution. All this goes to prove that the direct electrochemical oxidation is capable of oxidizing just partially the MO solution, that's why it's interesting to optimize this process to reach the dye total degradation.

The decolourisation kinetics can be quantitatively described as the first order with respect to the dye concentration. The rate values and the statistical correlation parameter are shown in table2.

TABLE II : KINETICS COEFFICIENTS FOR A FIRST ORDER ELECTRO DEGRADATION REACTION OF DYES

Dye	k (x 10 ⁻³) (min ⁻¹)	R ²
Methyl Orange	1.99	0.987
Congo Red	9.67	0.939
Methyl Green	16.99	0.962

The kinetics coefficient indicated the same results decolourisation rate obtained of MG, CR and MO.

B. Decolourisation of dyes mixtures

Real effluents often include more than one component and the study of the possible interactions between different chromophores will be very useful. Here we tested mixture of azo dye (MO) and triphenyl methane dye (MG). The UV/visible spectrum of mixtures of dyes shown in figure 3. The decolourisation rate of each dye changed when the technique was applied to the mixture. Significant differences on decolourisation rate of MO and MG was observed due to the class of each dye.

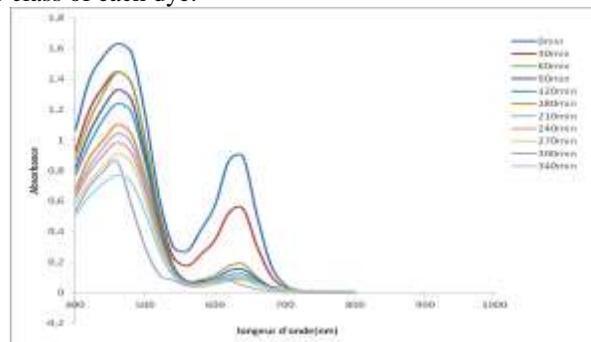


Fig. 3 : Direct electrodecoulourisation of dyes mixtures

The Methyl Orange reached decolourisation percentage of about 48% after 240 minutes in monocomponent oxidation and 40% after the same time. The reached decolourisation rate of about 96% after 180 minutes of MG in the monocomponent dye solution, only 84% was observed in solution mixture. This can explain by the competition between the two dyes at anode electrode.

IV. INDIRECT OXIDATION

It's well established that the redox mediators such as (Fe^{2+/3+}, Ce^{3+/4+}, Co^{2+/3+}) are able to generate electrochemically oxidizing species capable of inducing degradation of dyes [12]. Therefore, it is interesting to consider the redox catalyst effect on MO oxidation. We started with the couple Ce^{3+/4+} catalyst, no significant change was observed in terms of dye disappearance, this is probably due to its moderate oxidation potential (1.72 V). The second attempt was performed using the couple Co^{2+/3+} with a slightly higher oxidation potential (1.92 V) [12]. We tested its effect on MO, CR and MG electro-degradation.

A. Evolution of monocomponent dye solution absorption spectra

In terms of experimental conditions, the study was performed by adding a solution of CoCl₂ (10⁻⁷ M) to the initial dyes solutions (45 µM), basic initial pH using the same platinum electrodes. In figure 5 we presented the percentage of

dyes decolourisation according to the different treatment time during the indirect oxidation.

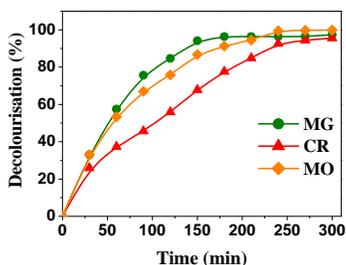


Fig.4: Decolourisation rate of dyes in the presence of $Co^{2+/3+}$ catalyst.

B. Photocatalytic Degradation of MB in aqueous solution by TiO_2/SL and ZnO/SL

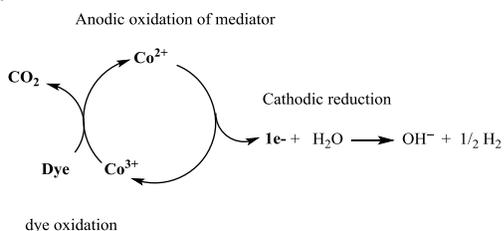
The most striking result shows that the almost complete dyes decolourisation after 250 minutes against low decolourisation of MO in the case of the direct oxidation. This reflects the substantial role played by the catalyst in the electrochemical process to increase the dye decolourisation percentage.

These results demonstrate that a small amount of cobalt (10^{-7} M) is largely enough to effectively catalyze the electrochemical reaction of dyes. Furthermore, in terms of reaction kinetics, the indirect oxidation is first-order kinetics. The rate constant of the reaction is deduced from the curve representing $(\ln C_0/C$ versus time). The rate constant values and statistical correlation are shown in table3.

TABLE 2 : Kinetics coefficients for a first order electro degradation reaction of dyes in presence of Co^{2+} mediator

Dye + Co^{2+}	k_1 ($\times 10^{-3}$) (min^{-1})	R^2
Methyl Orange + Co^{2+}	11.9	0.999
Congo Red + Co^{2+}	3	0.998
Méthyl Green + Co^{2+}	10	0.995

In this process, metal ions are oxidized anodically from a stable oxidation state to reactive species, which in turn, are capable of oxidizing organic substances to CO_2 [10]. The electro-degradation mechanism is presented by the following scheme.



Scheme 2: Mechanism of dyes oxidation with redox mediator Co^{2+}

Following these results, we can say that the redox mediator acts as a catalyst for the complete decolourisation of methyl orange Figure 4.

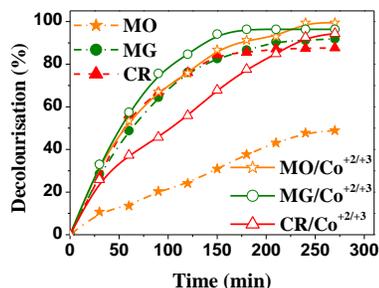


Fig. 5: Comparison between the dyes decolourisation rate (with and without catalyst).

C. Decolourisation of dyes mixtures in the presence of redox mediator

At the same dyes mixtures used above, the $CoCl_2$ solution (10^{-7} M) was added to the solution of the initial concentration of $45 \mu M$ mixture. The evolution of the dyes mixtures of the absorption spectrum for discoloration figure 4 shows a significant difference compared with that found for the direct discoloration figure3. The using of redox mediator favors complete degradation of mixtures of dyes into simpler compounds or even reaching a complete mineralization.

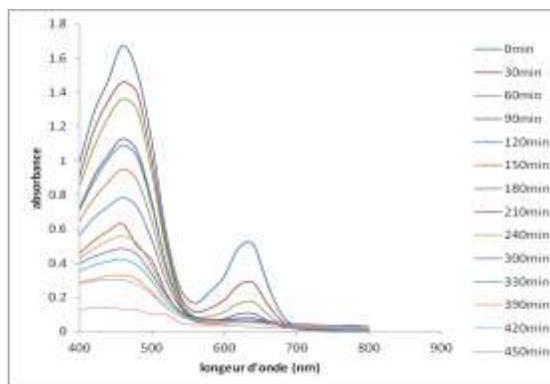


Fig. 6: Indirect electrochemical decolourisation of dyes mixtures in presence of Co^{2+}

The voltammogram (CV) of free Methyl Green in KCl on Pt electrode at scanning rate $100 mVs^{-1}$ shows the presence of an irreversible oxidation peak at a potential of $1.1 V / SCE$ and irreversible reduction peak at $-0.4 V / SCE$. After complete discoloration of the dye, the recorded voltammogram shows the disappearance of the oxidation peak, and occurrence of an irreversible reduction peak at a potential of $0.2 V / SCE$ and a reversible system with an anodic peak potential (Epa) to $-0.3 V / SCE$ and cathodic peak potential (Epc) of $-0.6 V / SCE$. The resulting irreversible redox system is probably due to the reduction of CO_2 mineralization occurs in the following half reaction: $CO_2 + e^- \rightarrow CO_2^{\cdot-}$.

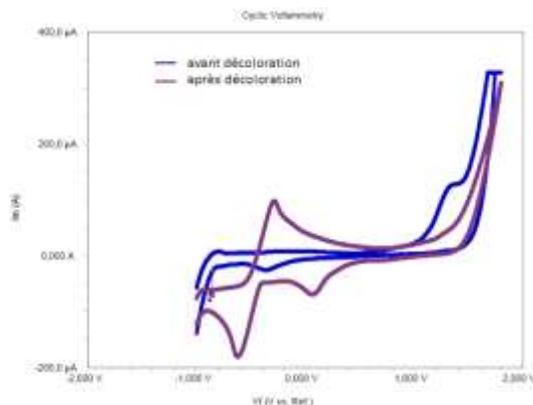


Fig. 7 : Voltammogram of MG before and after decolourisation

V.CONCLUSION

The study in this work shows that the electrochemical oxidation process is effective under our experimental conditions for the treatment of wastewaters dyes of azo type and triphenylmethane type. This method allows to eliminate or reduce the quantity of chemical reagents in producing oxidants directly into the medium by electrochemistry. By its environmental compatibility, it is an efficient and clean solution to the objectives of green chemistry and sustainable development. Electrochemical treatment of dye solutions in the presence of the redox mediator $\text{Co}^{2+} / \text{Co}^{3+}$ plays an important role on the speed of electrodegradation the dye and the decolourisation rate.

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