



Effect of the mixing velocity and the active chlorine concentration in anolyte on the indirect electrochemical oxidation of the Acid Red35 dye.

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Received 9Jan 2017,
Revised 5Apr 2017,
Accepted 7Apr 2017

Keywords

- ✓ Acid Red35 dye,
- ✓ indirect electrochemical oxidation,
- ✓ anolyte,
- ✓ stirred tank,
- ✓ active chlorine

Abbreviations

- ✓ AR35: Acid Red35
- ✓ ECA: ElectroChemical Activation
- ✓ RMSE : Root Mean Square Error
- ✓ NRMSE: Normalized Root Mean Square Error

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Abstract

The main objective of this work is to study the effect of the agitation rate and the concentration of active chlorine on the efficiency of the degradation of the Acid Red35(AR35) dye by indirect electrochemical oxidation. The experimental tests were carried out in a stirred tank with a reaction volume of approximately 350 mL. The Reynolds number is set to a high value so that the mixture is perfect. The synthetic solution of the dye at a concentration of 20 mg·L⁻¹ and the initial pH of the anolyte used for the treatment is between 3.2 and 4.4. The stirring velocity has a very limited effect on the degradation of the dye for a 16.6% added anolyte volume fraction containing 210 ppm of active chlorine. For the same volume fraction of anolyte and a stirring velocity of 300 rpm, the temporal evolution of the dye concentration shows that the time required for an 80% reduction has increased from 3 to 40 minutes for Chlorine, respectively, of 440 and 120 ppm. The effectiveness of the treatment of the synthetic solution of the AR35 dye increases as the concentration of active chlorine increases. In addition, empirical correlations expressing the results were developed based on curve fitting. These correlations estimate the time required for the degradation of the AR35 dye as a function of the volume added of the anolyte and the yield of the discoloration as a function of the reaction time for different concentrations of active chlorine.

1. Introduction

The water quality entering to sewage treatment plants is increasingly affected by the contamination of persistent organic compounds from different branches of industry, chemical, pharmaceutical, agri-food, etc. Pollutants commonly found in industrial and urban discharges include synthetic dyes, which causes many disturbances to aquatic fauna and constitute a risk to human health. With a view to degrading this pollution, several processes have been subject of researches, and the choice of the most suitable technology depends, in part, on the physico-chemical characteristics of the effluent, on its final destination and on the economic feasibility of the process. Special attention has been paid to electrochemical oxidation processes (direct or indirect oxidation) for the treatment of these effluents. These techniques are clean and flexible for the development of new methods for the treatment of wastewater [1,2]. For direct oxidation, there is a direct effect on a species in solution when the electron is exchanged exclusively on the electrode, while the indirect oxidation consists in generating a powerful oxidizing agent which reacts with organic pollutants. Among these oxidizing agents, there is Ag²⁺ and Co³⁺ [3,4]. The indirect action may also be obtained by oxidation of the halides (Cl⁻, Br⁻ or I⁻) or by reduction of the dissolved oxygen, the reactions of which make it possible to generate strong oxidants such as HClO, HBrO, IOH. In particular, Canizares and al. [5] have proved that hypochlorite acid (HClO) is a strong oxidant capable of oxidizing and modifying the structure of organic molecules and producing less toxic components. The *in situ* generation of active chlorine has been widely applied in the treatment of sewer water [6], dyes such as methyl violet (MV2B), Eosin Yellowish (EOY), Trypan Blue (TRB) ACridine Orange (ACO) [7], textile dyes [8], tannery wastewater [9], and pesticides such as atrazine [10]. Indeed, the electrolytic production of active chlorine is one of the most important industrial electrochemical reactions [8, 11] and its use for the disinfection of drinking water has expanded greatly [12,13]. Then, the research of Zaviska and al. [7,10] demonstrated that the direct effect of *in situ* generation of active chlorine is only 10%, whereas the indirect effect

is predominant. For this reason, the electrochemical activation technique (ECA) shows promise from an environmental and economic point of view. The method consists in chemically activating of brine in order to generate in the anode compartment of the electrochemical cell a solution called anolyte. It is composed of active molecules such as active chlorine, which can reach a concentration of 500 ppm (for an initial concentration of NaCl between 800 and 1000 ppm), free radicals and highly reactive ions [14]. Although chlorine gas is the initial product of electrochemical oxidation of chloride ions, other species may be formed depending on the pH of the system. Consequently, active chlorine is a term used to designate the concentration of three highly oxidizing chlorine species, namely molecular chlorine (Cl_2), hypochlorous acid (HOCl) and hypochlorite (OCl^-) ions [15]. All are collectively called active chlorine.

Some authors have pointed out that several other radicals such as chlorine radicals (Cl° , ClO° and Cl_2°) can be formed during the electrochemical generation of active chlorine and have higher oxidation potentials than active chlorine $\text{Cl}^\circ / \text{Cl}^- = 2.410 \text{ V} / \text{ENH}$, $\text{E}^\circ \text{Cl}_2^\circ / 2\text{Cl}^- = 2.090 \text{ V} / \text{ENH}$, $\text{E}^\circ \text{Cl}_2 / 2\text{Cl}^- = 1.395 \text{ V} / \text{ENH}$ [16,17]. With all these active elements, the anolyte is capable of reacting rapidly and non-selectively on most persistent organic compounds [18]. Design considerations and operational factors for systems using chlorine are still being studied to optimize these systems.

In this study, the anolyte generated from the electrochemical activation process of brine is the oxidizer used for the indirect oxidation of the AR35 textile dye in a stirred tank at atmospheric pressure and ambient temperature. This type of dye was chosen as the target compound because it is found abundantly in the liquid effluents of the textile industries. The effect of different parameters on the evolution of the coloration removal efficiency as a function of the reaction time is discussed in order to show the importance of each parameter and to elaborate useful correlations for the sizing of the reactors. The parameters followed are the stirring speed, the volume fraction in added anolyte, the pH and the concentration of active chlorine in the anolyte.

2. Materials and methods

2.1. Materials

Anolyte: supplied by the company Alternattech subsidiary of "Enviolyte France", is a solution recovered from the anode part of the Electrochemical Activation system ECA, it is a colorless liquid, its pH is very acid from (2 to 4.5), with a characteristic odor of chlorine. The anolyte is characterized by a high oxidation potential in the range +1200 to +1500 mV. It is made up of several efficient and non-selective oxidizing agents: chlorine (Cl_2 dissolved), hypochlorite acid (HClO), hydrogen peroxide (H_2O_2), ozone (O_3), hydroxyl radicals and chlorine radicals, which contribute to the powerful oxidizing properties of the anolyte. The various dissolved chlorine species (molecular chlorine (Cl_2), hypochlorous acid (HOCl) and hypochlorite ions (ClO^-) are called active chlorine [19, 28, 29]. The relative amount of each of these forms of free chlorine is dependent on the pH of the anolyte and temperature. At room temperature, Cl_2 (aq) is the dominant species under very acidic conditions, HOCl predominates at $3.3 < \text{pH} < 7.5$, while ClO^- is the main species at $\text{pH} > 7.5$. Starting with $\text{pH} = 4$, the hypochlorite is transformed into hypochlorous ions (ClO^-) less active than HOCl and Cl_2 . Control of the pH of the anolyte is a critical factor for the operation of the reactor for treating water containing a dye.

Acid Red35 dye: The synthetic solution of AR35 dye of chemical formula $\text{C}_{19}\text{H}_{15}\text{N}_3\text{Na}_2\text{O}_8\text{S}_2$ (CAS 6441-93-6). Its chemical structure was given in **Figure 1** is used to simulate industrial wastewater. For all the experiments carried out in this study, the initial solution is prepared by diluting 20 mg of the dye, in powder form, in one liter of distilled water ($C_0 = 20 \text{ mg}\cdot\text{L}^{-1}$).

Potassium iodide, acetic acid, sodium thiosulfate and starch (analytical grade-SigmaAldrich) are used for titration of active chlorine contained in the anolyte.

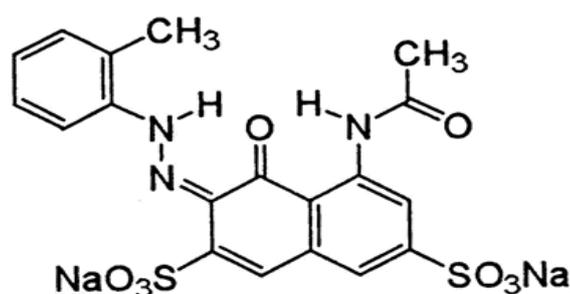


Figure1. Chemical structure of AR35.

2.2. Methods

The measurement of the active chlorine content is very important in our case because the quality of the anolyte is controlled by its concentration of active chlorine and its pH.

The concentration of active chlorine present in the anolyte is determined via the iodometric standard volumetric method by titration with thiosulfate [19]. And the initial pH of the anolyte is measured by a pH meter of brand-name (PHM 240 PH / ion meter Meterlab™). The pH of the reaction mixture after addition of the anolyte remains virtually neutral during the treatment of the colored solution.

The degradation of the dye is carried out by the addition of the anolyte which is realized in a vessel that has a diameter of 80 mm as shown in **Figure 2**. The mixture is provided by a magnetic bar of cylindrical shape with a length of 28 mm and a diameter of 5 mm and stirring speed is adjusted by a magnetic stirrer from the brand (AGIMATIC N). The absorbance is monitored by a UV / visible spectrophotometer (HITACHI High-Technologies Co., Tokyo-Japan, model U5100 RATIO BEAM) using a 10 mm wide quartz cell. IR spectra were obtained on a FTIR (Bruker Vector 22 spectrometer) and reported in wave numbers (cm^{-1}).

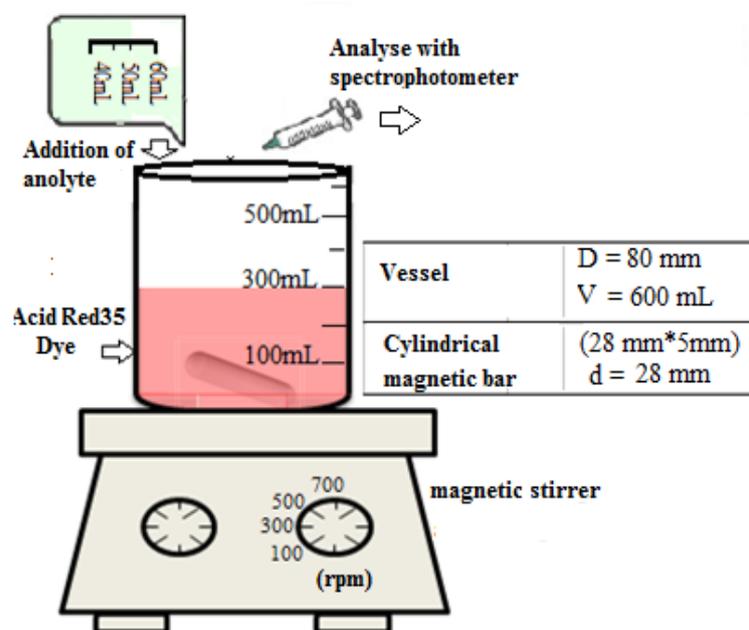


Figure 2: Experimental design

In this study, the residual AR35 dye concentration was measured to evaluate the performance of the treatment by addition of the anolyte to various operating conditions: agitation velocity, the amount of added anolyte and the concentration of active chlorine in the anolyte. The dye concentration is determined indirectly by measuring the absorbance at a wavelength of 515 nm which corresponds to a peak in the absorption spectrum. The volume of the synthetic solution of the dye is fixed at 300 mL.

3. Results and discussion

3.1. UV-VIS analysis

Figure 3 shows the temporal evolution of the absorption spectrum of the reaction mixture consisting of the synthetic solution of the AR35 dye with an initial concentration of 20 mg.L^{-1} ($C_0 = 20 \text{ mg.L}^{-1}$), and a volume of 50 mL of the anolyte with a concentration of 480 ppm of active chlorine. The rate of stirring is set at 300 rpm. The scanning is carried out between the wavelengths 200 and 700 nm. An absorption peak is located in the visible spectrum between 430 and 610 nm with a maximum absorbance at the wavelength 515 nm ($\lambda_{\text{max}} = 515 \text{ nm}$). After three minutes of reaction, the absorbance increases from 0.3 (before the addition of the anolyte) to 0.035, this corresponds to an 88% decrease in absorbance. During the processing time, the absorbance becomes very low for wavelengths that are greater than 400 nm. The evolution of the absorbance in the visible range is synonymous with a chemical transformation of the synthetic solution by indirect oxidation of the dye by the oxidants contained in the anolyte and particularly the active chlorine. Throughout the treatment, the

predominant peak corresponding to the wavelength $\lambda_{\max} = 515$ nm disappears after 37 min. Therefore, the absorbance at 515 nm can be used to evaluate the degradation performance of the dye.

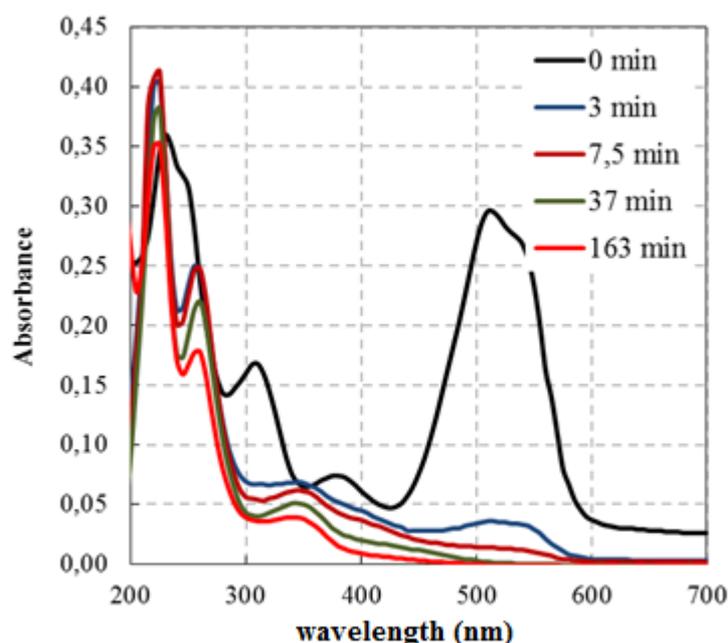


Figure 3: UV-vis spectrum at different treatment times ($\tau_r = 3, 7.5, 37.3$ and 163 min) with $C_0 = 20$ mg.L⁻¹, 50mL of anolyte of 480 ppm of active chlorine, and a rate of stirring of 300 rpm

In the UV range, where the wavelength is included in our study between 200 and 400 nm, three net absorption peaks are observed for the synthetic solution of the dye before the addition of the anolyte. These peaks are located at 230, 310 and 380 nm. Indeed, the intensities of the bands at 310 and 380 nm decreases greatly, this is mainly caused by changes in the centers of aromatic character in the dye molecule [20]. After three minutes of oxidation of the dye, an absorption peak appears at 345 nm and is greatly decreased. Another one appears at 220 nm and the absorbance remains virtually identical to this wavelength until a treatment time of 7.5 minutes ($\tau_r \leq 7.5$). For $\tau_r \geq 37.3$, the absorbance begins to decrease slowly. This can be explained by the formation of a transient species during the fragmentation of the dye molecule and that this species requires a very long time to react compared to others. The absorbance peak at 260 nm may be associated with an excess of oxidants originally contained in the anolyte and formed during the reaction between Cl_2 and O_3 [21]. According to the same work [21], the disinfection by-product ClO_2^- is generated as an intermediate of the reaction between excess active chlorine and ozone, and that $(\text{Cl}_2 + \text{ClO}_2^-)$ absorbs at the wavelength 360 nm. In this study, the absorption peak at the wavelength 360 nm is not observed, so it can be concluded that there are no disinfection by-products (ClO_2^- and even ClO_3^- , which is generated by the reaction of active chlorine and ClO_2^- [22]). The formation of such undesired products has often been mentioned in the case of chlorination of wastewater (Sellar, 1974, Jolley, 1975). Generally, the incorporation of halogen atoms into an organic molecule results in increased risks in terms of toxicity, bioaccumulation or persistence. Arber et al. (1984) compare the effects of chlorination of wastewater with increasing chlorine levels at different positions on the breaking point curve according to bacteriological and chemical criteria. The best results in disinfection are obtained in the presence of free chlorine, a situation in which the formation of organochlorine derivatives, such as trihalomethanes, is also maximal. Whereas in our case several other investigations carried out on electrochemical oxidation by chlorine have proved the absence of its degradation by-products.

Indirect oxidation by the addition of anolyte generated by ECA appears to be suitable for discoloration of the synthetic solution of AR35 dye. In the rest of this study, we measured the absorbance at 515 nm for the evaluation of the performance of the treatment of the synthetic solution of the AR35 dye for various operating conditions because the variation in the absorbance at this wavelength is very important. Measurement of the

absorbance at $\lambda_{\max}=515$ nm for different dye concentrations between 0 and 20 mg.L⁻¹ made it possible to obtain a calibration curve whose evolution is linear. Therefore, the residual dye concentration is deduced from equation (1).

$$C_{(Red35)} = 62.03 * Abs_{(\lambda=515nm)} \quad (1)$$

The coefficient of determination R^2 for the establishment of this linear regression equation is almost equal to 1 ($R^2 = 0.9996$). Therefore, this equation explains 100% of the distribution of points with a very low error. The performance of the treatment of the AR35 dye is also evaluated by the yield calculated by equation (2).

$$R(\%) = \frac{C_0 - C_t}{C_0} * 100 = \frac{Abs_0 - Abs_t}{Abs_0} * 100 \quad (2)$$

With,

C_0 and Abs_0 are respectively the dye concentration and the absorbance at the wavelength 515 nm before the addition of the analyte ($\tau = 0$ s).

C_t and Abs_t are respectively the dye concentration and the absorbance at the wavelength 515 nm at a time τ after the addition of the analyte which corresponds to a reaction time τ_r .

3.2. IR analysis

The mechanism behind effective decoloration and degradation of AR35 dye was investigated by means of IR analyses of the treated solution.

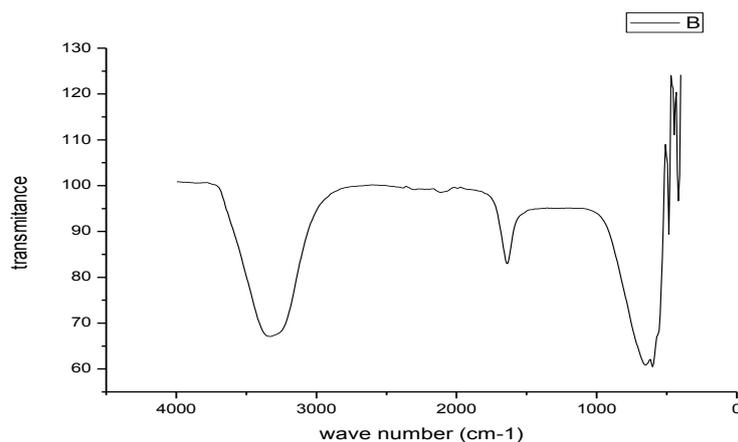


Figure 4: IR Spectrum of the treated solution of AR 35 dye

As shown in figure 4 the IR Spectrum contains three bands:

- a-Strong and very wide absorption band between 2900 and 3700 cm⁻¹
- b-Medium and sharp band at 1635cm⁻¹
- c-Strong band between 500 and 800cm⁻¹

After analyzing the spectrum (**Figure 4**) and verifying the existence of each of the conventional absorption bands (see document "IR analysis of the treated solution of the AR35 dye" attached). The spectrum is thus identified as that of a compound containing a characteristic group of a carboxylic acid. Indeed, there is a broad absorption band between 2900 and 3700 cm⁻¹, and a thin strip around 1635 cm⁻¹. An N-H bond may also be present because our spectrum contains a mean band between 1500-1700 cm⁻¹ which characterizes this bond. In addition, a strong band exists in our spectrum between 500-800 cm⁻¹ corresponds to the C-Cl bond as the treatment of the dye is carried out by analyte which contains active chlorine. So to conclude these last two connections can be existed with that of the carboxylic acids demonstrated at the top.

3.3. Effect of agitation on discoloration of the AR35 dye

The effect of agitation on the discoloration of the AR35 dye solution is evaluated by comparing the color reduction efficiencies at stirring rates of 100, 300, 500 and 700 rpm in a tank of a mixture containing 300 mL of the colored solution at 20 mg.L^{-1} . After the addition of a volume of 50 mL of anolyte with a concentration of 300 ppm of active chlorine and a pH of 3.2 (**Figure 5**), it is observed that the variation in the processing efficiency of the colored solution over time is quasi-identical for the different agitation speeds. In the first minutes of treatment, the change in the discoloration yield is linear and the discoloration is rapid whatever the speed of mixing. A reduction of 50% of the coloration is observed after about three minutes of treatment. Thereafter, the discoloration becomes less rapid, where the reaction time required is about 8 minutes to achieve 75% of the abatement. For a reaction time of more than 12 minutes, the discoloration of the solution becomes very slow, and for the increase in the discoloration from 86% to 92%, the reaction time increases from 12 to 30 minutes.

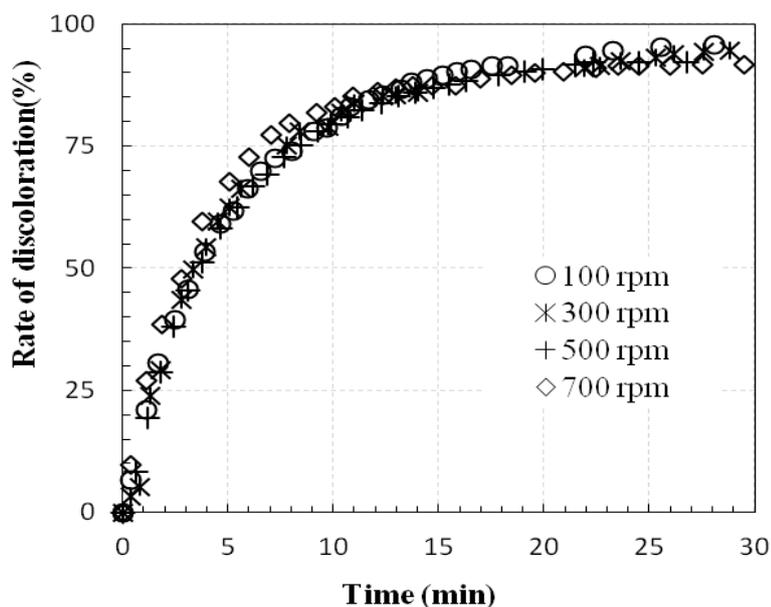


Figure 5: Time evolution of the discoloration efficiency for different agitation rates (300 ppm of active chlorine, pH = 3.2 ; volume of anolyte added 50mL and $C_0 = 20 \text{ mg.L}^{-1}$).

To minimize the loss of active chlorine by transfer of material to the ambient air, mixing must be carried out by a low mixing speed and preferably using a reactor with lid [21]. Therefore the study of the effect of the added amount of anolyte and the concentration of active chlorine is carried out by setting the mixing rate at 300 rpm to maintain a perfect mixture of the solution without vortex formation.

3.4. Effect of the amount of anolyte added on the discoloration of the AR35 dye

In order to study the effect of the amount of anolyte added on the discoloration of the AR35 dye solution, the active chlorine concentration was set at 210 ppm, the pH of the anolyte was 3, 4 and the stirring rate is maintained at 300 rpm. The time evolution of the discoloration yield for different volumes of anolyte (30, 40, 50 and 60 mL) is shown in **Figure 6**. It is observed that the addition of an anolyte volume of 60 mL gives rise to an increase in the discoloration yield very rapidly and reaches 75% within a treatment time of about 6 minutes. On the other hand, when the volume of anolyte added is 50 and 40 mL, the required reaction time is respectively equal to 12.6 and 22.1 minutes to achieve a yield of 75% as shown in Table 1. Also observed that for a treatment time of 40 minutes, respectively, a discoloration yield of 95%, 90%, and 86% was achieved for 60, 50 and 40 mL of added anolyte. While for an added amount of 30 mL, the yield is equal to 67% for the same treatment time. Thus, as the added volume of the anolyte increases, the abatement kinetic comes rapid.

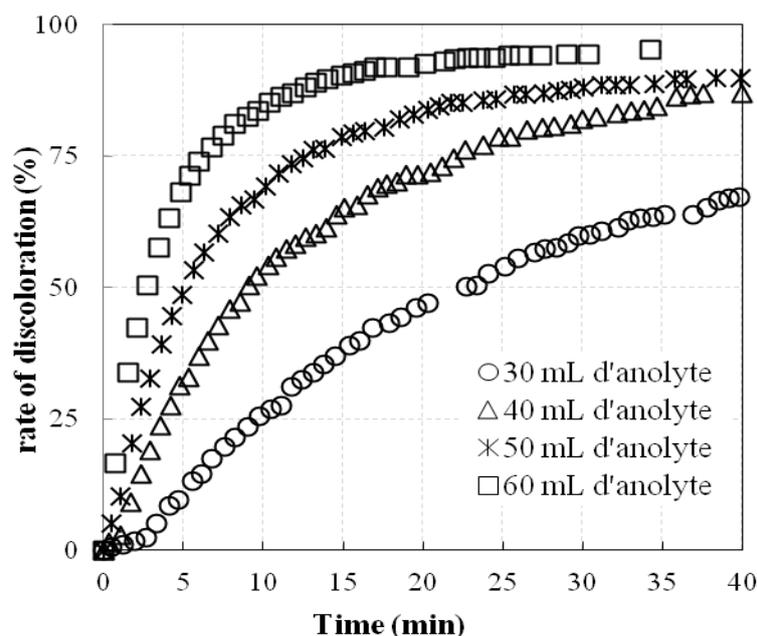


Figure 6: Time evolution of the discoloration yield for various volumes added to the anolyte (210 ppm of active chlorine, pH = 3.4, $C_i = 20 \text{ mg L}^{-1}$ and stirring speed of 300 rpm)

Table 1: Treatment time for different rates of discoloration (40, 50, 65 and 75%)

| Rate of discoloratio | Volume of anolyte added, V_a | τ_r (min) | $\tau_r/\tau_r(50 \text{ mL})$ | $V_a/50(\text{mL})$ | $\tau_r/\text{mod}(\text{min})$ | Error |
|----------------------|--------------------------------|----------------|--------------------------------|---------------------|---------------------------------|-------|
| 40% | 30 | 16.06 | 4.226 | 0.6 | 16.06 | 0% |
| | 40 | 6.6 | 1.737 | 0.8 | 6.77 | -3% |
| | 50 | 3.8 | 1 | 1 | 3.47 | 9% |
| | 60 | 1.99 | 0.524 | 1.2 | 2.01 | -1% |
| 50% | 30 | 22.7 | 4.408 | 0.6 | 22.53 | 1% |
| | 40 | 9 | 1.748 | 0.8 | 9.51 | 6% |
| | 50 | 5.15 | 1 | 1 | 4.87 | 5% |
| | 60 | 2.7 | 0.524 | 1.2 | 2.82 | 4% |
| 65% | 30 | 37.65 | 4.461 | 0.6 | 37.39 | 1% |
| | 40 | 15.05 | 1.783 | 0.8 | 15.77 | -5% |
| | 50 | 8.44 | 1 | 1 | 8.08 | 4% |
| | 60 | 4.42 | 0.524 | 1.2 | 4.67 | -6% |
| 75% | 40 | 22.1 | 1.754 | 0.8 | 22.53 | -2% |
| | 50 | 12.6 | 1 | 1 | 11.54 | 8% |
| | 60 | 6.3 | 0.5 | 1.2 | 6.68 | -6% |

The addition of an anolyte volume of 50 mL makes it possible to achieve a discoloration yield of 50% and 75% respectively at 5.15 and 12.6 minutes. These times may be considered reasonable for the treatment of water containing dyes. Indeed, the time $\tau_{1/2}$ for a similar treatment with the addition of H_2O_2 coupled with UV was the order of 5.8 min for the degradation of two acid dyes namely *Acid Red1* and *Acid Yellow23* at $20 \text{ mg}\cdot\text{L}^{-1}$ [23].

For a rate of discoloration of 75% in less than 13 min can satisfy the dimension of a reactor [24]. Indeed, a 15 min residence time is required for the pilot scale electrochemical treatment of the waste water with a current density of $3\text{mA}\cdot\text{cm}^{-2}$ and a feed rate of $0.3 \text{ m}^3\cdot\text{h}^{-1}$ [25]. Then, the addition of 50 mL of anolyte, which represents

about 16% relative to the volume of the colored water to be treated, can be considered as a reference state. An increase in the volume of anolyte by 10 mL, which corresponds to a 20% increase in volume, results in a reduction of about 50% in the reaction time. On the other hand, this reaction time increases by 75% when the volume of anolyte is reduced by 20%. For a 40% reduction in the amount of anolyte added, it is necessary to increase the reaction time by 4 times to reach 40, 50 and 65% on the rate of discoloration (Table 1).

The evolution of the reaction time as a function of the volume added to the anolyte, for different discoloration efficiencies, is identical and follows a power law (Figure 7). The correlation of the experimental points, using this law, made it possible to establish an equation making it possible to estimate the reaction time necessary to achieve a given discoloration yield (equation 3).

$$\tau_r = K_\tau * V_a^{-3} \quad (3)$$

The values of the constant K_τ are grouped in Table 2.

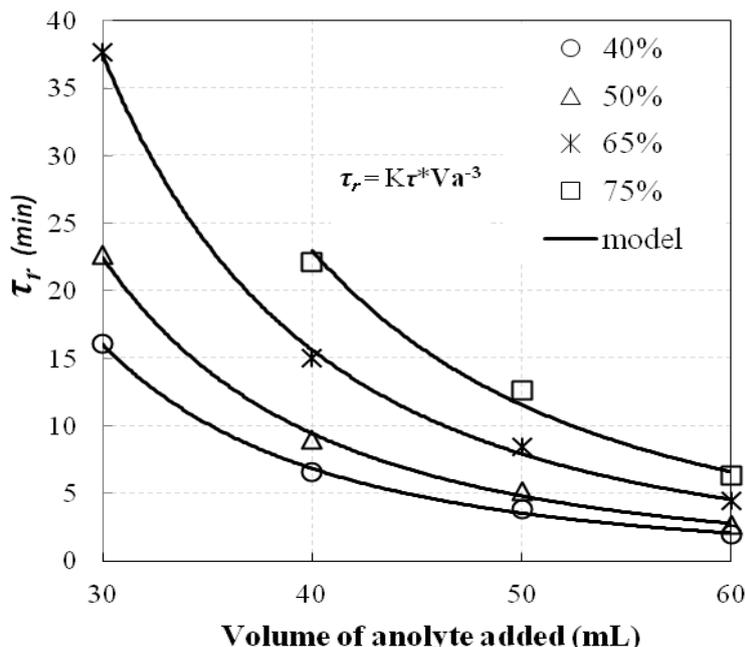


Figure7: Comparison of experimental and estimated effect of the volume of added anolyte on the reaction time

This correlation makes it possible to correctly estimate the reaction time (R^2 converges to 1) for the different discoloration yields. As shown in Table1, the maximum error for estimating the reaction time is 9%. This correlation can be used for dimensioning a colored water treatment reactor. Indeed, for a reaction time previously fixed as a function of the flow rate of the colored waters to be treated, it is possible to evaluate the amount of anolyte necessary to achieve a given discoloration yield.

Table 2: Values of constant K_τ for different rates of discoloration (40, 50, 65 and 75 %)

| <i>Rate of discoloration</i> | $K_\tau \times 10^{+5} (min. cm^{-3})$ |
|------------------------------|--|
| 40% | 4.34 |
| 50% | 6.08 |
| 65% | 10.10 |
| 75% | 14.42 |

The volume added to the anolyte is none other than the quantity of active chlorine used for the treatment of colored water. The effect of the active chlorine concentration in the anolyte on the reaction time required to achieve a given discoloration yield is studied by keeping the reference volume set at 50 mL which is about 16% of the volume of the colored water to be treated.

3.5. Effect of the active chlorine concentration of the anolyte on the discoloration rate

The effect of the active chlorine of the anolyte on the discoloration rate of the AR35 dye is investigated by adding 50 mL of anolyte and the mixture is assured at a rate of 300 rpm. The time evolution of the discoloration yield is similar for the different concentrations of active chlorine in the added anolyte as shown in **Figure 8**. After the addition of anolyte, the discoloration is very rapid and it is reduced by time. It is found that for a given treatment time, the discoloration yield increases as the active chlorine concentration of the anolyte increases.

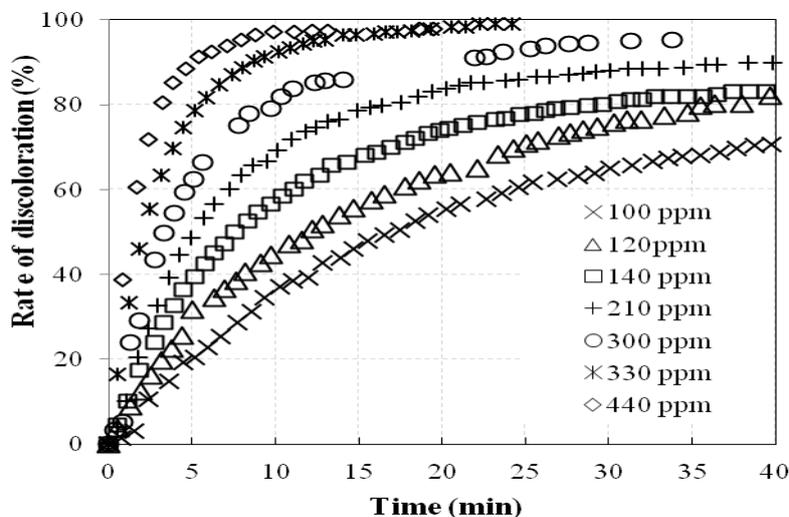


Figure 8: Time evolution of the discoloration efficiency for different active chlorine concentrations of the anolyte ($C_0 = 20 \text{ mg.L}^{-1}$, volume added of anolyte 50 mL and mixing speed of 300 rpm)

Indeed, for a very high active chlorine concentrations (330 and 440 ppm), the reaction time required is less than 5 min to achieve a yield of 75%. Starting from 10 min of reaction, the discoloration yield stabilizes at 90% and 97% respectively for 330 and 440 ppm of active chlorine. For active chlorine concentrations of 210 and 300 ppm, respectively, 13 and 8 minutes are required to achieve a 75% yield. From 20 min of reaction, this yield starts to stabilize to 90% and 95%, respectively. For low concentrations of active chlorine (120 and 140 ppm), it takes 30 minutes and 21 minutes, respectively, to achieve a yield of 75%, which stabilizes at about 80% after 40 min of treatment. On the other hand, for the very low active chlorine concentration of 100 ppm, the yield of 75% is not reached even after 40 min of reaction.

For a discoloration yield of 50%, the reaction time required $\tau_{1/2}$ decreases with increasing the concentration of active chlorine contained in the added anolyte. As shown in Table 3, the time $\tau_{1/2}$ increases from 5.15 to 1.27 minutes when the active chlorine concentration rises from 210 ppm (taken as a reference) to 440 ppm. Thus, an increase of almost 50% in active chlorine causes a reduction of about 75% of the reaction time $\tau_{1/2}$. On the other hand, this time increases more than 3 times when the concentration of active chlorine in the anolyte is reduced by approximately 50% as compared to the reference 210 ppm.

Table 3: Treatment time to achieve a discoloration yield of 50% for various active chlorine concentrations of the added anolyte

| Concentration of active chlorine in the anolyte (ppm) | $\tau_{r1/2}$ (min) | $\tau_{r1/2}/\tau_{r1/2}(210 \text{ ppm})$ |
|---|---------------------|--|
| 100 | 17.5 | 3.39 |
| 120 | 12 | 2.33 |
| 140 | 7.58 | 1.47 |
| 210 | 5.16 | 1.00 |
| 300 | 3.38 | 0.66 |
| 330 | 1.5 | 0.29 |
| 440 | 1.27 | 0.25 |

The residual active chlorine concentration should be minimized to avoid the production of disinfection by-products [11] in order to comply with environmental discharge standards and to reduce the operating cost of the water treatment plant. It is then preferred to use an anolyte with an active chlorine concentration of 120 ppm and an anolyte fraction of about 16% since the treatment time required to achieve a 50% discoloration yield is 12 minutes, or a low volume of anolyte highly concentrated in active chlorine.

Under the operating conditions cited above, the discoloration yield can be estimated by equation (4) which has been established by correlating the experimental points.

$$R_{mod} (\%) = \left[1 - \frac{1}{(1 + k_1 \tau_r)^{k_2}} \right] \times 100 \quad (4)$$

τ_r : reaction time of discoloration of AR35 dye by anolyte (min),

k_1 and k_2 : are constants that depend on the active chlorine concentration and the initial C_0 concentration.

The determination of the constants k_1 and k_2 , which depends on the active chlorine concentration, is carried out by iterative calculation by minimizing the error between the experimental discoloration yield of the AR35 dye and that estimated by equation (4). The values of these constants are grouped in Table 4.

To show that the correlation established (equation 4) correctly estimates the discoloration efficiency as a function of the reaction time for the different concentrations of active chlorine, three indices of concordance are used: the coefficient of determination R^2 , RMSE (Root Mean Square Error) and NRMSE (Normalized Root Mean Square Error). The description of a real process by a mathematical model is better when the coefficient of determination R^2 converges to 1, RMSE and NRMSE are close to 0. These are often used in the literature [26,27] given by the following formulas:

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_{i \text{ exp}} - y_{i \text{ mod}})^2}{\sum_{i=1}^n (y_{i \text{ exp}} - \bar{y}_{\text{exp}})^2} \quad (5)$$

$$RMSE = \left(\frac{\sum_{i=1}^n (y_{i \text{ exp}} - y_{i \text{ mod}})^2}{N} \right)^{1/2} \quad (6)$$

$$NRMSE = \frac{RMSE}{\left[(y_{i \text{ exp}})_{\text{max}} - (y_{i \text{ exp}})_{\text{min}} \right]} \quad (7)$$

With:

N: number of points compared;

$y_{i \text{ exp}}$: experimental value;

$y_{i \text{ mod}}$: value obtained by applying the model;

\bar{y}_{exp} : mean experimental value;

$(Y_{i \text{ exp}})_{\text{max}}$ and $(Y_{i \text{ exp}})_{\text{min}}$: maximum and minimum experimental value.

For each concentration of active chlorine, the values of the two constants k_1 and k_2 are determined as shown in Table 4. It is noted that the coefficient of determination R^2 is very close to 1, and that the two indices of concordance RMSE and NRMSE are close to 0, irrespective of the concentration of active chlorine. Then, it can be considered that the discoloration yield estimated by the model (equation 4) is very close to the experimental yield as shown in **Figure 9**.

Table 4: Constants k_1 and k_2 of the correlation and the coefficients RMSE, NRMSE and R^2

| Concentration of active chlorine of the anolyte (ppm) | $k_1 \cdot 10^{-2}$ | k_2 | RMSE | NRMSE | R^2 |
|---|---------------------|-------|-------|-------|--------|
| 100 | 3.52 | 1.47 | 0.011 | 0.015 | 0.997 |
| 120 | 5.65 | 1.37 | 0.010 | 0.013 | 0.998 |
| 140 | 10.9 | 1.15 | 0.089 | 0.010 | 0.957 |
| 210 | 18.1 | 1.11 | 0.025 | 0.027 | 0.990 |
| 300 | 8.63 | 2.63 | 0.028 | 0.029 | 0.993 |
| 330 | 9.5 | 3.83 | 0.003 | 0.003 | 0.9998 |
| 440 | 16.9 | 3.80 | 0.005 | 0.005 | 0.9996 |

Using this correlation (equation 4), it is also possible to determine the reaction time required to achieve a given discoloration yield:

$$\tau_r(\text{min}) = \frac{1}{k_1} \left[-1 + \left(1 - \frac{R_{\text{mod}}(\%) }{100} \right)^{-1/k_2} \right] \quad (8)$$

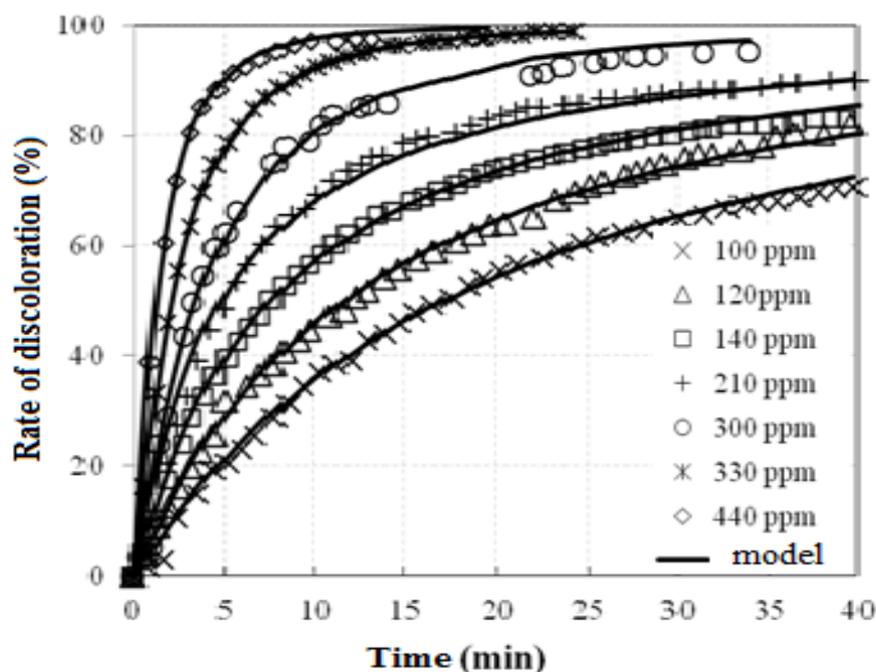


Figure 9: Comparison between the temporal evolution of the experimental discoloration yield of AR35 dye and estimated by the mathematical model (equation 4)

It has been demonstrated by Zaviska et al. that the predominant reaction mechanism is the indirect effect of the electric current corresponding to the oxidation of MV2B by the active chlorine (the 10% reduction would only be related to the direct effect of the electric current). This indicates that the higher the initial concentration of MV2B, the greater the active chlorine concentration required. The maximum active chlorine concentration produced by their system was 150 ppm (after 1 h of 2A electrolysis with Ti / IrO₂ as anodic electrode material). It was also possible for Flavio et al. to produce up to 60 mg L⁻¹ of active chlorine on a Ti / Sn_{0.99}Ir_{0.01}O₂ anode. The discoloration of a red 29 acidic textile dye (CI 16570) was also investigated in situ with electro-active chlorine. The best conditions were found to be: NaCl pH 4, 25 mA.cm⁻² and 6 h of electrolysis. It is important to emphasize that in such a treatment (in-situ), the electrochemical kinetics can be limited either by the process of supplying electro-activated species of the solution to the electrode, the solubility of chlorine gas in the solution. Because chlorate can be generated by parasitic reactions of solution hypochlorite (transfer of matter) cases of Zaviska et al. and Flavio et al. or by the electron transfer process (electrochemical reaction). Indeed, a difference in the concentration of active chlorine produced can be explained by a difference in limitations. In our present study, the concentrations of active chlorine employed at pH values of less than 4.5, ranging from 90 ppm up to 440 ppm batchwise, are relatively high, thus avoiding any limitation on the transfer of matter. Nevertheless, in the case of the Nagata et al. study, the process is limited by an electronic transfer caused by an accumulation of the ionic species in the vicinity of the electrodes, thus forming a diffusion layer.

Conclusion

The addition of acidic anolyte with a pH of between 3 and 4 allowed a discoloration of the synthetic solution of the dye AR35. The mixing rate does not have a significant effect on the discoloration efficiency. On the other hand, the volume of the added anolyte is a key parameter for reactor operation because the reaction time is inversely proportional to the volume of anolyte at power 3 (V_a³). The active chlorine concentration in the anolyte has a remarkable effect on the processing time and the discoloration yield.

For a good operation of the reactor for treating this water containing the AR35dye, it is necessary to avoid the formation of the disinfection by-products. It is preferable to use an anolyte with an active chlorine concentration of 120 ppm and an anolyte fraction of approximately 16% since the processing time necessary to achieve a discoloration yield of 50% is acceptable ($\tau_{r1/2} = 12$ min) or a low volume of anolyte highly concentrated in active chlorine.

Acknowledgments-The authors thank Zakia ZMIRLI for the help with the experimental apparatus. Thanks also to H. Labjer for her contribution in IR analyses.

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(2017) ; <http://www.jmaterenviromsci.com/>