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Abstract

The coupling of an electrochemical process with a biological treatment for the degradation of methylene blue (MB) and basic yellow 28 (BY28) considered separately or in mixture on a glassy carbon electrode was examined in this study. It was shown that color removal efficiency and mineralization yield of MB, BY28 and their mixture increased with the working potential and decreased with the initial dye concentration. The optimal conditions were found to be E = 2.4 V/SCE, $[MB]_0 = 50$ mg L^{-1}, $[BY28]_0 = 50$ mg L^{-1}, pH = 2, T = 25°C and ω = 600 rpm, which led to 100% color removal after 120 and 240 min of reaction time for BY28 and MB, respectively. Under these optimal conditions, the mineralization yield of BY28, MB and their mixture (50 mg L^{-1} of each dye) were close to 59 %, 57% and 54% within 360 min of reaction time, respectively. The BOD_5/COD ratio increased substantially after 360 min of pre-treatment from 0.04 to 0.27 for the dyes mixture. Microbial degradation was therefore performed for the pre-treated mixture solution and the results showed significant mineralization yields leading to an overall DOC decrease of 78% for the coupled process. It was therefore shown the presence of residual refractory compounds at the end of the culture which was illustrated by the decrease of the BOD_5/COD ratio (0.045) obtained for the final solution. However Biodegradability was

improved after a recycling of the solution in the electrochemical oxidation pre-treatment during 180 min, leading to a BOD_5/COD ratio of 0.73.

Keywords: Methylene Blue; Basic Yellow 28; Electrochemical process; Glassy carbon electrode; Biological treatment.

1. Introduction

The recent United Nations World Water Development Report has given prominence to the growing concern on dyeing industrial effluents [1, 2]. Large volumes of these wastewaters with high dye contents are daily discharged into water bodies, thus causing not only aesthetic problems but also toxic effects on aquatic organisms and humans [3-13], including proven carcinogenic, mutagenic and bactericide activities [1-3].

With the aim of removing theses organic toxic compounds from wastewater, a lot of physico-chemical techniques were studied such as adsorption, biosorption, ozonation, advanced oxidation processes (AOPs) including O_3/H_2O_2, UV/O_3, UV/H_2O_2, H_2O_2/Fe^{2+}, etc. [10-14]. To remediate groundwater contaminated by such non-biodegradable organic compounds, direct and indirect electrochemical processes can be implemented [15-28]; while biological processes which are the most cost-effective appear not always relevant for the remediation of such recalcitrant compounds [20-28].

Consequently, the implementation of a combined approach coupling direct electrochemical oxidation and biological process for the degradation of dye effluents could become an interesting alternative [23-28]. The potential advantages of the strategy of combining physico-chemical and biological processes to treat contaminants in wastewater have been previously suggested [21-28]. When used as a pre-treatment, physico-chemical processes can modify the structure of the pollutants leading to by-products which are expected to be more biodegradable and less toxic, allowing a subsequent biological treatment. The second strategy consists in the implementation of a biological pre-treatment to remove the biodegradable part, keeping the physico-chemical process for the treatment of the non-biodegradable part of the effluent [23-28]. MB is a widely used dye for cotton, wool, acrylic and silk [8, 9]; it is highly stable and non-biodegradable [8, 9]. Among the cationic dye family, BY28 which is commonly used in dying industries was selected [6, 7]. The degradation of MB and BY28 by the combination of an electrochemical oxidation using Pb/PbO2 electrode to a biological treatment was studied and the results were reported in our previous papers [26, 28], showing the efficiency of the proposed combined process; which however shows a crippling drawback owing to the slight dissolution of lead in the treated solution and hence less pollutant electrode materials such as carbon and glassy carbon electrodes could be an attractive alternative. In this work, a biological process was therefore tested in combination with an electrochemical process on a glassy carbon electrode to remove methylene blue (MB) and basic yellow 28 (BY28) considered separately or in mixture in aqueous solutions. The impact of the initial MB and BY28 concentrations and the working potential on the color removal and the mineralization yield were examined and the electrochemical pre-treatment was optimized.

2. Materials and Methods

2.1. The experimental set-up

The experimental set-up is described in Figure 1; it is mainly composed of the following parts: (1) potentiostat/Galvanosta VoltaLab; (2): glassy carbon anode (50 mm x 40 mm x 1 mm); (3): reference electrode (saturated calomel electrode-SCE); (4): graphite carbon cathode (188mm² of geometrical surface area); (5): magnetic bar-stirrer; (6): magnetic stirrer; (7): jacketed reactor; (8): water circulation "in"; (9): water circulation "out".

Electrolysis of the aqueous methylene blue (MB), basic yellow 28 (BY28) and their mixture solutions were carried out in a one-compartment Pyrex glass cell of 200 mL volume.The reference electrode (saturated calomel electrode-SCE) was positioned in the middle of the glass cell, between the anode and the cathode. The working potential control was performed using a potentiostat/Galvanostat VoltaLab PZG301. BY28 and MB degradation experiments were conducted in batch mode and the distance between electrodes was 10 mm.

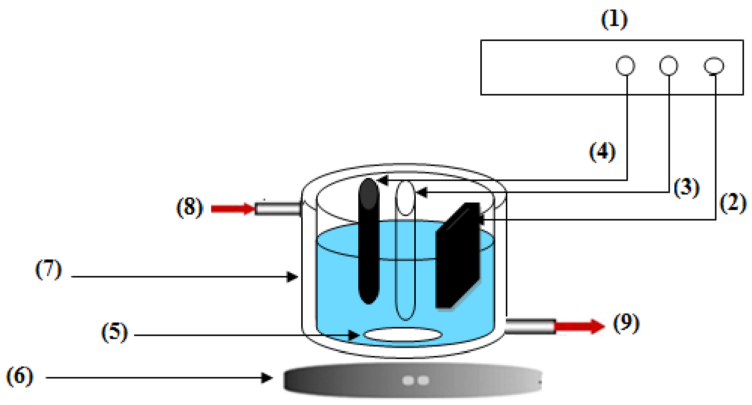
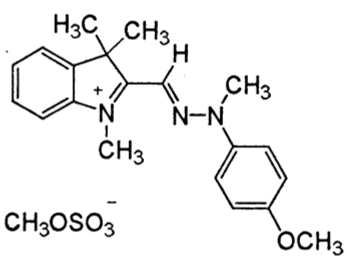


Figure 1. Experimental set-up

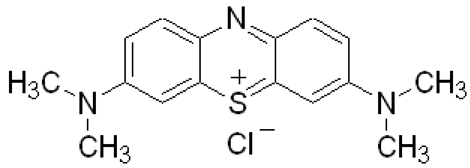
(1) Potentiostat/Galvanosta VoltaLab; (2): Plate anode (glassy carbon electrode); (3): saturated calomel electrode (SCE); (4): Graphite carbon electrode as cathode; (5): Magnetic bar-stirrer; (6): Magnetic stirrer; (7): Jacketed reactor; (8): Water circulation in; (9): Water circulation out.

2.2. Target compounds

The synthetic dye solution of BY28 was supplied by a Textile Factory (Alfaditex Remila – Bejaia, Algeria). Methylene blue was obtained from Biochem Chemopharma (Montreal, Quebec, Canada). Their chemical structures are given in figure 2.



Basic Yellow 28



Methylene Blue

Figure 2. Molecular structure of Methylene Blue and Basic Yellow 28

2.3. Analytical methods

2.3.1 Color removal efficiency measurements

Concentrations of dyes (MB and BY28) in the aqueous solution was spectrophotometrically determined at the maximum absorption wavelength (665 nm and 412 nm for BY28 and MB, respectively) using an ultraviolet-visible light (UV−vis) system (UV–vis A SAFAS SP2000 Monaco, Principality of Monaco) [25, 26, 28]. Sulphuric acid (H_2SO_4; 96 % purity form Biochem Chemopharma (Montreal, Quebec, Canada)) has been used both as supporting electrolyte and to adjust the pH of the solutions to 2 and all the dyes solutions were prepared with ultra-pure water (PurelabOptions-Q7/15, Elga, 18.2 MΩ cm^{-1}). All experiments were conducted at 30 °C and 200 mL volume solution. When considered separately, two different initial dye concentrations were studied, 50 and 100 mg L^{-1}; and for the mixture solution 50 mg L^{-1} of each dye was used.

2.3.2 Dissolved organic carbon (DOC) measurements

Dissolved organic carbon (DOC) was measured by TOC-$V_{CPH/CPN}$ (Total Organic Analyzer Schimadzu). Samples were taken and filtered through 0.45 μm membrane syringe filter

(Satorius Stedim biotech Gmbh, Germany) for the measurement of dissolved organic carbon (DOC) [26-28].

2.3.3 COD and BOD_5 measurements

Chemical oxygen demand (COD) and biological oxygen demand in 5 days (BOD_5) were measured by Nanocolor 500D photometer type (Macherey-Nagel, Hoerd, France); all COD and BOD_5 measurements were duplicated. The determination of BOD_5 was carried out into tube tests in the presence of added nutrients according to the EN 1899-1-H51. Additionally, probable influence of nitrification processes is inhibited by *N*-allythiourea which was also added. Samples incubation was carried out directly in the test tubes and the determination of oxygen dissolved in water was carried out after 5 days in accordance to the Winkler method EN25813-G21 by photometric evaluation of iodine-color. The COD was measured by means of Kits Nanocolor® 15-160 mg L^{-1} COD according to DIN ISO 15705 at 148 °C. The amount of oxygen required for the oxidation of the organic and mineral matter was quantified after oxidation with $K_2Cr_2O_7$ at acidic pH and heating at 148 °C for 2 h [26-28].

2.4. Media and culture conditions

Biodegradability tests and biological treatments were duplicated and were carried out on MB, BY28 and their mixture (MB and BY28) electrochemically degraded under the following conditions: 25 °C, 2.4 V/CSE, 600 rpm and 50 mg L^{-1} of dye (50 mg L^{-1} each in the case of the mixture).

Biological treatment was only performed on a mixture of dyes (50 mg L^{-1} each) electrolyzed under the optimal conditions for 360 min. Batch cultures were carried out at 25 °C during 30 days in shake flasks (250 mL) containing 0.5 g L^{-1} of activated sludge and the following mineral basis were added in the flasks: 0.5 mL of KH_2PO_4 (43.8 mg L^{-1}) and Na_2HPO_4 (33.4 mg L^{-1}), 0.150 mL of $CaCl_2$ (27.5 g L^{-1}), $MgSO_4$, $7H_2O$ (22.5 g L^{-1}) and NH_4NO_3 (3 g L^{-1}). 0.5 mL of trace elements was added to all solutions ($FeSO_4$,$7H_2O$: 1.36 g L^{-1}, $CuSO_4$,$2H_2O$: 0.24 g L^{-1},

$ZnSO_4,5H_2O$: 0.25 g L^{-1}, $NiSO_4,6H_2O$: 0.11 g L^{-1}, $MnSO_4$ H_2O: 1.01 g L^{-1}, H_3BO_3: 0.1 g L^{-1}). The pH was adjusted to 7.0 with 1 mol/L NaOH solution [26-28].

3. Results and Discussion

3.1. Effect of the working potential

The effect of the working potential on the color removal efficiency was examined at 1.5, 1.8 and 2.4 V/SCE (Fig.3). Comparison of the data for 2.4 V/SCE with those for 1.8 SCE/V and 1.5 V/SCE reveals that the degradation rate increased with increasing working potential; a significant effect was observed for both initial dye concentrations tested. Dyes were completely or nearly completely removed (> 90% color removal efficiency) within a reaction time of 360 min for 2.4 V/SCE. This effect should be related to the production of oxidizing •OH with increasing the working potentials [25-32].

$$H_2O \longrightarrow {}^{\bullet}OH + H^+ + e^- \qquad (Eq.\ 1)$$

Fig.3

For the electrolysis carried out at 1.5 V/SCE, it can be assumed that the degradation of BY 28 and MB was due to their direct oxidation at the electrode surface thus leading to low mineralization yield. Glassy carbon can be considered as an active electrode where chemisorbed “active oxygen” reacts with the dyes even if it is generally accepted that carbon electrodes have not a satisfactory stability [33, 34]. The part of chemisorbed “active oxygen” increased with the potential (Eq. (1)) (Gattrell et al. [32]), leading to higher degradation and mineralization yields at 2.4 V/SCE.

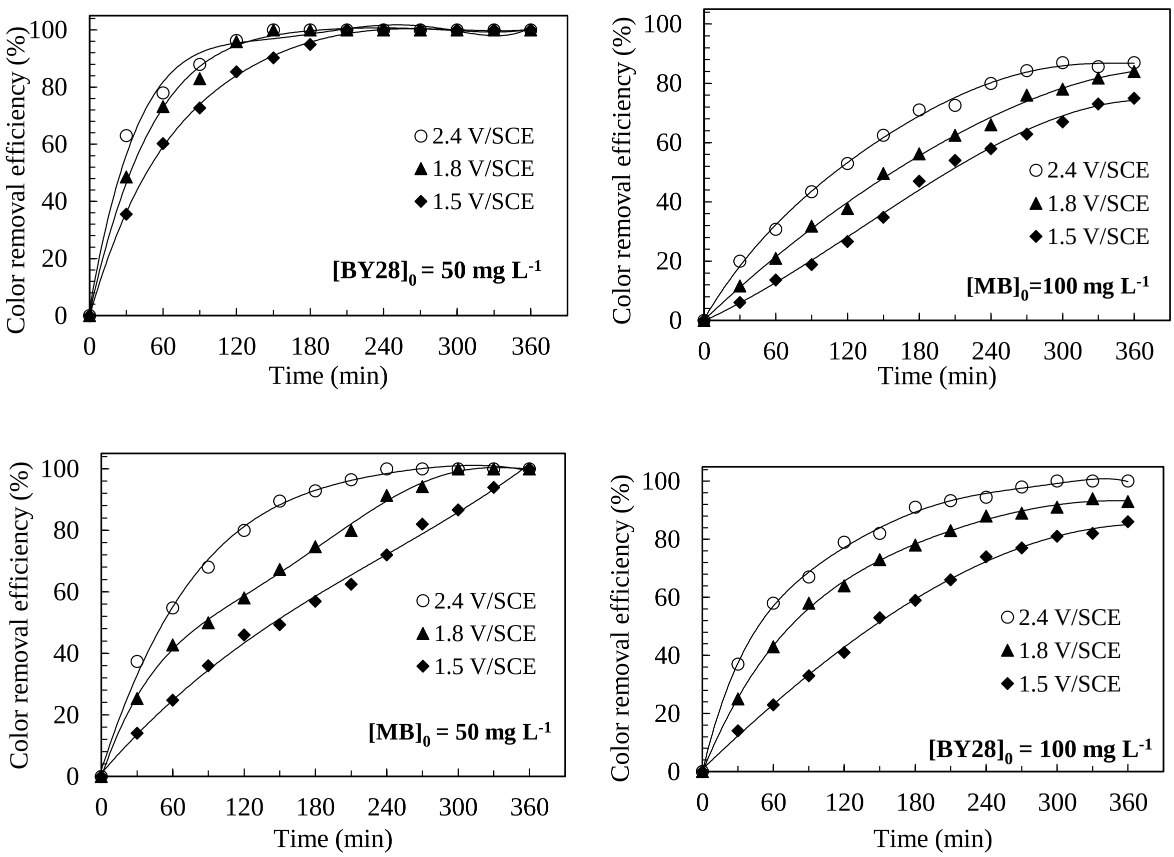


Figure 3. Influence of the working potential on Methylene Blue and Basic Yellow 28 degradationT= 25 °C, ω = 600 rpm and pH 2

3.2. Effect of initial BY28 and MB concentrations

Time-courses of ($[BY28]_t/[BY28]_0$) and ($[MB]_t/[MB]_0$) at various initial BY28 and MB concentrations were shown in the Figure 4 and the corresponding parameters are collected in Table 1. The values of the apparent rate constant (K_{app}) and the apparent mass-transfer coefficient (K_m) were determined from the slope of the straight line obtained by plotting $\ln([MB]_0/[MB]_t)$ and $\ln([BY28]_0/[BY28]_t)$ versus time (Figure 4) and Eq. 2 [18-21], respectively.

$$K_m = \frac{K_{app}\, V}{S} \qquad (2)$$

Where V is the volume of the solution (mL) and S the anode surface (cm^2). Removal efficiencies of BY28 and MB decreased with increasing initial dye concentrations (Fig.3). This could be attributed to the competitive consumption of oxidizing $^{\bullet}OH$ radicals between the considered dye and the generated intermediates formed; this result is in agreement with other findings [21, 25-30]. The kinetics of disappearance of BY28 and MB are displayed in Fig. 4. First order kinetic model was determined as follows:

$$\ln \frac{C_0}{C_t} = kt \quad (3)$$

Where C_0 and C_t are the initial dye concentration and its concentration at a given time t, t is the decolorization time (min), and k is the first order decolorization rate constant (min^{-1}), which corresponds to the linear fit between $\ln C_0/C_t$ and the decolorization time. Parameters k and R^2 (correlation coefficient) are given in table 1.

According to Figure 4, for the considered dye concentration (50 mg L^{-1}), total color removal was observed after 150 and 240 min for BY28 and MB dyes, respectively. Figure 5 illustrates the absorption spectra of dyes before and after the electrochemical pretreatment in the optimal conditions, showing nearly complete removal of the color of the solutions. A gradual disappearance of the peaks was observed during the electrolysis (Fig.5) but without modification of the shape of the spectra, namely a modification of the number of peaks. Total disappearance of absorption peaks at the end the treatment showed the total degradation of the main chromophores in accordance with results from figure 4.

Table 1 Apparent rate constant (K_{app}), apparent mass-transfer (K_m) coefficients and R^2 values

Solutions	mg L^{-1}	K_{app}(min^{-1})	K_m (cm min^{-1})	R^2
BY28	50	0.0262	0.1310	0.9792
	100	0.0131	0.0655	0.9885
	200	0.0079	0.0399	0.9744
MB	50	0.0132	0.0660	0.9947
	100	0.0063	0.0315	0.9963
	200	0.0034	0.0170	0.9942

Wang et al. [9] proposed an oxidation mechanism of methylene blue by hydroxyl radicals. From this mechanism, MB chromophore groups such as –C=C-C=C- and –C=N- didn't react first with hydroxyl radicals. On the contrary, in the case of the basic yellow 28 [35], chromophore groups namely –C=N- double bonds, seemed to react first with hydroxyl radicals. The total decolorization of BY28 before MB can then be assumed. Regarding mineralization, similar yields were obtained for the two molecules (BY28 and MB), close to 57 % after 6 h of electrolysis (Fig.6). It should be noted that under the optimal conditions, the mineralization yield of the mixture solution (50 mg L^{-1} of each dye) was about 54% within 360 min reaction time (Fig.6).

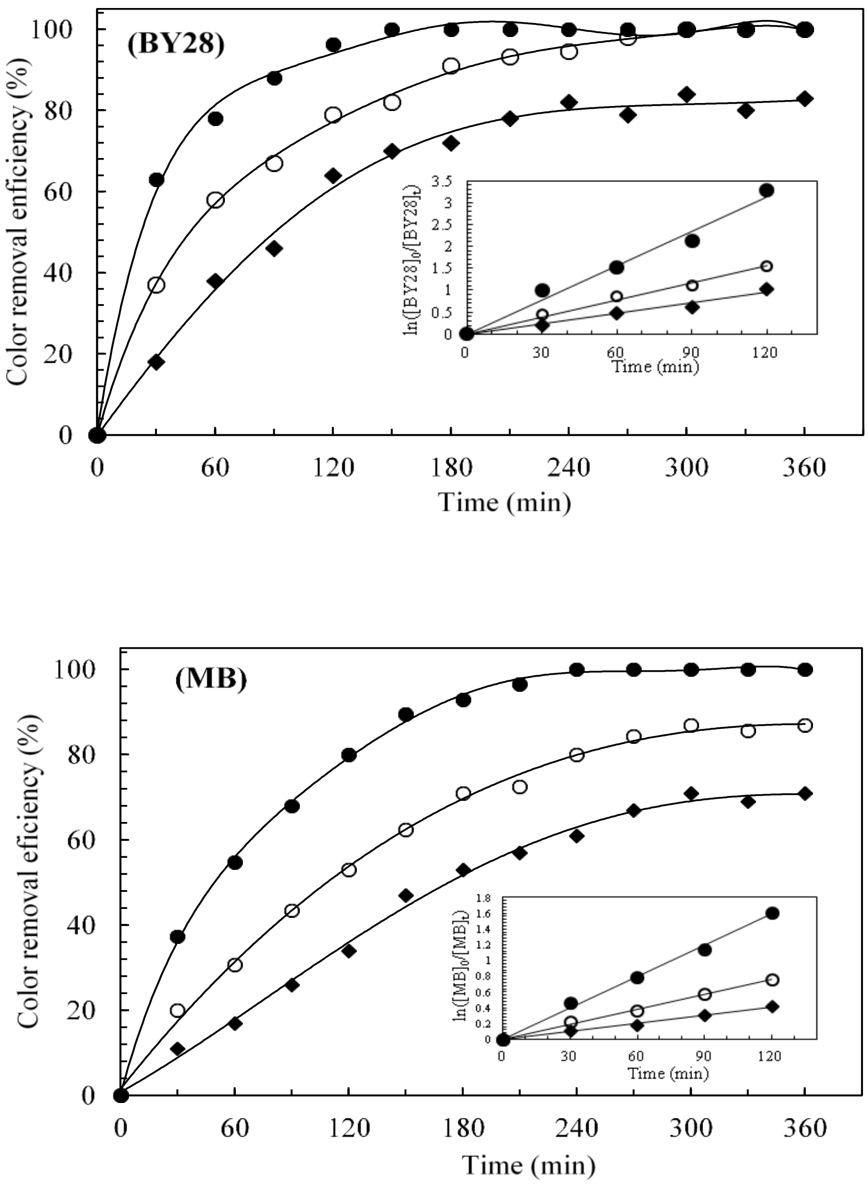


Figure 4

Figure 4. Influence of the initial concentration of of Methylene Blue and Basic Yellow 28 on the color removal efficiency

E= 2.4 V/SCE, T= 25 °C, ω = 600 rpm and pH 2

(•): 50 mg L^{-1}, (○):50 mg L^{-1} and (♦): 200 mg L^{-1}

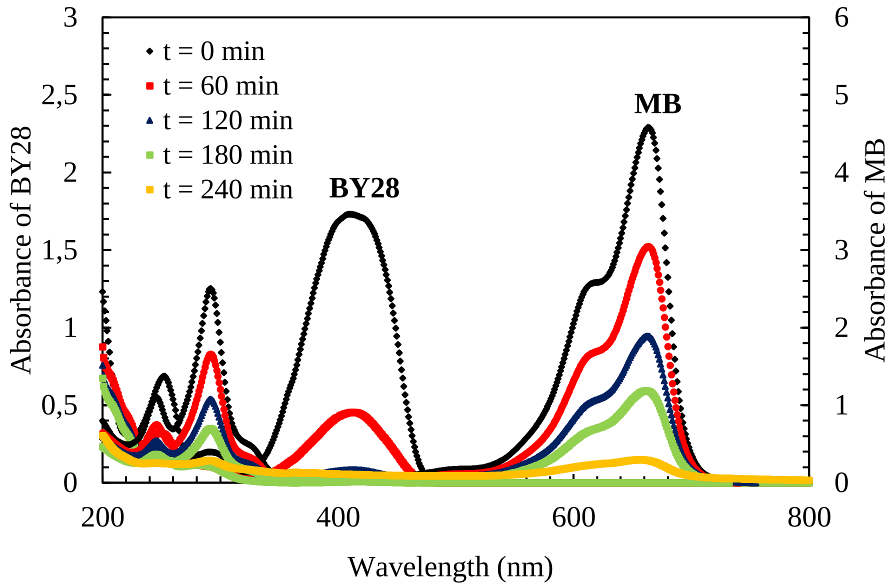


Figure 5. Absorbance spectra of BY28 and MB recorded before the electrochemical pretreatment and after different electrolysis times in the optimized conditions: $[BY28]_0 = 50$ mg L^{-1}, $[MB]_0 = 50$ mg L^{-1} E= 2.4 V/SCE, T= 25 °C, ω = 600 rpm and pH 2

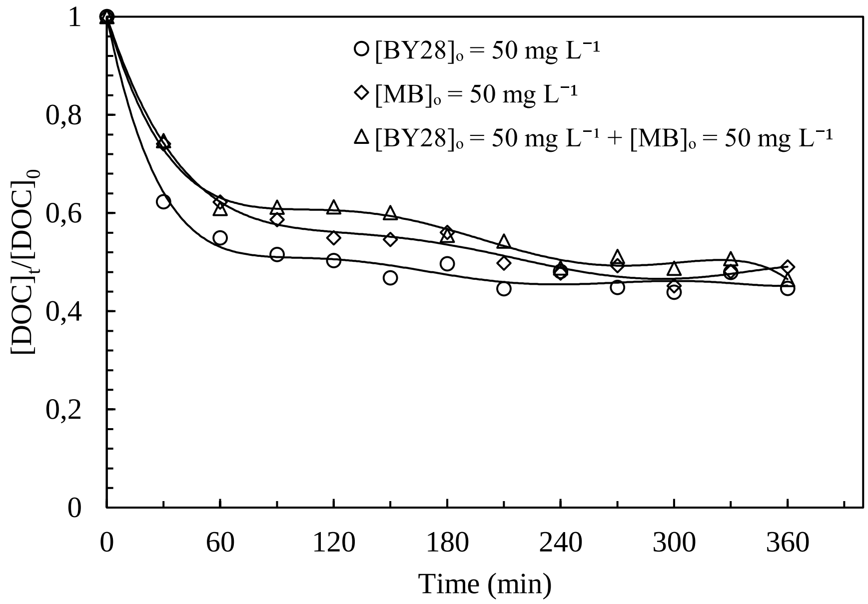


Figure 6. Time-courses of mineralization during the electrochemical pretreatment under the optimal conditions for Methylene Blue, Basic Yellow 28 and the dyes mixture

E= 2.4 V/SCE, T= 25 °C, ω = 600 rpm and pH = 2

3.3. Biological treatment

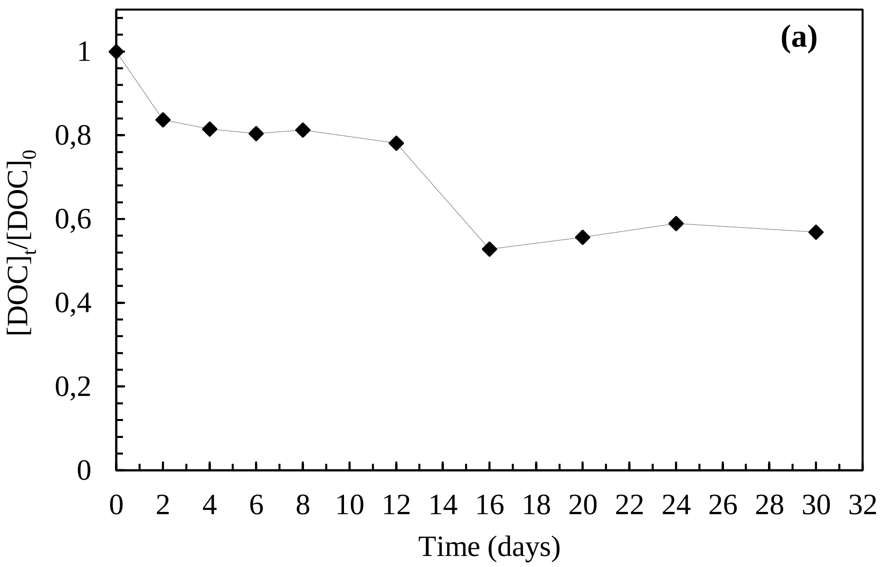
3.3.1. Biodegradability tests

Biodegradability tests were realized on the solutions electrolyzed in the optimal conditions, namely E= 2.4 V/SCE, T= 25 °C, ω = 600 rpm and pH = 2 and 50 mg L^{-1} of BY28 or MB or the mixture solution containing 50 mg L^{-1} of each dye. The biodegradability tests showed a substantial increase of the BOD_5/COD ratio, from 0.08 initially to 0.50, from 0.07 to 0.26 and from 0.04 to 0.27 after 6 h for MB, BY28 and their mixture respectively (Table 2), namely above the limit of biodegradability (0.4) for MB and close to the limit of biodegradability for BY28 and the mixture of the two dyes. These results were in favor of the proposed combined process.

3.3.2. Biological treatment

Biological treatment (made in duplicates) was only realized for the mixture solution (50 mg L^{-1} of each dye), after electrolysis under the optimal conditions. The electrochemical pre-treatment allowed 43% mineralization yield, which had to be completed during the subsequent biological treatment. A rapid decrease of the [DOC]t/$[DOC]_0$ ratio was observed within the two first days of culture, from 1.0 to 0.84 (Fig. 6-a), which correspond to the combination of two phenomena, the biosorption of intermediates compounds formed on activated sludge and their degradation by activated sludge, namely nearly 11% (Fig. 6-b) and 5 % DOC, respectively. The weak $[DOC]_t/[DOC]_0$ decrease observed in a second part of the culture, from roughly 2 to 8 days (Fig. 6-a), appeared not really significant; it correspond most likely to an acclimation of the activated sludge to the recalcitrant intermediate compounds generated by the electrochemical oxidation pre-treatment. According to figure 6-a, after 16 days, DOC decrease reached approximately 47.1% and then remained almost constant until the end of culture (30 days) (Fig.6). This recalcitrant DOC corresponds most likely to the formation of recalcitrant intermediate compounds generated by the electrochemical oxidation pre-treatment. Indeed, the determination of the BOD_5/COD ratio of the final culture solution (30 days) showed a value of 0.045, namely significantly lower than the value obtained at the end of the electrochemical pre-treatment (0.27).

Therefore, the combination of an electrochemical pre-treatment to a biological treatment led to an overall decrease of 78% of the dissolved organic carbon. It is noteworthy that a recycling of the solution in the electrolysis cell for 3 h after the biological treatment led to an impressive increase of the BOD_5/COD ratio, from 0.045 to 0.73, showing that a succession of electrolyses and biological treatments to achieve a complete refractory compounds removal may be promisingly considered.



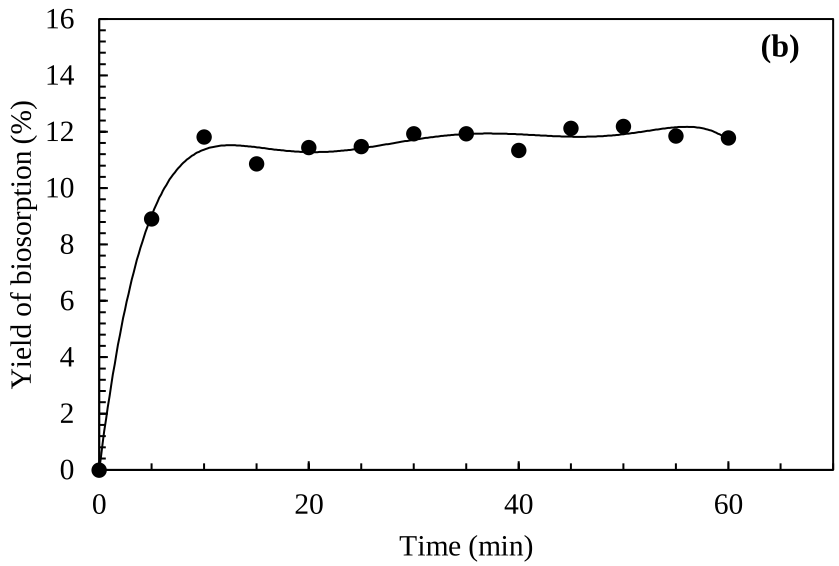


Figure 7. (a):Time-courses of $[COD]_t/[COD]_0$ values during activated sludge culture of the dyes mixture pretreated during 6 h (◊). **(b)** Biosorption on activated sludge of intermediate compounds formed after the electrochemical oxidation of the dyes mixture (○).

4. Conclusion

Aqueous solutions of dyes (MB and BY28) considered separately or in mixture have been effectively treated by the electrochemical process on a glassy carbon electrode coupled to a biological treatment. The effects of the current density and the initial dye concentration were investigated in order to optimize the process. The color removal efficiency decreased with the initial dye concentration, while it increased with the current density. Biodegradability tests realized on the solution electrolyzed in the optimal conditions showed a clear improvement of the (BOD_5/COD) ratio, from 0.076 initially to 0.50, from 0.068 to 0.26 and from 0.04 to 0.27 after 6 h of electrolysis for MB, BY28 and their mixture, respectively. From this, a biological treatment was considered, leading to an overall DOC decrease of 78 % by means of the combined process. Residual refractory compounds were shown at the end of the culture, illustrated by the decrease of the BOD_5/COD ratio (0.045); biodegradability was however subsequently improved (0.73) after a recycling of the solution in the electrochemical pre-treatment during 3 h.

Acknowledgements

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