Electrochemical Oxidation of Bromothymol Blue: Application to Textile Industrial Wastewater Treatment

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Abstract:

In this study, electrochemical oxidation of Bromothymol blue (BTB) was studied in an aqueous medium (pH = 3) by electro-Fenton process (EFP). This chemical compound belongs to the family of sulfone phthalein, widely used for dyeing in the textile industry. EFP generates in a catalytic way hydroxyl radicals (•OH) which are powerful oxidant species (E^0(•OH/H_2O) = 2.8 V/NHE) used for the oxidation of organic pollutants. The kinetics of BTB degradation and the mineralization efficiency of its process are investigated through the effect of some operating parameters. The value of 300 mA as applied current, Fe^{2+} as a catalyst with a concentration of 0.2 mM and a temperature of 40 °C are found to be the optimum operating parameters. The reaction kinetic follows a pseudo-first order with an absolute rate constant of $3.36 \times 10^{10}\ M^{-1}\ s^{-1}$. The efficiency of EFP is confirmed by the decrease of the molecule concentration during the treatment until its total disappearing. The chemical oxygen demand (COD) analyses indicate after 6 h a mineralization degree of 94% for the BTB synthetic solution, 91% for the effluent provided from a small Tunisian textile industry and 41% for the wastewater provided from a medium one. The energy consumption per unit COD mass (EC_{COD}) of the EFP is determined for the treatment of BTB synthetic solution and for the two real effluents. Concerning the BTB synthetic solution, the energetic cost is equal to 1.02 kWh (g COD)$^{-1}$ at the beginning of the electrolysis and it has decreased to reach 0.30 kWh (g COD)$^{-1}$ after 6 h. For the first effluent, the energy consumption rises from 1.20 to 0.36 kWh (g COD)$^{-1}$. An opposite phenomenon is observed for the second effluent.

Keywords: Bromothymol blue, electrochemical oxidation, electro-Fenton process, mineralization, textile industrial wastewater

Introduction

Textile industries (especially dyeing and impression) are one of the biggest consumers of water (1). Therefore they reject large quantities of wastewaters. These wastewaters contain toxic dyes and pigments harmful to human health and to the ecosystem (2). Indeed, the existence of dyes in wastewaters causes the generation of various hazards such as mutagenic and carcinogenic problems for living organisms and reduces the photosynthesis by limiting the oxygen penetration to water (3). These effluents are treated by several methods (biological, physicochemical, chemical) (4). However, the biological treatments are ineffective in the presence of toxic and non-biodegradable dyes and produce large quantities of sludge and the physicochemical methods possess a fairly high cost of investment (5). These limitations entail the development of new efficient processes.

Several studies were reported on the destruction of dyes with electrochemical advanced oxidation processes (EAOPs) (6). These techniques seem to be interesting in decontamination of textile wastewaters because of their relatively low cost and high efficiency without adding harmful chemical reagents to the solution to be treated. Among these EAOPs, electro-Fenton (EF) has been successfully applied to mineralize various persistent, toxic and non-biodegradable organic pollutants such as dyes (7, 8), pharmaceutical products (9), pesticides (10).

Electro-Fenton process (EFP) is an indirect electrochemical method that consists on the production of powerful oxidant species, such as •OH, via Fenton's reaction (1) in which one of the Fenton reagents (H_2O_2) is produced electrochemically whereas Fe^{2+} is added in catalytic quantities and regenerated in situ.

$$Fe^{2+}{}_{(aq)} + H_2O_{2(aq)} \rightarrow Fe^{3+}{}_{(aq)} + OH^-{}_{(aq)} {}^\bullet OH_{(aq)} \qquad (1)$$

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O_2 or air gas is injected into the reaction medium up to saturation. It was reduced at the cathode to generate H_2O_2 via reaction (2):

$$O_{2(g)} + 2H^+_{(aq)} + 2e^- \rightarrow H_2O_{2(aq)} \quad (E^0=0.69V/SHE) \quad (2)$$

Soluble Fe^{3+} can be cathodically reduced to Fe^{2+} by reaction (3), wish is known as electrochemical catalysis, with E^0 = 0.77 V/SHE.

$$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)} \quad (E^0 = 0.77\ V/SHE) \quad (3)$$

The fast regeneration of Fe^{2+} by reaction (3) accelerates the production of •OH from Fenton's reaction (1). This enhances the decontamination of organic solutions achieved with these EAOPs.

Using an undivided electrolytic cell for the EFP, the organic compounds can be also destroyed by heterogeneous hydroxyl radicals (M(•OH)) produced at the anode surface (M) from water oxidation following the reaction (4) thus accelerating the mineralization rate of the pollutants (11-13).

$$M_{(s)} + H_2O_{(l)} \rightarrow M(\bullet OH)_{(aq)} + H^+_{(aq)} + e^- \quad (4)$$

Bromothymol blue (BTB) also known as 3,3'-dibromothymolsulfonephtalein, is a textile dye derivative and often deployed as a pH indicator (14, 15). Due to its wide application (16, 17) and hazards associated with dyes (especially azo based dyes), its mineralization is considered as necessary. In order to decrease risks of its toxicity in wastewater, the degradation of this molecule until its mineralization were investigated by several authors (14-17, 18). Except that according to literature, no study has shown the degradation of BTB using EFP.

In this study, EFP is used to remove BTB from textile effluents of Tunisian industries. For a clear understanding of the efficiency of the electrochemical oxidation set-ups, the effect of some operating parameters (applied current, chemical nature and concentration of catalyst and temperature of the reaction medium) on the removal of BTB was investigated. The optimum operating conditions were applied to the treatment of two textile effluents. The initial chemical oxygen demand (COD) value of the first effluent provided from a small Tunisian textile industry was 349 mg O_2 L^{-1}. Concerning the second effluent from a medium Tunisian textile industry, the initial COD value was equal to 556 mg O_2 L^{-1}. The energy consumption per unit COD mass (EC_{COD}) of the EFP was determined for the treatment of BTB synthetic solution and for the two real effluents.

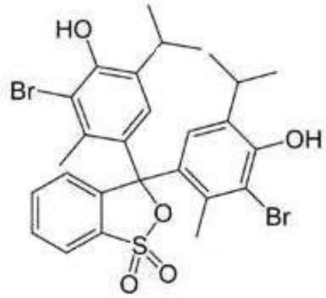

Figure 1. Chemical structure of BTB.

Materials and Methods

Chemicals

BTB ($C_{27}H_{28}Br_2O_5S$) was purchased from REACTIFS RAL. The chemical structure of BTB is given in Figure 1. Heptahydrated ferrous sulfate ($FeSO_4 \cdot 7H_2O$) was used as a ferrous ion source (catalyst), supplied by VWR BDH Prolabo. Anhydrous sodium sulfate (Na_2SO_4) was used as an inert supporting electrolyte, purchased from Acros organics. All the other chemicals were analytically graded from VWR BDH Prolabo and Sigma-Aldrich. Chemicals used in this work were all analytical grades and were used without further purification.

Electrochemical Apparatus and Procedure

Dye solution was prepared containing 100 mg L^{-1} (1.6 x 10^{-4} M) of BTB. The ionic strength was maintained constant adding 50 mM of Na_2SO_4. Ferrous ions (Fe^{2+}) were introduced to the synthetic samples prepared just before the beginning of the electrolysis.

The experiments were performed in an open, undivided and cylindrical cell containing 250 mL of BTB solution (synthetic or real). The carbon-felt piece (Carbone Lorraine RVG 4000 Mersen) was used as a cathode (60 cm^2). It was placed on the inner wall of the cell covering the totality of the internal perimeter. The cylindrical platinum anode (0.78 cm^2) was placed on the center of the cell. The distance between electrodes was 5 cm. The initial pH of the solutions, measured with a Mettler Toledo EL20 pH-meter, was adjusted to 3 by adding sulfuric acid (H_2SO_4). Prior to the electrolysis, a moderate compressed air was bubbled for 10 min through the cell to saturate the solution in oxygen, which was stirred continuously by a magnetic stirrer. The bubbling was maintained throughout all the experiment. The temperature of the reaction medium was kept constant by using a thermostated bath. Electrolyses were carried out under current controlled conditions. The current was kept at the desired level with a GWINSTEK GPS-3303 stabilized power supply and samples were withdrawn at regular electrolysis times.

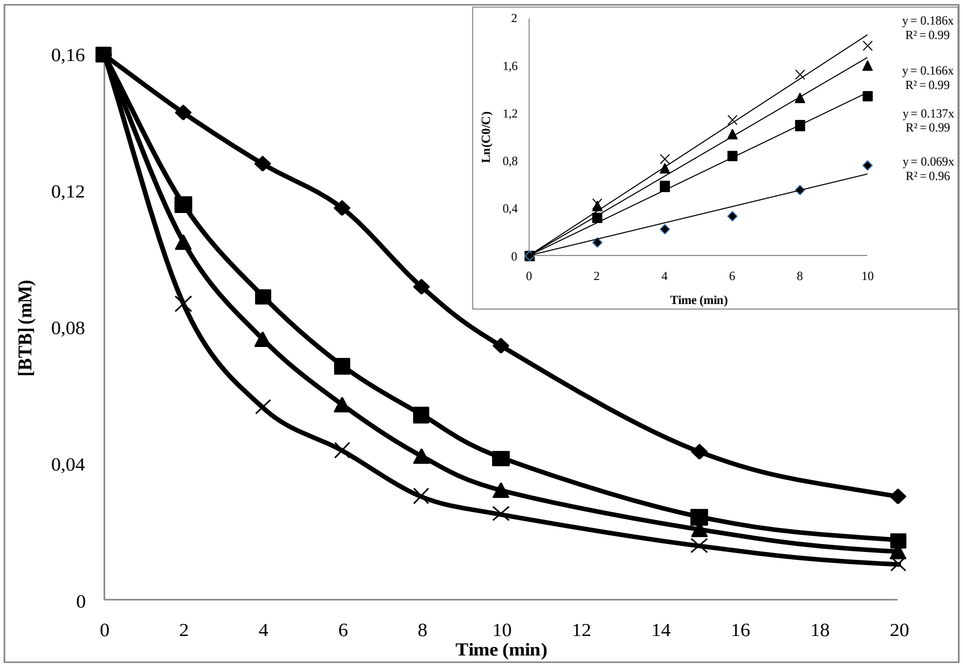

Figure 2. Effect of applied current on the degradation of BTB with EFP. I: 100 (□), 200 (Δ), 300 (ˣ) and 500 (◊) mA. $[BTB]_0 = 1.6 \times 10^{-4}$ M, $[Fe^{2+}] = 0.2$ mM, $[Na_2SO_4] = 50$ mM, pH = 3, V = 250 mL.

Analytical Methods

The color removal was monitored by measuring the decrease in absorbance using Jouan VP1020 UV spectrophotometer at an absorbance detection of 433 nm which is the λ_{max} of the acid form of BTB (18).

The color removal degree of the investigated solutions was determined using the following formula (5) (19):

$$\%\ \text{Color removal} = \left(1 - \left(\frac{C_t}{C_0}\right)\right) * 100 \qquad (5)$$

Where C_0 is the initial concentration of BTB and C_t is its concentration at treatment time t (min).

COD measurements were taken every 1 h of electrolysis, by sampling 2 mL of the electrolyzed solution. Then, aliquots of an acidic solution (1 mL) containing $K_2Cr_2O_7$ and $HgSO_4$ were added to the electrolyzed samples followed by the addition (3 mL) of concentrated H_2SO_4 containing $AgSO_4$. These solutions were heated at 150 °C for 2 h in a COD block reactor to complete the oxidation of the remaining organic matter. Finally, the COD value was monitored using HANNA photometer COD.

COD removal percentage was estimated using the following formula (6) (20):

$$\%\ \text{COD removal} = (1 - \left(\frac{COD_t}{COD_0}\right)) * 100 \qquad (6)$$

Where COD_0 and COD_t are the measures of oxygen equivalent to the organic matter of a sample that is susceptible to oxidation by a strong chemical oxidant at reaction time 0 and t of EF treatment of BTB (real or synthetic) solution, respectively.

Results and Discussion

Decay Kinetics of BTB's Degradation with EFP

Effect of Applied Current on BTB's Degradation

The effect of applied current on the decay kinetics of BTB's degradation with EFP was investigated at different current values in a range of 100 to 500 mA. The results are depicted in Figure 2.

It can be seen from Figure 2 that the concentration of BTB decreases exponentially for all current values and that the degradation rate increases by rising the applied current from 100 to 300 mA. This result is due to the oxidizing power associated with the enhancement of H_2O_2 electro-generation and Fe^{2+} regeneration rates according to reactions (2) and (3) and, therefore, to the possibility of continuous Fenton reaction thus continuous hydroxyl radicals generation.

However, a decrease in the degradation efficiency is observed at a current value of 500 mA. This phenomena results from the increase of the applied current, promoting the parasitic reactions in the bulk, simultaneously with the hydrogen evolution at the cathode according to reaction (7):

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad (7)$$

Similar observations were already reported in other studies (21, 22).

Figure 2 shows also that the decay of [BTB] in function of the electrolysis time is exponential indicating that the oxidation reaction obeys to pseudo-first order kinetics. The reaction of BTB with hydroxyl radicals can be described by pseudo-first order kinetics model, assuming a quasi-stationary state for hydroxyl radical •OH concentration:

$$\mathrm{BTB}_{(s)} + \bullet\mathrm{OH}_{(aq)} \rightarrow \text{Oxidation products} \qquad (8)$$

$$V = \frac{-d[\mathrm{BTB}]}{dt} = k_{abs}[\bullet\mathrm{OH}][\mathrm{BTB}] = k_{app}[\mathrm{BTB}] \qquad (9)$$

With BTB Bromothymol blue, k_{abs} absolute rate constant and $k_{app} = k_{abs}[\bullet\mathrm{OH}]$ apparent rate constant.

The pseudo-first order reaction rate constant, k_{app}, was calculated (Table 1) from linear regression of the pseudo-first order kinetic model with related co-efficients equal to 0.99 (insert Figure 2).

Effect of Catalyst Nature and Concentration on BTB's Degradation

In order to understand the effect of the catalyst nature, its influence on the degradation of BTB with EFP was investigated. In fact, the electrolysis was carried out using ferrous sulfate ($FeSO_4$), copper sulfate ($CuSO_4$) and silver sulfate (Ag_2SO_4) (Figure 3).

Figure 3 shows that the degradation of BTB is more efficient using ferrous sulfate as catalyst nevertheless it is slower by using copper and silver. When copper sulfate was used, a metal deposition was observed causing a decrease of the catalyst concentration and therefore a decrease in the production of hydroxyl radicals •OH according to the following reaction (10) (23):

$$\mathrm{M^{n+}}_{(s)} + \mathrm{H_2O_{2(aq)}} \rightarrow \mathrm{M^{(n+1)+}}_{(s)} + \mathrm{OH^-}_{(aq)} + \bullet\mathrm{OH}_{(aq)} (10)$$

Copper cathodic deposition is justified based on the values of the potential standard reduction of Cu^{2+} ($E^0_{(Cu2+/Cu(s))}$ = 0.34 V/ENH and $E^0_{(Cu+/Cu(s))}$ = 0.52 V/ENH). However, the reduction potential of ferrous and ferric ions is much more important ($E^0_{(Fe2+/Fe(s))}$ = -0.44 V/ENH and $E^0_{(Fe3+/Fe(s))}$ = -0.04 V/ENH) (24, 25).

In relation with the two other tested catalysts, silver sulfate does not accelerate the degradation of BTB. In addition, it is an expensive and a toxic element. Consequently, its use is incompatible with the development of a new ecologic and economic technique (26).

These results highlight the fact that the use of ferrous sulfate is a very important condition to the degradation of BTB by EFP. This is in good agreement with previous work (27, 28).

Table 1. Pseudo-first order kinetic constants for BTB degradation at various current values

Current values I (mA)	Apparent rate constant k_{app} (min^{-1})	Related coefficients R^2
100	0.137	0.99
200	0.166	0.99
300	0.186	0.99

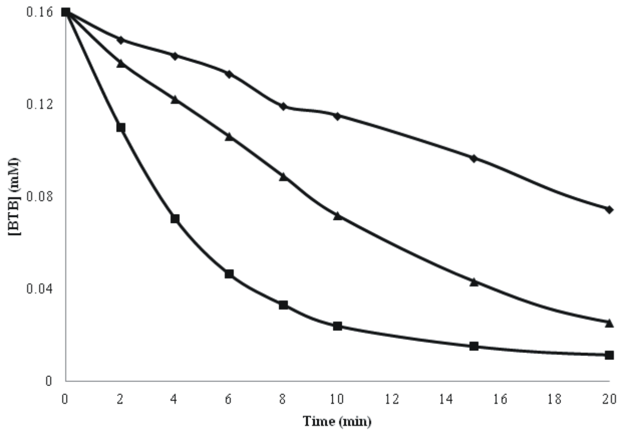

Figure 3. Effect of the chemical nature of the catalyst on the degradation of BTB with EFP. Catalysts: $FeSO_4$ (□), $CuSO_4$ (Δ), Ag_2SO_4 (◊). $[BTB]_0 = 1.6 \times 10^{-4}$ M, [Catalyst] = 0.2 mM, $[Na_2SO_4]$ = 50 mM, pH = 3, V = 250 mL, I = 300 mA.

The amount of hydroxyl radicals generated by EFP and therefore the efficiency of the system depends not only on the type of catalyst used but also its concentration. For this reason, solutions of BTB were electrolyzed in an acid medium (pH = 3) in the presence of ferrous sulfate concentrations ranging from 0 to 1 mM in order to determine the concentration of the catalyst which is the most adapted to the degradation of BTB (Figure 4).

As can be seen on Figure 4, the optimal ferrous sulfate concentration is 0.2 mM. Similar observations were reported by some publications (29, 30).

Low BTB removal from the solution is observed without the addition of Fe^{2+}, this is due to the low ability of the hydrogen peroxide to oxidize the BTB, even though it has a high oxidant power. The oxidizing power of the hydrogen peroxide is highly enhanced by the addition of iron generating the Fenton reaction (11), leading to the generation of active intermediates (such as •OH and •OOH radicals) by the iron catalyzed decomposition of the hydrogen peroxide (31).

The inhibition of BTB removal rate in the presence of higher catalyst concentration can be explained by the increase of the rate of parasitic reactions (32-34):

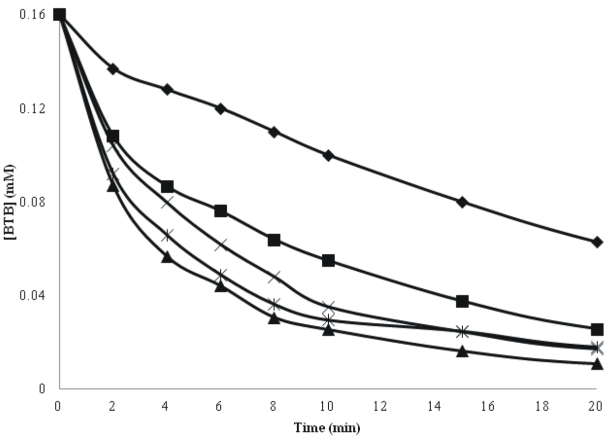

Figure 4. Effect of catalyst concentration on the degradation of BTB with EFP. $[Fe^{2+}]$: 0 (◊), 0.1 (□), 0.2 (Δ), 0.5(ˣ), 1 (*) mM. $[BTB]_0 = 1.6 \times 10^{-4}$ M, $[Na_2SO_4]$ = 50 mM, pH = 3, V = 250 mL, I = 300 mA.

$$Fe^{2+}{}_{(aq)} + \bullet OH_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + OH^{-}{}_{(aq)} \qquad (11)$$

$$Fe^{2+}{}_{(aq)} + \bullet OH_{(aq)} \rightarrow FeOH^{2+}{}_{(aq)} \qquad (12)$$

$$Fe^{3+}{}_{(aq)} + H_2O_{2(aq)} \leftrightarrow Fe - OOH^{2+}{}_{(aq)} + H^{+}{}_{(aq)} \qquad (13)$$

Excess of ferrous ions can react with •OH leading to the consumption of •OH with a high oxidation potential inducing a decrease of the ferric reduction efficiency and affects the color removal rate during EFP.

Consequently, the value of 0.2 mM was selected as catalyst concentration for the following experiments.

Effect of Temperature on BTB's Degradation and Determination of the Activation Energy

The effect of temperature on the degradation of BTB was studied at 20, 30 and 40 °C and the obtained results are shown in Figure 5. The degradation kinetics improves when the temperature increases from 20 to 40°C. This result shows that the reaction of hydroxyl radicals oxidizing BTB could be favored by an increase in the temperature. Indeed, the solution temperature influences both electron transfer and mass transfer rate and affects the regeneration of Fe^{2+}. Other research work (35) proved that Fe^{2+} regeneration is favored at high temperatures. Our work is in good agreement with literature and the most appropriated of tested temperatures for the faster degradation of BTB is 40 °C.

Drawbacks of temperature on the production of hydrogen peroxide could result in a lower concentration of dissolved oxygen and a self-decomposition of hydrogen peroxide. In fact, the concentration of hydrogen peroxide decreased when the temperature increased because of oxygen solubility in the wastewater. In addition, the rate of self-decomposition of the hydrogen peroxide to water and oxygen, increased with the temperature (36).

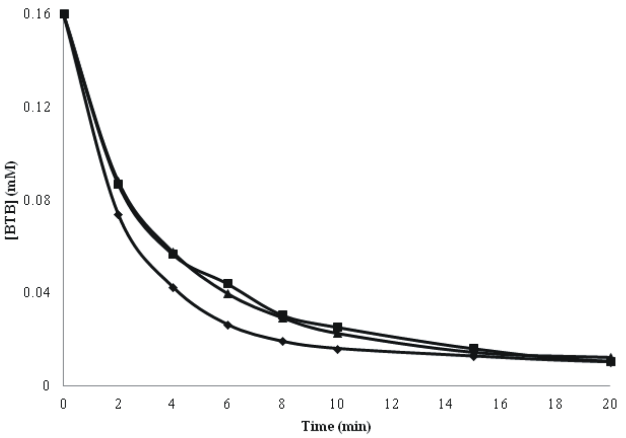

Figure 5. Effect of the temperature of the reaction medium on the degradation of BTB with EFP. T: 20 (□), 30 (Δ) and 40 (◊) °C. $[BTB]_0 = 1.6 \times 10^{-4}$ M, $[Fe^{2+}]$ = 0.2 mM, $[Na_2SO_4]$ = 50 mM, pH = 3, V = 250 mL, I = 300 mA.

The apparent kinetic rate constants (k_{app}) of the degradation of BTB obtained at 20, 30 and 40 °C are respectively 0.203, 0.212 and 0.262 min^{-1}. According to the apparent kinetic rate constants at various temperatures, the apparent activation energy E_a for the degradation of BTB by EFP was calculated with Arrhenius law (14) (37):

$$k = A \exp\left(\frac{-Ea}{RT}\right) \qquad (14)$$

Where k is the apparent kinetic rate constant (min^{-1}), A is the pre-exponential factor, E_a is the activation energy (J mol^{-1}), R is the ideal gas constant (8.314 J $mol^{-1} K^{-1}$) and T is the reaction temperature (K).

The activation energy was determined from the Arrhenius plot of ln k_{app} versus 1/T and the application of the Arrhenius law (38). It was found to be 9.66 kJ mol^{-1}. The activation energies of the degradation of Reactive Brillant Blue and Acid Red 73 by advanced Fenton oxidation process are respectively 25.21 kJ mol^{-1} (39) and 31.98 kJ mol^{-1} (40). These results imply that the degradation of BTB in aqueous solution by EFP requires low activation energy and hence can be easily achieved.

Determination of the Absolute Rate Constant of BTB's Degradation

In order to determine the absolute rate constant of BTB's degradation by hydroxyl radicals, the competition kinetic method is applied (41, 42) using benzoic acid (BA) as standard competitor ($k_{BA} = 4.3 \times 10^9$ M^{-1} s^{-1}) (43). Electrolyses of a mixture of BTB and BA were carried out under optimal conditions determined with I = 300 mA, $[Fe^{2+}]$ = 0.2 mM and T = 40 °C.

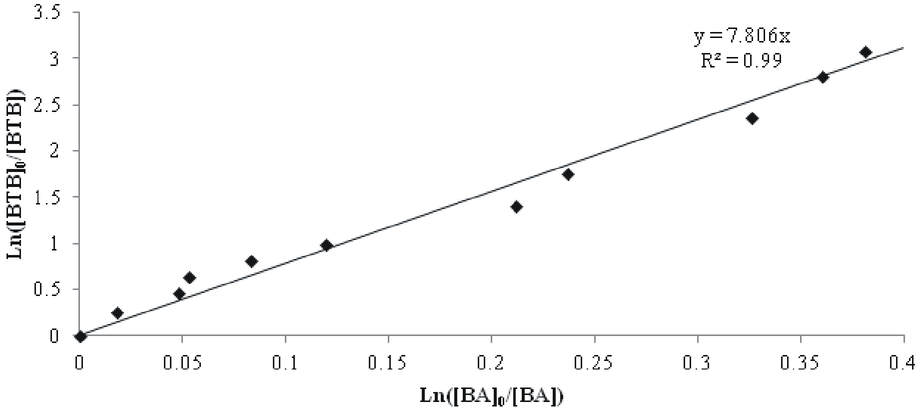

Figure 6. Kinetic analysis for the pseudo-first order reaction of BTB and BA with hydroxyl radicals. $n_{BTB}=n_{BA}$. $[BTB]_0 = 1.6 \times 10^{-4}$ M, $[Fe^{2+}] = 0.2$ mM, $[Na_2SO_4] = 50$ mM, pH = 3, V = 250 mL, I = 300 mA.

The absolute rate constant k_{BTB} was then calculated following the data of Figure 6 and equation (15):

$$k_{BTB} = k_{BA}\,\frac{\mathrm{Ln}\frac{[BTB]_0}{[BTB]}}{\mathrm{Ln}\frac{[BA]_0}{[BA]}} \tag{15}$$

The value of 3.36×10^{10} M^{-1} s^{-1} was found for the absolute rate constant of BTB oxidation reaction. This value is in agreement with k_{abs} values for hydroxylation reactions of aromatic compounds with hydroxyl radicals, and it is of the same order of magnitude (between 10^9 and 10^{10} M^{-1} s^{-1}) as was reported by many authors (44, 45).

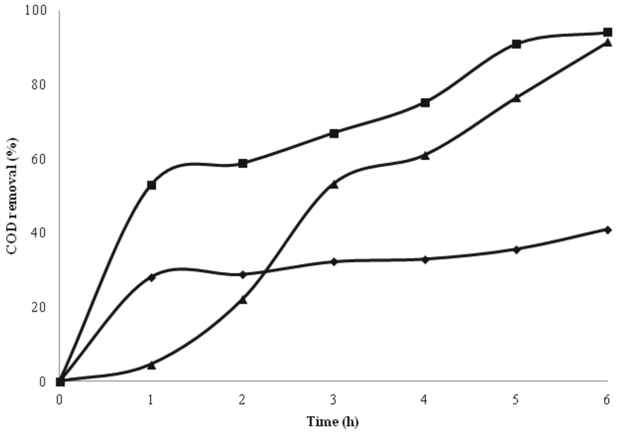

Figure 7. Evolution of the COD removal percentage of a synthetic solution of BTB and industrial effluents containing BTB. Synthetic solution of BTB (□), Industrial effluent 1 (Δ), Industrial effluent 2 (◊).

Mineralization of BTB and Industrial Effluents Wastewaters Containing BTB

Evolution of COD Removal

Mineralization of aqueous BTB solution and those of effluents wastewaters from two Tunisian textile industries (small and medium industries) containing BTB were monitored by solution COD abatement during EF treatment. Mineralization experiments were carried out under optimal operating conditions determined previously as described above in this work.

The evolution of the COD removal percentage during the mineralization of BTB in aqueous solution and in the two industrial effluents by EFP is shown in Figure 7 as a function of treatment time.

For the synthetic solution of BTB, the initial COD value of 121 mg O_2 L^{-1} decreased quickly at the beginning of the electrolysis giving rise to a removal of more than 50% in only 1 h whereas the removal gradually slows reaching a poor removal rate at the end of treatment. This is due to the formation of hardly oxidizable compounds such as short-chain carboxylic acids (46). Nevertheless, an abatement of 94% of the initial COD value is reached at the end of 6 h of electrolysis. The final value of COD obtained (8 mg O_2 L^{-1}) complies with the Tunisian law NT.106.002 (47) for effluent discharges into the aquatic environment which sets a value equal to 90 mg O_2 L^{-1} for maritime public domain and public hydraulic areas and a value of 1000 mg O_2 L^{-1} for the utility pipes.

The initial COD value of the first effluent provided from a small Tunisian textile industry is 349 mg O_2 L^{-1}. It decreased through the treatment time and reaches 30 mg O_2 L^{-1} after 6 h. This value is consistent with the Tunisian standard (47). Consequently, the COD removal percentage is higher than 90%. This satisfactory result can be explained by the fact that EFP achieves an effective removal of the refractory organic matter.

Concerning the second effluent that comes from a medium Tunisian textile industry, the initial COD value is 556 mg O_2 L^{-1}. The COD decreased along the mineralization process with lesser abatement rates compared to the synthetic BTB solution and reached a value of 329 mg O_2 L^{-1}. This final COD value complies with the law concerning discharges into public drains (47). Consequently, the COD removal percentage at the end of 6 h of treatment is only 41% of initial solution COD value. This value seems poor compared with that of synthetic solution and indicates that the industrial effluent is not formed dominantly by BTB but rather by hardly oxidizable compounds. Another reason for this low COD removal efficacy can be related to the high initial COD value which may require long treatment time to reach high mineralization efficiency. The use of boron doped diamond anode instead of Pt can enhance the mineralization efficiency of this effluent because of its significantly higher oxidizing power compared to Pt anode (48, 49).

Evolution of Color Removal

The evolution of the color removal percentage during the mineralization of BTB in aqueous solution and in the two industrial effluents by EFP is shown in Figure 8 as a function of treatment time. A total color removal was achieved at the end of the mineralization of BTB synthetic solution. For the treatment of the textile wastewaters, the color removal was respectively 93% and 88% for the first effluent provided from a small industry and the second one which provided from a medium one. For all these cases, the results obtained are consistent with the Tunisian law NT.106.002 for the protection of the environment (47). Similar observations were already reported for the treatment of textile wastewaters (50). Indeed, the effectiveness of Fenton oxidation for the treatment of wastewaters generated by an Egyptian and a Turkish textile industries was analyzed. The results obtained reaching 100% and 89% color removal respectively for the Egyptian textile effluent and the Turkish one. These results proved that Fenton oxidation could be used for the treatment of such industrial wastewaters without further treatment, since the final effluent complies with the law for water reuse under a restricted category.

Energy Consumption

Energy-related parameters are essential figures of merit for comparing the viability of EFP and related methods between them and against other electrochemical technologies. Operating at constant applied current, EC_{COD} is obtained from equation (16) (51):

$$EC_{COD} = \frac{E_{cell}\, I\, t}{(\Delta COD)_t V_s} \qquad (16)$$

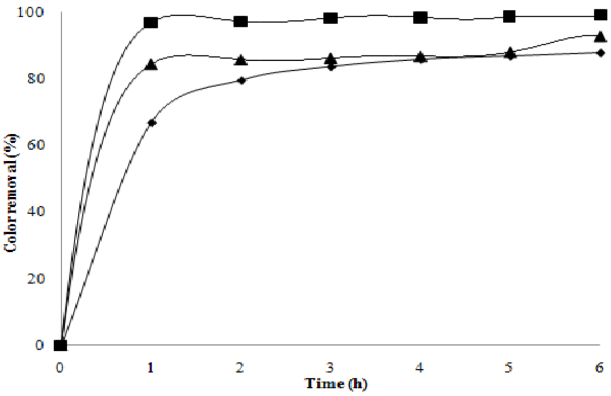

Figure 8. Evolution of the color removal percentage of a synthetic solution of BTB and industrial effluents containing BTB. Synthetic solution of BTB (□), Industrial effluent 1 (Δ), Industrial effluent 2 (◊).

Table 2. Energy consumption of EFP

Time (h)	1	6
EC_{COD}(BTB) (kWh(g COD)$^{-1}$)	1.02	0.30
EC_{COD}(Industrial Effluent 1) (kWh(g COD)$^{-1}$)	1.20	0.36
EC_{COD}(Industrial Effluent 2) (kWh(g COD)$^{-1}$)	0.12	0.51

Where EC_{COD} is the energy consumption per unit COD mass (kWh(g COD)$^{-1}$), E_{cell} is the average cell voltage (V), I is the applied current (A), t is the electrolysis time (h), $(\Delta COD)_t$ is corresponding decays in COD (mg O_2 L^{-1}), V_s is the solution volume (L).

The EC_{COD} of the EFP was calculated for the mineralization of the synthetic solution of BTB and for the two industrial effluents (Table 2).

Concerning the BTB synthetic solution, the energetic cost was equal to 1.02 kWh (g COD)$^{-1}$ at the beginning of the electrolysis and it decreased to reach 0.30 kWh (g COD)$^{-1}$ after 6 h, in agreement with the findings of some authors (52). This decrease was the consequence of a good mineralization of the solution.

At the beginning of the electrolysis of the first industrial effluent, the EC_{COD} was high (1.20 kWh (g COD)$^{-1}$). However, at the end of the mineralization of this real effluent, the EC_{COD} reached 0.36 kWh (g COD)$^{-1}$. This decrease confirms that this textile effluent was well mineralized. Moreover, this is the same phenomena as that observed for the mineralization of BTB synthetic solution (53).

For the second textile effluent, the EC_{COD} increased with time. This tendency seems contradictory to the previous EC evolutions found for the BTB synthetic solution and the first real effluent. This could be explained by the hardly oxidable by-products generated during EFP, by the initial compounds present in this wastewater or by the formation of by-products which consume hydroxyl radicals as is proved by the following parasite reactions (54):

$$2\bullet OH_{(aq)} \rightarrow H_2O_{2(aq)} \quad (17)$$

$$H_2O_{2(a)} + \bullet OH_{(a)} \rightarrow HO_2^{\bullet}{}_{(aq)} + H_2O_{(l)} \quad (18)$$

Conclusion

In this study, we demonstrated that BTB can be efficiently destroyed in aqueous medium with the EFP. Indeed, the complete degradation of 100 mg L^{-1} of BTB requires only 20 min when the optimal experiment conditions (pH = 3, I = 300 mA, $[Fe^{2+}]$ = 0.2 mM and T = 40 °C) are applied.

We showed that the kinetics of the oxidation reaction of BTB by hydroxyl radicals follow a pseudo-first order. Using competition kinetics method, we determined the absolute rate constant of the oxidation reaction which is 3.36×10^{10} M^{-1} s^{-1}.

Concerning the mineralization of a synthetic solution of BTB, we obtained a COD removal percentage of 94% and a total color removal after 6 h of treatment under optimal operating conditions. We applied these conditions to the mineralization of Tunisian textile effluents. After 6 h of treatment, we obtained a COD removal percentage of 91% and a color removal of 93% for the effluent provided from a small industry but only 41% for the COD removal and a color removal of 88% for the effluent provided from a medium one. This second result can be enhanced by using new electrode materials, for example, the boron doped diamond anode instead of platinum one.

We determined the EC_{COD} of the EFP for the treatment of the synthetic and real solutions of BTB.

Concerning the synthetic solution of BTB, the energetic cost was equal to 1.02 kWh (g COD)$^{-1}$ at the beginning of the electrolysis and it decreased to reach 0.30 kWh (g COD)$^{-1}$ after 6 h. For the first effluent, it decreased from 1.2 kWh (g COD)$^{-1}$ to 0.36 kWh (g COD)$^{-1}$. And for the second one, the EC_{COD} increased with time. These results confirm that the mineralization of the synthetic solution of BTB and the first industrial effluent were good. However, for the second textile effluent, the evolution of the EC_{COD} seems contradictory compared to previous. This could be explained by the formation of by-products which consume hydroxyl radicals.

The results obtained confirm that the treatment by EFP is a significant removal pathway for dyes because of its relatively low cost and high efficiency without adding harmful chemical reagents to the solution to be treated.

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