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Chloride ions as an agent promoting the oxidation of synthetic dyestuff on BDD electrode

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ABSTRACT

The effect of the presence of chloride ions on anodic oxidation of synthetic dye solution was investigated and compared to other anions (NO_3^-, HCO_3^- and SO_4^{2-}). A boron-doped diamond electrode was used as an anode in bulk electrolysis. Dye degradation was monitored following the relative absorbance removal related to discolouration and aromatic derivates degradation and chemical oxygen demand (COD) removal. The study results showed that not only fast discolouration ($k = 76.8$) but also dye mineralisation is obtained with addition of chloride thanks to the electrogeneration of active chlorine ($HClO/ClO^-$). The comparison effect using others support electrolytes such as nitrates and hydrogen carbonate revealed strong inhibition for NO_3^- concerning dye degradation. Average current efficiency and energy consumption (E) were also investigated. An addition of low chloride concentration (0.02 M) in Na_2SO_4 electrolyte significantly enhances the degradation rate of Cibacron Yellow. An optimised concentration of 0.05 M NaCl leads to an increase by 42% of COD removal after 20 min of treatment and decreases the consumption of energy by 333 kWh (kg COD)$^{-1}$. This result presents Cl^- as a promoting agent of the mineralisation of the dye and is very interesting for a subsequent potential industrial application to dyeing waste water treatment for recycling.

Keywords: Active chlorine; Anodic oxidation; Azo dye; BDD electrode; ACE

1. Introduction

Advanced oxidation methods offer an attractive and powerful alternative to traditional methods of wastewater treatment *in situ* thanks to highly reactive oxidants production [1,2]. Among these methods, some technologies offer an alternative of indirect electro-oxidation for the removal of organic pollutants with different strong agents. The most commonly known and used oxidants are chlorine and chlorine–oxygen species such as HClO and ClO^-, which are traditionally used as an added chemicals products for treating industrial wastewater [3,4]. The electrochemical generation of chloride ion *in situ* from direct oxidation using suitable anodes presents major advantages such as the limitation of the transport and storage of chlorine and faster destruction of organic matter comparing to chemical oxidation. Yet, some disadvantages can be observed such as the formation of toxic chloro-organic derivates as well as chlorine–oxygen by-products with a high health-risk for living being [5].

A reduced number of anodes have been used to compare the colour removal and chemical oxygen demand (COD) reduction of azo dye with active

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chlorine, essentially DSA ($Ti/TiO_2–RuO_2–PbO_2$) [6]. Basically two processes occurred at the anode [5]:

(i) direct oxidation linked to the electrocatalytic activity of the anode and
(ii) oxidation via surface mediator on the anodic surface (indirect electrolysis).

In the case of boron-doped diamond (BDD) electrode, organic pollutants can be removed by generating *in situ* chemical reactants with different oxidising powerful species other than $OH^{\cdot}$ radical with higher powerful oxidising power. Anodic oxidation of dyes has been widely investigated with BDD electrode [5–7].

In indirect electro-oxidation, chloride salts are added to the electrolyte for better conductivity and to the generation of active chlorine which are known as the main oxidising agents, in the form of gaseous chlorine (Cl_2), hypochlorous acid (HClO) or hypochlorite ions (ClO) [6]. The kind of species generated depends on complex operative conditions (chloride concentration, stirring or flow rate, temperature, current density and essentially solution pH). Each produced species can oxidise on the anode (ClO_3^-, ClO_4^-) and/or reduce on the cathode [5].

Many papers agree that the use of sodium chloride as electrolyte has a positive effect due to active chlorine, HClO and/or ClO, which depends on the pH medium [8,9]. The active chlorine formation can occur in alkaline medium according to the following reactions:

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (1)$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (2)$$

$$HOCl \rightarrow H^+ + OCl^- \quad (3)$$

In neutral pH, HClO is the preponderant species. Some authors [10,11] have described acceleration in dye destruction in the presence of chloride. However, others [5] have demonstrated that no improvement is detected with the generation of active chloride when BDD is used. Persulphates ($S_2O_8^{2-}$) can also be generated using Na_2SO_4 electrolyte.

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \quad (4)$$

In general, contradictory results on the importance of oxidative role of active ions generated from electrolyte as chlorine species or persulphates ($S_2O_8^{2-}$) are presented in literature; in fact, some authors confirm similar decolourization rate with chloride or sulphate as electrolyte and consider that the contribution of other oxidants is minor when oxidation takes place via $^{\cdot}OH$ [5].

Other species can be formed from the oxidation of salts contained in synthetic support electrolyte or real wastewater like bicarbonate and phosphate as follows [5,12];

$$2HCO_3^- \rightarrow C_2O_6^{2-} + 2H^+2e^- \quad (5)$$

$$2PO_4^{3-} \rightarrow P_2O_8^{4-} + 2e^- \quad (6)$$

Complete colour removal is often the first satisfactory result we got referring to the process efficiency. However, it is known that the discolouration of azo dyes produces different by-products; and the formation of chlorinated derivatives from the attack of active chlorine dye has been observed [13]. It should be noted that several studies have shown that the formation of chlorate and perchlorate on BDD anodes oxidation is an important parameter to consider, because of its effect on the environment and human health, especially for drinking water disinfection [14,15]. Cañizares et al. [16] have described acceleration of dye degradation essentially in the case of chloride solution, but this behaviour is not found with others electrolytes.

The influence of several parameters on the electrochemical oxidation of dyes (cleavage of –N=N– and/or oxidation of aromatic derivates) is different from one dye molecule to other. Therefore, it is important to understand the limits of process efficiency and the influence of each parameter on kinetic oxidation behaviour.

In electrochemical processes, the type and concentration of electrolyte contents are of crucial importance. In fact, during dyeing process, high quantities of salts are added to improve dye fixation. Consequently, textile wastewater contains significant quantities of NaCl and/or Na_2SO_4, added during dyeing, as well as carbonates present in the water processing [17]. This high concentration of salts decreases the efficiency of many wastewater treatment processes such as coagulation or biological ones. However, this high concentration might be an advantage for electrochemical oxidation process due to: (i) high conductivity and (ii) generation of active species, which decrease the negative aspects. It is therefore of interest to study the performance of the electrochemical oxidation as textile wastewater treatment for recycling.

The purpose of this work is to study the efficiency of electrochemical oxidation using BDD electrode combined with the generation of active species, especially active chlorine, for Cibacron Brillant Yellow (CY) degradation as a model of complex azo dye and dyeing wastewater. The effect of several operating parameters such as initial pH solution, current density, chloride ion concentration on discolouration and mineralisation rate was investigated. In particular, the effect of limited addition of NaCl to electrolyte as promoting agent of the mineralisation of the CY is studied.

2. Materials and methods

2.1. Chemicals and dye

The selected pollutant model is an azo dye used in the textile industry called Cibacron Brillant Yellow (CY) 3G-P obtained from Aldrich. Its molecular structure is illustrated in Fig. 1a. Based on the given molecular weight of 873 g mol^{-1}, dye concentration is fixed at 0.05 mmol L^{-1} for all experiments. UV–vis spectra present two absorption bands at 414 and 270 nm related respectively to the azo group (–N=N–) and aromatic derivates. The positions of the two bands are stable under pH variation (Fig. 1b). Discolouration of the dye and degradation of the aromatics derivates of the azo dye CY will be monitored, according to the decrease of the related bands during electrochemical oxidation.

Na_2SO_4 (0.1 mol L^{-1}) was used as electrolyte and different concentrations of NaCl from 0.02 to 0.2 mol L^{-1} was added. Salts (NaCl, $NaNO_3$ (Merck), Na_2SO_4 (scharlau), NaClO, $NaHCO_3$ (Biotechnical), NaOH and sulphuric acid (H_2SO_4 at 98%) used for reactivity or pH regulation correspond to analytical quality. Table 1 presents the electrical conductivity of the different electrolyte supports.

2.2. Electrolysis cell

2.2.1. Presentation of BDD electrode

Experiments were conducted in a mini-Diacell provided by Adamant Technologies: an electrolytic cell composed of a BDD electrode. It is polycrystalline diamond layers synthesised on silicon high purity p-type wafer by microwave plasma enhanced chemical vapour deposition in a conventional reactor [18]. Doping concentration in the diamond layers, as estimated from Raman spectroscopy measurements [19], was in the range of 10^{18} to 10^{20} cm^{-3}. The film resistivity was equal to or less than 1 Ω cm as measured with a four-point probe. The polycrystalline diamond film consists of randomly oriented crystallites of few microns size and with predominantly cubic (1 0 0) and triangular (1 1 1) faces.

2.2.2. Electrolysis system

Experiments were conducted in a mini-Diacell provided by Adamant Technologies: an electrolytic cell composed of a BDD electrode as an anode and stainless steel as a cathode with a 3 mm gap between electrodes. The electrode is monopolar p-silicon covered by BDD (2–3 μm thick) with a 12.5 cm^2 rectangular surface (50 × 25 mm). The reactivity of the BDD electrode is guaranteed by 1 M of H_2SO_4 solution circulation during 30 min, prior to each electrolysis [20–22]. The mini-Diacell is supplied with the dye solution from a reservoir tank ($V_0 = 1{,}000$ mL) using a Peristaltic pump working in recycling mode. The flow rate depends on the applied current density in order to prevent temperature increase ($T < 60$°C) and electrode failure. For the used current range (from 8 to 48 mA cm^{-2}) corresponding flow rate varies from 0.23 to 3.38 L min^{-1}.

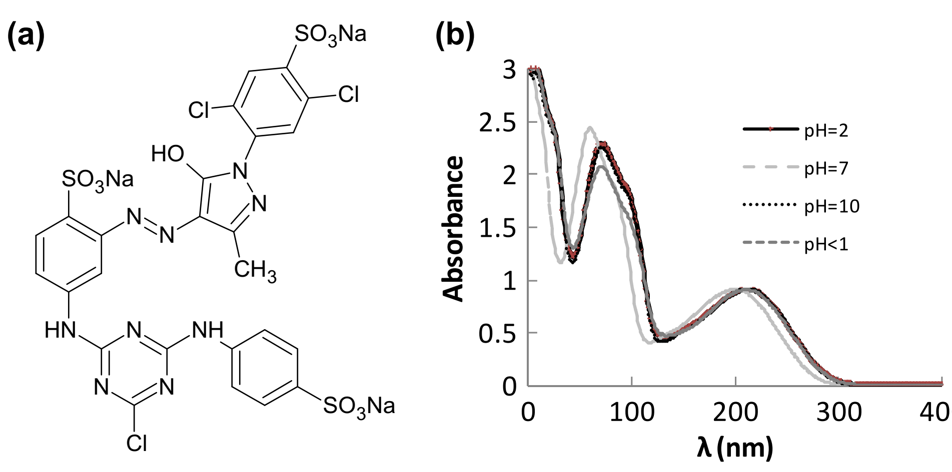

Fig. 1. (a) The molecular structure of Cibacron Brillant Yellow 3G-P and (b) effect of pH on initial absorbance.

Table 1
Conductivity, pH and apparent kinetic constants values (k) and correlation coefficient (R^2) at 414 ± 5 and 270 ± 2 nm obtained from the oxidation of 0.05 mM on the BDD electrode in the different electrolyte (0.1 M)

Salts	Na_2SO_4	$NaHCO_3$	$NaNO_3$	NaCl
pH	6.79	6.81	6.85	6.2
Conductivity (mS cm^{-1})	14.06	5.23	9.4	9.98
$k_{Abs412\pm5nm.}$ (h^{-1})	0.76 ($R^2 = 0.94$)	0.28 ($R^2 = 0.95$)	0.21 ($R^2 = 0.95$)	76.8 ($R^2 = 0.85$)
$k_{Abs270\pm5nm}$ (h^{-1})	0.32 ($R^2 = 0.98$)	0.21 ($R^2 = 0.93$)	–	–
$k_{COD}.10^3(h^{-1})$	6.91 ($R^2 = 0.94$)	2.5 ($R^2 = 0.87$)	0.65 ($R^2 = 0.81$)	24.7* ($R^2 = 0.94$)

Note:*initial rate (electrolysis time 4 min)

2.3. Anodic oxidation experiments

The anodic oxidation of Cibacron Yellow (CY) was performed galvanostatically. The oxidation degradation of the dye was monitored by withdrawing 20 mL of samples at selected times, from the reactor outlet and measuring the absorbance in the UV–vis spectrophotometer (*Thermospectronic UV1*). As shown in Fig 1b, the 414 nm wavelength in the visible region was selected to monitor the colour removal; and the wavelength detected in UV region (270 nm) is related to the absorbance of aromatic derivatives.

2.4. Analysis

The evaluation of global degradation related to organic matter was determined by measuring the COD during the experiments. COD is analysed using dichromate standard method.

The average current efficiency (ACE) for the anodic oxidation was calculated from the values of the COD using the following relationship [5].

$$\%\mathrm{ACE} = \frac{[(\mathrm{COD})_0 - (\mathrm{COD})_t]\mathrm{FV}_s}{8I\triangle I \times 100} \qquad (7)$$

Where $(COD)_0$, $(COD)_t$ (mg O_2 L^{-1}) are the CODs at electrolysis times 0 and t (h), respectively. I is the current (A), F the faraday's constant (96,487 C mol^{-1}) and V_s is the volume of electrolyte (L).

Energy consumption per amount of COD destroyed can be obtained as follows [5]:

$$E(k\mathrm{Wh}(\mathrm{gCOD})^{-1}) = \frac{IVt}{V_s\triangle(\mathrm{COD})} \qquad (8)$$

Where V is the average cell voltage (V), ΔCOD is the COD decay.

3. Results and discussion

3.1. Na_2SO_4 electrolyte (0.1M)

The Na_2SO_4 electrolyte is generally used to study the degradation of dyes by BDD electrodes due to its moderate effect concerning degradation rate [23]. It will also be considered in this case as reference to compare or extract the effect of other oxidative species and especially active chlorine. The concentration of azo dye was set at 0.05 mM and the initial pH was not modified (natural pH 6.2). Current density is equal to 40 mA cm^{-2}.

Fig. 2a presents the UV–vis spectra variation during oxidation of CY dye. As expected, a decrease of the main UV–vis absorption bands characterising the dye are observed during the time. The colour removal followed at 414 nm wavelength appears more rapid than aromatic derivatives detected in UV region (270 nm) in accordance with other studies [24]. However, no absorbance is detected after 164 min. It is proved that oxidation with $OH^{\cdot}$ is not the only oxidation mechanism occurring on BDD anodes but peroxodisulphates also can contribute to the oxidation process. They are formed during electrolysis with the BDD electrode following the reaction previously described in the introduction and as explained by several authors [10,25,26]. Obtained removal kinetics related to 414 and 270 nm are exposed in the following paragraphs.

3.2. Comparison with others salts (0.1M)

Degradation of CY, on others salts as electrolytes, is presented in this paragraph. Na_2SO_4 electrolyte is compared to chloride, nitrates and hydrogen carbonates salts. Same concentrations of CY (0.05 mM), electrolyte salts (0.1 M) and current density (40 mA cm^{-2}) are applied. pH values of electrolyte salts are presented in Table 1.

3.2.1. Effect on relative absorbance

As with SO_4^{2-}, a progressive decrease in absorbance of main CY peaks was observed in presence of HCO_3^- (Fig. 2b) during time. However, after 3 h of oxidation, absorbance at 414 nm and 268 nm did not disappear totally. Complete discolouration and complete aromatic degradation are partially inhibited by hydrogen carbonates ions. This result seems to be

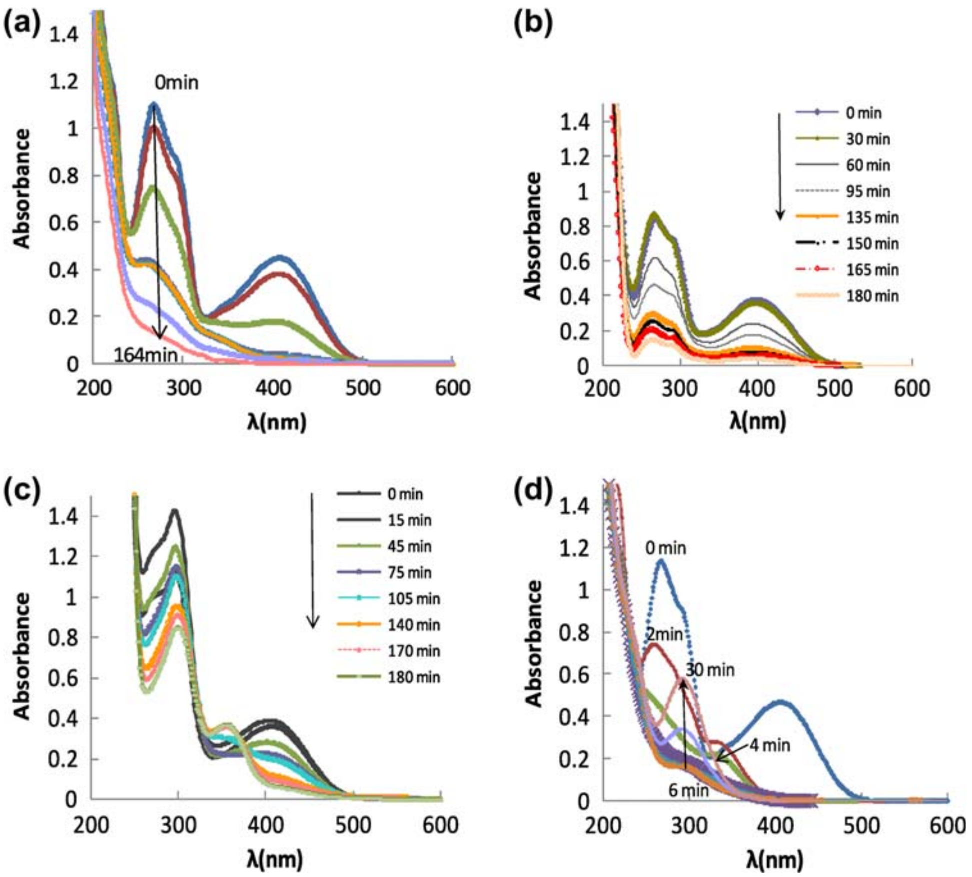

Fig. 2. Salt effect on absorbance spectra of aqueous solutions of 0.05 mM CY at 40 mA cm^{-2}, (a) Na_2SO_4, (b) $NaHCO_3$, (c) $NaNO_3$ and (d) NaCl.

related to the interference of HCO_3^- with $^{\cdot}OH$ radicals following the reaction [27]:

$$HCO_3^- + OH^{\cdot} \rightarrow CO_3^{\cdot} + H_2O \qquad (9)$$

and producing less powerful oxidant. However, it is important to note that HCO_3^- electrolyte has lower EC compared to other salts (Table 1).

Using nitrate salt as electrolyte (Fig. 2c), also leads to the decrease of the main UV–vis absorption peaks characterising the CY, but with the appearance of new peak at wave length ($\lambda = 355$ nm). The intensity of this absorption band decreased against electrolysis time and becomes stable from 140 to 180 min. It was observed that the dye colour is partially removed after 3 h of electrolysis and complete colour removal was not reached with nitrate electrolyte. Partial removal can be explained by the absence of the electrogeneration of powerful oxidising species from nitrates [23].

Concerning UV band, an increase of absorbance was detected during electrolysis. An absorbance spectrum of $NaNO_3$ electrolyte solution presents an absorption band at 304 nm (figure not shown) which interferes with UV band (270 nm).

The effect of NaCl electrolyte on the electrochemical oxidation of CY on BDD can be shown in Fig. 2d with the absorbance spectra obtained after different times of electrolysis. In this case, complete discolouration was obtained after few minutes (high decrease of relative absorbance at λ equal to 414 nm). Compared to Na_2SO_4 electrolyte, this phenomenon is linked to the electrogeneration of active chlorine which is expected yielding to hypochlorite at neutral pH [28].

However, the solution pH equal to 6.2 at the beginning of the electrolysis increased and reached (8.79) at the end of electrolysis. Active chlorine is expected to be present in solution under $ClO^-/HClO$ forms with potentials 1.29 V/SHE and 0.89 V/SHE, respectively [5].

Concerning the UV region, new bands are detected during the electrolysis, essentially at wave length $\lambda = 290$ nm ($t \geqslant 6$ min). It could be attributed to CY by-products formation or chlorine species generation. In

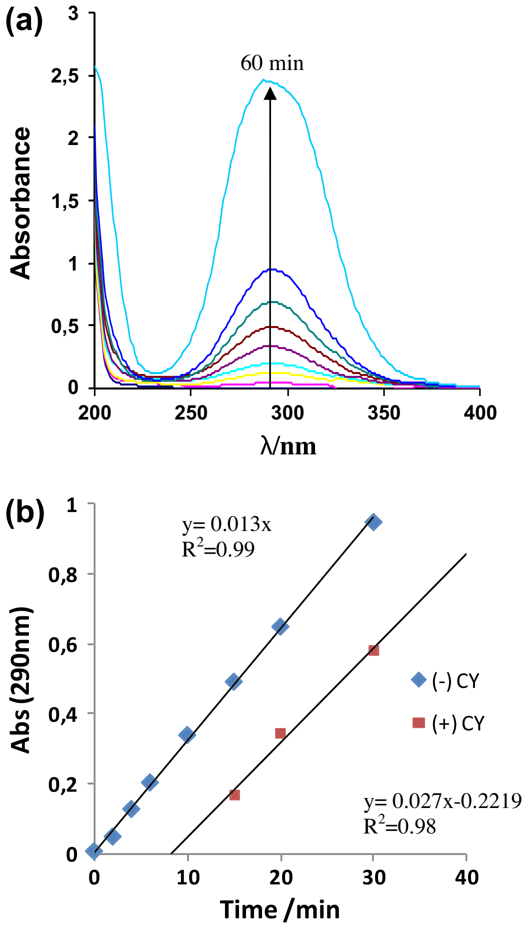

Fig. 3. (a) Absorbance spectra of aqueous solutions of [NaCl] = 0.1 M without dye and (b) absorbance band (290 nm) evolution function of time with (+) and without (–) CY; $j = 40\,\text{mA.cm}^{-2.}$

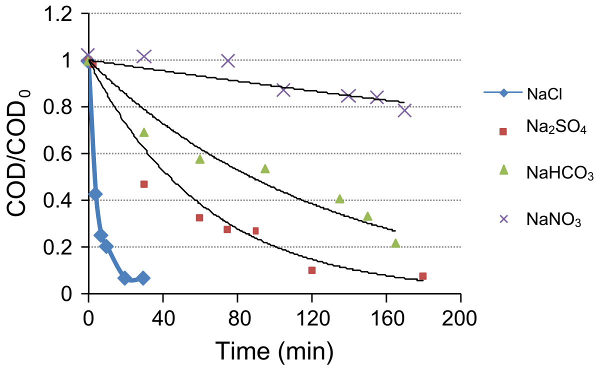

Fig. 4. Salt effect on COD removal, CY 0.05 Mm, $J = 40$ mA. cm^{-2}.

order to confirm this last hypothesis, the anodic oxidation by BDD of NaCl electrolyte (0.1 M) was performed without CY at the same condition. As shown in Fig. 3, the absorbance band obtained at 290 nm wave length increased with electrolysis time (60 min). This finding confirms the electrogeneration of chlorine species during CY electrolysis in NaCl electrolyte following zero order (Fig. 3b). In the presence of CY, dye similar rate is observed (Fig. 3b).

3.2.2. Effect on COD removal

During electrochemical oxidation of CY using Na_2SO_4 as electrolyte, COD removal efficiency reached 93% (Fig. 4). The observed inhibitive effect of HCO_3^- decreased this removal percentage to 80%, while only 20% are reached with nitrate salt. Nitrate appears as strong inhibitor to CY dye degradation. It is important to notice that a decrease of electrical conductivity of $NaHCO_3$ electrolyte is observed compared to others media (Table 1), which may affect oxidation process. The most interesting result is obtained with NaCl while COD removal curve has different trend. A strong decrease was observed rapidly equal to 88% of COD removal (until 3 min) followed by slow decrease until 25 min with final COD removal of 95%. Active chlorine has powerful action for mineralisation of CY molecule.

3.2.3. Kinetic degradation

Dye discolouration rate followed pseudo-first-order reaction in all media as the values of ln(abs/abs$_0$) was well fitted to the pseudo-first kinetic equation. Only for NaCl electrolyte, $R^2 = 0.85$ is obtained due to limited number of experimental data (Fig. 2d). Discolouration rate is considered only for comparison and equal to 76.8 h^{-1} (Table 1) which reflects the powerful bleaching action of active chlorine (101 times sulphate *k*). Kinetic constants (*k*) confirmed the inhibitor effect of nitrate and HCO_3^- ions on colour removal (decrease by 3.6 and 2.7 of *k* compared to $Na_2\ SO_4$).

Concerning the relative absorbance removal at 270 nm, only the related kinetics linked to sulphates and hydrogenocarbonates were determined due to strong variation observed in UV domain for nitrates and chlorides electrolytes as already explained. Inhibition effect of HCO_3^- is less pronounced in this case than colour removal, compared to SO_4^{2-}. Referring to obtained values of *k*, degradation of aromatic compounds needs more time to be mineralised.

Total mineralisation ratio was estimated by COD analysis. However, production of intermediaries' compounds and electrolyte salts (especially Cl^- and NO_3^-) could interfere, which explains the variation of COD curves leading to low R^2 (< 0.9) for first-order law application. However, Table 3 represents the calculated pseudo-first-order kinetic constant k for comparison. Estimated constants related to global mineralisation confirmed the partial degradation in the presence of HCO_3^- and the inhibitive effect of NO_3^-. Due to the special trend of COD curve for NaCl electrolyte, only the initial COD pseudo constant is calculated (4 min) and demonstrates the exceptional rate of the CY degradation.

3.2.4. ACE and energy consumption

Table 2 depicts the different values of ACE and energy (E) estimated after 1 h of electrolysis. In the presence of chloride, after 5 min of electrolysis, when 59% of COD removal is obtained, very higher value of current efficiency is obtained (91%) with limited consumption of energy (0.03 kWh $gCOD^{-1}$). This result is very interesting for potential industrial application to dyeing wastewater.

Little values of ACE detected by other salts can be ascribed to the partial removal of aromatic derivatives (UV 270 nm) and gradual formation of short carboxylic acids which are considered as the most persistent by-products [5]. Inhibitive effect of nitrates led to high energy consumption (66.37 kWh $gCOD^{-1}$), which can limit potential application.

3.3. Effect of current density and chloride concentration

The enhancement of CY degradation by active chlorine, generated during oxidation using BDD, is clear and worth being investigated.

3.3.1. Effect of current density on active chlorine efficiency

Current density was decreased to 8 mA cm^{-2} (superior to current limit equal to 0.65 mA cm^{-2}) and impact on relative absorbance on 414 nm during CY electrochemical oxidation is shown in Fig. 5. Thus, bleaching effect is immediate and independently on current value. However, UV absorbance at 270 nm was strongly affected by current decrease. Since the beginning of CY oxidation, high bleaching activity (96% colour removal) was observed but in parallel, a pseudo plateau corresponding to only 17% of UV absorbance removal was obtained at $t < 7$ min. Then, this ratio increased to 60% after 16 min of oxidation. As shown in Fig. 5, 82% of UV absorbance removal was obtained after 7 min of oxidation, when the current is five times more important. The obtained behaviour at low current can be explained by limited generation of active chlorine, as 8 mA cm^{-2} is superior to current limit, which are firstly used for bleaching reaction rather than participating to aromatic derivatives degradation considered as more recalcitrant compounds.

3.3.2. Effect of chloride concentration (without Na_2SO_4)

Experiments were carried on NaCl electrolyte with chloride concentrations from 0.02 to 0.2 mol L^{-1}.

The general evolution of colour removal (Fig. 6a) is similar for all chloride concentrations with strong discolouration since the beginning of the electrolysis.

Table 2
Salt effect on ACE and energy consumption (E) during electrolysis, $i = 40$ mA cm^{-2}, $C_{dye} = 0.05$ mmol L^{-1}

	Electrolysis time/min	COD removal %	ACE %	E kWh $(gCOD)^{-1}$
Na_2SO_4	60	53	5.94	0.64
$NaHCO_3$	60	30	4.62	1.44
$NaNO_3$	60	0.5	0.05	66.37
NaCl	25	95	9.7	0.43

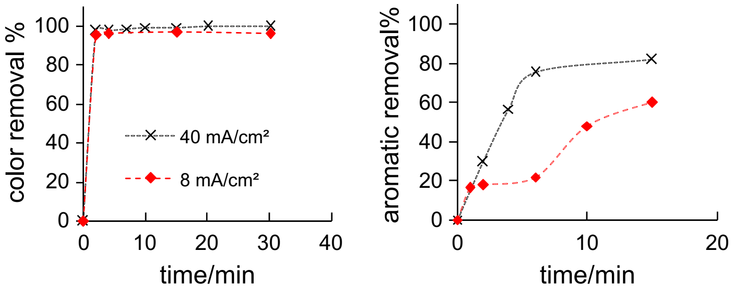

Fig. 5. Effect of current density on dye degradation decay for 0.05 Mm CY at natural pH with 0.1 M Nacl as support electrolyte.

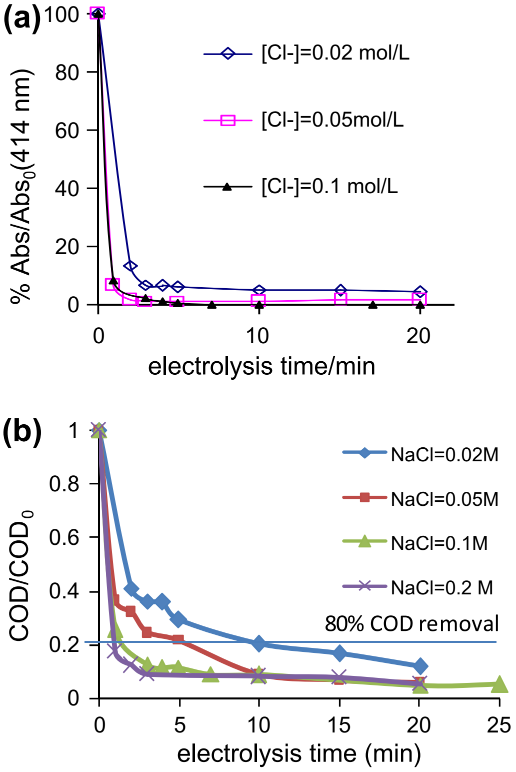

Fig. 6. Influence of chloride concentration on (a) discolouration rate and (b) COD removal with time.

Similar trend is observed in Fig. 6b, where COD removal becomes higher when chloride concentration increases. Higher Cl^- contents promote faster destruction of dyes with the consequent detrimental in ROS (reactive oxygen species) [5]. Nevertheless, no improvement is obtained with chloride concentration higher than 0.1 M, where residual COD is observed (5%). COD removal is more than 80% after 10 min of electrolysis (95.25 % COD removal).

3.3.3. Effect of chloride addition (with Na_2SO_4)

In the one hand, the effect of chloride ions on the electrochemical oxidation of CY on BDD was very powerful for discolouration and aromatic compounds degradation. In this case, more than 95% of COD removal is obtained only after 10 min. In the other hand, the degradation kinetic in Na_2SO_4 electrolyte is very slow compared to NaCl; 93% of COD removal can be obtained after 160 min (Fig. 4). Our purpose is to study the possibility to enhance degradation rate by adding different concentration of chlorine to Na_2SO_4 electrolyte.

Experiments were carried with the addition of different Cl^- concentrations from 0.02 to 0.2 mol L^{-1} in Na_2SO_4 electrolyte support (0.1 mol L^{-1}). Colour removal is presented in Fig. 7.

As observed in Fig. 7a, obtained trend is equivalent to the one of chloride and demonstrate clearly that addition of small quantity of chloride ion act directly on solution bleaching. Increasing chloride concentration will only decrease the necessary time for total discolouration. Due to rapid discolouration rate during electrochemical oxidation (Fig. 7b), only initial degradation rate (v_0) was considered. An increase in chloride concentration from 0.02 to 0.2 mol L^{-1} accelerated electrochemical degradation and v_0 fits well a logarithmic law function of initial chloride concentration. In the presence of sulphates, a small addition of chloride is necessary to obtain the best rate of discolouration.

Concerning COD decays, comparison of curves of Fig. 8 demonstrated that the trend is different from the one obtained without chloride. COD removal as well as degradation rate is higher in the presence of Cl^-. Nevertheless, comparison with chloride electrolytes (Fig. 6) shows that the chlorine effect on COD decrease is partially inhibited. Obtained degradation

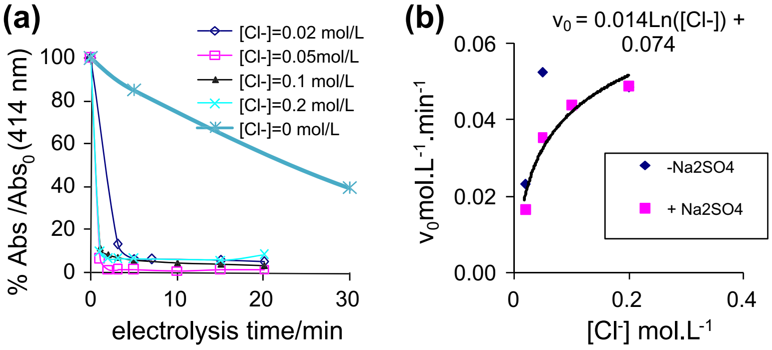

Fig. 7. Effect of chloride on degradation processes, (a) abs/abs$_0$ (414 nm) as a function of time reaction in the presence of Na_2SO_4, (b) initial discolouration rate (v_0) as a function of chloride concentration in presence (+) and absence (–) of Na_2SO_4. $C_{dye} = 0.05$ mM, $j = 40$ mA cm^{-2}.

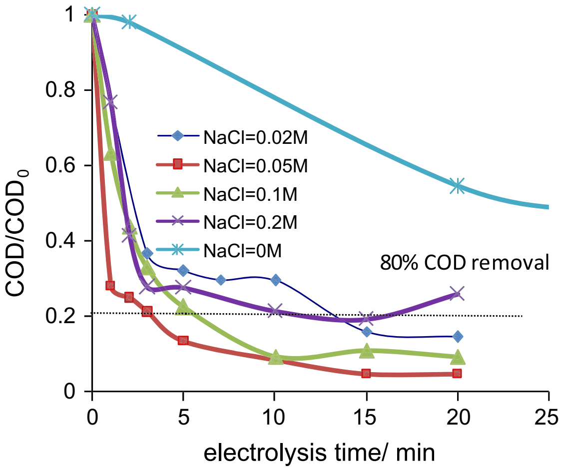

Fig. 8. Influence of chloride concentration on COD decay in the presence of Na_2SO_4, 0.05 mM CY, $j = 40\ mA\ cm^{-2}$.

rate is higher without Na_2SO_4 (Fig. 6). An optimum effect is observed due to the decrease of obtained COD removal at high value of Cl^- (> 0.05 M).

Addition of small quantity of chloride has a strong effect on discolouration, i.e. it improves the mineralisation rate of the CY dye and decreases the necessary electrolysis time.

This interesting finding deserves to be compared to other publication related to dyes oxidation. Table 3 summarises the percentage of COD removal and energy consumption values obtained for selected dyes at different electrolytes (NaCl or Na_2SO_4) in several papers from literature [29,30,8,31]. High COD removal is reached in this study with limited electrolysis time compared to other works presented in Table 3 [8]. Also, when energy consumption by COD removal (*E*) is indicated [31], lower value is obtained when 0.02 M of NaCl is added in Na_2SO_4 medium.

4. Conclusion

Throughout this study, the effect of different anions (NO_3^-, HCO_3^-, Cl^-) on anodic oxidation of azo dyes was studied in comparison with Na_2SO_4 electrolyte using BDD as anode. The main findings are as follows:

- A partial degradation action is obtained for HCO_3^- and strong inhibitive effect is detected in the case of NO_3^- essentially with regard to COD removal.
- On the contrary, a powerful bleaching action of active chlorine electrogenerated from chloride medium is obtained at the beginning of electrolysis and

Table 3
Examples of COD removal and energy consumption (*E*) obtained by authors for the oxidation of dyes in different electrolyte supports

Dye	C_0	Anode	Electrolyte	Electrolysis time/min	j/ mA cm^{-2}	COD removal %	*E* kWh kg COD^{-1}	Ref.
Cibracron yellow	0.05 mmol L^{-1}	BDD	0.1 M Na_2SO_4	30	40	53	365.85	This work
			0.1 M NaCl	20		95.25	34.66	
			0.05 M NaCl + 0.1 M Na_2SO_4	20		95.16	32.66	
			0.02 M NaCl + 0.1 M Na_2SO_4	20		85	60.97	
Amaranth	100 mg L^{-1}	BDD	0.07 M Na_2SO_4	60	200	62	Not determined	[29]
Black 5 dye	50 mg L^{-1}	BDD	0.02 M Na_2SO_4	25	1	51	36.95 kwh m^{-3}	[30]
Acid black 210	500 mg L^{-1}	BDD	0.1 M NaCl	60^a	25	–	55 kwh m^{-3}	[28]
Basic blue 9	80 mg L^{-1}	Ti/ RuO_2	0.02 Cl^{-a}	120^a	20	94	Not determined	[8]
Reactive red 120	100 mg L^{-1}	Ti/ TiO_2	0.025 NaCl^a	1,260^a	20	68.1	316	[31]
Reactive yellow 84	100 mg L^{-1}	Ti/ TiO_2	0.025 NaCl^a	720^a	20	63.8	400	[31]

[a] Calculated by authors.

high COD removal rate is observed at current electrolysis of 40 mA.cm^{-2}.

- The most interesting funding is an enhancement of COD removal by 42% and energy consumption by 333 KWh/kg of COD after the addition of 0.05 mol of NaCl (optimum concentration) to Na_2SO_4 electrolyte.

To conclude, chloride presence in dying wastewater can be an advantage for electrochemical oxidation process application as it is leading to high rate of solution bleaching and degradation rate. Small concentration (0.02 mol L^{-1}) is sufficient to promote dye mineralisation and multiply degradation rate by 1.54. Additionally, strong decrease in energy consumption (kWh COD^{-1}) is obtained as compared to other studies.

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