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Degradation of EDTA by in-situ electrogenerated active chlorine in an electroflotation cell

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ABSTRACT

Ethylenediaminetetraacetic acid (EDTA) is a chelating agent widely used for its ability to form stable water-soluble complexes with metals. Yet, it is among refractory and poorly degradable organics. Its degradation is indubitably becoming a major environmental concern. In this work, electrochlorination of EDTA on Ti/RuO_2 anode proved to be effective for such an aim, and thus this electrochemical process may be a promising alternative to conventional EDTA treatments. The effects of NaCl concentration, EDTA concentration, current intensity, and the presence of metallic ions on the EDTA oxidative degradation were investigated. The results herein reported showed that a complete degradation of EDTA was achieved under the following conditions: EDTA concentration, 400 mg.L^{-1}, NaCl concentration, 10 g.L^{-1}; time, 2 h, current intensity 800 mA. In the absence of chloride ions, no degradation was observed, whereas significant extents of degradation were obtained in their presence. Thus, the oxidation of EDTA took place in the bulk solution by the electrolytically generated active chlorine. Increasing the current intensity and NaCl concentration significantly increased EDTA decomposition. Initial pollutant concentration also affected the process efficiency; large amounts of EDTA in the solution slowed down the degradation extent. It was also found that the presence of metallic ions had a negative effect on the oxidation kinetics.

Keywords: Active chlorine; EDTA; Electrochemical degradation; Electrochlorination; Ti/RuO_2 anode

1. Introduction

Ethylenediaminetetraacetic acid (EDTA) is a strong and versatile metal sequestering agent, widely employed in industries such as metal finishing, cleaning process, photography, nuclear processes, detergents, paper, textiles, food, etc. [1,2]. Indeed, large amounts of EDTA in forms of complexes or free states are released in wastewaters which unfavorably harm the environment. Because of its capacity to enhance the mobility and the solubility of heavy metals, the removal of the latter species defies all classical treatment techniques. Owing to its easy complexation with metals, the existence of EDTA in the effluents would hamper their treatment by conventional techniques, mainly the precipitation process [3].

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It is well known that EDTA is a recalcitrant and poorly biodegradable substance [2,4], and its destruction by means of chemical oxidation techniques is not always successful. Moreover, EDTA presents a significant solidity towards photolysis [5]. Its high concentration in waters could entail disturbing effects to the environment such as eutrophization and metal leaching into water, thus ensuing a long-term toxicity for microorganisms [6]. In fact, its degradation remains a major environment-linked problem, and several technical issues need to be circumvented in laboratory and industrial scales. Different EDTA degradation methods reported in the literature, including chemical oxidation [7], advanced oxidation processes (AOP), photocatalysis [5,8], Fenton's process [9], sonochemical processes [10,11] and their combinations [12] were confined either to its lowering chelating/sequestering ability or to its mineralization. Although these techniques provide substantial degradation of EDTA, they suffered from some drawbacks: long operation time, fine pH adjustment, addition of external oxidizing agents, etc.

However, the electrochemical methods were quite successful in destroying the refractory organic pollutants from wastewaters [13–21]. These techniques involved either a direct or an indirect oxidation of the pollutants. In the former oxidation, the pollutants were first adsorbed onto the anode surface and then underwent oxidation reaction with the anode, whereas the indirect oxidation of the pollutants occurred by the *in situ* formed strong oxidizing agents such as active chlorine or hydrogen peroxide [13,14]. The oxidative removal of EDTA by the direct electro-oxidation using a platinum-made anode [15] or a boron-doped diamond anode (BDD) [16] was studied. Despite its success, this variation was impaired by, at least, two shortcomings: the slowness of the transport process of the species from the bulk solution to the electrode, and the fouling of the latter. On the other hand, the indirect electro-oxidation of the pollutants by active chlorine molecules generated from chloride ions present in the solutions, a process called electro-chlorination, was also claimed to powerfully destroy organic pollutants [17–20].

In the work herein presented, a study of the EDTA degradation by the active chlorine formed in an electroflotation cell equipped with a Ti/RuO_2 anode and steel-made cathode was undertaken. The effects of the initial EDTA concentration, NaCl concentration, applied current density and the presence of external metallic ions Ni (II), Cu(II)) on the EDTA degradation efficiency were examined.

2. Experimental

2.1. Chemicals

The chemicals used in this work were: Titriplex III (EDTA-Na_2, $2H_2O$) (Merck); NaOH (Merck); anhydrous sodium sulfate (Na_2SO_4) (Prolabo); NaCl (Prolabo); concentrated H_2SO_4 (Prolabo).

2.2. Materials and set-up

The experimental set-up is comprised of the following units:

- A 28 cm × 8 cm × 38 cm Plexiglas-made reactor.
- Two 7 cm × 19 cm electrodes, distant from each other by 1 cm, mounted at the bottom of the reactor. The ruthenium oxide-coated titanium grid used as an anode was placed on top, and the sheet steel as cathode was underneath.
- A current generator, Stratron 3217 type (10 A, 30 V).
- A Tacussel millivoltmeter MVN 75.
- A Tacussel amperemeter universal MAR-U.
- A pH-meter Ino-lab.

2.3. Procedure and analyses

The tests were realized in a batch experiment mode using 3 L solutions. The latter solutions contained EDTA, 5 g.L^{-1} of Na_2SO_4 solution, and a known amount of NaCl. Addition of either NaOH or H_2SO_4 for adjusting the pH at 9.5 was made. Electrolysis course was conducted in a galvanostatic mode.

The analyses were performed as follows: during the run, a 2-mL sample was removed from a site of the solution located 4 cm above the electrodes. EDTA concentrations were determined by colorimetry using xylenol zirconium-orange complex [22], and by means of a double beam UV-Visible spectrophotometer, Shimadzu 1602 type.

The results are expressed in removal efficiency, η (%), given by the following relation:

$$\eta\ (\%) = (C_0 - C_t)/C_0 \times 100$$

where C_0 and C_t are the initial concentration in mg.L^{-1} of the pollutant and its concentration at a time *t* of the operation, respectively.

3. Results and discussion

3.1. Effect of added chloride ions

In the aim of ascertaining the effectiveness of the indirect electro-oxidation of EDTA by the active chlorine, an intensity current of 1000 mA was applied to two aqueous solutions, each containing 600 mg.L^{-1} of EDTA and 5 g.L^{-1} of Na_2SO_4 (as an inert electrolyte), but to one of them 5 g.L^{-1} of NaCl were added. The results shown in Fig. 1 indicate that no degradation occurred in the presence of sulfate ions only; however, a significant decomposition was observed when chloride ions were added. A quantitative degradation (~100%) was observed after 4 h of electrolysis. The set of reactions involved in such oxidative degradation of EDTA by the *in situ* generated active

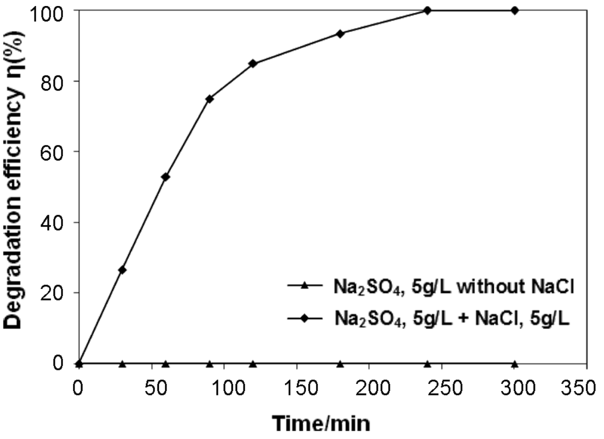

Fig. 1. Effect of the presence of chloride on EDTA degradation. EDTA concentration, 600 mg.L^{-1}; current intensity, 1000 mA.

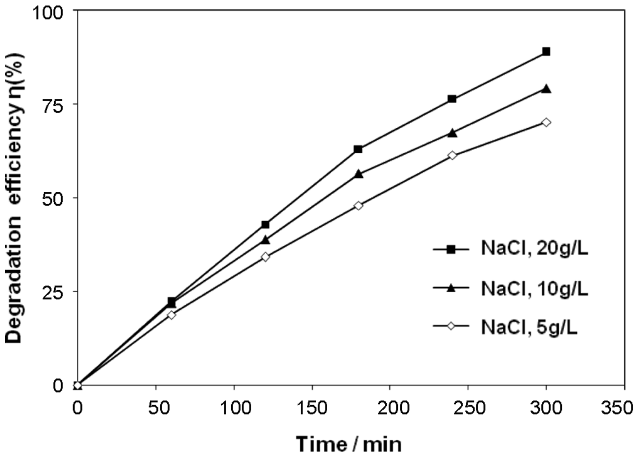

Fig. 2. Effect of the NaCl concentration on EDTA degradation. EDTA concentration, 400 mg.L^{-1}; current intensity, 200 mA.

chlorine is given below [20,23]. Reactions (3), (4), and (5) took place in the solution and were pH-dependent. An acidic pH would be more favorable for the degradation than an alkaline one. Yet, the choice of the working pH was based on the real conditions, that is, in the presence of metallic ions [24].

At the catode: $$2H_2O + 2\,e \rightarrow H_2 + 2OH^- \tag{1}$$

At the anode: $$2Cl^- \rightarrow Cl_2 + 2e \tag{2}$$

In the solution: $$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \tag{3}$$

$$HClO \rightarrow ClO^- + H^+ \tag{4}$$

$$\text{Organic pollutant} + ClO^- \rightarrow \text{Products} \tag{5}$$

As to the probable and concomitant direct oxidation, both the yield of EDTA oxidation and its kinetics were undetectable. The reason is that a small mass transfer coefficient would have limited the kinetics. In addition, the Ti/RuO$_2$ electrodes would have been involved more in water oxidation (evolution of oxygen) than in the direct oxidation of organic substances, and, thus, a degradation yield was annihilated [25].

3.2. *Effect of chloride ion concentration*

To assess the influence of chloride ion concentration on the course of the EDTA degradation, electrolysis experiments were carried out for three NaCl concentrations: 5, 10 and 20 g.L^{-1} The initial concentration of EDTA was 400 mg.L^{-1} and the intensity of the current applied was 200 mA. The results of such effect are illustrated in Fig. 2. It can be seen that the higher the NaCl concentration, the greater the degradation efficiency. The amount of active chlorine produced during the electrolysis increased as the mass transfer process was enhanced by a higher NaCl concentration, implying a faster flux of the chloride ions from the solution towards the anode surface [23]. More chlorine molecules than oxygen molecules were formed by raising the chloride ion concentration, and two competitive redox reactions, (6) and (7), would have occurred as shown below [26].

$$Cl_2 + 2e \rightarrow 2Cl^- \qquad E° = 1{,}358\ \text{V/SHE} \tag{6}$$

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \qquad E° = 1{,}229\ \text{V/SHE} \tag{7}$$

Our findings agreed with the results reported by Arikawa et al. [27]. These authors showed that the speeds of reactions (6) and (7) over a Ti/RuO$_2$ anode were related to the chloride ion concentration in the electrolysis solution. Upon raising the chloride ion concentration, the overpotential of chlorine evolution dropped and that of the evolution of oxygen rose. Hence, the chlorine yield would have been enhanced over that of oxygen.

3.3. *Effect of the current intensity*

The impact of the current intensity on the EDTA degradation extent was examined and the results are shown in Fig. 3. It can be noticed that an increase in the current intensity speeded up the degradation. After 60 min of electrolysis, the degradation extent was estimated to be 21.4% for 200 mA and 74.3% for 800 mA. Best of all, the residual amount of EDTA in the tested solution was almost nil after 120 min of electrolysis working at 800 mA. According to [23], the produced amount of active chlorine went up by raising the current intensity, accelerating reaction (5) and, consequently, improving the degradation yield.

3.4. *Effect of EDTA initial concentration*

The effect of EDTA initial concentration on the degradation degree is illustrated in Fig. 4. The results suggested

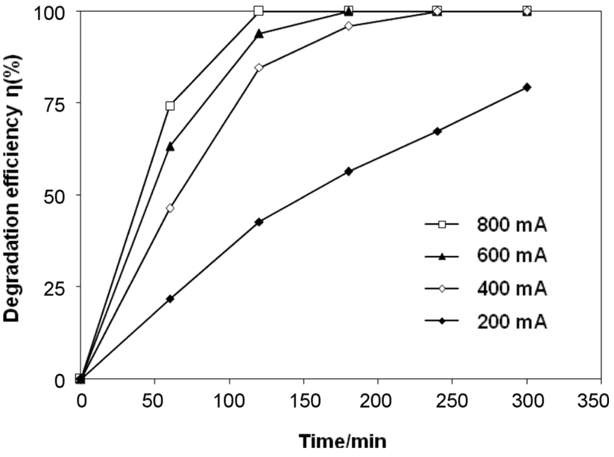

Fig. 3. Effect of the current intensity on EDTA degradation. EDTA concentration, 400 mg.L^{-1}; NaCl concentration, 10 g.L^{-1}.

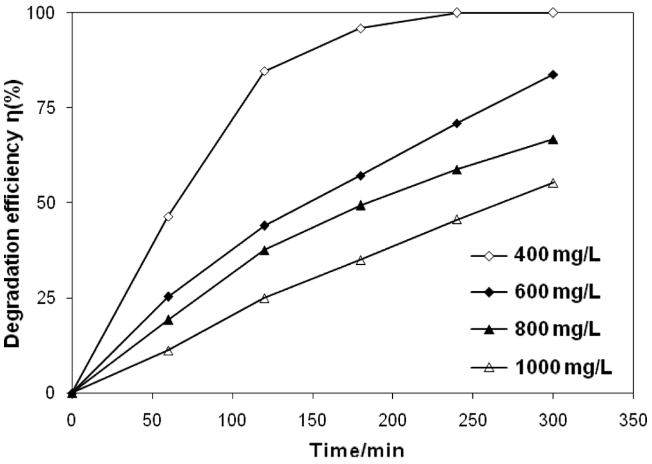

Fig. 4. Effect of the EDTA concentration on EDTA degradation. NaCl concentration, 10 g.L^{-1}; current intensity, 400 mA.

that the higher the EDTA initial concentration, the lower the degradation rate and η. Indeed, within a period of time of 120 min, the removal efficiency η was 84.7 and 22.7% for the concentrations of 400 and 1000 mg.L^{-1}, respectively. Furthermore, after 180 min of electrolysis, η was almost 100% for the former concentration and reached 35% only for the latter one.

It was rationalized [17–19,26] that in the electrochemical oxidation of an organic matter, the mineralization proceeded through several intermediate steps whose kinetics depended mostly on the oxidation-prone species, reaction (8).

$$\text{Organic pollutant} \xrightarrow{\text{rapid step}} \text{By-products} \xrightarrow{\text{slow step}} CO_2 + NH_3 + H_2O \tag{8}$$

It was found that increasing the organic pollutant initial concentration led to a drop of its degradation rate. The active chlorine molecules were not selective and could have attacked both the starting EDTA and the species of lower molecular weights (by-products) stemming from its degradation. Being stable and resistant to oxidation reaction, the mineralization of these species was very slow [28]. Under the galvanostatic conditions, set for providing constant active chlorine concentration, an increase in the EDTA initial concentration favored the formation of the decomposition intermediates, and, henceforth, a slow removal.

3.5. *Effect of the metallic ions*

As mentioned earlier, EDTA has a strong affinity towards metallic ions, forming stable complexes. For divalent metallic ions, M^{2+}, the complexes are formed according to reaction (9) [29].

$$H_2Y^{2-} + M^{2+} \rightarrow MY^{2-} + 2H^+ \tag{9}$$

where H_2Y^{2-} and MY^{2-} are the EDTA anion and the formed complex, respectively.

To assess the effect of the metallic ion on the course of EDTA degradation, Ni(II) and Cu(II) were added separately into the EDTA aqueous solutions, and the [EDTA]/[M^{2+}] molar ratio was set at 1. Fig. 5 illustrates the effect of these metallic ions on the kinetics of the degradation of EDTA. It is clear that the addition of metallic ions into the EDTA solution reduced its decomposition. While a complete degradation of EDTA from a solution exempt of metallic ions, was achieved after 3 h of electrolysis, only 45.8 and 57.7% of degradation were accomplished for solutions containing Ni(II) and Cu(II), respectively. Not only would the formation of a stable complex M(II)–EDTA account for the degradation efficiency lowering but also on the complexed metallic ion, in this order Cu (II)–EDTA >Ni (II)–EDTA. A plausible explanation to the degradation-related difference would be to the difference

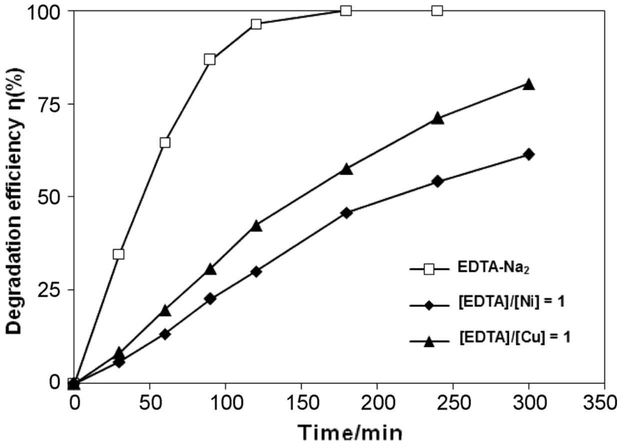

Fig. 5. Effect of the presence of metallic ions on EDTA degradation. EDTA concentration, 600 mg.L^{-1}; NaCl concentration, 10 g.L^{-1}; current intensity, 1000 mA.

in the extents of the free forms of the ions and their corresponding EDTA complexes. The strong coordinating bonds between the carboxylic groups and the metallic ion [30] would prevent the decarboxylation occurrence, which is a key step of the EDTA degradation. These results are in tune with those of Frim et al. [10], Motekaitis et al. [31], and Chaudhary et al. [32].

4. Conclusions

The above-presented results showed that the indirect electrooxidation via the electro-chlorination proved to be an efficient technique for the elimination of EDTA by degradation. This technique could be a convenient surrogate for the conventional ways of treatment of refractory substances and/or a pre-treatment step of a biological degradation. The EDTA oxidation occurs in the electrolytic bulk by the active chlorine electrochemically produced at the anode. In general, the degradation happens only in the presence of chloride ions, a source of active chlorine molecules. A high current intensity and a low EDTA concentration favor a substantial degradation within shorter times. On the opposite, the presence of metallic ions slows down the degradation process.

Our results showed that a complete degradation of EDTA was achieved under the following conditions: EDTA concentration, 400 mg.L^{-1} ; NaCl concentration, 10 g.L^{-1}; time, 2 h; current intensity, 800 mA.

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