Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.773862

51 (2013) 7555–7561
December

Taylor & Francis
Taylor & Francis Group

Photocatalytic degradation of EDTA with UV/Cu(II)/H_2O_2 process

Peng Liu[a], Chaolin Li[a,*], Xianghan Kong[a], Gang Lu[b], Jianhui Xu[a], Fei Ji[a], Xingang Liang[a]

[a]*Environmental Science & Engineering Research Center, Harbin Institute of Technology Shenzhen Graduate School, Shenzhen 518055, P.R. China*
Tel. +86 755 26032455; Fax: +86 755 26032455; email: lichaolin@hitsz.edu.cn
[b]*Department of Environmental Engineering, Jinan University, Guangzhou 510632, P.R. China*

Received 20 December 2012; Accepted 2 February 2013

ABSTRACT

In this study, degradation of ethylene diamine tetraacetic acid (EDTA) solution by the UV/Cu(II)/H_2O_2 process under various conditions was evaluated via chemical oxygen demand (COD) removal. The reactions were performed in a lab-scale batch photoreactor. The effects of different parameters such as H_2O_2 dosage, copper catalyst dosage, initial pH, and initial EDTA concentration on the oxidation efficiency of the process were investigated. The results indicated that the UV/Cu(II)/H_2O_2 process could effectively remove COD in both synthesized EDTA wastewater and real copper-plating wastewater. According to the experimental results, a reasonable mechanism was proposed to interpret the oxidation process. When treating real copper-plating wastewater (COD = 3,660 mg/L) catalyzed by self-contained 1.4 g/L copper, 98.6% of COD removal was obtained using 0.6 M H_2O_2 in 180 min. In addition to the removal of organic matter, copper complexes were decomposed to form easily removed free copper ions. This study shows that UV/Cu(II)/H_2O_2 is not only a powerful treatment method for COD removal of EDTA wastewater, but also an environmental friendly treatment process for copper-containing organic wastewater.

Keywords: UV/H_2O_2; EDTA; Copper-plating wastewater; Chemical oxygen demand (COD)

1. Introduction

Ethylene diamine tetraacetic acid (EDTA) is a common industrial and domestic water contaminant. It is used as an important decontaminating agent in the nuclear industry. Although EDTA itself is relatively risk-free to public health [1], it can increase the distribution of metals in the environment through the formation of very stable and mobile metal-EDTA complexes [2,3]. EDTA is not easily biodegradable [4] and hardly adsorbed by activated carbon and resistant to ozone oxidation [5,6]. Therefore, degradation of EDTA has attracted many researchers' attention during the last two decades. Several processes have been developed such as ultrasonic [7], electrochemical oxidation [8], photocatalysis [9,10], and UV/H_2O_2 [11,12].

Transition metals are often used to catalyze redox reactions [13]. Among the transition metals, copper has been found to possess high activity, and therefore, copper and copper-based catalysts have been widely studied [14]. Many researchers have reported the effectiveness of the homogeneous Cu^{2+} catalysts in the

---

*Corresponding author.

1944-3994/1944-3986

wet air oxidation of organic compounds [15,16]. Rodríguez et al. investigated degradation of methylene blue by catalytic wet air oxidation with Fe and copper catalysts supported on multiwalled carbon nanotubes. They found that the copper catalyst gave higher removal of TOC and color at different temperatures than the iron catalyst [17]. Some researches have compared the iron-based catalysts with copper-based catalysts; the results demonstrated that copper-based catalysts show better catalytic performance, and wider range of pH operations [18,19]. Moreover, with H_2O_2 present, homogeneous and heterogeneous copper catalysts have shown the ability to produce ·OH in a Fenton-like system [20,21]. Therefore, the catalytic activity of copper is greatly enhanced when H_2O_2 is present as the oxidant. However, few attempts were made in the case of addition of UV in the Cu/H_2O_2 process.

Most of the industrial wastewaters contain both toxic heavy metals and refractory organic compounds, such as electroplating wastewater, dyeing wastewater and so on. However, it is difficult to remove heavy metals by precipitation method due to the complexation of heavy metals by organic matter. Therefore, the research of using the heavy metals originally existing in the wastewater as catalyst to remove the refractory organic pollutants is very meaningful. Furthermore, with the removal of the organic pollutants, the heavy metals can be easily reduced by precipitation. Copper ion is one of the most common heavy metal contained in the industry wastewater.

Therefore, based on the above mentioned idea, the objective of this study was to clarify whether organic pollutants, as exemplified by EDTA, could be oxidized by $UV/Cu(II)/H_2O_2$ process. The effects of the key operating variables, such as H_2O_2 dosage, Cu^{2+} concentration, initial pH, and initial EDTA concentration were studied. The experiment was conducted by changing one variable at a time while keeping other parameters constant. The comparison with the direct UV photolysis and only Cu^{2+} in the presence of H_2O_2 were also studied. In addition, the oxidation effects of organic pollutants in real copper plating wastewater were also investigated.

2. Experimental

2.1. Material and analysis

Copper sulfate ($CuSO_4{\cdot}5H_2O$), Disodium EDTA (Na_2H_2EDTA), hydrogen peroxide (30%, w/w), sulfuric acid (98%, w/w) and sodium hydroxide were obtained from Tianjin Chemical (Tianjin, China). All chemicals were analytical grade reagents and were used as received without further purification. Distilled water was used to prepare all experimental solutions. The copper-plating wastewater was obtained from an electroplating plant in Shenzhen, China. The characteristics of the copper-plating wastewater were listed in Table 1. The pH of the solutions was adjusted with either H_2SO_4 or NaOH in all the experiments. The different concentrations of acid or base have been chosen in order to add the minimum quantity of these species to avoid the volume of the reaction mixture.

Even if EDTA concentration has dropped drastically, some by-products such as ethylenediaminediacetic acid (EDDA), iminodiacetic acid (IDA), and oxalic acid could be formed [12,22–24]. Therefore, in order to test the mineralization degree of EDTA, the degradation effect was reflected by measuring COD which was measured using Standard Method 5220D [25], and possible by-products formed during the EDTA degradation were not monitored. Copper was analyzed by atomic absorption spectroscopy (Shimadzu AA-6300C) using the direct aspiration flame method. The pH was measured by a pHs-25 instrument (Rex Analytical Instrument Co., Shanghai).

2.2. Photoreactor

A lab-scale photoreactor was designed for the batch experiments. The photoreactor had a capacity of 4 liters. The irradiation was provided by a low-pressure mercury lamp (Shenzhen Dohill Inc., 80 W electric power, and 314 cm^2 irradiation surface) with predominant UV intensity at 253.7 nm (75 mW/cm^2 at the surface of the lamp). The lamp was vertically located in the center of the photoreactor. During the experiments, compressed air was bubbled from the bottom at a flow rate of approximately 2,500 mL/min to achieve completely mixed batch conditions.

2.3. Experimental procedures

Fourliters of experimental solution was added to the photoreactor in each experiment. Then, initial pH of solution was adjusted to the desired pH by adding 1.0 M sulfuric acid and/or 1.0 M sodium hydroxide. From the beginning to the end of the reaction, predetermined amounts of H_2O_2 was continuously added

Table 1
Characteristics of copper-plating wastewater

Parameters	Value
pH	2.0
TDS (g/L)	19.0
Chemical oxygen demand (mg/L)	3,660
Copper (g/L)	1.4

into the reactor by a peristaltic pump at a desired constant flow rate. At each of appropriate time intervals, a 10-mL sample of the solution was removed from the photoreactor into the tubes for test. Any hydrogen peroxide, present in the samples after UV/H_2O_2 treatment, was quenched using catalase (3,050 units/mg solid, Sigma–Aldrich) extracted from bovine liver. All treated samples were settled for 60 min and diluted for further measurements. Each experiment was performed at least twice, except in the cases where the variation for replicate experiments exceeded 5%, more replications were performed. In order to eliminate the influence of volume changes caused by the added H_2O_2, the COD removal efficiency (R_{COD} in%) was calculated using Eq. (1):

$$R_{\mathrm{COD}} = \frac{\mathrm{COD}_{\mathrm{initial}} \times V_{\mathrm{initial}} - \mathrm{COD}_{\mathrm{sample}} \times (V_{\mathrm{initial}} + V_{\mathrm{H_2O_2}})}{\mathrm{COD}_{\mathrm{initial}} \times V_{\mathrm{initial}}} \times 100 \tag{1}$$

where R_{COD} is the COD removal efficiency (%); $\mathrm{COD}_{\mathrm{initial}}$ is the initial COD concentration (mg/L); $\mathrm{COD}_{\mathrm{sample}}$ is the COD concentration of the sample (mg/L); V_{initial} is the initial solution volume (L) $V_{\mathrm{H_2O_2}}$ is the added H_2O_2 volume (L).

All of the experiments and measurements were carried out at room temperature.

3. Results and discussions

3.1. Background experiment

Degradations of EDTA by UV, H_2O_2, UV/H_2O_2, Cu(II)/H_2O_2, and UV/Cu(II)/H_2O_2 were carried out, respectively, and the results are shown in Fig. 1. Single whether UV or H_2O_2 was very negligible to degradation COD of EDTA. There was no apparent COD removal when the solution was treated with Cu (II)/H_2O_2 process in the dark. The UV/H_2O_2 process was also insufficient to achieve excellent oxidation efficiency. However, when the reaction was carried out in UV/Cu(II)/H_2O_2 system, the best COD removal efficiency was observed and could reach up to 76.5%. Results illustrated that the EDTA degradation rate can be accelerated by using UV radiation, which suggested that UV was a key factor in the catalytic degradation process.

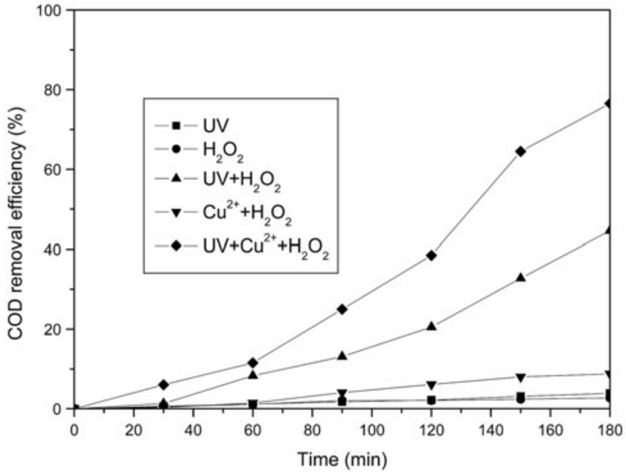

Fig. 1. Degradation efficiency of COD with different processes. Experimental conditions: initial EDTA concentration 5 g/L, H_2O_2 dosage 0.8 M, initial pH 3.0 and $CuSO_4{\cdot}5H_2O$ load 4 g/L.

In the UV/H_2O_2 process, $^{\cdot}OH$ can be produced by reaction (2), which is a strong oxidizing agent. However, $^{\cdot}OH$ can react with H_2O_2 molecules to produce hydroperoxyl radical ($HO_2^{\cdot}$), which is a weaker oxidizing agent [26]. Therefore, less $^{\cdot}OH$ was available for oxidation of the organic contaminants. However, the participation of the copper ions could improve the situation. In detail, Cu^{2+} could react with $HO_2^{\cdot}$·to form Cu^{+}, which could react with H_2O_2 to form $^{\cdot}OH$ (reactions 4 and 5) [27]. The kinetics of the UV/Cu (II)/H_2O_2 process was consistent with the following chain mechanism of the photocatalytic decomposition of H_2O_2 [28]:

$$H_2O_2 + UV \rightarrow 2^{\cdot}OH \tag{2}$$

$$^{\cdot}OH + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \tag{3}$$

$$HO_2^{\cdot} + Cu^{2+} \rightarrow Cu^{+} + O_2 + H^{+} \tag{4}$$

$$Cu^{+} + H_2O_2 \rightarrow Cu^{2+} + OH^{-} +^{\cdot} OH \tag{5}$$

Therefore, it is believed that $^{\cdot}OH$ was generated by the UV/Cu(II)/H_2O_2 process, and thus, the EDTA was oxidized by this strong oxidizing agent.

3.2. Effect of H_2O_2 dosage

The effects of H_2O_2 dosage on the oxidation of EDTA have been investigated. Experiments were carried out using different concentrations of H_2O_2 (0.2, 0.4, 0.8, 1.2 and 1.6 M), and the results are shown in Fig. 2. The degradation efficiency of EDTA increased with increasing H_2O_2 concentration. However, when H_2O_2 increased beyond a certain value of 1.2 M, the degradation efficiency increased insignificantly. At lower concentration, H_2O_2 could not generate enough ·OH and the oxidation rate was limited. With the increase of H_2O_2, the reaction rate was elevated as

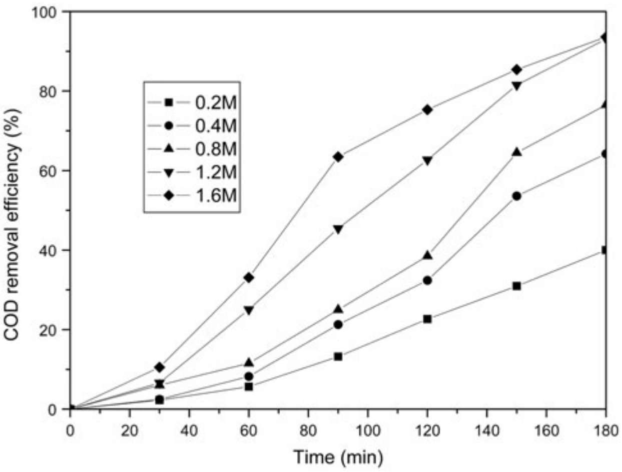

Fig. 2. Influence of H_2O_2 dosage on the degradation efficiency of COD. Experimental conditions: initial EDTA concentration 5 g/L, initial pH 3.0 and $CuSO_4{\cdot}5H_2O$ load 4 g/L.

more OH was formed. However, at higher H_2O_2 concentration, the OH scavenging effect occurred significantly [29]. According to the results, 1.2 M H_2O_2 is the best choice to deal with 5 g/L EDTA solution at initial pH of 3.0 and $CuSO_4{\cdot}5H_2O$ of 4 g/L. 93.1% of COD removal efficiency was achieved in 180 min.

3.3. Effect of Cu^{2+} dosage

The effect of Cu^{2+} was studied using different doses of $CuSO_4{\cdot}5H_2O$ from 2 to 8 g/L with a fixed dose of 0.8 M H_2O_2 (30%, w/v), and the results are shown in Fig. 3. The results indicated that the degradation efficiency of EDTA was significantly influenced by the dosage of Cu^{2+}. With increasing Cu^{2+} dose, COD degradation rate was also increased and the highest rate was achieved at the dosage of 6 g/L $CuSO_4{\cdot}5H_2O$. The reason is that the increase in Cu^{2+} dosage as catalyst can promote more ·OH generation, and thus elevates the degradation efficiency. However, higher copper concentrations (such as 8 g/L $CuSO_4{\cdot}5H_2O$) were found to lead to lower degradation rates. This was in agreement with the results reported in the literature [30]. The possible reason was that higher concentration of Cu^{2+} would increase color degree of the system, and thus decrease light UV penetration in the solution [31].

3.4. Effect of initial pH

To investigate the effect of the initial pH of solution, the experiments in the pH ranging from 2.0 to 11.0 were carried out. Fig. 4(b) indicated that the process was more efficient in the initial pH of 3.0.

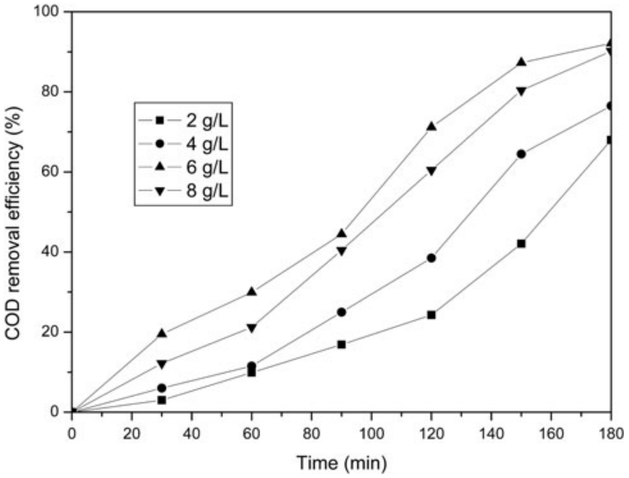

Fig. 3. Influence of $CuSO_4{\cdot}5H_2O$ dosage on the degradation efficiency of COD. Experimental conditions: initial EDTA concentration 5 g/L, H_2O_2 dosage 0.8 M and initial pH 3.0.

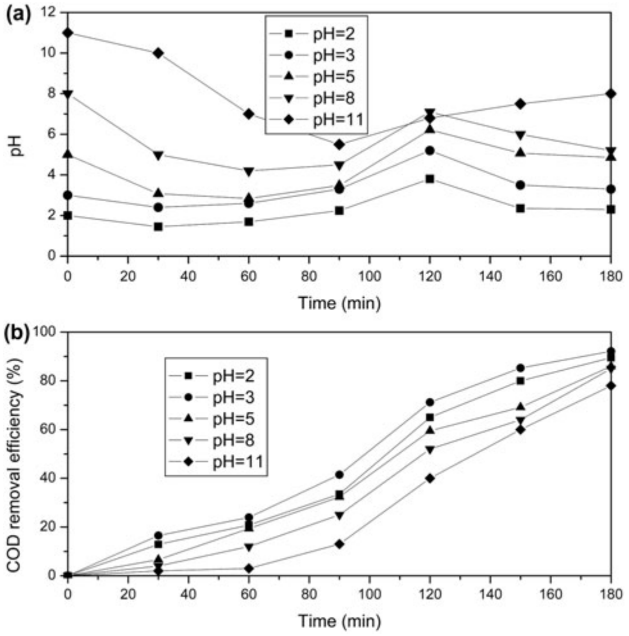

Fig. 4. Changes in the pH for its different initial values (a), and the influence of the initial pH on the degradation efficiency of COD (b). Experimental conditions: initial EDTA concentration 5 g/L, H_2O_2 dosage 0.8 M and $CuSO_4{\cdot}5H_2O$ load 4 g/L.

Under extreme acidic conditions (e.g. pH=2.0), the slower generation of OH from H_2O_2 decomposition lowered the oxidation rates. On the other hand, extreme alkaline conditions (e.g. pH=11.0) also resulted in the drop of oxidation rates. There may be two reasons: firstly, the self-decomposition rate of H_2O_2 (Eq. (6)) increased significantly with increasing solution pH [32]. Secondly, the formation of cupric hydroxide complexes led to a reduction of copper catalytic activity. Even when the initial pH was up to 8, 80% of COD removal could be achieved at the reaction time of 180 min.

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (6)$$

In addition, Fig. 4(a) showed that, pH dropped rapidly in the early stages of the oxidation process. The results can be explained by the formed acidic intermediates, such as EDDA, IDA, and oxalic acid. As further degradation of the acidic intermediates occurred, pH was gradually increased in the later stages of the oxidation process.

3.5. Effect of initial EDTA concentration

The effect of various initial EDTA concentrations on COD removal efficiency has been investigated. Fig. 5 indicated that with the increasing initial concentration of EDTA from 1 to 7 g/L, the COD removal efficiency decreased from 94.61 to 50.10% at the time of 180 min. At higher initial EDTA concentration, with constant photons entering into the solution, the relative concentration of ·OH was lowered, which consequently led to a decreased COD removal efficiency [33].

3.6. Treatment of copper-plating wastewater

Many previous researches have shown the degradation reactions with only synthesized EDTA wastewater, but few researches were demonstrated reactions of real wastewater. The real copper-plating wastewater COD removal was compared by four different pH UV/H_2O_2 processes: 2.0 (original value), 3.0, 8.0, and 11.0, which are catalyzed by the copper ions existing in the wastewater. As in the degradation of the synthesized EDTA, the best COD removal was found in the initial pH 3.0. The result was shown in Fig. 6(b). However, for the treatment of the real wastewater, the similar COD removal efficiency was obtained at the initial pH 2.0 and 3.0. The understandable reason could be easily found from the pH changes during the COD degradation process (Fig. 6 (a)). It shows that, regardless of the initial pH 2.0 or 3.0, the pHs of the solutions both changed in the range of 2.0–3.5 during the treatment process. According to the results, the UV/Cu(II)/H_2O_2 process can effectively remove organic auxiliary chemicals simultaneously contained in the copper-plating wastewater. At the reaction condition of original pH 2.0, H_2O_2 0.6 M, copper 1.4 g/L (existing in the wastewater itself), 98.6% of COD removal was obtained in 180 min. In addition to the removal of organic matter, copper complexes were decomposed to form free copper ions, which were beneficial to the subsequent copper removal.

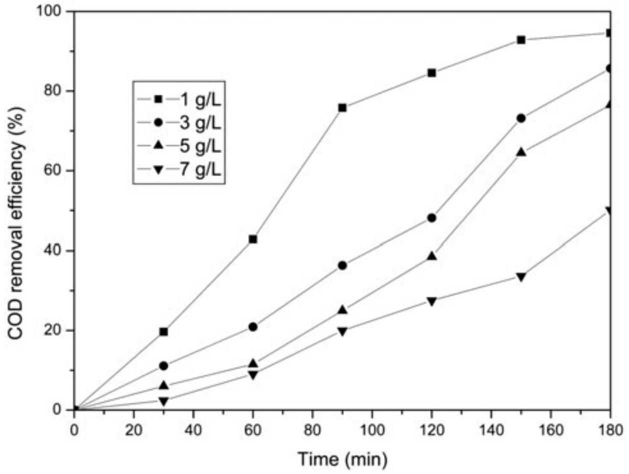

Fig. 5. Influence of initial EDTA concentration on the degradation efficiency of COD. Experimental conditions: H_2O_2 dosage 0.8 M, initial pH 3.0 and $CuSO_4{\cdot}5H_2O$ load 4 g/L.

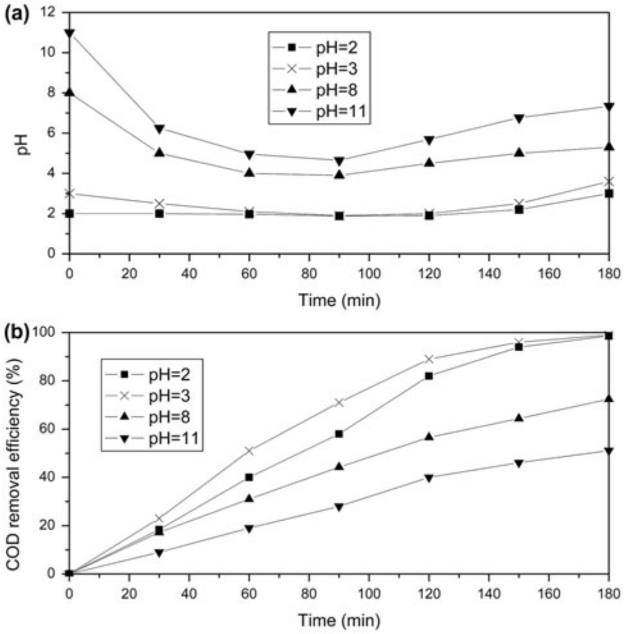

Fig. 6. Treatment of real-copper plating wastewater with UV/Cu(II)/H_2O_2 process at four different pHs. Experimental conditions: COD = 3,660 mg/L, H_2O_2 dosage 0.6 M and self-contained copper 1.4 g/L.

4. Conclusions

The UV/Cu(II)/H_2O_2 process can be used as an efficient method for the degradation of EDTA and its intermediate decomposition products, revealed by COD removal. The initial pH, initial H_2O_2, and Cu^{2+} dosage significantly influenced the degradation process. It was found that the process was more efficient in the initial pH of 3.0 and either too low (such as 2.0) or too high (such as 11.0) pH would lower the COD removal efficiency. When the initial EDTA concentration was 5 g/L, 93.1% of COD removal efficiency was achieved within 180 min with 1.2 M H_2O_2 and 4 g/L $CuSO_4{\cdot}5H_2O$ at the initial pH of 3.0. When treating real copper-plating wastewater, catalyzed by copper ions existing in the wastewater (1.4 g/L), 98.6% of COD removal was obtained in 180 min. In addition to the removal of organic matter, copper complexes were decomposed to form easily removed free copper ions. This study shows that UV/Cu(II)/H_2O_2 process is not only a powerful treatment method for COD removal of EDTA wastewater, but also an environmental friendly treatment method for copper-containing organic wastewater.

Acknowledgments

This study was supported by Grant 51178135 from the National Natural Science Foundation (P.R. China). The authors also extend thanks to the reviewers for constructive criticisms of an earlier version of this manuscript.

References

[1] P.J.M. Bergers, A.C. DE Groot, The analysis of EDTA in water by HPLC, Water Res. 28 (1994) 639–642.

[2] J. Cleveland, T. Rees, Characterization of plutonium in Maxey Flats radioactive trench leachates, Science 212 (1981) 1506–1509.

[3] J.L. Means, D.A. Crerar, J.O. Duguid, Migration of radioactive wastes: radionuclide mobilization by complexing agents, Science 200 (1978) 1477–1481.

[4] M.L. Hinck, J. Ferguson, J. Puhaakka, Resistance of EDTA and DTPA to aerobic biodegradation, Water Sci. Technol. 35 (1997) 25–31.

[5] S. Schullerer, H.J. Brauch, Oxidative und adsorptive Behandlung EDTA-und NTA-haltiger Wasser, Vom Wasser, 72 (1989) 23–29.

[6] E. Gilbert, S. Hoffmann-Glewe, Ozonation of EDTA in aqueous solution, influence of pH value and metal ions, Water Res. 24 (1990) 39–44.

[7] S. Chitra, K. Paramasivan, P.K. Sinha, K.B. La, Ultrasonic treatment of liquid waste containing EDTA, J. Clean. Prod. 12 (2004) 429–435.

[8] S. Balaji, V.V. Kokovkin, S.J. Chung, I.S. Moon, Destruction of EDTA by mediated electrochemical oxidation process: monitoring by continuous CO_2 measurements, Water Res. 41 (2007) 1423–1432.

[9] J. Yang, X. Hu, J. Zhang, Voltammetric monitoring photodegradation of EDTA based on carbon nanotubes-modified electrode, J. Hazard. Mater. 181 (2010) 742–746.

[10] T.H. Madden, A.K. Datye, M. Fulton, Oxidation of metal-EDTA complexes by TiO_2 photocatalysis, Environ. Sci. Technol. 31 (1997) 3475–3481.

[11] C. Baeza, A. Rossner, W.F. Jardim, M.I. Litter, H.D. Mansilla, Removal of EDTA by UV-C/hydrogen peroxide, Environ. Technol. 24 (2003) 1277–1281.

[12] Y. Ku, L.S. Wang, Y.S. Shen, Decomposition of EDTA in aqueous solution by UV/H_2O_2 process, J. Hazard. Mater. 60 (1998) 41–55.

[13] A.A.A. El-Raady, T. Nakajima, P. Kimchhayarasy, Catalytic ozonation of citric acid by metallic ions in aqueous solution, Ozone: Sci. Eng. 27 (2005) 495–498.

[14] F. Arena, R. Giovenco, T. Torre, A. Venuto, A. Parmaliana, Activity and resistance to leaching of Cu-based catalysts in the wet oxidation of phenol, Appl. Catal. B: Environ. 45 (2003) 51–62.

[15] S.T. Kolaczkowski, P. Plucinski, F.J. Beltran, F.J. Rivas, D.B. McLurgh, Wet air oxidation: a review of process technologies and aspects in reactor design, Chem. Eng. J. 73 (1999) 143–160.

[16] A. Santos, E. Barroso, F. Garc´ıa-Ochoa, Overall rate of aqueous-phase catalytic oxidation of phenol: pH and catalyst loading influences, Catal. Today 48 (1999) 109–117.

[17] A. Rodríguez, G. Ovejero, M. Mestanza, V. Callejo, J. García, Degradation of methylene blue by catalytic wet air oxidation with Fe and Cu catalyst supported on multiwalled carbon nanotubes, Chem. Eng. 17 (2009) 145–150.

[18] S. Caudo, G. Centi, C. Genovese, S. Perathoner, Copper- and iron-pillared clay catalysts for the WHPCO of model and real wastewater streams from olive oil milling production, Appl. Catal. B: Environ. 70 (2007) 437–446.

[19] T. Granato, A. Katovic, K.M. Valkaj, A. Tagarelli, G. Giordano, Cu-silicalite-1 catalyst for the wet hydrogen peroxide oxidation of phenol, J. Porous Mater. 16 (2009) 227–232.

[20] J.K. Kim, I.S. Metcalfe, Investigation of the generation of hydroxyl radicals and their oxidative role in the presence of heterogeneous copper catalysts, Chemosphere 69 (2007) 689–696.

[21] M.R. Maurya, S. Sikarwar, Oxidation of phenol and hydroquinone catalysed by copper (II) and oxovanadium (IV) complexes of N,N´-bis(salicyledene) diethylenetriamine (H2 saldien) covalently bonded to chloromethylated polystyrene, J. Mol. Catal. A: Chem. 263 (2007) 175–185.

[22] J.K. Yang, A.P. Davis, Photocatalytic oxidation of Cu(II)–EDTA with illuminated TiO_2: mechanisms, Environ. Sci. Technol. 34 (2000) 3796–3801.

[23] P.A. Babay, C.A. Emilio, R.E. Ferreyra, E.A. Gautier, R.T. Gettar, M.I. Litter, Kinetics and mechanisms of EDTA photocatalytic degradation with TiO_2, Oxidation technologies for water and wastewater treatment (II), Water Sci. Technol. 44 (2001) 179–185.

[24] C.A. Emilio, M.I. Litter, J.F. Magallanes, Semiempirical modeling for the photocatalytic reaction of EDTA over TiO_2 applying artificial neural networks, Helvetica Chim. Acta 84 (2001) 799–813.

[25] P.W. Wild, Modern Analysis for Electroplating, Fin. Pub., 1974, pp. 324–328.

[26] Y. Zhang, D.L. Li, Y. Chen, X.H. Wang, S.G. Wang, Catalytic wet air oxidation of dye pollutants by polyoxomolybdate nanotubes under room condition, Appl. Catal. B 86 (2009) 82–189.

[27] J.H. Baxendale, J.A. Wilson, The photolysis of hydrogen peroxide at high light intensities, Trans. Faraday Soc. 53 (1957) 344–356.

[28] O.N. Temkin, Homogeneous Catalysis with Metal Complexes: Kinetic Aspects and Mechanisms, John Wiley & Sons, Chichester, 2012, 518–519.

[29] S. Haji, B. Benstaali, N. Al-Bastaki, Degradation of methyl orange by UV/H_2O_2 advanced oxidation process, Chem. Eng. J. 168 (2011) 134–139.

[30] E.C. Butler, A.P. Davis, Photocatalytic oxidation in aqueous titanium dioxide suspensions: the influence of dissolved transition metals, J. Photochem. Photobiol. A: Chem. 70 (1993) 273–283.

[31] A. Doongr, W.H. Chang, Photodegradation of parathion in aqueous titanium dioxide and zero-valent iron solution in the presence of hydrogen peroxide, J. Photochem. Photobiol. A: Chem. 116 (1998) 221–228.

[32] B.F. Abramović, N.D. Banić, D.V. Šojić, Degradation of thiacloprid in aqueous solution by UV and UV/H_2O_2 treatments, Chemosphere 81 (2010) 14–119.

[33] S.P. Sun, C.J. Li, J.H. Sun, S.H. Shi, M.H. Fan, Q. Zhou, Decolorization of an azo dye orange G in aqueous solution by Fenton oxidation process: effect of system parameters and kinetics study, J. Hazard. Mater. 161 (2009) 1052–1057.