Desalination and Water Treatment
www.deswater.com

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doi: 10.1080/19443994.2012.693651

51 (2013) 495–502
January

Taylor & Francis
Taylor & Francis Group

Synergistic effects of chromium(VI) reduction/EDTA oxidization for PCB wastewater by photocatalysis combining ionic exchange membrane processes

Hung-Te Hsu[a], Shiao-Shing Chen[a,*], Wen-Shing Chang[a], Chi-Wang Li[b]

[a]*Institute of Environmental Engineering and Management, National Taipei University of Technology, No. 1, Sec. 3, Chung-Hsiao E. Rd., Taipei 106, Taiwan*
Email: f10919@ntut.edu.tw
[b]*Department of Water Resources and Environmental Engineering, Tamkang University, 151 Ying-Chuan Road, Tamsui District 25137, New Taipei City, Taiwan*

Received 30 March 2012; Accepted 10 May 2012

ABSTRACT

A new technology using the TiO_2 photocatalysis combining electrodialysis was proposed for the simultaneous oxidization of ethylenediaminetetraacetic acid (EDTA)/reduction of hexavalent chromium (Cr(VI)) by electron–hole (e^-–h^+) pairs. The application of a cationic exchange membrane in this system was used to enhance the efficiency for the prevention of the recombination of electrons with the electron hole. The following parameters were studied: current density, pH, hydraulic detention time (HRT), EDTA/Cr(VI) molar ratio, and oxygen contents (aerated by argon, air, and oxygen). The result showed that the optimum removal efficiency was observed at 4.0 mA/cm^2 and higher removal efficiencies were observed at a lower pH due to electrostatic attractions between the positively charged Ti–OH_2^+, and the negatively charged Cr(VI) and EDTA. A higher EDTA/Cr(VI) molar ratio enhanced the removal efficiency of Cr(VI) in the photocatalytic system, indicating that EDTA plays the role of a hole scavenger in the system. In addition, the removal efficiency of Cr(VI) was better for the system aerated with argon than those systems aerated with oxygen and air, since a lower direct oxygen or oxygen reduction potential (ORP) favors the reduction of Cr(VI). Moreover, an incomplete EDTA mineralization contributes to the occurrence of intermediates, including iminodiacetic acid, nitrilotriacetic acid, glyoxylic acid, glycine, oxalic acid, acetic acid, and formic acid, as identified by the GC/MS.

Keywords: Chromium; EDTA; Ionic exchange membrane; Photocatalysis; TiO_2

1. Introduction

Hexavalent chromium (Cr(VI)) is a carcinogenic and mutagenic pollutant, which greatly affects our environment due to its acute toxicity and high mobility in water. It is frequently found in wastewaters emanating from various industrial processes such as electroplating, leather tanning, paint making, printed circuit board (PCB) manufacturing, and others [1–3]. Chemical reduction, activated carbon adsorption, ion exchange, membrane separation, and UV light photo-

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*Corresponding author.

Presented at the International Conference on Desalination for the Environment, Clean Water and Energy, European Desalination Society, 23–26 April 2012, Barcelona, Spain

catalysis are the most common methods that are usually adopted for the disposal or the recovery of Cr(VI) for wastewater; but all these methods have their own advantages and disadvantages [4–8]. Ethylenediaminetetraacetic acid (EDTA) is a chelating agent that has been extensively used to enhance the solubilization of heavy metals during the production process involved in the making of detergents, photography, pulp and paper, agrochemicals, and the PCB industry; but the release of EDTA contributes to serious environmental problems, such as insolubility of a metal ion causing a high concentration of the metal in the solution to exceed the limit set for discharge regulation. As there are no regulations framed for the use of EDTA in most of the countries, typically no tailor-made treatment was applied in any of the above-mentioned industries. Quite a few researches have been conducted on a laboratory scale, and technologies such as Fenton, ozone, and H_2O_2 are some of the most popular methods [9–13]. Although Fenton, ozone and H_2O_2 are all effective, it is not feasible to apply them in small-scale industries. The reason for their nonuse can be attributed to the fact that they are strong oxidizing agents, which will require extra effort for transportation, storage, and safety issue. Since the titanium dioxide photocatalytic process has the synergic abilities of oxidizing/reducing pollutants simultaneously, a new technology of photocatalysis combining electrodialysis (ED) is proposed for the simultaneous oxidization of EDTA/reduction of Cr(VI) in the present research work. In the above-mentioned designed photocatalysis combining cationic exchange membrane (CEM) process, the energy consumption is low and no chemical reaction is altered, but higher treatment efficiencies of the contaminants could be achieved.

Using the oxidation/reduction capability, the TiO_2 removes the organic contaminants from the electric-hole pairs (e^-–h^+) of TiO_2 [8,14–16]. Theoretically, the UV light excited the electron-hole pairs to form a hole (h^+) on the surface and releases the electron (e^-) to the bulk solution. Consequently, TiO_2 can not only oxidize the pollutants with electric-hole pairs, but can also reduce the contaminants with the electrons. However, due to the charge-balance theory, it was very much possible for the negatively charged electron (e^-) to be very much present on the TiO_2 surface and recombine with the electron-hole pairs instead of reacting with the oxidizing pollutants. The application of ionic exchange membrane is able to enhance the oxidation/reduction efficiency for the prevention of the recombination of electrons with an electron hole.

The UV/DP-25 TiO_2 photocatalysis was investigated for environmental decontamination covering the oxidation of organic compounds and the reduction of metal ions [17–23]. When Cr(VI) is photocatalytically reduced alone, the reduction of Cr(VI) to Cr (III) proceeds slowly, but the addition of organic donors were demonstrated to act as hole scavengers on the TiO_2 surface to accelerate the Cr(VI) reduction in photocatalytic systems [18,20,24]. For example, Lee et al. [18] used illuminated DP-25 TiO_2 to treat wastewater containing both Cr(VI) and phenol, and Schrank et al. [20] reported that photo-induced Cr (VI) reduction and dye oxidation were observed in dye/Cr(VI)/DP-25 TiO_2 under UV irradiation. Both of them showed that the photoreduction of Cr(VI) and photodegradation of organic compound processed more rapidly in the mixture system than in the single-component system, due to the synergistic effect between the photocatalytic reduction of Cr(VI) and the photocatalytic oxidation of the organic compounds [23]. However, none of the researches had reported on the simultaneous removal of Cr(VI) and EDTA, two common pollutants from the PCB industry. Few studies have been reported on the EDTA removal in a low pH electroplating wastewater using the photocatalytic process. Seshadri et al. [25] reported that 95% of EDTA was removed by Degussa P-25 with UV after a 1-h reaction time and a complete removal of the EDTA was achieved after a 2.5-h reaction time with an initial pH of 4.4. The effects of loading H_2O_2 and TiO_2 were found to be crucial due to the impact on the production of hydroxyl radicals. Moreover, different processes contributed to different byproducts of the EDTA. Propoionic acid and iminodiacetic acid were observed in two studies [26,27]; but some disagreements were found where glyoxylic acid and formaldehyde were seen in one study [27], but oxalic acid was observed in the other [26].

In the present work, a new method to enhance the efficiency is also analyzed by placing an ionic exchange membrane with an electric field to prevent the re-oxidation of Cr(III) to Cr(VI) by the holes or oxygen containing radical species during the photocatalytic process. Since the ED is a membrane separation technique where ions are transported through ionic exchange membranes from one solution to another using an electric field as the driving force, the applied electric field can produce the transport of the cation, i.e. Cr(III), through the ionic exchange membrane toward the cathode. Therefore, the purpose of the CEM is to separate and prevent the recombination of the Cr(III) and holes, and the objectives of this study were to investigate: (1) effects of ionic exchange membrane and current density, (2) pH, HRT, EDTA/Cr(VI) molar ratio, and oxygen contents, and (3) mechanism of the TiO_2/Cr(VI)/ EDTA reaction.

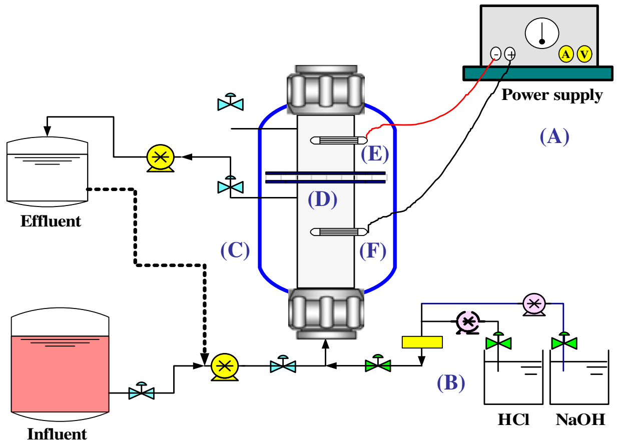

Fig. 1. Schematic diagram showing the photocatalytic reaction combining ionic exchange membrane processes: (A) DC power supply, (B) pH controller, (C) photocatalytic reactor, (D) CEM, (E) cathode and (F) anode.

2. Methods and materials

Fig. 1 is a schematic setup of the experimental system. The photocatalytic reactor system with membrane electrolysis was carried out in two compartments with the platinum placed in the cathode and anode. The application of the CEM is to separate the Cr(III), which was reduced from Cr(VI). The CEM used in this study is the Neosepta CMX membrane with an effective area of 50.2 cm^2, which was purchased from the Tokuyama Corporation . The physicochemical and electrochemical properties are presented in Table 1. Moreover, all the experiments were carried out at a constant applied cell voltage using the constant DC power supply (model GPC-3030D), while the current and cell voltage were recorded with a digital recorder. Under the electrical driving force, the reductive chromium or Cr(III) crossed the CEM toward the cathode. All photocatalytic reactions were conducted in a photocatalytic reactor system containing a Pyrex glass column with a diameter of 80 mm and a length of 300 mm, positioned parallel to the UV lamp. These black blue fluorescent UV lamps (wavelength of 253.7 nm), each with 8 W maximum output, were used as the UV light sources with an overall light intensity of 2.5 W/m^2. Degussa DP-25 TiO_2 with a dosage of 1 g/L was used throughout the study as it was tested in our previous study for this system [28]. A circulation pump was installed for maintaining the upflow velocity to fluidize the photocatalyst. The hydraulic detention time (HRT) was controlled by the flowrate of the influent and effluent pumps. Meanwhile, the system pH was controlled by a glass electrode and a pH controller, which controls the dosing of 1 M hydrochloric acid or sodium hydroxide. A cooling fan was also installed in the reactor to maintain the experimental temperature at 25.0 ± 1°C.

The present was research carried out in a fixed influent concentration of Cr(VI) of 0.01 mol. The following parameters were studied: current density (3, 4, 5, and 6 mA/cm^2), pH (2, 3, 7, and 10), HRT (1, 1.5, 2.5, 4, and 5 h), EDTA/Cr(VI) molar ratio (0, 0.5, 1, 2, 4, and 8), and oxygen contents (aerated by argon, air, and oxygen). The suspended particle was used in the photoreaction experiments. All the chemicals, including chloride ammonia, potassium dichromate, EDTA, hydrochloric acid and sodium hydroxide, were of analytical grade. Aqueous solutions were prepared with analytical grade Milli-Q water (Millipore). The total chromium concentration was measured by a flame atomic adsorption spectroscope (GBC 932, GBC Scientific Equipment, Australia), and hexavalent chromium was measured colorimetrically according to the methods 3,500-Cr listed in the 20th edition of the Standard Methods [29] using a UV-Vis spectrophotometer (HACH Model DR-4000). Trivalent chromium was calculated by deducting the hexavalent chromium from the total chromium. The EDTA concentration was analyzed using the high-performance liquid chromatography system with a 250 × 4.6 mm^2 model BDS C18 (5 μm) column (Thermo Hypersil-Keystone, Bellefonte, PA, USA). The total organic carbon (TOC) was measured using the Aurora 1030C TOC Analyzer purchased from the O.I. Analytical Corporation in the USA. The EDTA byproducts were measured by gas chromatography/mass spectrometry (GC/MS) equipped with a DB-5 column by the GC model Agilent 6890 N and the MS model Agilent 5973 N, respectively.

3. Results and discussion

3.1. Effect of the CEM and current density

Fig. 2 presents a comparison of removal efficiency for the (a) reduction of Cr(VI) and (b) oxidation of

Table 1
The properties of a cation-exchange membrane

Membrane	Type	Thickness (mm)	Ion-exchange capacity (meq/g of dry membrane)	Water content (%)
CMX	Strongly acidic	0.35	1.62	23

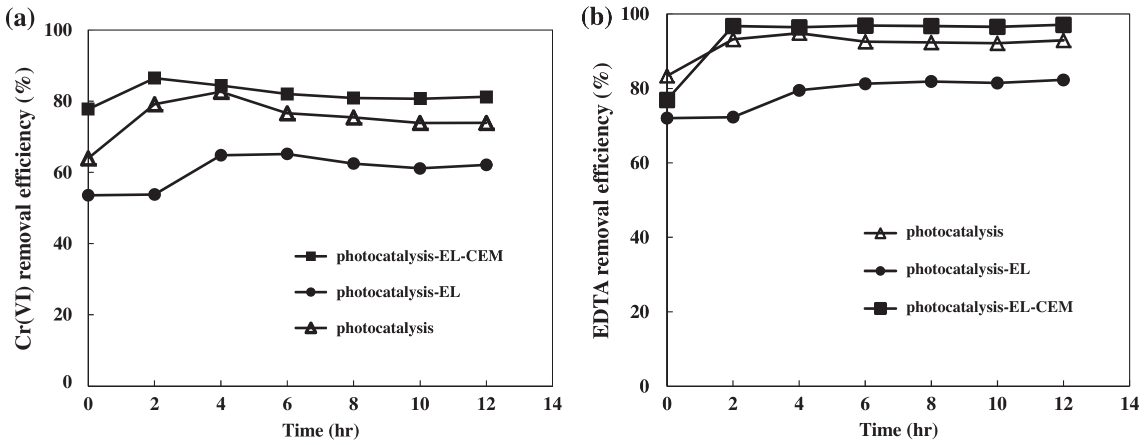

Fig. 2. A comparison of the removal efficiencies for the (a) reduction of Cr(VI) and (b) oxidation of EDTA with TiO_2 under UV irradiation with photocatalysis only, photocatalysis with electrolysis but without CEM (denoted as EL) and photocatalysis with CEM (denoted as EL-CEM) (Cr(VI) = 0.001 M, EDTA = 0.001 M, pH = 3.0, HRT = 4.0 h, with the aeration by air. Current density higher = 4.0 mA/cm^2 for EL and EL-CEM).

EDTA with TiO_2 under UV irradiation with photocatalysis only, photocatalysis with electrolysis but without CEM (denoted as EL) and photocatalysis with CEM (denoted as EL-CEM) for both Cr(VI) and EDTA = 0.001 M, pH = 3.0, HRT = 4.0 h with the aeration of air. The results show, with a current density of 4.0 mA/cm^2, removal efficiencies of about 20% higher were observed for both Cr(VI) and EDTA by photocatalysis in the presence of CEM. The application of the CEM is obviously effective for the separation of Cr(III) to prevent the re-oxidation of Cr(III) back to Cr(VI) by holes and various oxygen containing radical species during the photocatalytic process. Furthermore, since the applied electric field produced the transport of the Cr(III) toward the cathode, the enhanced efficiencies by providing the ED system for different current densities (3.0, 3.5, 4.0, 5.0, and 6.0 mA/cm^2) on the reduction of Cr(VI) and oxidation of EDTA were also investigated, as shown in Fig. 3. For Cr(VI), when the current density was controlled at 3.0 mA/cm^2, enhanced efficiency for the oxidation of EDTA was 24%. The enhanced efficiency was increased to 27% for a current density of 4.0 mA/cm^2 and leveled off for a current density higher than 4.0 mA/cm^2, due to less current efficiency observed at a higher current density. It was proven by observing the gases (O_2 and H_2) that are generated at the anode and the cathode during the experiment for a higher current density. Besides, at a higher current density, the more hydrogen ions are transferred through the CEM together with the Cr (III), which increases the pH and reduces the capacity of TiO_2 in the anode compartment. Therefore, as shown in the figures, optimization of the current density was 4.0 mA/cm^2 and was carried out throughout the rest of the experiment.

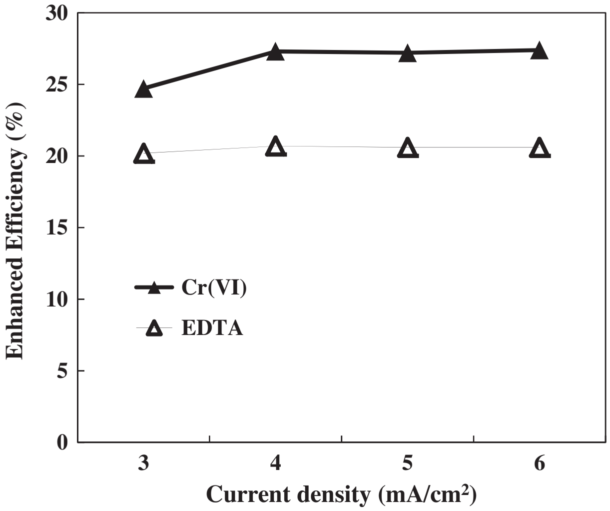

Fig. 3. A comparison of enhanced efficiencies for the (a) reduction of Cr(VI) and (b) oxidation of EDTA with TiO_2 under UV irradiation with the ED system (both Cr(VI) and EDTA = 0.001 M, pH = 3.0, HRT = 4.0 h with the aeration by air).

3.2. *Effects of pH and HRT*

The effect of pH is an important issue as it directly relates to the oxidative power of the EDTA by the photogenerated holes as well as the reduction of Cr(VI) and due to the amphoteric behavior of TiO_2. Fig. 4 present Cr(VI) and EDTA removals with the variation of pH at both Cr(VI) and

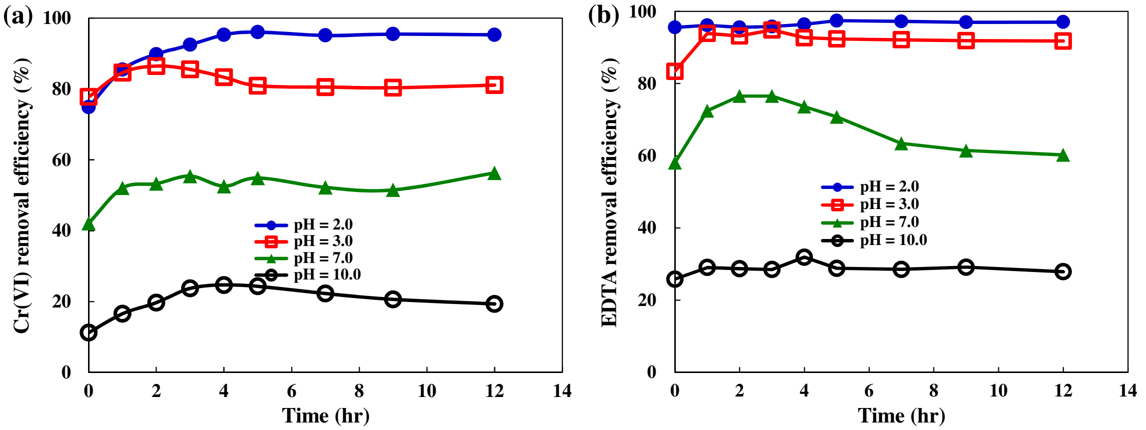

Fig. 4. A comparison of the removals of the (a) reduction of Cr(VI) and (b) oxidation of EDTA for different pHs with TiO_2 under UV irradiation with the ED system (both Cr(VI) and EDTA = 0.001 M, HRT = 4.0 h with the aeration by air).

EDTA = 0.001 M, and HRT = 4.0 h with the aeration of air. The results in Fig. 4 shows that the Cr(VI) removal efficiency increased from 25% for pH 10 to about 95% for pH 2, and the results in Fig. 4 show that the EDTA removal efficiency increased from 20% for pH 10 to about 94% for pH 2. The results were explained by the amphoteric behavior of the semiconductor oxides, i.e. TiO_2, affecting the surface charge of the photocatalyst. Since the pH value of a zero point charge (pHzpc) of TiO_2 (as Ti–OH) particles is equal to around 6.8, according to Eqs. (1) and (2), the TiO_2 surface charge becomes positively charged Ti–OH_2^+ when the pH is lower than 6.8 and becomes negatively charged Ti–O^- when the pH is higher than 6.8 [30]. Since the EDTA has $pK_1 = 1.99$, $pK_2 = 2.67$, $pK_3 = 6.16$ and $pK_4 = 10.26$, and $HCrO_4^-$ has pKa of 6.5, under basic conditions, electrostatic repulsions occurred between the negatively charged Ti–O^- and Cr(VI)(in the form of CrO_4^{-2}) and EDTA (in the form of $HEDTA^{3-}$ or $EDTA^{4-}$), resulting in a lower efficiency. Conversely, under acidic conditions, the electrostatic attractions happened between the positively charged Ti-OH_2^+ and the negatively charged Cr(VI) (in the form of $HCrO_4^-$) and EDTA (in the form of H_2EDTA^{2-} or H_3EDTA^-). Therefore, the removals of Cr(VI) and EDTA were more efficient under lower pH for all the results.

$$\text{Ti–OH} + H^+ \leftrightarrow \text{Ti–}OH_2^+ \quad \text{(Acidic Condition)} \qquad (1)$$

$$\text{Ti–OH} + OH^+ \leftrightarrow \text{Ti–}O^- + H_2O \ \text{(Basic Condition)} \qquad (2)$$

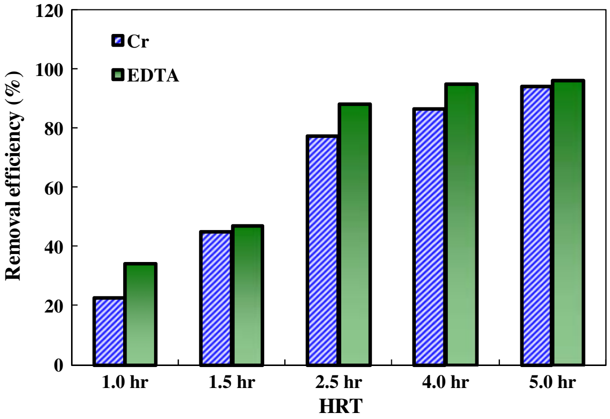

Fig. 5. A comparison of the removals of Cr(VI) and EDTA for different HRTs with TiO_2 under UV irradiation with the ED system (both Cr(VI) and EDTA = 0.001 M, pH = 3.0 with the aeration by air).

Fig. 5 shows the comparison of the removals of Cr (VI) and EDTA for different HRTs with TiO_2 under UV irradiation with the ED system (Cr(VI) = 0.001 M, EDTA = 0.001 M, pH = 3.0 with the aeration by air), since the HRT represents the land space requirement for the photocatalytic reactor. The results indicate that both reduction of Cr(VI) and oxidation of EDTA increased with an increase of HRT, but leveled off around HRT of 4 h, representing an optimum HRT of 4 h.

3.3. Effects of the molar ratio of EDTA/Cr(VI) and dissolved oxygen

Cr(VI) reduction and EDTA oxidation at different EDTA/Cr(VI) molar ratios from 0 to 8 were compared

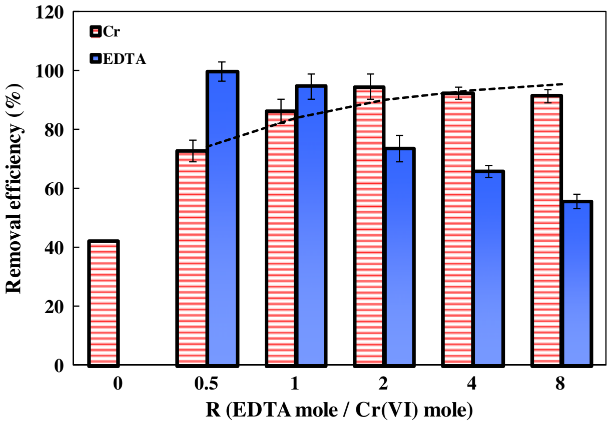

Fig. 6. Effects of the molar ratio of EDTA/Cr(VI) on their removal efficiencies with TiO_2 under UV irradiation with the ED system (pH = 3.0 and HRT = 4.0 h with the aeration by air).

in Fig. 6 for pH = 3.0, HRT = 4.0 h with the aeration of air. When the EDTA was absent, only 40.2% of Cr(VI) was removed. The addition of EDTA to a molar ratio of EDTA/Cr(VI) = 0.5 significantly increased the Cr (VI) reduction, in which EDTA was completely reduced. An almost complete Cr(VI) removal was observed when the molar ratio of EDTA/Cr(VI) increased to 2. This fact could be explained by the oxidation of EDTA consuming photo-excited holes promptly and efficiently to attenuate the electron–hole recombination and promote Cr(VI) reduction on the photocatalyst [30]. As the molar ratio of the EDTA/Cr (VI) increased to higher than 2, the reduction efficiency of Cr(VI) slightly decreased and the reduction efficiency of EDTA was decreased too. It was explained that at a high EDTA concentration, a significant amount of UV could be absorbed and covered by the EDTA molecules rather than the TiO_2 particles, resulting in a lower efficiency of the catalyst due to lower OH concentration radicals [30]. Therefore, increased of the EDTA concentration decreased the efficiency for both Cr(VI) and EDTA removals. Fig. 7 shows the comparison of the removal efficiencies for the (a) reduction of Cr(VI) and (b) oxidation of EDTA with TiO_2 under UV irradiation for different oxygen contents, aerated by argon, air and oxygen, respectively (both Cr(VI) and EDTA = 0.001 M, pH = 3.0, HRT = 4.0 h). The presence of argon enhanced the Cr (VI) reduction due to decrease of ORP to −100 mV instead of around 350 mV for aeration with oxygen

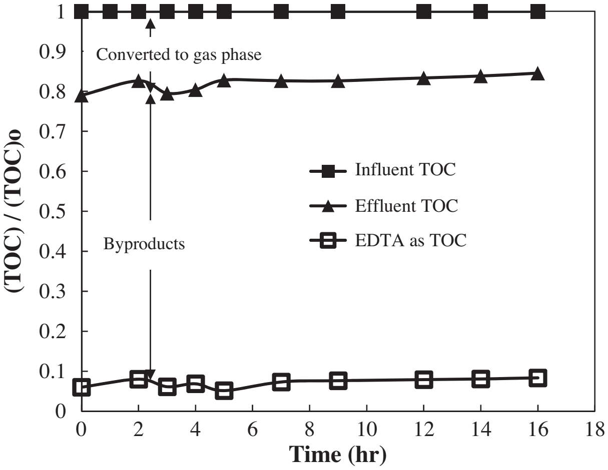

Fig. 8. TOC removal efficiencies for EDTA vs. time for influent, effluent TOC and EDTA as TOC with TiO_2 under UV irradiation (both Cr(VI) and EDTA = 0.001 M, pH = 3.0, HRT = 4.0 h with the aeration by air).

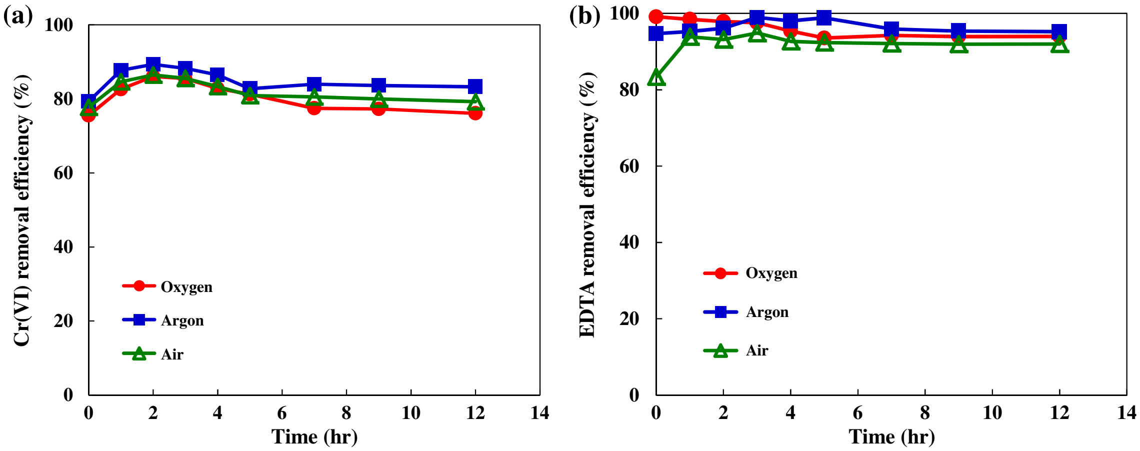

Fig. 7. A comparison of the removal efficiencies for the (a) reduction of Cr(VI) and (b) oxidation of EDTA with TiO_2 under UV irradiation for different oxygen contents, aerated by argon, air and oxygen, respectively (both Cr(VI) and EDTA = 0.001 M, pH = 3.0, HRT = 4.0 h).

and a lower ORP is favorable for the reduction of Cr (VI) [31,32].

3.4. Mechanism for TiO_2/Cr(VI)/EDTA reaction

Fig. 8 presents the TOC removal efficiencies for EDTA vs. time for influent, effluent TOC and EDTA as TOC with TiO_2 under UV irradiation (both Cr(VI) and EDTA = 0.001 M, pH = 3.0, HRT = 4.0 h with the aeration by air). First of all, the difference between influent and effluent TOC was the carbon converted to the gas phase due to complete mineralization. Besides, effluent EDTA was converted to TOC and shown as "EDTA as TOC" since 1 g of EDTA contains 0.415 g of TOC. If the "effluent TOC" and "EDTA as TOC" are exactly the same, then the reduced EDTA was converted to carbon dioxide. If not, then some byproducts were formed. The results show that there are some differences between the two, indicating that byproducts were formed in these experiments. Consequently, the end product after EDTA degradation was analyzed by the GC/MS, where iminodiacetic acid, nitrilotriacetic acid, glyoxylic acid, glycine, oxalic acid, acetic acid, and formic acid were observed.

4. Conclusions

TiO_2 photocatalysis combining ED was successfully used for the simultaneous oxidization of EDTA/ reduction of Cr(VI) by electron-hole (e^-–h^+) pairs. The result showed that the optimum removal efficiency was observed at 4.0 mA/cm^2 and higher removal efficiencies were observed at a lower pH due to the electrostatic attractions between the positively charged Ti-OH_2^+, and the negatively charged Cr(VI) and EDTA. The higher EDTA/Cr(VI) molar ratio enhanced the removal efficiency of Cr(VI) in the photocatalytic system, indicating that the EDTA plays the role of a hole scavenger in the system. In addition, the removal efficiency of Cr(VI) was better for the system aerated with argon than those systems aerated with oxygen and air, since a lower DO or ORP favors the reduction of Cr(VI). Moreover, an incomplete EDTA mineralization contributes to the occurrence of intermediates, including iminodiacetic acid, nitrilotriacetic acid, glyoxylic acid, glycine, oxalic acid, acetic acid, and formic acid, as identified by the GC/MS.

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