

Treatment of *o*-tert-Butyl Phenol Micro-Polluted Water with Electro-Oxidation and Microporous Aeration: Method Development, Performance Evaluation and Mechanism Study

Z. CHEN

Hangzhou No. 2 High School of Zhejiang Province, 76 Dongxin Avenue, Binjiang District, Hangzhou, Zhejiang Province, P.R. China

Corresponding author: Fax: +86 571 88320882; Tel: +86 571 88320881; E-mail: zhichen98@hotmail.com

Received: 30 July 2015;

Accepted: 22 September 2015;

Published online: 3 November 2015;

AJC-17627

This study investigated the treatment of organic micro-pollutants in drinking water using a combination of electro-oxidation and microporous aeration (EOMA) technique. Results indicated that microporous aeration enhanced the turbulence of reaction solution and improved the efficiency of organic contaminant removal two-fold *versus* electro-oxidation alone. *o*-tert-Butyl phenol (OTBP) was used as a representative pollutant. 1600 mL OTBP solution contained 160 mg sodium sulfate and 2 mL 30 % hydrogen peroxide. When the current density was 5 mA cm⁻², 1 and 2 mg L⁻¹ *o*-tert-butyl phenol was removed up to 98.0 and 75.1 %, respectively. The major intermediate products included trimethylacetic acid, succinic acid and other acid. These have much less toxicity than *o*-tert-butyl phenol. After 30 min, the organics were mineralized completely. Electro-oxidation and microporous aeration was applied to actual source water that was contaminated by complicated organics. No toxicity was shown to algae growth after 15 min of treatment and total organic carbon was removed completely after 30 min.

Keywords: Water treatment, Electro-oxidation, Microporous aeration, Organic micro-pollution, Removal mechanism.

INTRODUCTION

Quality water is a very important and basic issue that ensures the safety of urban living. The safety of drinking water is one of the top concerns of all countries. The technologies used to treat drinking water have been developed very fast. New techniques such as using ozone-biological activated carbon for deep treatment have overcome limitations of conventional methods that cannot efficiently remove organic pollutants [1]. However, as more pollution accidents occur, there is a further need to improve the safety of the water supply [2]. Moreover, there have been many reports about the abnormal smell of drinking water in some areas in China in recent years. Many of these were caused by leakage during chemical transportation or illegal industry wastewater discharge. Such pollution accidents cause major damage to the society, environment and economy.

Deep treatment process can only control regular organic pollutants with very limited control of water source contamination. Additional strategies are needed during these incidences. Some usual methods include introducing large amount of activated carbon or chemical pre-oxidation, but all of those methods have pros and cons [3-6]. The efficiency of activated carbon is very limited with poor or no absorbance

for certain organic pollutants. The addition of large amounts of carbon also requires long processing times. Pre-oxidation usually involves using chemicals such as potassium permanganate or chlorine oxidation and ozone—these chemicals can lead to other problems. Potassium permanganate-based oxidation is weak and overdoses of potassium permanganate can cause colour changes and manganese contamination. For chlorine oxidation, chlorine reacts with organic matter in water and produce large amounts of harmful chlorination byproducts. Though ozone is a strong oxidant and can oxidize most organic materials, it is difficult to store and transport. Thus, it must be prepared on site, which limits its application in many emergencies.

Electro-oxidation can deplete organic contaminant *via* the gain or loss of electrons on an electrode surface. It has been used widely applied for industrial wastewater treatment [7]. Our study was based on the electro-oxidation mechanism, which uses the microporous aeration technique to enhance electro-oxidation for the organic micro-pollutant water. This study investigated the efficiency of this technique to remove *o*-tert-butyl phenol (OTBP) and studied the critical parameters of the method followed by a hypothetical mechanism. The results will be useful for additional applications of microporous aeration that improve electro-oxidation.

EXPERIMENTAL

Fig. 1 shows a device designed in-house combining electro-oxidation and microporous aeration (EOMA). The device consists of a plexiglass reaction tank, a pump and a power supply. The plexiglass reaction tank is divided into two regions—a bottom region was installed with the aeration unit and was connected to the pump by a glass rotameter. The rest of the region was for electrolysis. This was installed with 3 cathode plates and 5 anode plates alternatively. The cathode and anode plates were connected *via* a wire and a power converter. The power converter converts AC power to DC constant output for an electro-oxidation reaction.

Methods

***o*-tert-Butyl phenol (OTBP) electrolysis test:** The efficiency of three different techniques on the removal of OTBP was tested. The OTBP solution (1.6 L; 5 mg L⁻¹) was added with sodium sulfate to a final concentration of 100 mg L⁻¹. This was then mixed with 2 mL 30 % hydrogen peroxide. Three treatment methods were tested: microporous aeration, electro-oxidation and both microporous aeration and electro-oxidation. The OTBP concentration was measured by a high performance liquid chromatography (HPLC) (USA Agilent Technologies, 1200 series).

Multiple experimental conditions were tested for the efficiency of microporous aeration to enhance electro-oxidation in a solution containing 1 mg L⁻¹ OTBP. The variables included the sodium sulfate concentration (50, 100, 150 and 200 mg L⁻¹), aeration rate (2, 3 and 4 L min⁻¹) and the amount of hydrogen peroxide (1.5, 2 and 2.5 mL). The final OTBP concentration was measured *via* HPLC.

The oxidation products after microporous aeration treatment were analyzed further. Electrolysis reaction was performed with a 1 mg/L OTBP solution under optimized experimental conditions obtained in the above optimization tests. A GC-MS (USA Waters, GCT Premier) was employed for the product analysis.

Electrolysis testing on a mixed organic-contaminated water sample: A contaminated water sample was used to make 1 mg L⁻¹ OTBP and 1,4-dichloroethane. The tests were performed with the optimized conditions but with different treatment times. The results were evaluated by measuring the

total organic carbon (TOC) with an analyzer (Shimadzu, TOCVCPH, Japan). A diluting plate count method was used to investigate the method disinfection efficiency. The study also checked the toxicity of a post-processing solution on chlorella to evaluate the ecological safety of the technique.

Analytical method: The key HPLC parameters included a C18 column (4.6 mm × 250 m, 5 μm), column temperature of 25 °C, mobile phase with a methanol-to-water ratio of 85/15 (v/v), flow rate of 1.0 mL/min, detection wavelength of 230 nm and a sample loading volume of 20 μL. GC-MS was used to measure OTBP products *via* SPME-GC/MS sample preparation. The SPME extraction head was CAR/PDMS with extraction and dissociation temperatures of 80 and 250 °C for 15 and 3 min, respectively. Chromatography employed a capillary column DB-5MS (30 m × 0.25 mm × 0.25 μm) and an injection temperature of 250 °C followed by a programmed temperature gradient at 50 °C for 2 min. This was dropped to 10 °C and then increased to 250 °C for 5 min. The ion source temperature was 230 °C, transfer tube was 250 °C and the electron collision energy was 70 eV. The ecological toxicity test used chlorella and was based on algae inhibition test methods from the National Environment Protection Department [8].

RESULTS AND DISCUSSION

Comparison of the three methods: The *o*-tert-butyl phenol (OTBP) solution was treated using the electro-oxidation and microporous aeration (EOMA) device shown in Fig. 1 with an applied current density of 5 mA cm⁻² and an aeration rate of 4 L min⁻¹. The sample was collected at 0, 7.5, 15, 22.5 and 30 min and the test results are shown in Table-1. The efficiency of only the OTBP microporous aeration technique was not clear—only 15 % of the OTBP was removed within 30 min. In comparison, using electro-aeration or microporous aeration assisted electro-aeration showed a much more pronounced change. The latter even showed as much change as twice of the former indicating that the microporous aeration enhanced electro-oxidation. This is because microporous aeration enhanced the reactive fluid turbulence and promoted transfer of material while improving the concentration of the dissolved oxygen [9]. Therefore, the microporous aeration technique can assist the electro-oxidation to remove the organic pollutant.

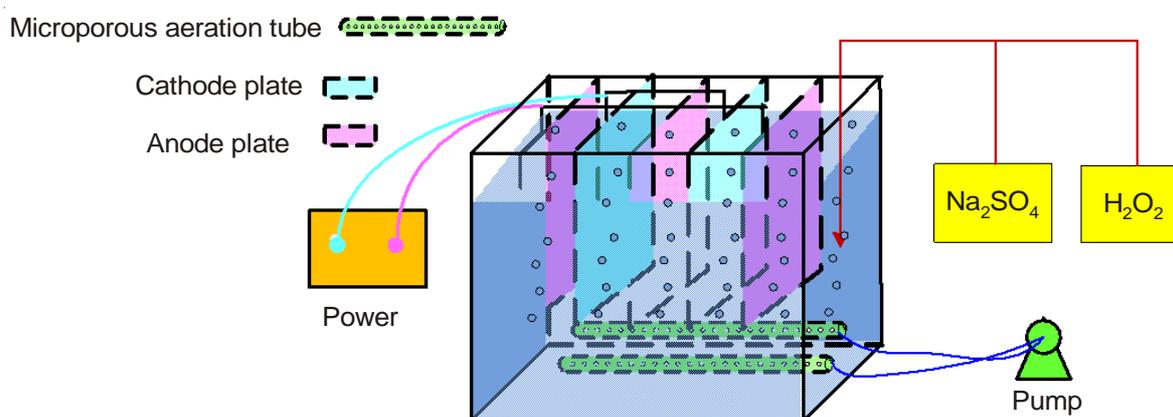


Fig. 1. Diagram of EOMA

Time (min)	MA	EO	EOMA
7.5	4.3	25.4	54.7
15.0	8.9	42.3	85.4
22.5	12.6	75.2	100.0
30.0	15.4	100.0	100.0

MA = Microporous aeration; EO = Electro-oxidation

Factors influencing removal of OTBP with EOMA:

The concentration of organic micro-pollution is typically very low in water and thus the concentration of OTBP was only 1 mg L⁻¹ in these experiments. A single factor method was used to select one experimental condition at a time for testing while keeping all other factors unchanged. HPLC was used for OTBP measurement of a sample at different sampling times.

Effect of sodium sulfate concentration: The current density directly affected the electrolysis during electro-oxidation and the current density was affected by electrolyte concentration. Because the electrolyte concentration in water is low and limited the electrolysis, additional sodium sulfate was added as an electrolyte. According to China's "Standards of Healthy Drinking Water" (GB5749-2006), the sulfate concentration should not exceed 250 mg L⁻¹. Therefore, our study tested 50, 100 and 200 mg L⁻¹ sodium sulfate to not affect water quality. Other parameters remained unchanged (aeration rate 4 L min⁻¹; 2 mL hydrogen peroxide; sampling time of 10 min).

Fig. 2 shows that the removal of OTBP increased significantly as the concentration of sodium sulfate increased from 50 to 100 mg L⁻¹. However, when the sodium concentration was further increased to 150 mg L⁻¹, the removal of OTBP did not change. The removal decreased when the sodium concentration increased to 200 mg L⁻¹. The current density was measured under different sodium sulfate concentrations and was 2.5, 5.0, 9.5 and 15 mA cm⁻². In theory, the increasing current density is in favour of the removal of organic contaminants. But when current density is too high, it may cause an oxygen evolution side reaction that reduces the removal efficiency [7]. This experiment used a microporous aeration technique that promoted the oxygen mass transfer. The oxygen evolution side reaction could occur at an even lower current

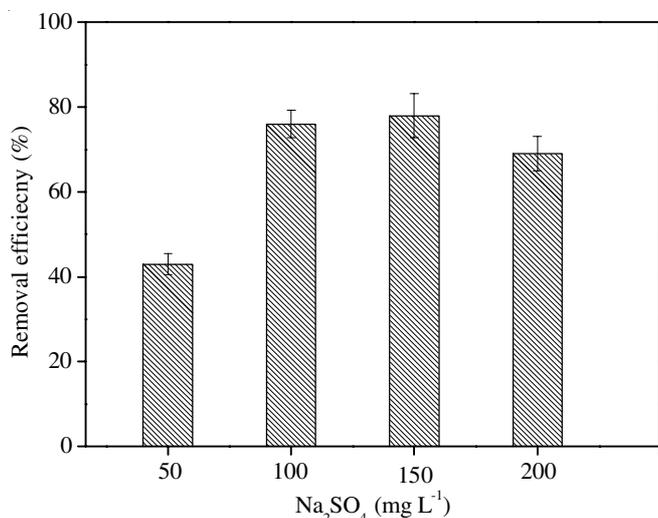


Fig. 2. Effect of Na₂SO₄ concentration on EOMA

density. Meanwhile, greater power was consumed at higher current density. Considering multiple factors such as the current efficiency, OTBP removal rate and effluent quality, the optimum concentration of electrolyte sodium concentration was 100 mg L⁻¹.

Microporous aeration flow rate: Increasing the amount of microporous aeration will speed up the mass transfer rate of dissolved oxygen and enhance the exchange rate of the electrode surface material. This improves the removal of OTBP. However, excessive aeration will make the reactants interact with the electrode surface with insufficient time. This moves more OTBP from the liquid phase into the gas phase, which is not favourable for removal. Therefore studying the impact of microporous aeration on OTBP removal is particularly important.

Aeration flow rates of 2, 3 and 4 L min⁻¹ were tested with other parameters remaining constant (sodium sulfate 100 mg L⁻¹; 2 mL of hydrogen peroxide). The sampling time was 10 min and the results were shown in Fig. 3. With aeration alone, the rate of aeration increase caused more OTBP removal due to stripping. This was because with fast airflow, the OTBP concentration between the gas phase and gas-liquid phase becomes large. This leads to an increase in the mass transfer driving force [10] and resulted in more OTBP turning into the vapour phase. Although the increase in aeration can reduce the OTBP in the aqueous phase, it causes a pollutant transfer between the different phases. This results in airborne pollutants. When both microporous aeration and electro-oxidation were applied, the removal of OTBP rate increased and then decreased as the aeration rate increased. This suggests the presence of an optimum aeration value. Conclusively, we selected 3 L min⁻¹ as the best aeration rate.

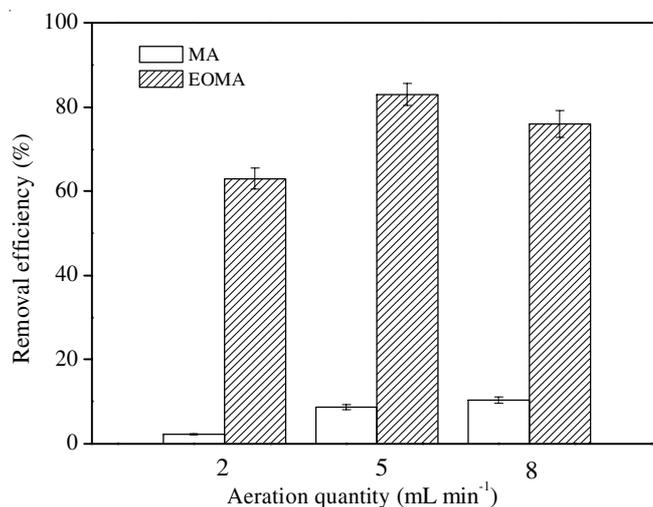


Fig. 3. Effect of aeration quantity on removal efficiency of OTBP

Amount of hydrogen peroxide: To increase the effect of microporous aeration-assisted electro-oxidation, 30% hydrogen peroxide was used. Hydrogen peroxide can produce more hydroxyl radicals (OH) in a relatively short period of time to strengthen the removal of pollutants. Four hydrogen peroxide volumes were studied—0, 1.5, 2.0 and 2.5 mL. Other parameters remained unchanged: sodium sulfate 100 mg L⁻¹, aeration rate 3 L min⁻¹ and total volume 1600 mL.

Fig. 4 shows that the addition of hydrogen peroxide dramatically improved the removal of OTBP. The OTBP removal rate was 54, 65, 82 and 76 % when the addition of hydrogen peroxide was 0, 1.5, 2.0 and 2.5 mL, respectively. This is because hydrogen peroxide forms radical $\cdot\text{OH}$ rapidly on the electrode surface to facilitate oxidation. More OH is produced when an excess of hydrogen peroxide is added, but too much H_2O_2 will react with $\cdot\text{OH}$ to produce H_2O and O_2 . This not only reduces the OH concentration, but also consumes H_2O_2 and makes hydrogen peroxide unable to participate in electro-oxidation [11]. Thus, the optimum amount of hydrogen peroxide was determined to be 2 mL.

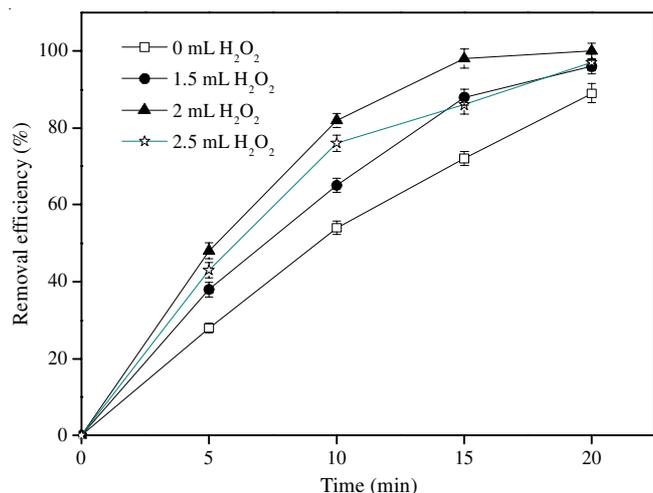
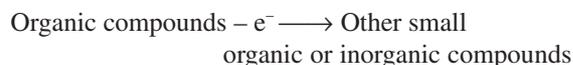
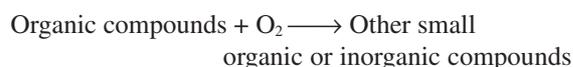
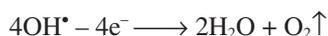
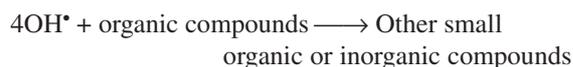


Fig. 4. Effect of H_2O_2 amount on removal efficiency of OTBP

Mechanism of removal of OTBP by EOMA: Electro-oxidation is an oxidation-redox reaction occurring on an electrode surface at an applied current. Organic molecules become harmless substances by losing electrons. Meanwhile, nascent oxygen can also oxidize the organic pollutants in water. The specific chemical reaction mechanisms are [12]:



We used hydrogen peroxide, which is not only a strong oxidant, but can also quickly generate other strong oxidizing materials such as oxygen and ozone. The mechanism for ozone production is below [13].



Based on the above analysis, two major mechanisms for removal of OTBP were involved in our study *i.e.*, direct electrolysis and electrolysis-produced strong active oxidant reagents including ozone and oxygen.

We studied OTBP at two concentrations (1 and 2 mg L⁻¹). All the other major parameters were optimized based on empirical tests. Ideal values were sodium sulfate 100 mg L⁻¹,

microporous aeration 3 L min⁻¹, 2 mL of 30 % hydrogen peroxide and a current density of 5 mA cm⁻². As shown in Fig. 5, 1 mg L⁻¹ and 2 mg L⁻¹ OTBP solutions had 98 and 75.1 % lower OTBP concentrations, respectively. No signal was detected after 30 min. *o*-*tert*-Butyl phenol is a phenol and produces a slight phenolic odor. After treatment for 15 min with EOMA, the odor was clearly reduced in both solutions and was removed completely at 30 min.

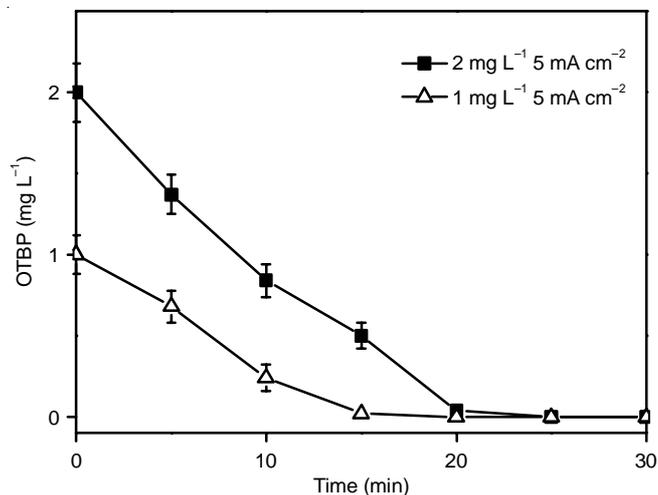


Fig. 5. Effect of initial concentration on OTBP removal efficiency by EOMA

The formed products from the OTBP solution after EOMA treatment were analyzed with headspace GC-MS (Table-2). The results indicated that the electrolysis reaction time affects the product type and amount directly. We proposed the following degradation mechanism according to the product eluting sequence and previous reports [14]. *o*-*tert*-Butyl phenol was first converted to *tert*-butyl-*o*-benzoquinone, which then generated trimethylacetic acid and succinic acid after ring opening. Both of these can be further oxidized to formic acid, acetic acid and other small organic molecules. These are eventually mineralized to CO_2 and H_2O at 30 min.

TABLE-2
MAIN INTERMEDIATES OF OTBP BY EOMA
WITH DIFFERENT TREATMENT TIMES

Time (min)	Main intermediates
10.0	Butyl benzoquinone
15.0	Pivalic acid, succinic acid
22.5	Formic acid, acetic acid, etc.
30.0	—

The contaminated water treated with EOMA is micro-polluted drinking water and thus the toxicity after treatment needs to be evaluated. Table-3 presents toxicity data for OTBP and major intermediate products [15]. The data shows that the toxicity of the intermediate products after treatment were lower than the OTBP indicating that the treatment process can quickly improve water safety and reduce toxicity.

Treatment of organic micro-pollutants in a practical water sample: A real water sample was provided by a water company in Hangzhou China. This was doped with 1 mg L⁻¹ OTBP and 1 mg L⁻¹ tetrachloroethane solution. After treating with our method, the depletion of organic molecules was analyzed

TABLE-3
TOXICITY OF OTBP AND ITS MAIN INTERMEDIATES

Substance	Acute toxicity
OTBP	Adult mouse abdominal cavity LD ₅₀ = 82 mg kg ⁻¹
Pivalic acid	Adult mouse abdominal cavity LD ₅₀ = 900 mg kg ⁻¹
Succinic acid	Adult mouse abdominal cavity LD ₅₀ = 2702 mg kg ⁻¹
Formic acid	Adult mouse abdominal cavity LD ₅₀ = 940 mg kg ⁻¹
	Young rat oral LD ₅₀ = 1100 mg kg ⁻¹
Acetic acid	Young rat oral LD ₅₀ = 3310 mg kg ⁻¹

by the total organic carbon in the solution and the ecological toxicity. The sample was assayed at 0, 7.5, 15, 22.5 and 30 min (Fig. 6). After 30 min, the original concentration of total organic carbon 2.1 mg L⁻¹ completely eliminated. This demonstrated that the technique can treat complicated polluted water by removing various organic contaminants.

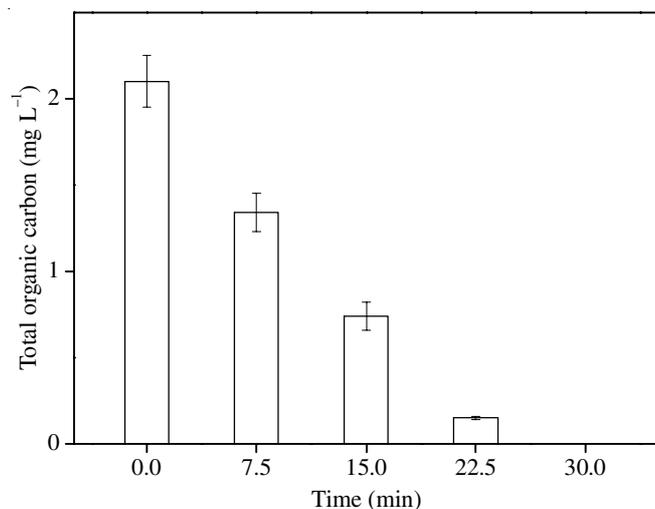


Fig. 6. Removal of OTBP and tetrachloroethane by EOMA

Ecological toxicity assays are the most direct method to evaluate ecological safety of chemicals [16]. Algae were the object of toxicological tests. Fig. 7 shows the growth of algae after different treatment times with EOMA. Algae in the post-treatment solution grew much better than those in the pre-treatment solution containing OTBP and tetrachloroethane. This indicates that the toxicity of the solution decreased as a function of treatment time. This concurs with the toxicity analysis of intermediate products. No changes are seen in algae growth after 15 min of treatment indicating that the toxicity of the test solution was minimal (Fig. 7).

Conclusion

We treated organic micro-polluted water with the EOMA technique. The data show that the EOMA method is twice as efficient in the removal of organic pollutants as electro-oxidation alone. We empirically optimized the parameters to be: 1600 mL total volume (1 mg L⁻¹ or 2 mg L⁻¹ OTBP) containing 100 mg L⁻¹ sodium sulfate and 2 mL 30 % hydrogen peroxide with a micro-porous aeration flow rate of 3 mL min⁻¹ and a current density of 5 mA cm⁻². *o*-tert-Butyl phenol solutions of 1 and 2 mg L⁻¹ were removed at 98.0 and 75.1 %, respectively. The major products include trimethylacetic acid, succinic acid, formic acid and acetic acid—these had much less toxicity than OTBP. After 30 min, the organics were mineralized completely with no odor detected.

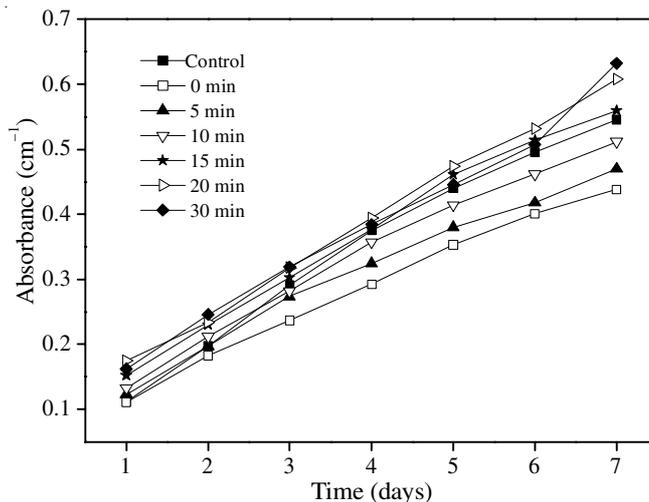


Fig. 7. Effect of reaction time on growth of algae

A water sample provided by a water company was doped with OTBP and tetrachloroethane to mimic organic micro-polluted drinking water and used to further evaluate EOMA. After 30 min, the total organic carbon value of 2.1 mg L⁻¹ at baseline was completely gone. Most microorganisms were removed indicating little or no disinfectant is needed. Ecological toxicity testing showed no decrease in algae growth after treating the solution for 15 min. This suggests that the solution was safe to aquatic ecosystems.

ACKNOWLEDGEMENTS

The author thanks Mr. Suhao Lin and Mr. Yanlong Chen from Hangzhou No. 2 High School of Zhejiang Province for their support. Thanks are also due to College of Biological and Environment Engineering, Zhejiang University of Technology for providing experimental materials and facilities.

REFERENCES

1. A. Matilainen, P. Iivari, J. Sallanko, E. Heiska and T. Tuhkanen, *Environ. Technol.*, **27**, 1171 (2006).
2. S.P. Dubey, K. Gopal and J.L. Bersillon, *J. Environ. Biol.*, **30**, 327 (2009).
3. E. Siswoyo, Y. Mihara and S. Tanaka, *Appl. Clay Sci.*, **97-98**, 146 (2014).
4. J. Benner, D.E. Helbling, H.P.E. Kohler, J. Wittebol, E. Kaiser, C. Prasse, T.A. Ternes, C.N. Albers, J. Aamand, B. Horemans, D. Springael, E. Walravens and N. Boon, *Water Res.*, **47**, 5955 (2013).
5. I. Ivancev-Tumbas, *Environ. Sci. Pollut. Res.*, **21**, 11794 (2014).
6. H. Zhao, L. Wang, Z.H. Zhang, B. Zhao, H.W. Zhang, H. Zhang and R. Ma, *Adv. Mater. Res.*, **777**, 472 (2013).
7. Y.F. Gao, J.W. Li, X.G. Li, X.G. Chen and F. Zhao, *J. Chem. Eng. Chinese Univ.*, **24**, 1052 (2010).
8. The Guidelines for the Testing of Chemical, Ministry of Environmental Protection of the People's Republic of China, 2004, China Environmental Science Press, Beijing, p. 172-181 (2004).
9. T. Luo, H.C. Wang, L. Qi and R.N. Xu, *Acta Sci. Circumstant.*, **32**, 2066 (2012).
10. M.R. Shah, R.D. Noble and D.E. Clough, *J. Membr. Sci.*, **241**, 257 (2004).
11. E. Brillias, R.M. Bastida and E. Llosa, *Electrochem. Sci. Technol.*, **142**, 1733 (1995).
12. J.H. Qu and H.J. Liu, *Electrochemical Theory and Technology of Water Treatment*, Science Press, Beijing (2007).
13. S.A. Snyder, E.C. Wert, D.J. Rexing, R.E. Zegers and D.D. Drury, *Ozone Sci. Eng.*, **28**, 445 (2006).
14. G. Mukesh, D. Ashutosh, K. Ravikummar and R. Nagarajan, *Res. J. Chem. Environ.*, **16**, 1922 (2012).
15. <http://www.drugfuture.com/toxic/search.aspx>
16. N. Gong, K.S. Shao, W. Feng, Z. Lin, C.H. Liang and Y.Q. Sun, *Chemosphere*, **83**, 510 (2011).