

Contents lists available at ScienceDirect

### Journal of Hazardous Materials



journal homepage: www.elsevier.com/locate/jhazmat

# Electro-scrubbing volatile organic carbons in the air stream with a gas diffusion electrode

## Ji Yang<sup>a,b,\*</sup>, Kaichen Liu<sup>b</sup>, Jinping Jia<sup>b</sup>, Limei Cao<sup>b</sup>

<sup>a</sup> School of Resources and Environmental Engineering, State Environmental Protection Key Laboratory of Environmental Risk Assessment and Control on Chemical Process, East China University of Science and Technology, Shanghai 200237, PR China

<sup>b</sup> School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China

#### ARTICLE INFO

Article history: Received 27 October 2010 Received in revised form 17 January 2011 Accepted 18 January 2011 Available online 26 January 2011

Keywords: Volatile organic carbon (VOC) Scrubbing Gas diffusion electrode (GDE) Activated carbon fiber (ACF) Waste gas

#### ABSTRACT

It is demonstrated that exposing the VOC air streams to the electro-scrubbing reactor with a gas diffusion electrode leads to an efficient removal of organics. The importance order of the influence factors on the electro-scrubbing reactor performance is: conductivity, voltage and air stream flow-rate. The effective conductivity and high voltages generally are beneficial to the removal process and the air flow-rate is not a significant factor compared with the other two, indicating that the reactor might have a consistently satisfying performance within a wide range of gas volumetric load. The mass transfer of both organics and oxygen in the reactor is estimated by mathematical model, and the calculation determines the concentration boundary conditions for the 2-ethoxyethyl acetate removal: if the 2-ethoxyethyl acetate concentration in the inflow air stream holds  $C_{G,i} \ge 0.7198\%$ , the controlling step will be the oxygen mass transfer from the air to the liquid in the electro-scrubbing reactor. The Apparent Current Efficiency of the electro-scrubbing reactor was also determined using COD data, which is significantly higher than some commercial metal oxide electrodes, showing that the reactor is energy efficient and has the promise for the future scale-up.

© 2011 Elsevier B.V. All rights reserved.

#### 1. Introduction

Volatile organic compounds (VOCs) are the major contaminants in the waste gas, some of which are common industrial solvents and by-products and these environmentally hazardous compounds are often carcinogens and mutagens and may deplete stratospheric ozone. USA air emissions amounted to about 0.6 Mt of pollutants in 2006 which corresponded to 33.1% of the total release of pollutants in the environment (air, land, water, and underground injection) [1,2]. Because of the public and corporate pressure, environmental legislation in all major industrialized countries is indeed posing increasingly stringent standards on VOCs emissions, the satisfaction of which requires significant improvement in the current removal technologies.

The air streams contaminated with VOCs are frequently characterized by the large volume and low, varying concentrations, which make VOC recovery not possible [3,4]. The most

pertinent strategy to treat these emissions is to destruct or transfer VOCs physico-chemically or biologically. The physicalchemical technologies including condensation, incineration, absorption/stripping, adsorption, and catalytic combustion have been extensively studied to remove VOCs from gaseous streams [5-7]. However, these technologies are either costly or they simply transfer VOCs from the gas phase to another phase. Bio-filtration systems have recently emerged as an efficient and cost-effective technology for the control of VOCs emission, which has been used in Europe for many years and is considered to be a best available control technology for treating contaminated gaseous streams, while it will not work for the poisonous VOCs and it usually requires relatively longer empty bed retention time. Furthermore, factors such as inflow fluctuation, packing materials and configurations, volumetric loading rates, nutrient feed flow rates, nutrient solution pH, and air flow patterns all may affect the final performance of bio-filtration systems and make the treatment not easy to manipulate.

Recent researches have demonstrated that electrochemical methods offer an attractive alternative to traditional routes for pollutants control [8–11], since the electrolytic process is easy to control by potential and current, and such process can operate at low temperature and pressure without adding other reagents. However, reviewing literature, it is fair to say that although elec-

<sup>\*</sup> Corresponding author at: East China University of Science and Technology, School of Resources and Environmental Engineering State Environmental Protection, 130 Meilong Road, P.O. 563#, Shanghai 200237, China. Tel.: +86 21 64250874; fax: +86 21 64250874.

E-mail address: yangji@ecust.edu.cn (J. Yang).

<sup>0304-3894/\$ -</sup> see front matter © 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2011.01.082



Fig. 1. The schematic diagram of the experimental setup (1) Pump; (2) Flow meter; (3) Stock solution bottle; (4) Electro-filter reactor; (5) Electricity supply; (6) Total Hydro-carbon Analyzer; (7) Sampling valve; (8) Air diffuser; (9) Washing bottle; (10) Stainless steal anode; (11) ACF cathode.

trochemical methods have been successfully commercialized, so far almost all of the efforts carried out on the electrochemical treatment pertain to the wastewaters, with primary objective of these studies being the development of appropriate parameters for contaminant removal, such as selection of electrode materials, electrolytic voltage or electrolytes [8–14]. There is a deficiency in research on the treatment of air streams containing VOCs based on electrochemical methods. It is in this context that the present study was undertaken with a primary view to propose the suitability of electrochemical methods in VOCs waste gas treatment under various conditions and explore the mechanism behind the process.

Consequently, an electro-scrubbing reactor was designed, and instead of using traditional electrodes made of metal oxide or graphite, activated carbon fiber (ACF) was employed as the cathode since it could behave as the gas diffusion electrode (GDE), which can accelerate oxygen reduction and thus have been introduced into gas consuming reactions to provide a larger reaction area and favorable conditions for gas diffusion processes [15-17]. GDEs have been widely studied in the design and manufacturing of fuel cells, especially of proton exchange membrane fuel cells and alkaline fuel cells [18-20]. The ACF GDE can greatly reduce fed oxygen in the air stream to produce hydrogen peroxide by two-electron reduction process, therefore was employed as the cathode in the electro-scrubbing reactor. The anode was stainless steel since it could leach Fe<sup>2+</sup> into the reactor and form electro-Fenton pair with  $H_2O_2$  produced at the cathode to destroy organics flowing into the reactor.

The significance of this research is trying to broaden the application of electrochemical method and explore possible industrial scale-up. The most relevant application of this strategy refers to treatment of off-gases from chemical plants, groundwater decontamination by air stripping followed by oxidation, odor emission control, and treatment of contaminated air in solvent evaporation processes. The major objectives of this study were as follows: (1) proposing an electrochemical process to remove VOCs in air streams; (2) exploring the mechanism behind the process; (3) obtaining reactor performance data under varying operating conditions such as electrolytic voltage, air flow-rate etc. and (4) calculating the current efficiency of the system. 2-Ethoxyethyl acetate (EEAc) was selected as the typical target VOCs for this study, since it is broadly used as a diluent and a cleaner in many industries because of its considerable hydrophilic and lipophilic properties, and it is known to produce spermotoxic, fetotoxic, teratogenic, hematological and immunological effects in rats and are suspected of producing hematological effects in humans. The National Institute for Occupational Safety and Health (NIOSH) suggest that exposures to glycol ethers should be reduced to the lowest extent feasible in order to protect workers from suspected teratogenic or reproductive effects.

#### 2. Experimental

#### 2.1. Electro-scrubbing reactor

The experimental setup employed is shown in Fig. 1. One piece of a round ACF felt with diameter of 86 mm was employed as cathode and a porous stainless steel (standard 304 steel according to ASTM A193) sheet of same size as anode with 0.1 mm thickness. The electrodes were situated 20 mm apart from each other and the height of the reactor was 130 mm.

The air was pumped into the stock solution bottle containing 200 ml EEAc solution with varying concentrations by a peristaltic pump (Model ACO-5503, Guangdong Haili Pump Company of China) to produce air streams containing EEAc for electroscrubbing reactor treatment. The flow-rate was controlled by a flow-meter (Model LZB-4, Zhejiang Zhenxing Flow-Meter Company of China). The air steam containing EEAc was then introduced into the electro-scrubbing reactor through a porous aerator at the center of the reactor bottom. The reactor was filled with 500 ml Na<sub>2</sub>SO<sub>4</sub> solution with a concentration of  $1 \text{ g L}^{-1}$ . The exiting gas of the reactor was absorbed by a series of two washing bottles containing 250 ml Na<sub>2</sub>SO<sub>4</sub> solution each to collect the escaping EEAc. At appropriate time intervals, samples of 10 ml were withdrawn from the reactor and analyzed to determine the intermediate properties of the reaction medium during the electrochemical conversion. A direct current voltage stabilized power supply (WYJ, Shanghai Songte Electrification Company of China) was connected to both the anode and cathode to control the potential.

#### 2.2. Materials and analysis

EEAc (CH<sub>3</sub>COOCH<sub>2</sub>CH<sub>2</sub>OC<sub>2</sub>H<sub>5</sub>, 98.5%) was obtained from Sinoreagent, and all the other reagents used were of analytical grade. Commercial ACF in cloth form was obtained from Nantong Sanyou



**Fig. 2.** (A) One typical example of the EEAc concentrations in the air stream exiting the stock solution bottle (flow-rate  $20 Lh^{-1}$ ); (B) the EEAc concentrations in the air stream exiting the electro-filter reactor (flow-rate  $20 Lh^{-1}$ . Effect of inflow concentration (voltage = 10 V)); (C) the EEAc concentrations in the air stream exiting the electro-filter reactor (flow-rate  $20 Lh^{-1}$ . Effect of inflow concentration in the stock solution bottle was 9600 ppm)) and (D) the EEAc concentrations in the effluent air stream from the electro-filter reactor (flow-rate  $20 Lh^{-1}$ , voltage = 0).

Environmental Technology Company of China. The average fiber diameter was around  $10-20 \,\mu\text{m}$  and the specific area between  $1000-1200 \,\text{m}^2 \,\text{g}^{-1}$ . The ACF electrode was soaked and rinsed in deionized water three times, and dried in oven at  $100 \,^{\circ}\text{C}$  before each experimental run.

The pH and dissolved oxygen (DO) in the solution was determined using pHS-3C pH meter (Shanghai Zhiguang Instrument Company of China) and Model 830A DO meter of Thermo Orion (USA). The ultraviolet (UV) was evaluated by the absorbencies of the solutions in the reactor using a UV/vis spectrophotometer (UNICO Instruments Company of China). Also chemical oxygen demand (COD) of solution samples in the electro-scrubbing reactor was obtained using potassium dichromate, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, as an oxidizing agent via Unico CT-50 COD Reactor (USA).

Gas chromatography–mass spectrometry (GC–MS) analysis process is as follows: the solution samples at different time interval were extracted using SPME [21] for GC–MS analysis. GC–MS analyses were performed using a GC MSQP 2010 apparatus (SHIMADZU Company of Japan), equipped withDB-5 MS column ( $30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$ ). The chromatographic conditions were as follows:  $50 \text{ cm s}^{-1}$  as the carrier gas (He) flow rate;  $40 \,^{\circ}\text{C}$  as initial temperature for 5 min;  $5 \,^{\circ}\text{C} \min^{-1}$  as temperature to  $280 \,^{\circ}\text{C}$  and keep the temperature for 6 min;  $280 \,^{\circ}\text{C}$  as injector and transfer-line temperature. The split ratio is 1:10. MS detects at voltage 1.01 kV, EI 70 eV, scan field  $33-200 \text{ mz}^{-1}$ , and ion source temperature 200  $\,^{\circ}\text{C}$ .

The organic concentration in the air steams was determined online by a hydrocarbon analyzer (51C-HT, Thermo, USA) every 2 min. The detector temperature was 200 °C, sampling pump pressure at 6.50 psi, air pressure at 15 psi, and hydrogen pressure at 9.5 psi<sub>0</sub>

#### 3. Results and discussion

#### 3.1. Degradation of EEAc in the air streams

Fig. 2A shows one typical example of the total hydrocarbon concentrations (THC) in the air stream exiting the EEAc bottle, which was filled with 9600 ppm EEAC solution. The data proves that passing through the stock solution bottle could introduce a relatively stable concentration of EEAc into the air for following electrochemical treatment. It could be seen that the concentration went up from almost zero to thousands quickly, indicating that the effluent from the EEAc stock solution bottle was diluted by the stagnant air in the tubing and instrument initially, but became stable around 3500 ppm after about 2 h. By integrating the THC within certain time interval, the total EEAc load in the air streams could be obtained. For all the following experiments, the total EEAc flowing into the electro-scrubbing reactor was obtained using this method.

To further verify the effect of electro-scrubbing reactor on the EEAc removal, experiments were performed with different voltages and different initial EEAc concentrations in the stock solution bottle, and the results were shown in Fig. 2.

It could be seen from Fig. 2B that as the initial concentration in the stock solution bottle goes up; the effluent concentration from the electro-scrubbing reactor also increases accordingly. This is reasonable since as the stock solution concentration goes up, more EEAc could be transferred into the reactor, while a linear relationship between the initial stock solution concentration and the effluent concentration could not be obtained, indicating that the electrochemical factor might make the difference. Fig. 2C shows the variation of the EEAc concentrations at the electro-scrubbing reactor outlet with time at different treating voltages. It is evident that

Table 1	
Orthogonal tests for EEAc removal in the electro-fi	lter reactor.

Factors sel	lected and the o	correspondingle	vels 1	2	3
А	Air flow-rate (L h <sup>-1</sup> )		20	24	16
В	Voltage (V)		20	25	30
С	$Na_2SO_4$ (g L <sup>-1</sup> )		0.5	1	1.5
Results					
	A	В	С	COD removal (%)	
1	1	1	1	56	
2	1	2	2	66	
3	1	3	3	56	
4	2	1	2	66	
5	2	2	3	63	
6	2	3	1	76	
7	3	1	3	45	
8	3	2	1	52	
9	3	3	2	47	
K <sub>1j</sub>	1.79	1.68	1.85		
K <sub>2j</sub>	2.05	1.82	1.80		
K <sub>3j</sub>	1.45	1.79	1.64		

as the voltage increases the effluent concentration from the reactor decreases, proving indirectly that electrochemical process plays an important role at decreasing the EEAc concentration. Although the figure exhibits that the EEAc decrease is more readily under higher voltages, the data alone could not demonstrate whether the EEAc is removed or not since the chemical could be absorbed by the solution in the electro-scrubbing reactor or adsorbed by the ACF electrodes. Therefore, direct evidence is needed before any further conclusion could be drawn.

Firstly, the effect of ACF adsorption was studied and the data was shown in Fig. 2D. It is evident in Fig. 2D that the adsorption by ACF electrode is trivial and negligible if the voltage is 0. Furthermore, another index was employed to study the removal of EEAc in the electro-scrubbing reactor. The COD of the solution in the reactor was examined and the total COD removal was calculated using following expression:

$$R_{\text{COD}}\% = \frac{(\text{COD}_0 - \text{COD}_S - \text{COD}_L)}{\text{COD}_0} \times 100$$
(1)

COD<sub>0</sub>: total COD entering the reactor

COD<sub>S</sub>: COD of the solution in the reactor

COD<sub>L</sub>: COD exiting the reactor

Orthogonal tests were performed to study the effect of some parameters on the EEAc removal in the electro-scrubbing reactor. Table 1 shows the factors selected and their corresponding levels. In orthogonal test, air flow-rate, voltage and eletrolyte concentration are considered as the main factors in electro-scrubbing reactor performance.

Table 1 shows the results of orthogonal test. It is evident in Table 1 that the electro-scrubbing reactor could remove a considerable amount of EEAc by mineralizing it. Since some of the organics were destructed while not totally mineralized, the apparent removal could be higher than COD removal. It was also found that in orthogonal test, the importance order of the influence factors on electro-scrubbing reactor performance was: C > B > A. The data manifests that effective conductivity in the solution is the most important factor to consider when it comes to the design of an electro-scrubbing reactor. Also, high voltages generally are beneficial to the removal process and the air flow-rate is not a significant factor compared with the other two, indicating that the reactor might have a consistent satisfying performance within a wide range of waste gas volumetric load, which is one important characteristic of the industrial VOC air streams.

#### 3.2. Mechanism of removal

To further elucidate the possible EEAc removal path in the electro-scrubbing reactor, UV and GC–MS were employed to analyze the samples. Fig. 3 shows the typical GC–MS and UV spectrum of the samples taken at 180mins from the electro-scrubbing reactor with 20 V. The control samples were taken with all the parameters kept the same except the voltage was 0. It can be learned from Fig. 3A that the adsorption around 230 nm in the UV spectrum of the control sample is from EEAc, and after 180 min electrolysis, the adsorption weakened significantly, indicating that most of it has been removed as a chemical entity. GC–MS results in Fig. 3B prove that the composition of the non-treated solution in the reactor is complex. After 180 min electrochemical treatment, the number of components decreased significantly, which together with COD data shown in Table 1 validates that mineralization and not other process dominates the EEAC removal process.

The mechanism of electrochemical treatment process is very complicated and not yet fully understood [22]. Usually, these mechanisms involved in treatment of organics are electro-floatation, electrocoagulation and electro-oxidation at the anode.

Previous work has proven that when air diffuses through active layer on the ACF as a cathode, oxygen is reduced to hydrogen peroxide [23–25]. The reduction of oxygen to form hydrogen peroxide happens with a high yield only on cathodic materials, including carbon, gold and mercury.

$$O_2(dissolved) + 2e + 2H^+ \rightarrow H_2O_2$$
<sup>(2)</sup>

The  $Fe^{2+}$  dissolves from anode could react with  $H_2O_2$  to form free radical for the oxidation of organics [26],

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH \bullet + OH^-$$
(3)

$$OH \bullet + H_2O_2 \to H_2O + HO_2 \bullet \tag{4}$$

$$Fe^{3+} + HO_2 \rightarrow Fe^{2+} + H^+ + O_2$$
 (5)

$$Fe^{2+} + HO_2 \rightarrow Fe^{3+} + HO_2^{-}$$
 (6)

$$Fe^{2+} + OH \bullet \to Fe^{3+} + OH^{-}$$

$$\tag{7}$$

It is a chain reaction, step (3) serving as chain initiation, steps (6) and (7) as termination. The cycle (3)–(4)–(5) forms the chain, which is the site of  $O_2$  evolution.

Based on the above THC, COD, UV and GC–MS results, it is reasonable to presume that electro-Fenton is the major pathway for EEAc removal as follows:

$$EEAC + OH^{\bullet} \rightarrow Intermediates \rightarrow CO_2 + H_2O$$
(8)

And the overall process of EEAc removal from air streams in electro-scrubbing reactor could be proposed as follows: absorption of EEAc by the solution in the reactor  $\rightarrow$  production of H<sub>2</sub>O<sub>2</sub> through the GDE  $\rightarrow$  dissolution of Fe<sup>2+</sup> from the anode  $\rightarrow$  formation of electro-Fenton pairs to produce OH•  $\rightarrow$  EEAc oxidized by OH• generated in the reactor as shown in Fig. 4. Therefore, the abovementioned electrochemical control is indirect: it arises from the reaction of species produced at the anode (Fe<sup>2+</sup>) and cathode (H<sub>2</sub>O<sub>2</sub>) to produce OH• which then oxidizes the VOC.

#### 3.3. Mass transfer boundary conditions

In commonly encountered situations, in which the desired final organic levels are low, and under the most frequently applied Galvan static operation conditions, the oxidation of the target organic compound may become mass transfer controlled either from the very beginning or soon after the start-up of the process. And this might reduce the current efficiency of the electrochemical reactor and waste the energy on water electrolysis. Therefore, the boundary conditions for the mass transfer should be explored for the reactor



**Fig. 3.** (A) The UV results of solutions in the electro-filter reactor (the initial EEAc concentration in the stock solution bottle was 9600 ppm, flow-rate 20 L h<sup>-1</sup>, voltage = 0, 20) and (B) the GC-MS results of solutions in the electro-filter reactor (the initial EEAc concentration in the stock solution bottle was 9600 ppm, flow-rate 20 L h<sup>-1</sup>, voltage = 0, 20).



Fig. 4. Degradation pathway of 2,4-DCP.

design. As shown in Eq. (4), the conversion of EEAc in the electroscrubbing reactor allows to regenerate continuously the scrubbing liquid and to maintain a driving force to improve mass transfer, while the consumption of DO could limit further mineralization. Therefore, the DO is critical for the efficient EEAc oxidation. Since the saturation level of DO is in the order of ppm, the transfer from the air stream is the dominant source for O<sub>2</sub> supply. When the VOC concentration is low in the air stream, the electro-scrubbing reactor could efficiently mineralize the organics as shown in above figure and table. However, if the organic concentration is high, the mass transfer of O<sub>2</sub> could be the limiting factor. As to how high the EEAc concentration could be for satisfying removal, the mass transfer for both EEAc and O<sub>2</sub> from gas phase to liquid phase should be calculated to estimate the boundary conditions.

Generally, the total mass transfer rate of  $O_2$  from air to liquid in the electro-scrubbing reactor could be described as:

$$\frac{dC_{O_2}}{dt} = K_L a_{O_2} \times (C_{G,O_2} - C_{L,O_2})$$
(9)

in which  $K_L a_{0_2}$  is the overall mass transfer coefficient between gas and liquid phase (S-1) for  $O_2$ ,  $C_{G,O_2}$  is the gas phase concentration and  $C_{L,O_2}$  is the liquid phase concentration. Eq. (5) could be simplified to following equation since  $C_{G,O_2}$  is around 21% for the air and  $C_{L,O_2}$  is about 8 ppm for water under room temperature.

$$\frac{dC_{O_2}}{dt} = 0.21 \times K_L a_{O_2}$$
(10)

The correlation proposed by Alexander and Shah [27] could be used to calculate the overall mass transfer coefficient of oxygen,  $K_L a_{0_2}$  from the gas phase to the liquid phase:

$$K_{\rm L}a_{\rm O_2} = 0.06371 \times (V_{\rm L}')^{0.3014} \times (V_{\rm C}')^{0.4484} \tag{11}$$

in which  $V'_{\rm L}$  equals liquid-phase superficial mass velocity  $(\text{kg m}^2 \text{ s}^{-1})$  and  $V'_{\rm G}$  is equal to gas-phase superficial mass velocity  $(\text{kg m}^2 \text{ s}^{-1})$ .

The mass transfer rate of EEAc from gas phase to liquid phase in the electro-scrubbing reactor is expressed as follows:

$$\frac{\mathrm{d}C_{\mathrm{i}}}{\mathrm{d}t} = K_{\mathrm{L}}a_{\mathrm{i}} \times (C_{\mathrm{G},\mathrm{i}} - C_{\mathrm{L},\mathrm{i}}) \tag{12}$$

in which  $K_L a_i$  is the overall mass transfer coefficient between gas and liquid phase (S<sup>-1</sup>) for EEAc,  $C_{G,i}$  is the gas phase concentration and  $C_{L,i}$  is the liquid phase concentration.

And the following equation can be derived from the two film theory and was used to calculate the overall mass transfer coefficient,  $K_L a_i$  for EEAc (S<sup>-1</sup>):

$$K_{\rm L}a_{\rm i} = K_{\rm L}a_{\rm O_2} \times \left(\frac{D_{\rm l,i}}{D_{\rm l,O_2}}\right)^{0.5} \times \left[1 + \frac{1}{H_{\rm i}(k_{\rm g,i}/k_{\rm l,i})}\right]^{-1}$$
(13)

in which  $K_L a_{O_2}$  is determined as shown above,  $D_{l,i}$  equals the liquid diffusivity of compound i (cm<sup>2</sup> s),  $D_{l,O_2}$  is equal to the liquid phase diffusion coefficient of oxygen (cm<sup>2</sup> s),  $H_i$  equals the Henry's law constant of EEAc (dimensionless), and  $k_{g,i}/k_{l,i}$  equals the ratio

ċ



Fig. 5. The DO in the electro-filter reactor (the initial EEAc concentration in the stock solution bottle was 9600 ppm, flow-rate 20 L h<sup>-1</sup>).

For the total mineralization of 1 mol EEAC, stoichiometrically 4.5 mol of  $O_2$  are needed. Therefore, to guarantee enough  $O_2$  supply for the oxidation, following condition must be hold:

$$\frac{dC_{O_2}}{dt} / \frac{dC_i}{dt} = \frac{0.21 \times K_L a_{O_2}}{K_L a_{,i} \times (C_{G,i} - C_{L,i})} \ge 4.5$$
(16)

Eq. (16) could be changed as follows:

$$\frac{dC_{O_2}}{dt} / \frac{dC_i}{dt} = \frac{0.21 \times \left[1 + (1/(H_i \times (k_{g,i}/k_{l,i})))\right]}{\left(D_{l,i}/D_{l,O_2}\right)^{0.5} \times (C_{G,i} - C_{L,i})} \ge 4.5$$
(17)

Insert Eq. (14) and Eq. (15) into Eq. (17), following relationship could be obtained:

$$\frac{|C_{0_2}|}{dt} / \frac{dC_i}{dt} = \frac{0.21 \times [1 + (1/3H_i)]}{((13.26 \times 10^{-5} / \mu^{1.14} \times V_b^{0.589}) / ((3.25 \times 10^{-5} \times 0.0089 \times \text{Temperature}) / 298.15 \times \mu))^{0.5} \times (C_{G,i} - C_{L,i})} \ge 4.5 \quad (18)$$

If the initial EEAc concentration in the electro-scrubbing reactor is zero, the highest air stream concentration of EEAc that the reactor could handle is:

$$C_{G,i} \le \frac{0.21 \times [1 + (1/3H_i)]}{4.5 \times ((13.26 \times 10^{-5}/\mu^{1.14} \times V_b^{0.589})/((3.25 \times 10^{-5} \times 0.0089 \times \text{Temperature})/298.15 \times \mu))^{0.5}}$$
(19)

of gas phase mass transfer coefficient to liquid phase mass transfer coefficient for EEAc (dimensionless). Methods for determining values for  $D_{l,i}$ ,  $D_{l,O_2}$ ,  $H_i$  and  $k_{g,i}/k_{l,i}$  are discussed below.

Hsieh et al. [28] reported that the ratio of  $k_{g,i}/k_{l,i}$  was relatively constant for bubble aeration and was observed to be between 2.2 and 3.6. Consequently, a conservative value of 3.0 was assumed for  $k_{g,i}/k_{l,i}$  because mass transfer was very fast.

 $D_{L,i}$  was determined from the correlation presented by Hayduk and Laudie [29]:

$$D_{\rm L,i} = \frac{13.26 \times 10^{-5}}{\mu^{1.14} \times V_{\rm b}^{0.589}} \tag{14}$$

in which  $\mu$  equals viscosity of liquid water (centipoise) and  $V_b$  is equal to molar volume at the normal boiling point (cm<sup>3</sup> g mol<sup>-1</sup>).  $D_{L,O_2}$  was adjusted with temperature and water viscosity ( $D_{L,O_2}$  at 25 °C (298.15 K) is  $3.25 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>, and the viscosity of water at 25 °C (298.15 K) is 0.0089 g cm<sup>-1</sup> s<sup>-1</sup>):

$$D_{\rm L,O_2} = \frac{3.25 \times 10^{-5} \times 0.0089 \times \rm Temperature}{298.15 \times \mu}$$
(15)

in which and temperature is in degrees Kelvin (K).

Assuming the temperature is 298.15 K, following result could be obtained:

$$C_{G,i} \le 0.7198\%$$
 (20)

and this is the concentration limit for controlling process: if  $C_{G,i} \le 0.7198$ %, the removal is electrochemical reaction controlled; if  $C_{G,i} \ge 0.7198$ %, the controlling step will be the oxygen mass transfer from air to liquid in the electro-scrubbing reactor. The result also proves that the electro-scrubbing reactor could handle VOC air stream with fairly wide concentration range, 0–0.7198%, which is another characteristics of the industrial VOC air streams.

Fig. 5 shows the typical DO levels in the electro-scrubbing reactor during treatment of the EEAc air streams. It could be learned that although the inflow THC in the air was around 3500 ppm, DO in the electro-scrubbing reactor remained stable and adequate, indicating that the treatment was electrochemical reaction controlled. It is also evident that the DO with 20 V was slightly lower than that with 10 V, and that could be attributed to the higher temperature caused by electrolyzing in the reactor with 20 V, which was about 10  $^{\circ}$ C higher averagely.

Table 2The ACEs of EEAc removal in the electro-filter reactor.

Voltage (V)	Flow-rate $(Lh^{-1})$	Stock solution concentration (ppm)	ACE (%)
10	20	9600	73.64
15	20	9600	58.43
20	20	9600	38.23

# 3.4. Apparent current efficiency (ACE) of the electro-scrubbing reactor

The ACE is one major consideration when it comes to the industrialization of the electrochemical reactor design. The ACE of the electrochemical processes is defined as the current fraction used for the organic compound oxidation [30]. The current efficiency is calculated according to the COD values of the samples, and could be determined as follows [30,31]:

$$CE(\%) = F \frac{(COD_0 - COD_S - COD_L)}{8I\Delta t} \times 100$$
(21)

where *I* is the current (A); *F* is the Faraday constant (96.487 C mol<sup>-1</sup>); *t* is the treatment time (s); *U* is the voltage (V).

Table 2 shows the changes of current efficiency with varying voltages. It could be seen that relatively higher ACE was achieved under lower flow-rate, while all of the data shows that the reactor has significantly higher energy efficiency than the reported values (10–21%) on other systems using commercially available electrode materials such as Ti/RuO<sub>2</sub>, Ti/IrO<sub>2</sub>, Pt, SnO<sub>2</sub>, PbO<sub>2</sub> and Si/BDD electrodes [32–34].

#### 4. Application prospect

An electro-scrubbing reactor is designed to meet two major challenges of the industrial VOC air steams: large volume and varying concentrations. It is demonstrated that exposing VOC air streams to the electro-scrubbing reactor leads to efficient removal of organics in the inflow. The ACE of the electro-scrubbing reactor was also determined using the COD data, showing that the reactor is energy efficient and has the promise for future scale up. In our future work, we will explore the possibility of applying this technique to treat various air streams containing environmentally important organic pollutants. Although the current research is still at lab scale stage, it has promise for application considering its energy efficiency, and the commercialization of this technique is a goal worth pursing.

#### Acknowledgements

This research is based upon work supported by the National Natural Science Foundation of China (Project No. 20777050), National 863 program (2009AA062603) and Shanghai Leading Academic Discipline Project (Project Number: B506). Any opinions, findings, conclusions, or recommendations expressed in this publication are those of the authors and do not necessarily reflect the view of the supporting organizations. The authors are grateful to Yalin Wang for advice and troubleshooting the experimental apparatus and sample analysis.

#### References

- USEPA, Toxic release inventory program "Air Emissions Trends-Continued Progress Through 2005" http://www.epa.gov/tri/index.htm.
- [2] Z.L. Cai, G.A. Sorial, Treatment of dynamic VOC mixture in a trickling-bed air biofilter integrated with cyclic adsorption/desorption beds, Chem. Eng. J. 151 (2009) 105–112.

- [3] E.N. Ruddy, L.A. Carroll, Select the best VOC control strategy, Chem. Eng. Prog. 89 (1993) 28–35.
- [4] F.I. Khan, A.K. Ghoshal, Removal of volatile organic compounds from polluted air, J. Loss Prevent. Proc. 13 (2000) 527–545.
- [5] S. Fukahori, Y. Iguchi, H. Ichiura, T. Kitaoka, H. Tanaka, H. Wariishi, Effect of void structure of photocatalyst paper on VOC decomposition, Chemosphere 66 (2007) 2136–2141.
- [6] P. Sabia, F. Romeo, M. de Joannon, A. Cavaliere, VOC destruction by water diluted hydrogen mild combustion, Chemosphere 68 (2007) 330–337.
- [7] S. Schmid, M.C. Jecklin, R. Zenobi, Degradation of volatile organic compounds in a non-thermal plasma air purifier, Chemosphere 79 (2010) 124– 130.
- [8] P. Dabo, A. Cyr, F. Laplante, F. Jean, H. Menard, J. Lessard, Electrocatalytic dehydrochlorination of pentachlorophenol to phenol or cyclohexanol, Environ. Sci. Technol. 34 (2000) 1265–1268.
- [9] F.C. Walsh, Electrochemical technology for environmental treatment and clean energy conversion, Pure Appl. Chem. 73 (2001) 1819–1837.
- [10] J. Casado, J. Fornaguera, M.I. Galan, Mineralization of aromatics in water by sunlight-assisted electro-Fenton technology in a pilot reactor, Environ. Sci. Technol. 39 (2005) 1843–1847.
- [11] A. Deligiorgis, N.P. Xekoukoulotakis, E. Diamadopoulos, D. Mantzavinos, Electrochemical oxidation of table olive processing wastewater over boron-doped diamond electrodes: treatment optimization by factorial design, Water Res. 42 (2008) 1229–1237.
- [12] A. Vlyssides, E.M. Barampouti, S. Mai, D. Arapoglou, A. Kotronarou, Degradation of methylparathion in aqueous solution by electrochemical oxidation, Environ. Sci. Technol. 38 (2004) 6125–6131.
- [13] Y.J. Liu, X.Z. Jiang, Phenol degradation by a nonpulsed diaphragm glow discharge in an aqueous solution, Environ. Sci. Technol. 39 (2005) 8512– 8517.
- [14] M. Mavros, N.P. Xekoukoulotakis, D. Mantzavinos, E. Diamadopoulos, Complete treatment of olive pomace leachate by coagulation, activated-carbon adsorption and electrochemical oxidation, Water Res. 42 (2008) 2883–2888.
- [15] D.B. Zhou, H.V. Poorten, Electrochemical characterization of oxygen reduction on Teflon-bonded gas diffusion electrodes, Electrochim. Acta 40 (1995) 1819–1826.
- [16] J.J. Yu, S.Y. Chou, Contaminated site remedial investigation and feasibility removal of chlorinated volatile organic compounds from groundwater by activated carbon fiber adsorption, Chemosphere 41 (2000) 371–378.
- [17] T.A. Metts, S.A. Batterman, Effect of VOC loading on the ozone removal efficiency of activated carbon filters, Chemosphere 62 (2006) 34–44.
- [18] K. Bolwin, E. Gulzow, D. Bevers, W. Schnurnberger, Preparation of porous electrodes and laminated electrode-membrane structure for polymer electrolyte fuel cells (PEFC), Solid State Ionics 77 (1995) 324–330.
- [19] E. Han, I. Eroglu, L. Turker, Performance of an alkaline fuel cell with single or double layer electrodes, Int. J. Hydrogen Energy 25 (2000) 157–165.
- [20] V. Mehta, J.S. Cooper, Review and analysis of PEM fuel cell design and manufacturing, J. Power Sources 114 (2003) 32–53.
- [21] L.Y. Liao, J. Yang, Y.L. Wang, T.H. Sun, J.P. Jia, Study on a novel circulating cooling solid-phase microextraction method, J. Chromatogr. A 1135 (2006) 1–5.
- [22] K. Rajeshwar, J.G. Ibanez, G.M. Swain, Electrochemistry and the environment, J. Appl. Electrochem. 24 (1994) 1077–1091.
- $\left[23\right]$  E. Yeager, Electrocatalysts for  $O_2$  reduction, Electrochem. Acta 29 (1983) 1527–1537.
- [24] D. Pletcher, Indirect oxidations using electrogenerated hydrogen peroxide, Acta Chem. Scand. 35 (1999) 745–750.
- [25] G. Kear, C. Ponce de León, F.C. Walsh, Reduction of dissolved oxygen at a copper rotating-disc electrode, Chem. Eng. Educ. 39 (2005) 14–21.
- [26] M.L. Kremer, Mechanism of the Fenton reaction. Evidence for a new intermediate, Phys. Chem. Chem. Phys. 1 (1999) 3595–3605.
- [27] B.F. Alexander, Y.T. Shah, Gas-liquid mass transfer coefficient for co-current upflow in packed beds-effect of packing shape at low flow rates, Can. J. Chem. Eng. 54 (1976) 556-559.
- [28] C.C. Hsieh, R.W. Babcock, M.K. Stenstrom, Estimating emissions of 20 VOCs. II. Diffused aeration, J. Environ. Eng. 119 (1993) 1099–1118.
- [29] W. Hayduk, H. Laudie, Prediction of diffusion coefficients for noneletrolyte in dilute aqueous solutions, AIChE J. 20 (1974) 611–615.
- [30] C.R. Costa, C.M.R. Botta, E.L.G. Espindola, P. Olivi, Electrochemical treatment of tannery wastewater using DSA electrodes, J. Hazard. Mater. 153 (2008) 616–627.
- [31] E. Emmanuel, G. Keck, J.M. Blanchard, P. Vermande, Y. Perrodin, Toxicological effects of disinfections using sodium hypochlorite on aquatic organisms and its contribution to AOX formation in hospital wastewater, Environ. Int. 30 (2004) 891–900.
- [32] M. Panizza, G. Cerisola, Electrochemical oxidation as a final treatment of synthetic tannery wastewater, Environ. Sci. Technol. 38 (2004) 5470–5475.
- [33] C.A. Martiĭnez-Huitle, A. De Battisti, S. Ferro, S. Reyna, M. Cerro-Loĭpez, M.A. Quiro, Removal of the pesticide methamidophos from aqueous solutions by electrooxidation using Pb/PbO<sub>2</sub>, Ti/SnO<sub>2</sub>, and Si/BDD electrodes, Environ. Sci. Technol. 42 (2008) 6929–6935.
- [34] O. Scialdone, A. Galia, G. Filardo, Electrochemical incineration of 1,2dichloroethane: effect of the electrode material, Electrochim. Acta 53 (2008) 7220–7225.