Int. J. Electrochem. Sci., 13 **(2018)** 1096 – 1104, doi: 10.20964/2018.01.78

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Electrochemical Oxidation Treatment of Wastewater Using Activated Carbon Electrode

Bo Yang[1,2] *and Jie Tang*[1,*]

[1] College of Environment and Resources, Jilin University, Changchun 130000, China
[2] Jilin Agricultural Science and Technology College School of Plant Science, Jilin 132011, China
[*]E-mail: tangjie0724@sina.com

Received: 24 June 2017 / *Accepted:* 20 November 2017 / *Published:* 16 December 2017

It has been widely accepted that wastewater contains low concentrations of organic pollutants and several inorganic salts after being biologically treated. This report presents a study of the synergic effects of electrosorption and electrochemical oxidation in the simultaneous removal of these substances. The electrochemical oxidization of phenol and sodium chloride occurred in the simulated wastewater in the presence of an anode made of activated carbon fibre (ACF) felt. We further studied the effect of anode structure and electrolytic conditions on the degradation of the wastewater. The removal of phenol was achieved by the synergic effect of electrochemical oxidation and adsorption, possibly maintained through the oxidization of hypochlorite and chlorine in either a direct or an indirect way. As degradation intermediates, chlorophenols were eventually converted into carboxylic acids. Desalination may be due to the ion electrosorption in the activated carbon electrode pores.

Keywords: Wastewater; Electrochemical oxidation; Activated carbon fibre; Water treatment; Environmental pollution

1. INTRODUCTION

As we know, shortages of water are harmful to the sustainability of human beings, and water recycling is essential to the resolution of this difficult issue. Wastewater, industrial wastewater, or municipal wastewater from household sources can be treated and recycled for potable and non-potable purposes. Treatment solutions differ according to the features and utilities of the wastewater [1]. For instance, coking wastewater, common in the steel industry, contains large numbers of pollutants, including phenolic compounds and ammonia [2]. The refractory organic compounds and inorganic ions (including the Cl^- ion) remain even after biological treatment, and the removal of these substances is essential in the case of wastewater reuse during production [3].

As an excellent and eco-friendly technique for the removal of persistent organic contaminants, electrochemical advanced oxidation processes (EAOPs) are ordinarily used with electrons as reagents. However, this technique suffers the primary disadvantage of high energy consumption and low current efficiency [4]. Direct or indirect oxidation (including chlorine and $S_2O_8^{2-}$) could cause damage to the organic pollutants [5]. DSA-type electrodes [6] and boron-doped diamond (BDD) electrodes [7] are the main anode materials used [7]. Carbon anodes have poor efficiency in oxidant (such as the hydroxyl radical) formation and a low O_2 evolution overpotential, which is why they have rarely been studied [8]. Fan and co-workers [9] studied amaranth azo dye degradation, in which the anode was activated carbon fibre (ACF). Positive and negative applied potentials were used for the electro-oxidation or electro-reduction of the pollutants, respectively.

The use of electrochemical oxidation techniques in wastewater treatment has been of great interest in recent years. In addition, the proposal of new anodes for organic compound degradation has attracted attention. Currently, the electrodes commonly used during electrochemical oxidation include graphite electrodes [10], iron electrodes [11], PbO_2 electrodes [12], noble metal electrodes [13, 14], dimensionally stable anodes (DSAs) [15-17] and boron-doped diamond electrodes (BDDs) [18-20]. The last two methods, which have been reported in recent years, are considered the most excellent ones. Increasing attention has been paid to the employment of DSA in indirect organic pollutant degradation, due to its high current efficiency in chloride ion oxidation [17]. However, the dyes would only be partially mineralized by the active chlorine (provided by the mixture of OCl^-, HOCl and Cl_2). Fortunately, via water oxidization, a substantial amount of hydroxyl radicals (OH·) with significant oxidant features could form on the surface of the BDD. Here, BDD electrodes could be used for thorough mineralization and colour removal. Cerisola and Panizza [21] presented a comparison in the catalytic activities of four electrode materials (BDD, PbO_2, Pt, and $TiRuSnO_2$) in the anodic oxidation of methyl red. As indicated in the bulk electrolysis, the use of BDD and PbO_2 led to thorough removal of colour and COD, whereas only a partial methyl red oxidation was observed using Pt and $TiRuSnO_2$. Chen and co-workers [22] further confirmed the better stability and activity of Ti/BDD electrodes compared with the Ti/SnO_2–Sb_2O_5 electrodes in the oxidization of the pollutants.

Three-dimensional electrodes have been proposed with the development of electrochemical technology [23]. The electrode area and the mass transfer of the solution may be enhanced by the porous structure of activated carbon fibre felt, the reticulated texture of a reticulated vitreous carbon electrode, and the particles of a packed bed electrode. Hence, activated carbon fibre (ACF) was used in the electrochemical treatment of wastewater as a new three-dimensional carbon electrode due to its desirable electric and catalytic performance, remarkable adsorption ability, and high specific surface area [9]. An applied potential of 1.7 V was obtained for the evolution of oxygen using an ACF electrode, nearly the same as that of a platinum electrode. Therefore, the dye can be electrochemically treated based on ACF (anode) under the synergic effect of electrochemical degradation and adsorption of dye on the anode, thus leading to an enhanced dye degradation efficiency along with an increase in the ACF life span.

This report used ACF electrode-based desalination as well as electrochemical oxidation to study the decontamination of wastewater that contained NaCl and phenol. We aim to develop a strategy that has potential application to the treatment of industrial wastewater as well as the ability to efficiently and simultaneously remove organic pollutants and inorganic salts.

2. EXPERIMENTS

2.1. Chemicals

Activation and carbonization involving the viscose fibre felts (precursors) were conducted to prepare viscose-based activated carbon fibre felts (VACFs), where the activation conditions were controlled to obtain a specific surface area range of 800–1700 m^2/g. A NaClO fresh solution from Fluka containing ∼13% active chlorine was used. It had a pH of ∼13, which was lowered to 10 by addition of 4 M HCl under the monitoring of a pH metre. Alizarin red S (ARS) obtained from Tianjin Xinchun Chemical Reagents Institute, China, was of analytical grade. All other test chemicals were of analytical reagent grade.

2.2. Electrochemical setup

Two ACF electrodes separated by a rubber gasket were parallel with each other in the undivided cell. A constantly recycling configuration was used for the batch mode tests. This configuration involved a conductivity/pH metre, a power supply, and a peristaltic pump, along with an electrochemical cell. Ordinarily, the feed solution was prepared by mixing phenol (1.1 mM) with NaCl (17.1 mM) to obtain a volume of 100 mL. The optimal temperature ranged from 28 to 48 °C, and the optimal potential ranged from 1.5 to 3.0 V, with a flow rate of 40 mL min^{-1}. N_2 or O_2 purging was conducted for the mixture for 0.5 h at 500 mL/min before tests, and the gas purging treatment was conducted throughout the polarization.

2.3. Characterization

An automated gas sorption analyser (Autosorb-iQ, Quantachrome) was used to record the nitrogen sorption isotherm at 77 K. The degassing of the specimen was conducted for 12 h at 120 °C prior to test. An electrochemical workstation (Autolab PGSTAT302 N, Metrohm) was used for the cyclic voltammetry (CV) measurement, which was conducted in NaCl (17.1 mM) under O_2 or N_2 bubbling at −1.0 to 1.5 V (vs. SCE) and a scan rate range of 1–50 mV/s. The working reference and counter electrodes were a 10 mm × 10 mm AC electrode (ca. 10 mg), a saturated calomel electrode (SCE), and a platinum sheet. The direct oxidization of phenol was assessed by adding phenol (1.1 or 5.5 mM) in certain cases.

2.4. Analytical methods

A conductivity metre (Orion 3-Star, Thermo Fisher Scientific Inc.) was used for constant monitoring of the effluent conductivity. High performance liquid chromatography (HPLC, 1200 infinity series, Agilent) was performed with a Zorbax SB-C18 column to obtain the concentration of phenol and its oxidation intermediates. The electrolyte influence analysis was conducted on a Na_2SO_4 solution with different concentrations. Prior to the tests, we measured the relationship of the concentration and conductivity. Methanol was mixed with water + H_3PO_4 (10 mM; 25%/75%, *V*/*V*) to yield the mobile phase. Through the batch experiments, the influences of electrolytic conditions, including the initial pH of solution, the current density, and the supporting electrolyte on the phenol degradation, were studied. The absorbencies of the tested solutions at 407 nm were determined at different time intervals to evaluate the colour removal efficiency. The COD removal efficiency could be derived from COD values of the original solution and the treated solution after 60 min of electro-oxidation. A TOC analyser (TOC-V_{CPH}, Shimadzu) was used to obtain the total organic carbon (TOC). The iodide strategy (350 nm) and potassium titanium (IV) oxalate reagent, using a spectrophotometric measurement (400 nm), were used to obtain the total concentration of possible oxidants (including chlorine and H_2O_2) and the concentration of H_2O_2, respectively [24]. The phenol oxidation process was conducted using NaClO. Specific quantities of a 1.668 M NaClO solution adjusted to pH 10 were added dropwise, while the pH of the reacting solution was monitored to 10 by dropwise addition of 0.5 M aq NaOH. The oxidation progress was monitored by the consumption of NaOH.

3. RESULTS AND DISCUSSION

A micropore surface area of 102 m^2/g and a BET specific surface area of 297 m^2/g were obtained. As indicated in the PSD profile, the majority of the pores were measured at greater than 1 nm, providing a desirable condition for the adsorption of ions. The AC electrode was characterized via the CV profiles (Fig. 1). The CVs recorded under O_2 and N_2 atmospheres are shown in Fig. 1A and Fig. 1B, respectively. When the sweep rate was 10 or 50 mV/s, no cathodic or anodic peaks were observed, whereas these peaks could be recorded when the sweep rate was low – at 1 mV/s. When the applied potential exceeded 1.2 V, a rapid increase in the anodic current was observed. This could possibly be ascribed to the oxidization of Cl^-. When 1.0 V was applied, we observed a cathodic peak. A comparison of the CVs at a scan rate of 1 mV/s under N_2 and O_2 atmospheres is presented in Fig. 1C. As indicated in Fig. 1D, another oxidization peak was observed after adding phenol when the potential was ca. 0.79 V, which increased as the concentration of phenol was increased. The main difference is that the cathodic current is higher under an O_2 atmosphere, as O_2 will be reduced at a negative potential [25]. The primary contributing factor of the appearance of this peak might be the oxidization of the phenol. The peak is possibly attributed to phenol oxidation. The direct phenol oxidation is viable by the electrochemical method [26].

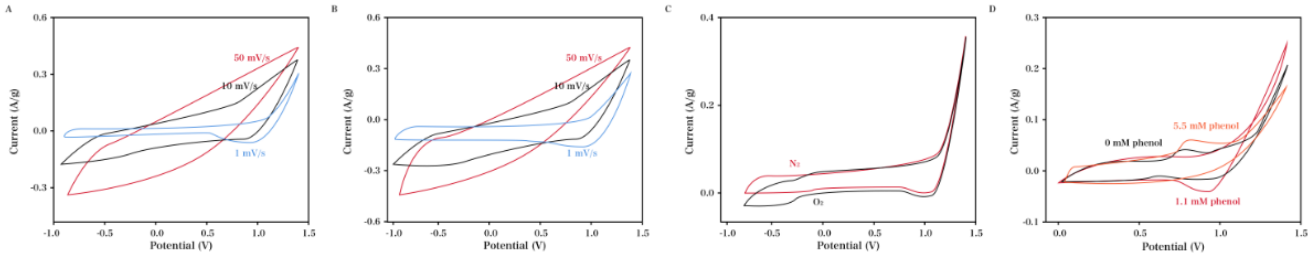

Figure 1. CVs of (A) nitrogen atmosphere and (B) oxygen atmosphere; (C) comparison of CVs under varying atmospheres at 1 mV/s; (D) comparison of CVs before and after adding phenol at 1 mV/s (Electrolyte: 0.12 M Na_2SO_4, pH: 4.5).

The removal of phenol was investigated at 28 °C and a potential of 0 or 2.0 V using varying concentrations of O_2, as indicated in Fig. 2A. A value of 39% was obtained as the phenol removal efficiency, where the adsorption was conducted under an open circuit condition. A similar removal efficiency was recorded with N_2 bubbling at 2.0 V, suggesting that the adsorption led to the removal. After polarization was performed for 300 min, the conversion of phenol was ca. 55% in the absence of any gas. However, the conversion of phenol was obviously enhanced in the presence of O_2 bubbling (flow rate: 500 mL/min). The possible oxidants in the solution, such as H_2O_2, Cl_2, and ClO^-, were detected [27]. The oxidants are mostly Cl_2 and ClO^- (as the solution pH is ~9.0), and H_2O_2 was not detected. An increase in the formation of chlorine-containing oxidants was observed with the increase in O_2 concentration, which possibly enhanced the phenol removal to a great extent [24]. Fig. 2C indicates the potential at the anode, where the SCE was used. It can be seen that a higher anodic potential (ca. 1.32 V) was obtained when O_2 was bubbled compared with that obtained in the absence of gas or N_2 bubbling, leading to the formation of Cl_2. To further elucidate the mechanism, a divided cell was constructed with the same AC electrode for the anode and the cathode, separated by a Nafion 117 cationic membrane. This experiment revealed that Cl_2 is produced in the anodic chamber, while H_2O_2 accumulates in the cathodic chamber when O_2 is bubbled instead of N_2.

A constant conductivity was maintained when 0 V was applied, whereas a significant decrease was observed at 2.0 V, as indicated in Fig. 2D, due to the electrosorption of ions onto the porous carbon electrode surfaces. When the concentration of O_2 was higher, the decrease in conductivity was more obvious. This phenomenon is contrary to the literature, which shows better desalination performance under a nitrogen atmosphere [28]. Unfortunately, potential Faradaic reactions could be prevented by the absence of oxygen, along with the low potential (0.9 V) in the previous experiments. Meanwhile, the consumed charge led to ion adsorption. However, it can be seen from the pH value variations that the reactions, including the oxidization of Cl^- and the reduction of oxygen, would occur due to the adequate oxygen and higher potential in this study. The above reactions might be the possible contributing factors to the salt removal improvement.

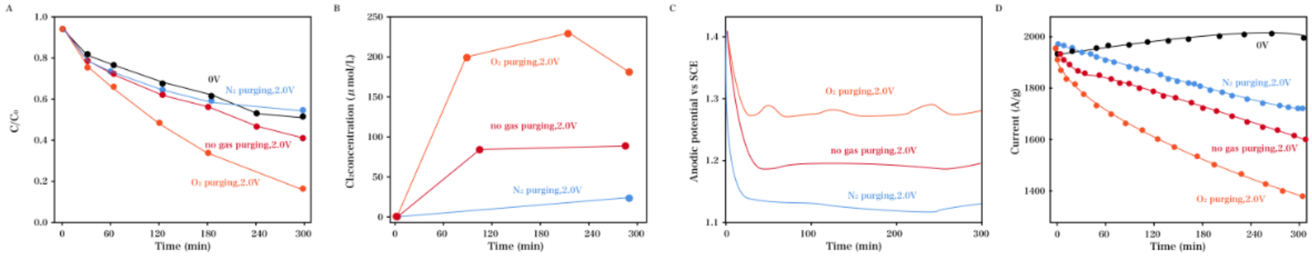

Figure 2. The profiles of (A) the concentration of phenol, (B) the concentration of chlorine, (C) anodic potential, and (D) conductivity when purged with nitrogen and oxygen and without gas purging (temperature: 28 °C, applied potential: 2.0 V).

The effect of the concentration of Na_2SO_4, the supporting electrolyte, on the wastewater degradation efficiency was investigated. After electrolysis for 1 h, all specimens showed identical colour and COD removal efficiency, as indicated in Fig. 3A and Fig. 3B, respectively. Hence, the degree of terminal degradation of the dye was slightly affected by the Na_2SO_4 concentration, since the Na_2SO_4 addition would lead to a solution conductivity increase and a cell voltage decrease, along with a reduction in electrical energy consumption. Nevertheless, we recorded a comparatively higher colour removal efficiency at the preliminary stage (below 40 min) with a higher Na_2SO_4 concentration. A gradual decline in this variation was observed when the electrolysis was further continued, due to the basically slight amount of electrogenerated persulfate and the corresponding non-decisive influence in the degradation of the wastewater.

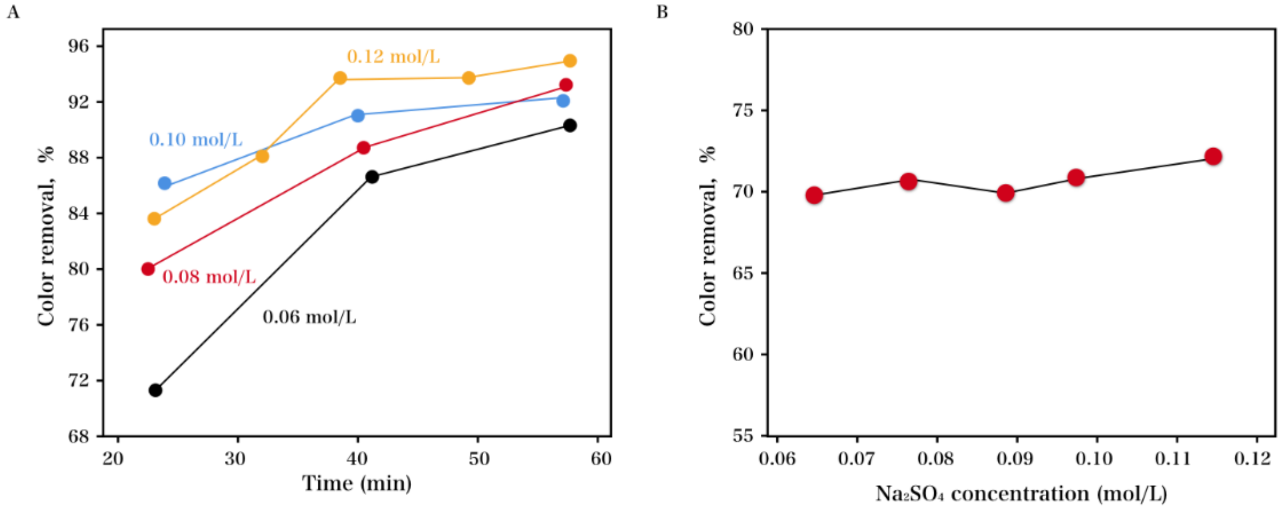

Figure 3. Effect of Na_2SO_4 concentration on the removal of (A) colour and (B) COD (temperature: 28 °C, applied potential: 2.0 V).

The degradation efficiency of wastewater can be enhanced by NaCl, as shown in Fig. 4. The efficiency removal of the COD and colour obtained after electrolysis for 1 h was observed to increase by 10.6% and 3.7%, respectively, after adding NaCl.

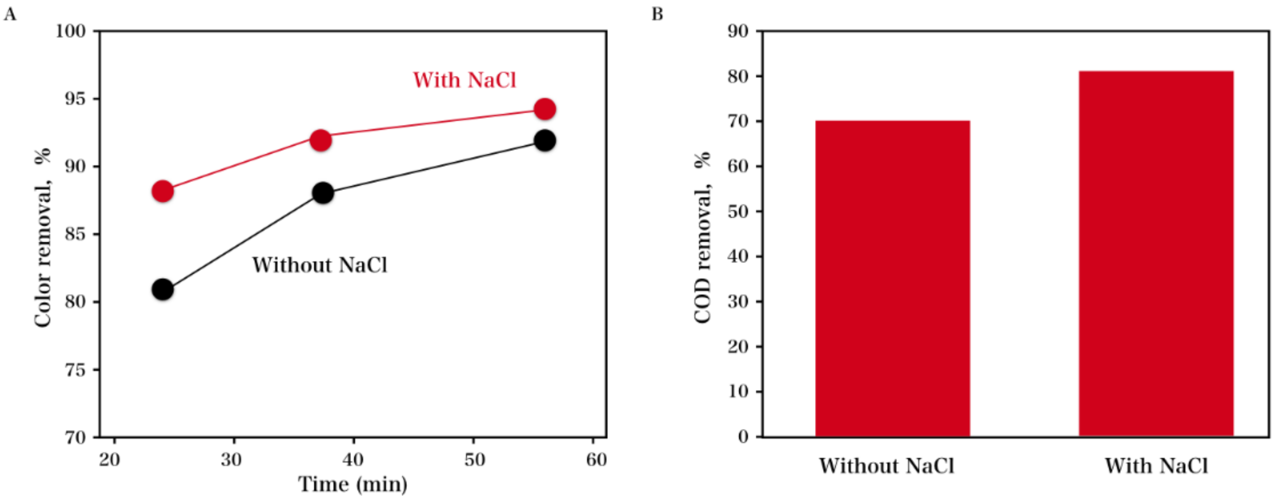

Figure 4. Effect of the NaCl addition on the removal of (A) colour and (B) COD (temperature: 28 °C, applied potential: 2.0 V).

Under an O_2 atmosphere, we determined various degradation intermediates. The intermediates were identified using high-performance liquid chromatography. Within the initial 3 min, an increase in the 2-chlorophenol (2-CP) and 4-chlorophenol (4-CP) concentration was observed, followed by a decrease after prolonged time (Fig. 5A).

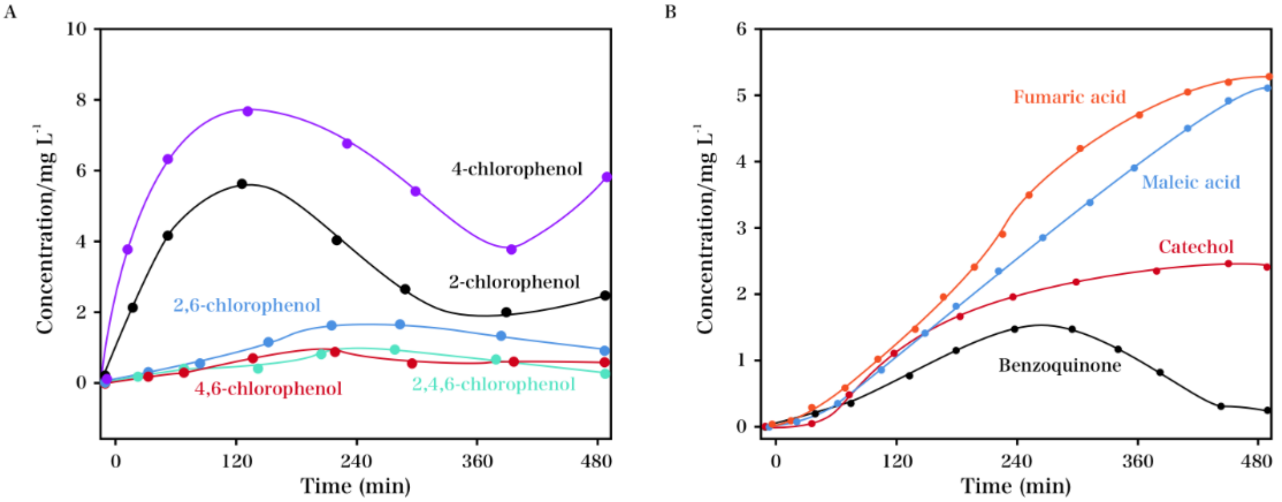

Figure 5. Development of (A) chlorophenols and (B) other degradation intermediates in the process of phenol electrolysis of 1.1 mM phenol in 17.1 mM NaCl at 28 °C and 2.0 V.

Trichlorophenols and dichlorophenols showed similar concentration variation trends. In addition, Fig. 5B indicates the increase in the fumaric acid and maleic acid concentrations as the measurement was continued. The concentrations of catechol and benzoquinone were low, suggesting the possibility of the direct oxidization of the phenol. We performed two tests to understand the mechanism in a better way. The *t*-butanol posed no inhibition of the degradation of phenol. Instead, it was promoted to some extent. Nevertheless, the conversion of phenol possibly occurred in the absence of the hydroxyl radical. We further carried out a test in which phenol was chemically oxidized using NaClO. These results suggested the oxidization of phenol into 2-CP and 4-CP, followed by the formation of 2,4,6-trichlorophenol and dichlorophenols. The electrochemical degradation of phenol in our system is possibly performed by two pathways. One is through indirect chlorine mineralization. Chlorophenols are formed as intermediates in this pathway and finally oxidized to carboxylic acids and CO_2. Another is through direct oxidation. Benzoquinone and catechol are generated by hydroxylation through this pathway [29, 30].

The charging/regeneration cycles were conducted for several successive runs using the electrodes. After the charging maintained for 3 min at phenol, 5 (1.1 mM) and NaCl (17.1 mM), a potential shift to −1.0 V was observed for 10 min, followed by 0 V (short circuit) for 110 min for the generation of the electrodes. After charging/regeneration cycles were conducted 5 times, a gradual reduction of salt and phenol removal efficiency was observed due to the organic fouling of the as-prepared electrodes.

4. CONCLUSIONS

In this work, the simultaneous removal of an inorganic salt (NaCl) and an organic pollutant (phenol) from solution by ACF electrodes was investigated. The phenol was removed by adsorption, direct electrochemical oxidation and chlorine-mediated oxidation. Meanwhile, the electrosorption of ions was significant. An ACF electrode that has a higher specific surface area and mesopore percentage can more effectively adsorb and concentrate target molecules from the solution on its surface, which facilitates the electro-oxidation degradation of wastewater. As a result, a higher removal efficiency can be obtained by using an ACF anode with a high surface area and high mesopore percentage.

ACKNOWLEDGEMENTS

This study was supported by the National Major Project of Science and Technology on water pollution control and management of China comprehensive treatment technology and research project on Liao river basin (NO. 2012 ZX072009).

References

1. Z. Chen, H. Ngo and W. Guo, *Critical Reviews in Environmental Science and Technology*, 43 (2013) 1446.
2. H. Li, H. Cao, Y. Li, Y. Zhang and H. Liu, *Water Science and Technology*, 62 (2010) 2096.
3. H. Li, Y. Li, H. Cao, X. Li and Y. Zhang, *Water Science and Technology*, 64 (2011) 63.
4. E. Brillas, I. Sirés and M. Oturan, *Chemical reviews*, 109 (2009) 6570.
5. C. Martinez-Huitle and S. Ferro, *Chemical Society Reviews*, 35 (2006) 1324.
6. E. Chatzisymeon, S. Fierro, I. Karafyllis, D. Mantzavinos, N. Kalogerakis and A. Katsaounis, *Catalysis Today*, 151 (2010) 185.
7. R. Daghrir, P. Drogui and J. Tshibangu, *Sep. Purif. Technol.*, 131 (2014) 79.

8. D. Ghernaout, M. Naceur and A. Aouabed, *Desalination*, 270 (2011) 9.
9. L. Fan, Y. Zhou, W. Yang, G. Chen and F. Yang, *Dyes and Pigments*, 76 (2008) 440.
10. Z. Shen, D. Wu, J. Yang, T. Yuan, W. Wang and J. Jia, *J. Hazard. Mater.*, 131 (2006) 90.
11. B. Körbahti, *J. Hazard. Mater.*, 145 (2007) 277.
12. H. Awad and N. Galwa, *Chemosphere*, 61 (2005) 1327.
13. J. Chen, M. Liu, J. Zhang, Y. Xian and L. Jin, *Chemosphere*, 53 (2003) 1131.
14. D. Doğan and H. Türkdemir, *Journal of Chemical Technology and Biotechnology*, 80 (2005) 916.
15. D. Rajkumar, B. Song and J.G. Kim, *Dyes and pigments*, 72 (2007) 1.
16. N. Mohan and N. Balasubramanian, *J. Hazard. Mater.*, 136 (2006) 239.
17. F. Oliveira, M. Osugi, F. Paschoal, D. Profeti, P. Olivi and M. Zanoni, *Journal of Applied Electrochemistry*, 37 (2007) 583.
18. E. Butrón, M. Juárez, M. Solis, M. Teutli, I. González and J.L. Nava, *Electrochimica Acta*, 52 (2007) 6888.
19. C. Saez, M. Panizza, M. Rodrigo and G. Cerisola, *Journal of Chemical Technology and Biotechnology*, 82 (2007) 575.
20. P. Cañizares, A. Gadri, J. Lobato, B. Nasr, R. Paz, M. Rodrigo and C. Saez, *Ind. Eng. Chem. Res.*, 45 (2006) 3468.
21. M. Panizza and G. Cerisola, *Appl. Ctatl. B-Environ.*, 75 (2007) 95.
22. X. Chen, F. Gao and G. Chen, *Journal of Applied Electrochemistry*, 35 (2005) 185.
23. P. Tissot and M. Fragniere, *Journal of Applied Electrochemistry*, 24 (1994) 509.
24. C. Kormann, D. Bahnemann and M.R. Hoffmann, *Environ. Sci. Technol*, 22 (1988) 798.
25. Q. Ping, Z. Huang, C. Dosoretz and Z. He, *Water research*, 77 (2015) 13.
26. J. Skowroński and P. Krawczyk, *Chemical Engineering Journal*, 152 (2009) 464.
27. H. Yuan, I. Abu-Reesh and Z. He, *Chemical Engineering Journal*, 270 (2015) 437.
28. F. Zhang and Z. He, *Desalination*, 360 (2015) 28.
29. Q. Ping, C. Zhang, X. Chen, B. Zhang, Z. Huang and Z. He, *Environmental Science & Technology*, 48 (2014) 13010.
30. H. Yuan and Z. He, *Bioresource Technology*, 195 (2015) 202