Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.24129

157 (2019) 53–61
July

Effects of $FeSO_4$ and H_2O_2 on earthed atomizing corona discharge technique for the styrene–butadiene rubber wastewater treatment

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Received 22 September 2018; Accepted 16 March 2019

ABSTRACT

In this work, earthed atomizing corona discharge (EACD) technique was used to dispose wastewater produced during the manufacture of styrene–butadiene rubber. The effects of discharge time, volume of H_2O_2 $\left(V_{H_2O_2}\right)$, and concentration of $FeSO_4$ $\left(C_{FeSO_4}\right)$ on turbidity (T_b), pH value, biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), and the biodegradability of styrene–butadiene rubber wastewater (SBRW) was investigated using the EACD technique treatment process. After a cumulative EACD treatment for 21 min (i.e., three discharge cycles), the COD and T_b values of SBRW both decreased by 67% (from 600.8 to 200.0 mg L^{-1} for COD and from 106.0 to 35.0 NTU for T_b). The pH value remained unchanged, while the BOD_5 value initially increased as the discharge time increased and then reached equilibrium. The COD value decreased subsequently to 80.0 mg L^{-1} after a cumulative EACD treatment of 21 min when $FeSO_4$ was added. Meanwhile, the total decrease in the efficiency of the COD value was about 86.7%. However, the results show that H_2O_2 had no impact on decreasing the COD value or improving the biodegradability. Therefore, the addition of $FeSO_4$ had a positive effect on decreasing the COD value for SBRW by cooperating with the EACD technique.

Keywords: Electrochemical technique; Organic wastewater treatment; COD; Biodegradability

1. Introduction

Since styrene–butadiene rubbers are widely used in various industrial manufacturing fields, a significant amount of styrene–butadiene rubber wastewater (SBRW) is produced during their manufacture and using process. SBRW has a complex composition, and it mainly consists of refractory degradation benzene compounds, chemical additives, and various aromatic hydrocarbon compounds. As a result, SBRW is a toxic and low-biodegradable refractory industrial wastewater [1–3] that should be treated before discharge, and significant efforts have focused on the best method to treat SBRW [1–15]. The technologies that have been proposed to dispose this wastewater include hydrolytic acidification [1], biological treatment technologies [2,4–7], microelectrolysis [3], membrane bioreactor method [8,9], ozone oxidize [10], aerobic granular sludge technology [11], Fenton reagent oxidation [12,13], coagulation–catalytic oxidation process [14], and coagulating sedimentation [14,15]. However, these methods have some drawbacks when used to treat SBRW, such as time-consuming and complicated operation and so on. Therefore, a new technique should be developed that is more effective and environmentally friendly to treat the refractory wastewater so it can be properly disposed.

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The application of discharge technology in the treatment of wastewater has recently received increased attention since it is both environmentally friendly and can be used to effectively treat organic pollutants [16–24]. A pulsed discharge plasma technique could improve the degradation efficiency of organic pollutants without secondary pollution, due to a variety of active species ($^{\bullet}OH$, $^{\bullet}O$, O_2^-, $^{\bullet}HO_2^-$, etc.) produced during the treatment process [16–21]. The EACD technique was recently adopted to treat oily wastewater, and this method reduces the required energy and reaction time because the plasma region was synchronized with the reaction zone, which also increases the effectiveness of the active species for wastewater treatment [19]. Because the contact surface area of the wastewater and active species was increased, the EACD technique improved the degradation of organic pollutants, suggesting that this method has advantages in using it to treat styrene–butadiene rubber wastewater.

In this work, the EACD technique was used to improve the degradation efficiency and biodegradability of organic pollutants present in SBRW. The research was carried out in our laboratory throughout the study and started in April 2018. The *I-V* characteristics of the method were studied to ensure a sufficient discharge voltage and appropriate inter-electrode distance was used during the advanced oxidation treatment of the SBRW. Two chemical reagents, H_2O_2, and $FeSO_4$, were used to investigate their influence on the SBRW treatment in this technique, and the effects of discharge time, $V_{H_2O_2}$ and C_{FeSO_4} on T_b, pH, biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), and biodegradability of SBRW were investigated to evaluate the quality of water. Besides, BOD_5, COD, T_b, and the pH values of the original SBRW and treated SBRW were measured. The results indicated that the EACD technique effectively reduced the COD and improved the biodegradability of SBRW.

2. Experiments

2.1. Materials and methods

H_2O_2 and $FeSO_4{\cdot}7H_2O$ were purchased from Sinopharm Chemical Reagent Co., P.R. China, and all chemicals were of analytical grade and used as received. The wastewater was sourced from Fushun petrochemical company of Petro China Co., China. COD, BOD_5, pH, and T_b of original wastewater were 600.8, 50.0 mg L^{-1}, 6.2, and 106.0 NTU, respectively.

The experimental setup used in this work to dispose SBRW by the EACD technique was based on the work of Du et al. [16] with a slightly modified procedure. The maximum output voltage, the maximum supply control current, and the power of the oil-immersed DC testing transformer high-voltage DC power supply (YDJ-50/50, Wuhan HV Hipot Electric, Co., Ltd., China) was 70 kV, 70 mA, and 5 kVA, respectively. The voltage supplied was regulated by using a voltage regulator.

The stainless steel line electrode with a 0.3 mm diameter was in the center of an iron tubular electrode, which had a diameter and height of 56 and 80 mm, respectively. It was linked to a low-voltage pole or earth pole with a power supply provided by an ammeter 1 (A1) (Yokogawa 201131 DC, Yokogawa Meters and Instruments Corporation, Japan, class 1.0) or ammeter 2 (A2) (C21/1-μA DC micro-ammeter, Yangzhou Subo Electric Co., Ltd., China). A1 was connected to the circuit, while A2 was unconnected from the circuit to measure the corona current. The maximum scale values of A1 and A2 were 3 and 150 μA, which each had a degree of precision of ±1%. The small-scale value of A1 observed was the onset voltage. The tubular electrode was connected to the high-voltage pole.

A WNY 600 speed micro metering pump (Chengdu Xinweicheng Technology Co., Ltd.) was used to pump the water from the bottom to the top of the tank, with a maximum lift, power, and water supply speed of approximately 2 m, 4.2 W, and 180 mL min^{-1}, respectively.

2.2. SBRW treatment experiment

First, the water voltage was identified as 0.0 V when it did not flow through the tubular electrode because the maximum discharge current of the ammeter was even smaller than 100 μA due to the presence of resistance. The voltage between the inter-electrode was monitored with a digital high-voltage DC divider (kV shown in Fig. 1; FRC-100, Shanghai Gongdian instrument Co., Ltd., China), with a resistance of 1,100 MΩ a 1,000:1 voltage division ratio, and an accuracy of 0.5%. The measurement range of the digital high-voltage DC divider was 0–100 kV.

Second, when A1 was connected to the circuit, the voltages between the line and tubular electrodes were slowly increased until the A1 electric current was higher than 0 μA, and the voltage measured then was recorded as the onset voltage. When voltage shown on the digital high-voltage DC divider was greater than the onset voltage, the A2 was connected into the circuit to measure the corona current, and the A1 disconnected.

Third, the water in the top water tank flowed down and evenly covered the surface of the line electrode, which was

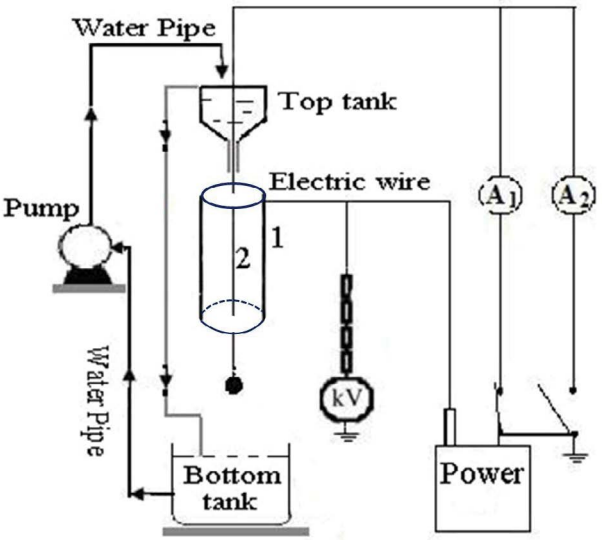

Fig. 1. Experimental setup [16], where the bottom and top tanks were made of plastic. The bottom tank and pump were placed on insulating rubber slabs. (1) Iron tubular electrode and (2) line electrode.

in the center of the water spout. Water circulation was maintained to ensure a stable flux velocity on the line electrode surface using the water pump. One circulation where 500 mL of the water samples (original SBRW or original SBRW with Fe_2SO_4 or H_2O_2) moved from the top tank to the bottom tank and back to the top tank was completed every 7 min with a water flux velocity of approximately 71 mL min^{-1}. As it can be seen, the water volume $\left(V_{H_2O}\right)$ during each circulation every minute was 14% of the total volume. In previous reports [12,21], the highest electric field intensity was present on the line electrode's surface, and a corona zone was formed around the line electrode when the onset voltage was exceeded.

2.3. Characterization

The biodegradability and water quality of the SBRW was determined by measuring the COD, BOD_5, T_b, and pH values after treatment by the EACD technique. The COD values of the water samples were determined by a chemical oxygen determiner (COD HH-6, Jiangsu, China) using a fast digestion spectrophotometric method (HJ/T 399–200). The BOD_5 value of water samples was determined using a BOD_5 rapid testing instrument (BOD_5-220A, Tianjing, China) equipped with a sensor for the rapid testing of microorganisms (HJ/T 86–2002). The T_b of water samples was determined using a turbidity meter (WGZ2000, Shanghai, China), while the pH values of the water samples were determined using a pH meter (InoLab pH 7200, Germany).

3. Results and discussion

3.1. Earthed atomizing corona discharge test

Discharge characteristic of the EACD technique for the SBRW was investigated. The voltage for the tubular electrode was separately provided by the positive and negative poles of a DC high-voltage power supply, and the effect of voltage (V) on the discharge current (I) is shown in Fig. 2. The results indicated that I of the corona discharging greatly exceeded the traditional corona discharge [16] for both the positive and negative electrodes using the same voltage, while the I produced by the negative pole was higher than that produced by the positive pole of the high-voltage power supply. This phenomenon may be caused by a Taylor cone which produced multiple cone-shaped jets that flowed when the surface water voltage increased on the line electrode, when the voltage of the tubular electrode reached a certain value [16]. For example, when the voltage of the tubular electrode >8 kV with circulating water or 10 kV without circulating water, I was produced that increased as the tubular electrode voltage increased. In addition, the peak voltage was 14 kV for both power poles, and the flow direction of I was from the negative pole to the positive pole of the earthed atomizing corona. The results obtained here agree with previous reports [16,25].

The effect of water flux on I is shown in Fig. 3, where the voltage of the tubular electrode was provided by the negative pole of the power supply and I is shown to increase as the voltage increased. When the water flux was >0 mL min^{-1}, I decreased as the water flux increased. These results show that a voltage of 11 kV ensures a sufficient I for 71 mL min^{-1} of water flux for the degradation of pollutants.

3.2. Effect of discharging time on SBRW treatment by EACD technique

The ways in which discharging affected the pH, COD, T_b, and BOD_5 of the original wastewater were investigated, and the results are shown in Fig. 4. The results show that the pH did not change and remained near 6.2, while both the COD and T_b values decreased as the discharging time increased. The BOD_5 value increased to about 70 mg L^{-1} after 21 min of discharging because the organic macromolecular pollutants were decomposed into small molecular biodegradable contaminants when the COD value decreased. Thus, the total number of organic compounds increased, which led to an increase in the BOD. In contrast, the COD value was reduced to nearly 200.0 from 600.8 mg L^{-1} with a reduction efficiency of approximately 66.7%. The T_b decreased from 106.0 to 35.0 NTU, and the reduction efficiency is approximately 67.0%.

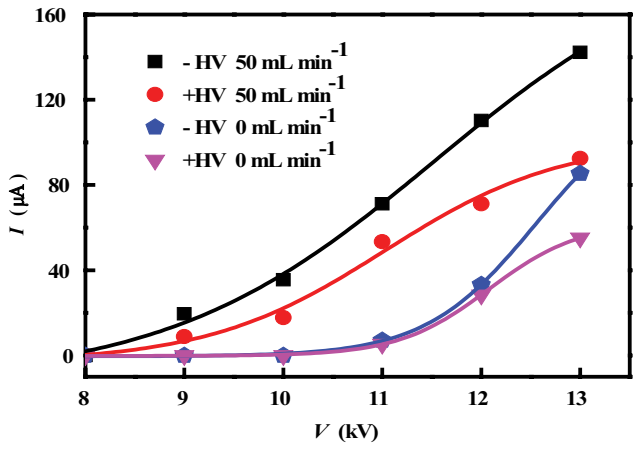

Fig. 2. Effect of voltage (V) on discharge current (I) for earthed atomizing corona discharge in this system.

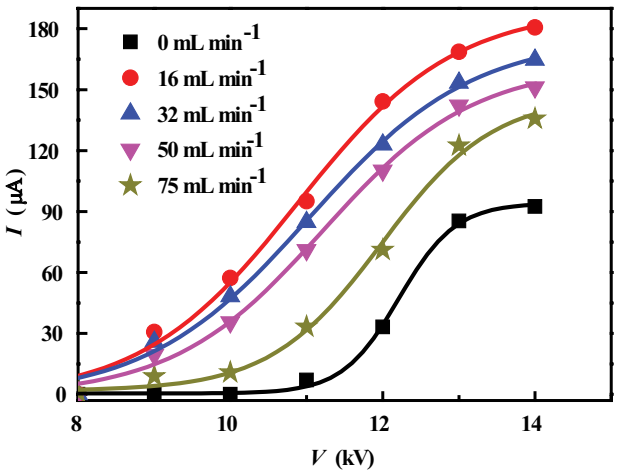

Fig. 3. Effect of water flux on discharge current (I).

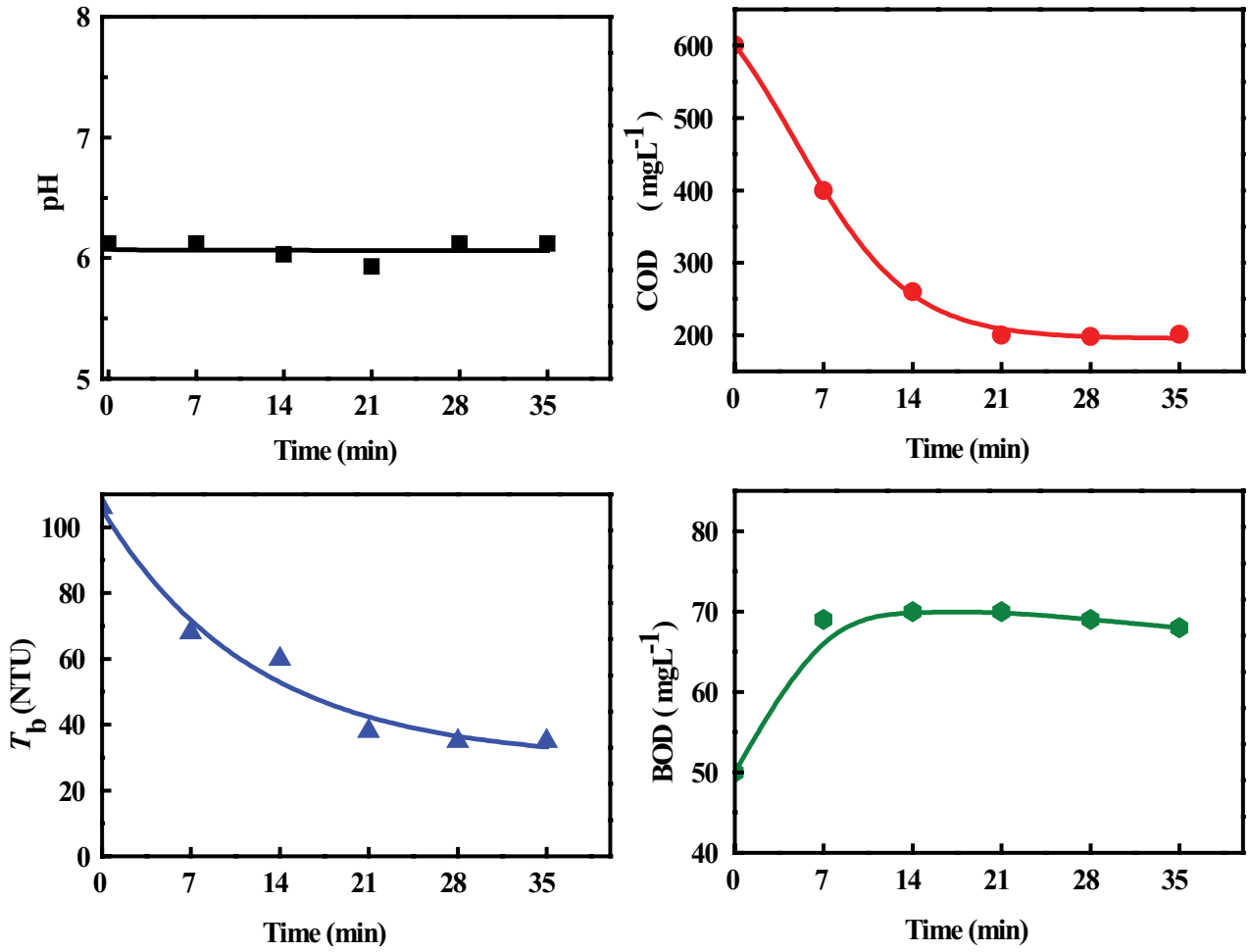

Fig. 4. Effects of discharging time on pH, COD, T_b, and BOD_5 of original SBRW.

The biodegradability was evaluated by calculating the ratio of BOD_5 to COD, shown in Fig. 5, which shows that the ratio of BOD_5 to COD increased from 0.08 to 0.35 after 21 min of cumulative discharging (i.e.. three cycles). The biodegradability was improved by approximately 77.0%, which indicates that the EACD technology can be used to effectively treat SBRW.

3.3. Effect of C_{FeSO_4} on SBRW treatment by EACD technique

The effects of C_{FeSO_4} on pH, COD, T_b, and the BOD_5 values of SBRW are shown in Fig. 6 after cumulatively discharging for 21 min. pH was nearly unchanged, while T_b showed a slight increase as the C_{FeSO_4} increased, since the color of the ferrous sulfate aqueous solution is light green, causing the color of the SBRW system to change slightly. The COD and BOD_5 values both decreased as the C_{FeSO_4} increased. This is consistent with the study by Lai et al. [2], in which the thousands of microscopic galvanic cells formed with iron on the surface of sponge iron can degrade the pollutants when contacted the wastewater. The COD value decreased by an

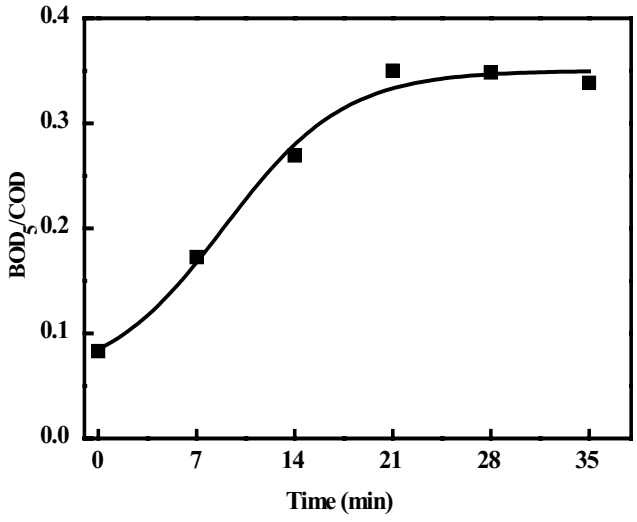

Fig. 5. Effects of discharging time on the ratio of BOD_5 to COD for original SBRW.

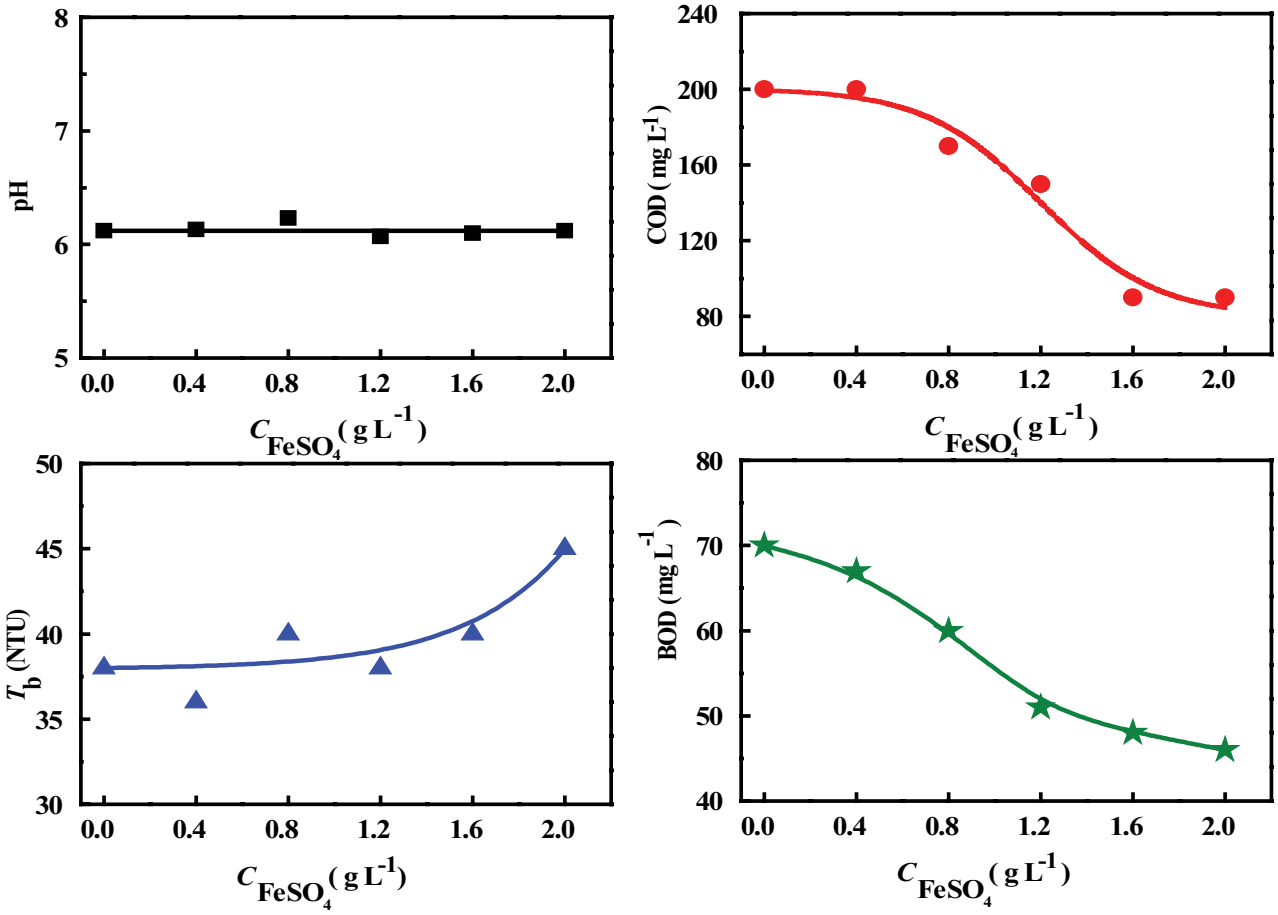

Fig. 6. Effect of C_{FeSO_4} on pH, COD, T_b, and BOD_5 values of the SBRW after discharging for 21 min.

additional 60.0%, from ~200.0 to ~80.0 mg L^{-1}, and the total reduction efficiency of the COD value was ~86.7% for the original SBRW. The BOD_5 value decreased by 34.3%, from ~70.0 to ~46.0 mg L^{-1} which is likely because the biodegradable organic pollutants were completely degraded when the COD value dropped below 100 mg L^{-1}.

Additionally, the ratio of BOD_5/COD increased ~57.1% after cumulatively discharging for 21 min with C_{FeSO_4} increasing, as shown in Fig. 7. The ratio of the BOD_5 to COD values increased from 0.35 to 0.54, which indicates that the addition of $FeSO_4$ significantly improved the biodegradability.

These results have shown that the $FeSO_4$ is an effective additive for the EACD technique for the treatment of SBRW. The concentration of Fe^{2+} $\left(C_{Fe^{2+}}\right)$ was unchanged before and after discharge, with a $C_{Fe^{2+}}$ value of 4.015 g L^{-1} before EACD, and a value of $C_{Fe^{2+}}$ = 4.003 g L^{-1} after the treatment, as measured by inductive coupled plasma emission spectrometer. This suggests that $FeSO_4$ played a role in the catalyzed electrical degradation.

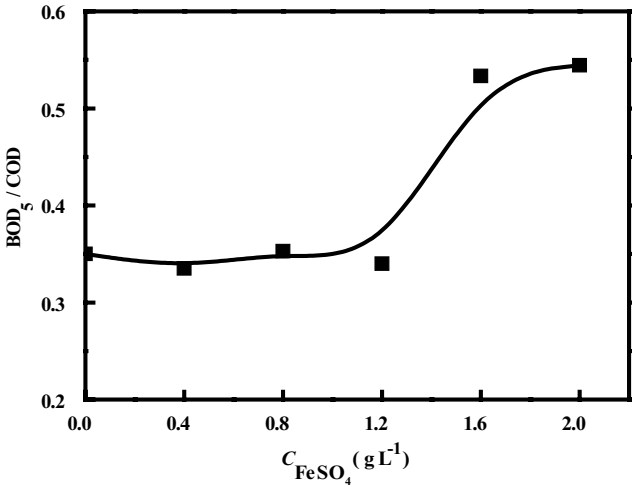

Fig. 7. Effect of C_{FeSO_4} on the ratio of BOD_5 to COD for SBRW after discharging for 21 min.

3.4. Effect of H_2O_2 on SBRW treatment by EACD technique

H_2O_2 was used as an oxidant in an attempt to further disintegrate the pollutants. First, the effect of discharging time on pH, COD, T_b, and BOD_5 value of the original SBRW was investigated at $V_{H_2O_2}$ = 3.0 mL, and the results are shown in Fig. 8. It was shown that the reaction reached equilibrium after plasma discharging for 21 min, while the results were

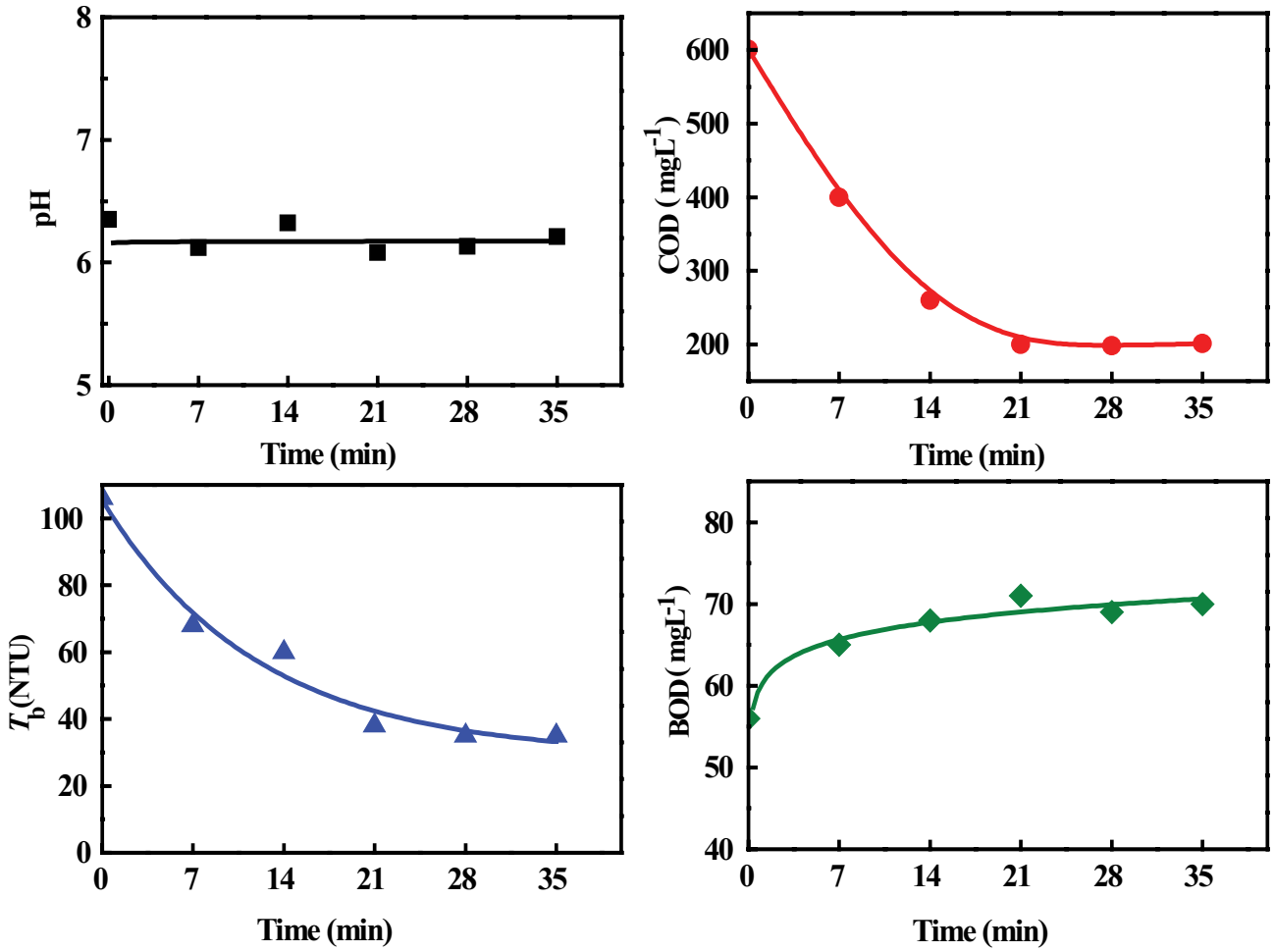

Fig. 8. Effects of discharging time on pH, COD, T_b, and BOD_5 of the original SBRW at $V_{H_2O_2}$ = 3.0 mL.

nearly unchanged at $V_{H_2O_2}$ = 3.0 mL, compared with samples without addition of H_2O_2 at an identical discharging time. The initial BOD_5 value showed a slight increase when H_2O_2 was added because the H_2O_2 oxidized the pollutants into small molecule organic material, which increased the number of intermediate products. The H_2O_2 can also be used to kill bacteria, which limits the magnitude of the BOD_5 increases.

The biodegradability was reflected from the ratio of the BOD_5/COD values shown in Fig. 9, which shows that an increase in the discharge time initially increased BOD_5/COD, which reached an equilibrium value at a discharge time of 21 min. However, the H_2O_2 did not contribute to the biodegradability of the system.

Fig. 10 shows the effect of $V_{H_2O_2}$ on pH, COD, T_b, and BOD_5 of the original SBRW after 21 min of discharging. The results showed that H_2O_2 did not affect the treatment of SBRW using the EACD technique, even at a C_{FeSO_4} = 1.6 g L^{-1} in the original SBRW (Fig. S1), and the biodegradability was also not affected by $V_{H_2O_2}$ (Fig. S2). The reason is still not clear. The possible reason is that the H_2O_2 and Fe^{2+} did not form the Fenton solution at the partial neutral condition and hydroxyl radicals were not produced. The H_2O_2 may decompose into the H_2O and O_2 in the system. Therefore, the H_2O_2 did not notably improve the SBRW treatment when the EACD technique was used.

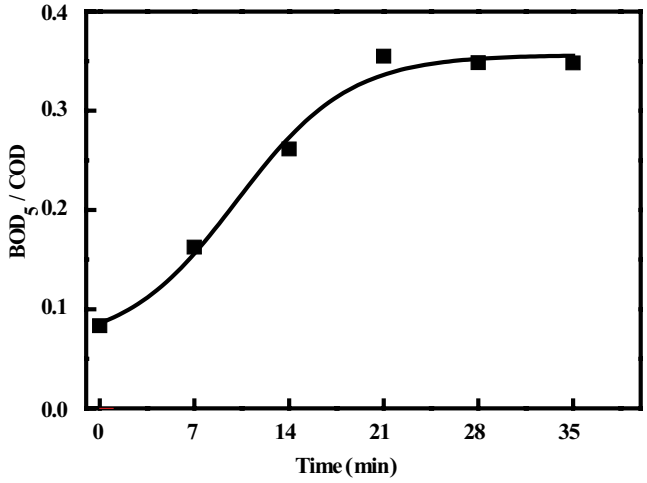

Fig. 9. Effect of discharging time on the ratio of BOD_5 to COD for original SBRW with 3.0 mL H_2O_2 addition.

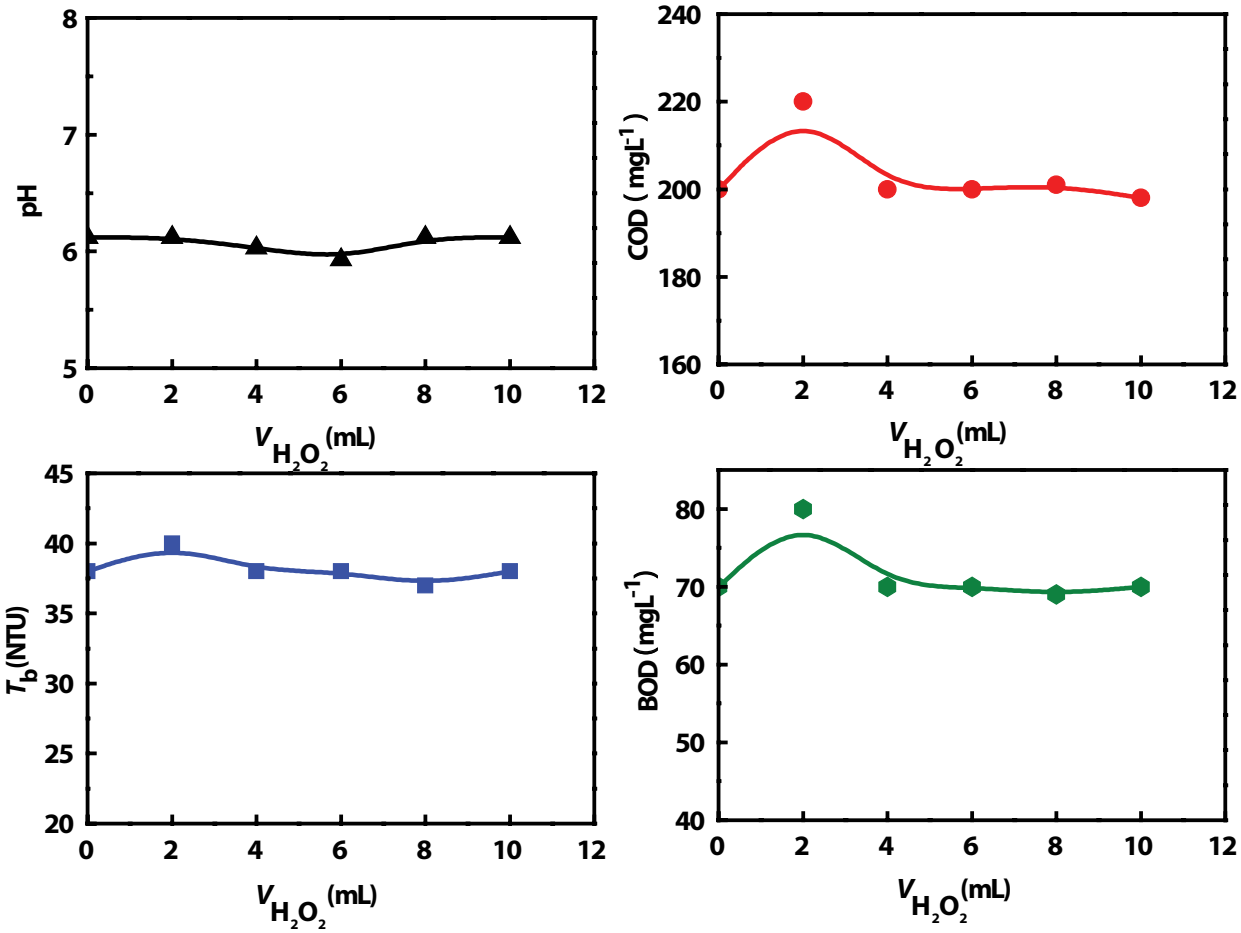

Fig. 10. Effect of $V_{H_2O_2}$ on pH, COD, T_b, and BOD_5 of SBRW after plasma discharging for 21 min.

4. Conclusions

This paper is the first report that describes the use of earthed atomizing corona discharge technique (EACD) to degrade SBRW. Two reagents, H_2O_2 and $FeSO_4$, were used to investigate their influence on the SBRW treatment in this technique. The effects of discharging time, $V_{H_2O_2}$, and C_{FeSO_4} on T_b, pH, BOD_5, COD, and biodegradability of SBRW were investigated to evaluate the water quality. It was found that the EACD technique was effective for treatment of SBRW, especially for both the COD and T_b reducing. After a cumulative discharge treatment of 21 min, the pH value remained largely unchanged, while the BOD_5 value initially increased and then reached equilibrium. Furthermore, the addition of $FeSO_4$ demonstrated a positive effect on the SBRW treatment and cooperated with the EACD technique. For example, the biodegradability was notably improved when the C_{FeSO_4} increased, and the COD value decreased to ~80.0 mg L^{-1} when $FeSO_4$ was added, to obtain a total decrease in the COD efficiency value of 86.7%. However, the H_2O_2 did not assist the EACD technique for the SBRW treatment in this study. This work improves the understanding of the application of the EACD technique for SBRW treatment from the styrene–butadiene rubber industry.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 51508342), Doctoral Start-up Fund of the Liaoning Province Natural Science Foundation (No. 201601335), Liaoning Provincial educational Fund of China (No. L2017LQN018), and the Talent Scientific Research Fund of LSHU (No. 2016XJJ-031).

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Supporting Information

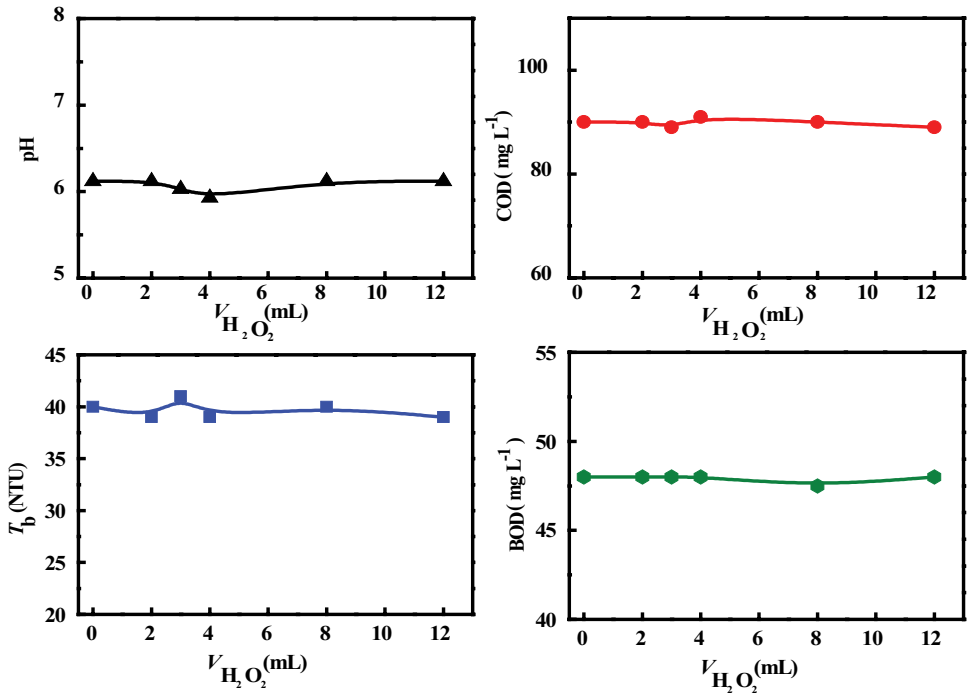

Fig. S1. Effects of $V_{H_2O_2}$ on pH, COD, T_b, and BOD_5 of SBRW after plasma discharging 21 min at C_{FeSO_4} = 1.6 g L^{-1}.

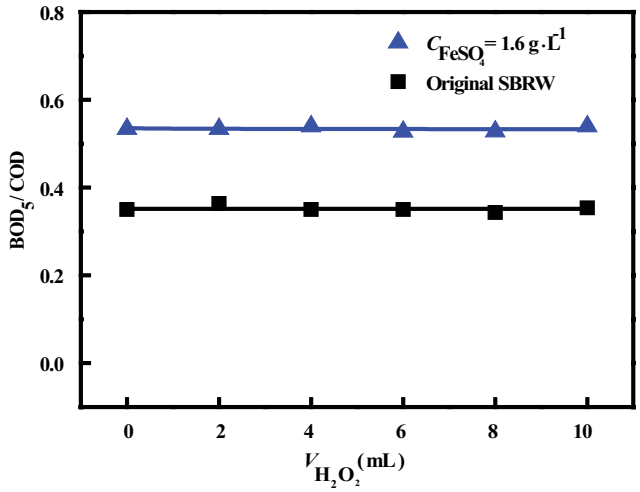

Fig. S2. Effect of $V_{H_2O_2}$ on the ratio of BOD_5 to COD for original SBRW with 0 and 1.6 g L^{-1} of $FeSO_4$.