

# Treatment of bactericide wastewater by combined process chemical coagulation, electrochemical oxidation and membrane bioreactor

Wei-Qing Han, Lian-Jun Wang\*, Xiu-Yun Sun, Jian-Sheng Li

*School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, China*

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## Abstract

Bactericide wastewater (BIW) contains isothiazolin-ones, high salinity, toxicity and non-biodegradable organic concentrations. In order to enhance biodegradable capacity, chemical coagulation and electrochemical oxidation were applied to pretreatment processes.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , pH 12 and 20 mmol/l were determined as optimal chemical coagulation condition; and 15 mA/cm<sup>2</sup> of current density, 10 ml/min of flow rate and pH 7 were chosen for the most efficient electrochemical oxidation condition at combined treatment. The wastewater which consisted mainly of isothiazolin-ones and sulfide was efficiently treated by chemical coagulation and electrochemical oxidation. The optimal pretreatment processes showed 60.9% of chemical oxygen demand (COD), 99.5% of  $\text{S}^{2-}$  and 96.0% of isothiazolin-ones removal efficiency. A biological treatment system using membrane bioreactor (MBR) adding powder-activated carbon (PAC) was also investigated. COD of the wastewater which was disposed using a MBR was lower than 100 mg/l.

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**Keywords:** Bactericide wastewater; Combined process; Isothiazolin-ones; Chemical coagulation; Electrochemical oxidation; Membrane bioreactor

## 1. Introduction

Isothiazolin-ones is a bactericide widely used in industry [1]. The bactericide wastewater contains a number of different kinds of pollutants such as greases, organic acids, organic sulfide, inorganic sulfide, salts and isothiazolin-ones. The concentration of isothiazolin-ones in the wastewater typically reaches as high as 120 mg/l and the concentration of sulfide reaches as high as 450 mg/l. And the concentration of COD is 25,000 mg/l. Conventional treatments of wastewater include biological degradation [2], advanced oxidation [3], incineration [4] and resin adsorption [5]. The biological treatment of wastewater is cheaper than the others. Unfortunately, isothiazolin-ones and sulfide in wastewater are very difficult to break down biologically, due partly to the toxicities of isothiazolin-ones and sulfide to microbes. The cost of advanced oxidation is relatively high, because of additional chemical requirements. The reaction condition is typically so severe that it is not feasible for practical application. The incineration is an expensive procedure, and

the hazardous wastes incinerating in incinerators change new toxic wastes giving off and into the air. The resin adsorption is applied to callback value substances. In an attempt to find treatments that do not have the aforementioned drawbacks, attention has been focused on chemical coagulation for sulfide and on electrochemical methods for isothiazolin-ones.

Recently, there has been increasing interest in the use of chemical coagulations and electrochemical methods for the treatment of recalcitrant toxic wastes. The cost of chemical coagulation is low, cheapness and widely used in treating wastewater.

The electrochemical methods are environmentally friendly and do not produce new toxic wastes. The organic matters and toxic pollutants are usually destroyed by anodic oxidation as a result of the production of oxidants such as hydroxyl radicals, ozone, etc. Electrolytic processes generally have lower temperature requirements than those of other equivalent non-electrochemical treatments, such as wet air oxidation, and there is no need for additional chemicals for advanced and Fenton oxidation. This electrochemical process requires neither chemical pre-testing nor chemical adjustment of the wastewater and little space, and produces fewer by-products or sludge. Recently, electrochemical methods have been successfully applied in the purification of several industrial wastewaters, such as fine chem-

\* Corresponding author. Tel.: +86 25 84315941; fax: +86 25 84315518.  
E-mail address: [wanglj@mail.njust.edu.cn](mailto:wanglj@mail.njust.edu.cn) (L.-J. Wang).

ical manufacturing effluent [6], landfill leachate [7], textile dyes and dyehouse effluents [8] and olive oil mill wastewaters [9]. However, few reports have been published on the treatment of bactericide wastewater by the electrochemical method. Generally, platinum-coated titanium electrodes (Pt/Ti) are suitable for the oxidation of organic substances, although their cost poses a major restriction for their widespread use [10]. On the other hand, cheaper substituents such as titanium electrodes coated with active oxides (e.g., RuO<sub>2</sub>, PbO<sub>2</sub>, SnO<sub>2</sub>, etc.) have been successfully used in order to oxidize the organic pollutants in aqueous media [11–13]. And lead dioxide coated titanium electrodes (PbO<sub>2</sub>/Ti) were widely used for the electrochemical oxidation of the organics.

This investigation extended the final work using a MBR. Membrane technology has attracted much attention from scientists and engineers in recent years as a new separation process in water and wastewater treatment. These separation processes have been applied to treat municipal and industrial wastewaters. Combining membranes with biological treatment is an attractive technique and has resulted in a new concept: MBR. The recent development of a new generation of more productive and less expensive ultrafiltration and microfiltration membranes makes this possible. In the MBR, the entire biomass is confined within the system, providing both exact control of the residence time for the microorganisms in the reactor (solids retention time) and the disinfection of the effluent.

MBR process offers numerous advantages over conventional biological processes, elimination of settling basins, independence of process performance from filamentous bulking or other phenomena affecting settleability [14,15]. The separation of biomass from effluent by membranes also allows the concentration of mixed liquor-suspended solids (MLSS) in the bioreactor to be increased significantly, thus giving good effluent and reducing its size for a given sludge. Effects of dilution of wastewater and adding adsorbent of PAC were studied using MBR treatment.

The treatment and safe disposal of hazardous organic waste material in an environmentally acceptable manner and at a reasonable cost is a topic of great universal importance. There is little doubt that biological processes will continue to be employed as a baseline treatment process for most organic wastewaters, since they seem to fulfil the above two requirements. However, biological processes do not always give satisfactory results, especially applied to the treatment of industrial wastewaters, because many organic substances produced by the chemical and related industries are inhibitory, toxic or resistant to biological treatment. Therefore, advanced technologies based on chemical oxidation may be the only viable options for decontaminating a biologically recalcitrant wastewater. Oxidation technologies may be used either for the complete mineralization of all pollutants to carbon dioxide, water and mineral salts or for the partial removal of certain target pollutants and their conversion to intermediates. In general, a chemical oxidation method aiming at complete mineralization might become extremely cost-intensive since the highly oxidized end-products that are formed during chemical oxidation tend to be refractory to total oxidation by chemical means. Total chemical oxidation of

these intermediates to carbon dioxide and water may be difficult and require severe oxidative conditions. Biological treatment of intermediates becomes more attractive than chemical oxidation of intermediates [16]. Then many combined processes chemical oxidation and biological treatment were suggested in these days. One of reported combined methods showed that green table olive wastewater was treated by the combined process (Fenton's reagent oxidation and aerobic biological treatment) [17]. And Lin and Peng [18] employed combined coagulation, electrochemical oxidation and activated sludge for textile wastewater treatment. And Alaton et al. [19] employed combined chemical and biological oxidation for penicillin formulation effluent treatment. Because of complicacy and toxic of BIW composition, it would be of more practical significance to BIW to operate the combined process.

However, no report has ever been published regarding treatment by combined process adopting chemical coagulation, electrochemical oxidation and MBR in BIW. This research suggests a combined process which is composed of chemical coagulation and electrochemical oxidation pretreatment, and MBR final-treatment. The purpose of this study was to investigate the performance of the combined BIW treatment.

## 2. Materials and methods

Wastewater used in this research was obtained from a fine chemical factory located in Xuzhou China. The characteristics of BIW were showed in Table 1.

The combined process for BIW treatment consists of chemical coagulation, electrochemical oxidation and MBR. A flow diagram of the combined BIW treatment system used in this study was shown in Fig. 1.

Chemical coagulation and electrochemical oxidation were placed before MBR treatment step. Before the continued test, jar-test at the laboratory scale was carried out in order to choose the adequate coagulant and the reaction condition (pH, dosage). Poly-AlCl<sub>3</sub>, FeCl<sub>3</sub>·6H<sub>2</sub>O and FeSO<sub>4</sub>·7H<sub>2</sub>O were tested as chemical coagulant candidates. One normal H<sub>2</sub>SO<sub>4</sub>, NaOH solution were added to adjust pH of the solution to the desired value. Chemical coagulant was added and mixed for 2 min under rapid mixing condition (250 rpm) and the solution was mixed at slow flocculation (40 rpm) for 5 min after rapid mixing. And then, COD, S<sup>2-</sup> and pH of supernatant were measured after settling for 30 min.

Three hundred milliliters of mixing tank and 7 l (Ø15 cm × 50 cm) of sedimentation tank were equipped

Table 1  
Characteristics of BIW

Parameter	Range	Average
pH	3–5	4
Temperature (°C)	40–25	43
COD (mg/l)	20,000–25,000	23,000
BOD <sub>5</sub> (mg/l)	200–250	225
S <sup>2-</sup> (mg/l)	400–450	430
Isothiazolin-ones (mg/l)	90–120	100

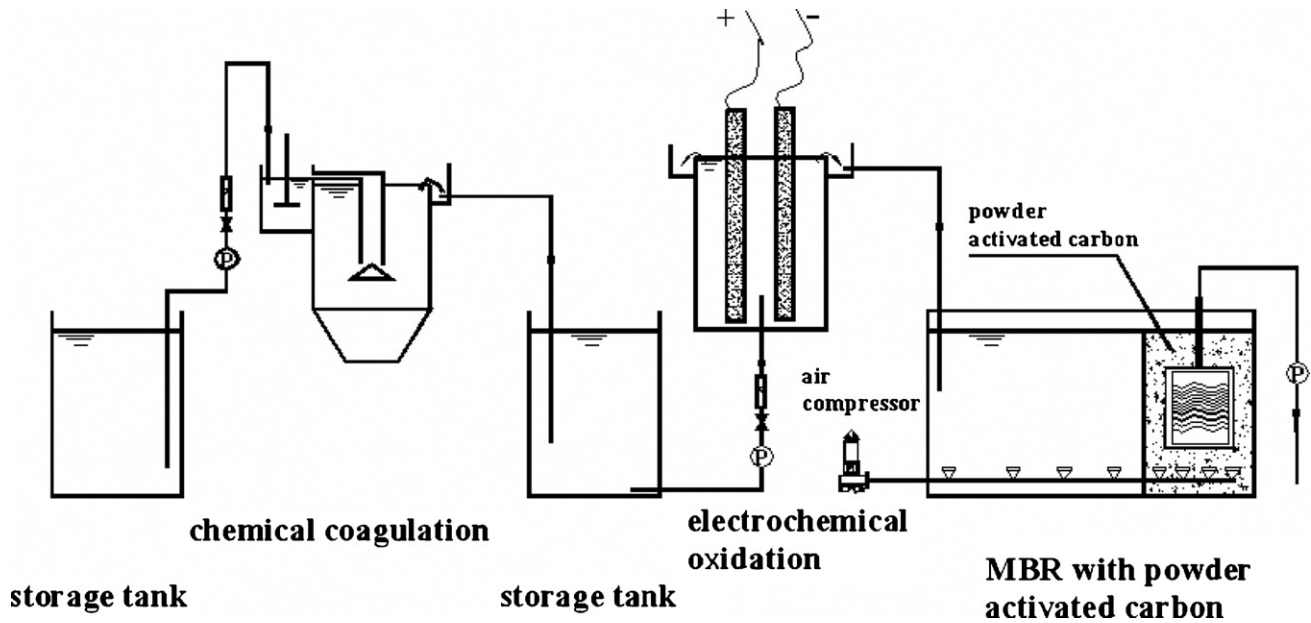


Fig. 1. Flow diagram of combined process for BIW treatment.

for pilot continued chemical coagulation. The solution was continuously fed to the mixing tank by peristaltic pump. The average flow range was 5–20 ml/min and thus the settling time was larger than 3 h. The hydraulic retention time (HRT) was sufficient to settle the coagulated sludge. The supernatant remaining after coagulated solids was put into the electrochemical reactor for continuous electrochemical oxidation process described in the next section.

Before the continuous test of all systems, the optimization of operating conditions of electrochemical oxidation was performed through the unit process study. The apparatus of electrochemical oxidation consisted of a reactor ( $\varnothing 10 \text{ cm} \times 25 \text{ cm}$ ) 1.8 l, a pairs of electrodes and dc rectifier. The anode was made of plate of titanium ( $6 \text{ cm} \times 22 \text{ cm}$ ,  $132 \text{ cm}^2$ ) coated with  $\text{PbO}_2$ , while plate of stainless steel ( $6 \text{ cm} \times 22 \text{ cm}$ ) was used as cathodes; the distance between electrodes was 2 cm.  $\text{Na}_2\text{SO}_4$  was added as an electrolyte.  $\text{H}_2\text{SO}_4$  solution is added to adjust pH of the solution to the desired value. The solution after chemical coagulation was continuously fed to the electrochemical reactor by peristaltic pump.

MBR treatment was placed after chemical coagulation and electrochemical oxidation step. Forty-five liters of anoxic activated sludge tank and 15 l of aerobic-activated sludge tank were equipped for pilot scale biological treatment. Hollow fiber membranes submerged in wastewater of aerobic-activated sludge tank. The hydraulic retention time of the bioreactor was set to 96 h for the majority of experiments. Effluent was threaded through membrane in aerobic-activated sludge tank by a peristaltic pump. The activated sludge was mixed by airflow. Excess sludge was withdrawn frequently in order to control the concentration of MLSS ( $4000 \pm 200 \text{ mg/l}$ ). Dissolved oxygen (DO) was supplied by diffuser at an airflow rate of 2.4 l/min. The concentration of sulfate was higher than the conventional wastewater. Tanaka and Takenaka [20] found that the volume of air injection required to inhibit the generation of hydrogen sulfide was

established in the anoxic zone. Therefore, the concentrations of dissolved oxygen were 1 mg/l in anoxic zone and 4 mg/l in aerobic zone.

Because of high COD (9000 mg/l), and high salinity in BIW. In order to improve biological treatability of the wastewater, methods of dilution and powdered activated carbon (PAC) as adsorbent were used as biological treatment. The range of powder-activated carbon concentration was 0.1–2.0 g/l.

The pH was controlled at 7.0–8.0 by means of the addition sodium hydroxide (NaOH). The temperature was maintained at room temperature ( $22 \pm 2 \text{ }^\circ\text{C}$ ).

The activated sludge was obtained from a wastewater treatment plant of chemical industry (Nanjing chemical industry company, China). The sludge was first acclimated at low concentrations for 15 days and then was incubated in the MBR.

Standard methods for examination of wastewater were used for the estimation of COD,  $\text{S}^{2-}$ , isothiazolin-ones and dissolved oxygen (DO). COD using a dichromate method after digestion of the samples in a COD reactor;  $\text{S}^{2-}$  was measured using iodine method; and DO using potassium permanganate amending method. The concentrate of isothiazolin-ones was analyzed by UV–visible spectrophotometer at a wavelength of 273 nm (TU-1901, China). The mechanism of isothiazolin-ones degradation was analyzed by MS.

### 3. Results and discussion

#### 3.1. Chemical coagulation

Chemical coagulation was placed first treatment step. Coagulation was employed as a pretreatment to electrochemical oxidation. The main purpose of chemical coagulation was decreasing the sulfide loading on post-treatment. The results of jar-test were shown in Table 2. The coagulation efficiency depended on the coagulation pH and the dosage amount of coag-

Table 2  
Results of jar-test for pH and dosage optimization of chemical coagulation

Coagulant	Optimization		Average of removal efficiency	
	Optimal pH	Optimal dosage (mmol/l)	S <sup>2-</sup> (%)	COD (%)
FeSO <sub>4</sub> ·7H <sub>2</sub> O	12–14	20.0–22.0	68.8	33.9
FeCl <sub>3</sub> ·6H <sub>2</sub> O	8.5–9.5	2.2–2.5	32.0	24.1
Polymer-AlCl <sub>3</sub>	9–10	2.5–2.8	28.0	22.3

ulant. As a result of jar-test in the laboratory, FeSO<sub>4</sub>·7H<sub>2</sub>O, pH 12 and 20 mmol/l were chosen as optimal chemical coagulation conditions for combined treatment.

### 3.2. Optimization of electrochemical oxidation

Jar-experiments were performed in order to investigate the effect of operating parameters and optimize the conditions of electrochemical oxidation in the combined process. The performances by the two pretreatment, namely, chemical coagulation was not carried out efficiently enough to satisfy the microbes in MBR process. Additional dosage of chemicals and longer HRT were not needed to decrease toxicity in the wastewater. The aqueous degradation of isothiazolin-ones has been reported was not degraded effectively at natural condition [21,22]. Therefore, the electrochemical oxidation process was employed as the pretreatment step in this study. In adopting the electrochemical oxidation process, it was intended to treat the pollutant efficiently as well as economically. The effects of electrolyte concentration, current density and pH and flow rate on electrochemical oxidation of BIW treatment were determined and then the overall combined system of continuous treatment was performed. The results of effects of operating parameters on combined process electrochemical oxidation were shown in Figs. 2–7.

#### 3.2.1. Effect of concentration of electrolyte

In this study, Na<sub>2</sub>SO<sub>4</sub> was added as an electrolyte. The effect of the electrolyte concentration on the removal efficiency of COD was determined as shown in Fig. 2. At applied electrolyte concentration of 0, 2.5, 5.0 and 10 g/l; the corresponding COD removal efficiencies were 40%, 39.1%, 39.2% and 35.1% after electrochemical oxidation of 180 min. Conductivity increase

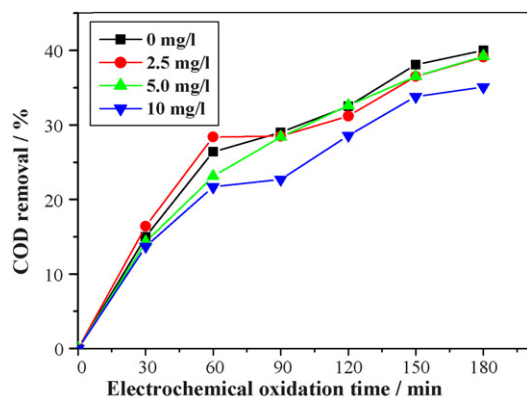


Fig. 2. Effects of electrolyte concentration on COD removal efficiency.

with concentration of Na<sub>2</sub>SO<sub>4</sub> and increase of electron transfer. But the concentrations of SO<sub>4</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup> and S<sup>2-</sup> in the raw wastewater were higher than that in conventional chemical wastewater. Overmuch salt resulted in adsorption of a mass of SO<sub>4</sub><sup>2-</sup> on an anode surface. It impeded creation of hydroxide radical. The effects of electrolyte concentration became noneffective. As the electrolyte concentration was increased, the electrochemical oxidation efficiency was not increased, but reduced.

As electrochemical oxidation of aqueous solutions, the anodic discharge of the water forming hydroxyl radicals which are absorbed on the active sites of the electrode surface PbO<sub>2</sub> [23,24]:



After this the absorbed hydroxyl radical oxidizes the organic matter:



where PbO<sub>2</sub>[ ] represents the active sites of anodic, and RO represents the oxidized organic matter which can be produced continuously by the hydroxyl radicals which are also continuously formed on anode, since the anodic discharge of the water goes on. The radicals [•OH] have a very short lifetime due to their high oxidation potential and oxidize organic compounds (i.e. direct oxidation), and are decomposed to other oxidants (such as O<sub>2</sub>, O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>) which diffused into the water away from anode thus continuing the oxidation process (indirect oxidation). The direct oxidation is effective pollutant degradation, because it is able to convert totally all the organic species into water

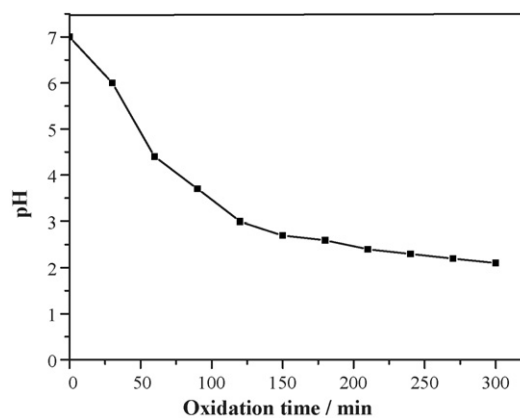


Fig. 3. pH reduction for isothiazolin-ones for 300 min of electrolysis at a current density of 15 mA/cm<sup>2</sup>, NaSO<sub>4</sub> concentration of 10 g/l and initial isothiazolin-ones of 100 mg/l.

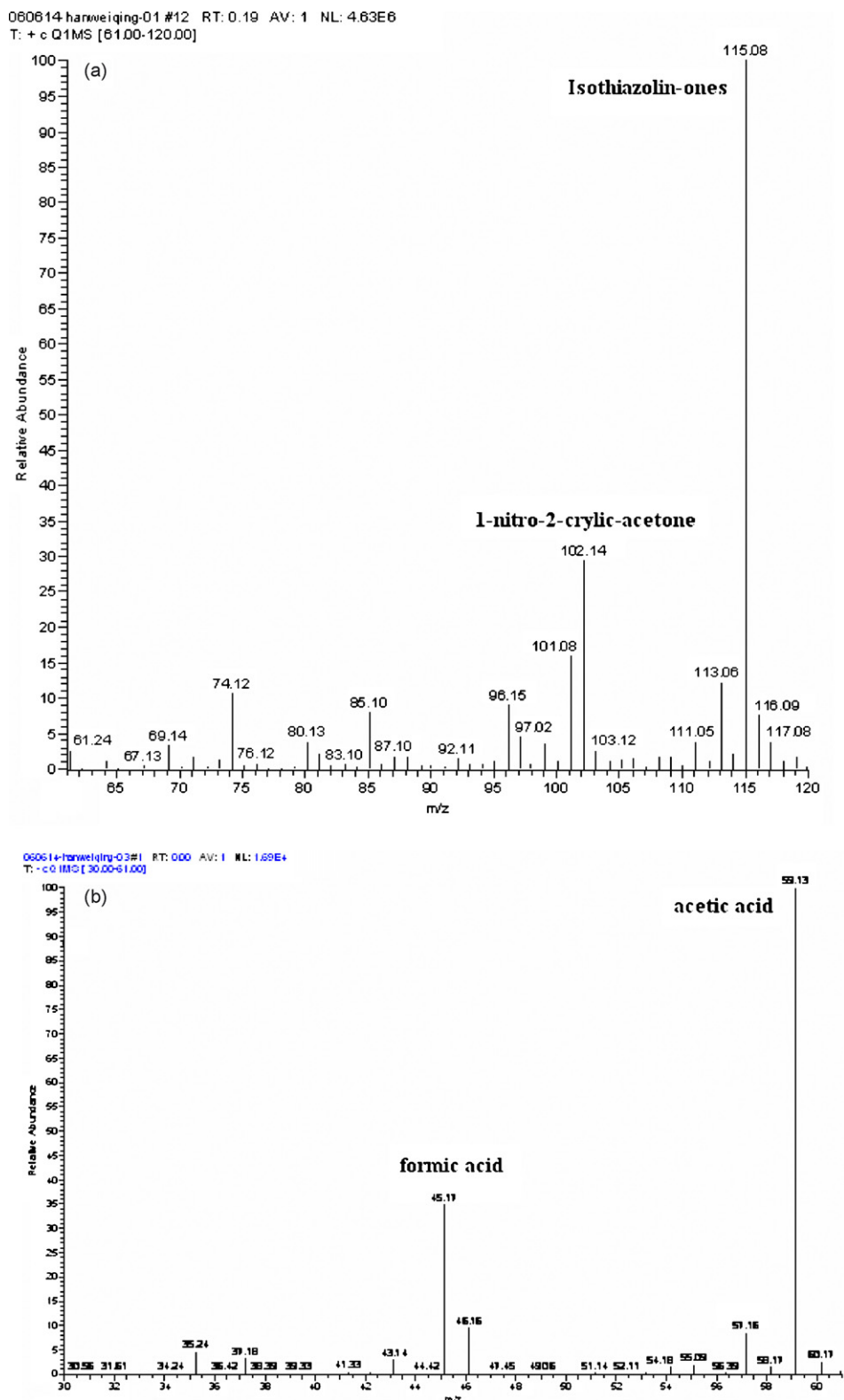


Fig. 4. Mass spectrum of the intermediates of electrochemical oxidation of isothiazolin-ones. (a) The positron ion and (b) the electronegative ion.

and carbon dioxide. The indirect oxidation is not.  $\text{PbO}_2$  electrodes can be highly effective for complete organic destruction [25]. Using a  $\text{PbO}_2/\text{Ti}$  anode, the pollutants are mainly removed by direct electrolyses mediated by electro-generated hydroxyl radicals; indirect electron-transfer oxidation is negligible.

### 3.2.2. Speculation of interaction mechanism

In order to understand the mechanism for the interaction of electrochemical oxidation with bactericide, pure solution (100 mg/l, isothiazolin-ones) was used to investigate the oxidation mechanism because the real bactericide wastewater



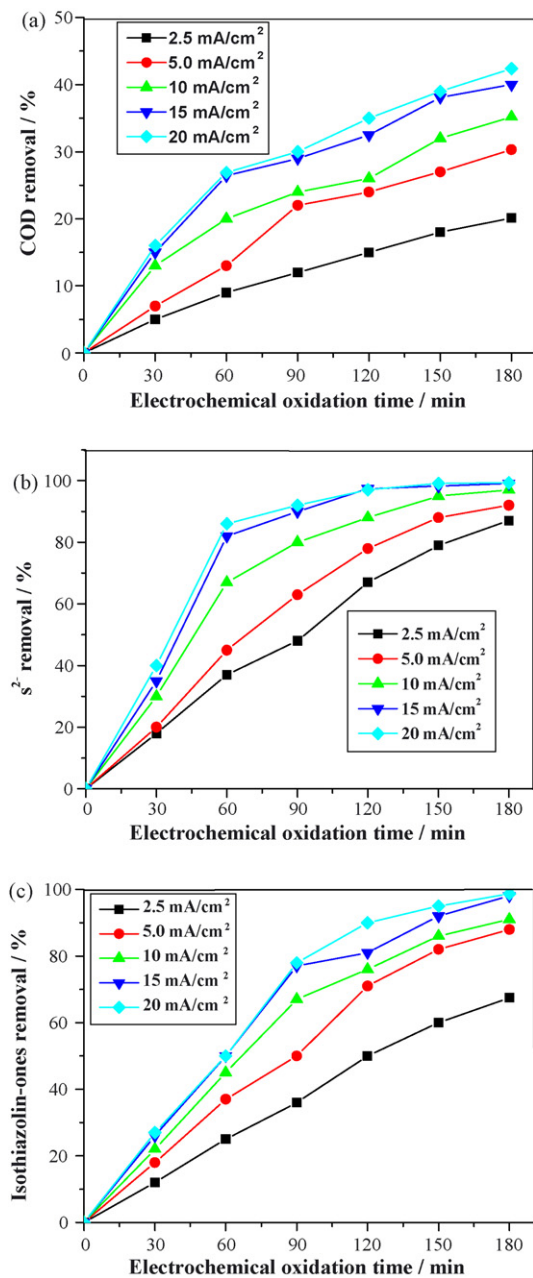


Fig. 5. Effects of current density on COD, S<sup>2-</sup> and isothiazolin-ones removal efficiency. (a) COD, (b) S<sup>2-</sup> and (c) isothiazolin-ones.

contained many complex substances. The continuous addition of high levels of organic acid in the electrolytic cell resulted in the drop of pH. The pH of the solution varying during electrolysis in aqueous solutions was shown in Fig. 3. The pH in 120 min of electrolysis was significantly reduced. Finally the solution became strong acidic (pH: 2.1). The pH dropped, during isothiazolin-ones degradation, was also noted from Kandavelu et al. [26] using photo-catalytic for the decomposition of isothiazolin-ones in aqueous solution. Electrochemical oxidation usually converts initially organics to organic acids firstly. But electrochemical oxidation of these organic acids to carbon dioxide and water may be difficult, require severe oxidative conditions and long oxidation time. It was also reported that while

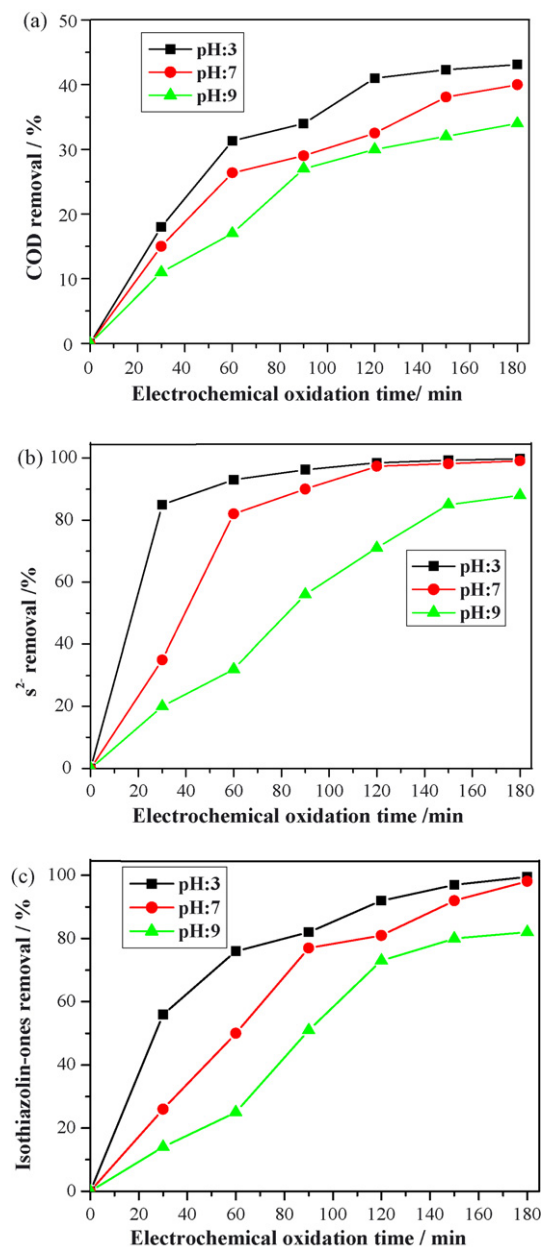


Fig. 6. Effects of solution pH on COD, S<sup>2-</sup> and isothiazolin-ones removal efficiency. (a) COD, (b) S<sup>2-</sup> and (c) isothiazolin-ones.

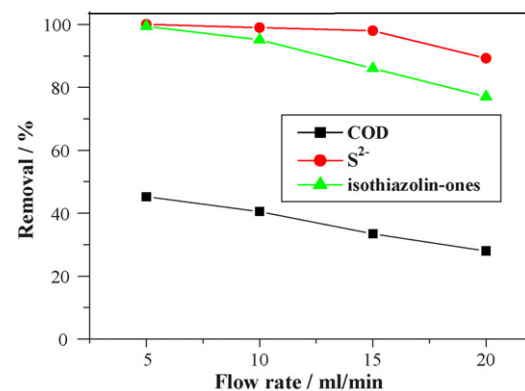
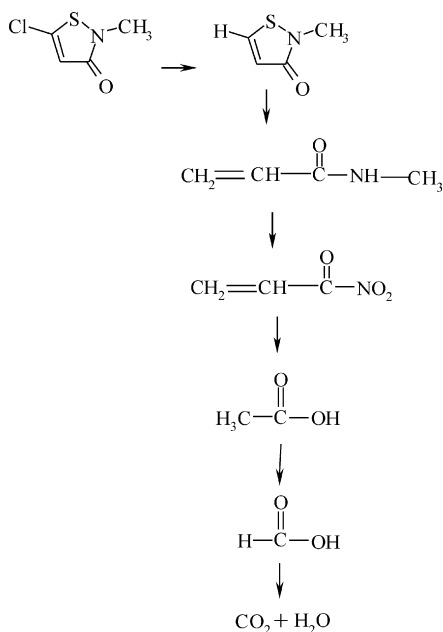


Fig. 7. Effects of flow rate on COD, S<sup>2-</sup> and isothiazolin-ones removal efficiency.

the mineralization goes to completion and the solution gets more and more acidic [27].

The temporal intermediates of reacting species during the electrochemical reaction in aqueous solution were analyzed by MS, and were shown in Fig. 4. Based on exact mass measurements, the elemental composition of this ion was determined to be isothiazolin-ones at  $m/z$  115. This elemental composition indicates that the isothiazolin-ones had lost a chloride ion. In the product ion spectrum, the most abundant fragment ions were detected at  $m/z$  102, 59 and 45. Using exact mass measurements, the elemental compositions of these product ions were determined to be 1-nitro-2-crylic-acetone, acetic acid and formic acid, respectively. These data clearly show that the degradation pathway of isothiazolin-ones. It proceeds via removal of chloride ion and ring opening through the nitrogen–sulfur bond. Subsequent oxidation leads to the formation of 1-nitro-2-crylic-acetone, acetic acid and formic acid, which slowly gets oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , along with the formation of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}_2$ .

The simplified degradation pathway of isothiazolin-ones by electrochemical oxidation was suggested to be in three steps: the initial step was the dissociation from chlorine and the formation of chlorine; the second step considered to be the attack on the N–S bond by hydroxyl radicals and the formation of sulfate ions and various organic intermediates; the third step was mineralization of intermediates; and shown below:



### 3.2.3. Effects of current density

The effects of current density were shown in Fig. 5. COD removal efficiency was increased to 20.1%, 30.3%, 35.2%, 40.0% and 42.4%, as the applied current densities were increased to 2.5, 5.0, 10, 15 and 20  $\text{mA}/\text{cm}^2$ , after 180 min of electrochemical oxidation time. But the  $\text{S}^{2-}$  and isothiazolin-ones removal efficiency were kept constant from 85.2% to 99.3% and from 67.5% to 98.7%, respectively, at the same condition, since the highest priority of electrochemical oxidation was  $\text{S}^{2-}$ , and it was oxidized to  $\text{SO}_4^{2-}$ . Isothiazolin-ones were oxidized to organic

acid secondly. The concentration of COD was caused by yet unoxidized organic compounds as well as the intermediates produced by electrochemical oxidation. Electrochemical oxidation of isothiazolin-ones and the other organic compounds was not removing COD efficiently. It could be seen that the effect of current density was significant between 2.5 and 15  $\text{mA}/\text{cm}^2$ ; and the rates of reaction increased dependent on the current density very steeply.

### 3.2.4. Effect of solution pH

Several wastewaters at pH between 3, 7 and 9 were tried and shown in Fig. 6. Lower initial samples pH value (pH 3) lead to oxidation efficiency highest of all. The removal efficiency of isothiazolin-ones decreased from 99.5% to 82.1% when the pH was increased from 3 to 9 and after oxidation time of 180 min. It appears that the increase of the pH decreased the potential oxygen generation obtained from  $[\bullet\text{OH}]$  radicals oxidation and consequently increased the flow rate of oxygen at the electrode surface. As a result, the diffusion flow of isothiazolin-ones towards the electrode decreased. Furthermore, it is well known that the decrease of the solution pH favors oxidation reactions; this can be indicated by the decrease of COD and  $\text{S}^{2-}$  removal measured between pH 3 and 9 too.

### 3.2.5. Effect of flow rate

The process of anodic oxidation of organic compound solution was a diffusion-controlled process [28]. The rapid inlet creates the mixing effects; it makes solution more homogeneous and allows hydrogen gas to easily escape from the surface of cathode. And the mixing effect resulting from rapid inlet increases the current efficiency. Otherwise the retention time is decreased while the flow rate is increased in a continuous process. Thus, optimal flow rate can be obtained.

From Fig. 7, as the inlet flow rate was increased to 5, 10, 15 and 20  $\text{ml}/\text{min}$ , the retention time directly decreased to 360, 180, 120 and 90 min. The COD removal efficiency decreased to 45.2%, 40.4%, 33.4% and 28.0%. With the flow rate increasing from 5 to 20  $\text{ml}/\text{min}$ , but the  $\text{S}^{2-}$  and isothiazolin-ones was maintained constantly in the range of 89.2–100% and 77.1–99.4%. It showed that the effects of inlet flow rate affected more significantly the  $\text{S}^{2-}$  and isothiazolin-ones removal than the COD removal. The optimal flow rate can be considered as 10  $\text{ml}/\text{min}$ .

Therefore, the optimal operating conditions for the electrochemical oxidation were 15  $\text{mA}/\text{cm}^2$  of current density, 10  $\text{ml}/\text{min}$  of flow rate, and not adding electrolyte and acid solution. Although it favors oxidation reactions in acid solution, Additional dosage of NaOH increased in MBR treatment. The pH 7 was determined as electrochemical oxidation condition in continues combined treatment.

## 3.3. Membrane bioreactor process

### 3.3.1. Effect of dilution of wastewater

The pretreated wastewater (COD about 9000  $\text{mg}/\text{l}$  after chemical coagulation and electrochemical oxidation) was diluted five, four, three and two times with domestic wastewater (COD about 500  $\text{mg}/\text{l}$ ) and the COD of these were around 2200, 2600, 3300

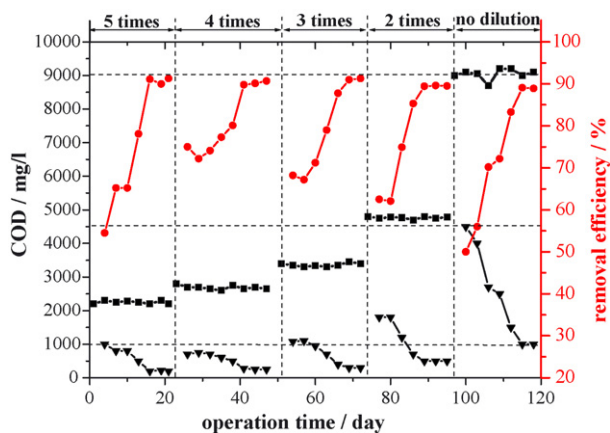


Fig. 8. Effects of the variation of diluted times of the wastewater on COD removal efficiency in the MBR treatment (■, influent ▼, effluent and ●, COD removal efficiency).

and 4750 mg/l, respectively. Its pH was adjusted to 7.0–8.0. Then the diluted five times wastewater (COD about 2200 mg/l) was charged full to the reactor. The activated sludge cultivated in a fermenter containing nutrient domestic wastewater and BIW was utilized to inoculate into the MBR. Microbial inoculums were introduced with concentration of around 4000 mg/l. After oxidation by supplying air for 36 h, a half of mixed liquid was drained off through membrane by a peristaltic pump; and then the same volume diluted five times pretreated wastewater was introduced for the next 36 h of the reaction. This procedure was repeated until COD of effusion was stability. Above tests were repeated adopting diluted four, three, two times and no dilution wastewater in file. Results were in Fig. 8. From Fig. 8, it could be see that COD of effluent was decreased to about 200, 250, 300, 500 and 1000 mg/l; and that COD of effluent was not lower than 100 mg/l, not diluting with domestic wastewater.

### 3.3.2. Membrane bioreactor process adding powdered activated carbon

From Fig. 8, it can be see, that biological treatment processes used for BIW after chemical coagulation and electrochemical oxidation resulted in low chemical oxygen demand (COD) removals mainly because of high COD (9000 mg/l), and also due to high salinity. In order to improve biological treatability of the wastewater which contains non-biodegradable organic concentrations and high salinity, dilution method was used as one of biological treatments; adopting dilution method, the biological treatment could be run effectively [29]. But dilution method resulted in the increasing of effluent. Adsorbent-added biological treatment of wastewater had been reported and could operate in high chemical oxygen demand (COD) removals. Nevertheless Adsorbent-added MBR of treated BIW has not been report; it is the major objective of the study to investigate the adsorptive MBR treatment of BIW using PAC as adsorbent. Treated BIW was subjected to PAC added aerobic biological treatment by MBR operation in an aeration tank. COD was quantified as a function of PAC concentration.

A set of experiments with different PAC concentrations (0.1–2 g/l) were conducted in an aeration tank operated using the

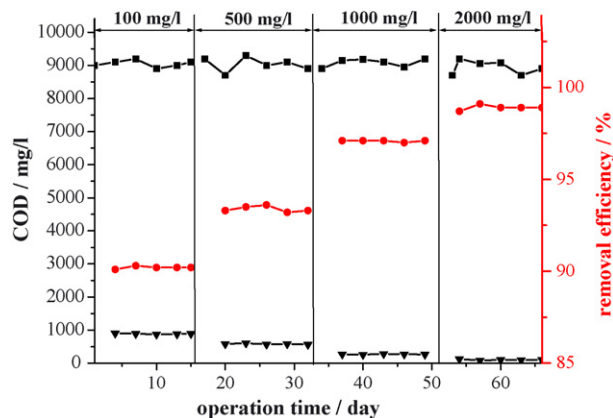


Fig. 9. COD removal efficiency with the variation of powder-activated carbon in the MBR treatment (■, influent ▼, effluent and ●, COD removal efficiency).

pretreated BIW. Simultaneous adsorption and biological treatment experiments were performed by addition of adsorbent to the aeration tank containing activated sludge organisms. The experiments were performed under the same initial and operating conditions. Feed COD content and flow rate (10 ml/min) were kept constant while the concentration of PAC changing. Amounts of PAC added in the biological reactor were 0.1, 0.5 1.0 and 2.0 g per liter of the wastewater; videlicet, the sum of wastewater treated in the biological reactor was 14.4 l (10 ml/min  $\times$  60 min  $\times$  24 h = 14.4 l/day) every day, amount of PAC added manually to the MBR was 1.44, 7.2, 14.4 and 28.8 g every day, respectively. Firstly the pretreated wastewater was charged to the biological reactor at flow rate of 10 ml/min, and for PAC amount of 1.44 g/day (added manually to the MBR every day). Treated water was drained off through membrane by a peristaltic pump continuously. This procedure was running for 12 days, and COD of effusion was measured. Above tests were repeated adding PAC of 7.2, 14.4 and 28.8 g/day in file. Fig. 9 shows COD removal with the variation of PAC. It was observed that removal efficiencies of COD increased from 90.1% to 98.9% adding from 0.1 to 2 g/l of PAC concentrations. An improvement of 8.8% of COD reduction was achieved by using PAC in this case.

By adding PAC, the PAC adsorbed activated sludge and the pollutant in water. Videlicet-activated sludge attached the powder-activated carbon which adsorbed pollutant; the pollutant was destroyed by the microbe in the activated sludge effectively. And COD was degraded effectively. The effective treatment of wastewater could be carried out using PAC in MBR. COD of the wastewater which using a membrane bioreactor adding 2.0 g/l of powder-activated carbon is lower than 100 mg/l.

Therefore, the optimal operating conditions for the MBR treatment were 96 h of hydraulic retention time and 2.0 g/l dosage of PAC.

### 3.4. Combined process for BIW treatment

Wastewater with 23,000 mg/l of COD, 430 mg/l of  $S^{2-}$  and 100 mg/l of isothiazolin-ones was continuously treated in continuous combined process of chemical coagulation, electro-



Table 3  
The effects on COD, S<sup>2-</sup> and isothiazolin-ones at the overall continuous combined process

Process unit	COD		S <sup>2-</sup>		Isothiazolin-ones	
	mg/l	Removal (%)	mg/l	Removal (%)	mg/l	Removal (%)
Raw	23,000	0 <sup>a</sup> (0) <sup>b</sup>	430	0 (0)	100	0 (0)
Chemical coagulation	15,100	33.9 (33.9)	135	68.6 (68.6)	100	0 (0)
Electrochemical oxidation	9,000	60.9 (40.4)	2.0	99.5 (98.5)	4.0	96.0 (96.0)
MBR (without powder-activated carbon)	1,000	95.7 (88.9)	0.8	99.8 (60.0)	0	100 (100)
MBR (with powder-activated carbon)	100	99.6 (98.9)	0.5	99.9 (75.0)	0	100 (100)

<sup>a</sup> Cumulative removal efficiency of overall process.

<sup>b</sup> Removal efficiency of unit process.

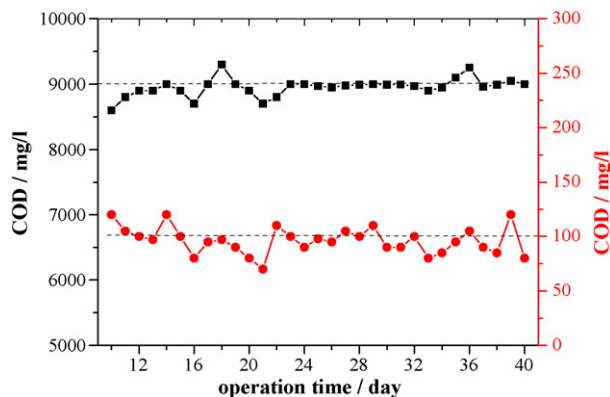


Fig. 10. The effects on the overall continuous combined process (■, effluent of pretreatment and ●, COD effluent of MBR treatment).

chemical oxidation and MBR (adding 2.0 g/l dosage of PAC) process. Running under optimal combining conditions, COD concentrations of effluent after chemical coagulation, electrochemical oxidation and membrane bioreactor process were 15,100, 9000 and 100 mg/l, respectively. The S<sup>2-</sup> of effluent after these combined process were 135, 2.0 and 0.5 mg/l, respectively. The isothiazolin-ones of effluent after the process were 100, 4.0 and 0 mg/l, respectively.

The effects of this on the overall continuous combined process were also shown in Fig. 10 and Table 3. COD removal of 99.6% was achieved by following MBR process after chemical coagulation and electrochemical oxidation treatment. S<sup>2-</sup> removal of 99.9% and isothiazolin-ones removal of 100% was also achieved by the same process as in the above case.

#### 4. Conclusions

The purpose of this study was to evaluate the effectiveness of combined process of chemical coagulation, electrochemical oxidation and member MBR for BIW treatment. The behavior studies, optimization of reaction conditions for unit process and overall combined processes operation was investigated.

The contribution of pretreatment of chemical coagulation, electrochemical oxidation to the overall system in terms of COD, S<sup>2-</sup> and isothiazolin-ones removal was 60.9%, 99.5% and 96.0%, respectively, by 20 mmol/l of FeSO<sub>4</sub>·7H<sub>2</sub>O concentration and pH 12 in the chemical coagulation process and by 15 mA/cm<sup>2</sup> of current density and 10 ml/min of flow rate and

pH 7 in the electrochemical oxidation process. The contribution of final treatment of MBR to COD was from 88.9% to 98.9% by adding PAC in biological treatment. COD, S<sup>2-</sup> and isothiazolin-ones removals of 99.6%, 99.9% and 100% were also achieved by the overall combined process of chemical coagulation, electrochemical oxidation and MBR adding PAC, respectively. It was concluded that the toxicity and non-biodegradable organic pollutant were removed and destroyed much effectively in pre-treatment of chemical coagulation, electrochemical oxidation. And the concentration of COD was much effectively decreased by adding PAC in MBR treatment. And this combined process of chemical coagulation, electrochemical oxidation and MBR adding PAC was successfully employed and was highly practicable.

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