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# Advanced treatment of pharmaceutical wastewater with combined micro-electrolysis, Fenton oxidation, and coagulation sedimentation method

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## ABSTRACT

Due to the inability of biochemical processes to remove refractory organic compounds from wastewater in pharmaceutical industrial parks, this research tried to find a new way to meet the requirement of the Discharge Standard in China. A combined process involving micro-electrolysis, Fenton oxidation, and coagulation was studied. Considering the removal efficiencies and operation costs, the reaction conditions were optimized. The COD concentration in the effluent after the combined treatment was less than the standard limit of 50 mg/L. Molecular weight distribution of organic compounds in wastewater was analyzed by sequential filtration and ultrafiltration. When treated by the combined process, the particulate fraction (particle size > 1,000 nm) decreased, and the soluble portion (particle size < 1 nm) increased significantly. Composition of the refractory organics was investigated using GC–MS. A total of 34 types of low-molecular-weight organics were identified in the effluent, among which phthalates, amides, heterocyclic compounds, and PAHs were the main organic pollutants. All these results show that the proposed method is promising for refractory wastewater because it is efficient and easy to operate.

*Keywords:* Pharmaceutical wastewater; Micro-electrolysis; Fenton oxidation; Coagulation sedimentation; COD component

## 1. Introduction

Wastewater produced from pharmaceutical manufacturing factories is characterized by high concentration of organic pollutants, color, and salinity, and its character and quantity varies depending upon the products and related manufacturing processes [1]. There are various organic pollutants in pharmaceutical wastewater, such as raw materials, drug intermediates, mycelium, and drug metabolites [2,3], which have strong toxic effect on environment. Kinds of techniques such as biodegradation, membrane

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filtration, adsorption, coagulation, classic Fenton's agent, and incineration have been developed to solve these pollution problems. The biological processes are commonly used for wastewater because these methods are economically and environmentally sound [4], but some components are not readily degraded by the conventional biochemical degradation method, even they may greatly inhibit the activities of microorganisms in activated sludge [5,6]. In the treatment of pharmaceutical wastewaters, it has always been troublesome to achieve more and more stringent effluent standards. Nowadays, the pharmaceutical wastewater treatments become more difficult than before. In order to effectively control the pharmaceutical wastewater pollution problems, there is a growing importance of developing some other technologies for the advanced treatment of pharmaceutical wastewater to meet the ever-increasing requirements of human beings [7–9]. Tracing those refractory components from production to discharge processes was also necessary, then introducing more targeted effective preprocessing techniques to reduce these matters.

Chemical and physical methods are not restricted by water quality. Micro-electrolysis and Fenton oxidation are advanced oxidation technologies. Micro-electrolysis is an alternative destructive treatment in which chemical species are reduced into smaller fragments. It is found to be successful in removing pollutants in various industrial wastewater [10–12]. Iron–carbon as a primary battery has been one of the most effective micro-electrolysis methods, among which the iron scrap was typically studied mainly for industrial wastewater treatment with the advantage of no need of power supply and addition of chemical agents. It is a promising technique with great potential for application. Hydrogen peroxide ($H_2O_2$) is a strong oxidant and its application in the treatment of various inorganic and organic pollutants is well established. Improvements can be achieved using transition metal salts (e.g. iron salts) or ozone and UV light can activate $H_2O_2$ to form hydroxyl radicals, which are strong oxidants. Oxidation processes utilizing activation of $H_2O_2$ by iron salts, classically referred to as Fenton's reagent is known to be very effective in the destruction of many hazardous organic pollutants in water [13]. Chemical oxidation processes are more effective to reduce or completely destroy the refractory organic compounds which have great chemical and biological stability. Previous studies have indicated the effectiveness of advanced oxidation processes to destroy refractory micropollutants [14,15]. Taking into account ferric produced during the abovementioned anode and Fenton oxidation has a flocculation effect, coagulation technology is acceded to further reduce the concentration of organic compounds after adjusting to neutral or weakly basic [16].

The effect of the combined treatment process involving micro-electrolysis, Fenton oxidation, and coagulation sedimentation on the influent of the sewage treatment plant in a pharmaceutical industrial park was evaluated in this work. The optimal reaction conditions were proposed. Under optimal reaction conditions, the effectiveness of the combined treatment was evaluated. Furthermore, refractory components were analyzed by gas chromatography–mass spectrometry (GC–MS). A basis was thus provided for establishing a new standard of revenue wastewater for the wastewater treatment plant, and technical support was provided for upgrading the process and improving the discharged wastewater to meet the emission standards.

## 2. Materials and methods

### 2.1. Wastewater sample collection

Wastewater samples were collected from a sewage treatment plant located in a pharmaceutical industrial park in northern China. Many large pharmaceutical companies are located in this zone, and their pretreated wastewater is discharged into the plant. Typical characterization data for raw wastewater taken from the plant are given in Table 1.

### 2.2. Materials

Iron scraps (5–10 mm in length and 1–2 mm in width) were purchased from Kemiou Chemical Reagent Co., Ltd (Tianjin, China). Iron scraps were soaked in sodium hydroxide solution (10%) for 12 h, allowed to react for 30 min with 10% sulfuric acid, then washed with deionized water. Granular activated carbon (GAC) was obtained from Tianjin University Chemical Experiment Plant (Tianjin, China). GAC was soaked in wastewater for 3 d to reach saturation, then rinsed with deionized water repeatedly before being used [17].

### 2.3. Micro-electrolysis, Fenton oxidation, and coagulation sedimentation

The experimental setup was composed of two reactors whose volumes were both 1 L. The two reactors were equipped with electric stirring device. Micro-electrolysis reaction proceeded in the first reactor. Fenton oxidation and coagulation sedimentation proceeded in the second reactor. A selected amount of wastewater was firstly channeled into the reactor (as

Table 1
Typical wastewater characterization

| Parameters | COD | B/C | $NH_3$-N | TN | TP | Acute toxicity ($HgCl_2$ equivalent) |
|---|---|---|---|---|---|---|
| Concentration range (mg/L) | 200–400 | 0.13–0.24 | 42–46 | 64–68 | 3–7 | 0.08–0.12 |

shown in Fig. 1), and the pH of the wastewater was adjusted. The saturated activated carbon and treated iron filings were mixed together and packed into the reactor. Subsequently, the wastewater was stirred with a stirring device to conduct the micro-electrolysis reaction. The micro-electrolysis reaction time (MRT) was kept 180 min. The effluent from the micro-electrolysis experiment was removed, and the pH was adjusted. Then, a selected amount of hydrogen peroxide was added. The pH of the effluent from Fenton oxidation was adjusted to 8–9, and the residual COD of the supernatant from each effluent was measured [18,19].

### 2.4. Sequential filtration and ultrafiltration

The collected wastewater samples were subjected to sequential filtration and ultrafiltration. Solvent filters were used as the filtration units and were operated under positive pressure (0.1 MPa, vacuum pump). Ultrafiltration was carried out in a continuous stirring-cell (Amicon, Model 8200) under positive pressure (maximum recommended pressure was 0.483 MPa; for membranes with MWCO 100 KDa, the maximum recommended pressure was 0.069 MPa; $N_2$ as the inert gas). Samples were filtered sequentially through conventional filters with pore sizes of 1,000–3,000 nm (quantitative filter paper, slow), 450 and 220 nm (Xingya Shanghai). Permeates from the 220-nm membrane were then filtered successively through ultrafiltration membranes with nominal molecular weight cut-off (MWCO) values of 100, 30, 10, 5, 3, and 1 kDa (PL series, Millipore, MA), respectively [20,21]. To provide consistency among the different size units of ultrafiltration and filtration, the nominal MWCO values given in kDa units were approximated to the corresponding particle size values defined in nm. Thus, the pore sizes of each level were 1,000, 450, 220, 13, 8, 5, 4, 3, and 2 nm, respectively.

### 2.5. Analytical method with GC–MS

Solid-phase microextraction (SPME) was used for the enrichment of pollutants from the 2-nm ultrafiltrate. At 40°C, the sample was stirred with a magnetic stirrer, allowed to sit for 5 min, and extracted for 30 min. Then, the SPME tip was injected into the GC–MS to be analyzed. The initial column temperature of 40°C held for 2 min, then the temperature was ramped at 15°C/min to 80°C, 10°C/min to 140°C, 15°C/min to final temperature 230°C. The final temperature was then held for 10 min [22].

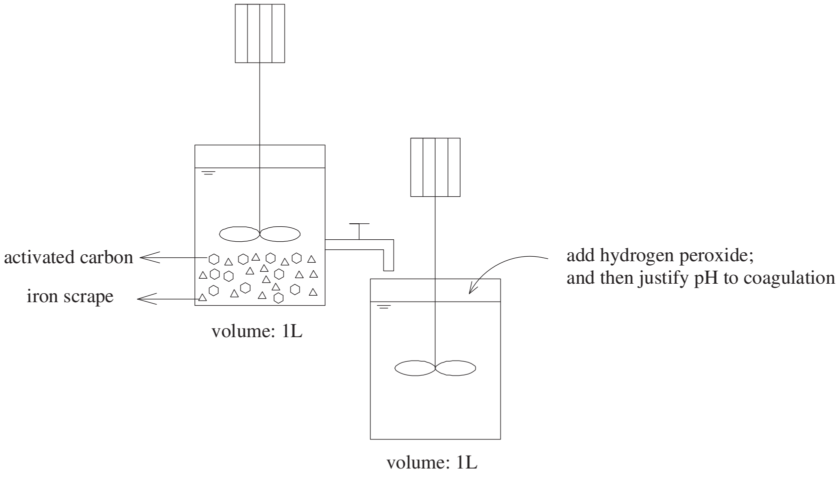

Fig. 1. The schematic diagram of the experimental setup.

## 3. Results and discussion

### 3.1. Performance of the micro-electrolysis process

By single-factor experiment, the optimum reaction conditions for micro-electrolysis of the studied wastewater were explored.

#### 3.1.1. Effect of reaction time on the micro-electrolysis treatment of wastewater

COD removal rates of samples were determined at various reaction times to observe the degradation level of the refractory organic matter and the consumption of iron. The results of this experiment were shown in Fig. 2(a). From Fig. 2(a), it could be seen that the MRT in the micro-electrolysis reactor had a great impact on the overall COD removal rate. COD removal efficiency ($R_{COD}$) increased sharply during the first 120 min, while the $R_{COD}$ of the micro-electrolysis system became stable after 120 min. This phenomenon means that the micro-electrolysis reaction could be completed in approximately 120 min. More reaction time could not contribute to any changes in COD but consumed more iron filings. Considering the removal efficiency and the processing costs, 120 min was enough for the reaction.

#### 3.1.2. Effect of Fe/C mass ratio on the micro-electrolysis treatment of wastewater

Owing to the strong effect of $Fe^0$/GAC on the discharge of [H] and $Fe^{2+}$ and the degradation efficiency, the RCOD of the influent to the sewage treatment plant was investigated under different $Fe^0$/GAC mass ratios. Fig. 2(b) showed the effects of different $Fe^0$/GAC values from Fig. 2(b), it can be observed that the RCOD was the highest when the $Fe^0$/GAC was 2:1, and the overall COD removal rate was 54%. The RCOD would decrease with higher or lower $Fe^0$/GAC (m/m) values. This was primarily because the amount of primary batteries produced by the micro-electrolysis reaction and the nascent hydrogen ([H]) was decreased under improper $Fe^0$/GAC, which would inhibit the degradation of organic pollutants [22]. Therefore, $Fe^0$/GAC mass ratio of 2:1 was selected in the following experiments.

#### 3.1.3. Effect of pH on the micro-electrolysis treatment of wastewater

In this electrochemical reaction, the pH affected the utilization of [H] and $Fe^{2+}$ significantly, so the micro-electrolysis experiments were conducted under various pH values. The effect of initial pH on $R_{COD}$ was displayed in Fig. 2(c). It showed that the $R_{COD}$ dropped dramatically when the initial pH was less than 5. This might be because micro-electrolysis was promoted in acidic conditions, but the mixture was alkaline in the reactor. When the initial pH dropped, the electric potential difference of the primary batteries produced by micro-electrolysis became larger and the electrode reaction proceeded more easily. Furthermore, the electrode oxidation–reduction reaction, electrocoagulation, and adsorption occurred more completely, which increased the $R_{COD}$. In addition, the lower the pH, the more ferrous ions were discharged, which promoted the electrochemical corrosion of iron and allowed the influence of anodic polarization to be overcome [23]. However, if the pH was too low, an excess of $Fe^{2+}$ would reduce the efficiency of micro-electrolysis and affect the determination of COD. Thus, there were no substantial changes in the $R_{COD}$ at pH values lower than 5. In summary, considering the removal efficiency of COD and the processing costs, initial pH was adjusted to 5.0 in the experiment.

#### 3.1.4. Effect of iron dosage on the micro-electrolysis treatment of wastewater

In the micro-electrolysis system, the iron filings, as an anodic metal, provided electrons for the destruction of COD, thus the $C_{Fe^0}$ value affected the activity of the galvanic cells. The $R_{COD}$ was measured at iron filing dosages of 15, 30, 60, 90, 120, 150, and 200 g/L, respectively. The results were presented in Fig. 2(d). When the dosage was less than 60 g/L or more than 90 g/L, degradation ratio dropped dramatically. When inadequate iron and carbon were present, there was only a small amount of primary batteries, which led to slow mass transfer and an inefficient process. Conversely, with increased iron, there were more primary batteries, which meant that the mass transfer speed was enhanced and the efficiency of the process improved. However, when the dosage was greater than 90 g/L, excessive $H_2$ was present in the negative electrode, and the pH of the liquid was increased. These changes inhibited the anodic reaction, and the $R_{COD}$ was reduced. Therefore, 90 g/L was chosen as the optimal $C_{Fe^0}$.

### 3.2. Performance of the Fenton oxidation process

Because the $Fe^{2+}$ in the effluent of the micro-electrolysis process can be used as the catalyst of Fenton oxidation, three factors of the Fenton treatment process were studied: the dosage of hydrogen peroxide ($C_{H_2O_2}$), initial pH, and MRT.

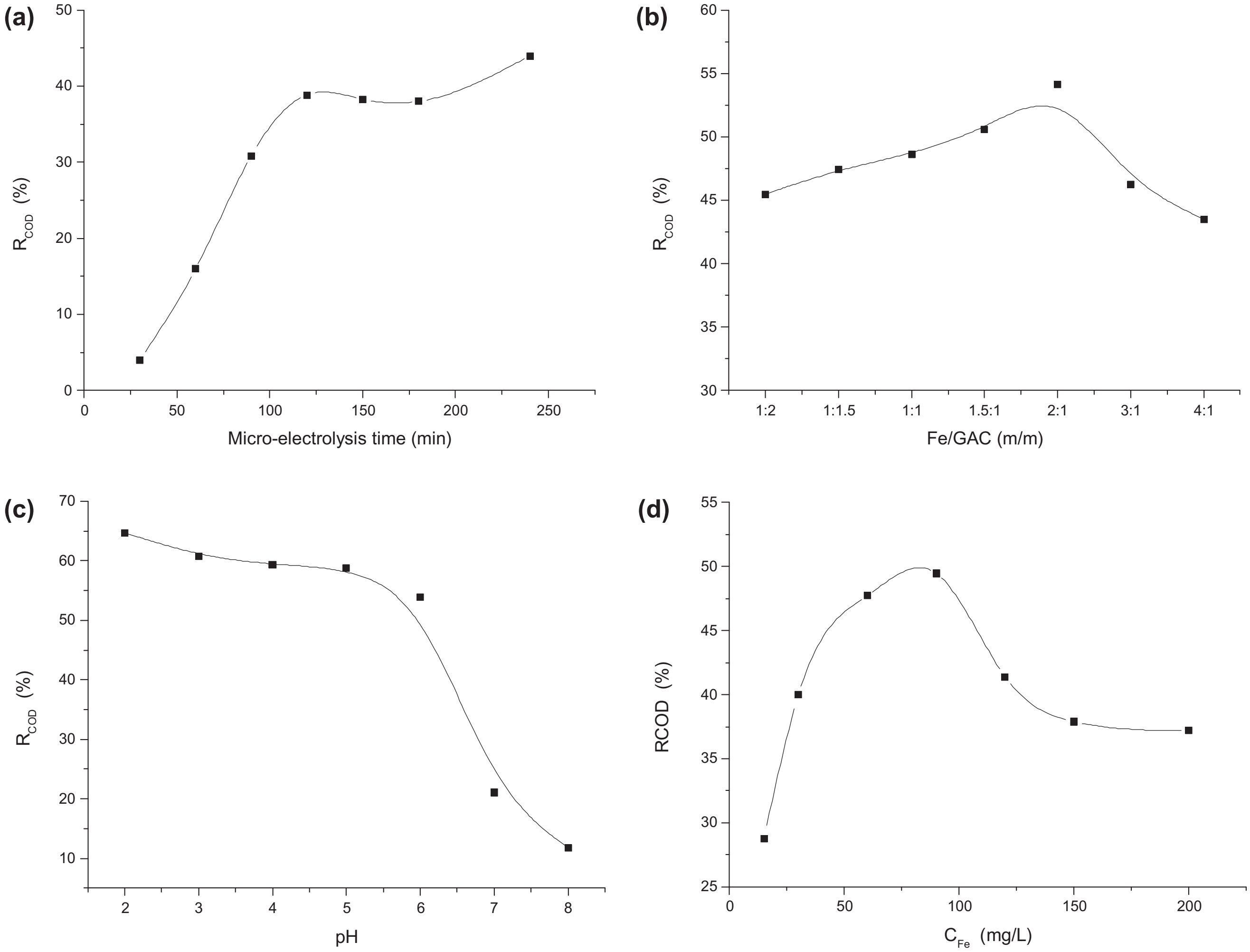

Fig. 2. Results of the single factor for the micro-electrolysis experiment: (a) effect of MRT on the removal of COD ($Fe^0$/GAC = 2:1, initial pH 3, $C_{Fe}$ = 90 g/L), (b) effect of $Fe^0$/GAC on the removal of COD (initial pH 3, MRT = 120, $C_{Fe}$ = 90 g/L), (c) effect of pH on the removal of COD ($Fe^0$/GAC = 2:1, MRT = 120, $C_{Fe}$ = 90 g/L) and (d) effect of $C_{Fe}$ on the removal of COD (initial pH 5, MRT = 120, $Fe^0$/GAC = 2:1).

### 3.2.1. *Effect of $H_2O_2$ dosage on the Fenton oxidation process*

$R_{COD}$ was determined at $H_2O_2$ dosages of 140, 160, 180, 200, 220, 240, and 260 mg/L, respectively. $R_{COD}$ during Fenton oxidation process at different $H_2O_2$ dosage were depicted in Fig. 3(a). Higher $H_2O_2$ doses generated more $^{\cdot}OH$, which, in turn, improved the $R_{COD}$. With an increase in $C_{H_2O_2}$ from 140 to 200 mg/L, the $R_{COD}$ increased from approximately 12–25%, and the $R_{COD}$ was the highest when $C_{H_2O_2}$ was 200 mg/L. With increased $H_2O_2$ doses, the excess $H_2O_2$ consumed enough $^{\cdot}OH$ to suppress the oxidation–reduction reaction, which led to the reduction in $R_{COD}$ [1]. Hence, 200 mg/L was chosen as the optimum $C_{H_2O_2}$ value.

### 3.2.2. *Effect of reaction time on the Fenton oxidation process*

The Fenton oxidation experiments were conducted under different MRT values to investigate the effect of MRT on COD removal. Fig. 3(b) depicted the experiment results, which showed that the MRT in the reactor had a great impact on the overall COD removal rate. With increased MRT, the organic pollutants were oxidized quickly and the $R_{COD}$ increased dramatically at the first 60 min. The $R_{COD}$ increased slowly after 60 min, reaching 35% when the reaction approached 150 min. Considering the processing efficiency and operational costs, 60 min was selected as the optimum MRT.

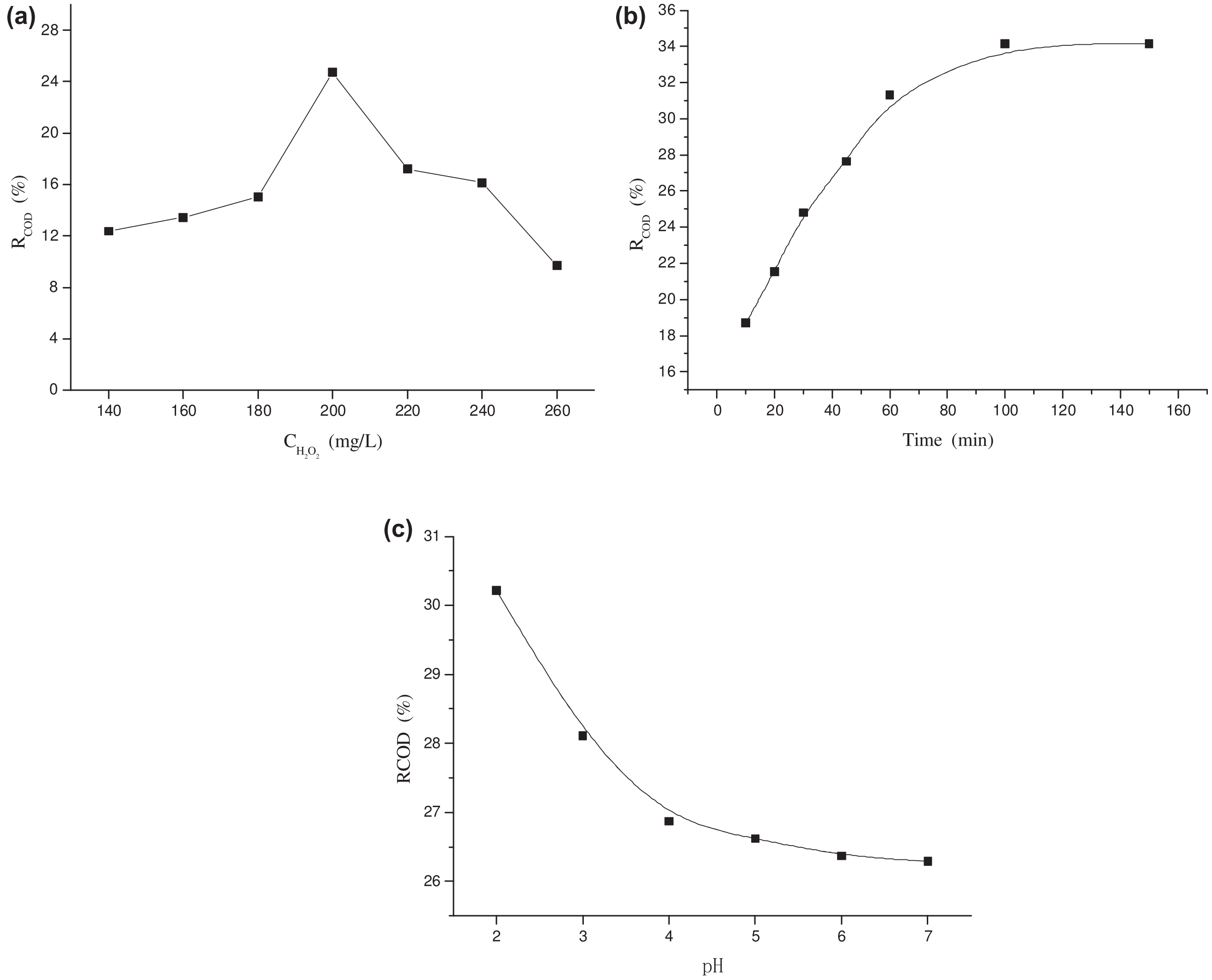

Fig. 3. Results of the single-factor experiment of the Fenton oxidation process: (a) effect of $H_2O_2$ on the removal of COD (initial pH 3, $C_{Fe} = 90$ g/L), (b) effect of MRT on the removal of COD (initial pH 3, $C_{H_2O_2} = 200$ g/L) and (c) effect of pH on the removal of COD ($C_{H_2O_2} = 200$ mg/L, MRT = 60 min).

### *3.2.3. Effect of initial pH on the Fenton oxidation process*

The $R_{COD}$ was measured under various initial pH values (2, 3, 4, 5, 6, and 7, respectively). The effect of initial pH was shown in Fig. 3(c). From Fig. 3(c), it could be seen that due to the inhibition of ·OH production caused by high pH values, the $R_{COD}$ was significantly higher in the mixture with lower initial pH. Considering the processing costs, the optimum initial pH was chosen as 3.0.

## *3.3. Analysis of the treatment efficiency and economic analysis*

The treatment efficiency of the influent of the wastewater treatment plant in a pharmaceutical industrial park by the combined micro-electrolysis, Fenton oxidation, and coagulation sedimentation process was measured under the above optimal reaction conditions. The pH of the effluent of the Fenton oxidation process was adjusted to approximately 8 and coagulated for 30 min.

The results of treatment by this combined process were presented in Table 2. The COD concentration in the effluent at the end of the combined treatment process was less than 50 mg/L, which met the requirement of the Discharge Standard of Pollutants for Municipal Wastewater Treatment Plants (GB18918-2002) of China.

In the micro-electrolysis process, the iron filings and activated carbon basically are one-time investment. The price of iron filings and activated carbon are 1,900 RMB and 5,800 RMB per ton, respectively. In the Fenton oxidation and coagulation process, hydrogen peroxide, sulfuric acid, and calcium hydroxide are consumables. The price of 30% industrial grade hydrogen peroxide, 98% industrial grade sulfuric acid, and industrial grade calcium hydroxide are 2,000 RMB, 1,500 RMB, and 380 RMB per ton. According to the dosing quantity under the optimum process conditions, the reagent cost is about 1–1.5 RMB per ton wastewater. Considering the electricity and labor cost, the treatment cost is about 1.3–1.8 RMB per ton wastewater. It is slightly higher than biochemical processes which priced about 0.8–1.0 RMB per ton wastewater. Due to the inability of biochemical processes to remove refractory organic compounds from the wastewater treatment plant in the pharmaceutical industrial park and the stricter discharge standards for the municipal wastewater treatment plant, non-biological processes such as physical and chemical methods appear promising.

### 3.4. *Analysis of fractionation changes of the organic pollutants in the wastewater*

To better understand the changes to the organic pollutants treated by the proposed micro-electrolysis/Fenton oxidation/coagulation sedimentation combined process, the molecular weight distribution of organic matter was measured using granular continuous filtering and ultrafiltration combined technology [21]. The particle size distribution (PSD)-based COD fractionation of the raw wastewater and effluent at the end of the combined process was visually presented in Fig. 4.

From Fig. 4, it could be seen that the particulate fraction (particle size > 1,000 nm) of the investigated wastewater decreased, and the COD content decreased from 29.5 to 2.54% after treated by the combined process. However, the soluble portion (particle size < 1 nm) increased significantly, and the COD content grew from 52.13 to 89.63%. It is possibly explained as the strong reduction of [H] produced by the electrode in micro-electrolysis has broken the bioresistant macromolecular organic compounds down into smaller biodegradable intermediates. In the Fenton oxidation experiment, at sufficiently low pH, $Fe^{2+}$ could catalyze $H_2O_2$ decomposition to $^{\cdot}OH$, which had an extremely high oxidizing ability and accelerated the oxidation of high-molecular-weight organics and bioresistant contaminants into smaller biodegradable materials. There was also a large amount of $Fe^{3+}$ in the effluent of the Fenton oxidation process, with a pH adjusted to 8, in order to generate $Fe(OH)_3$, which was easy to flocculate and highly stable. The small suspended colloid particles and macromolecular

Table 2
Treatment efficiency of the micro-electrolysis, Fenton oxidation, and coagulation sedimentation combined process

| | COD (mg/L) | | | |
|---|---|---|---|---|
| Sample | Raw wastewater | Effluent of micro-electrolysis | Effluent of Fenton oxidation | Effluent of coagulation sedimentation |
| Sample 1 | 267 | 162 | 113 | 47.7 |
| Sample 2 | 274 | 156 | 133 | 45.1 |
| Sample 3 | 267 | 163 | 133 | 49.2 |

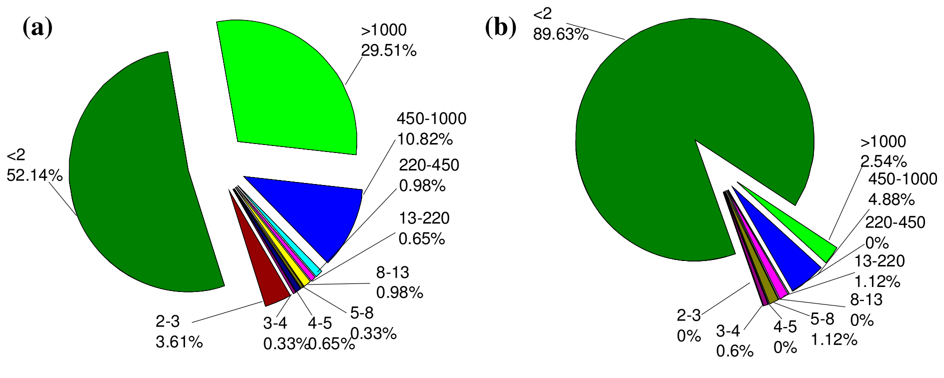

Fig. 4. Changes in the PSD of organic pollutants treated by the combined process: (a) PSD of the raw wastewater and (b) PSD of the effluent of the combined process.

organic pollutants were adsorbed or captured and precipitated out by flocculation, by which process the COD was effectively removed.

### *3.5. Analysis of COD components in the effluent of the end of the combined process*

According to the changes in the PSD of organic pollutants treated by the combined process, the refractory substances were mainly composed of the soluble fraction (particle size < 2 nm). In this study, GC–MS was used to analyze the soluble organics (molecular weight < 1 kDa) in the effluent at the end of the combined process.

Thirty-three types of organic pollutants were detected in the effluent after the combined process. These compounds belonged to seven types of classification and listed in Table 3. The area percentage demonstrated the relative content of the organic pollutants. According to the concentration from high

Table 3
Qualitative analysis results of organic pollutants in the effluent by GC–MS

| Classification | Substance | Percentage of area (%) |
|---|---|---|
| Siloxanes | Hexamethylcyclotrisiloxane | 5.34 |
| | Octamethylcyclotetrasiloxane | 6.44 |
| | Decamethylcyclopentasiloxane | 3.36 |
| | Dodecamethylcyclohexasiloxane | 0.89 |
| | Tetradecamethylcycloheptasiloxane | 0.65 |
| Phenols | 2,6-Di-tert-butyl-4-methylphenol | 1.93 |
| | 2,4-Di-tert-butylphenol | 0.59 |
| | 4-tert-Butyl-2,6-diisopropylphenol | 0.38 |
| | 2,5-Di-tert-butylphenol | 0.33 |
| Amides | (4-acetylphenyl) phenylmethane | 7.23 |
| | N-(diethylcarbamoyl)-N-methoxyformamide | 5.34 |
| | Acetamide, N-[3-(acetylamino) propyl]-N-3-butenyl- | 0.57 |
| | 4-Ethoxybenzamide | 2.58 |
| Phthalates | Bis(2-ethylhexyl) phthalate | 24.36 |
| | Dibutyl phthalate | 5.78 |
| | Phthalic acid, butyl 2-(2-methoxyethyl) hexyl ester | 1.62 |
| Heterocyclic | Dibenzofuran | 0.97 |
| | Diethyl(3-pyridyl)borane | 3.49 |
| | 4-(3-Methyl-1H-pyrazol-1-yl)-2-trifluoromethylbenzoic acid | 5.34 |
| | 2-Mercapto-4-phenylthiazole | 2.17 |
| | 4-(2-Chloroethyl)morpholine | 1.28 |
| PAHs | Naphthalene | 0.77 |
| | Fluorene | 1.83 |
| | Phenanthrene | 3.70 |
| | Anthracene | 1.20 |
| Others | 1H-Trindene, 2,3,4,5,6,7,8,9-octahydro-1,1,4,4,9,9-hexamethyl- | 1.48 |
| | 2,6-Di-tert-butyl-p-benzoquinone | 0.66 |
| | 2-Phenyltoluene | 0.57 |
| | Cedrol | 2.16 |
| | Benzeneacetic acid, α,3,4-tris[(trimethylsilyl)oxy]-, trimethylsilyl ester | 1.59 |
| | 2,2´,5,5´-tetramethylbiphenyl | 1.39 |
| | L-picein | 0.71 |
| | 3,5-Di-tert-butyl-4-hydroxybenzaldehyde | 2.27 |
| | Diphenylacetylene | 1.04 |

to low, the seven types of organics were ordered as follows: phthalates (31.76%) > siloxanes (16.68%) > amides (15.72%) > heterocyclic compounds (13.25%) > others (11.87%) > PAHs (7.5%) > phenols (3.23%). The phthalates, amides, and heterocyclic compounds were the main pollutants and made up 60.73% of the total, while the siloxanes might be derived from the losses from the GC column. Because almost all of the compounds listed in Table 3 were pharmaceutical intermediates, these substances could have come directly from pharmaceutical companies; furthermore, they had stable structures and could not be completely removed by the combined process.

## 4. Conclusion

Advanced degradation of pharmaceutical wastewater has attracted a lot of attention recently as a possible answer to the increasing need for stringent effluent standards. Chemical oxidation process displays certain advantages over conventional biochemical degradation in the treatment of biotoxic wastewaters. In this respect, developing more effective combined oxidation technology still needs to be undertaken.

After a batch of experiments, the optimal conditions for the combined treatment by micro-electrolysis/Fenton oxidation/coagulation sedimentation were determined. After the proposed process to treat the influent of the wastewater treatment plant in a pharmaceutical industrial park, the COD concentration in effluent was less than 50 mg/L, which met the requirement of the Environmental Standard GB18918-2002 in China.

The possible products of oxidative degrading organic matter were further discussed in this paper. Most of the particulate fraction with a particle size larger than 1,000 nm was removed, while the soluble portion was increased. This phenomenon revealed the pollutant transformation rule during the reaction. Finally, GC–MS was used to analyze the refractory soluble organics, and phthalates, amides, heterocyclic compounds, and PAHs were obtained as the main pollutants, which contributed approximately 70% to the total and had stable structures. These pollutants cannot be completely removed by the micro-electrolysis/Fenton oxidation/coagulation sedimentation combined process. The developed method has the advantages of less investment, operation cost, and convenient operation. It has a good effect and pushes forward the development of pollution treatment.

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