Using the Micro-Electrolysis Process to Pretreat PCB Etching Wastewater

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Abstract　Printed circuit board（PCB）etching wastewater is a type of industrial wastewater characterized by its high concentration and challenging treatment processes. The primary pollutants present in the water include ethylic acid，polyethylene，and copper ions（Cu^{2+}）. A ferric-carbon micro-electrolysis（ME）process is usually employed to treat the PCB etcheting wastewater. Since the ME process produces iron ions（Fe^{2+}）dispersed in the solution，Fenton oxidation can be performed after ME by simply adding hydrogen peroxide. This study conducted experiments to determine the optimal process parameters for both ME and Fenton oxidation. The total removal efficiencies for chemical oxygen demand（COD）and Cu^{2+} were 66. 34% and 99. 71%，respectively. To enhance COD degradation efficiency，various strengthened ME methods were investigated，including ultrasonic Fe-C ME，MnO_2 catalytic Fe-C ME，and Fe-Al-C ternary ME. The COD removal efficiencies were increased to 78. 3%，76. 5%，and 82%，respectively. Among these methods，Fe-Al-C ME proved to be the simplest and most effective approach for enhancing COD removal. Additionally，the reaction kinetics of Fe-Al-C ME were analyzed. Furthermore，the passivation of ME fillings was examined，as it is the most common factor affecting the stability of the ME process.

Key words　Printed circuit board（PCB）etching wastewater，Micro-electrolysis（ME），Fenton oxidation，Strengthened ME，Fillings passivation

0　Introduction

In recent years，the rapid development of the electronics industry has led to a significant increase in the production of printed circuit boards（PCBs）in China. Consequently，the volume of PCB wastewater has also risen sharply. Etching wastewater is a primary type of the PCB wastewater. It is characterized by a low pH value，a high chemical oxygen demand（COD），and elevated concentrations of heavy metals. Notably，the COD value can reach several tens of thousands mg/L. It is quite challenging to meet the discharge standards set by the *Wastewater Integrated Discharge Standard*（GB 8978-1996）in China. Consequently，pretreatment is commonly employed to reduce the COD to levels below 2 000 mg/L and to remove most heavy metals. After this pretreatment，the effluent can be directed to a municipal sewage treatment plant for further biochemical processing[1].

Recent research on the treatment of PCB etching wastewater focuses on pretreatment methods that include electrolysis，ion exchange，catalytic oxidation，micro-electrolysis（ME），absorption，and coagulation，*etc.* [2-4]. Among these methods，the ME process has emerged as a significant research focus. There are three primary reasons for this：（i）one of the working conditions of ME occurs in acidic solutions，which aligns with the characteristics of

PCB etching wastewater；（ii）in addition to degrading COD pollutants，ME can convert metal ions into elemental forms by providing electrons，allowing for their removal through the absorption and filtration of ME fillings[5-6]；（iii）one of the ME fillings—iron scraps—constitutes mechanical processing waste，making it a low-cost option that is advantageous for treating large volumes of industrial wastewater.

When the PCB etching wastewater is treated by ME，a significant amount of Fe^{2+} is produced in the wastewater. Consequently，a Fenton oxidation system can be easily established by adding hydrogen peroxide（H_2O_2）to the effluent from the ME process，which further degrades COD pollutants. The Fe^{3+} produced from the Fenton oxidation process，along with residual Fe^{2+}，can effectively coagulate pollutants in wastewater under weak alkaline conditions[7].

Although the ME process offers numerous advantages for treating PCB wastewater，particularly in the removal of heavy metal ions，some literature indicates two significant drawbacks：one is the relatively low COD removal efficiency，and the other is the instability of this process[8]. The latter issue arises from the formation of a compacted and passivated film on the surface of Fe-C fillings during the ME process.

This study aimed to investigate the treatment efficiency of the ME process for pretreating PCB etching wastewater. Experiments were conducted to determine the optimal process parameters for both the ME and Fenton oxidation methods，with treatment indices including COD and Cu^{2+} concentration. To enhance COD removal efficiency，three enhanced ME methods were employed for comparison and analysis.

1　Materials and methods

1.1　Properties of PCB etching wastewater

The PCB etching wastewater was collected from a domestic appliance factory located in the Yangtze River Delta, China. This wastewater had been sent to a solid waste management company for treatment as solid waste for many years prior to 2022. However, this method of treatment has been prohibited due to the issuance of new environmental policies. The wastewater generated during the PCB etching and washing processes contains a significant amount of ethyl acid and various organic matters leached from the PCB materials. This results in a low pH value (pH < 1, as determined by a pH meter) and a high COD value of 20 200 mg/L (as determined by the chemical reflux method). As a crucial material in PCBs, copper can dissolve into wastewater as Cu^{2+}. Its concentration was determined to be 817 mg/L using an atomic absorption spectrometer (AAS), and the resulting color of the wastewater was light blue.

1.2　Experimental systems and procedure

Fig. 1 illustrates the ME experimental system, which consists of a 500 mL beaker and a micro-hole aerator placed inside the beaker. Iron scraps (collected from a machine factory) and activated carbon powder (from Zhuxi Company, Jiangsu Province) were mixed evenly at a specific mass ratio, which can be adjusted according to the experimental design.

1.2.1　ME-Fenton oxidation-coagulation procedure. Firstly, iron scraps were treated using the following steps: they were soaked in a 5% NaOH solution for 30 min, followed by soaking in a 5% HCl solution for 1 h. The scraps were then washed with distilled water until neutral, dried, and had an average diameter of approximately 0.2 mm[9]. Activated carbon powder was soaked in wastewater for 1 h before the experiment, which made it sorptively saturated. Approximately 50 g of ME fillings were placed in a beaker (labeled 1#). Sodium hydroxide (NaOH, AR) was then added to 200 mL of PCB etching wastewater, adjusting the pH to 3. The effluent was discharged into beaker 2# after 1 h of aeration. 5 mL of 30% H_2O_2 (AR) was added to beaker 2#, which contained a small micro-hole aerator. The effluent was then transferred to beaker 3# after 1 h of aeration. Beaker 3# was placed on a magnetic stirring apparatus. NaOH (AR) was gradually added to beaker 3# until the pH reached 8. After 30 min of stirring, the stirring apparatus was turned off, and the mixture was allowed to stand for 30 min for static precipitation. A 5 mL effluent sample was collected from beaker 1#, 2#, and 3# after the completion of the ME, Fenton oxidation, and coagulation operation steps, respectively, to determine the COD and Cu^{2+} concentration.

1.2.2　Strengthened ME process. (i) Ultrasonic Fe-C ME. The beaker 1# containing Fe-C ME fillings and PCB etching wastewater was placed in the cleaning tank of the VGT-2127QT ultrasonic cleaner (Shenzhen Goot Company). The power switch was turned on, the moderate intensity button was pressed, and the device was turned off after 1 h of aeration. A total of 5 mL of the effluent sample was collected to determine the COD value. Five types of experiments were conducted in this step to evaluate whether ultrasonic waves enhance the COD removal efficiency of Fe-C ME: Fe-C ME for 2 h (experiment 1), ultrasonic treatment for 2 h (experiment 2), Fe-C ME for 1 h + ultrasonic treatment for 1 h (experiment 3), ultrasonic treatment for 1 h + Fe-C ME for 1 h (experiment 4), Fe-C ME and ultrasonic treatment simultaneously for 2 h (experiment 5).
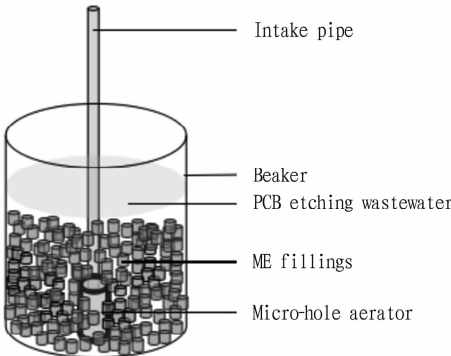

Fig. 1　ME experimental system

(ii) Catalytic Fe-C ME. A series of MnO_2 powders (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 g) were added to beaker 1#, which contained Fe-C ME fillings and PCB etching wastewater. After 1 h of aeration, 5 mL of the effluent sample was collected to determine the COD value.

(iii) Fe-Al-C ternary ME. Approximately 50 g of ME fillings (with a Fe/Al/C mass ratio of 1 : 1 : 2) were added to beaker 1# containing PCB etching wastewater. After 1 h of aeration, 5 mL of the effluent sample was collected to determine the COD value.

1.2.3　ME fillings compaction and passivation treatment. The treatment effect of the Fe-C ME process will diminish due to the compaction and passivation of the fillings during wastewater treatment. A backwashing method was employed to restore its functionality. Following the ME process, the ME fillings were rinsed with distilled water that was forced through a 10W small pump. Approximately 2 g of filling samples were collected before and after backwashing for characterization analysis using scanning electron microscopy and energy-dispersive spectroscopy.

2　Results and analysis

The optimal process parameters experiments for ME and Fenton oxidation were investigated to achieve the best process efficiency.

2.1　ME

2.1.1　pH of raw wastewater. A series of solid NaOH pellets were added to beaker 1#, resulting in pH of 2, 3, 4, 5, and 6, respectively. After the aforementioned ME procedure (Section 1.2), the treated water samples were collected to determine the COD value, and the results are presented in Table 1.

Table 1　Effect of pH on Fe-C ME

Item	pH				
	2	3	4	5	6
COD // mg/L	12 360	12 060	12 440	13 200	13 840
COD removal efficiency // %	38.20	39.70	37.80	34.00	30.80

Commonly, the COD removal efficiency of ME under acidic conditions is superior to that under alkaline conditions. In acidic environments, Fe readily dissolves and converts to ferrous ions (Fe^{2+}), which is helpful to the ME process[10]. The highest removal efficiency of COD is 39.7% at a relatively low pH of 3. However, under extremely low pH conditions, an excess of H^+ reacts with the ferrous hydroxide [$Fe(OH)_2$] produced during the ME process. These ferrous hydroxides can coagulate to remove

pollutants from water, including organic matter, thereby diminishing the effectiveness of the treatment.

2.1.2 Fe/C mass ratio. Under a pH of 3, a series of 50 g of ME fillings with Fe/C mass ratios of 4 : 1, 5 : 2, 2 : 1, 4 : 3, 1 : 1, and 2 : 3 were added to beaker 1#. After the ME procedure, the treated water samples were collected to determine the COD value, and the results are shown in Table 2.

Table 2 Effect of Fe/C mass ratio on ME

Item	Fe/C mass ratio					
	4 : 1	5 : 2	2 : 1	4 : 3	1 : 1	2 : 3
COD // mg/L	13 760	12 580	11 140	10 100	8 700	8 620
COD removal efficiency // %	31.20	37.10	44.30	49.50	56.50	56.90

As the Fe/C mass ratio decreased, the COD removal efficiency increased, reaching a steady state when the ratio fell to 1 : 1. This trend suggests that the quantity of microbatteries formed by iron and activated carbon reaches a relatively high level after the 1 : 1 ratio.

2.1.3 Dosage of fillings. Under a pH of 3, a series of ME fillings with masses of 20, 30, 40, 50, and 60 g were added to beaker 1#, respectively, maintaining a Fe/C mass ratio of 1 : 1. After the ME procedure, the treated water samples were collected to determine the COD value, and the results are presented in Table 3.

Table 3 Effect of iron dosage on ME

Item	Iron dosage // g				
	10	15	20	25	30
COD // mg/L	13 840	9 520	8 500	6 840	6 848
COD removal efficiency // %	30.80	52.40	57.50	65.80	65.78

Generally, the COD removal efficiency increases with the dosage of fillings. However, it reached a relatively stable state at 25 g, as an excessive amount of iron scraps and activated carbon led to the accumulation of fillings, which could not sustainably enhance the removal efficiency.

After the optimal process parameters for ME were established, the PCB etching wastewater was treated accordingly. The determination results indicated that the COD of the raw wastewater decreased from 20 200 to 6 840 mg/L, reflecting a COD removal efficiency of 65.80%. Additionally, the concentration of Cu^{2+} was reduced from 817 to 6.30 mg/L, and the pH increased from 3 to 4.

2.2 Fenton oxidation process

2.2.1 H_2O_2 volume. The effluent from the ME process, under its optimal parameters, was collected in beaker 2#. Volumes of 3.0, 3.5, 4.0, 4.5, and 5.0 mL of H_2O_2 were added to the beaker, respectively. Following the Fenton oxidation procedure described in Section **1.2**, the treated water samples were collected to determine the COD value, and the results are presented in Table 4.

Table 4 Effect of H_2O_2 volume on Fenton process

Item	H_2O_2 volume // mL				
	3.0	3.5	4.0	4.5	5.0
COD // mg/L	4 830	4 795	4 704	4 627	4 613
COD removal efficiency // %	26.60	27.13	28.51	29.68	29.89

During the range of 3.0 to 5.0 mL of H_2O_2, the COD removal efficiency increased as the volume of H_2O_2 increased, reaching a relatively stable state after 4.5 mL. The added H_2O_2 reacted with Fe^{2+} to produce hydroxyl radicals, which are effective in degrading organic matters. Therefore, the optimal volume of H_2O_2 depended on the concentration of Fe^{2+} in the wastewater. An excessive amount of H_2O_2 could react with hydroxyl radicals to produce perhydroxyl radicals, which would diminish the degradation capacity of the Fenton oxidation system. This is because the degradation ability of perhydroxyl radicals is lower than that of hydroxyl radicals[11].

2.2.2 pH. The effluent from the ME process, under its optimal parameters, was collected in beaker 2#. A total of 4.5 mL of H_2O_2 was added to the beaker. Following the Fenton oxidation procedure described in Section **1.2**, the treated water samples were collected to determine the COD value, and the results are presented in Table 5.

Table 5 Effect of pH on Fenton process

Item	pH				
	2	3	4	5	6
COD // mg/L	4 900	4 494	4 263	4 200	4 774
COD removal efficiency // %	25.53	31.70	35.21	36.17	27.45

From Table 5, it was found that pH significantly affected the COD removal efficiency. As the pH increased from 2 to 5, the removal efficiency also increased. The pH is related to the concentration of H^+ in the wastewater, which can promote the reaction between Fe^{2+} and H_2O_2, leading to the production of hydroxyl radicals.

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + \cdot OH \qquad (1)$$
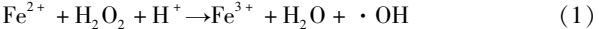
However, an excess of H^+ in the wastewater leads to the reaction of hydroxyl radicals with these ions, which diminishes the degradation capacity of the Fenton system for organic pollutants[12].

$$\cdot OH + H^+ + e^- \rightarrow H_2O \qquad (2)$$

The effluent from the ME process was treated using Fenton oxidation under optimal process parameters. The determination results indicated that the COD value decreased to 4 200 mg/L, representing a COD removal efficiency of 36.17%. The concentra-

tion of Cu^{2+} remained at 6.30 mg/L, and the optimal pH was 5.

2.3   Coagulation process   The effluent treated by the Fenton oxidation process was added to beaker 3#, into which NaOH reagent was introduced to increase the pH value. This adjustment facilitates the coagulation effect of Fe^{2+} and Fe^{3+} in the water. After the coagulation procedure, the treated water samples were collected to determine the COD value and Cu^{2+} concentration. The results indicated that the COD value was 2 760 mg/L, corresponding to a COD removal efficiency of 34.29%, while the Cu^{2+} concentration was 2.3 mg/L.

After successive treatment with the Fe/C ME process, Fenton oxidation and coagulation processes, the total COD removal efficiency was 86.34%, and the total Cu^{2+} removal efficiency was 99.71%. However, the COD value of 2 760 mg/L was excessively high and unsuitable for subsequent biochemical treatment. As the ME process was the primary method for disposing of COD matter, several measures were implemented to enhance the ME's ability to remove COD matter.

2.4   Strengthened Fe-C ME methods   Strengthened ME methods, such as ultrasonic-Fe/C ME, can significantly improve the effectiveness, thereby enhancing the efficiency of the ME process. This enhancement is typically attributed to the increased potential difference resulting from the synergistic interaction between ultrasonic waves and ME. A greater potential difference facilitates the decomposition of specific organic pollutants during the ME process. In this paper, three strengthened methods, including ultrasonic treatment, MnO_2 intermingling, and Fe-Al-C ternary ME, were employed to improve the removal efficiency of COD in the PCB etching wastewater through the Fe/C ME process.

2.4.1   Ultrasonic strengthened Fe-C ME. Ultrasonic treatment decomposes COD in wastewater through two mechanisms: thermolysis and strong hydroxyl oxidation. The hydroxyl radicals are generated from the decomposition of H_2O by ultrasonic waves[10]. Five experiments were designed to treat 200 mL of PCB etching wastewater to investigate whether ultrasonic waves enhance Fe-C ME, including Fe-C ME for 2 h (experiment 1), ultrosonic treatment for 2 h (experiment 2), Fe-C ME for 1 h + ultrasonic treatment for 1 h (experiment 3), ultrasonic treatment for 1 h + Fe-C ME for 1 h (experiment 4), Fe-C ME and ultrasonic treatment simultaneously for 2 h (experiment 5). The results are displayed in Fig. 2.

Fig. 2 demonstrates that the COD removal efficiency of experiment 5 was 78.3%, the highest among all experiments. This efficiency was 17.3% greater than that of experiment 1, indicating that the combination of ME and ultrasonic treatment has a synergistic effect on the treatment of PCB etching wastewater. Firstly,

the micro-jets and blast waves produced by ultrasonic waves can agitate the wastewater, increasing the contact opportunities between iron and carbon particles, thereby enhancing the quantity of galvanic cells. Secondly, ultrasonic waves prevent the surface passivation of Fe-C filling particles, which could otherwise reduce the efficiency of the ME treatment[12].
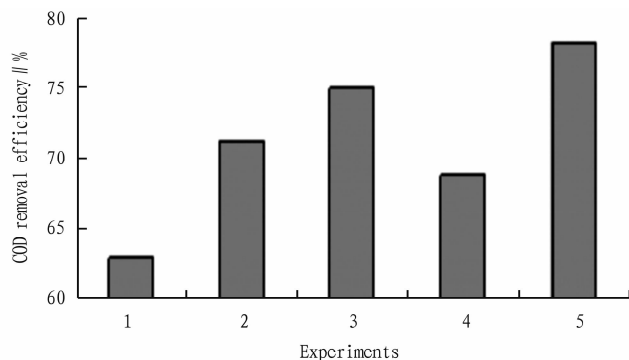
Fig. 2   Effect of various ultrasound methods on COD removal efficiency

2.4.2   Catalytic strengthened ME. MnO_2 solid reagent was added to the Fe-C ME system to investigate the effect of ME on wastewater treatment. MnO_2 was found to enhance the COD removal efficacy of the ME process. A series of dosages of MnO_2 (0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 g) were added to the Fe-C ME system under optimal process parameters. When the dosage of MnO_2 was 2.5 g for 200 mL of PCB etching wastewater, the COD removal efficiency reached 76.5%, which was 10.7% greater than that of the Fe-C ME process. MnO_2 can reduce the activation energy of the ME reaction, making the redox reaction of ME easier.

2.4.3   Fe-Al-C Ternary ME. Ternary ME system can be structured by incorporating an additional material into the Fe-C system. In this study, Al scraps that were pretreated using the same procedure as the Fe scraps were utilized.

When Al scraps were added to the Fe/C system, Al provided a greater electron driving force that accelerated electron transfer, resulting in improved COD removal efficiency compared to that of the Fe-C ME process[13]. However, if an excessive amount of Al was added, the surface of Fe became coated with Al particles, which reduced the contact opportunities between Fe and wastewater. When the mass ratio of Fe/Al/C was 1 : 1 : 2, the COD removal efficiency was optimal at 82%, 16.20% higher than that of the Fe-C ME process (Table 6).

Table 6   Effect of ternary ME with different mass ratios on COD removal efficiency

Item	Mass ratio of Fe/Al/C				
	1 : 0 : 1	1.5 : 0.5 : 2	1 : 1 : 2	0.5 : 1.5 : 2	0 : 1 : 1
COD in effluent // mg/L	6 840	4 323	3 636	3 979	3 959
COD removal efficiency // %	65.80	79.60	82.00	80.30	80.40

2.4.4   Comparison of three strengthened ME methods. Comparing the three strengthened ME processes mentioned above, the Fe-

Al-C ME method proved to be the most effective for treating PCB etching wastewater for two reasons: first, it achieved the highest

COD removal efficiency at 82% ; second, Al scraps are readily available and the least expensive among the three methods[13-14].

Based on previous experimental results, the optimal parameters for the Fe-Al-C ME process in treating PCB etching wastewater were as follows: the pH was 3, the Fe-Al-C mass ratio was 1 : 1 : 2, and the dosage of fillings was 50 g for 200 mL of raw wastewater. After 1 h of reaction, the COD of the wastewater decreased to 3 636 mg/L, while the concentration of Cu^{2+} reduced to 5.75 mg/L. The removal efficiencies for COD and Cu^{2+} were 82% and 99.30%, respectively. Additionally, it was observed that the Cu^{2+} removal efficiency of the Fe-Al-C ME process was slightly higher than that of the Fe-C ME process.

Finally, Fe-Al-C ME was chosen to replace Fe-C ME, in conjunction with Fenton oxidation and coagulation, to treat the PCB etching wastewater. The effluent had a COD value of 1 525 mg/L and a Cu^{2+} concentration of 2.1 mg/L, resulting in total removal efficiencies of 92.45% for COD and 99.74% for Cu^{2+}, respectively.

2.5 ME fillings passivation Although the Fe-Al-C ME-Fenton oxidation-coagulation process can be used to pretreat PCB etching wastewater, the effluent parameters meet the requirements for biological treatment. Another limitation of ME is its instability. It was found that the treatment efficiency decreased when the ME fillings, which had been used once, were employed again to treat PCB etching wastewater[15]. Some research indicates that the passivation of ME fillings during the wastewater treatment process leads to a reduction in treatment efficiency[16-18]. The backwashing method is a common approach to recover the effectiveness of the ME fillings[19]. The data from five ME experiments indicated a gradual decline in COD removal efficiency, decreasing from 82% to 39.70%. Following a backwashing treatment, the efficiency increased to 74.11% ; however, it subsequently decreased to 42.82% after three additional ME experiments. Upon the application of backwashing treatment once more, the COD removal efficiency was restored to 71% (Table 7).

Table 7 COD removal efficacy of raw wastewater after ME treatment

No.	COD of raw wastewater // mg/L	COD of effluent after ME treatment // mg/L	COD removal efficiency // %
1	20 200	3 636	82.00
2	20 200	3 948	80.46
3	20 200	5 796	71.31
4	20 200	8 694	56.96
5	20 200	12 180	39.70
6	20 200	5 229	74.11
7	20 200	7 077	64.97
8	20 200	8 820	56.34
9	20 200	11 550	42.82
10	20 200	5 859	71.00
11	20 200	8 190	59.46
12	20 200	12 159	39.81

NOTE No.6-12 are backwashing treatments.

The curves (Fig. 3) indicated that the treatment effect of COD decreased rapidly as the duration of the experiment increased. This finding suggested that the ME fillings were passivated after the ME system operated for a certain period. When the removal efficiency of ME decreased to a certain level, a high-intensity backwashing of the ME fillings could be employed. Consequently, the COD removal efficiency improved, although this enhancement was sustained only for a brief period. Therefore, the passivation process of the iron and activated carbon fillings was investigated using scanning electron microscopy (SEM).
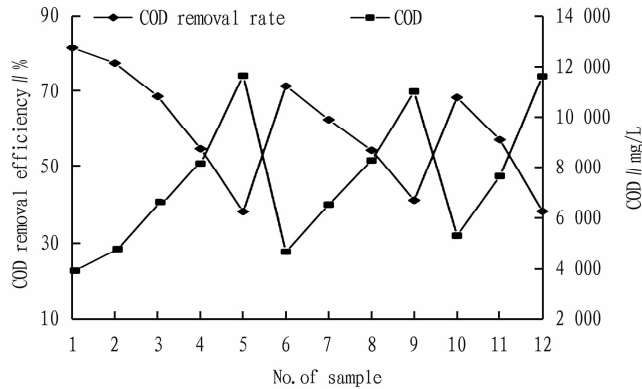

Fig. 3 Changes in wastewater COD before and after backwashing

The surfaces of unreacted iron, passivated iron with a ME reaction efficiency reduced to less than 50% , and iron after backwashing were analyzed using SEM. The SEM images of the unreacted iron surface are presented in Fig. 4. The surface of the unreacted iron appeared smooth and exhibited a distinct texture.
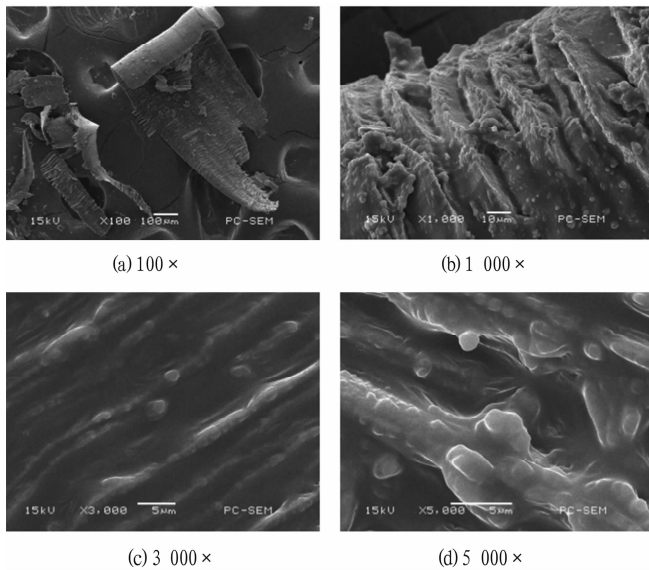

(a) 100 ×

(b) 1 000 ×

(c) 3 000 ×

(d) 5 000 ×

Fig. 4 SEM images of unreacted iron surface

The smoothness of the passivated iron significantly decreased, and a layer of passivation film was clearly observable (Fig. 5). The film demonstrated a strong tendency to agglomerate (Fig.5c-5d).
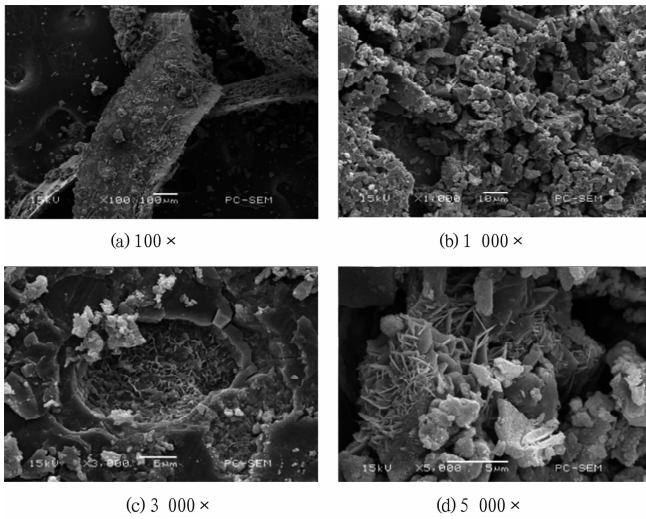
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<tr><td>(a) 100 ×</td><td>(b) 1 000 ×</td></tr>
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Fig. 5　SEM images of passivated iron surface

<table>
<tr><td>(a) 100 ×</td><td>(b) 1 000 ×</td></tr>
<tr><td>(c) 3 000 ×</td><td>(d) 5 000 ×</td></tr>
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Fig. 6　SEM images of iron surface after backwashing

The surface of iron after backwashing (Fig. 6) was smoother than that of passivated iron (Fig. 5). The texture of the former was distinctly visible, while the passivation film could not be clearly observed. Fig. 6c-6d further confirmed the disappearance of the agglomerate and flake film. This finding may be ascribed to the effects of backwashing.

The SEM images of the iron surface revealed that iron and carbon can be encapsulated by the agglomerated passivation film during the ME process. To clarify the characteristics of the film, its components were analyzed using energy-dispersive spectroscopy (EDS). The EDS patterns for the Fe-C fillings before and after ME are illustrated in Figs. 7-8.
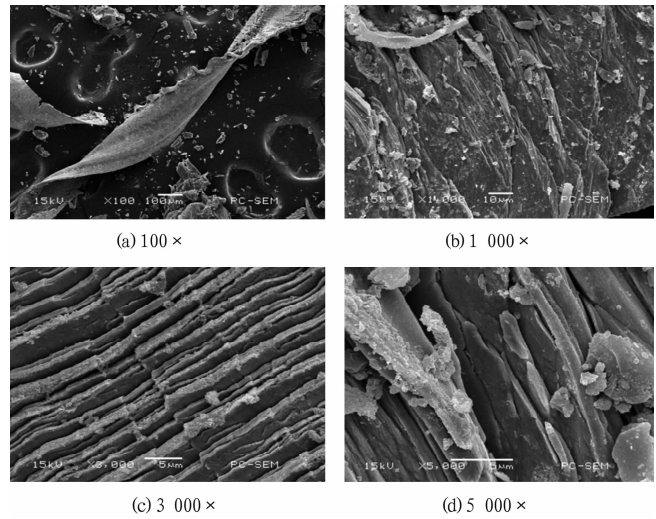
A detailed elemental composition is presented in Fig. 7. The characteristic peaks of Fe, O, C, and Na, the principal elements of the passivation film, were observed. The surface of this material appeared loose and porous (Fig. 5b-5d), which may be attributed to the presence of iron oxides, such as Fe_2O_3 and Fe_3O_4. Additionally, the detected characteristic peaks of C, Na, and Si may indicate the presence of impurities within the material. Such porous materials can be penetrated by wastewater, which may cause the iron to clump together. This clumping significantly hinders the interaction between iron and carbon, thereby preventing the formation of Fe-C primary battery in wastewater. Consequently, this can diminish the effectiveness of the ME treatment process.
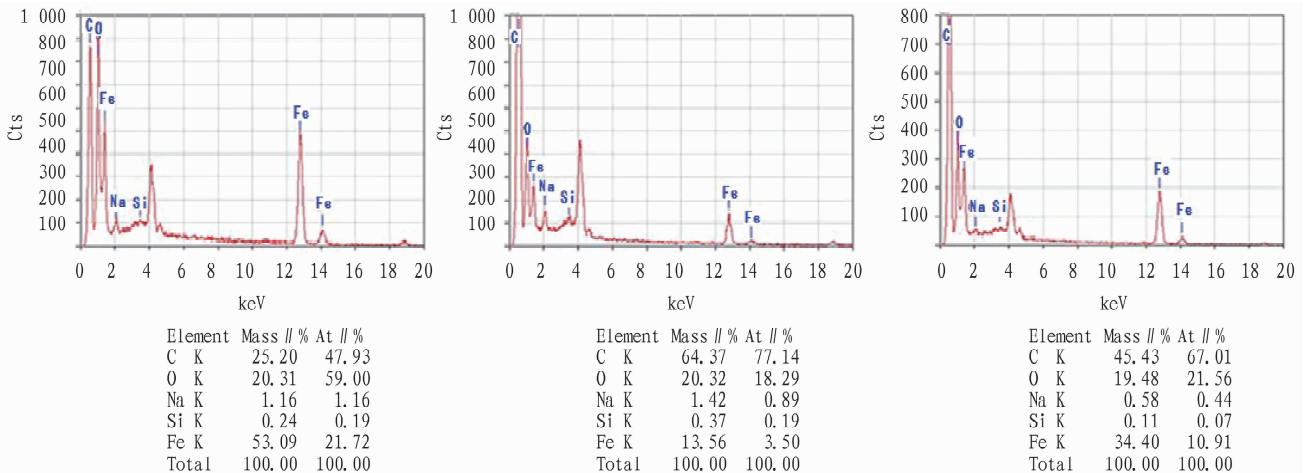

Element	Mass ∥ %	At ∥ %
C K	25.20	47.93
O K	20.31	59.00
Na K	1.16	1.16
Si K	0.24	0.19
Fe K	53.09	21.72
Total	100.00	100.00

Element	Mass ∥ %	At ∥ %
C K	64.37	77.14
O K	20.32	18.29
Na K	1.42	0.89
Si K	0.37	0.19
Fe K	13.56	3.50
Total	100.00	100.00

Element	Mass ∥ %	At ∥ %
C K	45.43	67.01
O K	19.48	21.56
Na K	0.58	0.44
Si K	0.11	0.07
Fe K	34.40	10.91
Total	100.00	100.00

Fig. 7　EDS patterns of passivated iron surface

Fig. 8 illustrates the primary characteristic peaks of Fe, O, C, Si, and Cr on the surface of the iron. However, the amount of oxygen on the iron surface after backwashing significantly declined (Fig. 7), providing direct evidence that the removal of the passivation film was caused by the backwashing process. Although backwashing partially removed the iron oxide film, some iron oxides could still adhere to the iron surface. Given the incomplete removal of the passivation film and its higher surface activity or viscosity, the passivation of the fillings was more likely attributed to oxidation and compaction[20-21].

The treatment effect diminished during the ME process due to the formation of an iron oxidation passivation film. This film can compact iron and carbon, thereby hindering the development of Fe-C primary battery[22]. The passivation film can be more effectively removed during backwashing. Therefore, the backwashing procedure should be taken into account when designing the ME reactor.
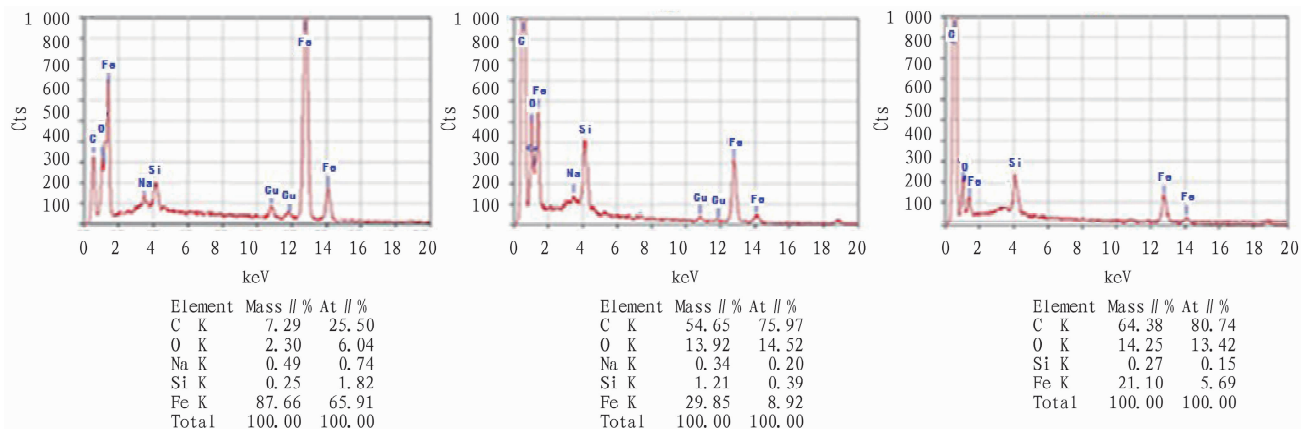
Fig. 8　EDS patterns of iron surface after backwashing

3　Conclusions

In this study, the successive treatment with the Fe/C ME process, Fenton oxidation and coagulation processes was employed to treat PCB etching wastewater. The results of the effluent analysis indicated a COD value of 2 760 mg/L and a Cu^{2+} concentration of 2.3 mg/L. The total COD removal efficiency was 86.34%, while the Cu^{2+} removal efficiency reached 99.71%. These findings suggest that the ME-Fenton oxidation-coagulation combination process can effectively pretreat PCB etching wastewater.

To enhance the ME's ability to decompose COD matter in PCB etching wastewater, three enhanced ME methods were investigated. Among these, the Fe-Al-C method was found to be the most effective.

The successive treatment processes, including the Fe-Al-C ME process, Fenton oxidation, and coagulation, were employed to treat the PCB etching wastewater. The COD value and Cu^{2+} concentration in the effluent were 1 525 and 2.1 mg/L, respectively. The total removal efficiencies for COD and Cu^{2+} were 92.45% and 99.74%, respectively.

The treatment effect of the ME process was diminished due to iron oxidation passivation and compaction. The passivation film can be partially removed during backwashing.

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