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Fenton Oxidation Combined with Iron–Carbon Micro-Electrolysis for Treating Leachate Generated from Thermally Treated Sludge

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Abstract: In this study, Iron–Carbon Micro-Electrolysis (ICME), Fenton oxidation, and their combination were investigated to treat the leachate obtained from a wastewater treatment plant located in southern China. The results show that the Fenton-ICME process was the most efficient one. After the leachate was treated with the Fenton-ICME process, the COD concentration was reduced from the initial 35,772 mg/L to 13,522 mg/L, and the removal efficiency was up to 62.2%. In addition, the biological oxygen demand (BOD) to COD ratio increased by 40% at optimal conditions. This suggests that the biodegradability of the leachate has been increased, facilitating the biodegradation of the leachate after it is mixed with the raw wastewater. By studying the characteristic variation of the leachate treated with the Fenton-ICME process, it was found that the combined process mainly removes organic compounds such as aromatic compounds, ketones, and aldehydes. The separated sludge does not have a crystalline structure, and the iron in it mainly exists in the form of trivalent iron. It reveals that the Fenton-ICME process has great potential to be used as a pretreatment of leachate.

Keywords: sludge leachate; iron–carbon micro-electrolysis; Fenton oxidation; wastewater treatment

Citation: Dong, X.; Liu, H.; Li, J.; Gan, R.; Liu, Q.; Zhang, X. Fenton Oxidation Combined with Iron–Carbon Micro-Electrolysis for Treating Leachate Generated from Thermally Treated Sludge. *Separations* **2023**, *10*, 568. https://doi.org/10.3390/separations10110568

Academic Editor: Dimosthenis Giokas and Manolis Manos

Received: 29 October 2023
Revised: 10 November 2023
Accepted: 12 November 2023
Published: 14 November 2023

1. Introduction

At present, most of the sewage treatment plants in China generally use the activated sludge method as the basic method of sewage treatment. In the process of treatment, a large amount of residual sludge is inevitably generated [1]. Thermal treatment is generally used to pretreat sludge for enhancing the dewatering. The essence of the thermal treatment of the sludge is the process of destroying the water-holding structure of the sludge by using high temperatures and high pressures, which can release the bound and adsorbed water in the sludge efficiently, and the intracellular products of the sludge also release and finally enter into the leachate. Therefore, the leachate has a complex composition and high chemical oxygen demand (COD) [2]. It is enriched with various pollutants, and contains more toxic, harmful substances with high salinity, which are capable of inhibiting the growth and reproduction of microorganisms. In addition, the biological oxygen demand (BOD) to COD ratio (B/C) is about 0.30, which suggests that the leachate has poor biodegradability.

Generally, the leachate is mixed with the raw sewage wastewater and treated in the wastewater treatment. However, the COD concentration of the leachate is normally in the range of 5000~50,000 mg/L [3,4]. There is great concern on that the high COD concentration of the leachate treated along with the raw wastewater will increase the COD loading to the wastewater treatment processes and thus may cause the effluent quality to exceed the discharging regulation. In fact, it has already been found that the COD concentration of the effluent of a wastewater treatment plant in Guangdong province of China was occasionally over the required maximum discharge concentration (50 mg/L). This suggests that there is risk for the plant. Therefore, pretreatment on the leachate is necessary before it is sent to mix with the raw sewage wastewater for treatment.

So far, some physicochemical methods, including coagulation adsorption, advanced oxidation, etc., have been introduced for leachate treatment; however, it is rather costly due to the large amount of chemical addition [5–7]. Biological treatment has also been tested to treat the leachate, but the efficiency is very low as the bioavailability of the leachate is quite low [8]. Therefore, these technologies are still mainly in the initial exploration stage. It suggests that cost-effective treatment techniques are highly needed.

Iron Carbon Micro-Electrolysis (ICME) technology is an advanced wastewater treatment technology based on electrochemical principles, and its reaction system has a variety of processes, including galvanic cell reaction, redox reaction, coagulation precipitation, electrochemical enrichment, adsorption, etc. Thus, ICME can decompose multi-ring and multi-chain organic matters in wastewater, and thus improves the B/C value of the wastewater. ICME technology is considered to be a good wastewater treatment process [9,10], which can provide conditions for subsequent biochemical treatment. For example, Han et al. (2023) applied ICME technology to the treatment of aniline wastewater, and after 1 h of reaction, the COD removal rate reached more than 70% [11]. In addition, it can effectively reduce the toxicity of water [12].

A wastewater treatment plant of Guangdong province has adopted ICME as a pretreatment to treat the leachate from the dewatering of sludge that has been thermally treated. However, the COD concentration in the effluent of the wastewater treatment was observed as being greater than 50 mg/L sometimes. This suggests that ICME alone cannot ensure the good performance of the leachate treatment as the leachate is different from the general sewage wastewater. It is more complex and difficult to degrade. Advanced oxidation is an efficient method for treating refractory organic pollutants [13]. Common oxidation methods include sodium persulfate (PS) and the Fenton process. Yao et al. used ICME combined with Fenton technology to treat the wastewater generated from pigment production and have achieved a COD removal of 90% [14]. Wang et al. added H_2O_2 to the ICME system to effectively degrade fused aromatic hydrocarbon pollutants in wastewater [15]. The study reveals that the coupling of ICME and oxidation methods could be an efficient method to treat the leachate generated from the dewatering of the thermally treated sludge.

In this study, ICME and its combination with Fenton oxidation have been employed to treat the leachate generated from the dewatering of the thermally treated sludge in a wastewater treatment plant. The work explored the treatment efficiency and impact factors. The optimal treatment condition was investigated. The characteristics of the leachate before and after treatment were studied using Gas Chromatography-Mass Spectrometry (GC-MS), and 3-Dimension Excitation Emission Matrix (3D-EEM), and the generated Fenton sludge was analyzed via Fourier Transform Infrared Spectroscopy (FTIR).

2. Methodology

2.1. Materials

The leachate used in this study was collected from a wastewater treatment plant of Guangdong Province, China. In this plant, the wastewater sludge was first thermally treated with steam, and then the residue solid was separated via plate and frame filter press from the liquid. The liquid is the leachate, which contains a high COD concentration. The leachate sample was placed in a 30 L sewage bucket and stored at 4 °C. The color of the leachate is black as paint, and the pungent smell is persistent. The leachate characteristics are as follows: the COD concentration is 25,000~57,000 (mg/L); the BOD_5 concentration is 11,100~17,000 (mg/L); the NH_4^+–N content is 1000~2500 (mg/L); the B/C ratio is 0.28–0.35; and the pH is 5.15–6.30.

The iron–carbon fillers used to carry ICME in the experiment were purchased from Pingxiang Shangyuan Environmental Protection Chemical Co., LTD. Jiangxi Province, China. The iron–carbon fillers were placed in the dark and sealed for storage. This filler was made of iron powder (45~50%), carbon powder (15%), and other metal catalysts through combustion. The selected iron–carbon filler has less density, good strength, good flow permeability, and small flow resistance; it does not easily produce the phenomenon of compaction and passivation and has a longer service life compared to other tested iron–carbon fillers. Its surface color is gray-black, and its main properties are shown in Table 1.

Table 1. The main properties of the fillers.

Property	Value	Property	Value
Product Model	TMIE-1	Cylinder compressive strength (MPa)	≥ 5
Appearance	Spherical three holes with grooved side	Packing density (g/cm^3)	0.9~1.0
Size Deviation (mm)	± 0.50	Polymetallic content (%)	60~65
Specific surface area σ (m^2/g)	≥ 2	Carbon content (%)	15~20
Porosity ε (%)	50~55	Catalyst content (%)	≥ 3

2.2. Leachate Treatment

The ICME process: The iron–carbon fillers were washed with clean water 1 to 2 times before the experiment (except for special instructions), and then soaked in the leachate for 1 h before use. A total of 100 mL of the filtrate was placed in a 250 mL conical flask. The initial pH of the filtrate was adjusted to 3.5, and the dosage of the filler was 800 g/L. It was placed on a constant temperature shaker, and an oscillation speed of 180 rpm was set. After sampling at 0, 0.5, 1.0, 2.0, 4.0, 6.0, and 8.0 h, the pH value of the effluent was measured and adjusted to alkaline via the addition of NaOH. After precipitation, the supernatant was taken to measure the COD concentration and the ratio of BOD to COD.

The Fenton oxidation process: H_2SO_4 and NaOH were used to adjust the pH of the leachate to a suitable value, and then a certain amount of the leachate and solid $FeSO_4 \cdot 7H_2O$ was placed into a 250 mL beaker. Stirring was performed until $FeSO_4 \cdot 7H_2O$ was completely dissolved. Then, a certain amount of 30% H_2O_2 solution was added to the solution and agitated at 500 rpm. After 1 h of reaction, the sample was taken, and a certain amount of NaOH solution was added to adjust the pH. The supernatant was taken to determine the COD concentration after settling.

ICME-Fenton combination process: In this process, ICME was carried out first and then Fenton oxidation followed. The procedures of ICME and Fenton oxidation are as described above.

Fenton-ICME combination process: In this process, Fenton oxidation was carried out first and then ICME followed. The procedures of Fenton oxidation and ICME are as described above.

2.3. The Optimization of the Processes

For the ICME process, the impact of reaction pH, iron–carbon dosage, and oscillation velocity on the COD removal of the leachate were investigated. For the Fenton oxidation process, the influences of H_2O_2 dosage, dosage ratio, wastewater pH, and reaction time on the COD removal of the leachate were investigated, respectively. As for the ICME-Fenton combined process, the study investigates the influences of H_2O_2 dosage, pH, and reaction time. For the Fenton-ICME combined process, investigation of filler dosage, wastewater pH, and reaction time were carried out.

2.4. The Composition Variation of the Leachate

Gas Chromatography-Mass Spectrometry (GC-MS, Agilent, US), Fourier Transform Infrared Spectroscopy (FTIR, Thermo Scientific), and Three-Dimension Excitation Emission Matrix (3D-EEM) were employed to analyze the composition variation of the leachate before and after Fenton-ICME treatment, as well as the precipitates obtained via Fenton oxidation. The apparent morphology, material structure, and elemental composition of the sludge were also analyzed.

A total of 10 mL of original or treated leachate sample was added into a 250 mL funnel, and 50 mL of n-hexane was added. The mixture was covered and placed in a shaker for 10 min. Thereafter, it was allowed to stand for separation, and the top layer was collected. The extraction was performed three times, and the collected extractant was united, dehydrated with anhydrous Na_2SO_4, and finally concentrated to 5 mL by evaporation. Thereafter, it was injected into a GC-MS with a HP-5MS quartz capillary column (30 m $\times$ 0.25 mm $\times$ 0.25 μm, Agilent, US.). The initial column temperature was set to 40 °C and heated to 280 °C at a rate of 15 °C/min, the injection port temperature was 250 °C, the split ratio was 10:1, the carrier gas (N_2) flow rate was 3 mL/min, and the ion source temperature was 250 °C. During the test, the scanning mode was selected for qualitative analysis, and the data collection was compared with the NIST11.L standard and poor's library.

Dried sludge samples were tested with FTIR, and the number of absorption peaks was used to determine the type of chemical bond expansion and contraction vibration or functional group. The measurement mode was ATR mode, the measurement wavenumber range was 400~4000 cm^{-1}, the measured value was absorbance, and the absorbance and transmittance can be converted in Omnic software according to actual needs.

3D-EEM can rapidly analyze dissolved organic matter (DOM). The original or treated leachate sample was filtered with a 0.45 μm membrane as a pretreatment and then was diluted to a COD concentration between 20 to 100 mg/L, and the UV254 value was read. It was then placed in a 10 mm quartz cuvette and scanned with a 3D fluorescence analyzer. The excitation wavelength (Ex) was set at 220~500 nm, the emission wavelength (Emission, Em) was 200~600 nm, the sampling time interval was 1 nm, and ultrapure water was used as the blank reference zeroing. After the detection was completed, the data were normalized against the UV254 values.

3. Results and Discussion

3.1. The Leachate Treated by Different Processes

3.1.1. ICME Process

The treatment effect of ICME technology is affected by many factors, including filler dosage, iron–carbon ratio, reaction pH, dissolved oxygen, reaction time, etc. After a single variable pre-experiment, the optimal process parameters of ICME were determined as follows: the initial pH value was 3.5, the iron–carbon dosage was 800 g/L, and the oscillation speed was 180 r/min. The results are shown in Figure 1.

According to Figure 1a, after 8 h of reaction, the COD concentration of the leachate decreased from 40,095 mg/L to 24,558 mg/L, and the COD removal rate reached 38.8%. The pH, in fact, is a very important parameter as it impacts on the redox potential of iron. Therefore, the pH variation during the treatment was followed. It can be seen that the pH value of the reaction system increased rapidly to more than 6.0 within 2 h (Figure 1b). This is due to the fact that the iron in the filler is continuously consumed, and $OH-$ is continuously produced in the system, resulting in a continuous increase in pH value. It can be seen that the COD reduction and B/C increasing mainly occurred in the first 2 h. This is due to the fact that low pH increases the potential difference of ICME and thus enhances the treatment efficiency. According to the XPS analysis, the major iron compound was Fe_3O_4 with a $pH < 5.5$, but the major iron compound became FeOOH with a $pH > 5.5$. The redox potential of $FeOOH/Fe^{2+}$ and Fe_3O_4/Fe^{2+} are -274 mV and -314 mV [16]. The higher the redox potential is, the better performance is. Hence, low pH showed better COD removal efficiency. From Figure 1c, it can be seen that the ratio of BOD to COD of the filtrate after ICME treatment increased from 0.31 to 0.33. Although it increased, the range was not high. Therefore, the effect of microelectronics technology on improving the biodegradability of the leachate is not obvious.

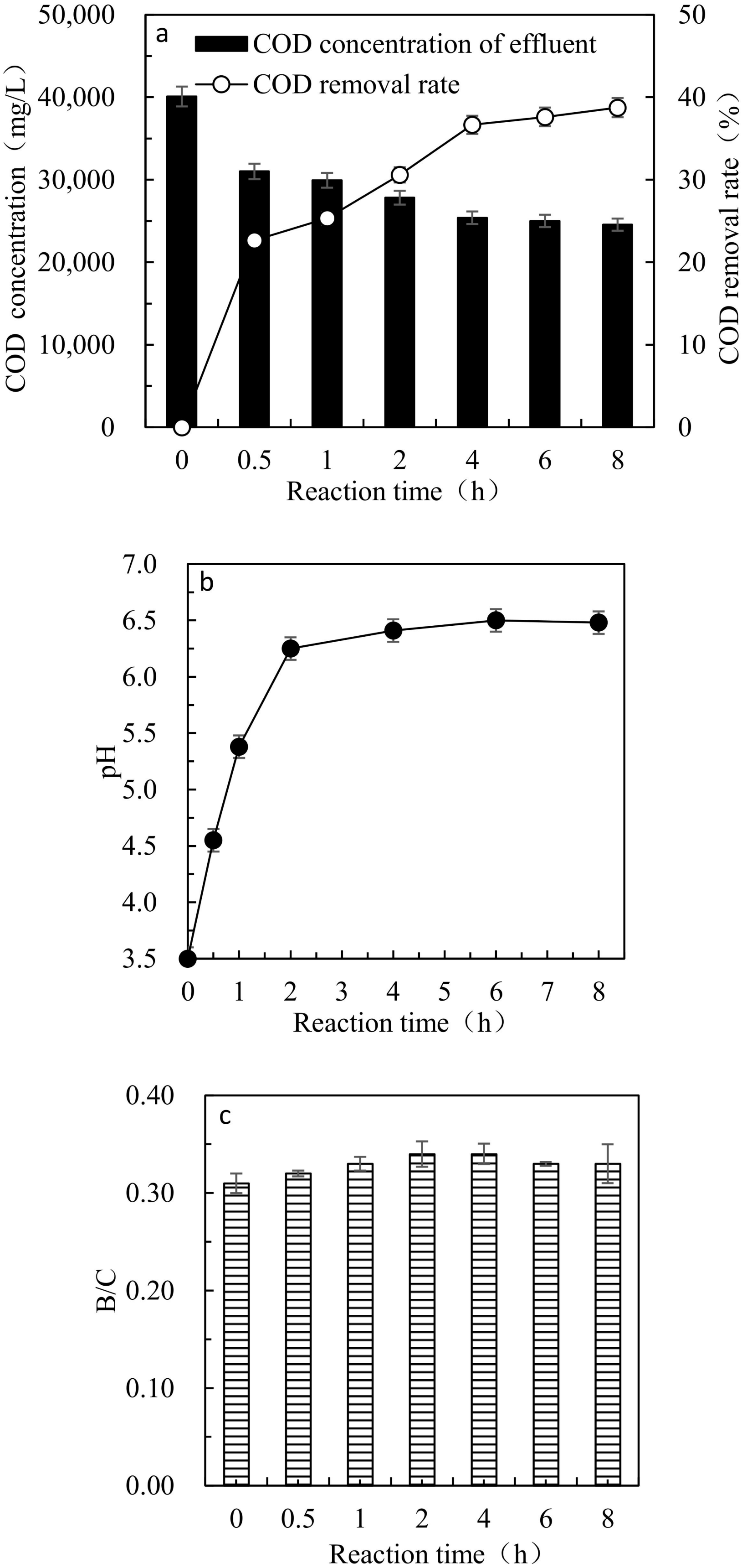


Figure 1. The COD removal (**a**), pH variation (**b**), and the ratio of BOD to COD (**c**) of leachate before and after ICME treatment.

3.1.2. ICME-Fenton Combined Process Research

The effects of H_2O_2 dosage, dosage ratio, pH, reaction time, and other factors on the COD removal rate of the leachate were investigated. After a single variable pre-experiment (results are not shown here), the optimum process parameters of Fenton oxidation were determined as follows: the dosage of H_2O_2 was 0.20 mol/L, the reaction pH value was 4.0, the ratio of H_2O_2 to Fe^{2+} was 4:1, and the reaction time was 15 min.

In order to explore whether the combined process of Fenton and ICME can play a role in strengthening the treatment effect of the ICME process, the leachate was treated via single process and combined process, respectively. The single process includes the single Fenton oxidation process at optimal conditions and the single ICME process at optimal conditions, and the combined process is the ICME-Fenton process. The experimental results are shown in Figure 2.

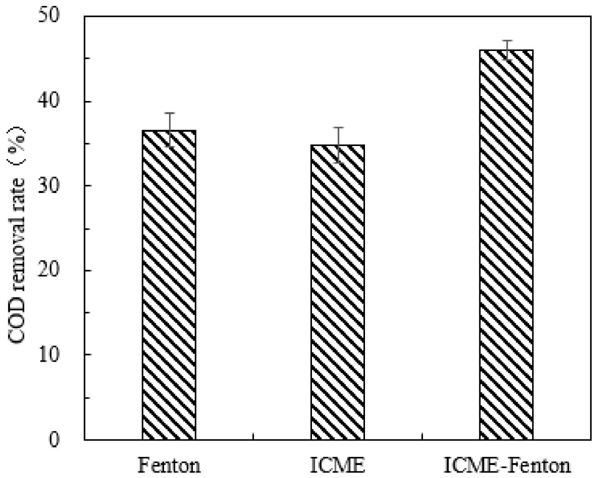


Figure 2. The COD removal via Fenton oxidation, ICME, and ICME-Fenton process.

The COD removal rate of Fenton, ICME, and ICME-Fenton were 36.57%, 34.78%, and 46.03%, respectively (Figure 2). During the ICME reaction, a large amount of iron ions and ferrous ions are dissolved in the system. Ferrous ions can form Fenton's reagent with H_2O_2, and Fenton's reagent can further oxidize organic pollutants. Therefore, it is considered that the combination of the Fenton process after the ICME process can not only reuse iron resources, but also improve the COD removal rate.

In order to enhance the treatment effect of the ICME-Fenton combined process on the leachate, the H_2O_2 dosage, pH, and reaction time were optimized. From Figure 3a, it can be seen that when the dosage of H_2O_2 was 0.15 mol/L, the treatment performance was the best. The COD concentration was reduced to 19,942 mg/L, and the COD removal efficiency reached 43.3%. It can be seen from Figure 3b that the treatment efficiency was the highest when the pH of the ICME effluent was adjusted to 4.0. In this case, the COD concentration of the leachate was reduced to 19,132 mg/L, and the COD removal rate was 45.6%. Therefore, the pH value of ICME effluent was adjusted to 4.0 in the ICME-Fenton combined process. It can be seen that when the Fenton oxidation was used following the ICME process, and the reaction rate was very fast (Figure 3c), after about 30 min, the COD removal rate was stable. Therefore, the Fenton oxidation reaction time in the ICME-Fenton combined process was only 30 min.

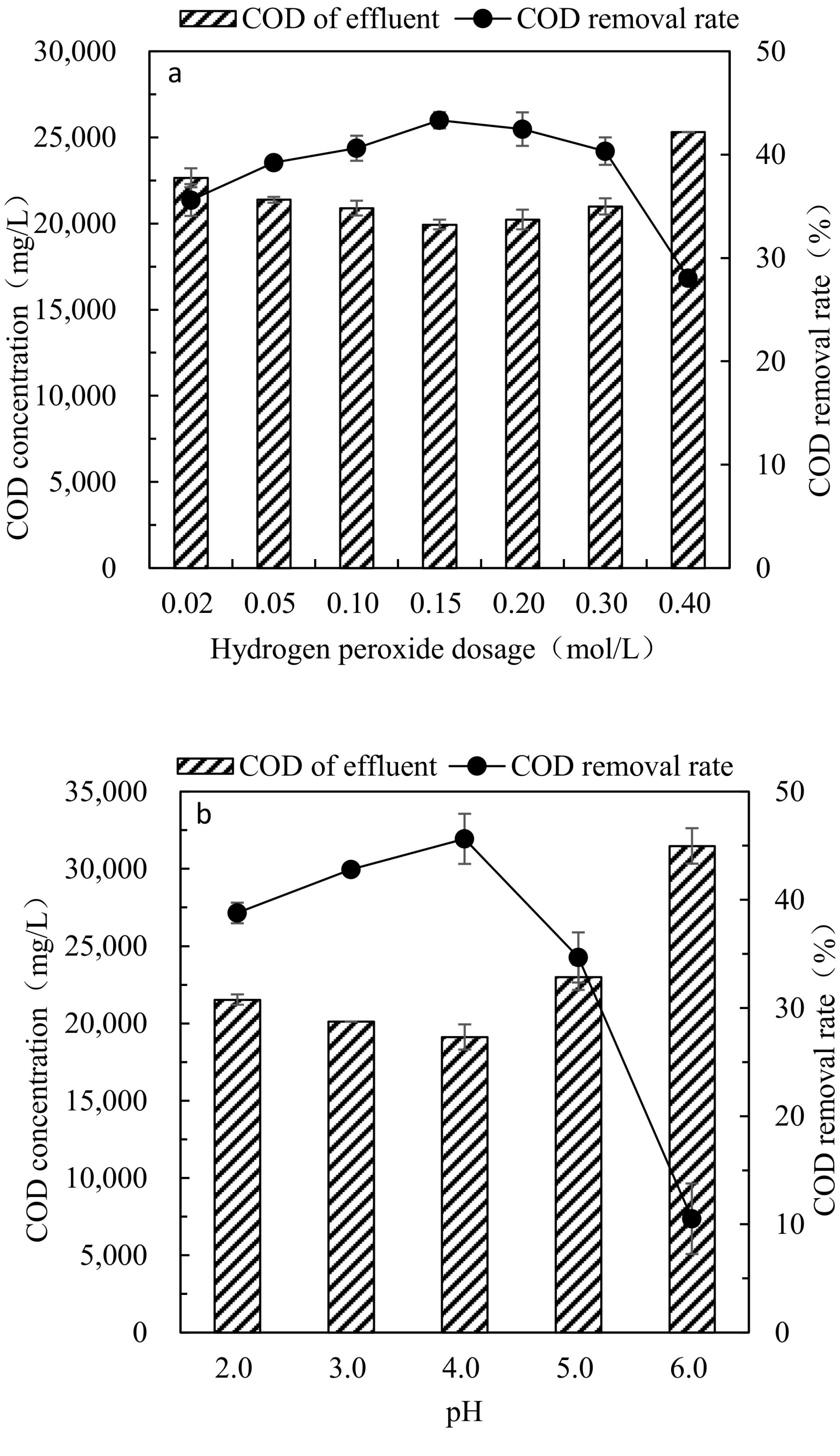


Figure 3. *Cont.*

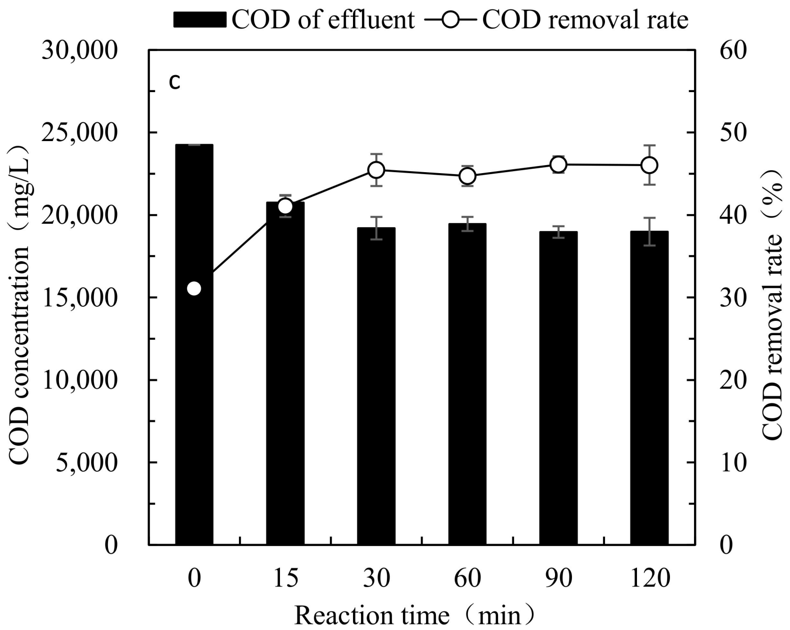
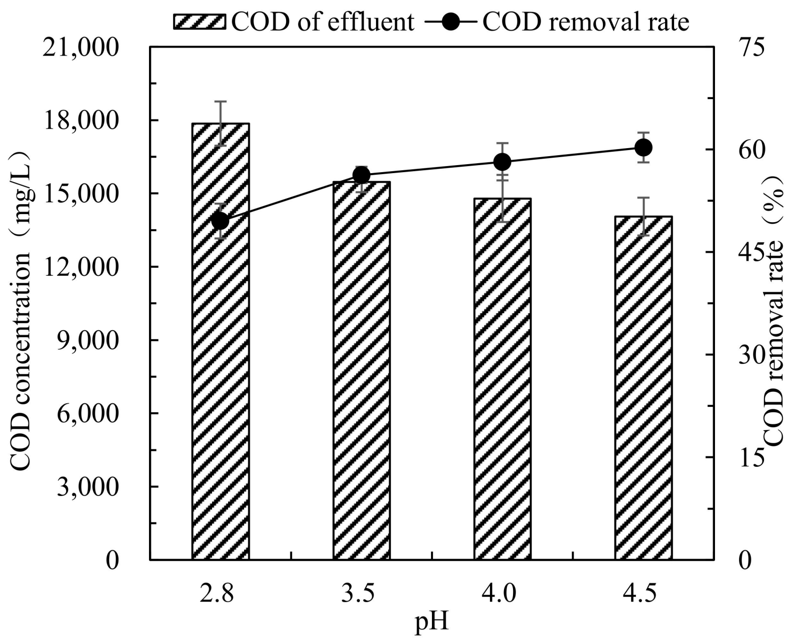


Figure 3. Effect of relevant parameters on COD removal from leachate via the ICME-Fenton combined process: (**a**) H_2O_2 dosage, (**b**) pH, (**c**) reaction time.

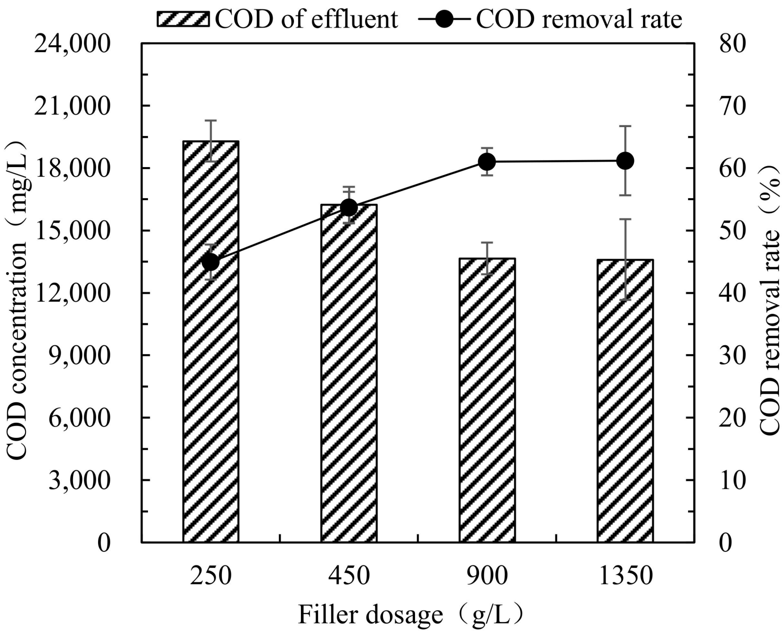
3.1.3. Fenton-ICME Process

The leachate treated with the Fenton oxidation process only needs a small amount of alkali to adjust the pH to the optimal value required by the single ICME process. In addition, the residual H_2O_2 in the leachate can continue to react with Fe^{2+} produced by ICME. Therefore, using the Fenton oxidation process before the ICME process would not only reduce the amount of acid and alkali, but also may improve the COD removal. In order to explore the treatment effect of the Fenton-ICME combined process on the leachate, the related parameters of pH value, filler dosage, and reaction time were optimized. The results of parameter optimization are shown in Figure 4.

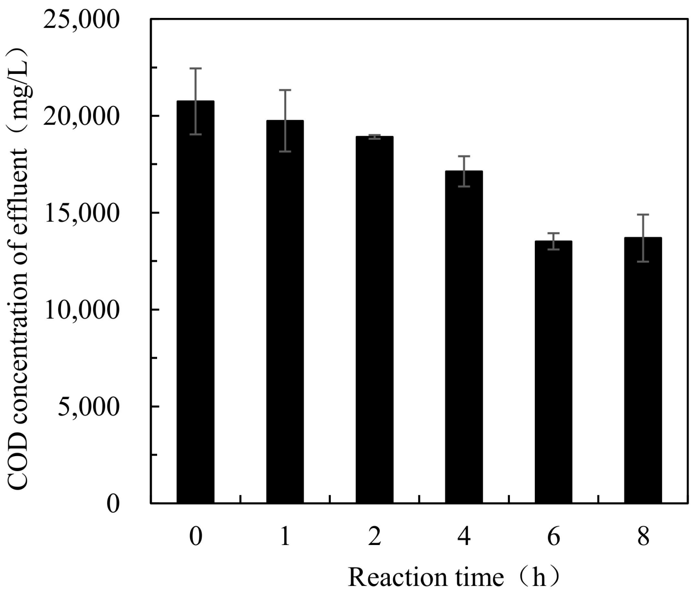


(**a**)

Figure 4. *Cont.*



(**b**)

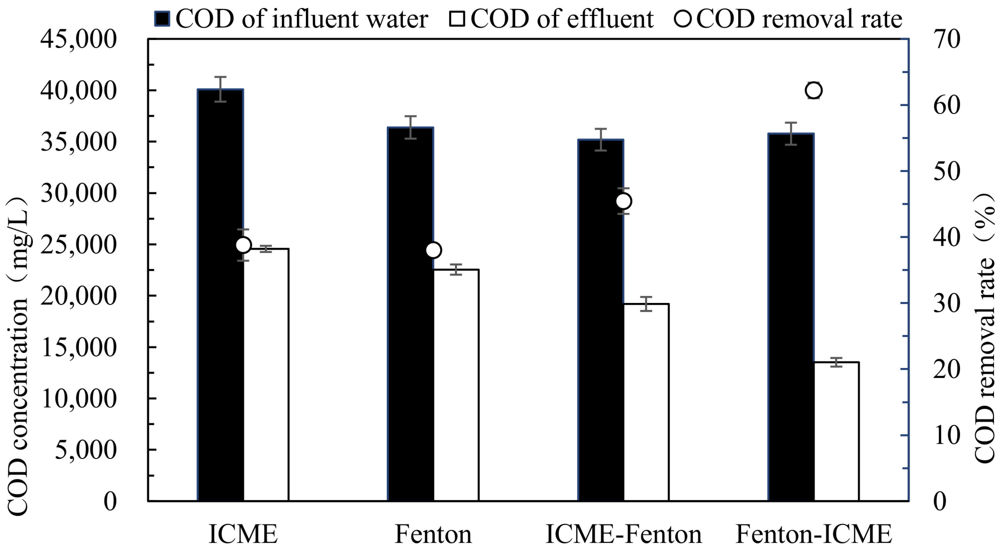


(**c**)

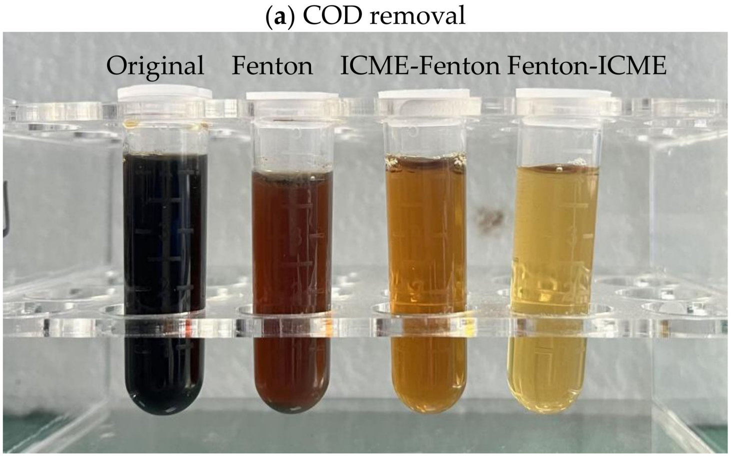
Figure 4. Effect of relevant parameters on COD removal of the leachate via the Fenton-ICME combined process: (**a**) pH value, (**b**) the filler dosage, (**c**) reaction time.

Studies have shown that changes in pH value have little effect on the removal rate of COD (Figure 4a). Therefore, in order to reduce the used amount of alkali, it is more appropriate to adjust the pH of the Fenton effluent to 3.5 in the Fenton-ICME combined process. It can be seen from Figure 4b that when the amount of filler was increased to 900 g/L, the COD concentration of the leachate was decreased to 13,660 mg/L, and the COD removal rate reached 61.0%. Thus, it reveals that in the Fenton-ICME combined process, when the iron–carbon filler dosage is 900 g/L, a stable treatment effect can be guaranteed. From Figure 4c, it can be seen that with the reaction proceeding, the treatment performance became better and better. After 6 h of reaction, the COD removal rate reaches stability. Therefore, the optimal ICME reaction time in the Fenton-ICME combined process is 6 h.

As shown in Figure 5a, by comparing the single ICME process, the single Fenton process, the ICME-Fenton combined process, and the Fenton-ICME combined process, the combination of ICME and Fenton could improve the removal rate of COD. Among them, the single ICME process could obtain a COD removal of 38.8%, and the COD concentration was reduced from 40,095 mg/L to 24,558 mg/L. The single Fenton process obtained a COD removal of 38.0%, and the COD concentration was reduced from 35,383 mg/L to 22,546 mg/L. The ICME-Fenton combined process achieved a COD removal of 45.4%., and the COD concentration decreased from 35,189 mg/L to 19,198 mg/L. The Fenton-ICME process obtained a COD removal rate of 62.2%, and the COD concentration decreased from 35,772 mg/L to 13,522 mg/L. In summary, from the perspective of COD removal efficiency, the combination of Fenton-ICME has a better effect on the treatment of sludge filtrate. Compared with the single ICME process, the COD removal rate can be increased from 38.8% to 62.2%.

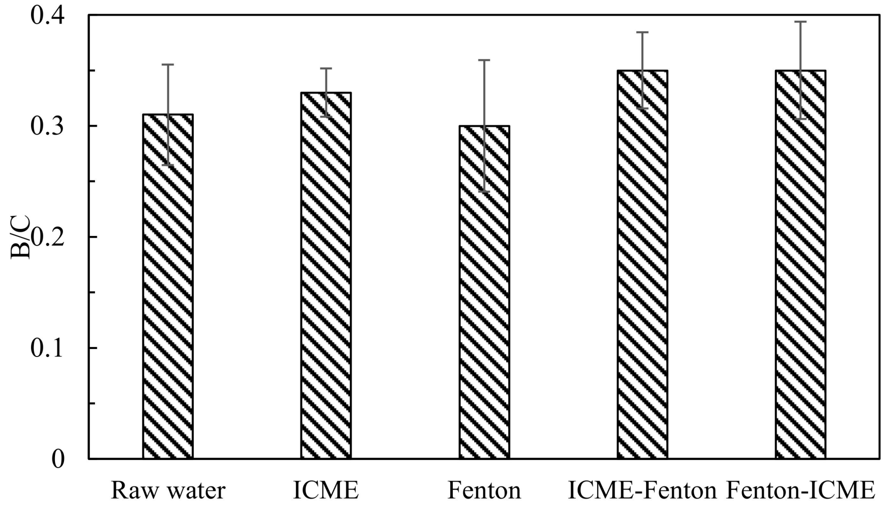


(**a**) COD removal

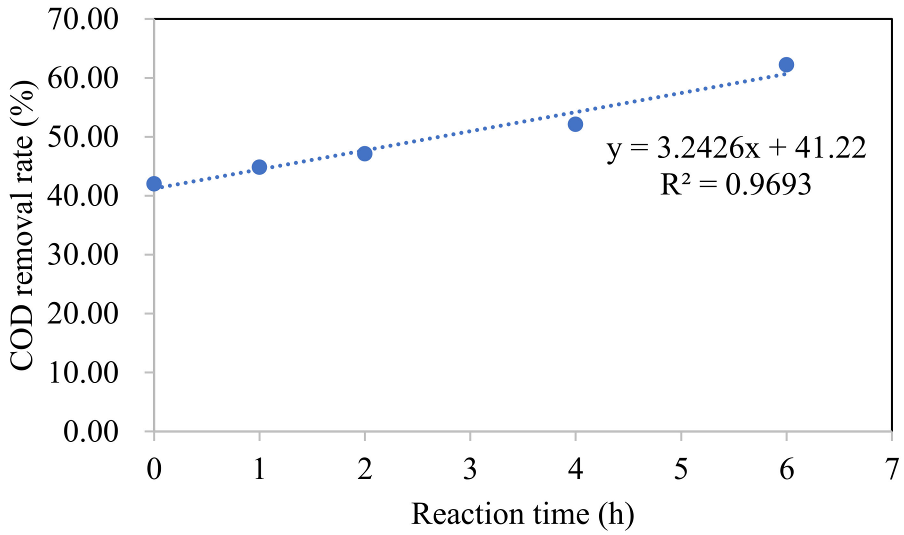


(**b**) Effluent color

Figure 5. *Cont.*



(**c**) B/C ratio



(**d**) the correlation coefficient of COD removal

Figure 5. The performance comparison of different process: (**a**) COD removal, (**b**) effluent color, (**c**) B/C ratio, (**d**) the correlation coefficient of COD removal.

It can be seen from Figure 5b that the original leachate was dark black, turned into brown after the Fenton treatment, turned yellow after the ICME-Fenton treatment, and turned light yellow after the Fenton-ICME treatment. From the apparent results, Fenton-ICME has the best treatment effect.

From Figure 5c, it can be observed that the single Fenton oxidation process did not improve the B/C ratio, which was 0.31 and 0.30 before and after the treatment, respectively. Meanwhile, the ICME-Fenton process and the Fenton-ICME process both increased the BOD/COD value of the effluent from 0.31 to 0.35.

In summary, the Fenton-ICME combined process is more suitable for treating the leachate obtained from the dewatering of thermally treated sludge. Compared with the single ICME process, the Fenton-ICME combined process increased the COD removal efficiency from 38.8% to 62.2%, and the B/C ratio was increased from 0.31 to 0.35. This suggests that the leachate has a better biodegradability after being treated with the Fenton-ICME combined process.

To further investigate the dependence of COD removal on time, as mentioned before, samples were taken during 8 h of study. It was found that the removal was gradually increased till 6 h, after which it saw almost no change (Figure 4c). This suggests that 6 h reaction time is sufficient for COD removal, and further increases of the reaction time will not bring higher removal but only consume more energy. From the analysis of the COD removal rate during the 6 h treatment, it can be seen that the linear correlation coefficient was around 0.97 (Figure 5d). This reveals that the reaction time has a great impact on the COD removal and should be considered in similar studies.

According to the treatment capacity and leachate production rate, by calculating the COD impact on the raw wastewater COD after the leachate being sent back to the influent of the wastewater treatment plant, the COD would remain lower than 32 mg/L based on the current COD removal efficiency of the plant, which is lower than the regulation (50 mg/L).

3.2. The Characteristics of the Leachate after Fenton-ICME Treatment

3.2.1. Organic Matter in the Leachate before and after Treatment

In order to explore the changes in the organic matter composition after the treatment of the leachate with the Fenton-ICME process, GC-MS was used, the NIST11.L standard library was used to retrieve and compare the characteristic ions, and the relevant data with a matching degree of more than 90% were selected, as shown in Table 2.

Table 2. GC-MS analysis of the leachate before and after being treated with the Fenton-ICME process.

Peak Number	Substance	Before		After	
		Time (min)	Peak Area	Time (min)	Peak Area
1	Heptane, 2, 4-dimethyl-	—	—	4.929	97,431
2	Octane, 4-methyl-	—	—	5.616	26,169
3	Pyrazine, 2, 5-dimethyl-	6.320	306,193	—	—
4	1H-Pyrrole-2-carboxaldehyde	7.659	162,964	—	—
5	Decane, 4-methyl-	7.830	264,951	7.830	69,510
6	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	7.899	224,655	—	—
7	p-Cresol	8.437	671,385	—	—
8	Benzene, 1-methyl-3-(1-methylethyl)-	8.614	138,834	—	—
9	Phenol, 2-methoxy-	8.654	453,017	—	—
10	Benzene, 1, 2, 3, 5-tetramethyl-	9.015	348,810	9.020	43,653
11	Phenol, 4-ethyl-	9.450	1,054,345	—	—
12	Undecane, 2, 6-dimethyl-	—	—	9.947	62,421
13	Dodecane, 4-methyl-	10.028	189,918	—	—
14	Dodecane, 4, 6-dimethyl-	10.354	174,253	—	—
15	Odecane, 2, 6, 10-trimethyl-	—	—	10.817	40,755
16	Phenol, 2, 6-dimethoxy-	11.309	542,295	—	—
17	Decane, 3, 8-dimethyl-	13.735	158,398	—	—
18	Sulfurous acid, butyl heptadecylster	—	—	13.821	37,787
19	Heneicosane, 11-(1-ethylpropyl)-	14.880	166,580	—	—
20	Heptadecane, 2, 6, 10, 15-tetramethyl-	—	—	16.819	186,213
21	9-Octadecenamide, (Z)-	18.399	310,423	—	—
22	Phenol, 2, 2′-methylenebis[6-(1, 1-dimethylethyl)-4-methyl-	18.776	207,837	18.776	144,798

According to the data in Table 2, it can be seen that the type of organic matter in the leachate changed greatly after treatment with the Fenton-ICME process. A total of 16 organic compounds with a matching degree greater than 90% were detected in the leachate before treatment, including long-chain alkanes such as Heneicosane and aromatic compounds such as Pheno, 2,6-dimethoxy-, Benzene, and 1-methyl-3-(1-methylethyl)-. A total of nine kinds of organic matters with a matching degree greater than 90%, mainly including alkanes such as Heptadecane, 2,6,10,15-tetramethyl- and complex esters such as sulfurous acid and butyl heptadecylster, were found in the leachate after being treated with Fenton-ICME.

In addition, comparing the same pollutants contained in the leachate before and after treatment, it can be seen that the peak area of the effluent was greatly reduced. This suggests that the organic matter content in the leachate was significantly reduced after the treatment with Fenton-ICME. Moreover, it was found that some new small molecular organic matters were also produced, such as decane. Comparing the types of organic matter in the leachate before and after treatment, it can be seen that the types of organic matter decreased after treatment. This indicates that Fenton-ICME could remove some complex organic matter. Fenton-ICME could be used to remove organic matter in the leachate, which has a certain effect on reducing the content and type of organic matter.

3.2.2. FTIR Analysis

The leachates, before and after being treated with Fenton-ICME, were scanned with FTIR. As shown in Figure 6, a large peak was observed at a wavenumber of about 3195 cm^{-1} for the original leachate, which was mainly attributed to the stretching vibration of C–H in aromatics. A weak vibration peak was observed at a wavenumber of 2968 cm^{-1}, which was related to the stretching of CH_2 and CH_3 groups [17], indicating the presence of long-chain aliphatic hydrocarbons in the stock solution. The peak at about 1660 cm^{-1} is mainly attributed to the stretching vibration of C=C [18], the peak at about 1402 cm^{-1} is mainly attributed to –COOH [19], the peak at about 1112 cm^{-1} is mainly attributed to the stretching vibration of C=O [20], and the peak at about 618 cm^{-1} is mainly attributed to the stretching of N–H and O–N=O [17] and may also be related to Fe–O [21]. This reveals that the main organic compounds in the filtrate are long-chain aliphatic hydrocarbons, aromatic compounds, ketones, and amides. It can be seen that the FTIR spectral analysis results of the original leachate are essentially consistent with the results of GC-MS (as shown in Table 2).

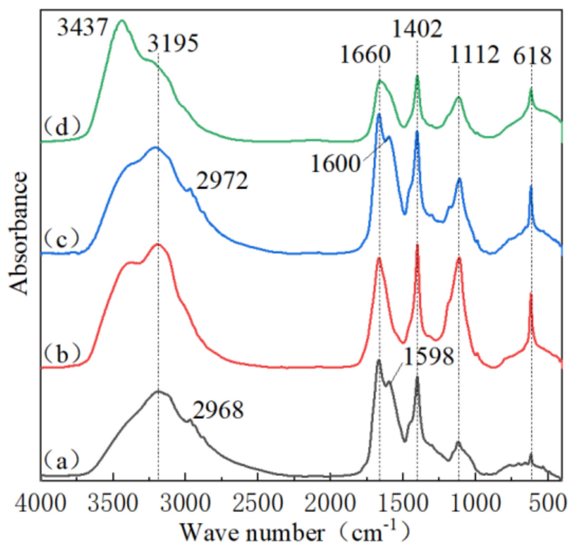


Figure 6. FTIR spectra of filtrate and effluent: (**a**) original leachate; (**b**) Fenton-treated; (**c**) ICME-treated; (**d**) Fenton-ICME-treated.

The (b) line in Figure 6 shows the FTIR spectrum of the leachate after the single Fenton treatment. All the peaks are similar to those of the original leachate, except for the peak with a wave number of 1660 cm^{-1}. The peak intensity of other peaks increased, which means that the Fenton oxidation may convert part of the C=C into a saturated bond. The (c) line of Figure 6 shows the FTIR spectrum of the leachate treated with the single ICME treatment. All the peaks were the same as the original leachate, and the peak intensity of the related peaks increased, which means that the ICME process did not have the effect of directly degrading organic matter.

The (d) line of Figure 6 is the FTIR spectrum of the leachate treated with the Fenton-ICME treatment. The broad peak at 3437 cm^{-1} corresponds to the O–H bond, which is mainly attributed to the adsorption of water on the sample surface [22]. The peak at 3195 cm^{-1} disappeared, indicating that the Fenton-ICME process could decompose or convert most of the aromatic compounds. Comparing (a), (b), (c), and (d), it can be seen that the peak intensity of the related peaks in the (d) line decreased significantly. This indicates that the Fenton-ICME process can remove more organic pollutants.

3.2.3. The 3D-EEM Analysis

The three-dimensional fluorescence spectra of the original leachate, Fenton-treated leachate, ICME-treated leachate, and Fenton-ICME-treated leachate are given in Figure 7.

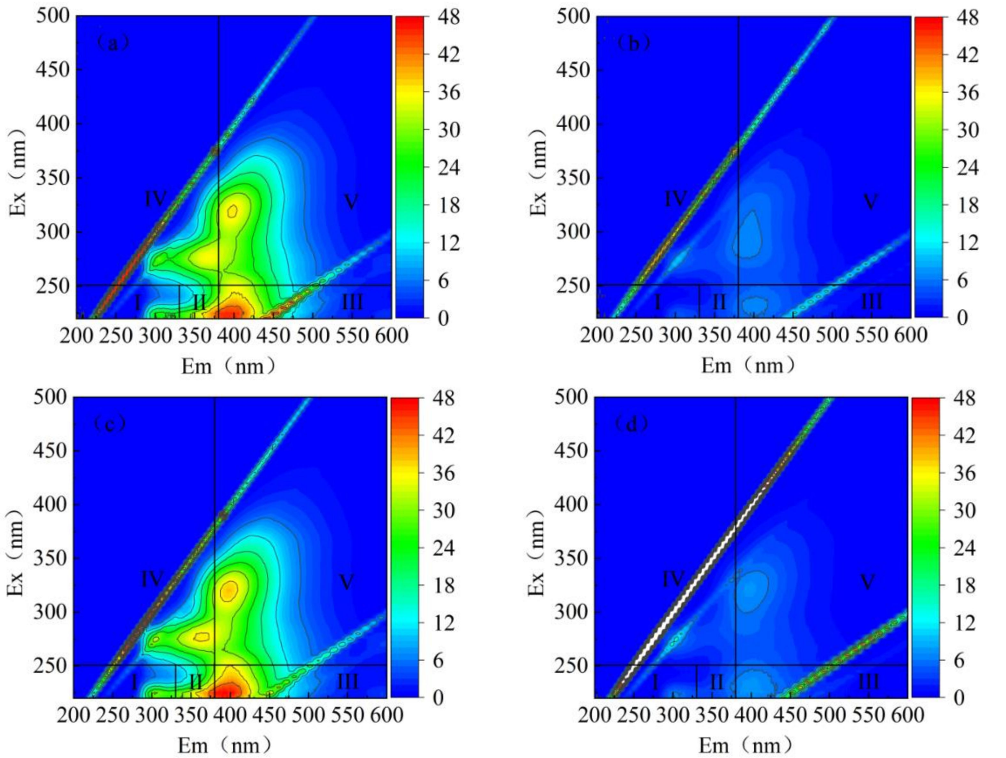


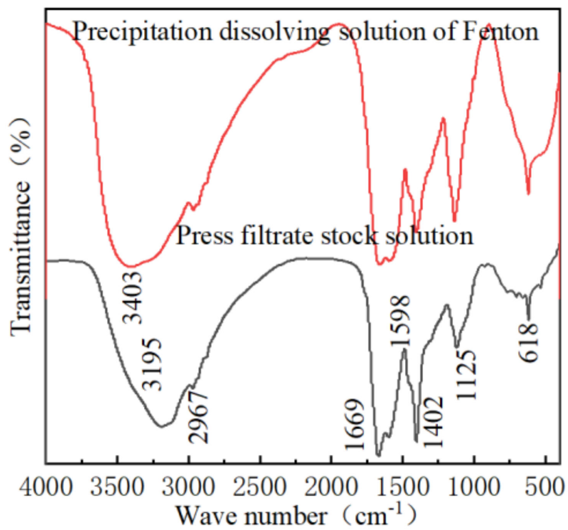
Figure 7. Three-dimensional fluorescence images of the leachates: (**a**) original leachate, (**b**) treated with Fenton oxidation, (**c**) treated with ICME, (**d**) treated with the Fenton-ICME process.

The 3D-EEM provides the category of the compounds in the sample, as each excitation wavelength corresponds to a specific emission wavelength. Among them, zone I and zone II mainly refer to aromatic protein substances, zone III mainly refers to fulvic acid substances, zone IV mainly refers to soluble microbial products, and zone V mainly refers to humic acid substances [23]. It can be seen from Figure 7a that the substances with relatively high concentrations in the filtrate are fulvic acids, followed by humic acids and soluble microbial products, while the content of aromatic proteins is lower. Comparing Figure 7a,c, it can be seen that the three-dimensional fluorescence image of the leachate treated with the ICME process was similar to that of the original leachate, indicating that the treatment performance of the single ICME process is not good. By comparing Figure 7b,d, it can be seen that the single Fenton process and the Fenton-ICME process can remove most of the various substances, and that the Fenton process plays a significant role in organic matter removal [24].

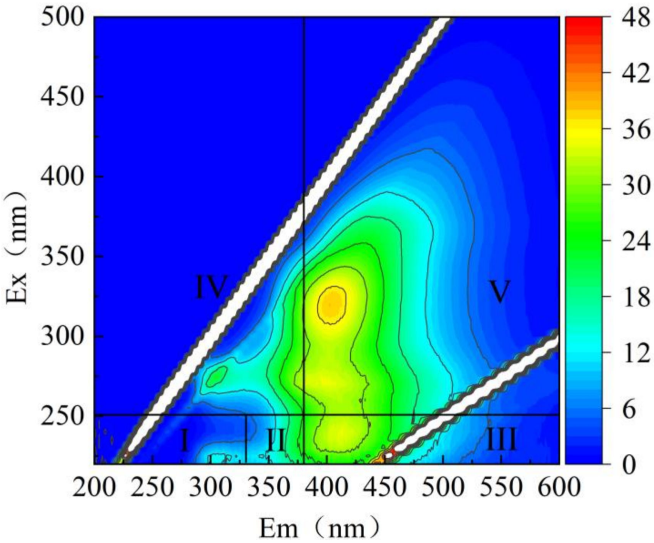
3.3. Characteristics of Fenton Precipitation Solution

In order to explore the characteristics of the Fenton precipitation, a small amount of NaOH solution was added to the Fenton precipitation to dissolve it into a liquid, which was called Fenton precipitation solution. The Fenton precipitation solution was dark black-brown with an extremely pungent smell, strong in viscosity, and the COD concentration was about 36,000 mg/L.

The Fenton precipitation solution was scanned with Fourier transform infrared spectroscopy, and the spectra are shown in Figure 8a. It can be seen that the peak with a wave number of 3403 cm^{-1} in the dissolved solution of the Fenton precipitation could be attributed to the stretching of O–H. Compared with the original leachate, except for the peak with wave number of 3195 cm^{-1}, which disappeared, the other peaks were not significantly different. It can be considered that the composition of the Fenton precipitation solution and the original leachate is highly similar, and special attention should be paid to pH control in practical engineering applications. Three-dimensional fluorescence scanning was performed on the Fenton precipitation solution, and the spectrum is shown in Figure 8b.



(**a**)



(**b**)

Figure 8. Fenton precipitate solution: (**a**) FTIR diagram, (**b**) three-dimensional fluorescence.

It can be seen that the main substances contained in the Fenton precipitation are humic acids, followed by fulvic acids, and there are fewer aromatic proteins and soluble microbial products (Figure 8b). Comparing Figures 7a and 8b, it was found that the content of fulvic acids in the III region was significantly reduced. It was speculated that the Fenton process converted some fulvic acids into humic acids, and this portion of humic acids entered the precipitate, thereby removing pollutants [25].

4. Conclusions

In this study, ICME and Fenton oxidation were employed to treat the leachate obtained from the dewatering of thermally treated wastewater sludge. After comparation, it was found that Fenton-ICME was the most efficient technology for the leachate treatment compared to single ICME, Fenton oxidation, and ICME-Fenton. The optimal treatment condition was as follows: the reaction pH is 4.0, the H_2O_2 dosage is 0.20 mol/L, the H_2O_2 and Fe^{2+} dosage ratio is 4:1 and the reaction time is 15 min for the Fenton step, and the reaction pH is 3.5, the iron–carbon dosage is 900 g/L, and the reaction time is 6 h in the following ICME step. The COD removal was mainly due to the removal of aromatic compounds, ketones, and aldehydes from the leachate. The study has proposed a reliable method for treating the leachate obtained from the dewatering of thermally treated wastewater sludge. It can prevent the effluent COD from exceeding regulations when the leachate is sent to mix with raw wastewater and treated in the treatment plant.

Author Contributions: Conceptualization, J.L. and X.Z.; methodology, X.D. and H.L.; software, Q.L.; validation, H.L., R.G. and Q.L.; formal analysis, H.L. and R.G.; investigation, H.L.; resources, J.L.; data curation, Q.L.; writing—original draft preparation, X.D.; writing—review and editing, X.Z.; visualization, R.G.; supervision, J.L.; project administration, J.L. and X.Z.; funding acquisition, J.L. and X.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Shenzhen Science and Technology Innovation Commission grant number [GJHZ20220913143007014, JCYJ20200109113006046 and KCXFZ20211020163404006].

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to the project contact requirement.

Acknowledgments: Sincere thanks to Shenzhen Science and Technology Innovation Commission for the support.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Okan, B.; Aksoy, A.; Erguder, T.H. Model-based comparison of biological wastewater and sludge treatment combinations for nutrient removal, sludge and biogas production. *J. Water Process Eng.* **2023**, *55*, 104198. [CrossRef]
2. Bonu, R.; Anand, N.; Palani, S.G. Impact of thermal pre-treatment on anaerobic co-digestion of sewage sludge and landfill leachate. *Mater. Today Proc.* **2023**, *72 Pt 1*, 99–103. [CrossRef]
3. Zanona, V.R.C.M.; Barquilha, C.E.R.; Braga, M.C.B. Removal of recalcitrant organic matter of landfill leachate by adsorption onto biochar from sewage sludge: A quali-quantitative analysis. *J. Environ. Manag.* **2023**, *344*, 118387. [CrossRef] [PubMed]
4. Skrzypczak, D.; Lale, D.; Mikula, K.; Izydorczyk, G.; Połomska, X.; Matejko, M.; Moustakas, K.; Witek-Krowiak, A.; Chojnacka, K. Maximizing the potential of leachate from sewage sludge as a sustainable nutrients source to alleviate the fertilizer crisis. *J. Environ. Manag.* **2023**, *338*, 117794. [CrossRef]
5. Kanmani, S.; Bharathi Dileepan, A.G. Treatment of landfill leachate using photocatalytic based advanced oxidation process—A critical review. *J. Environ. Manag.* **2023**, *345*, 118794. [CrossRef] [PubMed]
6. Faggiano, A.; De Carluccio, M.; Cerrato, F.; Junior, C.A.G.; Proto, A.; Fiorentino, A.; Rizzo, L. Improving organic matter and nutrients removal and minimizing sludge production in landfill leachate pre-treatment by Fenton process through a comprehensive response surface methodology approach. *J. Environ. Manag.* **2023**, *340*, 117950. [CrossRef] [PubMed]
7. Xu, X.; Zhong, Y.; Shao, Z. Double Perovskites in Catalysis, Electrocatalysis, and Photo(electro)catalysis. *Trends Chem.* **2019**, *1*, 410–424. [CrossRef]
8. Ilmasari, D.; Yuniarto, A.; Khen, C.; Purba, L.D.A.; Lei, Z.; Yuzir, A. Microalgal-bacterial aerobic granular sludge for old leachate treatment: Development, performance, and lipid production. *J. Clean. Prod.* **2023**, *417*, 138053. [CrossRef]
9. Yang, X. Interior Microelectrolysis oxidation of polyester wastewater and its treatment technology. *J. Hazard. Mater.* **2009**, *169*, 480–485. [CrossRef]

10. Chen, X.; Liang, S.; Tao, S.; Yu, W.; Yuan, S.; Jian, S.; Wan, N.; Zhu, Y.; Bian, S.; Liu, Y.; et al. Sludge-derived iron-carbon material enhancing the removal of refractory organics in landfill leachate: Characteristics optimization, removal mechanism, and molecular-level investigation. *Sci. Total Environ.* **2023**, *904*, 166883. [CrossRef] [PubMed]
11. Han, Y.; Xu, H.; Zhang, L.; Ma, X.; Man, Y.; Su, Z.; Wang, J. An internal circulation iron–carbon micro–electrolysis reactor for aniline wastewater treatment: Parameter optimization, degradation pathways and mechanism. *Chin. J. Chem. Eng.* **2023**, *63*, 96–107. [CrossRef]
12. Hu, M.; Luo, T.; Li, Q.; Xie, Y.; Liu, G.; Wang, L.; Peijnenburg, W.J.G.M. Remediation of low C/N wastewater by iron–carbon micro-electrolysis coupled with biological denitrification: Performance, mechanisms, and application. *J. Water Process Eng.* **2022**, *48*, 102899. [CrossRef]
13. Li, S.; Yang, Y.; Zheng, H.; Zheng, Y.; Jing, T.; Ma, J.; Nan, J.; Leong, Y.K.; Chang, J.-S. Advanced oxidation process based on hydroxyl and sulfate radicals to degrade refractory organic pollutants in landfill leachate. *Chemosphere* **2022**, *297*, 134214. [CrossRef] [PubMed]
14. Yao, Q.-S.; Huang, C.; Wang, M.-K. Treatment of Water Hyacinth Anaerobic Fermentation Wastewater by Combining Fe-C Micro-Electrolysis with Fenton Reaction. *J. Environ. Chem. Eng.* **2020**, *8*, 104157. [CrossRef]
15. Wang, Y.; Wu, X.; Yi, J. Pretreatment of printing and dyeing wastewater by Fe/C Micro-Electrolysis combined with H2O2 Process. *Water Sci. Technol.* **2018**, *2017*, 707–717. [CrossRef] [PubMed]
16. Thamdrup, B. Bacterial manganese and iron reduction in aquatic sediments. In *Advances in Microbial Ecology*; Schink, B., Ed.; Kluwer Academic/Plenum Publishers: New York, NY, USA, 2000; Volume 16, pp. 41–84.
17. Lai, B.; Zhou, Y.; Qin, H. Pretreatment of wastewater from acrylonitrile-butadiene-styrene (ABS) resin manufacturing by micro-electrolysis. *Chem. Eng. J.* **2012**, *179*, 1–7. [CrossRef]
18. El Farissi, H.; Talhaoui, A.; Bachiri, A.E.L. Cistus shells used as a sustainable matrix for bioenergy production through slow pyrolysis process: Kinetic and thermodynamic study. *Renew. Energy* **2023**, *218*, 119337. [CrossRef]
19. Tang, M.; Wang, L.; Li, H. Promoting effect of FeOx addition on the mechanochemically prepared vanadium-based catalyst for real PCDD/FS removal and mechanism insight. *J. Environ. Sci.* **2022**, *137*, 478–487. [CrossRef]
20. El Farissi, H.; Beraich, A.; Lamsayah, M.; Talhaoui, A.; El Bachiri, A. The efficiency of carbon modified by phosphoric acid (H_3PO_4) used in the removal of two antibiotics amoxicillin and metronidazole from polluted water: Experimental and theoretical investigation. *J. Mol. Liq.* **2023**, *391*, 123237. [CrossRef]
21. Yuan, L.; Shen, J.; Chen, Z. Role of Fe/Pumice composition and structure in promoting ozonation reactions. *Appl. Catal. B Environ.* **2016**, *180*, 707–714. [CrossRef]
22. Liu, H.; Sha, W.; Cooper, A.T. Preparation and characterization of a novel silica aerogel as adsorbent for toxic organic compounds. *Colloids Surf. A Physicochem. Eng. Asp.* **2009**, *347*, 38–44. [CrossRef]
23. Chen, W.; Westerhoff, P.; Leenheer, J.A.; Booksh, K. Fluorescence Excitation−Emission Matrix Regional Integration to Quantify Spectra for Dissolved Organic Matter. *Environ. Sci. Technol.* **2003**, *37*, 5701–5710. [CrossRef] [PubMed]
24. Ghernaout, D.; Elboughdiri, N.; Ghareba, S. Fenton technology for wastewater treatment: Dares and Trends. *Open Access Libr. J.* **2020**, *7*, 1–26. [CrossRef]
25. Dong, Q.F.; Jin, H.L.; Sen, G. Biochar enhanced the degra- dation of organic pollutants through a Fenton process using trace aqueous Iron. *J. Environ. Chem. Eng.* **2020**, *9*, 104677.