

# Degradation of Oil Pollution in Seawater by Bipolar Electro-Fenton Process

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## Abstract

The fast development of oil products leads to growing waste emissions and oil spill accidents. Oil dissolved in water causes many immediate and potentially chronic adverse effects on marine habitats and coastal ecosystems. Electro-Fenton technology possesses many significant advantages for treatment of refractory material from water. The possibility of using in situ electrochemical reaction of the bipolar electro-Fenton process for solving oil pollution problems in seawater is investigated. The study shows that the bipolar electro-Fenton technology is feasible for treatment of oily seawater. In the process of the bipolar electro-Fenton, operating current density and pH have effects on the removal efficiency of oil pollution from seawater. Higher current density is favorable for removal of oil pollution, and the optimum pH was 2.5-3.5. Under the optimum pH value of 3.5 and current density of 25 mA/m<sup>2</sup>, the oil and COD concentration decreased about 90-95%. By process of the bipolar electro-Fenton, most of the components of oil were degraded to smaller molecular compounds. In addition to indirect oxidation, electro flocculation and adsorption is inevitable for the removal of pollutants when using bipolar electro-Fenton.

**Keywords:** bipolar electro-Fenton, oil pollution, advanced oxidation process, electro flocculation, adsorption

## Introduction

With mass exploitation and the use and transportation of petroleum products, more and more waste emissions and oil spill accidents occur [1-4]. According to statistics, the current annual production of crude oil is 86 million barrels per day [5], and approximately 50% of the oil being transported by sea [6]. The estimated average amount of oil entering into marine environment from ships and other sea-based activities is about 1,245,200 tons per year [7]. Crude oil is a mixture of many different types of hydrocarbons, such as aliphatic and aromatic compounds, and many of the constituents with acute or long-term toxic effects and, as such, represent a threat to exposed wetland and estuarine

ecosystems [5]. The short-term and long-term impacts of oil pollution are significant [8]. Due to the immediate and potential chronic adverse effects inflicted on marine habitats and coastal ecosystems, pollution of accidental oil spills and emissions has become a global concern [9]. The solubility of oil in water is very low, so treatment for oil accidents usually focuses on floating oil and less for dissolved oil. But oil dissolved in water has reverse impacts. Attention to treatment for dissolved oil should not be ignored.

In recent years, the electro-Fenton technique has been studied for organic pollutant destruction in water extensively, and has achieved preferable development [10-13]. Electro-Fenton mainly relies on *in situ* and catalytic electro generation of Fenton's reagent – a mixture of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and ferrous iron (Fe<sup>2+</sup>) – to produce hydroxyl

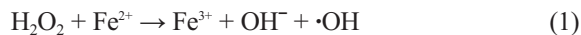
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Table 1. Characteristics of oily water.

Oil concentration (mg/L)	COD concentration (mg/L)	Conductivity (ms/cm)	pH	Cl <sup>-</sup> concentration (mg/L)
18.35-26.38	764-1272	50.1	7.6	12045

radicals ( $\cdot\text{OH}$ ) and react with organic pollutants in water, finally leading to their destruction (as formulas 1-4).



In this work, oil pollution dissolved in seawater was treated by a bipolar electro-Fenton process. Through systematic analysis, the feasibility of the technology has been discussed, and at the same time the destruction of oil compositions and the mechanism of pollutant removal have been discussed.

### Materials and Methods

Electrolysis was performed in batch mode in an undivided glass cell under vigorous stirring performed by a magnetic stirrer with 1,000 mL of solution. The anode used was a 10 cm×8 cm×0.5 cm sheet iron, and cathode was 10 cm×8 cm activated carbon fiber, and the distance between the anode and cathode was 5 cm. Compressed air was fed to the cathode by an air pump with 250 mL/min for 5 min before the power was on and was maintained during the process of electrolysis. The oily seawater was simulated water with diesel dissolved in seawater under ultrasound for 4 h, and the characteristics of oily water were seen in Table 1.

The experiments were performed at room temperature, and pH of water was adjusted by the addition of solution of 0.1 mol/L sulfuric acid and sodium hydroxide.

The oil concentration in water was measured with an infrared oil-measuring instrument. 20 mL sample water was extracted with 5 mL  $\text{CCl}_4$ . The resulting organic phases were decanted, and were then dehydrated by  $\text{Na}_2\text{SO}_4$ . The collected organic solution was analyzed using IR. The wave numbers used were mainly 2,930  $\text{cm}^{-1}$ , 2,960  $\text{cm}^{-1}$ , and 3,030  $\text{cm}^{-1}$ . Chemical oxygen demand (COD) was evaluated using Merck Cell tests. The destruction and change of chemical compositions of oil under the study were followed by GC-MS analysis.

The removal efficiency for oil or COD was calculated as follows:

$$R = \frac{C_0 - C}{C_0} \times 100\%$$

...where  $C_0$  and  $C$  are initial concentration and final concentration of oil and COD.

## Results and Discussion

### Effect of Current Density on the Degradation of Oil

As shown in Fig. 1, oil degradation depends on the current density. When the current density increased from 5  $\text{mA}/\text{m}^2$  to 25  $\text{mA}/\text{m}^2$ , the degradation rate of oil increased, and at 120 minutes the removal efficiency increased from 72.3% to 93.1%. That is to say that high applied current is favorable for oil degradation. But on the other hand, high current would increase the cost of energy. In later experiments the current density was stabilized at 20  $\text{mA}/\text{m}^2$ .

### Effect of pH on Removal Efficiency for Oil Pollution

pH has an effect on treatment efficiency of the electro-Fenton process. In this study, pH was adjusted to 2.5, 3.5, 4, 5, 6, and 7 beforehand to study the effect of pH on removal efficiency for oil pollution. The electrolysis time was 120 minutes. Operating current density was 20  $\text{mA}/\text{cm}^2$ .

### Effect of pH on Oil Removal

Fig. 2 shows the removal efficiency for oil at different pH values. It could be seen that pH had some effect on the removal efficiency for oil. The removal efficiency for oil decreased with increased pH value. When pH was 2.5, oil concentration decreased from 22.391 mg/L to 1.699 mg/L

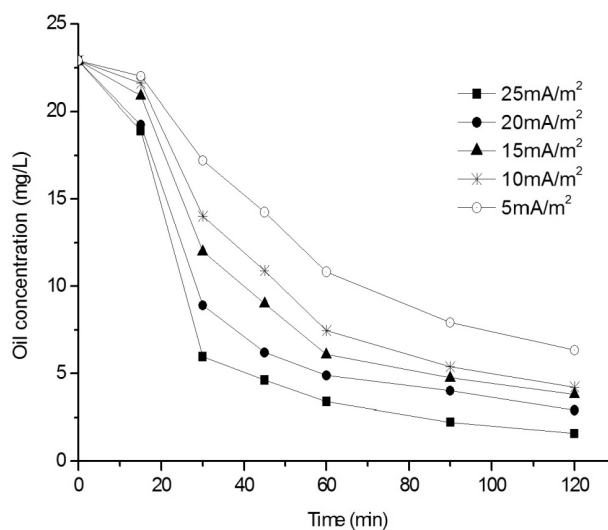


Fig. 1. Effect of current density on oil degradation.

in 120 minutes, and removal efficiency was 92.4%. When pH increased to 6.0 and 7.0, oil concentration decreased from 22.391 mg/L to 3.212 mg/L and 3.254 mg/L in 120 minutes, and removal efficiency was 85.7%, 85.5, respectively. It could be seen that though removal efficiency decreased with the increase of pH, the removal efficiency for oil at high pH was still very high. Traditionally, the electro-Fenton process was conducted under low pH as 2-4 to ensure the production of hydroxyl radicals. But with the development of electro-Fenton technology, some researchers found that in the process of electro-Fenton, the pollutants were not only removed by oxidation of radicals, but by other factors such as electro-flocculation and adsorption, and so on. In this experiment, a sheet of iron was used as an anode, and some Fe<sup>2+</sup> and Fe<sup>3+</sup> may have hydrolyzed and taken flocculation and adsorption at high pH, so the removal efficiency for oil at high pH was reduced little.

From oil removal efficiency at the end of 30 and 120 minutes of electrolysis in Fig. 3, it could be concluded that the optimum pH value in this experiment was 2.5-3.5.

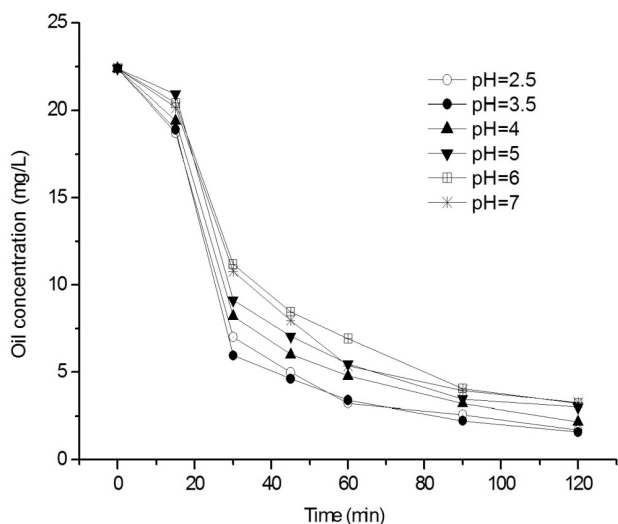


Fig. 2. Effect of pH on oil removal.

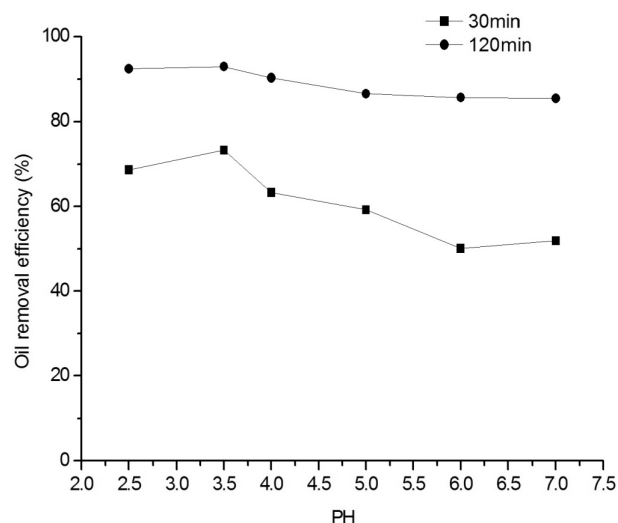


Fig. 3. Terminal concentration of oil at different pH.

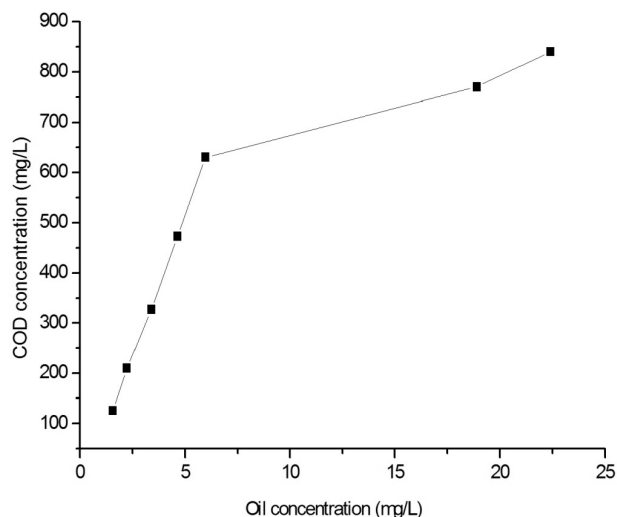


Fig. 4. Relation between oil and COD.

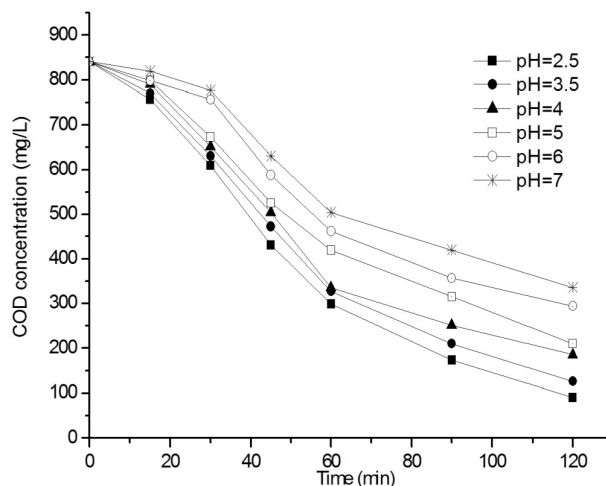


Fig. 5. Effect of pH on COD removal.

Studies have shown that the best pH value in Fenton's reaction was 2~4. Because iron ion would precipitate at high pH values, and at the same time, H<sub>2</sub>O<sub>2</sub> would be decomposed to H<sub>2</sub>O and O<sub>2</sub> and thus decreased the efficiency of Fenton's reaction [14-17].

### Effect of pH on COD Removal

In general, chemical oxygen demand (COD) was used to show the relative contents of organic matters in water. Oil was composed of organic compounds of hydrocarbons, so oil concentration would be correlated with that of COD. The correlation between COD and oil concentration was shown in Fig. 4. The graph shows that COD concentration decreased with the decrease of oil concentration in water, and COD has good correlation with oil concentration. Oil was composed of a variety of organic compounds, so COD could be used to show the relative contents of these matters.

COD removal results at different pH values in Fig. 5 show that, as the same as that of oil, the removal efficiency

for COD decreased with the increase of pH. When pH increased from 2.5 to 7.0, the removal efficiency for COD decreased from 89.2% to 60.0% at 120 minutes.

PH has an effect on removal efficiency for oil pollution from water in the process of the bipolar electro-Fenton, and the optimum pH value of the experiment is 2.5-3.5. Later, pH of water was stabilized at 3.5.

### Oil Pollution Removal Efficiency with Electrolysis Time

Oil was degraded by reagents of Fenton generated on electrodes along the electro-Fenton process. Fig. 6 presented oil removal efficiency versus time at pH value of 3.5. The graph shows that oil concentration decreased along with the process of the bipolar electro-Fenton. In the first, oil was degraded fast and the removal efficiency for oil reached up to 75% at 30 minutes. Then the degradation rate slowed down, and the removal efficiency increased to 90% at 120 minutes. The reason may be because at first, oil concentration in water was high, and the degradation rate was high, so the removal efficiency was high and reached 75%

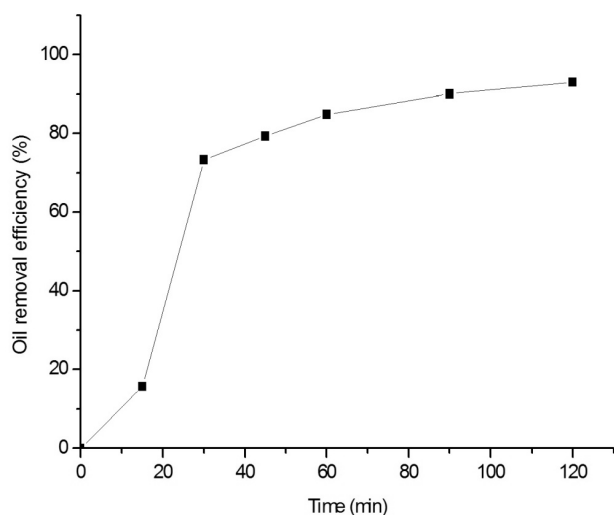


Fig. 6. Removal of oil at electro-Fenton process.

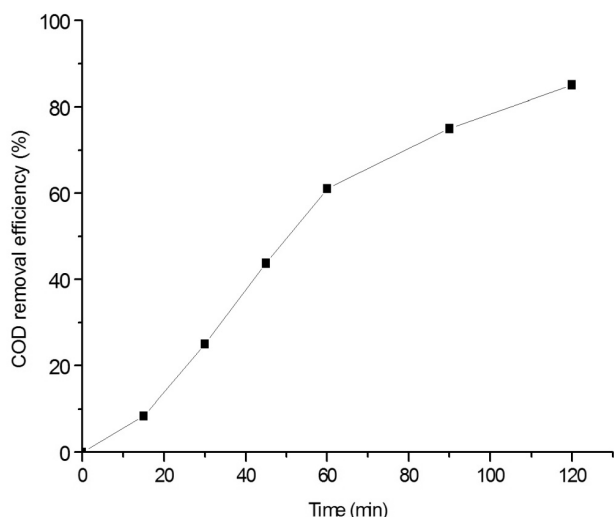


Fig. 7. Removal of COD at electro-Fenton process.

in 30 min. Then, with the decrease of oil concentration, the degradation rate slowed down and removal efficiency increased slowly.

### COD Removal Efficiency with Electrolysis Time

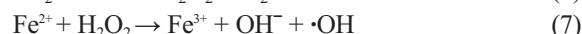
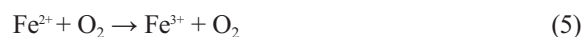
The removal efficiency for COD versus time in the bipolar electro-Fenton process was shown in Fig. 7.

It could be seen that the removal efficiency for COD versus time was the same as that for oil. At first, the removal rate for COD was fast, though removal efficiency was not very high. In the first 60 minutes, the removal efficiency for COD reached 50%. Then the removal rate slowed down and increased to 80% at 120 minutes.

From Figs. 6 and 7 it could be seen that, compared to oil, the removal rate for COD was slow in the first 30 minutes and slightly increased in the later 30 minutes. This may be due to the fact that oil was mainly composed of large molecular and complex compounds, and these complex compounds were difficult to be oxidized. With the process of the electro-Fenton, these complex compounds were degraded to simpler products and then further decomposed to simpler and lower molecules. In contrast, simpler intermediates were easier to be oxidized and decomposed by chemical oxidation, so compared to that of oil, the removal rate for COD was not very fast at the beginning and then increased and persisted over a long period of time.

### GC-MS Analysis Results

In the process of electro-Fenton,  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  generated on electrodes in situ and reacted with each other to produce  $\cdot\text{OH}$  (as Formulas 5-7) [18]. At the same time, with the process, pH of water increased, then some of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  would precipitate and form some flocs [19], and the flocs of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  would absorb some polluted matters along with the process of the electrolysis.



In the experiments, we found that some flocs formed during process of the electrolysis. Along with the electrolysis, the change of pH was studied and the results were shown in Fig. 8. It could be seen that, at first, pH value was low, so  $\text{Fe}^{2+}$  would react with  $\text{H}_2\text{O}_2$  to produce  $\cdot\text{OH}$  *in situ*. While along with the process, there would more and more  $\text{OH}^-$  be produced, and the pH value increased, then some of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  would hydrolyze step-by-step to produce flocs of more hydroxyl complex and then the flocculation and adsorption would play a role to some extent for pollutant removal. Some researchers have shown that flocculation has a preferential effect in removal of organic matters in Fenton's reaction, and Fenton's reaction is known as enhanced flocculation reaction [20].

From what has been discussed above, we know that in the process of the bipolar electro-Fenton, the oil pollutants could be removed to some extent. In the process of the

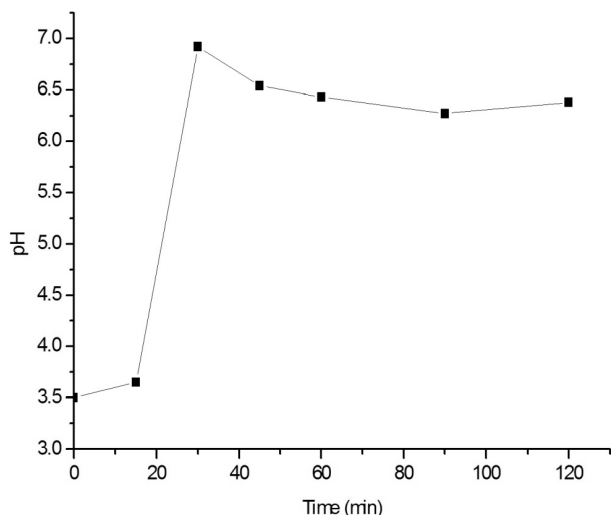


Fig. 8. The pH-varied scheme in electro-Fenton reaction with time (initial pH was 3.5).

bipolar electro-Fenton,  $Fe^{2+}$  reacts with  $H_2O_2$  to produce  $\bullet OH$ , and some are oxidized to  $Fe^{3+}$  and precipitate to form some flocs.

In order to identify the effect of flocculation and adsorption of the flocs, the degradation and change of oil chemical compositions were analyzed by GC-MS. 250 mL sample water was extracted three times with 15 mL  $CH_2Cl_2$ . The resulting organic phases were decanted, and were then dehydrated by  $Na_2SO_4$ . The collected organic solution was evaporated and the remaining solid was dissolved in 5 mL of methanol. Helium was used as the carrier gas. A temperature gradient was used in the separation. The temperature was maintained at  $50^\circ C$  for 2 min and then increased to  $300^\circ C$  at a rate of  $6^\circ C/min$ .

GC-MS analysis was done for three samples. Sample 1 was raw oily water, sample 2 was clarified water treated by the process of the bipolar electro-Fenton, and in which the flocs formed in the process had been removed through cen-

trifugal separation, and sample 3 was treated water that contained the flocs and the flocs had been dissolved into water with hydrochloric acid. Which means that in sample 2, the pollutants were removed by oxidation and flocculation and adsorption of flocs, while in sample 3 the pollutants were removed only by oxidation and did not think about the flocculation and adsorption of flocs. Through analysis of the three samples, the effect of oxidation and flocculation and adsorption of flocs could be identified.

In this experiment, the initial concentration of oil was 22.39 mg/L, pH of water was 3.5, and the operating current density was  $20\text{ mA/cm}^2$ . Reaction time of the electrolysis was 30 minutes.

Table 2 shows the change of chemical compositions of hydrocarbon components of oil, and the paraffin (PHs) results are shown in Fig. 9, while polycyclic aromatic hydrocarbon (PAHs) results are shown in Fig. 10.

From the results of PHs in Fig. 9 it could be seen that there were more than 20 peaks in sample 1, which showed that the PH components of oil were complex. For sample 2 the peak numbers and heights decreased significantly, which showed that the complex components of oil have been degraded in the process of electrolysis, and the PH components decreased not only in classes but in contents. For sample 3, the peak numbers and heights decreased compared to that in sample 1, but increased compared to that in sample 2. In sample 2, the water was treated water and the flocs were separated, meaning that the pollutants were removed by oxidation and flocculation and adsorption. While in sample 3, the water was treated, but the flocs were not separated but were dissolved into the water, and this means that the pollutants were removed only by oxidation, but not by flocculation and adsorption. The contrast results of the 3 samples show that the PH components were not only removed by oxidation, but some were removed by flocculation and adsorption of flocs formed in the electrolysis process.

The results of PAHs in Fig. 10 was the same as that of PHs in Fig. 9.

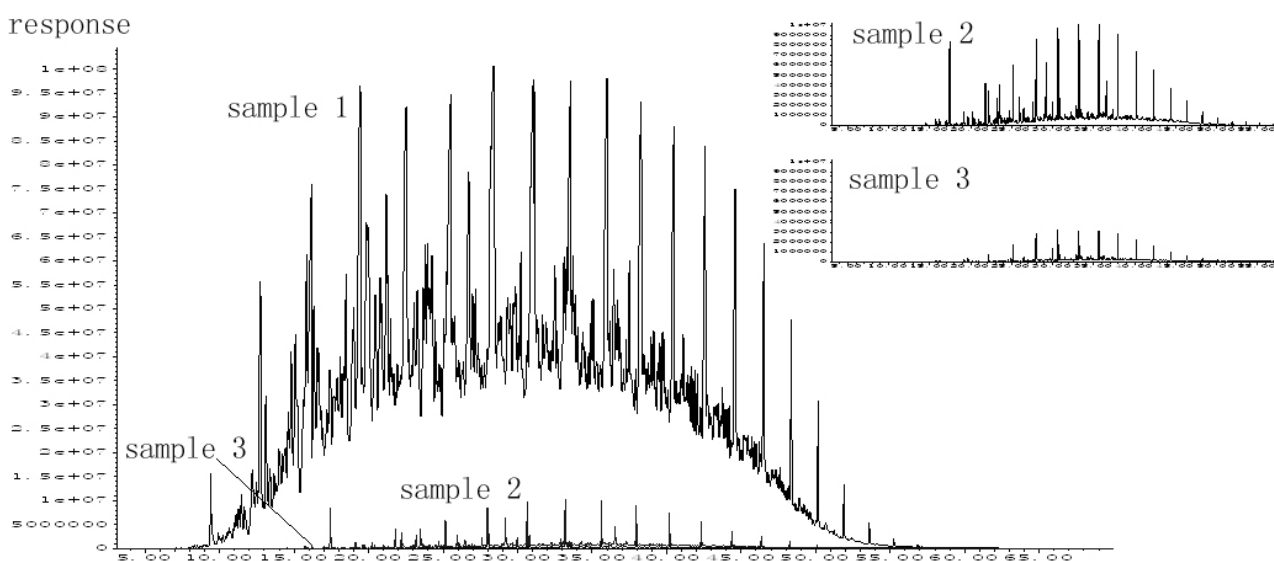


Fig. 9. The paraffin compound results treated by the bipolar electro-Fenton.

Table 2. The change of hydrocarbon components of the three samples.

Detected substances	Responses			Response time (Min)
	Sample 1	Sample 2	Sample 3	
Naphthalene	10,029.38	64.55	138.57	4.096
Diacenaphthene	2,075.78	60.39	69.88	7.187
Acenaphthene	3,376.63	139.59	388.68	7.754
Fluorene	9,437.46	316.86	426.96	9.205
Phenanthrene	30,432.27	1,166.57	1,507.71	12.137
Anthracene	31,037.09	119.32	172.95	12.295
Carbazole	3,585.04	481.24	480.28	12.926
Fluoranthene	2,009.70	87.55	125.28	17.498
Pyrene	9,038.01	151.43	261.94	18.602
Benzo [a] anthracene	1,664.18	107.56	195.60	23.080
Benzo [b] fluoranthene	120.08	78.54	91.01	27.431
Benzo [k] fluoranthene	95.24	55.72	67.59	27.431
Benzo [a] pyrene	104.41	66.65	72.10	28.503
Indeno [1,2,3-cd] pyrene	84.24	81.77	84.36	33.360
Dibenzo [a, h] anthracene	87.16	N.D.	83.12	33.580
Benzo [g, h, i] Perylene	74.45	N.D.	71.65	34.747
C14	3,513.03	473.30	2,268.86	19.107
C15	5,244.94	1,122.24	4,751.61	22.207
C16	25,452.24	2,449.16	8,419.66	25.151
C17	4,035.65	4,084.85	12,863.97	27.962
Pristane	3,280.60	3,486.67	11,134.54	27.962
C18	3,567.53	4,276.26	13,117.41	30.639
Phytane	2,262.69	1,274.13	4,059.96	30.783
C19	55,287.01	4,558.77	14,313.18	33.194
C20	15,262.94	4,379.81	13,661.47	35.627
C21	4,967.40	4,014.83	12,978.43	37.949
C22	3,358.18	3,378.05	10,764.23	40.182
C23	10,060.06	2,691.85	8,845.59	42.326
C24	1,492.51	2,012.33	6,173.87	44.371
C25	21,427.99	1,511.50	5,100.12	46.348
C26	125,577.73	1,109.97	3,552.25	48.259
C27	81,404.55	780.33	2,462.60	50.092
C28	32,397.43	543.34	1,871.30	51.870
C29	16,080.60	599.82	1,889.78	53.581
C30	8,319.08	556.43	1,787.72	55.236

These results show that in the process of the bipolar electro-Fenton, some of the organic components were decayed by chemical oxidation, but some were removed by flocculation and adsorption of the flocs generated in the process of electrolysis.

Composition analysis results in Table 2 showed that in sample 2, in addition to C17, C18, pristane, C22, C24, the content of all the rest of the components were reduced compared with that in sample 1, and some even were not checked out. This result expressed that the components of

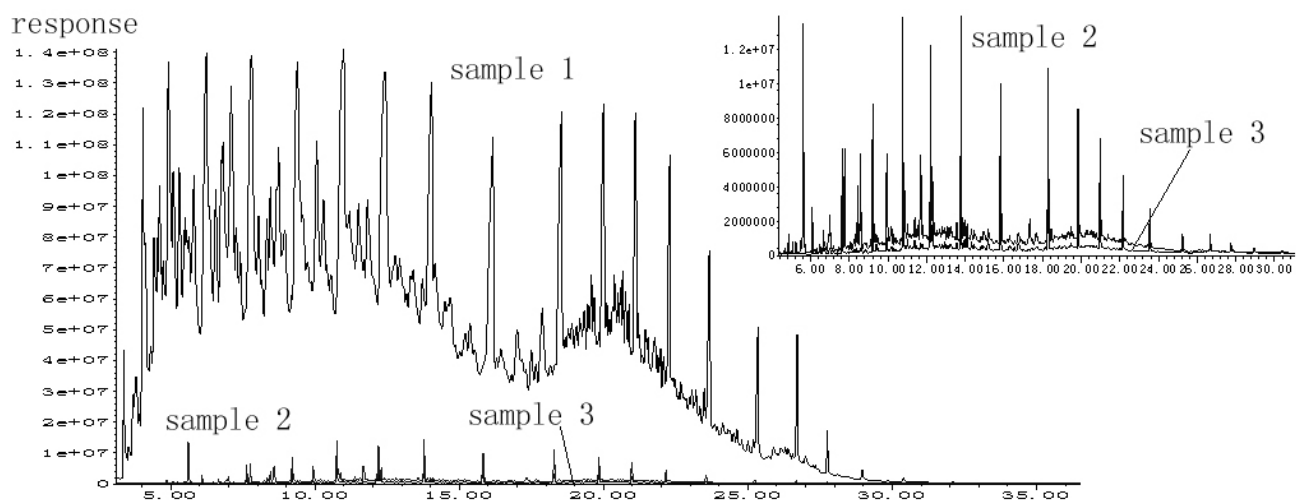


Fig. 10. The polynuclear aromatic compounds results treated by the bipolar electro-Fenton.

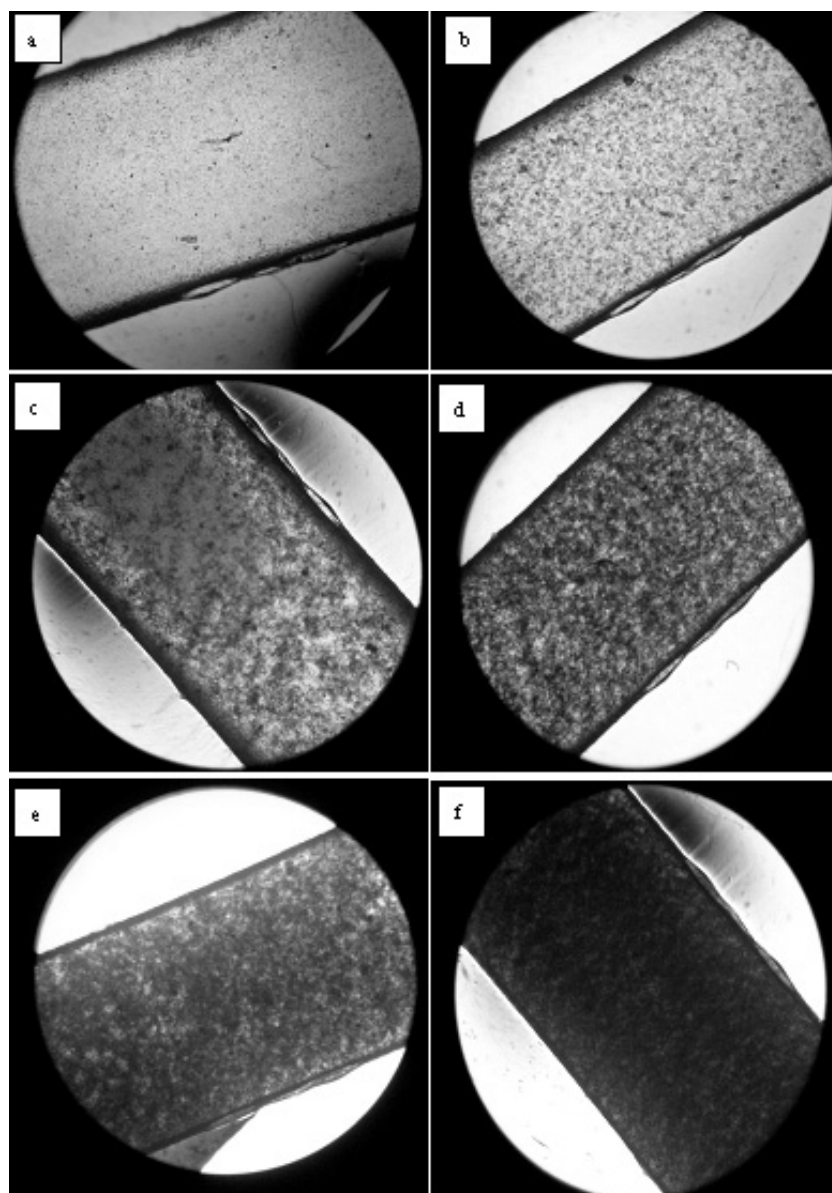


Fig. 11. Flocs formed in the process of the bipolar electro-Fenton: a – flocs formed at 15 minutes, b – flocs formed at 30 minutes, c – flocs formed at 45 minutes, d – flocs formed at 60 minutes, e – flocs formed at 90 minutes, f – flocs formed at 120 minutes.

oil were removed in great degree by electro-Fenton process oxidation. At the same time, it could be seen that in sample 3, as the same as that in sample 2, nearly all the components decreased compared to that in sample 1, while they slightly increased compared to that in sample 2. This showed that most of the organic matters were removed by oxidation in the process, but some were removed by flocculation and adsorption of flocs. By the way, it could be seen that, compared with that in sample 1, some polycyclic aromatic and macromolecular compounds such as naphthalene, anthracene, and phenanthrene in sample 2 decreased greatly. While most smaller molecules of hydrocarbons decreased gently, some of the small molecular compounds increased instead. This showed that by the process of the bipolar electro-Fenton, the polycyclic aromatic and macromolecular compounds of oil were degraded to smaller hydrocarbons and even to H<sub>2</sub>O and CO<sub>2</sub> by the advanced oxidation process.

The GC-MS analysis results showed that in the bipolar electro-Fenton process, the compounds of oil were removed not only by oxidation, but also by flocculation and adsorption of flocs formed during the process. From the results of pH changes during the process in Fig. 8, it could be known that the pH of water increased with the electrolysis process, and with the increase of pH some flocs formed. The flocs formed during the electro-Fenton process were studied and the results of 15, 30, 45, 60, 90, 120 minutes are shown in Fig. 11. It could be seen that at 15 minutes the flocs formed, and the flocs increased with the increase of electrolysis time. The flocs of Fe<sup>2+</sup> and Fe<sup>3+</sup> hydroxyl complexes have good flocculation and adsorption for pollutants from water, and used for pollutants removal in water treatment usually. The CC-MS analysis results have shown the effect of the flocs of Fe<sup>2+</sup> and Fe<sup>3+</sup> for oil pollution removal during the process of bipolar electro-Fenton.

### Conclusion

This work focused on the study of degradation of oil components with technology of bipolar electro-Fenton in seawater. The results show that:

The technology has a high effect on treatment for oil pollution in water. The removal efficiency for oil and COD could be up to 90-95% and 80-90%, respectively.

PH has an effect on the removal efficiency for oil pollution from water. The removal efficiency for oil increased with the decrease of pH, and the optimum pH value in the experiment was 2.5-3.5.

This technology affects component degradation of oil. In the process of the bipolar electro-Fenton, some polycyclic aromatic and macromolecular compounds of oil were degraded into smaller molecular hydrocarbons and even to final products of H<sub>2</sub>O and CO<sub>2</sub>.

In the process of the bipolar electro-Fenton, pH value of water increased, and some flocs generated in the process, and the flocs has some effect for oil pollution removal.

The oil pollution was removed not only by indirect oxidation, but also by flocculation and adsorption of flocs gen-

erated during the process. Oxidation was the main factor in removal for oil pollution.

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