

Study on COD removal mechanism and reaction kinetics of oilfield wastewater

Xian-Qing Yin, Bo Jing, Wen-Juan Chen, Jian Zhang, Qian Liu and Wu Chen

ABSTRACT

The chemical oxygen demand (COD) removal mechanism and reaction kinetics were mainly studied in the treatment of oilfield oily sewage containing polymer by three-dimensional electrode reactor. The results proved that the residual active oxides O_3 , H_2O_2 , $\bullet OH$ and active chlorine in the system of electrochemical reaction could be effectively detected, and the COD removal mechanism was co-oxidation of active oxides; Under these experimental conditions: the electrolysis current of 6 A, surface/volume ratio of $6/25(\text{cm}^2 \cdot \text{L}^{-1})$, the reaction time of 50 min, the COD_{cr} of treated sewage was no more than $50 \text{ mg} \cdot \text{L}^{-1}$; the removal reaction of COD conformed to apparent second-order reaction kinetic model, the correlation coefficient R^2 was 0.9728, and the apparent reaction rate constant was $k = 3.58 \times 10^{-4} (\text{L} \cdot \text{min}^{-1} \cdot \text{mg}^{-1} \cdot \text{m}^{-2})$. To reach the goal, the COD_{cr} was no more than $50 \text{ mg} \cdot \text{L}^{-1}$ in treated sewage, and the theory minimum processing time was 45.73 min. The verification of experimental results was consistent with kinetic equations.

Key words | mechanism, reaction kinetics, sewage containing polymer, three-dimensional electrode

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INTRODUCTION

Injecting polymer is the key to efficient exploitation technology for oil fields. Adding demulsifiers, water clarifiers and other various chemicals makes the composition of oily sewage containing polymer complex in the process of oil-water separation and sewage treatment (Chen *et al.* 2012a, 2012b, 2013; Jiang & Fang 2012; Yin *et al.* 2012; Xiao *et al.* 2013). After oil-water separation effluent sewage should be treated and the key control indicator of COD_{cr} is no more than $50 \text{ mg} \cdot \text{L}^{-1}$. An environmental protection sewage treatment technology of efficient advanced oxidation has been rapidly developed in recent years, especially the three-dimensional electrode reactor. It shows several advantages in the treatment of complex sewage (Chen 2007; Qi *et al.* 2011; Chen *et al.* 2012a, 2012b; Yang *et al.* 2014). However, the chemical oxygen demand (COD) removal mechanism has not been reported, especially the active oxides detection. Dimensional electrode reactor which is an advanced electro-catalytic oxidation technology with high efficiency, easy operation and environmental friendly features can decompose various pollutants in sewage by direct oxidation and indirect oxidation (Körbahti & Artut 2010; Kushwaha *et al.* 2010; Santos *et al.* 2013; Zhang *et al.* 2013). Structural features are as follows:

filling with activated carbon or other particles between the main electrodes to improve the efficiency of absorption and mass transfer (Drogui *et al.* 2009; Mao *et al.* 2010; Wang *et al.* 2014). Filled particles contacting with the electrodes or charged by the electric field form many micro cells. The larger surface provides more reactive active bits, so the current efficiency and the treatment effect of the three-dimensional electrode is higher and better than the two-dimensional electrode. PFR (plug flow reactor) fixed bed electrochemical reactor was firstly applied in the deep treatment of COD in oil field sewage, and the COD removal reaction kinetics (Lin *et al.* 2016; Ertugay & Acar 2017) in oily sewage containing polymer from a macro perspective could be researched in the study.

EXPERIMENTAL

Experimental instruments and chemicals

DR1010 COD tester (HACH COMPANY, USA) and HACH-COD preformed tube agent ($15\text{--}150 \text{ mg} \cdot \text{L}^{-1}$), Agilent 5975C Chromatography-Mass Spectrometer, UV-2450 UV-Vis

spectrophotometer (Shimadzu), ZD-3A automatic potentiometric tester, CH-II mini continuous sewage treatment equipment, Homemade PFR electrochemical reactor. Water quality analysis method was in accordance with 'wastewater discharge standards' (GB8978-2002) in this study.

The main quality indicators of water samples

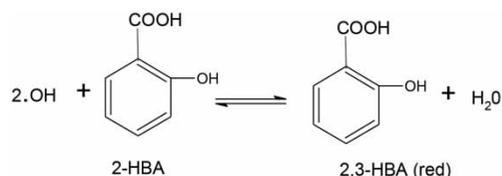
Experimental water sample was taken from biochemical pool import water samples in the oil field sewage treatment process, and the concentration of Cl^- was up to $5,436.34 \text{ mg}\cdot\text{L}^{-1}$. The results are shown in Table 1. The results were the mean of three parallel test samples.

The detection method of active oxides

It is very important to detect the presence of strong oxidizing active groups such as H_2O_2 , $\cdot\text{OH}$, O_3 , as well as a class of oxidative active species (collectively referred to residual chlorine) like HClO , ClO^- or in the form of elemental chlorine and chlorine-containing in sewage treatment process of electrochemical degradation of organics, and it is an important means of studying the degradation of COD. The detection of active intermediates H_2O_2 (Chen & Mei 2013) could use Ti (IV)-(5-Br-PADAP), the basic principle is based on the high coordination number of Ti(IV), and it can cooperate with (5-Br-PADAP) and H_2O_2 , respectively. Moreover, the space volume of H_2O_2 is less than (5-Br-PADAP), so the ternary complexes spatial effect of Ti(IV) and H_2O_2 with (5-Br-PADAP) is good, and it can form a stable ternary complex in the range of low pH, and there is an obvious absorption peak of this ternary color system at about 561 nm whose absorption coefficient $\epsilon_{561\text{nm}} = 7.3 \times 10^4 \text{ (L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})$. Within the range of $0.2\text{--}10 \mu\text{mol}\cdot\text{L}^{-1}$ H_2O_2 the Beer-Lambert Law is conformed. However, the pH value stable range of this ternary complex is very narrow, and it has significant absorption peak of pH in the range of 1–1.5, and any slight error in the experimental operation will lead to be unable to detect H_2O_2 .

Trace active intermediate $\cdot\text{OH}$ (Chen & Mei 2013) could be indirectly detected by colorimetric determination. Red 2,3-dihydroxybenzoic acid (2,3-HBA), the reaction product of trace active intermediate $\cdot\text{OH}$ and salicylic acid

(2-HBA), has a maximum absorption peak at 510 nm, and its absorption coefficient $\epsilon_{561\text{nm}}$ is $271.3 \text{ (L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})$. When there is absence of $\cdot\text{OH}$ in the sewage, it does not produce 2,3-HBA and the absorbance is zero; when it produces trace active intermediate $\cdot\text{OH}$, it can react with 2-HBA and produces red 2,3-HBA. The reaction principle is as follows:



O_3 and residual chlorine were detected by colorimetric determination: since the solubility of O_3 in water was limited and O_3 was unstable, the concentration of ozone was measured using the *N,N*-diethyl-*p*-phenylene diamine (DPD) reagent. The principle is as follows: DPD - potassium iodide method, that is to say, ozone reacts with DPD into red, the depth of color is proportional to the concentration of ozone in the water in the catalytic effect of potassium iodide. DPD reagent tablet containing disintegrating agents can be quickly dissolved. The products with a dedicated colorimetric tube is highly sensitive to ozone, the precision of it is to $0.05 \text{ mg}\cdot\text{L}^{-1}$, configuring DPD method is corresponding to the colorimetric levels of the solution. Colorimetric card is made by precise color separation.

A class of oxidative active species containing chlorine is collectively referred to residual chlorine, which is characterized by strong oxidation in water and is very instability. Experiments used DPD residual chlorine test tube in accordance with the national standard GB/T5750-2006. The principle is DPD rapidly reacts with free residual chlorine in water into red. Take 1 mL water sample into the test tube, shake it, and after the reaction for 2–3 min, compare with the standard colorimetric board to determine the concentration of residual chlorine, and the concentration of residual chlorine is proportional to the color depth of the solution.

Experiment process

Plexiglas three-dimensional electrode reactor ($260 \times 250 \times 256 \text{ mm}$) was designed with dual electrodes, shown in

Table 1 | Wastewater characteristics

Parameters	Salinity/ $\text{mg}\cdot\text{L}^{-1}$	Conductivity/ $\mu\text{ s}\cdot\text{cm}^{-1}$	$\text{COD}_{\text{cr}}/\text{mg}\cdot\text{L}^{-1}$	Polymer/ $\text{mg}\cdot\text{L}^{-1}$	Oil/ $\text{mg}\cdot\text{L}^{-1}$	Redox potential/mV
Mean values	9374.34	16.82	226.0	89.5	12.2	264

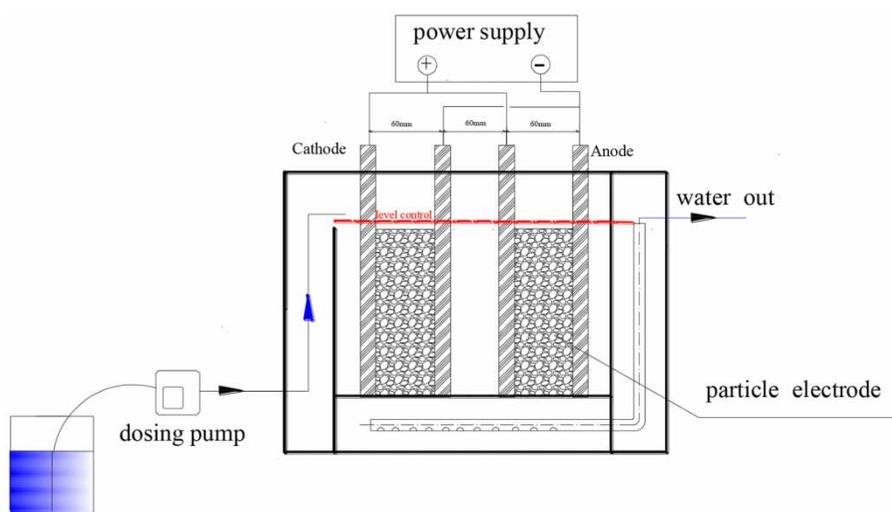


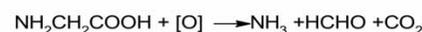
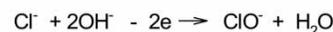
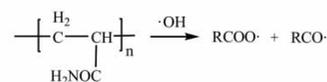
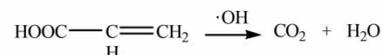
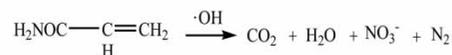
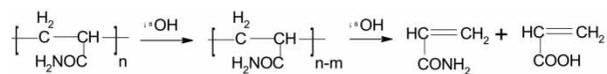
Figure 1 | Three-dimensional electrode experimental device process.

Figure 1. Titanium mesh electrode plates were used and treated by Ir/Ru oxide coating as double electrodes, and surface/volume ratio of $6/25(\text{cm}^2 \cdot \text{L}^{-1})$. The water flowing state of it was similar to that of PFR reactor. The three-dimensional electrode reactor consisted of rod activated carbons (after pretreatment of saturated adsorption) and a certain amount of insulative particles of quartz sand and glass beads which were filled between positive and negative electrode plates. The insulative particles improved the contact state of the particles with each other, and more particles were isolated from each other to reduce effectively the short-circuit current between particles corresponding to increasing the Faraday current so that the efficiency of the reaction was improved.

The principle of COD removal

The degradation of organic pollutants in the process of electrochemical treatment of sewage divides direct and indirect oxidation. Indirect oxidation refers to making use of active groups with strong oxidation in the anode reaction, such as H_2O_2 , $\cdot\text{OH}$, O_\cdot , O_3 , etc. It will generate hypochlorous acid (HClO), hypochlorous acid (ClO^-) and other products in wastewater of high concentration of Cl^- . These active substances, which have the characteristics of short life and strong oxidation, can effectively oxidize and decompose pollutants to achieve the purpose of removal of pollutants. If these active oxides can be detected in the system, it indicates the existence of indirect oxidation. In different sewage systems, these oxidizing active groups exist as a very small amount, whether active oxides are generated in the process of sewage treatment by electrolysis or

the concentration affects the electrolytic sewage treatment. Since the active oxides are very unstable, how to detect the presence of it in the experimental system is an important factor to analyze the mechanism of COD degradation. Here is the principle of COD removal by three-dimensional electrode reactor: anode produces high active intermediates (Ramalho *et al.* 2010; Rocha *et al.* 2012; Zhao *et al.* 2014) such as H_2O_2 , $\cdot\text{OH}$, O_3 and ClO^- in the sewage at the influence of external currents. Organics occur oxidative chain scission reaction in the anode, and organics occurs oxidation reaction with $\cdot\text{OH}$ of strong oxidizing ability. Organics of low molecular weight may also be directly oxidized into CO_2 and H_2O on anode. The chain scission product of organics is further oxidized in the reaction zone by ClO^- , O_3 and so on. For example, the degradation principle of the polymer PAM and organics in the sewage are as follows:



RESULTS AND DISCUSSION

The detected results and analysis of residual active oxides during the reaction

The detected results of active oxides at different times are shown in Figures 2 and 3, when the experiment reached steady state. Because of the poor stability of $\cdot\text{OH}$, the solution showed significant pale pink and then gradually disappeared in detection of $\cdot\text{OH}$. The results indicated that the amount of $\cdot\text{OH}$ was little in electrolysis water samples, and $\cdot\text{OH}$ disappeared because of oxidizing pollutants in the sewage. As it can be seen from Figures 2 and 3, there were residual active oxides such as H_2O_2 , O_3 , residual chlorine and so on in the sewage. The concentration of these rose in different degrees with the increasing of reaction time.

$\cdot\text{OH}$ is the most strong oxidizing oxygen radicals, the oxidative potential of it is up to 2.80 V, and it is significantly higher than O_3 (2.07 V), H_2O_2 (1.77 V) and residual chlorine (1.5 V). $\cdot\text{OH}$ can react with the vast majority of organic contaminants in sewage, and it can make these contaminants decompose into small biodegradable molecules until CO_2 and H_2O . Because the amount of active oxides was shown by detected residual amount, it was difficult to judge which kind of active oxides had greater importance in indirect oxidation. The detected results showed that there existed indirect oxidation in the degradation of COD in sewage, and it was the result of synergistic effect of these active oxides.

The removal effect of COD

COD value changes of water samples with different processing time were studied to research the kinetics of COD

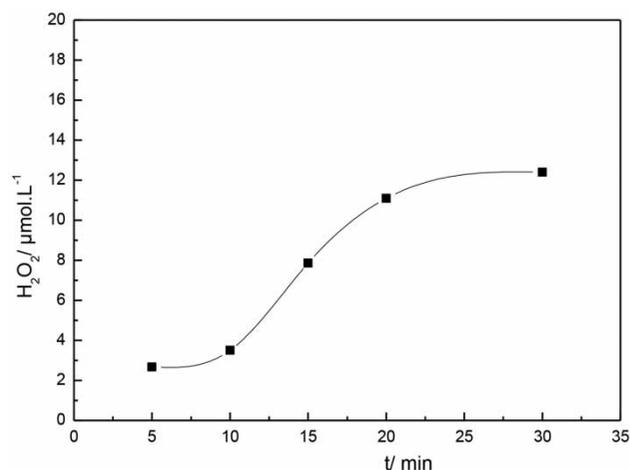


Figure 2 | The concentration changes of residual H_2O_2 in a water sample with treated time.

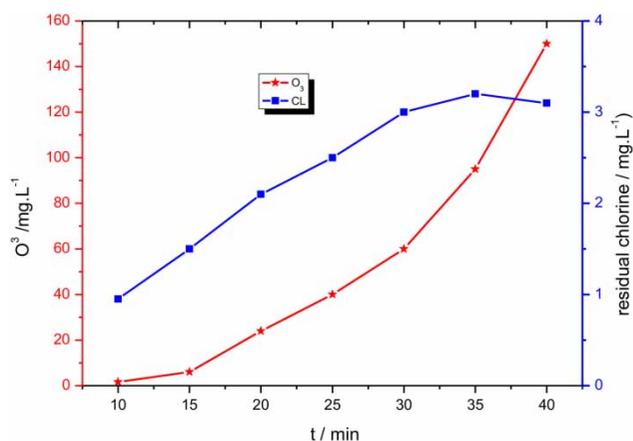


Figure 3 | Concentration change trends of residual O_3 and residual chlorine during the process of sewage treatment.

removal through a continuous flow experiment at steady flow state in the process of sewage electrochemical treatment and, according to the results, kinetic equation of COD degradation could be established.

The optimum conditions of electrochemical treatment of oily sewage containing poly by three-dimensional electrode were according to early optimized experiments (Yang *et al.* 2017): 40–60 mm of plate distance, 4 L of effective treated water, $6/25$ ($\text{cm}^2\cdot\text{L}^{-1}$) of surface/volume ratio, and 6A of the regulated voltage output current. A stable pump was used to input oily sewage containing polymer, and a water sample was taken at different times at the outlet of the reactor to analyze the COD value.

The COD value changes of sewage at different treated time are shown in Figure 4. It can be seen from Figure 4 that COD removal rate from the initial three-dimensional electrode electrochemical treatment was up to 55% within 15 min, indicating that the rapid degradation of PAM and small molecule organics led to rapid decrease of COD.

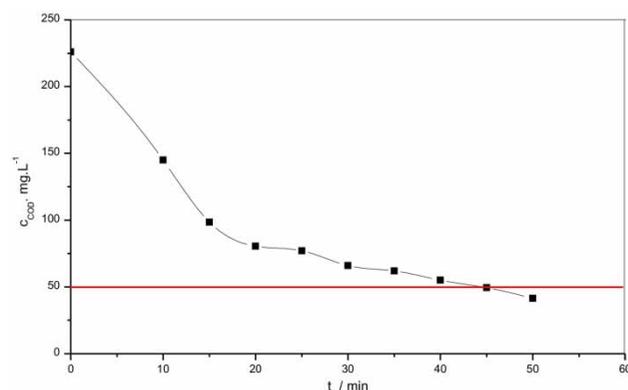


Figure 4 | Trend of $t\text{-COD}_{\text{Cr}}$ at different processing times.

The COD value declined slowly after processing time of 20 min, and the efficiency of COD removal decreased. COD removal rate was 35.8% from 15 to 35 min. The COD removal rate improved with the processing time. COD value could be reduced to 50 mg·L⁻¹ or less to reach emission standard when the electrochemical reaction proceeded to 45 min. It was reported that bio-activated sludge method and sanding filter method (Wang et al. 2010; Chen et al. 2016) can both remove COD, however, these methods need a long treatment time, and quite high site requirements. In this study, the deep treatment of the sewage was limited by the venue, time and space, so a simple and fast and efficient method, electrochemical method, was used to remove residual COD, and only by extending the appropriate reaction time could achieve the target, so obviously, bio-activated sludge method and so on was not suitable.

Changes of t- C_{COD} in the reaction system

As to the three-dimensional electrode reactor in certain experimental operating conditions and steady-state flow, the COD degradation rate was related to specific surface area of a three-dimensional electrode as the reaction conditions of experiment 3.2, and its macroscopic kinetic equation could be expressed as:

$$r = -\frac{dc}{dt} = -akc^{\alpha}$$

wherein a was specific surface area of a three-dimensional electrode, α was apparent reaction order, k was the reaction rate constant, and c was COD concentration of sewage.

Through continuous flow experiments by the type CH-II mini continuous sewage treatment equipment, variations of the data about COD value of the water sample at different processing times was established, and then kinetics of COD degradation was analyzed.

Establishment of reaction kinetic model

COD degradation could be considered as an irreversible reaction, thus the impact of the reverse reaction could be ignored. The t-C_{COD} variation parameter could be obtained from the experimental results. Based on the linear relationship, trial and error method was used to assume the order of reaction α value, plot, then the order of reaction in the system was determined in turn. Provided that, in the process of sewage electrochemical treatment COD degradation kinetics were, respectively, zero-order kinetics, one-order

Table 2 | Data analysis of t- C_{COD} at steady processing state

t /min	0	10	15	20	25	30	35	40	45	50
C _{COD} /mg·L ⁻¹	226	146	101.3	91.3	87	76	65	54	51.5	43.5
-ln c	-5.4205	-4.9836	-4.6181	-4.5142	-4.4659	-4.3307	-4.1744	-3.9889	-3.9416	-3.7728
1/c	0.004425	0.006849	0.009872	0.01095	0.01149	0.01316	0.01538	0.01852	0.01942	0.02299
1/c ²	1.9579 × 10 ⁻⁵	4.6913 × 10 ⁻⁵	9.7450 × 10 ⁻⁵	1.1997 × 10 ⁻⁴	1.3210 × 10 ⁻⁴	1.7310 × 10 ⁻⁴	2.3670 × 10 ⁻⁴	3.4290 × 10 ⁻⁴	3.7700 × 10 ⁻⁴	5.2850 × 10 ⁻⁴

Table 3 | Fitting results of kinetic parameters under steady state

Assumption reaction order	Kinetic equations	Rate constant
Zero-order kinetics	$c = -3.13t + 178.73$ ($R^2 = 0.8068$)	$k = -3.13$
One-order kinetics	$-\ln c = 0.03076t - 5.2516$ ($R^2 = 0.9579$)	$k = 3.076 \times 10^{-2}$
Two-order kinetics	$1/c = 0.000358t + 0.00363$ ($R^2 = 0.9728$)	$k = 3.58 \times 10^{-4}$
Three-order kinetics	$1/c^2 = 9.62 \times 10^{-6} t - 5.22 \times 10^{-5}$ ($R^2 = 0.8817$)	$k = 4.81 \times 10^{-6}$

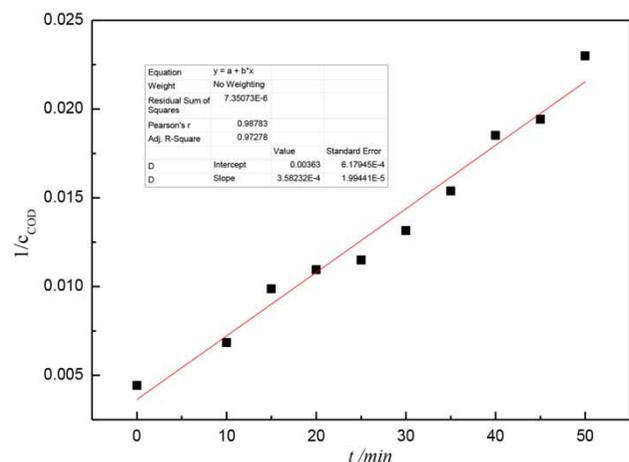
kinetics, two-order kinetics and three-order kinetics, which α was corresponding to 0, 1, 2 and 3, and made fitting linear for c - t , $-\ln c$ - t , $1/c$ - t and $1/c^2$ - t relationship according to experimental data processing results of Table 2. Table 3 shows different orders of reaction kinetic equations.

From the experimental data fitting results in Table 3, the correlation coefficient of the apparent second-order kinetic equation was optimal. Good linear relationship can be seen in Figure 5, so the COD decomposed reaction was consistent with second-order reaction kinetics model.

The reaction rate constant was $k = 3.58 \times 10^{-4}$, and the kinetic equation was:

$$r = -\frac{dc}{dt} = -3.58 \times 10^{-4} \cdot a \cdot c^2 \quad (1)$$

As can be seen from the above reaction model, the small reaction rate constant of the system was internal causes of slow rate of COD degradation, and affecting factors of COD rapid degradation had great relationship with the specific surface area of a three-dimensional electrode filler. Increasing the filling specific surface area of the three-dimensional electrode could improve the reaction rate effectively, which was favorable to the rapid degradation of

**Figure 5** | Fitting curve of apparent second-order kinetic equation.

pollutants. The degradation rate became slow with the decline of COD concentration when the reaction was carried out to a later period, and extending electrochemical processing time had no obvious enhancement effect on the COD removal rate.

Application of kinetic equations

Experimental results and theoretical calculated results from kinetic equation are compared in Table 4. It shows that to achieve a certain effect, the actual processing time was basically the same as the theoretical required processing time, and it indicated that the fitting kinetic equations was consistent with the actual COD degradation process; according to the kinetic equations, to reach the goal the COD was no more than $50 \text{ mg}\cdot\text{L}^{-1}$ in treated sewage, the theory minimum processing time was 45.73 min.

Analysis of organic pollutants in sewage before and after treatment

The components and contents of organics in the extracted sewage before and after electrochemical treatment were analyzed by gas chromatography–mass spectrometry (GC-MS). The analytical results are shown in Tables 5 and 6.

It can be seen from Table 5 that the contents of 10 aromatic organics such as naphthalene, phenanthrene, thiophene, biphenyl, furan, flexor, pyrene, fluorene triaryl steroidal and other (C27–29) organics in sewage were significantly reduced by electrochemical treatment, and the total concentration was decreased from $126.0 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ to

Table 4 | Results of verification and application of kinetic equations

Experimental treated time – t_t /min	35	40	45	50
COD value of treated sewage – $C_{\text{COD}}/\text{mg}\cdot\text{L}^{-1}$	65	54	51.5	43.5
Calculated value of kinetic equations – t_t /min	32.82	41.59	44.11	53.08

Table 5 | Content comparison of aromatic organic pollutants before and after treatment ($\mu\text{g}\cdot\text{L}^{-1}$)

Organics	Content before treatment	Content after treatment	Removal rate%
Naphthalene organics	18.2976	1.1765	93.57
Phenanthrene organics	36.5334	0.7828	97.86
Thiophene organics	5.4253	0.0941	98.27
Biphenyl organic	2.1687	0.33940	84.35
Furan organics	1.8839	0.21893	88.38
Flexor organics	11.4187	0.1065	99.06
Pyrene class organics	4.2731	0.2894	93.23
Fluorene organics	8.2115	0.5445	93.37
Triaryl steroidal organics	14.9043	0	100
Other (C27–29) organics	22.8832	0	100

$3.5523 \mu\text{g}\cdot\text{L}^{-1}$, the total removal rate was up to 97.18% after electrochemical treatment. No triaryl steroids and other (C27–29) organics were detected in the electrochemically treated sewage, and it showed the best efficiency. The aromatic hydrocarbon with the lowest removal efficiency was biphenyl organics, and the removal rate was 84.35%. Therefore, the electrochemical advanced treatment technology could significantly reduce the types and contents of aromatic organic pollutants in sewage.

It can be seen from Table 6 that the content and type of straight chain organics in the sewage were significantly increased after electrochemical treatment, the total concentration of straight chain organics increased from $4.52 \mu\text{g}\cdot\text{L}^{-1}$

to $20.04 \mu\text{g}\cdot\text{L}^{-1}$, and the number of straight chain organics increased by 9 from C14–C30 to C14–C39. A large amount of active free radicals might be produced during the electrochemical treatment process, resulting in the degradation of aromatic organics in the sewage. The content of generated straight chain hydrocarbons or molecular fragments increased with the decrease in the types and content of aromatic organics in the aqueous solution. The concentration and types of straight chain organics in aqueous solution increased markedly, and it showed an opposite trend with the decrease in the types and content of aromatic pollutants in Table 6.

Table 6 | Content comparison of straight-chain organics before and after treatment ($\mu\text{g}\cdot\text{L}^{-1}$)

Organics	Content before treatment	Content after treatment	Organics	Content before treatment	Content after treatment
nC14	0.1074	0.1531	nC27	0.1902	1.7661
nC15	0.1621	0.5674	nC28	0.1585	1.3701
nC16	0.1599	1.1364	nC29	0.1305	1.1245
nC17	0.3085	0.9966	nC30	0.1125	0.8459
nC18	0.2252	0.4602	nC31	0.0000	0.6520
nC19	0.3178	0.3317	nC32	0.0000	0.4628
nC20	0.2520	0.2696	nC33	0.0000	0.2970
nC21	0.3098	0.4183	nC34	0.0000	0.2664
nC22	0.3386	0.5735	nC35	0.0000	0.2576
nC23	0.3428	0.8626	nC36	0.0000	0.3203
nC24	0.8429	1.2187	nC37	0.0000	0.1441
nC25	0.3169	1.6929	nC38	0.0000	0.1430
nC26	0.2456	1.9087	nC39	0.0000	1.7661

CONCLUSIONS

Three-dimensional electrode treatment of oilfield oily sewage containing polymer was a green, efficient and fast method without adding chemicals, COD removal in the sewage was the result of synergistic indirect oxidation effect of these active oxides, such as O_3 , H_2O_2 , $\cdot\text{OH}$ and residual chlorine. COD was $43.5 \text{ mg}\cdot\text{L}^{-1}$ after the electrochemical treatment time of 50 min, it reached the discharge standard. The experimental results were basically consistent with the theoretical calculations of kinetic equations. The main pollutants of COD in oily sewage containing polymer were from aromatic organics and straight chain organics. The removal rate of aromatic organics was 84.35–99.06% after treatment by three-dimensional electrode reactor, while the total concentration of small molecule straight chain organics increased from $4.52 \mu\text{g}\cdot\text{L}^{-1}$ to $20.04 \mu\text{g}\cdot\text{L}^{-1}$. The kinetic model of COD degradation in oilfield wastewater was as

follows: $r = -dc/dt = 3.58 \times 10^{-4} a c^2 + 0.00363$. It was consistent with the apparent secondary reaction kinetics, and the apparent correlation coefficient R^2 was 0.9728, the small apparent reaction rate constant k value was the main cause of the slow COD removal rate.

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