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Photoelectrocatalytic decontamination of oilfield produced wastewater containing refractory organic pollutants in the presence of high concentration of chloride ions

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Abstract

The feasibility study of the application of the photoelectrocatalytic decontamination of high saline produced water containing refractory organic pollutants was investigated in the slurry photoelectrocatalytic reactor with nanometer TiO_2 particle prepared with sol–gel method using the acetic acid as hydrolytic catalyst. The efficiency of the photoelectrocatalytic decontamination of produced water was determined with both COD removal from the tested wastewater and the decrease of mutagenic activity evaluated by Ames tests. The experimental results showed that the photoelectrocatalysis is a quite efficient process for decontaminating the produced water, although there are high concentration of salt existed in oilfield wastewater. We found that the COD removal efficiencies by photoelectrocatalytic process are much higher than that of by photocatalytic or electrochemical oxidation individually in the photoelectrocatalytic reactor. The COD removal can be substantially improved by the added H_2O_2 and the generation of active chlorine from high concentration chlorides in the wastewater. The effects of various operating conditions, such as initial COD concentration, applied cell voltage, catalyst amount and initial pH value of solution, on the photoelectrocatalytic efficiencies, is also investigated in detail. The results showed that when the raw produced wastewater was diluted in a 1:1 (v/v) ratio, there is a highest COD removal efficiency. And the photoelectrocatalytic degradation of organic pollutants in saline water is much favored in acidic solution than that in neutral and/or alkaline solution.

Keywords: Photoelectrocatalysis; Oilfield wastewater; Active chlorine; COD removal; Toxicity

1. Introduction

Produced water is defined as the water (brine) brought up from the hydrocarbon bearing strata during the extraction of oil and/or gas and can include formation water, injection water, and small volumes of condensed water and trace amounts of treatment chemicals [1]. That is, produced waters are co-produced during the exploitation and production operation of crude oil and natural gas, and are considered the largest volume of waste stream in the exploitation and production process. In the most oilfields, the volumes of produced water can be more than 10 times the volume of hydrocarbon produced [2]. For instance, an EPA study [3] reported that 11.7 billion barrels of produced water are generated in the US annually. However, the amount of produced water always depends on the extraction technology utilized, the reservoir characteristics and the rate of oil extraction. The amount of water produced alone with the oil is normally low in the early stages of oil production, but as the increase of the oilfield ages the water volume can increase to several times the volume of oil produced. In most Chinese large oilfields, such as Daqing oilfield, Shengli oilfield and Liaohe oilfields, are now all in their mid-or final-stage of development and the produced oil also contains a very large volume of water as high as 90% [4]. However, this produced water contains significant levels of organic and inorganic compounds, such as oil, heavy metals, especially organic substances varying widely between

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fields or even within the same field. But this produced water have the same characteristics such as containing oil and the suspended solids (SS), high temperature, high salts concentration, high corrosion rate and so on.

Generally, most of produced waste water was reused and reinjected into the underground for enhancing oil recovery after certain treatment, but there are also large amounts of produced wastewater were discharged directly into the environment. However, in recent years, the arising ecological problems connected with crude oil pollution in the presence of oil derivatives in the environment have been observed because of the complex composition of produced water. Thus these containing pollutants, especially refractory organic pollutants, are high toxic and not easily degraded in the environment. The wastewater may represent potential harmful impacts on both environment and human beings if the large amounts of produced water were discharged into the environment without treatment or with improper treatment.

Traditional produced water treatment technologies are focused on the removal of dispersed oil and grease which can easily be removed by filtration or an alternate commercial treatment with good removal efficiency [4,5], but the other components such as the dissolved or soluble refractory organic pollutants that contribute to the high Chemical oxygen demand (COD) of the water are difficult to treat. The COD always cannot meet the China national discharge standard of produced water (100 mg L^{-1}), therefore it often become a difficult problem for oilfield produced water discharge. Conventional physical–chemical methods are often unsatisfactory for treating oilfield wastewater, in that the pollutants may be only removed from the aqueous phase, but could not be fully destroyed, resulting in a problem of subsequent disposal of these pollutants [6]. However, biological treatment is an economical method for this kind of wastewater, and many bacteria have been reported to treat the dissolved organic pollutants in the produced water [7–9]. But one matter of concern is the high NaCl content in the produced water because it poses great difficulties for treatment processes, particularly biological treatment method, by inhibiting the growth of microorganisms. Thus it may be demand an increasing effort towards the development of technologies for the cleanup of such produced wastewater.

Heterogeneous photocatalytic process using semiconductor catalysts is a good advanced oxidation technology for degradation of organic pollutants, and recently have attracted considerable attentions [10]. The appeal of this technology is the prospect of complete mineralization of the pollutants into harmless compounds [7,11]. However, there are only a few researches to report the photocatalytic decompose the oil contaminated water [12–14]. Grzechulska et al. [12] first applied the photocatalytic technology to decompose the bilge oil water permeated by ultrafiltration process, and they found that the complete oil (ca. 6 ppm) decomposition was achieved after 2 h of UV illumination with the photocatalyst content of 0.5 g dm^{-3}. Ziolli and Jardim [13] found that the degradation reached 90% under irradiation of TiO_2/UV–vis after 7 days for seawater-soluble crude oil compounds in water containing 9–45 mg Cl^{-1}. And Bessa et al. [14] used H_2O_2 to assist the photocatalytic decomposition of pollutants present in the oilfield produced waters from Campos Basin, Brazil. Their GC/MS results showed that there was a sharp reduction in the number of substances present in the effluent. Thus, the photocatalysis seem to be a feasible process for the degradation of oilfield produced water. However, the application of TiO_2 photocatalytic process is often low efficiency due to the high-speed recombination of photogenerated electron and hole. Moreover, high concentration chloride ions containing in produced water have been found to be an effective scavenger for heterogenous photocatalytic process by competing for surface active sites and forming weaker Cl radical [15,16]. Furthermore, a large amount of electrolytes existed in produced water may have a strong deleterious effect on photocatalysis. That is, only a few of TiO_2 was dispersed in solution for photocatalysis because of the coagulation role of electrolytes for TiO_2 slurry solution. Thus the photocatalytic may be very inefficient to treat this kind produced wastewater due to above mentioned reasons.

More recently, photoelectrochemical technology with anode bias appears to be a newly emerging research front of photocatalytic degradation of organic pollutants, and many academic interests have been focused on this area to decontaminate toxic organic contaminants in wastewater [17–20] because the applied cell voltage can greatly accelerate the separation and suppress the recombination of photogenerated electrons and holes [21,22]. What's more, in our previous research [23] and in others research work [24], it is found that chloride ions had an obvious enhancement effect on the photoelectrocatalytic degradation of organic pollutant in saline water by the generation of active chlorine. Thus it may be supposed that the photoelectrocatalytic technology have good removal efficiency for these produced waters with high concentration of chloride ions. However, there is few research to investigate the photoelectrocatalytic degradation of the produced water up-to date.

Thus the present paper is to focus on investigating the feasibility of the photoelectrocatalytic decontamination of high saline produced water containing organic pollutants assisted by active chlorine generated from the chloride ions abundantly existed in the produced water in the slurry photoelectrocatalytic reactor, and evaluating the degradation efficiency at different operating parameter variables. Additionally, toxicity studies before and after photoelectrocatalytic degradation of organic pollutants in the produced water were compared using the Ames test.

2. Experimental

2.1. Reagents and apparatus

Dexon was purchased from Sigma. Titanium tetraisopropoxide was chemical pure reagent, and other chemicals such as dichloromethane and glacial acetic acid were all analytic grade reagents and were used without further purification. COD was carried out according to the standard methods for examination of water and wastewater (using $K_2Cr_2O_7$ as oxidant). A 500 W high-pressure mercury lamp was used as an illuminant, and the cell voltage across the reactor in the photoelectrochemical experiments was supplied with a potentiostat (Dongfang, Yangzhou). The micropore titanium plate was used as electrodes

after dealt with diluted sulfuric acid and then washed with deionized water twice. X-ray diffraction (XRD) was measured using a D/Max-IIIA Diffractometer (Rigaku Corporation, Japan) with radiation of Cu target ($K \propto 1$, $\lambda = 1.54056$ nm) to determine the crystal phase composition of the nanometer TiO_2 at room temperature. Scanning electron micrographs were obtained on a HITACHI S520 mode reflection electronic microscope. Inorganic metal ions in the produced water were characterized by ICP-MS (model ELAN 6000, America). Organic compounds components were analyzed by a Hewlett-Packard (HP)-6890 equipped with a 50 m HP-5 capillary column coupled to a HP-5972 mass spectrometer.

2.2. Preparation of catalyst

Titanium dioxide nanometer particles were prepared by the sol–gel technology using the acetic acid as hydrolytic catalyst showed as follows: Titanium tetraisopropoxide was added dropwise into vigorously stirred acetic acid solution so as to give a 1:10:40 molar ratio of titanium tetraisopropoxide, acetic acid and water. Then the white slurry gradually formed during the reaction, and the resulting slurry was peptized by further stirring for 3 h to get a completely transparent sol solution. The sol solution was further deposited 60 h for the aging process, then the obtained gel was dried over at 100 °C and then calcined at 450 °C for 4 h to obtain an nanometer TiO_2 photocatalyst.

2.3. Oilfield produced water sample and photoelectrochemical procedures

The real effluent of oilfield produced water was sampled in Xianhe Shouzhan, Shengli Oilfield and it was preserved by adding sulfuric acid to keep its at pH < 2.0. Prior to photoelectrocatalysis, the produced water was deposited naturally and then the transparent supernatant was used to conduct the photoelectrocatalytic experiments. At certain conditions, diluted solution of H_2SO_4 and NaOH were used to adjust the pH value of solution.

The used setup is a efficient slurry photoelectrochemical reactor as published in previous literature [25], and the distance between anode and cathode in the reactor was 23.5 cm. And the photoelectrocatalytic reaction procedures are showed as following: A 350.0 mL produced water containing certain amount of nanometer TiO_2 photocatalyst was fed into the photoelectrochemical reactor each run. The reactor was timed starting when the dc power, illumination and compressed air supply were switched on. Except as indicated, general treating conditions were 30.0 V cell voltage, 0.05 MPa airflow, 2 g L^{-1} catalyst, pH value 7.0, initial COD value of 316.9 mg L^{-1} and reaction interval 60 min. At certain interval, the sample solutions were collected, then the sample solution was natural stood for sedimentation, and then the transparent supernatant was used for COD analyses with potassium dichromate. The concentration of active chlorine produced in the electrochemical and photoelectrocatalytic process was determined by the DPD (*N*,*N*,-diethyl-*p*-phenylenediamine) colorimetric method as early publication [26].

2.4. GC–MS analysis

Two hundred fifty millilitre samples were extracted three times with 10 mL dichloromethane (DCM) as solvent each time by liquid–liquid extraction and then the three extracted samples were mixed and rotary-evaporated at ≤35 °C nearly dryness. Then the extract were transferred to a screw cap vial and removed the remaining solvent with a gentle stream of nitrogen. Then the dry extracts were re-dissolved in 50 μL of DCM to perform GC–MS analysis. The samples were analyzed using a Hewlett-Packard (HP)-6890 gas chromatograph with mass selective detection (GC–MS) equipped with a 50 m HP-5 capillary column coupled to a HP-5972 mass spectrometer operated in the electron impact mode (70 eV). The chromatographic conditions were as follows: the carrier gas was Helium at a constant flow rate of 2.2 mL min^{-1}. Sample of 1 μL was injected with splitless model, and mass range at 50–500 was used for quantitative determinations. Injector temperature, 280 °C; ion source temperature, 180 °C; The column temperature was programmed at 60 °C for 5 min, and then ramped up to 290 °C at the rate of 3 °C min^{-1}, then maintained for 30 min. Data acquisition and processing were controlled by a HP Chemstation data system. Chromatographic peaks of samples were identified by GC–MS analysis and the compounds were identified by the retention indices and the library mass spectra.

2.5. Salmonella mutagenicity assay—Ames test

In order to test the mutagenicity of the sample, 1.7 L produced water were extracted three times with 30 mL dichloromethane (DCM) each time, and three extracts was mixed and dried with a gentle nitrogen gas. Then the dried extracts were re-dissolved in different volume of dimethyl sulfoxide (DMSO) to prepare a certain concentration of organic pollutants. *Salmonella* mutagenicity tests were performed using the standard plate incorporation method [27] with the *Salmonella typhimurium* strains TA98 and TA100. Three plates were prepared for each test condition. The revertant colonies on each plate were counted after 48 h incubation at 37 °C in a sealed container. Known mutagen, Dexon, was used as the positive control, while solvent and blanks controls were also conducted in each assay. The mutagenic index (*M*) was also calculated for each dose; that is, the average number of revertants per plate divided by the average number of revertants per plate for the negative control (solvent). A sample was considered mutagenicity when the *M* was equal to or greater than 2 for at least one of the tested doses and if it had a reproducible dose–response curve.

3. Results and discussion

3.1. Characterization of photocatalyst

The XRD pattern of the prepared nanometer TiO_2 powder calcined at 450 °C is as shown in Fig. 1. From the figure, we can easily see that the profile is a typical figure of anatase crystal phases TiO_2, moreover the XRD peak at 25.3 is very sharp. The mean crystallite sizes of the TiO_2 powder can be calculated by

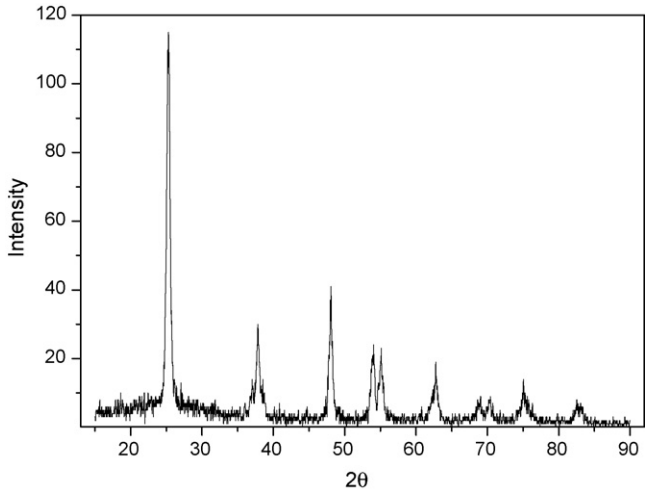

Fig. 1. The XRD pattern of the nanometer TiO_2 powder calcined at 450 °C.

Scherrer formula [28], and the mean sizes of prepared nanometer TiO_2 is 16.9 nm. The transmission electron microscopy (TEM) technology was employed to characterize the surface morphology of prepared nanometer photocatalyst. The TEM microimage of the TiO_2 powders magnified with 100,000 and 250,000-folds are given in Fig. 2, respectively. From the TEM photograph we can obviously see that the prepared TiO_2 powder is also nanometer scale particle about the mean sizes of 15–17 nm, which is in reasonable agreement with the results obtained from the XRD.

3.2. Oilfield wastewater characteristics

Produced water always contains a complex mixture of organic and inorganic materials similar to those found in crude oil and natural gas, whose composition varies with the location and over the life of a producing field. However, the basic components can be grouped into following main categories: oil, heavy metals, radionuclides, chemicals, salt, and dissolved oxygen [14]. In the paper, the physical–chemical characteristics of oilfield wastewater sampled from Shengli oilfield were summarized in Table 1. From the table, we can easily see that the components of oilfield produced wastewater also can be grouped into the following main categories: oil, salt, metals ions and other dissolved organic matter. In Table 1, the primary constituent of inorganic materials, salt content (salinity), expressed as chloride ions at the concentration of ca. 19 g L^{-1}, usually higher than the seawater's salinity. Besides chloride ions, certain heavy metals and other chemicals, other inorganic material in produced wastewater are high levels sodium, calcium, barium, strontium, magnesium, potassium, etc. A high COD value in the produced water also indicates that the produced water contains numerous dissolved organic pollutants. In order to understand the components of COD, the GC–MS was employed to identify the dissolved organic compounds in water, and the total ion current (TIC) profile was shown in Fig. 3. From the figure, we can identify large quantity of organic compounds, but mainly groups as phenol, substituted phenols and *n*-alkanes. This observation conforms to the Chapelle's conclusion that the most prevalent

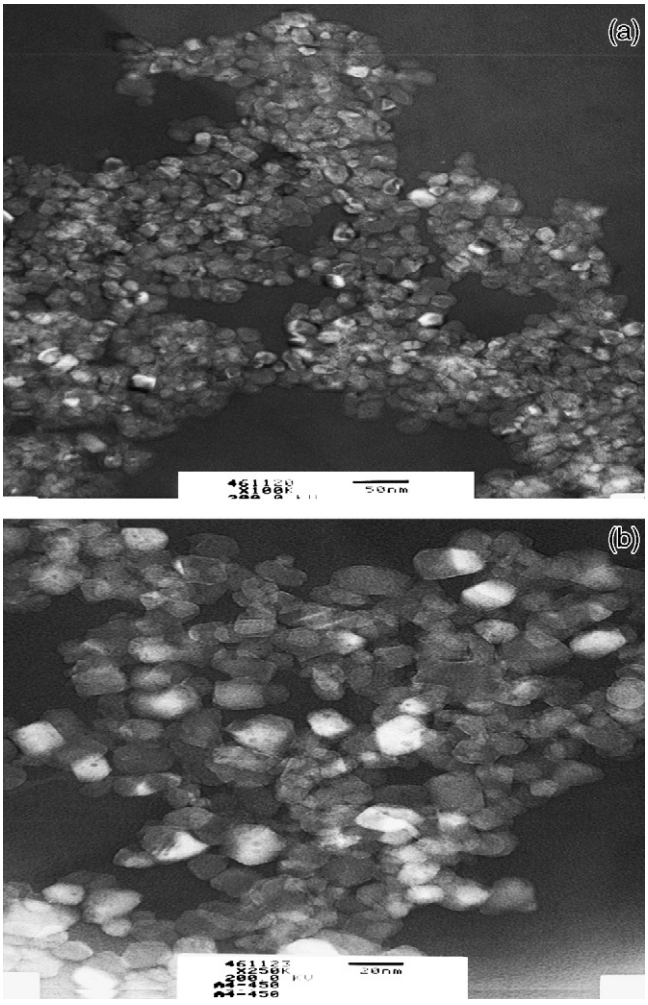

Fig. 2. The TEM photographs of nanometer TiO_2 photocatalyst. (a) Magnified with 100,000-folds and bar length of 50 nm; (b) magnified with 250,000-folds and bar length of 20 nm.

(approximately 90%) groups detected within produced waters are C_{10}–C_{30} straight chain alkanes [29]. Moreover, the peak in TIC figure of *n*-alkanes first increased gently from C_{14} to C_{18}, present a maximum at C_{18}, then gradually decreased with further increasing chain length to C_{34} in this produced water. This change trend of alkane in TIC figure is also very similar to the reference [30].

3.3. Comparison of different degradation processes

Taking the COD removal as an index, the photoelectrocatalytic degradation of organic pollutants in produced water was investigated as compared with two single degradation process, for example photocatalytic and electrochemical process, and the COD removals within 60 min were shown in Fig. 4. In this profile, it is obvious that the COD removal efficiency with different processes varied differently. For the raw effluent (COD concentration: 645 mg L^{-1}), the removal efficiency of photoelectrocatalysis is the best (47.4%), and the remaining COD concentration is 339 mg L^{-1}. While the removal efficiency of photocatalysis take second place (38.0%), and the electro-

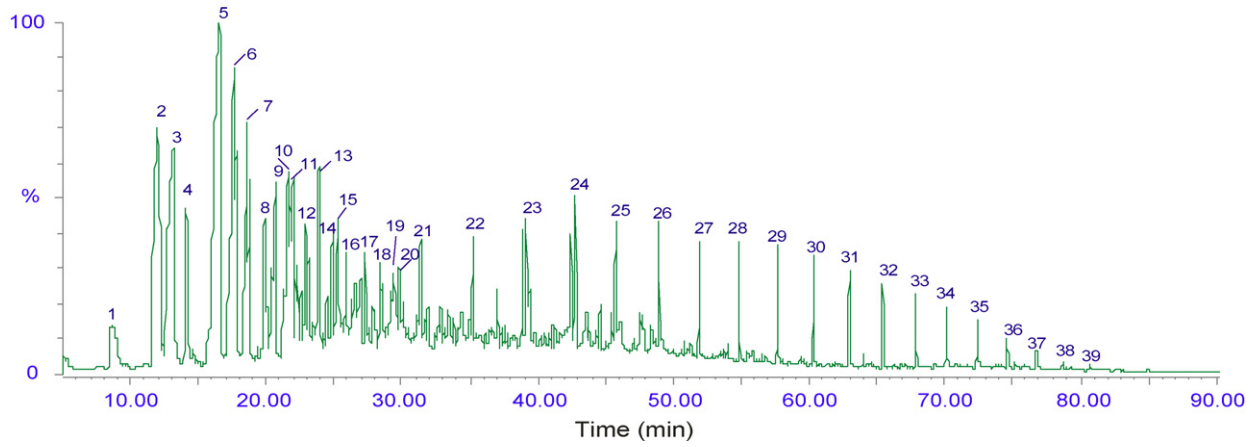

Fig. 3. GC–MS TIC spectra of the oilfield wastewater [peak number: 1, phenol; 2, 2-methyl-phenol; 3, 3-methyl-phenol; 4, 2,4-methyl-phenol; 5, 2,5-methyl-phenol; 6, 3-ethyl-phenol; 7, 2-ethyl-4-methyl-phenol; 8, 2,3,5-trimethyl-phenol; 9, 2-(1-methylethyl)-phenol; 10, 2-ethyl-4-methyl-phenol; 11, 2,3,6-trimethyl-phenol; 12, 2-(1,1-dimethylethyl)-phenol; 13, 2-(2-propenyl)-phenol; 14, 4-(2-propenyl)-phenol; 15, 3-methyl-6-propyl-phenol; 16, 2-methyl-6-(2-propenyl)-phenol; 17, *n*-C14; 18, 2-methyl-6-(2-propenyl)-phenol; 19, 2-methyl-6-(2-propenyl)-phenol; 20, 1-chloro-hexadecane; 21, *n*-C15; 22, *n*-C16; 23, *n*-C17; 24, *n*-C18; 25, *n*-C19; 26, *n*-C20; 27, *n*-C21; 28, *n*-C22; 29, *n*-C23; 30, *n*-C24; 31, *n*-C25; 32, *n*-C26; 33, *n*-C27; 34, *n*-C28; 35, *n*-C29; 36, *n*-C30; 37, *n*-C31; 38, *n*-C32; 39, *n*-C33].

oxidation process is the poorest one (13.5%). The remaining COD concentrations are obtained as 400 and 558 mg L^{-1} for two processes, respectively. Although the removal efficiencies are very low for these three processes, the net COD removal was obtained 306, 245 and 87 mg L^{-1} for photoelectrocatalytic, photocatalytic and electrochemical processes within 60 min, respectively. Moreover, we can conclude that photoelectrocatalysis is a much more efficient technology than the other two processes. This may be interpreted that the application of an anodic bias to TiO_2 electrode provides a potential gradient within the electrode to drive away the photogenerated holes and electrons in different directions efficiently [31,32]. Another important reason is that in the photoelectrocatalytic reactor, many other active oxidants—active chlorine, such as chlorine (Cl_2) and hypochlorites (OCl^-), are electrolytically generated from the chloride ions abundantly existed in the produced water. In our previous publication [23], we have found that chloride ion had an obvious enhancement effect on the photoelectrocatalytic degradation of organic pollutants in saline water rather than a scavenging effect on the photocatalytic degradation. Zanoni et al. [24] also have investigated photoelectrocatalytic oxidation of chloride ions to generate free chlorine in NaCl solutions, and found the free chlorine can easily be obtained on the photoelectrocatalytic electrodes. Thus, in this paper, the generation of active chlorine in photoelectrocatalytic reactor was also attempted compared with in the electrochemical reactor at different conditions, and the measured results were shown in Fig. 5. From the figure, we can see that these data were obtained by evaluating the amount of active chlorine generated as a function of time, in aliquots of the electrolyzed sample removed each 15 min during the electrolysis and analyzed instantaneously by the DPD colorimetric method. We also can observe that the active chlorine generated by photoelectrocatalytic process is slightly higher than that of electro-oxidation, indicated that the active chlorine was gen-

Table 1
Composition of the oilfield wastewater

Parameters	Concentration
pH	7.0
COD	645 mg L^{-1}
Oil	31.56 mg L^{-1}
Cl^-	19000 mg L^{-1}
Na	14150.143 mg L^{-1}
Ca	581.758 mg L^{-1}
Ba	314.224 mg L^{-1}
Sr	223.604 mg L^{-1}
Mg	105.850 mg L^{-1}
K	85.405 mg L^{-1}
Si	11.349 mg L^{-1}
P	8.784 mg L^{-1}
Fe	2.237 mg L^{-1}
Cu	0.279 mg L^{-1}
Mn	0.135 mg L^{-1}
Al	0.095 mg L^{-1}
Pb	0.074 mg L^{-1}
Cr	0.072 mg L^{-1}
Zn	0.059 mg L^{-1}
V	0.027 mg L^{-1}
Ni	0.017 mg L^{-1}
Cd	0.002 mg L^{-1}

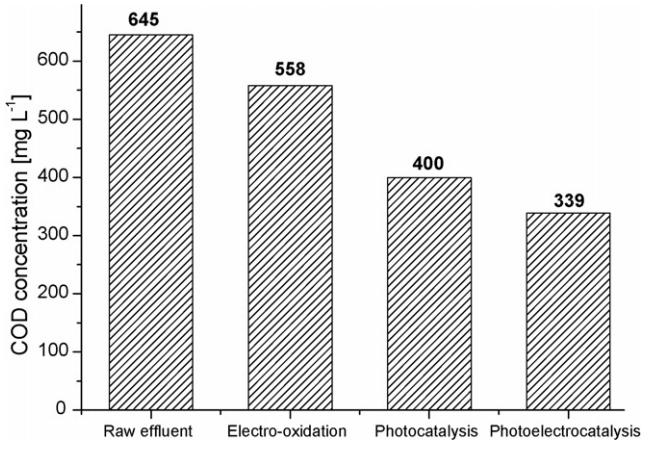

Fig. 4. Effect of different degradation processes (initial COD: 645 mg L^{-1}).

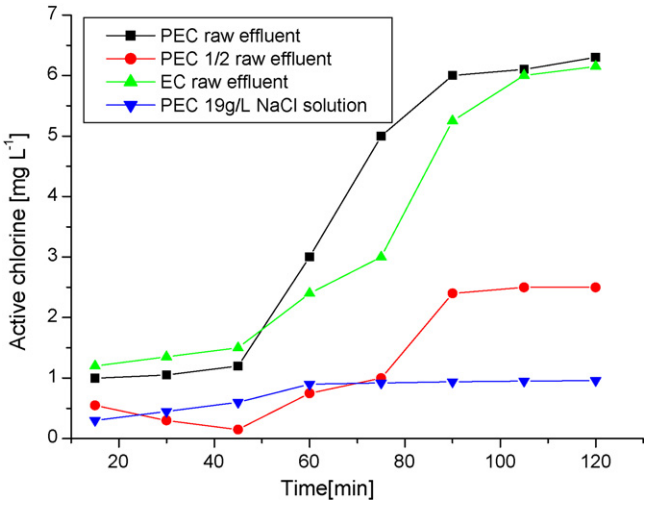

Fig. 5. The concentration of active chlorine generated at various conditions.

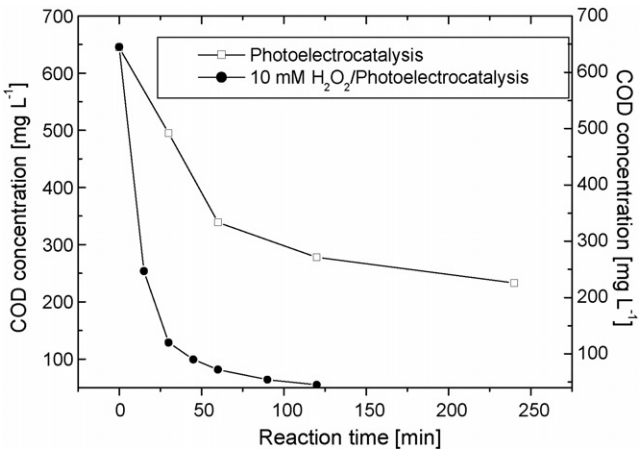

Fig. 6. Photoelectrocatalytic kinetic curves with and without H_2O_2 (initial COD: 645 mg L^{-1}).

erated mainly by electro-oxidation process. Furthermore, the produced active chloride can improve the COD removal efficiency in the photoelectrocatalytic process. The results showed that, on the whole, the concentration of active chlorine was increased much slower at the first stage of the process, then increased faster and finally reached a maximum value after a longer period of time at any different treatment conditions. But different samples displayed different specific trends. The concentration of active chlorine generated in the raw effluent was much higher than that in simulated NaCl solution with the same concentration of chloride ions, even when the raw effluent was diluted. This may be interpreted that other various inorganic ions existed in the raw effluent can improve the generation of active chlorine used as supporting electrolyte for the photoelectrocatalytic degradation. So, we found that the photoelectrocatalysis is an efficient and great economical technology for oilfield wastewater with the use of generated active chlorine.

3.4. Effect of H_2O_2 on photoelectrocatalytic kinetics

During the course of photocatalytic degradation, hydrogen peroxide often been choosed added into the photocatalytic systems with small concentration [14,33,34] to investigate the enhancement effects on the removal efficiency of organic pollutants because the •OH can be produced easily by the illumination of hydrogen peroxide [35]. However, Liao and Gurol [36] found that there should be an optimal dosage of chemical oxidant H_2O_2 because there are two opposing effect on the steady-state concentration of •OH, i.e. •OH is generated through photolysis of H_2O_2 but is also consumed by H_2O_2. Many previous researches have showed that optimal H_2O_2 concentration is 4–10 mM [33,34,37]. Thus, in this paper, in order to further improve the COD removal of raw oilfield wastewater, the experiments were conducted with the photoelectrocatalytic process to examine the effect of added oxidant H_2O_2 (10 mM) on the degradation of organic pollutants. The COD removal kinetics curves with or without H_2O_2 were presented in Fig. 6. From the figure, it is easy to see that the photoelectrocatalytic degradation rate of organic pollutants containing in produced water can be greatly enhanced by the added H_2O_2. In the H_2O_2 assisted photoelectrocatalytic process, a significant high COD removal efficiency was observed in comparison to the photoelectrocatalytic experiments without H_2O_2. More than 80% of COD removal was obtained within 30 min of photoelectrocatalysis/H_2O_2 system, while there is only 23.3% COD removal in photoelectrocatalysis. The average COD removal rate with 17.5 mg L^{-1} min^{-1} for photoelectrocatalysis/H_2O_2 system is much higher than that of the system without H_2O_2 system (5.0 mg L^{-1} min^{-1}). That is, the average COD removal rate for the former system is 3.5 times for the latter system. However, with increase of the reaction time, the degradation rate of photoelectrocatalysis/H_2O_2 became slow. At the end of 60 and 120 min, the COD removals of produced water were obtained as 88.9% and 93.0%, respectively, while the COD removal efficiency only reached as 47.4% and 56.9% for single photoelectrocatalysis. The phenomena can be interpreted as following two reasons: First, H_2O_2 is an oxidant and has a direct oxidative action on organic pollutants. Moreover, H_2O_2 also can be easily decomposed to generate •OH under the illumination of UV light in the photocatalytic system [35]. Second, H_2O_2 has been reported as an electron acceptor having a higher activity and efficiency in this role than oxygen for the titania conduction-band electrons [38]. Thus the added H_2O_2 can substantially improve the photoelectrocatalytic degradation rate of organic pollutants containing in water.

3.5. Effect of initial COD concentration of oilfield wastewater

The effect of the initial COD concentration on the removal efficiency was investigated by diluted raw effluent. Five different initial COD concentrations with 158.5, 211.3, 316.9, 422.5, 645.0 mg L^{-1} were chosen to carry out the experiments. Results presented in Fig. 7 clearly show that the COD removal efficiency strongly depends on the initial COD concentration of produced wastewater. It is found that initial COD concentration has a significant effect on the removal efficiencies in the photoelectrocatalytic process. The degradation efficiency increased

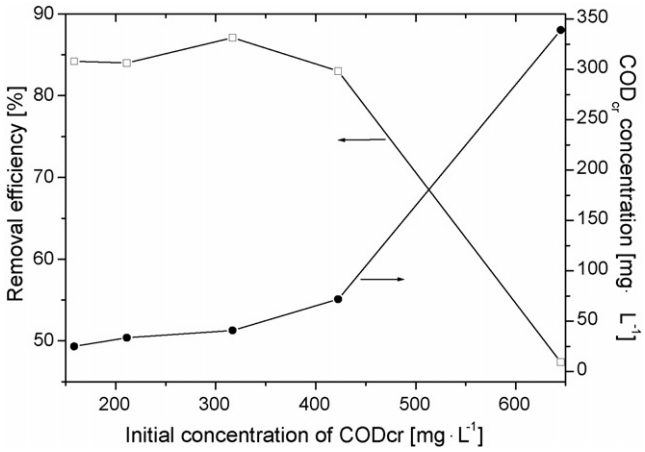

Fig. 7. Effect of initial COD concentration.

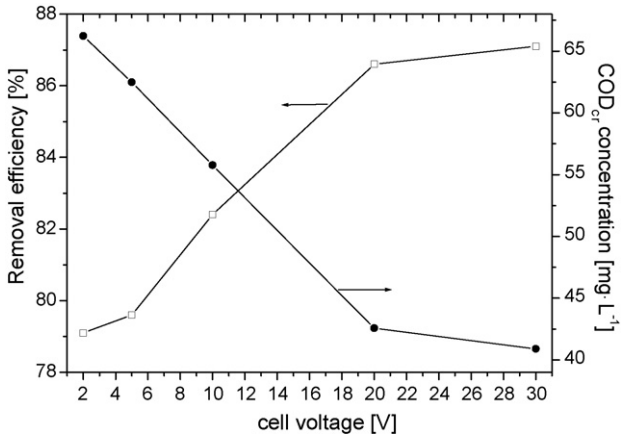

Fig. 8. Effect of cell voltage.

slightly firstly with increasing the initial COD of wastewater, then reached a maximum value, 87.1%, at initial COD 316.9 mg L^{-1}. As the initial COD increases further, the removal efficiency decreased sharply from 87.1% down to 47.4% at initial COD of 645.0 mg L^{-1}. These results can interpret as follow: The primary oxidant responsible for most photocatalytic oxidation processes is •OH, while the lifetime of •OH is very short (only a few nanoseconds), they can only react at or near the location where they are formed. At certain degree, high pollutant concentration can enhance the probability of collision between organic pollutants and the catalyst, leading to an increase in the degradation rate [39]. However, at higher pollutant concentration, too much of the pollutant adsorbed on the catalyst and inhibited the reaction of reactant molecules with the photoinduced positive holes or •OH. That is, the saturation of TiO_2 surface is achieved gradually, since there is not a direct contact of the semiconductor with them.

3.6. Effect of applied cell voltage

In photoelectrocatalytic process, the COD removal efficiency was significantly affected by cell voltage, in that the application of anode bias has been proven to be effective in not only enhancing the photocatalytic oxidation efficiency by minimizing the recombination of electron–hole pairs, but also providing the capability for direct or indirect electrochemical oxidation of the organic pollutants [31]. Thus, in this paper, the effect of cell voltages on the photoelectrocatalytic degradation of 1:1 diluted oilfield wastewater was investigated. As shown in Fig. 8, the COD removal efficiencies increased with increasing the cell voltage from 2.0 to 30.0 V. However, the COD removals increase more sharply with increase in applied cell voltage less than 20.0 V, while the cell voltage exceeded 20.0 V, the COD removal efficiency increase more gently with increase in applied voltage, and the removal efficiency obtained up to 87.1% at 30.0 V finally. This increase trend possible due to that the parasitic reactions, such as the generation of O_2 and H_2 gas, can consume much more current at high cell voltage than that at low cell voltage, in the photoelectrocatalytic reactor. Anyway, the photoelectrocatalytic degradation of oilfield wastewater was much more favored at higher cell voltages. And this enhancement effect in the photoelectrocatalytic process may be attributed to both the capturing effect of photogenerated electrons and direct oxidation effect by external electric field, which promotes faster organic pollutants decomposition. Furthermore, more active chlorine produced in the photoelectrocatalytic reactor can further assist the degradation of organic pollutants when the cell voltage is higher. Thus, in all further experiments, the 30.0 V cell voltages were chosen as best for the degradation of the oilfield wastewater.

3.7. Effect of catalyst amount

To investigate the effect of catalyst concentration on COD removal efficiency of oilfield wastewater, and determine the optimal content of catalyst in the reaction mixture, the photoelectrocatalytic reaction was carried out with the catalyst content in the range from 0.5 to 2.5 g L^{-1}. Results represented in Fig. 9 showed that the COD removal efficiency increased with the increase in the catalyst concentration up to an optimum loading. Further increase in the concentration of the catalyst showed a negative effect on the COD removal efficiency. When the concentration was above 2.0 g L^{-1}, there was no significant change in the COD removal of oilfield wastewater. The similar results were

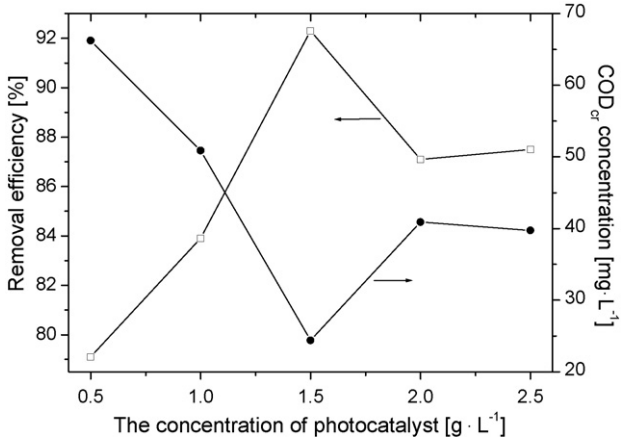

Fig. 9. Effect of catalyst amount.

obtained in Lathasree's experiments [40]. The change trend of optimal catalyst concentration observed in the experiment can be interpreted as following: as the weight of the catalyst increased, the numbers of pollutant molecules adsorbed are increased and at the same time the catalyst creates more active sites for the photoelectrocatalytic reaction owing to the increase in the number of catalyst particles. Thus the COD removal efficiency was enhanced firstly. As the weight of the catalyst increases further, the catalyst was up to a certain level, and the COD removal efficiency became highest. After exceeding the optimal amount of catalyst, the suspended catalyst particles might intercept the penetration of light toward the solution, and the UV light might be scattered by suspended catalyst [12,41].

3.8. Effect of initial pH value

The pH value is a key factor for the photocatalytic and photoelectrocatalytic degradation of charged organic pollutants because the pH value of solution will change the existed configuration of degraded species and surface charges of catalysts. The iso-electric point of TiO_2 is at pH between 4 and 6, hence, at more acidic pH values, the catalyst surface is positively charged while at pH value above 6, it is negatively charged [42]. Thus, for charged substrates, pH value will have a significant effect on photocatalytic degradation of organic pollutants while the effect is rather insignificant for neutral substrate [43]. The relationship between pH value and the COD removal efficiency of photoelectrocatalytic degradation of the produced wastewater in the reactor was studied by adjusting the initial pH values. The COD concentration and its removal profiles were all shown in Fig. 10. As shown in Fig. 10, we can easily see that the COD removal efficiencies decreased sharply with the increase of pH value, especially when the pH value is between 3 and 8.5, but decreased slightly after pH value reached ~8. That is, from these results, it is obvious that the photoelectrocatalytic degradation of this produced water is much favored in acidic solution than that in neutral and/or alkaline solution. Thus we can conclude that the pH value of oilfield wastewater has a dominant effect on the photoelectrocatalytic reaction because the dissociation of pollutants and the semiconductor's surface charge state, are all strongly pH dependent.

In this oilfield produced water, from mentioned above, the main substrates are grouped as phenol, substituted phenols and *n*-alkanes. All *n*-alkanes are existed in the water as neutral substances, while phenol and substituted phenols are all existed in water as weak organic acid. Thus phenol and substituted phenols may be presented in different forms depending on the pH value in the solution. Therefore, the pH value would have no effect on *n*-alkanes but have a significant effect on the adsorption–desorption properties of phenols at the catalyst's surface, and the initial pH value of solution might be an important parameter in photoelectrocatalytic degradation of this produced water. This reason can be explained that, the adsorption of substances onto TiO_2 is probably the first step in the process of photoelectrocatalysis like photocatalysis. Used phenol as a preventative of all phenolic compounds, at low pH values, phenol molecules presented in the neutral form may be easily be adsorbed onto the surface of TiO_2 with positive charges. When the pH value is larger than 8, the surface of TiO_2 gradually becomes negatively charged, and the adsorption of phenolic compounds onto TiO_2 becomes much more difficult than that at low pH values due to the repellent effect of two anionic species between the negatively charged surface of TiO_2 and the negatively charged dissociated phenolic compounds at high pH.

3.9. Toxicity assessment

In order to assess the photoelectrocatalytic decontamination of produced water, the toxicity of organic extracts of raw effluent and the degradation products at the reaction time of 240 min were studied by Ames tests with two strains of *S. typhimurium*, for example TA98 and TA100. The dose–response curves of extracts sample were presented in Fig. 11. From the figure, one can observe the extracts from raw effluent showed a significant mutagenic activity both in strains TA98 and TA100, and the detectable concentrations were 4, and 5 μg/plate for two strains, respectively. While the toxicity of extracted sample decrease greatly when the raw produced water was treated by photoelectrocatalytic technology for 240 min. The results showed that

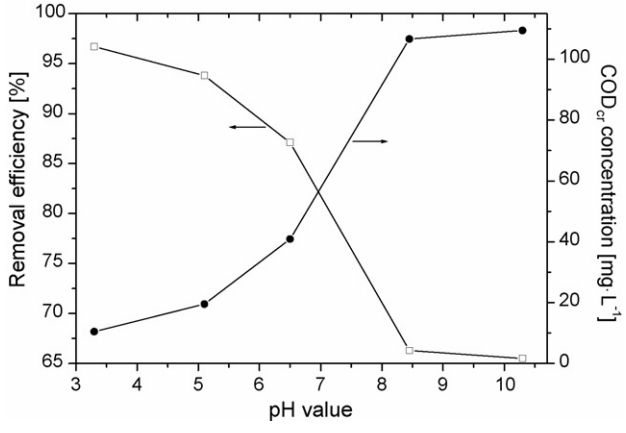

Fig. 10. Effect of initial pH value.

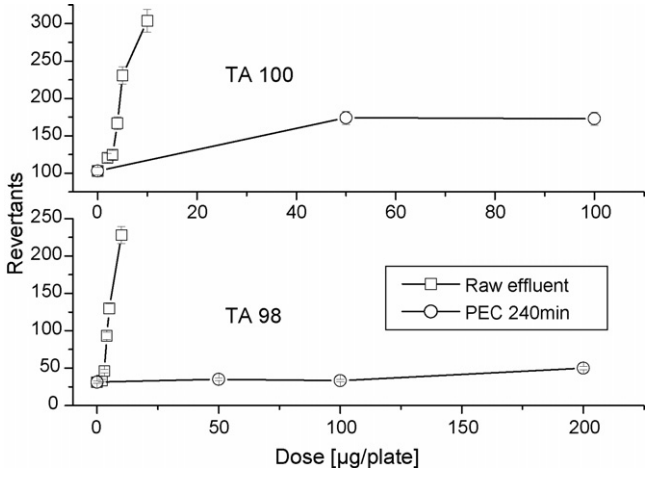

Fig. 11. Dose–response curves of extracted sample.

there is not any mutagenic activity even if the concentration is higher up to 200 μg/plate for strain TA98 or 100 μg/plate for strain TA100, respectively.

Therefore, it may be concluded that the photoelectrocatalysis is a quite efficient process for decontaminating the produced water, although there are high concentration of salt existed in oilfield wastewater. However, the complete understanding of toxicity change trend and the decontamination mechanism of produced water during different photoelectrocatalytic degradation stages will be published elsewhere.

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