

# Treatment of oilfield produced water with electrocoagulation: improving the process performance by using pulse current

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## ABSTRACT

The main aim of this study is to investigate the technical and economic feasibility of the pulse electrocoagulation (PE) process on the treatment of oilfield alkali/surfactant/polymer flooding produced water. By using an Fe electrode, the performance of the PE process was analyzed in terms of operating parameters such as pulse duty cycle, current density, pulse frequency, electrode distance, and reaction time with removal efficiencies, some of which are presented in figures and others are given in tables due to the numbers of parameters. Under the optimal conditions of a pulse duty cycle of 0.3, current density of 35 mA/cm<sup>2</sup>, pulse frequency of 3.0 kHz, electrode distance of 1.0 cm, and reaction time of 40 min, the removal efficiencies of chemical oxygen demand (COD), oils and greases, turbidity, total suspended solids, and polyacrylamide reach 98.3, 99.0, 98.8, 98.1 and 94.3%, respectively, with an energy consumption of 0.19 kWh/kg COD<sub>removed</sub> and an electrode consumption of 3.1 kg Fe/kg COD<sub>removed</sub>. The quality of the final effluent could satisfy the requirement of the national discharge standard. Compared with the traditional direct current method, the PE process could save 76% of the energy. Moreover, the treatment performance of PE is much better than traditional chemical coagulation treatment using polymeric ferric sulfate.

**Key words** | electrocoagulation, passivation, produced water, pulse current

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## INTRODUCTION

Oilfield produced water has become a hot research topic within the area of environmental engineering and applications in wastewater treatment due to its vast yield and potential hazards (Lu *et al.* 2009). To enhance oil recovery, alkali, polymers, surfactants and some other chemicals are increasingly widely used through injection into oil reservoirs, especially heavy oil reservoirs (Chang *et al.* 2006). These actions result in the production of a large quantity of wastewater with highly complex compositions and recalcitrant nature (Li *et al.* 2013). Effective treatment and a reuse

of produced water can mitigate scarcity of fresh water, especially in arid areas.

Alkali/surfactant/polymer (ASP) flooding produced water (AFPW) contains large amounts of residues of alkali, surfactants, polymers (mainly polyacrylamide, PAM), and emulsified oil. PAM can increase the viscosity of produced water and enhance the stabilization of oil-water emulsions, therefore raising the difficulty of the demulsification process and the subsequent treatment (Lu & Wei 2011). Traditionally, coagulation, sedimentation, filtration and their combinations are employed to treat produced water in Chinese oilfields. However, these processes have a low performance towards AFPW because of the high viscosity and very small oil droplet size in the wastewater, making the effluent quality not satisfy the reuse requirement for reinjection in oilfields (He *et al.* 2016). Effective treatment of AFPW is

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one of the difficult problems in the popularization and application of ASP flooding.

Wastewater treatment using electrochemical technologies has drawn extensive research attention in recent years due to several advantages including high energy efficiency, amenability to automation, easy handling, safety and versatility (Brillas & Martínez-Huitle 2015). These technologies mainly comprise electrodeposition, electrocoagulation, electroflotation, electrooxidation, electroreduction, electrochemical oxidation, etc. Among these approaches, electrocoagulation has gradually been used for wastewater treatment because of its advantages such as efficient and rapid organic matter separation, no need for pH control, easy availability of electrode materials, low requirement of chemicals, low sludge production, low operating costs (Martinez-Huitle & Brillas 2009). Electrocoagulation (EC) utilizes soluble metal (like Al and Fe) electrodes to form metal hydroxides by using current between immersed metal electrodes in wastewater, and these metal hydroxides serve as coagulants and/or adsorbents to remove inorganic and organic pollutants and pathogens. Electrocoagulation mechanisms may involve oxidation, reduction, decomposition, deposition, coagulation, adsorption, precipitation, and flotation.

Usually, direct current is used in electrocoagulation systems. In this case, an impermeable oxide layer may form on the cathode material as well as corrosion formation on the anode material because of oxidation. This passivation prevents the effective current transfer between the anode and cathode, so the performance of the electrocoagulation reactor declines in continuous operation mode (Martinez-Huitle & Brillas 2009). Fortunately the development of pulse electrocoagulation (PE) has been explored in recent years (Ren *et al.* 2011). PE uses 'on-off-on' power supply mode for electrolysis under the action of the electric field applied. In comparison with direct current electrocoagulation (DE), the electrode reaction is intermittent during PE, which is beneficial for the electrode surface diffusion, thus efficiently preventing electrode passivation caused by the concentration polarization phenomenon. Moreover, an intermittent power supply mode could greatly reduce energy consumption, since the actual electrification time is much less than the total EC reaction time (Ren *et al.* 2011).

In this study, the effects of pulsed voltage applications on EC performance were investigated using AFPW. The operating parameters were optimized through single-

factor experiments. Additionally, PE, DE, and chemical coagulation (CC) were compared in terms of treatment efficiency and energy consumption.

## MATERIALS AND METHODS

### Materials

The main reagents were analytical grade and used as received without further purification. Solutions were prepared using MilliQ-grade ( $>18.0\text{ M}\Omega/\text{cm}$ ) water. Commercial grade polymeric ferric sulfate (PFS) (purity: 98%) was obtained from Dongfang Water Purification Material Co., Ltd, Gongyi, China.

### Wastewater

The actual AFPW sample used in this study was collected from Daqing oilfield located in Heilongjiang province, China. The wastewater was allowed to settle for 24 h, the floating oil was skimmed off using filter paper, and then preserved at  $4\text{ }^{\circ}\text{C}$  before use. The wastewater quality parameters are listed in Table 1.

### Experimental set-up

A bench-scale reactor of 0.5 L with a virtual volume of 250 mL was made of Plexiglas® and used throughout the experiments.

**Table 1** | Characteristics of the AFPW used in the present study

Parameter	Unit	Value
pH	/	8.7
COD	mg/L	4,264
O&G	mg/L	156
Viscosity	mPa·s	1.48
Conductivity	mS/cm	3.52
Turbidity	FTU	317
$\text{CO}_3^{2-}$	mg/L	538
$\text{HCO}_3^-$	mg/L	4,263
Total dissolved solids	mg/L	8,346
TSS	mg/L	224
PAM	mg/L	330

The unit consisted of two pairs of electrodes made of plate steel with an effective area of 16 cm<sup>2</sup> for each electrode. The electrodes were arranged vertically in the reactor and the distance between the electrodes was adjustable. The reactor content was continuously mixed by a magnetic stirrer. The pulse current was supplied by numerically controlled dipulse galvanization power (model YS-9000D, Yisheng Electronic Science & Technology Co., Ltd, Shanghai, China). Direct current was provided using a digital direct current power supply (model YS900S, Yisheng Electronic Science & Technology Co., Ltd, Shanghai, China). The direct current power supply has an input of 220 V and a variable output of 0–30 V, with a variable current of 0–4 A being used.

All experiments were conducted at a constant temperature of 25 °C. In each run, 250 mL of wastewater was placed inside the EC reactor. Conductivity of the wastewater itself was used and no supported electrolyte was added. Before each run, electrodes were washed in a solution prepared by mixing 100 mL of HCl solution (36.5%) and 200 mL of hexamethylenetetramine aqueous solution (2.8%) to remove the oxide and passivation layers from the electrodes (Eyvaz *et al.* 2009). After each run, electrode surfaces were removed by dipping for 1 min in the abovementioned solution and washed thoroughly with deionized water to remove any solid residues on the surfaces, followed by drying and re-weighing. Electrocoagulated wastewater was filtered through a Whatman #40 filter paper after each run and then the filtrate was analyzed. At the end of each experiment, the amount of formed sludge (metal hydroxide flocs together with removed pollutants) was calculated by weighing the dried solid residue on the filter paper.

During PE experiments, the influences of peak current density, duty cycle and pulse frequency on treatment performance were investigated.

The CC experiments were conducted using jar test apparatus. In each run, 250 mL wastewater was added to a 500 mL beaker. The wastewater was stirred rapidly at 200 rpm for 2 min after a certain amount of PFS was dosed. After slow stirring at 50 rpm for 5 min, the wastewater was allowed to settle for 15 min. The supernatant samples were taken and analyzed.

In this study, each experiment was conducted in three replications to calculate the mean value and standard deviations.

## Analytical methods

Chemical oxygen demand (COD), oils and greases (O&G), turbidity, alkalinity, and total suspended solids (TSS) were determined by the procedure described in *Standard Methods for the Examination of Water and Wastewater* (APHA 2005). O&G measurements were performed with a Soxhlet extractor. The turbidity tests were performed with a HACH 2100AN turbidimeter (Hach Company, Loveland, CO, USA). The instrument was calibrated against formazin reference suspensions and thus the results are expressed as formazin turbidity units (FTU). Conductivity was measured with a portable conductivimeter (model SX713, Sanxin Instrument Factory, Shanghai, China). pH was measured using a portable pH meter (model PHS-3C, Leici Instrument Factory, Shanghai, China). The concentration of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> was measured by the titrimetric alkalinity method. PAM was measured by starch-CdI<sub>2</sub> spectrophotometry (Scoggins *et al.* 1979).

Energy and electrode consumptions are the main components of the operating cost. Thus, specific iron electrode consumption  $q$  (kg Fe/kg COD) and specific energy consumption  $Q$  (kWh/kg COD) was calculated according to Equations (1) and (2), respectively:

$$q = \frac{(m_0 - m_t)}{(\text{COD}_0 - \text{COD}_t)} \quad (1)$$

where  $m_0$  and  $m_t$  are the mass of the iron electrode at  $t = 0$  and  $t$ , respectively;  $\text{COD}_0$  and  $\text{COD}_t$  are the concentration of COD at  $t = 0$  and  $t$ , respectively.

$$Q = \frac{VIt\theta^2}{(\text{COD}_0 - \text{COD}_t)} \quad (2)$$

where  $V$  is peak voltage,  $I$  is peak current,  $t$  is reaction time, and  $\theta$  is pulse duty cycle (in the DE process there is  $\theta = 1$ ).

Pulse duty cycle  $\theta$  is defined as the ratio of power-on time to the whole cycle time (Equation (3)) (Ren *et al.* 2011):

$$\theta = \frac{t_{\text{on}}}{T} = \frac{t_{\text{on}}}{t_{\text{on}} + t_{\text{off}}} \quad (3)$$

where  $T$  is the pulse cycle time,  $t_{\text{on}}$  is the power-on time,  $t_{\text{off}}$

is the power-off time. Then the mean current value  $I_{\text{mean}}$  and the peak current value  $I$  have a relationship  $I_{\text{mean}} = I \times \theta$ .

## RESULTS AND DISCUSSION

### Effect of peak current density on PE

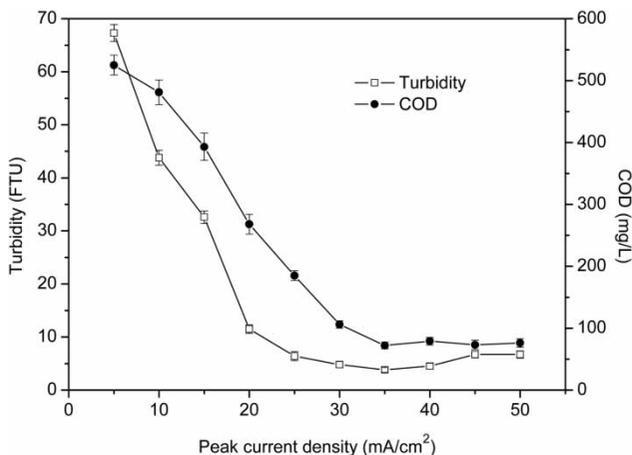
In all electrochemical processes, current density is the most important parameter for reaction controlling in the reactors. Current density can affect the growth of flocs by determining the production rates of flocs, and altering the size and pace of bubbles produced (Mollah *et al.* 2004). To investigate the effect of peak current density on PE performance, a series of experiments were carried out with current density being varied from 5 to 50 mA/cm<sup>2</sup> under the following conditions: pulse duty cycle of 0.3, pulse frequency of 3.0 kHz, electrode distance of 1.0 cm, and reaction time of 40 min.

The values of COD and turbidity versus the current density are presented in Figure 1. Obviously, the removal efficiencies of COD and turbidity are improved gradually with an increase in the current density. Higher current density promotes anode dissolution, producing more flocs in a fixed time (Ren *et al.* 2011). The presence of flocs in solution contributes to an enhancement of oil removal efficiency by flotation of the oil droplets, reduction of electrostatic repulsion between the air bubble and oil droplets and an increase

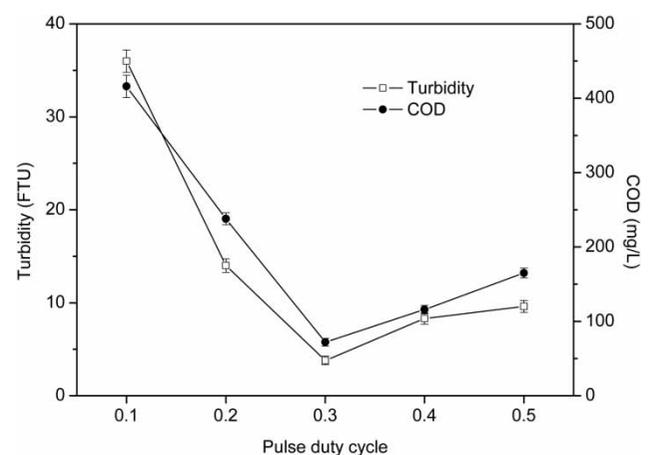
in oil droplet hydrophobicity. Moreover, the generation rate of bubbles increases and the bubble size decreases with current density. In addition, higher current density could provide some oxidation actions. These effects are favorable for destabilization of the emulsion and pollutant removal efficiencies. The removal efficiencies of COD and turbidity reach the maximum percentages of 98.3 and 98.8% separately at the current density of 35 mA/cm<sup>2</sup> (current of 0.56 A) (Figure 1). However, the treatment performance is not improved when the current density is further increased from 35 to 50 mA/cm<sup>2</sup>. Too high current density could increase the consumption of energy and electrode material and result in the formation of excessive flocs, which in turn would prolong the settling time. Therefore, the optimum current density of 35 mA/cm<sup>2</sup> was selected for the next experiments considering efficiency and cost of the process.

### Effect of pulse duty cycle on PE

PE treatments were carried out at a pulse duty cycle ranging from 0.1 to 0.5 under the following conditions: peak current density of 35 mA/cm<sup>2</sup>, pulse frequency of 3.0 kHz, electrode distance of 1.0 cm, and reaction time of 40 min. It can be noticed in Figure 2 that as the COD and turbidity decline the duty cycle is increased in the range of 0.1–0.3, and their lowest values are reached at the duty cycle of 0.3.



**Figure 1** | Effect of peak current density on variations in COD and turbidity during PE experiments. Conditions: pulse duty cycle of 0.3, pulse frequency of 3.0 kHz, electrode distance of 1.0 cm, and reaction time of 40 min. Error bars represent standard error from three independent trials.



**Figure 2** | Effect of pulse duty cycle on variations in COD and turbidity during PE experiments. Conditions: peak current density of 35 mA/cm<sup>2</sup>, pulse frequency of 3.0 kHz, electrode distance of 1.0 cm, and reaction time of 40 min. Error bars represent standard error from three independent trials.

Nevertheless, the COD and turbidity increase slightly when increasing the duty cycle from 0.3 to 0.5.

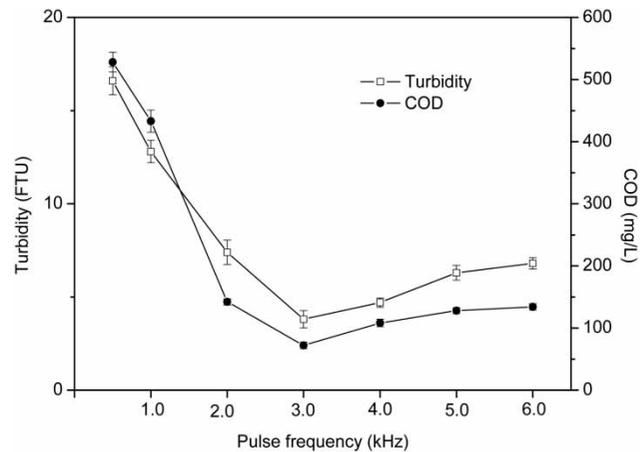
The pulse duty cycle is a particular parameter in PE compared to DE. According to Equation (2), energy consumption would be reduced with a low pulse duty cycle. Additionally, the dissolution of the Fe electrode was stopped during the power gap, thus Fe consumption could be greatly reduced. However, treatment duration would be prolonged with a lower duty cycle. At a higher duty cycle, the performance of PE is similar to that of DE due to the short power gap. The electrode surface proliferation is inefficient, leading to concentration polarization caused by electrode passivation. Moreover, the change of duty cycle may also affect the demulsification efficiency. AFPW is an oil-in-water emulsion with a high degree of emulsification because of the presence of a large number of amphiphilic molecules (such as PAM) and a large amount of oil. Emulsion has its critical breakdown field strength, and when the applied electric field intensity exceeds this critical value, the short circuit phenomenon may occur in the solution (Liu & Zhu 2003). The short circuit of emulsion would result in the formation of smaller-sized and more dispersed droplets, which increases the difficulty of demulsification. During PE treatment of AFPW, the short circuit of emulsion can be prevented by controlling the pulse parameters, rendering the pulse output time (pulse width) less than the short-circuit formation time and the pulse interval greater than the short-circuit disappearing time. Considering the treatment efficiency and energy consumption, the pulse duty cycle was controlled at 0.3 in this study.

### Effect of pulse frequency on PE

Pulse frequency ( $f$ ) is defined as the reciprocal of the cycle time:

$$f = \frac{1}{t_{on} + t_{off}} \quad (4)$$

Figure 3 shows the COD and turbidity values versus pulse frequency in the PE process under the following conditions: peak current density of 35 mA/cm<sup>2</sup>, pulse duty cycle of 0.3, electrode distance of 1.0 cm, and reaction time of 40 min. In the pulse frequency range of 0.5–3.0 kHz, the COD and



**Figure 3** | Effect of pulse frequency on variations in COD and turbidity during PE experiments. Conditions: peak current density of 35 mA/cm<sup>2</sup>, pulse duty cycle of 0.3, electrode distance of 1.0 cm, and reaction time of 40 min. Error bars represent standard error from three independent trials.

turbidity decrease with the increase of pulse frequency, and reach the lowest point at a pulse frequency of 3.0 kHz. However, higher pulse frequencies (3.0–6.0 kHz) cause decreased treatment efficiency (Figure 3). In the case of fixed peak current density and duty cycle, changing the pulse frequency would only affect pulse width and pulse interval. There are more cycles of current pulses at higher frequencies, which give a better chance for floc formation and thus higher pollutant removal efficiency. Nevertheless, the time of power-on and power-off time is reduced with the increase in pulse frequency. Thus, the anodic passivation caused during power-on duration can not be eliminated owing to the shorter pause time at higher pulse frequency. That is the probable reason why the removal efficiencies of COD and turbidity drop with the increase in pulse frequency from 3.0 to 6.0 kHz.

### Effect of electrode distance on PE

Electrode distance is an important variable in order to optimize the operating costs of electrolysis systems. The drop in ohmic potential of a cell is proportional to the electrode distance. The distance between electrodes also affects electrolysis energy consumption, and when the conductivity of the effluent is high, a larger spacing between the electrodes is possible. On the other hand, when conductivity is low, the spacing should be smaller (Drouichea *et al.* 2011). To determine the effect of electrode spacing, PE treatments were carried out at an electrode distance ranging from 0.5

to 2.5 cm under the following conditions: peak current density of 35 mA/cm<sup>2</sup>, pulse frequency of 3.0 kHz, pulse frequency of 3.0 kHz, and reaction time of 40 min.

As shown in Figure 4, the COD and turbidity fall down at first and then ascend with the increase in electrode distance. The removal efficiencies of COD and turbidity reach 98.3 and 98.8% separately at the optimum electrode distance of 1.0 cm. Short electrode distances inhibit ion diffusion between electrodes, and thus reduce the coagulation efficiency. On the contrary, the ion generation rate declines with the increase in electrode distance, and it is prone to generate larger and looser flocs that could enhance the coagulation performance (Ren *et al.* 2011). However, the electrode reaction rate could drop at an electrode distance above 2.0 cm. In addition, the electrical resistance and voltage increase with the increase in electrode distance, which causes higher energy consumption. Therefore, the electrode distance of the PE process was kept at 1.0 cm for efficiency, energy consumption and resource considerations.

### Effect of reaction time on PE

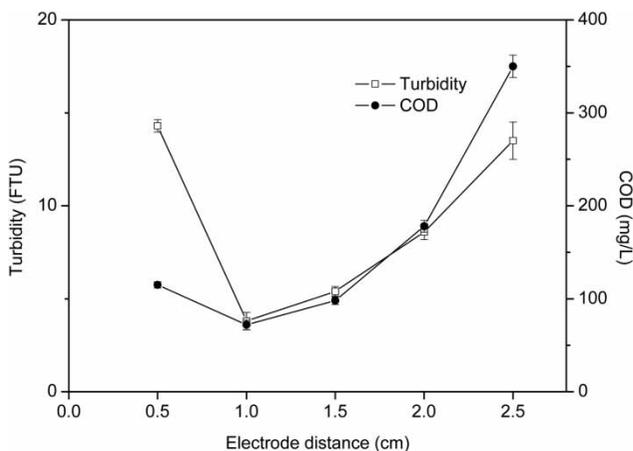
Similar to the current density influence on electrode dissolution, reasonable electrolysis duration should be provided to assure adequate current is applied to the sacrificial electrodes where the metal ions released by the dissolution form metal hydroxide species in the EC reactor. Meanwhile, energy and electrode material consumption increase with electrolysis

time, so it is essential to determine the optimum reaction time. To investigate the effect of reaction time on the PE, optimum parameters obtained from the former experiments were used: peak current density of 35 mA/cm<sup>2</sup>, pulse duty cycle of 0.3, pulse frequency of 3.0 kHz, and electrode distance of 1.0 cm.

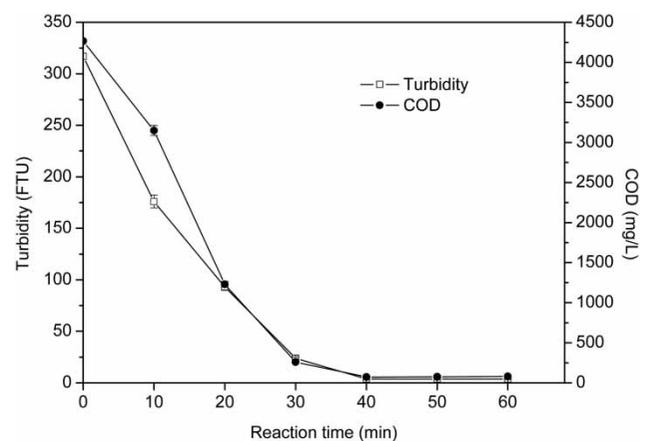
As shown in Figure 5, COD and turbidity exhibit regular variations, with a continuous decrease with time, reaching a constant value. The first 20 min gives a considerable removal of COD and turbidity (above 70%) of the initial wastewater. The increment in reaction time gives better results for the removal efficiencies, reaching 98.3% COD and 98.8% turbidity after just 40 min. However, with an increase in reaction time, the COD and turbidity remain constant and the emulsion becomes visually very clear. Only about 25% of removals are contributed by the latter 40 min. Therefore, the optimum reaction time was chosen as 40 min, considering the treatment efficiency and the economic factor. Based on the above investigations, the optimum conditions of PE were determined: pulse duty cycle, 0.3; current density, 35 mA/cm<sup>2</sup>; pulse frequency, 3.0 kHz; electrode distance, 1.0 cm; electrolysis time, 40 min.

### Effect of current density on DE

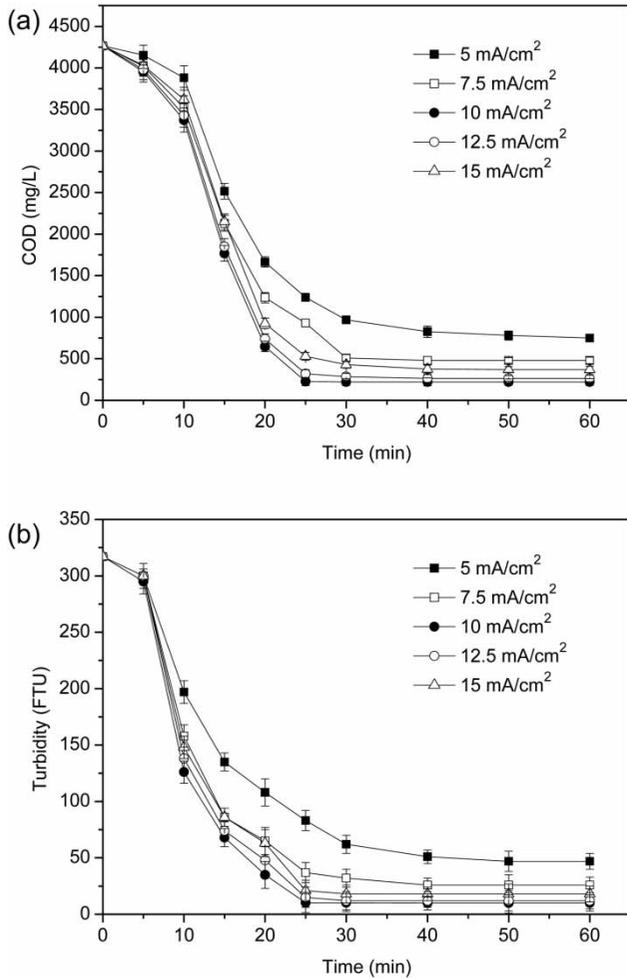
DE treatments were conducted using the same reactor for the PE process but with a direct current at an electrode distance of 1.0 cm. Figure 6 shows the influence of current



**Figure 4** | Effect of electrode distance on variations in COD and turbidity during PE experiments. Conditions: peak current density of 35 mA/cm<sup>2</sup>, pulse duty cycle of 0.3, pulse frequency of 3.0 kHz, and reaction time of 40 min. Error bars represent standard error from three independent trials.



**Figure 5** | Effect of reaction time on variations in COD and turbidity during PE experiments. Conditions: peak current density of 35 mA/cm<sup>2</sup>, pulse duty cycle of 0.3, pulse frequency of 3.0 kHz, and electrode distance of 1.0 cm. Error bars represent standard error from three independent trials.



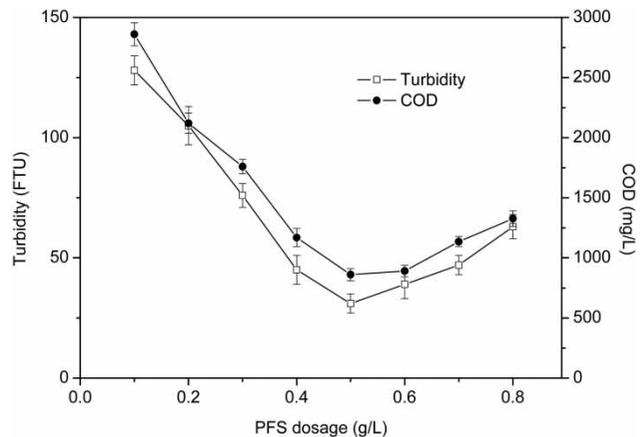
**Figure 6** | Effect of current density on variations in (a) COD and (b) turbidity with time during DE experiments. Electrode distance is 1.0 cm. Error bars represent standard error from three independent trials.

density on residual COD and turbidity with time at various current densities in the range of 5–15 mA/cm<sup>2</sup>. It may be seen that the current density of 10 mA/cm<sup>2</sup> gives the lowest COD and turbidity values (226 mg/L and 10.5 FTU, respectively) in 25 min, corresponding to removal efficiencies of 94.7 and 96.9%, respectively. After 25 min, the COD and turbidity reach constant levels at a current density of 10 mA/cm<sup>2</sup>. It is also observed that COD (or turbidity) removal is sluggish within the initial 5 min and later the removal becomes fast, followed by a very slow removal period again. This initial period of sluggish removal may be called the induction period. The induction period is smallest for a current density of 10 mA/cm<sup>2</sup>. At this current density, a thick oily layer is found at the top of the reactor.

### Effect of PFS dosage on CC

It has been demonstrated that coagulation is the most applicable and effective method for oil–water separation (Ma *et al.* 2013; Zhang *et al.* 2014). PFS is a pre-hydrolyzed coagulant, prepared by partial neutralization of ferric sulfate. PFS contains poly-nuclear complex ions, such as Fe<sub>2</sub>(OH)<sub>2</sub><sup>4+</sup>, Fe<sub>3</sub>(OH)<sub>4</sub><sup>5+</sup>, formed by the OH bridges and large number of inorganic macromolecular compounds with high positive charge, resulting in more efficient coagulation than the respective non-polymerized ferric coagulant (Zouboulis & Moussas 2008).

Figure 7 illustrates the effect of PFS dosage on COD and turbidity removal. It shows that as the coagulant dosage increases, the COD and turbidity decrease noticeably until the coagulant dosage of 0.5 g/L is reached. In addition, as the dosage is increased above 0.5 g/L, there is an increment in the COD and turbidity levels. Therefore, the optimum treatment efficiency is achieved at the dosage of 0.5 g/L, where the COD and turbidity values are 860 mg/L and 28.3 FTU, respectively. Figure 7 shows that there is a sharp decrease in the treatment efficiency as the coagulant dosage is increased from 0.5 to 0.8 g/L. The reason for the worsening performance with the increase of coagulant concentration is the overdosing effect, which is based on the chain bridging mechanism (Zhu *et al.* 2012). The polymer chains are attached to the particle surface at several points by adsorption to unattached segments that extend into the bulk of the liquid; the chain may loop back and attach to



**Figure 7** | Effect of PFS dosage on variations in COD and turbidity during CC experiments. Error bars represent standard error from three independent trials.

the same particle and other particles, eventually linking particles together to form an aggregate (Zhu *et al.* 2012). Therefore, the polymer would bridge between the particle surfaces only when the coagulant concentration is sufficiently small compared with the amount of saturated adsorption points. However, with less coagulant, the adsorption/bridging role would not work.

### Comparison of DE, PE and CC

Table 2 lists the effluent values of various parameters in the AFPW for DE, PE and CC processes under respective optimized conditions. It can be observed that only the effluent quality of PE treatment could meet the national discharge standard of China, the COD and O&G levels of DE treatment exceed the discharge limits, whereas only the TSS concentration reaches the discharge standard for CC. These results demonstrated that PE treatment has higher treatment efficiency than DE and CC processes towards the AFPW.

Electrocoagulation is proposed as an effective technique when metal hydroxides are used as coagulant, because it provides 100 times greater adsorption capacity on *in situ* hydroxides rather than on preprecipitated hydroxides (Mollah *et al.* 2004). When an iron electrode is used as the anode in an electrocoagulation reactor, it produces iron hydroxide,  $\text{Fe}(\text{OH})_n$ , where  $n = 2$  or  $3$ . At the cathode,  $\text{H}_2$  evolution occurs by the following reaction (Equation (5)):



These tiny bubbles contribute to flotation of the flocculated particles to the surface of the wastewater. Moreover, the presence of NaCl in wastewater makes feasible the anodic oxidation of  $\text{Cl}^-$  to active chlorine species such as  $\text{Cl}_2$ ,  $\text{HClO}$  and  $\text{ClO}^-$ , which can oxidize organics (Wei *et al.* 2012). Moreover, no additional chemicals are needed in electrocoagulation processes, since the ‘electron’ is the main reagent in the electrolytic reactor. This minimizes sludge generation and eliminates the detrimental effects of reagents and chemicals used in the conventional CC process (Mollah *et al.* 2004).

In this study, PE exhibits higher performance than DE (Table 2). This is because the electrode passivation in PE could be avoided or lessened relative to DE (Ren *et al.* 2011). As observed in previous research, the electrode surface was more seriously corroded and uniform in PE than that in DE (Ren *et al.* 2011). In the DE process, the anode electric potential is raised and  $\text{Fe}^{2+}$  is continuously generated, so the  $\text{Fe}^{2+}$  concentration around anodes is increased and a dense oxide layer is formed on the electrode surface. However, in PE,  $\text{Fe}^{2+}$  could diffuse into solution and the oxide layer could be dissolved by  $\text{H}^+$  near the electrode, which succeeds in avoiding electrode passivation and thus improves current efficiency (Ren *et al.* 2011).

Table 3 shows that under the respective optimum conditions, the energy consumption of PE is much lower than that of DE, and the PE process could save 76% of the energy relative to the DE process. There is no obvious difference in specific iron electrode consumption and sludge yield in these two processes.

**Table 2** | Performance comparison of DE, PE and CC processes

Parameter	Effluent value			Removal (%)			Discharge standard <sup>a</sup>
	DE	PE	CC	DE	PE	CC	
COD (mg/L)	226	72	860	94.7	98.3	79.8	≤100 mg/L
O&G (mg/L)	5.9	1.6	25.7	96.2	99.0	83.5	≤5 mg/L
Turbidity (FTU)	10.5	3.7	28.3	96.9	98.8	91.1	≤15 FTU
TSS (mg/L)	10.1	4.3	17.5	95.5	98.1	92.2	≤20 mg/L
PAM (mg/L)	44.2	18.8	71.6	86.6	94.3	78.3	–

<sup>a</sup>Chinese discharge standard for water pollutants (GB18918-2002). DE conditions: current density, 10 mA/cm<sup>2</sup>; electrode distance, 1.0 cm; electrolysis time, 25 min. PE conditions: pulse duty cycle, 0.3; current density, 35 mA/cm<sup>2</sup>; pulse frequency, 3.0 kHz; electrode distance, 1.0 cm; electrolysis time, 40 min. CC conditions: PFS dosage, 0.5 g/L.

**Table 3** | Comparison of DE and PE regarding electrode consumption, energy consumption, and sludge yield

Item	DE	PE
Electrode consumption (kg Fe/kg COD <sub>removed</sub> )	3.4	3.1
Energy consumption (kWh/kg COD <sub>removed</sub> )	0.78	0.19
Sludge yield (kg/kg COD <sub>removed</sub> )	5.5	5.3

DE conditions: current density, 10 mA/cm<sup>2</sup>; electrode distance, 1.0 cm; electrolysis time, 25 min. PE conditions: pulse duty cycle, 0.3; current density, 35 mA/cm<sup>2</sup>; pulse frequency, 3.0 kHz; electrode distance, 1.0 cm; electrolysis time, 40 min.

## CONCLUSIONS

The results of the present study demonstrate that the PE technique can efficiently treat AFPW. Under the optimized conditions, the effluent meets the national discharge standard. This process shows much higher performance than CC using PFS, and it has an obvious advantage over DE process regarding energy saving.

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