

Advanced Treatment of Biologically Pretreated Coking Wastewater by Electro-Coagulation: Degradation Behavior and Mechanism

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Abstract

In the present study, the electro-coagulation (EC) process has been first applied to advanced treatment of biologically pretreated coking wastewater (BPCW), and the degradation behavior and mechanism were investigated by means of a lab-scale EC in static methods. The results showed that the percent COD and color removal can reach 80.5% and 95.4%, respectively, under optimal conditions (initial pH 8.0, reaction time 30 min, current density 14.0 mA/cm², and NaCl dosage 1.6 g/L). The pseudo-second-order kinetic model fit well with the kinetic data of COD in the treatment of BPCW by EC process. The compositional evaluation of EC flocks and treated wastewater by FT-IR and UV-Vis indicates that the residual organics from BPCW might be removed through electro-oxidation, chemical complexation, and EC sludge adsorption. The energy consumptions per unit of pollutants were obtained as 12.26 kW·h/kg COD (RMB ¥ 6.13 /kg COD). It is proved that the treatment of BPCW using the EC process is very effective with a lower operating cost.

Keywords: coking wastewater, electro-coagulation, advanced treatment, electrochemical treatment

Introduction

Coking wastewater originates from the process of destructive distillation of coal at high temperature in the absence of air. The composition of coking wastewater is very complex due to various factors, such as the quality of coal, coking temperature, recovery technology for coking product, and so on. And it is refractory to be treated by conventional biological processes since it contains high concentrations of toxic compounds (such as phenols, cyanides, thiocyanate) [1-2]. Moreover, more and more attention has been paid to the removal of persistent

organic pollutants (POPs) such as polycyclic aromatic hydrocarbon (PAHs) in coking wastewater due to the long-term environmental toxicity in spite of extremely low concentrations in coking wastewater [3].

Nowadays in China, some advanced biological treatment processes such as anaerobic-anoxic-oxic (A-A-O), anoxic-oxic (A-O), and sequencing batch reactor (SBR) with long hydraulic retention time have still been extensively used in most coking wastewater treatment plants for the reason of lower operating costs. However, the presence of concentrations of toxic, refractory, and inhibitory compounds (e.g., phenols, sulfides) in the coking wastewater sometimes has resulted in effluents containing high concentrations of chemical oxygen demand (COD) and other toxic pollutants [4-7].

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It should be noted that coal is still treated as one of the main energy sources in China, and the discharge of biological pretreated coking wastewater (BPCW) into the environment has caused serious health risks in major coal areas in recent years [8]. Hence, it is very important to choose effective and economical processes for advanced treatment of coking wastewater. The present study shows that some new processes have achieved positive progress, which has been extensively applied in advanced treatment on coking wastewater in order to fulfill environmental discharge requirements. These technologies include biological enhancement, adsorption, advanced oxidation processes, etc. [9-20].

Electro-coagulation (EC) is an electro-chemical method of treating wastewater. It depends on dissolving sacrificial anodes to generate active coagulant precursors (usually iron/aluminum cations), then react with negatively charged particles in the solution to form flocks. The gases produced at the cathode during the electrolysis of water and metal dissolution allow the resulting flocks to float. It was usually used for the removal of both color and colloidal particles [21-23]. The mechanism of EC process is generally considered to involve three possible behaviors: electro-coagulation, electro-flotation, and electro-oxidation [24-25]. As electro coagulation processes do not require the addition of any chemical coagulants, it has been successfully applied on the industry of effluent treatment, which has been proven to be an economical and effective process [26-34].

To our best knowledge, little work in the existing literature has carefully and quantitatively addressed the advanced treatment process of BPCW via EC technology. In order to improve the removal of organic pollutants from BPCW, the effects of various operating conditions such as current intensity, reaction time, electrolyte dosage, and initial pH on the elimination of COD and color were investigated. The compositional evaluation of EC sludge production and treated wastewater by EC was assessed by UV-Vis and FT-IR, respectively. In addition, energy consumption per unit weight COD during the EC process were also evaluated. The objective of this study was to investigate the optimal conditions and removal mechanisms for advanced treatment of BPCW by the EC process. Particularly, this information is essential for scaling up the treatment to the industrial level.

Materials and Methods

Raw Wastewater

The tested sample was obtained from the effluent well of coking wastewater treatment (floatation-anaerobic-anoxic-oxic) plant located in Wuhu city (Anhui Province in China). Its color is deep dark red with a certain level of turbidity. It was characterized by the following relevant parameters, and the wastewater characteristics are given in Table 1. It is obvious that the effluent is much too refractory for further biological treatment ($BOD_5/COD < 0.085$).

Table 1. Characteristics of coking wastewater used in all experiments.

| | |
|-------------------------------------|-------------------------|
| pH | 6.0~9.0 |
| COD (chemical oxygen demand) | 425~490 mg/l |
| TOC (total organic carbon/) | 312~334 mg/l |
| BOD_5 (biochemical oxygen demand) | 34.5~39.2 mg/l |
| NH_4-N (ammonia nitrogen) | 8.2~22.4 mg/l |
| TN (total nitrogen) | 24~37 mg/l |
| TSS (total suspended solids) | 136~182 mg/l |
| Color | 350~267 ADMI color unit |
| TDS (total dissolved solids) | 1857~2245 mg/L |
| Volatile phenol | 0.03~0.07 mg/l |
| Total cyanide | 0.15~0.23 mg/l |
| Oil and grease | 0.58~1.25 mg/l |
| Turbidity | 152-179 NTU |

Analysis Methods

COD were measured according to the standard methods for examination of water and wastewater [35]. Color was determined by the APHA platinum-cobalt method using a spectrometer (721 N, Beijing, China) set at 455 nm wavelength [27], and distilled water was used as a blank. pH of solution was measured by a pH meter (PHS-3C, Leici, Shanghai). The UV-vis spectrum of tested wastewater sample was analyzed using UV-vis spectrophotometer (UV-2550, Shimadzu, Japan). FT-IR analysis of EC treatment flocks were carried out by FT-IR spectrometer (IRPrestige-21, Shimadzu, Japan) using potassium bromide pellets (sample: KBr=1:50) in range 4000-400 cm^{-1} with 2 cm^{-1} resolution. In order to avoid interference from suspended matter with the result, the wastewater sample was centrifuged before examination. The efficiency of the EC process was determined in terms of the COD/color of the initial and treated sample, which was calculated using Eqs. (1):

$$\text{Removal (\%)} = (C - C_0) / C_0 \quad (1)$$

...where C_0 and C are the initial and final COD/color values of the tested samples, respectively.

Equipment and Experimental Procedure

The EC treatment for tested wastewater was performed in a cylindrical glass cell with a working volume of 500 mL. The contents in the reactor were agitated by a magnetic stirrer to avoid concentration gradients with stirring at constant speed (150 r/min). The electrodes were kept 10 mm above the bottom of the reactor. The

wastewater was adjusted to the desired pH for each experiment using sodium hydroxide or sulfuric acid. The monopolar iron (Fe) plate electrodes (150 mm×50 mm×2 mm) were employed owing to its innocuity compared with Al^{3+} ions. The distance between both electrodes was 20 mm. Before each test case, electrodes were polished thoroughly, washed with 0.1 mol/L HCl and 0.1 mol/L NaOH solution to remove surface rust and grease, and rinsed with distilled water and dried naturally for use. The electrodes were connected to terminals of a DC power supply with an actual total effective immersion area of 130 cm². After the electro-coagulation process, the treated wastewater sample was measured for color removal efficiency, adjusted pH to 9.6, and filtered by 0.45 μm filter membrane to diminish the interference of Fe^{2+} for COD measurement. All experiments were carried out in duplicate three times and in static and batch modes at room temperature.

Results and Discussion

Effect of Initial pH

Fig. 1 shows actual appearance of the coking wastewater before and after treatment, showing that the effluent is clear and transparent compared with raw water. It has already been established that the initial pH is one of the key parameters influencing the performance of electro-coagulation [36]. Fig. 2 depicts the influence of percent COD and color removal on initial pH from 4.0-11.0. It can be seen that the effect of COD removal rate could be improved when the initial pH value increased from 4.0 to 7.0, and then there was a decrease with the increase of initial pH from 7.0 to 11.0. The higher COD removal efficiency was obtained in neutral and alkaline medium, especially within a 7.0-9.0 range. The maximum percent COD removal rate was 79.4 % when initial pH was 8.0. However, percent color removal had a similar increasing trend by increasing initial pH from 4.0 to 8.0, and is almost constant from 8.0-11.0. The optimum percent color removal rate of 92.5% was observed at pH of 9.0.

This phenomenon can be explained by the fact that iron hydroxide precipitates, iron complexes, and iron cations could be replied significantly on the pH of solution [37]. $Fe(OH)^{2+}$, $Fe(OH)_2^+$, and $Fe(OH)_3$ species may be presented under acidic conditions. Under alkaline conditions, $Fe(OH)_4^-$ and $Fe(OH)_6^-$ ions may also be present. When the acidity of the solution is too high, the binding capacity of H^+ and OH^- is stronger than Fe^{2+}/Fe^{3+} in the strong alkaline solution. The cathodic reaction is suppressed, then current intensity decreased, and the anode is difficult to be dissolved to generate Fe^{2+}/Fe^{3+} . Therefore, the amount of polymeric species will decrease sharply and the negatively charged organic pollutants macromolecule would not be easily adsorbed onto the positively charged precipitates, resulting in the lower removal rate [38]. The difference between initial and final pH values diminishes

for the initial $pH > 9.0$, suggesting that electro-coagulation exhibits some pH buffering capacity. These results were observed also by other investigators [39]. Considering the simultaneous percent COD and color removal, pH 8.0 was adjusted before electrochemical treatment in the following experiments.

Electrolyte Dosage

Experiments were carried out at various electrolyte dosages in order to verify the effect of electrolyte on COD and color removal efficiency. As can be seen in Fig. 3, percent COD removal rate increased from 52.5% to 81.2% with increasing the NaCl dosage from 0.2 to 1.6 g/L, and a further increase in the NaCl dosage between 1.6-2.4 g/L did not yield any improvement on the percentage COD removal. Then COD removal efficiency decreased from 81.7 % to 71.2 % with the continuously increasing NaCl dosage. However, we found that there was an increasing percent color removal from 55.4% to 95.4% with the increase of NaCl dosage from 0.2 g/L to 2.4 g/L, and then

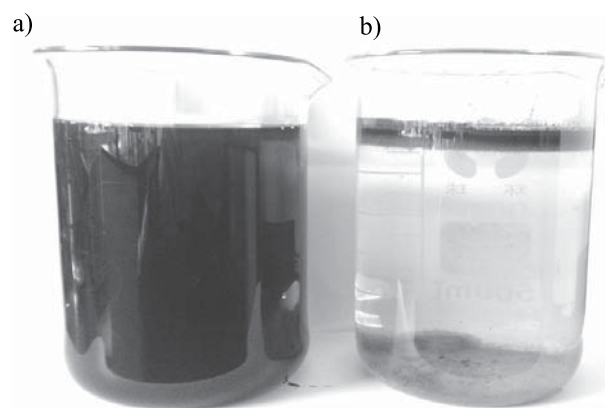


Fig. 1. Raw wastewater and effluent of electro coagulation treatment (a. raw wastewater, b. treated effluent).

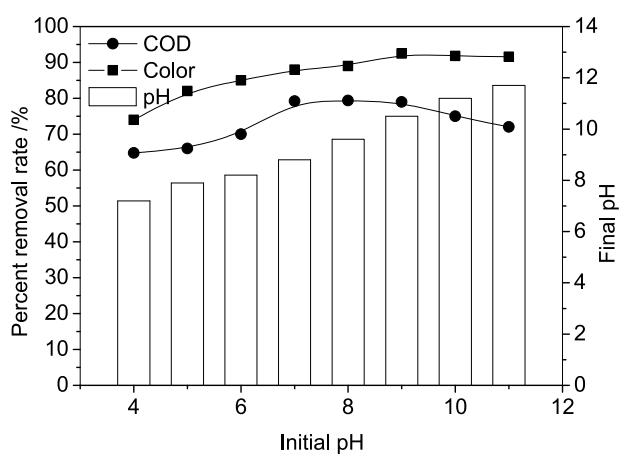
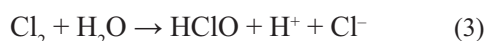


Fig. 2. Effect of COD and color removal on initial pH (conditions: reaction time=40 min, NaCl electrolyte dosage=1.0 g/L, electrode distance=2 cm, initial COD concentration=468 mg/L, current density=20 mA/cm²).

remained constant. The optimum color removal rate was attained at NaCl dosage of 2.4 g/L.

The previous studies show that secondary reactions (see Eqs. 2-4) may also occur using NaCl as an electrolyte if anode potential is sufficiently high [40]. Therefore, the enhancement of color removal in this experiment may imply that the removal of macromolecule organic pollutants was due to the intensity of the break of chromogenic chemical bonds by electro-chemical degradation as a result of the indirect oxidation by hypochlorite. A similar observation was also found by Daneshvar et al. [21], who reported that the color removal was enhanced by electro-coagulation when treating dyed wastewater. However, excessive NaCl addition causes the production of extra ClO^- , which would oxidize ferrous ion and polymeric species into ionic hydroxide and small molecular soluble substance in water so as to reduce COD adsorption, complexation properties and floatation performance, but contribute to color removal [41]. Furthermore, the addition of NaCl can effectively reduce the voltage of electrolyzer under the stable current density, thereby reducing energy consumption. Hence the optimal NaCl dosage is 1.6 g/L in terms of the running cost and pollutant removal efficiency.



Effect of Current Density

It has already been reported by several authors that current density has significant influence on the efficiency of the electro-coagulation process [42]. The influence of COD and color removal efficiency on current density was investigated. The results are shown in Fig. 4. It was found that the COD removal efficiencies can reach 35.4% at current density of 4 mA/cm², and then increased

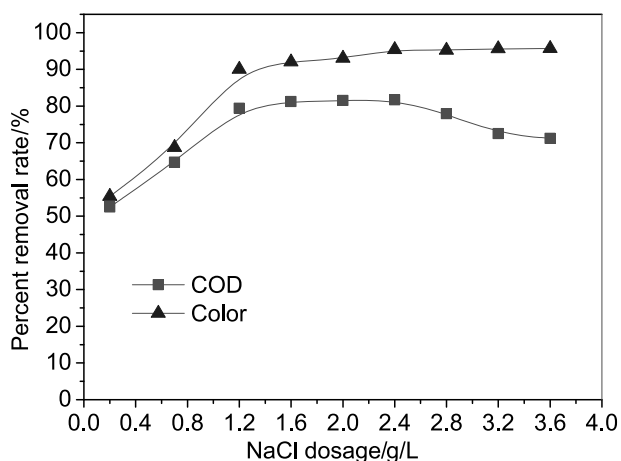
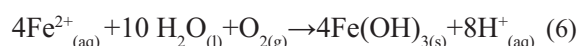
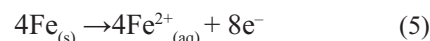


Fig. 3. Effect of current density on COD and color removal (pH=8.0, reaction time=40 min, electrode distance=2 cm, initial COD concentration=479 mg/L, current density=20 mA/cm²).

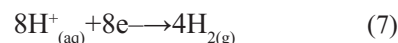
significantly to around 80.5% when the current density ascended to 14.0 mA/cm². It reached the maximum percentages of 81.7% at current density of 18 mA/cm², and then remained nearly constant with a continuous increase of current density. These results were similar to those observed with industrial wastewater [43-44]. The color removal efficiencies also shows a similar variation and it was evident that the rapid color elimination of 94.5% can be achieved during 4.0~14.0 mA/cm², then percent color removal efficiency present a slow rise as the current density was raised. Energy consumption went up to 0.01 and 0.26 kW·h/kg COD, increasing current density from 4.0 to 34.0 mA/cm², and then increased sharply with a current density increase from 34.0 to 38.0 mA/cm².

This may be attributed to the fact that a higher current density would provide a higher oxidation action [45] and higher rates of anode dissolution, affecting the production of hydroxyl compounds, complex compounds with hydroxyl iron, and the growth of coagulant (flocks formation) [46], thus pollutant removal from BPCW was influenced by complexation, electrostatic attraction, and adsorptions, and then COD removal efficiency was enhanced (see Eq. 5-7) [47],

Anode:



Cathode:



It was obvious that the decolorization rate was greater than COD at the same current density, which indicates that electric-oxidation process by EC just broke the chemical bond of chromogenic substance from BPCW, and produced some small organic molecules. Furthermore, a higher percentage color removal at a lower current density might account for the electro-oxidation process being the

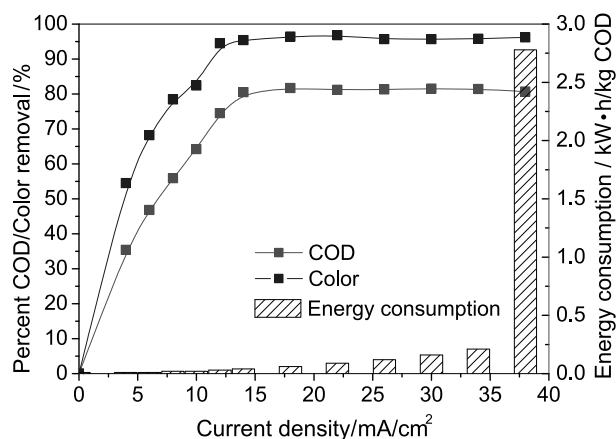


Fig. 4. Effect of current density on COD and color removal (conditions: pH=8.0, reaction time=40 min, electrode distance=2 cm, NaCl electrolyte dosage=1.6 g/L, initial COD concentration of raw wastewater=485 mg/L).

main EC reaction mechanism, and increasing high current density resulted in an increase of energy and electrode material consumption. Therefore, the optimum current density of 14 mA/cm² (current of 1.8 A, voltage of 2.5 V) was selected, taking into account energy consumption and COD removal efficiency.

Effect of EC Reaction Time and Reaction Kinetics

Fig. 5 illustrates that the effect of COD removal efficiency on reaction time at the different initial COD concentrations of wastewater. A series of experiments were performed where the reactor performance was as follows: current density of 14 mA/cm², pH of 8.0, NaCl dosages of 1.6 g/L, electrode distance of 2.0 cm, and initial COD concentration of 228-457 mg/L. It was obviously found that a fast COD reduction around 75% in the first 30 min was observed, and then decreased gradually, ranging

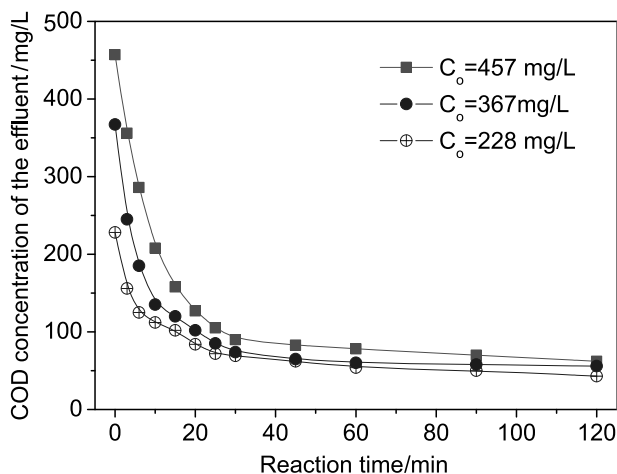


Fig. 5. Effect of reaction time on COD and color removal (initial pH=8.0, NaCl electrolyte dosage=1.6 g/L, electrode distance of 2.0 cm and current density=14.0 mA/cm², initial COD concentration=457 mg/L).

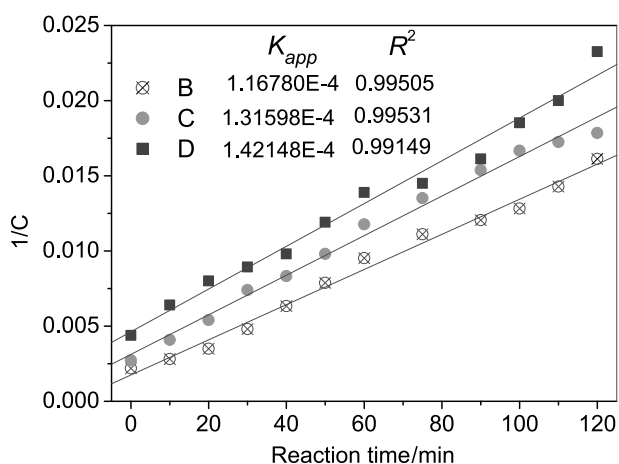


Fig. 6. The pseudo-second-order rate linear fitting constants.

30-120 min. Only 5-11% of removals were contributed by the following 90 min.

In general, the kinetics for the removal of COD were evaluated with the pseudo-second-order kinetic model represented in Eqs. 8-9, and the equations can be simplified by assuming the generation of aluminum/ferric hydroxide constant for a given current density.

$$\frac{dC}{dt} = -k_{ap} C^n \quad (8)$$

$$\frac{1}{C} - \frac{1}{C_0} = k_{ap} t \quad (9)$$

...where C_0 , C is the influent and effluent COD concentration respectively (mg/l), t is the reaction time (min), and k_{ap} is the pseudo-second-order reaction rate constant (min⁻¹), which can be estimated from the plot $[1/C]$ versus reaction time.

Obviously, k_{ap} is mainly related to the initial concentration of wastewater, which is presented in Fig. 6. The results show that the kinetics modeling fitted very well with all reactions ($R^2 > 0.95$), demonstrating that the electro coagulation degradation of coking wastewater is adequately described by the pseudo-second order kinetics model. Moreover, it can be observed that k_{ap} of COD degradation decreased gradually with continuous increase of C_0 from 228 mg/L to 457 mg/L.

UV-Vis

The UV-Vis spectra of the raw and the treated wastewater with different reaction time are shown in Fig. 7. It can be seen from raw wastewater that there are many strong peaks over the range of 275-370 nm, which corresponds to the maximum absorption wavelength band of reprehensive pollutants for single-ring aromatic compounds such as phenol, polycyclic aromatic hydrocarbons, and heterocyclic

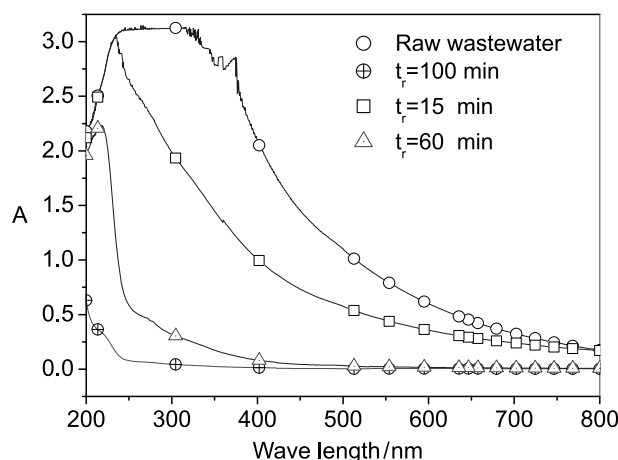


Fig. 7. UV-vis absorption spectra of raw and treated wastewater (Conditions: initial pH=8.0, NaCl electrolyte dosage=1.6 g/L, electrode distance of 2.0 cm and current density=14.0 mA/cm, initial COD concentration=464 mg/L).

nitrogen compounds such as naphthalene, quinoline, insole, and acridine. Furthermore, it is interesting to note that the overall absorbance of the curve decreased significantly with the increase of EC treatment reaction times ascended, which may be due to the removal of colloidal and suspended particles. However, there are no peaks in the spectra corresponding to components of the treated wastewater with reaction time of 100 min, but only a continuous rise over the range of 240-300 nm. Compared with the percent COD/color removal and UV-Vis at the different EC reaction times (15 min, 60 min, 100 min), this suggests that the refractory compounds from BPCW have been oxidized and decomposed, and not completely mineralized to CO_2 and H_2O [48]. Some small molecule organic compounds were produced in the EC reaction, although chromophoric groups have been destroyed. Meanwhile, it can be found that the effect of reaction time on the decolorizing coking water is significant.

FT-IR of Sludge

Fig. 8 shows the FT-IR spectrum of the EC flocks generated at optimum reaction conditions. Peaks at $3,442\text{ cm}^{-1}$ corresponding to H–O–H bond stretching at $1,637\text{ cm}^{-1}$ to hydroxyl bending and $\gamma(\text{OH})$ water bending vibration or overtones of hydroxyl bending [49], which indicates that hydroxide species were the prominent form of the generated flocks [50]. A band around $2,062\text{ cm}^{-1}$ represents the complex of CN-Fe precipitates [51], and a band of $1,521\text{ cm}^{-1}$ shows the skeleton-stretching benzene. Bands at $1,091$ and $1,043\text{ cm}^{-1}$ were attributed to the bending vibration of Fe-OH of the lepidocrocite surface. The previous studies show that wavelengths of 893 cm^{-1} and 795 cm^{-1} represent the generation $\alpha\text{-FeOOH}$, which is the distinguished proof of $\alpha\text{-FeOOH}$ instead of $\alpha\text{-Fe}_2\text{O}_3$ by IR spectroscopy [52-53]. Thus it can be considered that the organic pollutants might be removed through complexation and adsorption by the iron hydroxide precipitates.

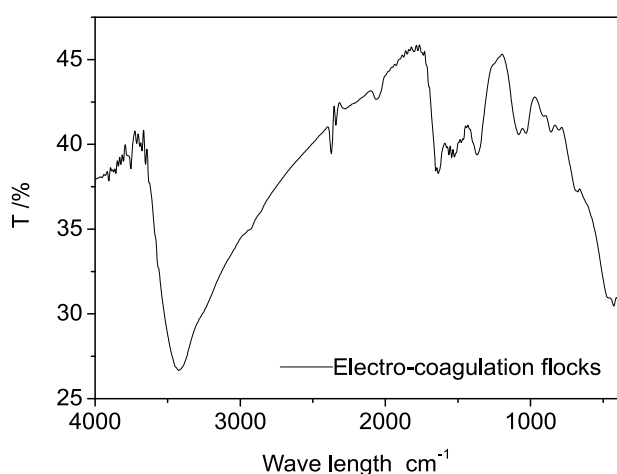


Fig. 8. FT-IR of flocks (conditions: initial pH=8.0, NaCl electrolyte dosage=1.6 g/L, electrode distance of 2.0 cm and current density=14.0 mA/cm², initial COD concentration=464 mg/L, reaction time=100 min).

Cost Analysis

The cost of the electro-coagulation operation mainly depends on the sacrificial electrode weight loss and the electrical energy consumption per unit of removed pollutants. Energy consumption mainly composed of the electrical energy consumed as kW·h/kg COD and the electrical energy price as RMB/kW·h. Eq. 10 can be used to calculate the cost of electro-coagulation in this experiment per unit of kg COD.

$$E = \frac{(\int J \cdot A_e \cdot U \cdot dt) \cdot P_e + L_{Fe} \cdot P_{Fe}}{60 \cdot V \cdot (C_i - C_e)} \quad (10)$$

...where E is the cost per unit removed COD (RMB/kgCOD), U is the applied voltage (V), J is the current density (mA/cm²), A_e is the effective superficial area (cm²), t is retention time (h), P_e is the electrical energy price (RMB/kW·h), L_{Fe} is the sacrificial electrode (Fe) per unit removed pollutants (kg Fe/kgCOD), P_{Fe} is the price of Fe (RMB/kg Fe), C_i is the initial COD concentration (mg/L), C_e is the concentration value of COD (mg/L) at time t , and V is total volume of the wastewater (L).

In general, short contact time is preferred for operational costs per unit pollutants removal [54]. Fig. 9 represents the operating cost analysis of coking wastewater treatment by electro-coagulation at an optimum current density of 14.0 mA/cm^2 by varying the electrolysis time from 0 to 120 min. It could be concluded from the figures that the most economical percent COD removal of 80% was attained at the reaction time of 30 min, taking into account the achievement of effluent discharge standards. When the applied current density is applied as 14 mA/cm^2 , unit energy consumptions were obtained as $12.26\text{ kW}\cdot\text{h/kgCOD}$ (RMB ¥ 6.13 /kg COD)-treated biologically treated wastewater. The total consumed electricity should be $0.225\text{ kW}\cdot\text{h}$ and the sacrificial electrode loss is 9.54 g of iron when 0.018 kg COD was removed.

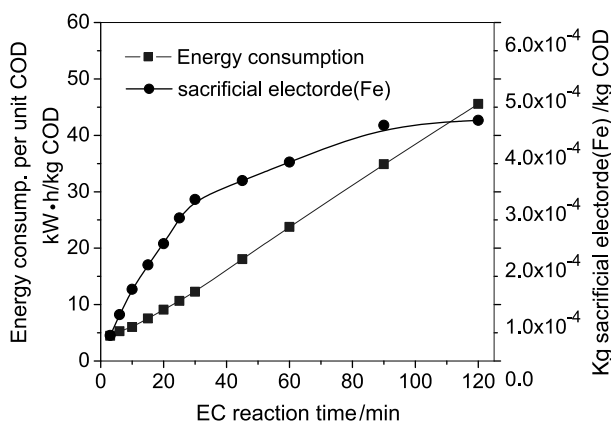


Fig. 9. Cost analysis and sacrificial electrode mass of EC reactor (Conditions: initial pH=8.0, NaCl electrolyte dosage=1.6 g/L, electrode distance of 2.0 cm and current density=14.0 mA/cm², initial COD concentration=457 mg/L).

Conclusions

From this work, the following conclusions can be drawn:

1. The electro-coagulation process has been applied to the advanced treatment of biologically pretreated coking wastewater. The results about the discolorations and organic pollutant degradation showed that the removal efficiencies of COD and chlorite of organic pollutants were significantly influenced by initial pH, reaction time, current density, and electrolyte dosage.
2. Under the optimal conditions (initial pH 8.0, electro coagulation reaction time 30 min, current density 14.0 mA/cm², electrolyte dosage of NaCl 1.6 g/L), the percent removal of COD and color can reach 80.5% and 95.4%, respectively. The kinetic results indicate that electro coagulation can be adequately described by a pseudo-second-order kinetics model that fit well with all reactions.
3. The UV-Vis analysis suggests that organics produced in the reaction have been oxidized into small molecule acids not completely mineralized to CO₂ and H₂O, although chromophoric groups have been destroyed. The FT-IR spectrum of the electro coagulation sludge revealed that the refractory organics might be removed through electro-oxidation, complexation, and adsorption with the iron hydroxide precipitates.
4. When the applied current density is 14 mA/cm², unit energy consumptions were obtained as 12.26 kW·h/kg COD (RMB ¥ 6.13 /kg COD) biologically treated wastewater. The total consumed electricity is 0.225 kW·h, and the sacrificial electrode loss is 9.54 g of iron when 0.018 kg COD was removed. This indicated that the advanced treatment of biologically pretreated coking wastewater by the EC process is effective for a lower operating cost (1.11 RMB/kgCOD, 1.25 kg RMB / m³) than normal advanced treatment technologies.

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References

1. ZHANG M., TAY J.H., QIAN Y., GU X.S., Coke plant wastewater treatment by fixed biofilm system for COD and NH₃-N removal, *Water Res.* **32**, 519, **1998**.
2. KIM Y.M., PARK D., LEE D.S., PARK J.M., Inhibitory effects of toxic compounds on nitrification process for cokes wastewater treatment, *J. Hazard. Mater.* **152**, 915, **1998**.
3. WU Z., ZHU L., Removal of polycyclic aromatic hydrocarbons and phenols from coking wastewater by

- simultaneously synthesized organobentonite in a one-step process, *J. Environ. Sci.* **24**, 248-253, **2012**.
4. LAI P., ZHAO H.Z., ZENG M., NI J.R., Study on treatment of coking wastewater by biofilm reactors combined with zerovalent iron process, *J. Hazard. Mater.* **162**, 1423, **2009**.
5. YU H.Q., GU G.W., SONG L.P., The effect of fill mode on the performance of sequencing-batch reactors treating various wastewaters, *Bioresour. Technol.* **58**, 46, **1996**.
6. LEE M.W., PARK J.M., Biological nitrogen removal from coke plant wastewater with external carbon addition, *Water Environ. Res.* **70**, 1090, **1998**.
7. LAI P., ZHAO H.Z., ZENG M., NI J.R., Study on treatment of coking wastewater by biofilm reactors combined with zerovalent iron process, *J. Hazard. Mater.* **162**, 1423, **2009**.
8. WANG JIANLONG, QUAN XIANGCHUN, WU LIBO, QIAN YI, WERNER HEGEMANN, Bioaugmentation as a tool to enhance the removal of refractory compound in coke plant, *Process biochem.* **38**, 777, **2002**.
9. QI R., YANG K., YU Z.-X., Treatment of coke plant wastewater by SND fixed biofilm hybrid system, *J. Environ. Sci.* **19**, 153, **2007**.
10. ZHAO W.-T., HUANG X., LEE D.-J., Enhanced treatment of coke plant wastewater using an anaerobic-anoxic-oxic membrane bioreactor system, *Sep. Purif. Technol.* **66**, 279, **2009**.
11. WEI-LING SUN, YAN-ZHI QU, QING YU, JIN-REN NI, Adsorption of organic pollutants from coking and papermaking wastewaters by bottom ash, *J. Hazard. Mater.* **154**, 595, **2008**.
12. MO HE ZHANG, QUAN LIN ZHAO, XUE BAI, ZHENG FANG YE, Adsorption of organic pollutants from coking wastewater by activated coke, *Colloid Surf. A-Physicochem. Eng. Asp.* **362**, 140, **2010**.
13. CHU L., WANG J., DONG J., LIU H., SUN X., Treatment of coking wastewater by an advanced Fenton oxidation process using iron powder and hydrogen peroxide, *Chemosphere* **86**, 409, **2012**.
14. WANG F., HV., GUO C., HUANG W., LIU C.Z., Enhanced phenol degradation in coking wastewater by immobilized laccase on magnetic mesoporous silica nanoparticles in a magnetically stabilized fluidized bed, *Bioresour. Technol.* **110**, 120, **2012**.
15. NING P., BART H. J., JIANG Y., DE HAAN A., TIEN C., Treatment of organic pollutants in coke plant wastewater by the method of ultrasonic irradiation, catalytic oxidation and activated sludge. *Sep. Purif. Technol.*, **41**, 133, **2005**.
16. LAI P., ZHAO H.Z., WANG C., NI J.R., Advanced treatment of coking wastewater by coagulation and zero-valent iron processes, *J. Hazard. Mater.* **147**, 232, **2007**.
17. CHU L., WANG J., DONG J., LIU H., SUN X., Treatment of coking wastewater by an advanced Fenton oxidation process using iron powder and hydrogen peroxide. *Chemosphere*, **86**, 409, **2012**.
18. ZHU X., TIAN J., LIU R., CHEN L., Optimization of Fenton and electro-Fenton oxidation of biologically treated coking wastewater using response surface methodology. *Sep. Sci. Technol.* **81**, 444, **2011**.
19. ZHAO W. T., HUANG X., LEE D. J., WANG X. H., SHEN Y. X., Use of submerged anaerobic-anoxic-oxic membrane bioreactor to treat highly toxic coke wastewater with complete sludge retention. *J Membrane Sci.* **330**, 57, **2009**.
20. ZHU X., NI J., LAI P., Advanced treatment of biologically pretreated coking wastewater by electrochemical oxidation using boron-doped diamond electrodes, *Water Res.* **43**, 4347, **2009**.

21. DANESHVAR N., OLADGARAGOZE A., DJAFARZADEH N., Decolorization of basic dye solutions by electrocoagulation: an investigation of the effect of operational parameters, *J. Hazard. Mater.* **129**, 116, **2006**.
22. ESSADKIA.H., BENNAJAH M., GOURICH B., VIAL CH., AZZI M., DELMAS H., Electrocoagulation/electroflotation in an external-loop airlift reactor – application to the decolorization of textile dye wastewater: a case study, *Chem. Eng. Process.* **47**, 1211, **2008**.
23. KHATAEE A.R., VATANPOUR V., GHADIM A.R.A., Decolorization of C.I. Acid Blue 9 solution by UV/Nano-TiO₂, Fenton Fenton-like, electro-Fenton and electro coagulation processes: a comparative study, *J. Hazard. Mater.* **161**, 1225, **2009**.
24. MOLLAH, M.Y.A., MORKOVSKY P., GOMES J.A.G., KESMEZ M., PARGA J., COCKE D.L., Fundamentals, present and future perspectives of electro-coagulation. *J. Hazard. Mater.* **114**, 199, **2004**.
25. MOLLAH M.Y.A., SCHENNACH R., PARGA J.R., et al . Electro-coagulation (EC)-science and applications. *J. Hazard. Mater.* **84**, 29, **2001**.
26. ALINSAFI A., KHEMIS M., PONS M.N., LECLERC J.P., YAACOUBI A., BENHAMMOU A., NEJMEDDINE A., Electro-coagulation of reactive textile dyes and textile wastewater, *Chem. Eng. Process.* **44**, 461, **2005**.
27. SENGIL I.A., OZACAR M., Treatment of dairy wastewaters by electro coagulation using mild steel electrodes, *J. Hazard. Mater.* **137**, 1197, **2006**.
28. YAVUZ Y., EC and EF, processes for the treatment of alcohol distillery wastewater, *Sep. Purif. Technol.* **53**, 135, **2007**.
29. JING-WEI F., YA-BING S., ZHENG Z., Treatment of tannery wastewater by electrocoagulation, *J. Environ. Sci.* **19**, 1409, **2007**.
30. WANG C.H., CHOU L.W., KUO Y.M., Removal of COD from laundry wastewater by electrocoagulation/electroflotation, *J. Hazard. Mater.* **164**, 81, **2009**.
31. GARCÍA-GARCÍA P., LÓPEZ-LÓPEZ A., MORENO-BAQUERO J.M., Treatment of wastewaters from the green table olive packaging industry using electro-coagulation, *Chem. Eng. J.* **170**, 59, **2011**.
32. MEIJIE REN, YONGHUI SONGA, SHUHU XIAO, PING ZENG, JIANFENG PENG, Treatment of berberine hydrochloride wastewater by using pulse electro-coagulation process with Fe electrode, *Chem. Eng. J.* **169**, 84, **2011**.
33. BALASUBRAMANIAN N., TOSHINORI KOJIMA, SRINIVASAKANNAN C., Arsenic removal through electrocoagulation: Kinetic and statistical modeling, *Chem. Eng. J.* **155**, 76, **2009**.
34. APHA, AWWA and WPCF. Standard methods for the examination of Water and Wastewater Washington, DC: American Public health association, **1998**.
35. A.P.H.A., A.W.W.A., W.E.F. Standard methods for the examination of water and wastewater, 18th ed. Washington, DC: American Public Health Association, **1992**.
36. LACASA E., CANIZARES P., SAEZ C., FERNANDEZ F.J., RODRIGO M.A. Electrochemical phosphates removal using iron and aluminium electrodes, *Chem. Eng. J.* **172**, 137, **2011**.
37. VASUDEVAN S., SOZHAN G., RAVICHANDRAN S., JAYARAJ J., LAKSHMI J., SHEELA S.M., Studies on the removal of phosphate from drinking water by electro coagulation process, *Ind. Eng. Chem. Res.* **47**, 2018, **2008**.
38. GAO S., YANG J., TIAN J., MA F., TU G., DU M., Electro-coagulation-flotation process for algae removal, *J. Hazard. Mater.* **177**, 336, **2010**.
39. CHEN X., CHEN G., YUE P.L, Separation of pollutants from restaurant wastewater by electrocoagulation, *Sep. Purify. Technol.* **19**, 65, **2000**.
40. KOBYA M., CAN O.T., BAYRAMOGLU M. Treatment of textile wastewaters by electro-coagulation using iron and aluminum electrodes , *J. Hazard. Mater.* **B100**, 163, **2003**.
41. KAN YETILMEZSOY, FATIH ILHAN, ZEHRA SAPCIZENGİN, SULEYMAN SAKAR, TALHA GONULLU M., Decolorization and COD reduction of UASB pretreated poultry manure wastewater by electro-coagulation process: A post-treatment study, *J. Hazard. Mater.* **162**, 120, **2009**.
42. MAHESH S., PRASAD B., MALL I.D., MISHRA I.M., Electrochemical degradation of pulp and paper mill waste water. Part I. COD and color removal, *Ind. Eng. Chem. Res.* **45**, 2830, **2006**.
43. İNAN H., DIMAGLO A., SIMSEK H., KARPUZCU M., Olive mill wastewater treatment by means of electro-coagulation, *Sep. Purif. Technol.* **36**, 23, **2004**.
44. KABDAŞL I., VARDAR B., ARSLAN-ALATON I., TÜNAY O., Effect of dye auxiliaries on color and COD removal from simulated reactive dyebath effluent by electro coagulation, *Chem. Eng. J.* **148**, 89, **2009**.
45. DANESHVAR N., OLADGARAGOZE A., DJAFARZADEH N., Decolorization of basic dye solutions by electrocoagulation: an investigation of the effect of operational parameters, *J. Hazard. Mater.* **B129**, 116, **2006**.
46. MERZOUK B., GOURICH B., SEKKI A., MADANI K., CHIBANE M., Removal turbidity and separation of heavy metals using electro coagulation-electro flotation technique: a case study, *J. Hazard. Mater.* **164**, 215, **2009**.
47. STUCKI P. Electrochemical wastewater treatment using high over voltage anodes. *J. Appl. Electrochem.* **21**, 34, **1991**.
48. JI-JIE H., JUN-XIA X., YUAN R., ZHAN-JI T., CHAO-FEI W., CHAO-HAI W., Adsorption process of organic contaminant in untreated coking wastewater by powdered activated carbon, *Environmental Science* **29**, 1567, **2008** [in Chinese].
49. TIAN-ZAN O., ZHEN-HUA Z., XIAO-MAN G., FTIR Study on the Adsorption of Bensulfuron-methyl by Goethite, *Spectrosc. Spect. Anal.* **23**, 1097, **2003** [in Chinese].
50. AOUJ S., KHELIFA A., DROUCHE N., HECINI M., HAMITOCHE H., Electro-coagulation process applied to wastewater containing dyes from textile industry, *Chem. Eng. Process.* **49**, 1176, **2010**.
51. XIA L., MCCREERY R.L., Structure and function of ferricyanide in the formation of chromate conversion coatings on aluminum aircraft alloy, *J. Electrochem. Soc.* **146**, 3689, **1999**.
52. RUAN H.D., FROST R.I., KLOPRGGE J.T., DUONG L., Infrared spectroscopy of goethite dehydroxylation III: FTIR microscopy of in situ study of the thermal transformation of goethite to hematite, *Spectrochim Acta A* **58**, 967, **2002**.
53. MARCO J.F, GRACIA M., GANCEDO J.R., MARTÍN-LUENGO M.A., JOSEPH G., Characterization of the corrosion products formed on carbon steel after exposure to the open atmosphere in the antarctic and easter island, *Corros Sci.* **42**, 753, **2000**.
54. RAJKUMAR D., PALANIVELU K., Electrochemical treatment of industrial wastewater, *J. Hazard. Mater.* **B113**, 123, **2004**.