



Depth treatment of coal-chemical engineering wastewater by a cost-effective sequential heterogeneous Fenton and biodegradation process

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Abstract

In this study, a sequential $\text{Fe}^0/\text{H}_2\text{O}_2$ reaction and biological process was employed as a low-cost depth treatment method to remove recalcitrant compounds from coal-chemical engineering wastewater after regular biological treatment. First of all, a chemical oxygen demand (COD) and color removal efficiency of 66 and 63% was achieved at initial pH of 6.8, 25 mmol L^{-1} of H_2O_2 , and 2 g L^{-1} of Fe^0 in the $\text{Fe}^0/\text{H}_2\text{O}_2$ reaction. According to the gas chromatography-mass spectrometer (GC-MS) and gas chromatography-flame ionization detector (GC-FID) analysis, the recalcitrant compounds were effectively decomposed into short-chain organic acids such as acetic, propionic, and butyric acids. Although these acids were resistant to the $\text{Fe}^0/\text{H}_2\text{O}_2$ reaction, they were effectively eliminated in the sequential air lift reactor (ALR) at a hydraulic retention time (HRT) of 2 h, resulting in a further decrease of COD and color from 120 to 51 mg L^{-1} and from 70 to 38 times, respectively. A low operational cost of 0.35 $\text{\$ m}^{-3}$ was achieved because pH adjustment and iron-containing sludge disposal could be avoided since a total COD and color removal efficiency of 85 and 79% could be achieved at an original pH of 6.8 by the above sequential process with a ferric ion concentration below 0.8 mg L^{-1} after the $\text{Fe}^0/\text{H}_2\text{O}_2$ reaction. It indicated that the above sequential process is a promising and cost-effective method for the depth treatment of coal-chemical engineering wastewaters to satisfy discharge requirements.

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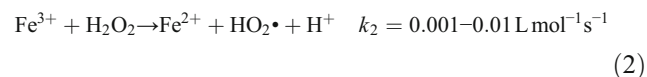
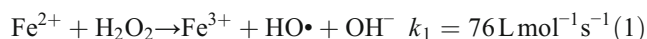
Keywords Zero valent iron · $\text{Fe}^0/\text{H}_2\text{O}_2$ reaction · Depth treatment · Coal-chemical engineering wastewater · Air lift reactor

Introduction

Wastewaters from coal-chemical engineering industry such as coking industries, synthesis of oil and chemical industries are typically refractory to individual biological treatment (Wei et al. 2012). These wastewaters usually contain a variety of organic and inorganic pollutants including ammonia nitrogen, cyanide, thiocyanate, oil, phenols, and polynuclear aromatic hydrocarbons (PAHs) (Chen et al. 2012). Conventional approach for this type of wastewater comprises physico-chemical pre-treatments and regular biological treatment. The physico-chemical pre-treatments include solvent extraction of phenolic compounds, steam stripping of ammonia nitrogen, flotation removal of oil, and coagulation of suspended solids (Lai et al. 2007). The regular biological treatment includes anaerobic treatment and aerobic treatment, which possess the advantage of low cost and high removal efficiency.

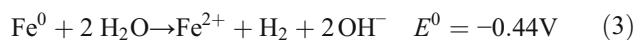
And they are used to degrade the bio-available compounds (Wei et al. 2012; Chen et al. 2012; Lai et al. 2007) including cyanide, thiocyanate, and phenols as well as heterocyclics and acyclic compounds. However, effluents from the above approach are frequently unable to meet the national discharge standard of China due to the presence of recalcitrant compounds (Liu et al. 2010). Hence, there is increasing interest in developing effective depth treatment measures to remove recalcitrant compounds from coal-chemical engineering wastewaters after bio-treatments.

Among various depth treatment methods, such as adsorption, membrane separation, and advanced oxidation (Liu et al. 2010; Bermejo and Cocero 2006; Mohammed and Smith 1992), Fenton reaction is widely reported to be effective and efficient for the removal of recalcitrant pollutants from aqueous solutions (Gogate and Pandit 2004a, b; Gallard and Laet 2000) by generating hydroxyl radicals (HO•) from the decomposition of H₂O₂ with Fe²⁺ oxidized to Fe³⁺ (Eq. 1) (Neyens and Baeyens 2003). Fenton reaction is a complex process in which iron also acts as catalyst in a redox cycle. Other reports suggested that H₂O₂ could act as a reducer and reduce Fe³⁺ into Fe²⁺, yielding a HO₂• (Eq. 2) (Lee and Yoon 2004). In this process, iron is the catalyst and H₂O₂ is transformed into radicals. The HO• radicals have a high reduction potential of 2.8 V and they are able to decompose most of the recalcitrant pollutants to CO₂, H₂O, or intermediate products such as organic acids with a series of rapid chain reaction.

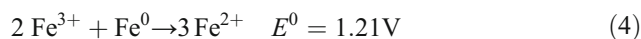


Equations 1 and 2 form a Fe³⁺/Fe²⁺ cycle which is essential for maintaining Fe²⁺ concentration and generating HO• during the reaction. The regeneration of Fe²⁺ is negligible since *k*₂ is insignificant as compared to *k*₁, far excess of stoichiometric Fe²⁺ is needed to produce enough HO• for efficient degradation of pollutants (Deng and Englehardt 2006). This leads to the production of a huge amount of iron-containing sludge after the reaction. Moreover, acidation and neutralization before and after the reaction requires extra cost because Fenton reaction is usually operated at the optimal pH of 3 (Chen et al. 2010). Hence, it is expected to develop a novel Fenton catalyst that has a wide application range of pH without the production of a huge amount of iron-containing sludge.

Zero valent iron (Fe⁰) can be an alternative catalyst for Fenton reaction (Fu et al. 2014; Huang et al. 2012). According to Eq. 3, the in situ generated Fe²⁺ from Fe⁰ corrosion can react with H₂O₂ to produce HO•.



The main advantage of the Fe⁰/H₂O₂ reaction is the conversion of Fe³⁺/Fe²⁺ at the Fe⁰ surface (Eq. 4).



In situ generation of Fe²⁺ from Fe⁰ corrosion and fast conversion of Fe³⁺ by Fe⁰ reduction can avoid ferric ion accumulation during the reaction and thereafter reduce ferric hydroxide precipitation after the reaction. With this advantage, the Fe⁰/H₂O₂ reaction has been proven to be effective for the treatment of refractory wastewaters such as landfill leachate (Martins et al. 2012), methyl *tert*-butyl ether (MTBE) wastewater (Bergendahl and Thies 2004), and phenol wastewater (Bremner et al. 2006). Besides, the Fe⁰/H₂O₂ reaction has a much wider application range of pH as compared to conventional homogeneous Fenton reaction due to the fast conversion of Fe³⁺/Fe²⁺ at the Fe⁰ surface (Martins et al. 2012; Bergendahl and Thies 2004; Bremner et al. 2006).

During the Fe⁰/H₂O₂ reaction, recalcitrant pollutants are usually transformed to short-chain organic acids. These short-chain organic acids are resistant to the attack of HO• for further degradation (Zhuang et al. 2015), but they are easily degradable substrates for the growth of microorganisms, in which they may be completely degraded into CO₂ and H₂O in a short period of time with oxygen as electron acceptors (Yu et al. 1997). Hence, the combined Fe⁰/H₂O₂ reaction and aerobic biodegradation process is expected to be an effective way for the depth treatment of coal-chemical engineering wastewaters.

It is known that traditional aerobic reactors have their own technical or economic limits such as low oxygen transfer rate (Jin et al. 2006; Hallas and Alexander 1983). Recently, air lift reactor (ALR) has been developed as an efficient aerobic reactor with high oxygen and mass transfer rates due to the intense turbulence and circulating flows inside the reactor (Rubio et al. 2001). In comparison with stirred tanks or bubble columns, shear stress can be more constant and milder in the ALR (Wang et al. 2011), promoting microbial growth and accelerating the degradation of substrates. Additionally, since the pH value of the Fe⁰/H₂O₂ reaction effluent normally ranges between 6 and 8, this Fe⁰/H₂O₂ reaction effluent may be suitable for further treatment using ALR reactor.

In this study, a sequential Fe⁰/H₂O₂ reaction and ALR process was employed as a depth treatment method for coal-chemical engineering wastewater by evaluating chemical oxygen demand (COD) and color removal efficiency. The change of recalcitrant compounds were analyzed by gas chromatography-mass spectrometer (GC-MS) and gas chromatography-flame ionization detector (GC-FID) to predict their fate and the relation to COD and color removal during the reaction. The operational cost of this sequential process was also evaluated.

Materials and methods

Wastewater and chemicals

An effluent from a coal-chemical engineering wastewater treatment plant was obtained and its characteristic quality is listed in Table 1. The concentrations of COD and color both were much higher than those of the national first class emission standard of China (GB18918-2002, China). A low ratio of biological oxygen demand (BOD₅) to COD was observed as 0.09, implying that further degradation of the recalcitrant compounds in the effluent was hard to be achieved in the above wastewater treatment plant.

The iron powder (Guangzhou Metals Company) was approximately 0.05 mm in diameter with a metallic glaze surface and was pretreated with 10 mmol L⁻¹ HCl for 5 min to remove the oxide film on its surface, then washed three times with deionized water and dried at 60 °C for 12 h. Hydrogen peroxide (30% (w/w) H₂O₂) was purchased from Sinopharm Chemical Reagent Co., Ltd. Silver sulfate, mercury sulfate, potassium dichromate, ammonium ferrous sulfate, and others conventional reagents such as H₂SO₄, NaOH, and NaHCO₃ were analytical grade and obtained from Guangzhou Chemical Reagent Factory.

Fe⁰/H₂O₂ reaction

Batch experiments were conducted in 250-mL conical flasks with 200 mL wastewater. The initial pH was adjusted by 0.1 mol L⁻¹ H₂SO₄ and NaOH when necessary. After the addition of 25 mmol L⁻¹ H₂O₂ and 2 g L⁻¹ Fe⁰, the flask was capped with a rubber plug and agitated in an isothermal shaker (120 rpm, 25 °C). At regular intervals, 6 mL solution was withdrawn with a syringe. A few drops of 0.1 mol L⁻¹ NaOH and trace manganese dioxide were added to avoid the interference of residual Fe²⁺ and H₂O₂ before filtered with a 0.45-μm membrane, followed by an immediate analysis of COD and color. The effects of initial pH, H₂O₂ dosage, and Fe⁰ dosage on the COD and color removal was conducted on the basis of the above benchmark experiment. After the reaction, the pH of the solution was measured and 10 mL solution with a limited iron concentration of 60 mg/L was collected for

Table 1 The characteristics of effluent from a coal-chemical engineering wastewater treatment plant and discharge standard

Parameter	Effluent quality	National first class discharge standard
COD	341 ± 6 mg L ⁻¹	100 mg L ⁻¹
BOD ₅	30 ± 3 mg L ⁻¹	30 mg L ⁻¹
Color	180 times	50 times
pH	6.8	6–9

leaching iron measurement. Each experiment was conducted in triplicate and an average value was shown in this study. The transformation of recalcitrant compounds was detected by GC-MS and the bio-available short-chain organic acids were measured with GC-FID.

Sequential biodegradation

The schematic diagram of the air lift reactor (ALR) (Wu et al. 2014) is shown in Fig. 1. And the operative conditions of the ALR reactor were based on our previous study (Wu et al. 2014). It had an effective volume of 1.5 L with a diameter and height of 11 cm and 26 cm, respectively. The diameter and height of the inner cylinder were 8.5 and 20 cm, respectively. The inlet and outlet were set at 5 and 23 cm above the bottom of the reactor. Dissolved oxygen (DO) concentration was controlled at 1–2 mg L⁻¹ with a flow of compressed air (4 L h⁻¹) introduced via a micro-pore diffuser at the bottom of the reactor. The reactor was maintained at room temperature of 25 ± 3 °C. Seed sludge was obtained freshly from a secondary sedimentation tank of a local sewage treatment plant, which was inoculated in the ALR reactor at an initial sludge concentration (SS) of 3 g L⁻¹. The sludge was acclimated for 60 days at a hydraulic retention time (HRT) of 2 h in the ALR reactor by feeding synthetic wastewater, which contained 150 mg L⁻¹ glucose (COD) as carbon and energy source, 26 mg L⁻¹ NH₄Cl, 6 mg L⁻¹ K₂HPO₄, 30 mg L⁻¹ MgSO₄·7H₂O, 4 mg L⁻¹ CaCl₂, 200 mg L⁻¹ NaHCO₃, 21 mg L⁻¹ FeSO₄·7H₂O, and 0.3 mg L⁻¹ trace metals including CoCl₂·5H₂O, CuCl₂·2H₂O, MnCl₂·4H₂O, NiCl₂·6H₂O, NH₄MO₃, and ZnSO₄, respectively. The sludge concentration in the reactor was kept at 3 g L⁻¹ by wasting 25 mL of sludge every day with a siphon method after settling for 30 min without feeding and bubbling.

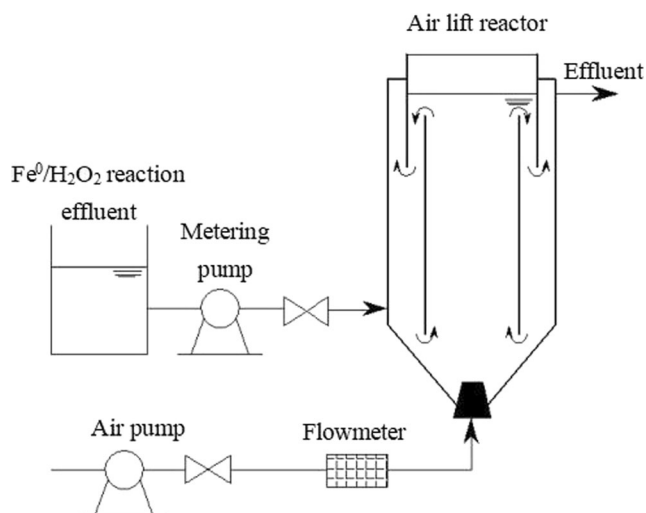


Fig. 1 The schematic diagram of the ALR reactor

After 2 months of acclimation, the effluent of the $\text{Fe}^0/\text{H}_2\text{O}_2$ reaction conducted in a 20-L bucket at the optimal condition obtained in the $\text{Fe}^0/\text{H}_2\text{O}_2$ experiment was collected and the residual hydrogen peroxide was eliminated in the $\text{Fe}^0/\text{H}_2\text{O}_2$ reaction before pumping into the ALR reactor at an HRT of 2 h. It took about 3 months for the reactor to obtain a steady-state condition. Water samples from the influent and effluent pipes of the ALR reactor were collected with a syringes, filtered with a 0.45 μm membrane after centrifugation (3000 rpm) for 20 min, followed the immediate analysis of COD, color, and pH. These parameters were measured every 2 days until their variation within 10% of the average value. Subsequently, the concentrations of COD, color and pH were measured every day for 20 days and average values were shown in this study.

Analytical methods

The concentrations of COD, BOD₅, SS, and color were determined according to the standard methods for the examination of water and wastewater (Rice 2012). The pH value was monitored using a pH meter (PHS-3C, Sanxin, China). The concentration of Fe^{2+} after the reaction was quantified using a phenanthroline method modified by Fadrus and Malý (1975). Total Fe concentration was determined after Fe^{3+} was reduced to Fe^{2+} by hydroxylamine hydrochloride.

The organic compounds in the wastewater were determined by a GC-MS (HP5890II GC/5972MSD, Agilent Technologies), which was conducted in a temperature programming mode with a DB-5 capillary column (30 m \times 0.25 mm \times 0.25 μm). The initial column temperature was 70 $^\circ\text{C}$ for 2 min, increased linearly at 5 $^\circ\text{C min}^{-1}$ to 280 $^\circ\text{C}$ and held for 10 min. The temperature of the injection port was 280 $^\circ\text{C}$. A sample of 1 μL was sequentially extracted with methylene chloride and *n*-hexane and then injected into the GC-MS with an automatic sampler. Ion source in the mass spectrometer was an electron bombardment source (EI). The electron multiplier voltage was 1600 eV and the emission electron energy was 50 eV. The scanning quality range (*m/z*) was 50–550 amu. Nitrogen was used as a carrier gas at a flow rate of 2.0 mL min^{-1} .

The concentrations of organic acids were determined by a GC (A90 Shanghai Yimeng Electronic Technology Co., Ltd) equipped with a flame ionization detector (FID) and a 30 m \times 0.320 mm capillary column (DB-FFAP). The oven temperature was kept at 80 $^\circ\text{C}$ for 1 min then increased to 90, 112, and 200 $^\circ\text{C}$ at a rate of 5, 11, and 10 $^\circ\text{C min}^{-1}$, respectively. Finally, the oven temperature was kept at 200 $^\circ\text{C}$ for 7 min. Nitrogen was used as a carrier gas at a flow rate of 5 mL min^{-1} . The flow rate of dry air and hydrogen was 450 and 40 mL min^{-1} , respectively. The injector and detector temperature was kept at 200 and 250 $^\circ\text{C}$, respectively. The sample of 1 μL was sequentially extracted with methylene chloride

and *n*-hexane. The concentrations of organic acids were quantified with the external reference method.

Results and discussion

$\text{Fe}^0/\text{H}_2\text{O}_2$ reaction

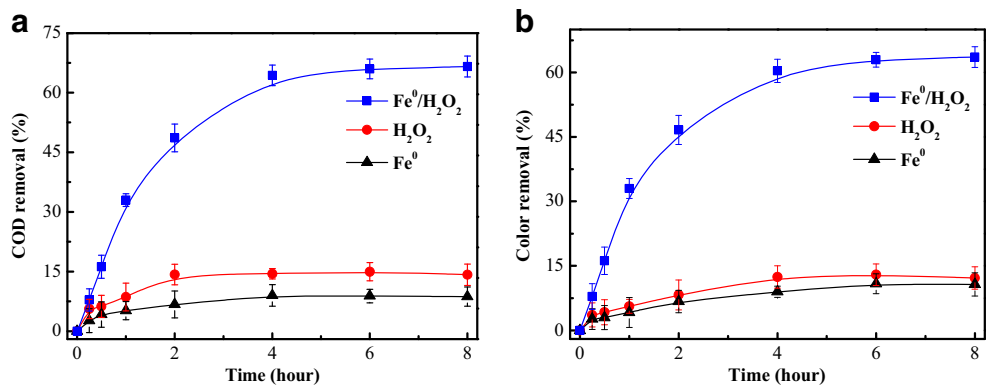
Comparison experiments

The degradation experiments were conducted with Fe^0 , H_2O_2 , and $\text{Fe}^0/\text{H}_2\text{O}_2$, respectively. As shown in Fig. 2, a COD and color removal efficiency of 9 and 10% was achieved after 8 h reaction time in the Fe^0 system, which was attributed to the adsorption of pollutants onto the Fe^0 surface (Wu et al. 2012) and the reductive transformation of chromophores of the surface-bounded pollutants by the Fe^0 due to its low redox potential ($E^0 = -0.44$ V) (Luo et al. 2013). Though a slight higher COD and color removal efficiency of 14 and 12% was achieved after 8 h reaction time in the H_2O_2 system respectively, it suggested that the H_2O_2 was unable to degrade the recalcitrant compounds in the wastewater because of its lower reduction potential ($E^0 = 1.78$ V) as compared to $\text{HO}\cdot$ and $\text{HO}_2\cdot$. For the $\text{Fe}^0/\text{H}_2\text{O}_2$ system, a significantly higher COD and color removal efficiency of 66 and 63% was achieved after 8 h reaction time respectively, as compared to the Fe^0 and H_2O_2 system. This superior performance of the $\text{Fe}^0/\text{H}_2\text{O}_2$ system was ascribed to the Fe^{2+} released from the Fe^0 corrosion and then the H_2O_2 molecules were promptly decomposed to powerful $\text{HO}\cdot$ (Eqs. 1–4). These radicals had an extremely high reduction potential of about 2.80 V and played an important role in the elimination of recalcitrant compounds to CO_2 , H_2O , or intermediate products such as organic acids with a series of rapid chain reaction.

Effect of initial pH

The effect of initial pH on the COD and color removal was studied over a pH range from 2 to 8 (Fig. 3). When the initial pH decreased from 8 to 3, the COD and color removal efficiency increased from 31 to 98% and from 2 to 100%, respectively. It was attributed to the fact that acid media promoted the in situ Fe^{2+} generation and consequently accelerated the production of hydroxyl radicals. In addition, H^+ also cleared up the passivated layer accumulating on the surface of Fe^0 such as $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ (Liang et al. 2009), which has low efficiency to decompose hydrogen peroxide into hydroxyl radical (Kang and Hwang 2000). Besides, hydrogen peroxide was increasingly unstable and it could be decomposed to produce H_2O and O_2 when the pH value was higher than 4, leading to less $\text{HO}\cdot$ being available to attack the recalcitrant compounds in a higher pH (Du et al. 2008). However, the COD and color removal efficiency decreased from 98 to 93% and from 100 to

Fig. 2 The COD and color removal in three systems. (Initial pH 6.8, H₂O₂ 25 mmol L⁻¹, Fe⁰ 2 g L⁻¹, 25 °C)



98%, respectively as the initial pH further decreased from 3 to 2. This phenomenon could be explained that excessive H⁺ was easily captured by H₂O₂ to produce H₃O₂⁺ and restrained the reaction between H₂O₂ and Fe²⁺ (Eq. 5) (Gogate and Pandit 2004b).



The concentrations of leaching ferric and ferrous ions in the solution after the reaction were measured and the result is showed in Fig. 3b. It was observed that the concentration of leaching ferric ion increased from 0.39 to 13.8 mg L⁻¹ after 8 h reaction time as the initial pH decreased from 8 to 2. This phenomenon was consistent with the expected results that more iron was dissolved under acid condition (Martins et al. 2010). When the initial pH was 6.8, a low leaching ferric ion concentration of 0.71 mg L⁻¹ and a relatively high COD and color removal efficiency of 66% and 63% could be achieved. Moreover, the pH value after the reaction increased from 6.8 to 7.3, which was an appropriate range for the growth of microorganisms in the sequential biodegradation. Hence, the initial (original) pH value of 6.8 was thereafter selected for further experiments.

As compared to traditional homogeneous Fenton processes, two obvious advantages were achieved in this Fe⁰/H₂O₂ system. Firstly, an effective COD and color removal efficiency was achieved at the original pH of 6.8, and the addition of acid

and alkali can be avoided before and after the reaction with Fe⁰ used as catalyst since the effluent from the coal-chemical engineering wastewater treatment plant is usually neutral or weakly acidic. Secondly, the generation of iron-containing sludge in the Fe⁰/H₂O₂ system was much less than that in traditional homogeneous Fenton reaction because the remaining ferric ions in the Fe⁰/H₂O₂ effluent were nearly negligible (less than 0.8 mg L⁻¹ at the original pH of 6.8). These results indicated that Fe⁰/H₂O₂ reaction is a cost-effective and environmentally friendly depth treatment method for coal-chemical engineering wastewaters.

Effect of iron and hydrogen peroxide dosage

The effect of Fe⁰ and H₂O₂ dosage was investigated by increasing the Fe⁰ dosage from 0.1 to 4 g L⁻¹ and the H₂O₂ dosage from 5 to 50 mmol L⁻¹, respectively. As shown in Fig. 4, the COD and color removal efficiency increased from 25 to 66% and from 40 to 63%, respectively, after 8 h reaction time with an increase of Fe⁰ dosage from 0.1 to 2 g L⁻¹. Since more reactive sites were available and more Fe²⁺ ions were released into the solution at higher Fe⁰ dosage, the decomposition of hydrogen peroxide into hydroxyl radicals was enhanced and higher COD and color removal efficiency was achieved. However, the COD and color removal efficiency decreased from 66 to 59% and from 63 to 58%, respectively, when the Fe⁰ dosage further increased from 2 to 4 g L⁻¹. It was

Fig. 3 The effect of initial pH on the COD, color removal, and iron leaching. (H₂O₂ 25 mmol L⁻¹, Fe⁰ 2 g L⁻¹, 25 °C)

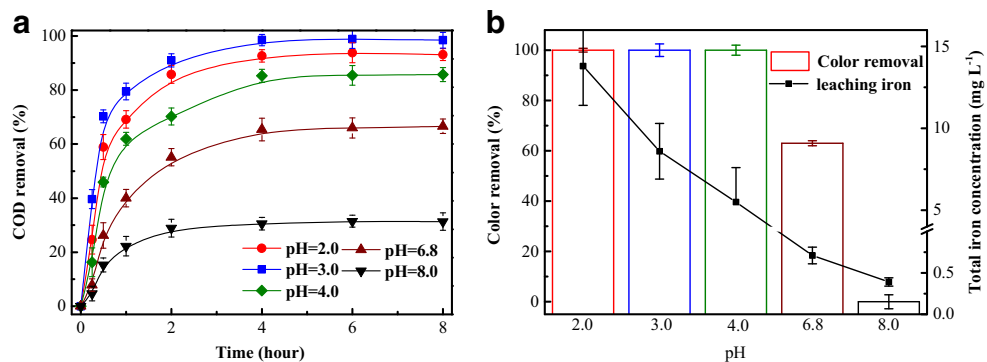
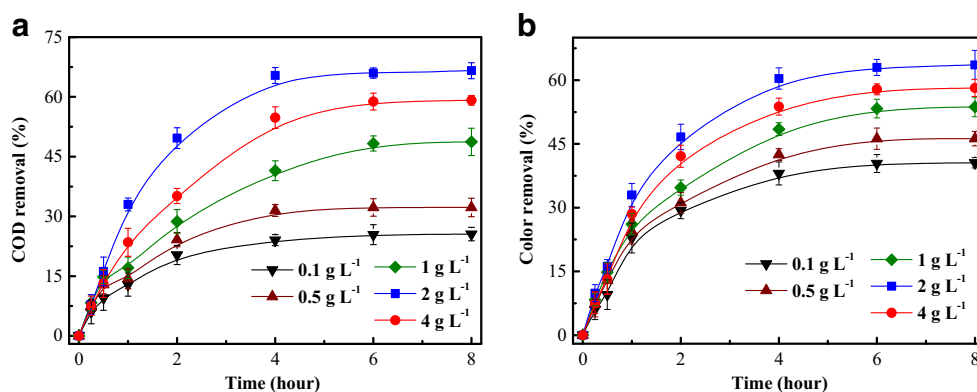


Fig. 4 The effect of Fe^0 dosage on the COD and color removal. (Initial pH 6.8, H_2O_2 25 mmol L^{-1} , 25 °C)



largely due to the parallel reaction between hydroxyl radicals and excessive ferrous ions released from over-loaded Fe^0 that impeded the degradation of recalcitrant compounds by hydroxyl radicals (Eq. 6).

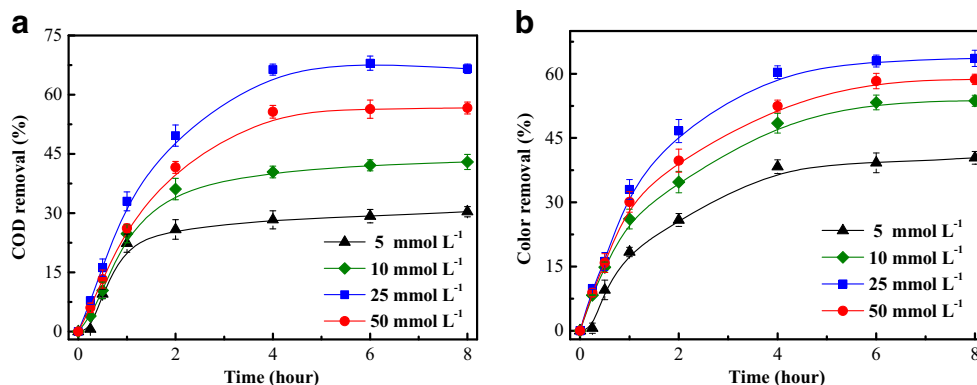


Similarly, the COD and color removal efficiency increased with H_2O_2 dosage from 30 to 66% and from 40 to 63%, respectively, within 8 h with an increase of H_2O_2 dosage from 5 to 25 mmol L^{-1} (Fig. 5). It can be explained that more hydroxyl radicals were generated at higher H_2O_2 dosage and the COD and color removal efficiency was thereafter improved. However, the COD and color removal efficiency slightly decreased from 66 to 58% and from 63 to 59%, respectively, as the H_2O_2 dosage further increased to 50 mmol L^{-1} . This phenomenon was attributed to the scavenging of hydroxyl radicals by excessive H_2O_2 to produce weaker $\text{HO}_2\cdot$ and these radicals would further deplete $\text{HO}\cdot$ (Eq. 7–8) (Chou and Huang 1999).



Therefore, with the above results, the optimal Fe^0 and H_2O_2 dosage was determined as 2 g L^{-1} and 25 mmol L^{-1} in the present study.

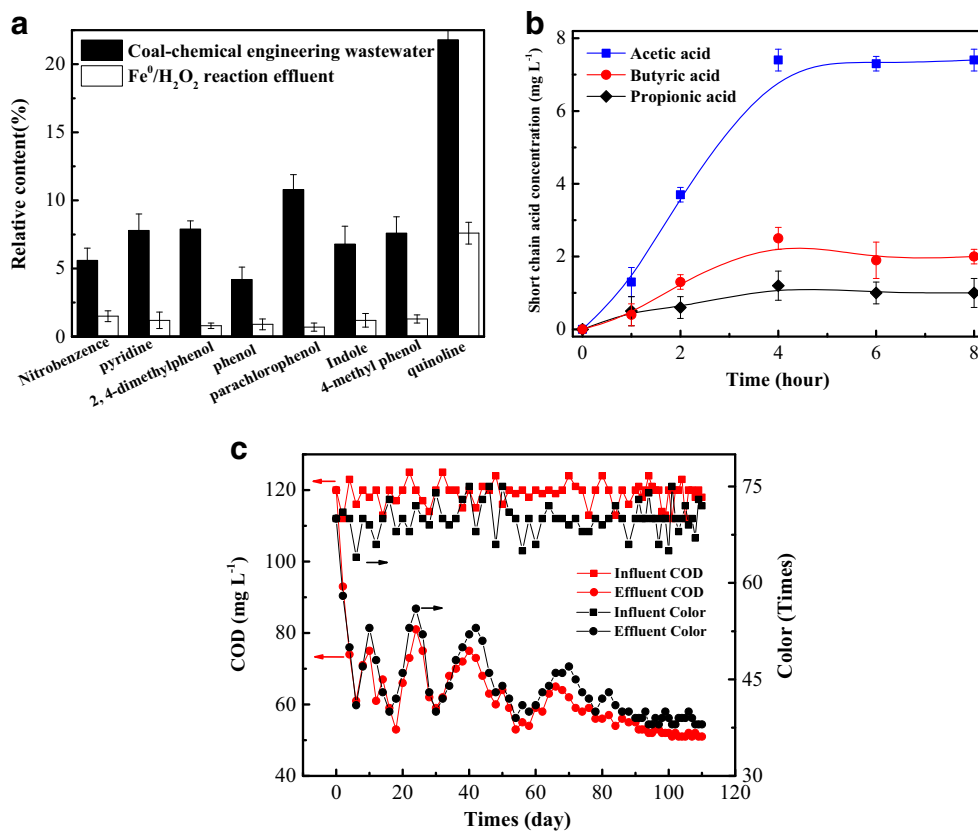
Fig. 5 The effect of H_2O_2 dosage on the COD and color removal. (Initial pH 6.8, Fe^0 2 g L^{-1} , 25 °C)



Sequential biodegradation

According to the results of the GC-MS analysis, the recalcitrant compounds in the effluent from the coal-chemical engineering wastewater treatment plant were confirmed as ring-shaped conjugated structure pollutants, such as nitrobenzene, pyridine, indole, quinoline, and phenols (Fig. 6a). Apparently, except for quinoline, these recalcitrant aromatic compounds were effectively degraded at a removal efficiency above 80% during the $\text{Fe}^0/\text{H}_2\text{O}_2$ reaction, leading to a significant decrease of COD and color and an increase of BOD_5 . The BOD_5 to COD ratio of this effluent was thereafter increased from 0.09 to 0.63 after the $\text{Fe}^0/\text{H}_2\text{O}_2$ reaction, which was higher than 0.3 for biological treatment. In order to identify the fate of the above recalcitrant aromatic compounds, the degradation products of the $\text{Fe}^0/\text{H}_2\text{O}_2$ reaction were measured with GC-FID. As shown in Fig. 6b, bio-available short-chain organic acids, including acetic acid (pK_a 4.76), propionic acid (pK_a 4.88), and butyric acid (pK_a 4.82) were produced and their concentrations increased with reaction time, reaching the maximum of 7.4, 2, and 1 mg L^{-1} in 4 h, respectively. According to the pK_a values of these short-chain organic acids, they were majorly in anionic forms at pH of 7.0. It indicated that the recalcitrant pollutants were degraded into bio-available substrates because the aromatic compounds were destroyed under electrophilic attack to unsaturated bond by hydroxyl

Fig. 6 **a** The relative content of aromatics compounds in the coal-chemical engineering wastewater before and after the $\text{Fe}^0/\text{H}_2\text{O}_2$ reaction, **b** the change of short-chain organic acids during the $\text{Fe}^0/\text{H}_2\text{O}_2$ reaction (initial pH 6.8, H_2O_2 25 mmol L^{-1} , Fe^0 2 g L^{-1} , 25 °C), and **c** the change of COD and color in the ALR reactor



radicals (Ruppert et al. 1993), which might result in consequential ring opening reaction (Bremner et al. 2006). However, the produced intermediates such as short-chain organic acids were resistant to the attack of hydroxyl radicals and remained in the solution even after 8 h reaction time.

In order to mineralize the remained intermediates in a short period of time without further consuming of reagents and reaction time, the effluent of the $\text{Fe}^0/\text{H}_2\text{O}_2$ reaction was fed into the ALR reactor. The experimental results showed that the concentrations of COD and color in the wastewater further decreased from 120 to 51 mg L^{-1} and from 70 to 38 times, respectively, at an HRT of 2 h and sludge concentration of 3 g L^{-1} (Fig. 6c). The concentrations of the above short-chain organic acids were under detection limit in the effluent of the ALR reactor. It suggested that these short-chain organic acids were favored carbon source for the microorganisms and they were effectively degraded to CO_2 and H_2O by the aerobic culture in a short period of time due to the high performance of the ALR reactor. It indicated that aerobic biodegradation after the $\text{Fe}^0/\text{H}_2\text{O}_2$ reaction was an effective and economic way to eliminate the remained intermediates from the advanced oxidation treatment of the coal-chemical engineering wastewater. After the treatment in the ALR reactor, the effluent COD and color satisfied the national first class emission standard of China (GB18918-2002, China).

Operational cost analysis

Recently, other methods such as electro-coagulation, chemical precipitation, electro-Fenton-biological activated carbon, and TiO_2 photocatalysis oxidation with moving bed bio-film reactor (MBBR) processes were reported to be effective for the depth treatment of coal-chemical engineering wastewaters. Their COD removal efficiency and operational cost are listed in Table 2, though a direct comparison of these processes with the sequential $\text{Fe}^0/\text{H}_2\text{O}_2$ -ALR process is difficult due to different experimental conditions used in each study. The operational cost of the sequential $\text{Fe}^0/\text{H}_2\text{O}_2$ -ALR process for the coal-chemical engineering wastewater mainly comprised the costs of reagents and electricity. The reagent cost mainly included the Fe^0 and H_2O_2 with a price of 0.5 and 0.27 \$ kg^{-1} , respectively. The Fe^0 dosage was 2 kg m^{-3} and the loss of Fe^0 was less than 0.02 kg m^{-3} in the $\text{Fe}^0/\text{H}_2\text{O}_2$ reaction, so the cost of Fe^0 was 0.01 \$ m^{-3} . The H_2O_2 dosage was 0.8 kg m^{-3} and the cost of H_2O_2 was 0.22 \$ m^{-3} . The electricity cost, mainly for the use of pump, mixing and aeration, was about 0.12 \$ m^{-3} . Thus, the total operational cost was 0.35 \$ m^{-3} . This cost was much cheaper than that of the coagulation and precipitation processes because it was free of pH adjustment and iron-containing sludge disposal. Table 2 also showed that the combined advanced oxidation and aerobic biodegradation process was an effective and cost-effective method for the

Table 2 Operational cost analysis

Depth treatment method	COD (mg L ⁻¹)	COD removal efficiency (%)	Operational cost (\$ m ⁻³)	Reference
Fe ⁰ /H ₂ O ₂ -ALR process	341 ± 6	85	0.35	This study
Electro-coagulation	/	> 90	2.19	(Oncel et al. 2013)
Chemical precipitation	/	> 90	5.02	(Oncel et al. 2013)
Electro-Fenton-biological activated carbon	140–190	81	0.16	(Hou et al. 2015)
TiO ₂ photocatalysis oxidation-MBBR process	150–200	87	0.41	(Xu et al. 2015)

depth treatment of coal-chemical engineering wastewaters because a high COD removal efficiency of more than 80% could be achieved with a low cost less than 0.5 \$ m⁻³. The COD removal efficiency and operational cost of the electro-Fenton-biological activated carbon and TiO₂ photocatalysis oxidation-MBBR processes were closed to that of the present study. However, the Fe⁰/H₂O₂-ALR process has a lower investment and is easier to be operated during the working time as compared to the above combined processes, suggesting that the sequential Fe⁰/H₂O₂-ALR process is a promising and cost-effective depth treatment technology for the coal-chemical engineering wastewater.

Conclusion

In this study, a sequential Fe⁰/H₂O₂-air lift reactor (ALR) process was employed for the depth treatment of coal-chemical engineering wastewater. It demonstrated that the recalcitrant compounds in the wastewater were effectively decomposed into short-chain organic acids such as acetic acid, propionic acid, and butyric acid with a COD and color removal efficiency of 66 and 63% at original pH 6.8, H₂O₂ 25 mmol L⁻¹, and Fe⁰ 2 g L⁻¹ in the Fe⁰/H₂O₂ reaction. The produced bioavailable organic acids were effectively eliminated by microorganisms in the ALR reactor, resulting in a total COD and color removal efficiency of 85 and 79%, respectively, which can satisfy the requirements of the national first class emission standard of China after this sequential process. In comparison with other depth treatment processes, this sequential Fe⁰/H₂O₂-ALR process could be selected as a cost-effective and environmentally friendly method with a total operational cost of 0.35 \$ m⁻³ because it could be operated under original conditions without pH adjustment and iron-containing sludge disposal since the leaching ferric ion concentration after the Fe⁰/H₂O₂ reaction was below 0.8 mg L⁻¹. This study demonstrated that the sequential Fe⁰/H₂O₂ reaction and biodegradation process is a promising and cost-effective depth treatment technology for coal-chemical engineering wastewaters.

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