Advanced treatment of biologically treated coking wastewater by persulfate oxidation with magnetic activated carbon composite as a catalyst

Xiulan Song, Chao Wang, Meiqin Liu and Miao Zhang

ABSTRACT

Advanced treatment of biologically treated coking wastewater (BTCW) using persulfate (PS) oxidation with magnetic activated carbon composite (CuFe₂O₄:AC w/w ratio of 1:1.5, denoted as 1.5-MACC) as a green catalyst was evaluated at ambient temperature (30 ºC). Effects of PS (K₂S₂O₈) and 1.5-MACC doses on PS decomposition and total organic carbon (TOC) removal in BTCW were also studied during 360 min. The results showed that the 1.5-MACC/PS system has a much better performance on TOC removal in BTCW than only 1.5-MACC or PS system. PS decomposition and TOC removal follow first-order kinetics in the 1.5-MACC/PS system. The optimum condition of the 1.5-MACC/PS system to treat BTCW is with a K₂S₂O₈ dose of 4 g L⁻¹ and 1.5-MACC dose of 5 g L⁻¹. Under this condition, TOC in the PS oxidation effluent is 20.4 mg L⁻¹ with a removal efficiency of 85.4%. TOC removal is a synergistic effect of adsorption and oxidation. TOC oxidation is due to the generation of ·SO₄ via the activation of PS by CuFe₂O₄ impregnated AC. The gas chromatography–mass spectrometry (GC-MS) analysis revealed that phenol compounds and esters were removed significantly by the 1.5-MACC/PS system. When 1.5-MACC was used for the fourth time in the 1.5-MACC/PS system, the removal ratio of TOC was still over 62.2% in 360 min reaction. Thus, the 1.5-MACC/PS system has a potential practical application in treatment of BTCW.

Key words | advanced treatment, biologically treated coking wastewater, magnetic activated carbon composite, persulfate oxidation, sulfate radical

INTRODUCTION

Coking wastewater, as a byproduct in the production of about 470 million tons of coke, is a severe environmental concern in China (Wei et al. 2012). It is a complex industrial wastewater containing large quantities of organic pollutants and inorganic pollutants, which usually include ammonia, cyanide, thiocyanate, phenolic compounds, nitrogen heterocyclic compounds (e.g., quinoline, pyridine, and indole), and polycyclic aromatic hydrocarbons (PAHs) (Ghose 2002; Park et al. 2008; Yang et al. 2013). Many of these constituents are refractory, toxic, mutative, and carcinogenic (Zhang et al. 2012; Ou et al. 2014).

The conventional treatment process of coking wastewater includes solvent extraction of phenolic compounds, steam stripping of ammonia, and biological treatment. At present, anoxic/oxic, anaerobic/anoxic/oxic (A²/O), and aerobic/anoxic/oxic/oxic (A³/O³) processes are the dominant biological treatment process in China for coking wastewater treatment because of the low cost, easy operation and maintenance (Bai et al. 2011; Jin et al. 2013; Ou et al. 2014; Zhou et al. 2014). Unfortunately, these aforementioned processes are not efficient in removing chroma and chemical oxygen demand (COD), resulting in failure to meet the emission standard of the coking chemical industry (GB16171-2012). The effluents from these processes still contain non-biodegradable organic pollutants, which are pyridine, alkylphenols, phthalate, PAHs, and so on (Xia et al. 2011). Therefore, advanced treatment of the biologically treated coking wastewater (BTCW) is necessary.

Recently, advanced oxidation processes (AOPs) have attracted more attention in the post-treatment of coking wastewater. The Fenton reaction is an effective method to remove refractory pollutants in coking wastewater. However, the chemical sludge generation and low pH might limit its application in coking wastewater treatment (Wu et al. 2010).
Persulfate (PS) oxidation that is based on sulfate radicals (SO₄⁻⁻) has exhibited great potential in degrading many refractory pollutants. SO₄⁻⁻ can be generated from the activation of PS by UV, heat, base, and transition metal ions (Kattel et al. 2011; Fang et al. 2017; Ma et al. 2017; Peng et al. 2017). Activated carbon (AC), widely used as an adsorbent in removal of contaminants in water, is not only an adsorption material, but also a catalyst carrier and a catalyst in heterogeneous catalysis (Szymanski 2008). The AC combined with PS system has been studied to degrade toxic organic pollutants for a long time, due to the fact that AC decomposes PS to produce SO₄⁻⁻ with stronger oxidation ability (Liang et al. 2009a; 2009b; Huling et al. 2011; Yang et al. 2011).

Spinel ferrites, expressed as MeFe₂O₄ (Me = Mn, Co, Ni, Cu, Mg, etc.), are actually magnetic materials widely employed in electronic applications, which could be separated easily from water under a magnetic field. Guan et al. found that CuFe₂O₄ was effective to activate peroxymonosulfate (PMS) among the ferrites with Mn, Co, Ni, Cu, and Zn (Guan et al. 2017). PS has a similar structure to PMS. We anticipate that CuFe₂O₄ can activate PS. AC is regarded as a good support for the ferrites due to its oxygen-containing functional groups. Thus, the performance of CuFe₂O₄ can be improved by supporting with AC. To date, limited work has been conducted to investigate the role of AC as the ferrites’ support for PS activation in BTCW treatment. Comparing with other advanced methods for treating BTCW, activation of PS via AC combined with CuFe₂O₄ might not produce secondary pollution, and the material including AC and CuFe₂O₄ is easy to separate from water for reuse.

Herein, the magnetic activated carbon composite (MACC) of CuFe₂O₄/AC was synthesized by a co-precipitation followed by the calcination method as reported previously (Oh et al. 2015). The MACC with a CuFe₂O₄:AC w/w ratio of 1:1.5 was denoted as 1.5-MACC, and had a good performance on removal of methylene blue (Oh et al. 2015). Therefore, we selected 1.5-MACC as the PS activator for pollutant removal from BTCW.

The objectives of this study are: (1) to demonstrate the feasibility of advanced treatment of BTCW using PS oxidation with 1.5-MACC as a green catalyst; (2) to investigate the effects of PS (K₂S₂O₈) and 1.5-MACC doses on total organic carbon (TOC) removal and PS decomposition in BTCW; (3) to identify the changes in organic pollutant composition of BTCW during PS oxidation qualitatively by gas chromatography–mass spectrometry (GC-MS); and (4) to evaluate reuse performance of 1.5-MACC. The results to be achieved in this study could provide a new alternative for the advanced treatment method of BTCW.

MATERIALS AND METHODS

Wastewater

The BTCW used in this study was collected from a coking factory located in Taiyuan City, Shanxi Province. The compositions of the BTCW were as follows: COD at 263–315 mg L⁻¹, TOC at 111–142 mg L⁻¹, NH₃-N at 1.44–1.85 mg L⁻¹, Cl⁻ concentration at 999–1,010 mg L⁻¹, and pH at 8.20–8.61. The effluent is difficult to be degraded by further biological treatment (BOD₅/COD < 0.05).

Materials

The chemicals used in this study were Cu(NO₃)₂·3H₂O, NaOH, Fe(NO₃)₃·9H₂O, K₂S₂O₈, Na₂S₂O₃, HCl, starch, phenolphthalein, Na₂CO₃, NaHCO₃, and KI, which are of analytical grade. They were purchased from Guang Fu Ltd (Shanghai, China). A commercial AC, which is bituminous-coal-based carbon (100 mesh, powder), was purchased from Tianjin Fine Chemical Plant.

Preparation of 1.5-MACC

Referring to the reference (Oh et al. 2015), 1.5-MACC was obtained by co-precipitation followed by calcination. The typical preparation process is described as follows. At first, 2 mmol of Cu(NO₃)₂·3H₂O and 4 mmol of Fe(NO₃)₃·9H₂O were dissolved in 50 mL of deionized water. Then 0.72 g of AC for CuFe₂O₄:AC w/w ratio of 1:1.5 was added into the solution followed by rapid stirring with a magnetic stirrer for 1 h, in which pH was maintained at 11 by adding NaOH. The solution was gradually heated to 100 °C, kept for 4 h under vigorous stirring, and then cooled down to room temperature. The resulting solid products were separated by filtration, washed with deionized water and dried in an oven at 60 °C for 12 h. Finally, the dried product was calcined in a muffle furnace at 300 °C for 1 h to improve the crystallinity and stability of the impregnated CuFe₂O₄.

Structure and magnetism of 1.5-MACC

The crystal structure of 1.5-MACC was determined using an X-ray powder diffractometer (XRD-6000, Shimadzu, Japan) at the scan rate of 8° min⁻¹ operating under 40 kV and
30 mA using Cu-Kα as the X-ray source. The magnetism of 1.5-MACC was determined using a vibrating sample magnetometer (VSM Bkt-4500, Beijing, China). The Brunauer-Emmett-Teller (BET) surface area of 1.5-MACC was determined by N2 adsorption/desorption using a 3H-2000PS2 apparatus (Beijing, China). The surface area and diameter of 1.5-MACC were 265 m²/g and 100–150 mesh, respectively.

**Experimental procedure**

Experiments were conducted using three systems (Systems A, B and C). System A was used to study TOC removal in different situations (only PS, only 1.5-MACC and 1.5-MACC/PS). Batch experiments were performed with 150 mL Erlenmeyer flasks. 100 mL of BTCW with 0.6 g of K₂S₂O₈ was added to the reactors respectively in the presence of, or without 1.5-MACC (0.5 g). 1.5-MACC (0.5 g) was mixed with 100 mL of BTCW to perform the adsorption experiment in the absence of PS. The reactors were opened and placed in an air shaker at 150 rpm and 30 °C for 360 min. Supernatant samples were taken periodically, and pH and TOC were measured. TOC was measured by a TOC-VCPH analyzer (TOC-VCPH, Shimadzu, Japan). pH was measured using a portable pH meter (Mettler Toledo FE-20). At the end of the experiment, 1.5-MACC was separated out from the suspensions using a magnet.

Two sets of experiments were run to study the effect of 1.5-MACC doses (4.5–5.5 g L⁻¹) and K₂S₂O₈ doses (3–6 g L⁻¹) on PS decomposition and TOC removal in System B. The preparation for these experiments was similar to the procedure described above. At each designated time interval, 20 mL of solution was collected, filtered through a 0.22 μm filter film for TOC and PS analysis. The PS concentration was measured by iodometric titrations (Kolthoff & Stenger 1949).

System C was to study the 1.5-MACC reuse performance under the optimum condition of 4 g L⁻¹ of K₂S₂O₈ and 5 g L⁻¹ of 1.5-MACC. 1.5-MACC was collected by magnetic separation after each run, washed several times with distilled water, and dried for 2 h at 105 °C before reuse. Then all the processes were carried out in the same operating conditions as before. Batch tests were carried out in duplicate. Under the optimum condition of 4 g L⁻¹ of K₂S₂O₈ and 5 g L⁻¹ of 1.5-MACC, GC-MS was performed to analyze the change in refractory organic compounds of the BTCW before and after PS oxidation catalyzed by 1.5-MACC. Samples were extracted using CH₂Cl₂ into acidic, neutral, and basic phases sequentially and then dried by the drying agent sodium sulfite and filtered using 0.45 μm syringe filters. The prepared samples were used for GC-MS analysis by a PerkinElmer Clarus 680/SQ8S GC/MS analyzer equipped with a DB-5MS capillary column with inner diameter of 0.25 mm, length of 30 m and film thickness of 0.25 μm. Temperature of the oven was maintained at 280 °C. The temperature control program was followed by retaining at 70 °C for 3 min and then increasing to 280 °C with an increment of 3 °C min⁻¹. The electron energy was 70 eV.

**RESULTS AND DISCUSSION**

**Structure and magnetism of 1.5-MACC**

Figure 1 shows the XRD patterns of pristine AC and 1.5-MACC. The XRD pattern of the pristine AC shows a typical amorphous structure from the broader diffraction peaks at 2θ ≈ 25 ° (Gao et al. 2014). In the XRD pattern of 1.5-MACC, the peak at 2θ ≈ 36 ° gives evidence of the presence of CuFe₂O₄ spinel with some impurity consisting of monoclinic CuO at 2θ ≈ 36 ° and 39 °. The broad XRD peaks suggest that CuFe₂O₄ consists of nano-sized particles. A sharp peak at 2θ = 27 ° for 1.5-MACC is due to impurities from AC.

The magnetic saturation moment per unit mass of 1.5-MACC was determined to be 10.9 emu g⁻¹ (Figure 2) compared to 0.289 emu g⁻¹ for pristine AC, which is attributed to the well-crystalline magnetic CuFe₂O₄ existing in 1.5-MACC. The presented magnetism value was higher than...
the samples prepared by Zhang et al. (0.97–5.93 emu/g), which were prepared without an additional calcination step (Zhang et al. 2007).

**Advanced treatment of BTCW by PS oxidation with 1.5-MACC as a catalyst**

**TOC removal in 1.5-MACC/PS system**

BTCW contains refractory organic pollutants. They can be absorbed by 1.5-MACC or can be oxidized by PS, as shown in Figure 3. Within 360 min, 43.4% of TOC is adsorbed in the 1.5-MACC system and 25.5% of TOC is oxidized in the PS system. Complete removal of refractory organic pollutants in BTCW needs a longer time and larger quantity of 1.5-MACC or PS. However, 88.1% of TOC is removed in the 1.5-MACC/PS system. That is to say that there is also a remarkable joint effect in the 1.5-MACC/PS system. TOC removal in these experiments is attributed to a simultaneous adsorption and oxidation. It has been reported that the impregnated CuFe2O4 in MACC as a catalyst generated ·SO4 from PMS for methylene blue and atrazine oxidation (Guan et al. 2016; Oh et al. 2015). PS is similar to PMS in structure. The impregnated CuFe2O4 in 1.5-MACC can catalyze PS to produce ·SO4 for TOC removal. The following reaction mechanisms are proposed (Zhang et al. 2013):

\[
\begin{align*}
\text{Cu(II)} - \cdot \text{OH} + \text{S}_2\text{O}_8^{2-} & \rightarrow \text{Cu(II)} - (\text{HO})\text{OSO}_3^{2-} + \text{SO}_4^{2-} \\
\text{Cu(II)} - (\text{HO})\text{OSO}_3^{2-} & \rightarrow \text{Cu(III)} - \cdot \text{OH} + \text{SO}_4^{2-}
\end{align*}
\]

(1)

(2)

AC is also an electron transfer catalyst and contains functional groups that can activate PS to produce ·SO4 as shown below (Liang et al. 2009b):

\[
\begin{align*}
\text{AC surface} - \cdot \text{OOH} + \text{S}_2\text{O}_8^{2-} & \rightarrow \text{AC surface} - \cdot \text{OO} + \cdot \text{SO}_4^{2-} + \text{HSO}_4^{-} \\
\text{AC surface} - \cdot \text{OH} + \text{S}_2\text{O}_8^{2-} & \rightarrow \text{AC surface} - \text{O} + \cdot \text{SO}_4^{2-} + \text{HSO}_4^{-}
\end{align*}
\]

(3)

(4)

Hence, it is possible to conclude that impregnated CuFe2O4 and AC are effective for PS activation and TOC is partly being degraded through oxidation.

**Effects of K2S2O8 dose on PS decomposition and TOC removal**

As shown in Figure 4(a), when the dose of 1.5-MACC remained at a fixed value (5 g L⁻¹), a remarkable increase in TOC removal was observed with an increase of K2S2O8 dose from 3 g L⁻¹ to 4 g L⁻¹, as opposed to the relatively slow growth of TOC removal with K2S2O8 dose increasing from 4 g L⁻¹ to 6 g L⁻¹. TOC degradation is of first-order (R² > 0.94), and its degradation rate constant increased from 0.0014 min⁻¹ to 0.0049 min⁻¹ with increasing K2S2O8 dose. However, the TOC degradation rate increased a little as the K2S2O8 dose was beyond 4 g L⁻¹. Thus a higher K2S2O8 dose resulted in an increase in TOC removal.
efficiency, but superfluous K$_2$S$_2$O$_8$ dose didn’t benefit the increase in TOC removal efficiency. The reason is that an excessive amount of PS in wastewater may compete with refractory organic pollutants on adsorption onto the surface of 1.5-MACC (Georgi & Kopinke 2005). In addition, SO$_4^-$ generated by catalysis of PS reacted with excessive PS to form SO$_4^{2-}$ (Sainen et al. 2011). As shown in Figure 4(b), the PS decomposition follows first order kinetics ($R^2 > 0.96$), and its decomposition constant rate decreases from 0.0124 min$^{-1}$ to 0.0030 min$^{-1}$ with increasing PS concentration, which is similar to the hydroxide decomposition on AC in other studies (Lücking et al. 1998; Huang et al. 2003). The remaining PS concentration increased sharply with K$_2$S$_2$O$_8$ dose from 3 to 6 g L$^{-1}$, but reached a lower level at a reaction time of 360 min with a K$_2$S$_2$O$_8$ dose of 4 g L$^{-1}$. Therefore, according to the TOC removal rate and the remaining PS concentration, the optimum K$_2$S$_2$O$_8$ dose was 4 g L$^{-1}$.

Effects of 1.5-MACC dose on PS decomposition and TOC removal

As shown in Figure 5(a), when the K$_2$S$_2$O$_8$ dose remained at a certain value (4 g L$^{-1}$), an increase in TOC removal was observed with the 1.5-MACC dose increasing from 4.5 g L$^{-1}$ to 5 g L$^{-1}$ at a reaction time of 360 min. However, further increase in the 1.5-MACC dose resulted in the saturation of the TOC removal, because the higher 1.5-MACC surface area increased the amount of active sites for adsorption and activation of PS. The TOC degradation constant rate increased quickly in the range of 4.5–5.0 g L$^{-1}$, but a little in the range of 5–5.5 g L$^{-1}$. The PS decomposition constant rate increased with increasing 1.5-MACC concentration from 4.5 g L$^{-1}$ to 5.0 g L$^{-1}$, and went up a little with further increase of 1.5-MACC dose. The result is similar to Lee’s study (Lee et al. 2015). The remaining PS concentration at the 1.5-MACC dose of 5 g L$^{-1}$ was near to that
with the 1.5-MACC dose of 5.5 g L\(^{-1}\) at a reaction time of 360 min (see Figure 5(b)). Then the optimum 1.5-MACC dose was 5 g L\(^{-1}\) according to the economic analysis. Moreover, TOC of the PS oxidation effluent with 5 g L\(^{-1}\) of 1.5-MACC was 20.4 mg L\(^{-1}\) and the TOC removal efficiency was 85.4%.

**Refractory organic compounds removal during PS oxidation**

Refractory organic compounds in the BTCW and oxidation effluent of the 1.5-MACC/PS system were determined by GC-MS analysis (see Supplementary Information, available with the online version of this paper). These compounds were mainly identified as alkane, alcohol, esters, long-chain acids, aldehyde, and phenol compounds. As a result of PS oxidation, 2-buten-1-ol, 2,4-di-t-butyl-6-nitro-phenol, 1-naphtha, diisobutyl phthalate, 2,4-di-tert-butylphenol, lauryl acetate, dibutyl phthalate, and n-hexadecanoic acid were removed significantly, which indicated that phenolic compounds and esters can be degraded by PS oxidation. The results are similar to those by Saputra et al. (Saputra et al. 2015) and Li et al. (Li et al. 2014). Furthermore, there were some new organic compounds generated, for example, heptane and 2,3,5-trimethyl.

**Reuse of 1.5-MACC**

The reuse experiment was carried out to understand the possibility of repeated use of 1.5-MACC. The results are shown in Figure 6. TOC removal efficiency for every reuse cycle gradually declined, but in the 1.5-MACC/PS system, when 1.5-MACC was used for the fourth time, the removal efficiency of TOC was still over 62.2% in 360 min reaction. It implied that the 1.5-MACC had been slightly deactivated and didn’t have a very bad recovery performance. This could be attributed to the following reasons: (1) the incompletely removed TOC adsorbed on the 1.5-MACC surface inhibited the interaction of PS and 1.5-MACC; (2) the adsorbed fraction of organics on the 1.5-MACC surface was almost unreactive (Oh et al. 2015). It was found that the concentration of leached Cu ion was about 2.06 mg L\(^{-1}\) at 360 min, accounting for 0.4% of the total Cu content in the catalyst. Although 1.5-MACC in this study showed good efficiency for TOC removal in BTCW in the presence of PS, there are still some common problems about Cu leaching, desorption and reuse of this material for its practical use. Thus further studies are needed in the future.

**CONCLUSION**

The 1.5-MACC was prepared by a two-step method of co-precipitation and calcination, which consisted of porous micro-particles with homogeneously distributed CuFe\(_2\)O\(_4\), and it possessed a high magnetic saturation moment (10.9 emu g\(^{-1}\)). In this study, the feasibility of advanced treatment of BTCW using PS oxidation catalyzed by 1.5-MACC was evaluated at ambient temperature (30 \(^\circ\)C). Effects of \(K_2S_2O_8\) and 1.5-MACC dose on refractory organics removal in BTCW and PS decomposition were investigated within 360 min. This study demonstrates that the 1.5-MACC/PS system has much better performance for the removal of TOC than only PS or 1.5-MACC. PS decomposition and TOC removal follow first-order kinetics in a 1.5-MACC/PS system. The optimum condition for a 1.5-MACC/PS system in BTCW is with 4 g L\(^{-1}\) of \(K_2S_2O_8\) and 5 g L\(^{-1}\) of 1.5-MACC. Under this condition, TOC in the PS oxidation effluent is 20.4 mg L\(^{-1}\) with a removal efficiency of 85.4\%, and TOC removal is a synergistic effect of adsorption and oxidation. TOC oxidation is due to the generation of \(\cdot SO_4\) via the activation of PS by CuFe\(_2\)O\(_4\) impregnated AC. GC-MS analysis results showed that phenol compounds and esters were removed significantly by the 1.5-MACC/PS system. 1.5-MACC could be reused several times in the 1.5-MACC/PS system. When 1.5-MACC was used for the fourth time, the degradation ratio of TOC was still over 62.2% in the 360 min reaction. Thus, the 1.5-MACC/PS system has a potential practical application in the treatment of BTCW.
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