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Heterogeneous persulfate oxidation of BTEX and MTBE using Fe_3O_4–CB magnetite composites and the cytotoxicity of degradation products

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ABSTRACT

Groundwater contamination by organic aromatic compounds such as gasoline fuel is a serious worldwide problem because of their carcinogenic and mutagenic potential. This study evaluated the use of Fe_3O_4–carbon black (CB) composites for persulfate (PS) oxidation of benzene, toluene, ethylene, and xylene (BTEX) and methyl *tert*-butyl ether (MTBE) compounds from the aqueous solution. The characterization results of environmental scanning electron microscopy coupled with energy-dispersive spectroscopy, X-ray diffraction, Fourier transform infrared spectroscopy, and a superconducting quantum interference device magnetometry evidenced the successful synthesis of Fe_3O_4–CB composites. In addition, the *in vitro* cytotoxic activity and apoptotic response of these composites were investigated before and after the Fe_3O_4–CB/PS processes test of the BTEX and MTBE samples was performed. The effects of various operating parameters were evaluated to optimize the oxidation process, including the PS concentration, initial pH, and Fe_3O_4–CB amount. The results showed that increasing PS and Fe_3O_4–CB dosage could accelerate BTEX and MTBE oxidation when PS and Fe_3O_4–CB concentrations increased to 15 g L^{-1} and 1.0 g L^{-1}, respectively, at a pH of 3.0. The degradation rate of BTEX and MTBE was strongly pH-dependent. Methyl thiazolyl tetrazolium assay was employed to perform a cytotoxicity study after Fe_3O_4–CB/PS processing treatment of BTEX and MTBE degradation products on the zebrafish (*Danio rerio*) embryonic cell line (ZF4), which revealed that a weak effect and apoptosis in cell viability ultimately leads to cell death. The results suggested that Fe_3O_4–CB assisted persulfate oxidation without elevating the temperature is a suitable and economic alternative for the *ex-situ* treatment of BTEX- and MTBE-contaminated aquatic environments.

1. Introduction

With the development of industry, vast attention has been paid to volatile organic petroleum contaminants such as gasoline hydrocarbons components—benzene, toluene, ethylbenzene, and xylenes (BTEX) and fuel additives—methyl *tert*-butyl ether (MTBE) because they are widely recognized as some of the most ubiquitous pollutants of the exposure of aquatic organisms are harmful to soil and groundwater, and contain high toxicity and hazardous materials when they exists in natural environments (Dangi and Abraham, 1997; Liang et al., 2009; Genuino et al., 2012; Khodaei et al., 2017). BTEX and MTBE, which have a complex aromatic molecular structure, are emitted in several processes, including those in the exhaust emissions from automobile, petroleum industry and paint, adhesives, and rubber production (Liang et al., 2008, 2010; Guisado et al., 2015; Chang et al., 2017). The potential ecotoxicological impacts of BTEX and MTBE are due to their highly mutagenic and carcinogenic compounds; therefore, they are a potential hazard to public health under ambient conditions, and their complete elimination from contaminated effluents is necessary (Croute et al., 2002; Wang et al., 2008; Li et al., 2009; da Silva and Corseuil, 2012; Liu et al., 2014, 2015; Lachner et al., 2015). Therefore, extensive study has been conducted to remove BTEX and MTBE from waste streams, and controlling BTEX and MTBE effluents is critical. There are many techniques options available for the removal of BTEX and MTBE from aqueous solutions successfully

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such as biodegradation, filtration, coagulation, ozonation, UV-light irradiation, electrocatalytic oxidation, and adsorption (Dangi and Abraham, 1997; Lin et al., 2007; Geng et al., 2012; Liao et al., 2013; Hu et al., 2014). However, conventional techniques are not readily amenable to detoxification of the pollutant to conform to stringent discharge regulations. Thus, an alternative treatment of the BETX- and MTBE-contaminated soils and groundwater is extremely urgent.

Owing to the limitations of the conventional process for BETX and MTBE, highly reactive sulfate radicals ($SO_4^{\bullet}$)–based advanced oxidation processes (AOPs) for persulfate (PS) have recently attracted attention because of their emerging and efficient in producing powerful oxidizing species, such as $SO_4^{\bullet}$, which can potentially be used for the degradation of organic contaminants (Tsitonaki et al., 2010). Although PS has been demonstrated more frequently than has hydrogen peroxide as an oxidant for the remediation of environments contaminated with recalcitrant organic pollutants at ambient temperature through *in situ* chemical oxidation (ISCO), the direct reaction of PS with most reductions is slow, which limits its large-scale applications (Yen et al., 2011). PS can be activated and converted to $SO_4^{\bullet}$, which is an effective approach to overcome these problems (Do et al., 2010). $SO_4^{\bullet}$ are one-electron oxidants that can potentially remove contaminants. Generally, PS can be activated chemically, using simple transition metals M^{n+} as catalysts or through heat or ultraviolet light activation to generate strong oxidizing species of $SO_4^{\bullet}$ that are utilized has been reported in the following processes (Ghauch et al., 2012):

$$S_2O_8^{2-} + M^{n+} \xrightarrow{chemical-activation} SO_4^{-\cdot} + SO_4^{2-} + M^{(n+1)+} \quad (1)$$

$$S_2O_8^{2-} \xrightarrow{thermal/UV-activation} 2SO_4^{-\cdot} (303K \le T \le 372K) \quad (2)$$

However, this crucial heterogeneous catalytic process has attracted considerable attention in materials chemistry, and Fe(II) additives can improve the effectiveness of the electron transfer process, which generates $SO_4^{\bullet}$ and hydroxyl free radicals (•OH) in a manner similar to that of Fenton's reaction.

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{-\cdot} + SO_4^{2-} + Fe^{3+} \quad (3)$$

$$SO_4^{-\cdot} + H_2O \rightarrow HO\bullet + HSO_4^- \quad (4)$$

Since these additives change the reaction characteristics in the PS approach, this may as well influence catalytic reactive species that can rapidly remove contaminants. Because of their engineering effectiveness, $SO_4^{\bullet}$-based AOPs selectively produce carbon dioxide and oxidize small molecules through aqueous-phase oxidation. Various types of catalyst have been enhanced in the treatment of BTEX- and MTBE-contaminated wastewater. Liang et al. (2008) reported the removal capabilities of citric acid (CA)-chelated Fe^{2+} BTEX in an aqueous solution. Their results showed that the degradation of BTEX was due to the PS oxidation process and the degradation rate constants of BTEX were found to increase with increased PS concentrations. Liang et al. (2009) observed that a complete removal of BTEX was achieved using Fe-activated PS chemical oxidation in conjunction with a wet scrubbing system. Additionally, $S_2O_8^{2-}$ can be activated using CA-chelated Fe^{2+} to generate $SO_4^{\bullet}$, which may rapidly degrade BTEX in the aqueous phase and result in continuous destruction of the BTEX gases. Kambhu et al. (2012) developed slow-release PS candles to treat BTEX-contaminated groundwater, and the activated PS transformed all the BTEX compounds tested. Jo et al. (2014) investigated the potential of the iron oxide immobilized MnO_2 composite as a heterogeneous catalyst to activate PS for the treatment of benzene- and carbon tetrachloride-polluted wastewater. Results reveal that for the PS and composite system, the same pH for the highest degradation rates of both carbon tetrachloride and benzene were observed and the pH was 9.0. Liang et al. (2010) applied the 3 g L^{-1} pyrite (FeS_2) as the source of ferrous ion with 5 g L^{-1} PS for the removal of MTBE, which exhibited generation and subsequent degradation of the primary MTBE intermediate products, including *tert*-butyl formate (TBF), *tert*-butyl alcohol (TBA), methyl acetate (MAC), and acetone after 4 h. Meanwhile, a possible reaction mechanism proposed that $SO_4^{\bullet}$ was the dominant active species taking part in the degradation of oxidation process indicates that MTBE destruction is most likely to be due to α-hydrogen abstraction through the $SO_4^{\bullet}$ attack in the intermediate methoxy group. Huling et al. (2011) reported that thermal activation of PS at a lower pH range (3.5–7.5) was effective and resulted in greater MTBE removal than did either alkaline activation or binary systems involving 30% H_2O_2 and 40 g L^{-1} of PS.

Functional carbon materials with a high surface area, such as activated carbon, carbon aerogel, and carbon black (CB), have received increased interest for their use as support materials for heterogeneous catalysts because of their performance in different industrial processes and their characteristics, including small pore diameter, large contact surface area, high dispersion of impregnated metal, and abundant functional groups (Lee et al., 2013; Mazaheri et al., 2015). The use of functional groups, including carboxylic ($-COOH_2^+$), phenolic ($-OH_2^+$), and chromenic groups, which enhances organics degradation through electrostatic attraction as an activator for mediating electron transfer and create more active sites within the carbonaceous matrix reactions on CB surfaces, is proposed as follows (Ghaedi et al., 2016; Guo et al., 2017):

$$CB_{surface} - OOH + S_2O_8^{2-} \rightarrow CB_{surface} - OO^{\cdot} + SO_4^{-\cdot} + HSO_4^- \quad (5)$$

$$CB_{surface} - OH + S_2O_8^{2-} \rightarrow CB_{surface} - O^{\cdot} + SO_4^{-\cdot} + HSO_4^- \quad (6)$$

To improve the performance of the catalyst, a combination of iron oxides and carbon materials, to be ideal candidates for these heterogeneous catalysts because of the combination of suitable magnetic properties with relatively low toxicity, biocompatibility and biodegradability, and environmentally friendly properties, and they can be promote the PS decomposition to generate reactive oxygen species for organic degradation (Tan et al., 2012). Because of its multifunctional properties, the environmental applications of magnetite (Fe_3O_4), such as the degradation of organic compounds in contaminated wastewaters, were investigated (Tang and Lo, 2013; Zhou et al., 2014; Kakavandi et al., 2016). Moreover, the interaction between magnetic iron nanoparticles in a CB matrix is complex. Among them, various metal interactions may exhibit a synergistic effect that in turn enhances the individual catalytic characteristics of the interacting compounds. Moreover, few studies have explored cell culture models for physiological and toxicological studies. The reported in cytotoxic effect to BTEX mixture toxicity has been extensively studied via various types of cells, such as A549 human lung adenocarcinoma cells (Groute et al., 2002), liver hepatoma (HepG2) cells (Groute et al., 2002; Liu et al., 2014, 2015), and in a zebrafish (*Danio rerio*) permanent hepatocyte cell line (ZFL) (Lachner et al., 2015), and the effect of MTBE compounds has been investigated in sertoli (Li et al., 2009) and rabbit tracheal epithelial cells (RTEs) (Wang et al., 2008). Furthermore, cumulative evidence has revealed that BTEX and MTBE induced free radical and reactive oxygen species (ROS) production that damages DNA molecules in human cells (Li et al., 2009; Lachner et al., 2015). The resulting hydroxyl radicals from ROS production