



Effective degradation of diatrizoate by electro-peroxone process using ferrite/carbon nanotubes based gas diffusion cathode



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ABSTRACT

In this study, ferrite modified carbon nanotubes (MFe₂O₄/CNTs, M: Fe, Mn) were prepared and employed as cathodic catalysts to assist electro-peroxone (i.e., combined ozonation with electrolysis process using a carbon-polytetrafluoroethylene cathode) treatment of emerging pollutant diatrizoate (DTZ) in aqueous solution. The structural and surface property of synthesized catalysts was studied, and the performance of electro-peroxone process using MFe₂O₄/CNTs based gas diffusion cathode (GDC) was systematically investigated from the kinetic and mechanistic viewpoints. Results show that the combination of ozonation and electrolysis exhibited synergistic degradation of DTZ. Approximately 71.9% DTZ had been degraded with MFe₂O₄/CNTs based GDC after 10 min, 13.2% higher than with bare CNTs based GDC, implying that the combined treatment efficiency could be enhanced by the presence of MFe₂O₄. The performance of MFe₂O₄/CNTs catalytic electro-peroxone process was positively correlated with inlet ozone concentration (10–30 mg/L), and an increase in applied current stimulated DTZ degradation at a low cathodic current density (5–40 mA/cm²) but inhibited the degradation at a high cathodic current density (40–60 mA/cm²). The MFe₂O₄/CNTs catalytic electro-peroxone treatment also showed a significant dependence on initial pH and reaction temperature, but was little affected by supporting electrolyte concentration. Higher removal efficiency was obtained at a lower initial DTZ concentration. The comparison tests reveal that peroxone reaction was the main pathway of hydroxyl radicals (HO[•]) production in the present system, and the presence of MFe₂O₄ at the cathode could promote HO[•] generation. These observations suggest that electro-peroxone is efficient for DTZ degradation in aqueous solution, and MFe₂O₄/CNTs are good and promising cathodic materials and catalysts for this process.

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1. Introduction

Diatrizoate (DTZ) is one of the most widely used iodinated X-ray contrast media (ICM), which are a group of pharmaceutical compounds that are used for imaging of organs or blood vessels [1]. Due to its heavy use and incomplete elimination, DTZ has been detected in hospital and domestic wastewater, treatment plant effluents, surface water, groundwater, and drinking water in ranges from ng/L to mg/L [2]. The presence of DTZ in aquatic environment exhibit a potential risk to ecological safety [3].

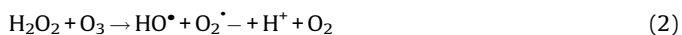
Unfortunately, because of its special chemical structure, DTZ has been found to be recalcitrant to conventional water treatment processes [4–6]. In particular, DTZ is the most persistent of the ICM compounds [7]. Advanced oxidation/reduction processes (AO/RPs) involve the generation of reactive species and either the reducing agents as the predominant species for the degradation of recalcitrant organic pollutants [8]. In this context, AO/RPs have been suggested as innovative removal technologies for DTZ [9,10], with many of them based on ozone and electrolysis application [11,12]. Ozone is an excellent oxidant, but only limited ozonation of DTZ has been reported [13]. Better DTZ degradation occurs during treatment with ozone-based AOPs (e.g., UV/O₃, O₃/H₂O₂) due to the promoted hydroxyl radicals (HO[•]) formation. However, DTZ continues to be detected at the end of these treatments [14].

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Combination of cathodic reduction and electro-oxidation is an efficient water treatment process [15]. Radjenovic et al. noted that cathodic DTZ deiodination combined with anodic oxidation provides benefits over oxidative treatment methods because it does not produce stable iodinated intermediates [16]. Nevertheless, its long time requirement may limit practical applications of electrolysis technology [17].

Recently, combining ozonation and electrolysis has emerged as a promising technology for treating waters contaminated with highly recalcitrant organic contaminants [18–20]. The presence of ozone during electrolysis brings about enhanced degradation of pollutants by the generation of highly reactive HO[•], and can mutually compensate the limitations of the two processes [21]. The applied electrode materials and process conditions that favor HO[•] formation have a pronounced positive effect on this combined treatment. Yuan et al. proposed to use carbon-based cathode to electrochemically generate H₂O₂ from O₂ in the bubbled ozone generator effluent, which contains both O₂ and O₃ gas [22]. The in-situ generated H₂O₂ can then react with O₃ to produce HO[•] via the peroxone reaction (Eqs. (1) and (2)) [23]:



The replacement of metal cathodes (e.g., Ti, stainless steel, and boron-doped diamond) with carbon based gas diffusion cathode (GDC) fundamentally changes the way of HO[•] generation in combined ozonation and electrolysis process and greatly enhances pollutant degradation [24–26]. To distinguish the combined process from the previous ozone-electrolysis process, the new process has been termed as electro-peroxone [22].

Accelerating the decomposition of ozone and H₂O₂ to generate HO[•] is critical for electro-peroxone treatment. In recent studies, carbon nanotubes (CNTs) based GDC has been demonstrated as an effective cathode in electro-Fenton and electro-peroxone processes [27–29]. Using spinel ferrites (MeFe₂O₄, Me = Mn, Co, Ni, Cu, Mg, etc.) as ozonation or Fenton-like reaction catalysts is promising in the field of environmental remediation due to their unique surface properties. Catalytic ozonation by ferrites was reported to destruct refractory organic pollutants [30]. Ferrites catalyzed H₂O₂ oxidation was efficient in synthetic dye degradation due to its contribution in the generation of HO[•] [31,32]. Furthermore, some studies have indicated that the combining of magnetic ferrites with carbon materials provides a potential catalytic route that meets the requirements of good adsorption capacity, high catalytic activity, high chemical stability and easy fixation for recovery and reuse [33,34]. Considering the excellent performance and low cost, ferrites might be applicable to activate electro-peroxone oxidation in water treatment. However, the effects of ferrite on the performance of GDC is largely unknown, and few systematic studies had examined the use of ferrite catalytic electro-peroxone process for treating DTZ containing wastewater.

This work is mainly focused on four aspects: (I) preparation and characterization of CNTs supported ferrite (MFe₂O₄/CNTs) catalysts; (II) effectiveness of electro-peroxone treatment of DTZ using MFe₂O₄/CNTs based GDC; (III) effects of operating variables in MFe₂O₄/CNTs catalytic electro-peroxone treatment of DTZ, including inlet ozone concentration, current density, initial pH, reaction temperature, supporting electrolyte concentration and initial DTZ concentration; (IV) investigation of the possible oxidation mechanism.

2. Materials and Methods

2.1. Chemicals and reagents

Multi-walled CNTs were purchased from Chengdu Organic Chemistry Co., Ltd, Chinese Academy of Sciences; DTZ (sodium salt), *p*-chlorobenzoic acid (pCBA), and *tert*-butanol (t-BuOH) were from Sigma Aldrich. In **Table S1**, the characteristics and structure of sodium DTZ are provided. Other chemicals (e.g., polytetrafluoroethylene, Na₂SO₄, Na₂S₂O₃ and KI) were analytical grade and purchased from Aladdin Industrial Co., China. All solutions were prepared using deionized-distilled water.

2.2. Preparation of MFe₂O₄/CNTs

CNTs were pretreated by sonication in aqueous 65 wt% HNO₃ solution for 2 h followed by aging at 130 °C for 4 h under refluxing conditions. The suspension was washed with distilled water and rinsed several times until the filtrate pH reached neutral. After acid treatment, the CNTs were separated by filtration and dried at 60 °C for subsequent use.

Since manganese ferrite can catalyze both ozone and H₂O₂ decomposition [35,36], it was employed to modify CNTs in this work. MFe₂O₄/CNTs hybrids were prepared by a simple impregnation – calcination method [37]. Briefly, 1.0 g CNTs were impregnated into a 100 mL solution mixture of 20 mmol/L Fe(NO₃)₃ and 10 mmol/L Mn(NO₃)₂. After sonication for 2 h, the suspension was then mixed continually at room temperature for 24 h. After that, the impregnated CNTs were filtrated and dried at 50 °C. Finally, the dried CNTs were treated at 600 °C for 2 h under inert condition of N₂. As Fe₃O₄ can also be fabricated by this method [37], the products were denoted as MFe₂O₄/CNTs (M: Fe, Mn).

2.3. Characterization of MFe₂O₄/CNTs

The metal loadings of the prepared samples were determined by X-ray fluorescence (XRF-1800, Shimadzu, Japan), and inductively coupled plasma optical emission spectrometry (ICP-OES, Prodigy, Leeman Labs Inc., USA) after their dissolution in a mixture of 65 wt% HNO₃ and 37 wt% HCl (1:1 v/v). The phase of the calcined catalysts was characterized by X-ray diffraction (XRD) with copper Ka radiation. The specific surface area was measured by Brunauer-Emmett-Teller (BET) apparatus (BeISorp-Mini, Japan), and the pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) method. A JEM-200CX transmission electron microscope operating at 200 kV accelerating voltage was used for transmission electron microscopy (TEM) images. Fourier Transform Infrared Spectroscopy (FT-IR) were recorded in KBr pellets instrument (Thermo Scientific Nicolet iS10, USA) in 400–4000 cm⁻¹ range. The pH at the point of zero charge (pH_{PZC}) of catalyst was determined by mass titration method [38].

2.4. Experimental set-up and conditions

Experiments were carried out in an undivided pmma reactor (100 mm length, 50 mm wide and 150 mm height) with 500 mL of solution, and a water jacket was employed for controlling reaction temperature (**Fig. S1** in Supplementary data). A 0.8 cm² Pt wire was employed as the anode, and a CNTs or MFe₂O₄/CNTs based GDC with effective area of 7.0 cm² (2.0 cm × 3.5 cm) was used as the cathode. The GDCs were prepared following the procedure described elsewhere [27]. The electrode gap was 30 mm, and a

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