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Removal of chlorpheniramine in a nanoscale zero-valent iron induced heterogeneous Fenton system: Influencing factors and degradation intermediates

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HIGHLIGHTS

- Removal of chlorpheniramine by nZVI/H_2O_2 was studied for the first time.
- The optimal reaction conditions were determined for chlorpheniramine degradation.
- Degradation pathway of chlorpheniramine in the nZVI/H_2O_2 system was proposed.
- NDMA was formed during the decomposition of chlorpheniramine by nZVI/H_2O_2.
- NDMA FP was significantly reduced by nZVI/H_2O_2 reaction.

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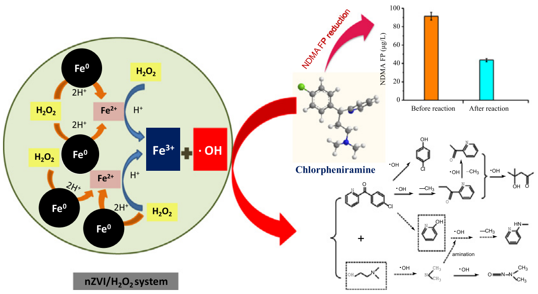
GRAPHICAL ABSTRACT



ABSTRACT

Removal of chlorpheniramine in a nanoscale zero-valent iron (nZVI) induced heterogeneous Fenton system was investigated. The removal efficiency of chlorpheniramine depended on its initial concentration, initial pH, H_2O_2 concentration and nZVI dose. Chlorpheniramine ($\leqslant 15$ mg/L) was completely removed after 60 min oxidation under the following optimal conditions: initial pH = 3.0, H_2O_2 concentration = 0.1 mM and nZVI dose = 22.4 mg/L. The degradation of chlorpheniramine fitted well with the pseudo first-order kinetics model, and the rate constants (k_{obs}) were obtained ($R^2 > 0.9$). Several degradation intermediates of chlorpheniramine were detected and confirmed, including 4-hydroxy-4-methyl-2-pentanone, 2-methylaminopyridine, 4-chlorophenol, 2-propionylpyridine, 2-acetylpyridine, 4-chlorophenyl-2-pyridyl ketone, dimethylamine (DMA) and N-nitrosodimethylamine (NDMA). Based on the identified intermediates, a tentative degradation pathway of chlorpheniramine in the nZVI/H_2O_2 system was proposed. After nZVI/H_2O_2 reaction, 52.2% of NDMA formation potential (FP) from chlorpheniramine was reduced. Therefore, nZVI as the catalyst used in the heterogeneous Fenton system is not only an alternative to remove chlorpheniramine, but also effective in reducing NDMA FP.

1. Introduction

Chlorpheniramine is the first-generation of alkylamine antihistamine used in the prevention of the symptoms of allergy, and it is one of the most commonly used antihistamines in small animal

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veterinary practice as well. It is classified as one category of drugs with high solubility and high permeability based on Biopharmaceutics Classification System [1]. Although the occurrence of chlorpheniramine in water and wastewater is rarely reported, its qualitative identification in samples collected from wastewater treatment plants (WWTPs) in New York that had more than 20% of inflow from pharmaceutical formulation facilities was confirmed [2]. Recently, chlorpheniramine was also found to be an important potential precursor of N-nitrosodimethylamine (NDMA), an emerging disinfection byproduct during chloramination or chlorination [3–9]. It is well known that NDMA is a potential carcinogen and mutagen. Therefore, it may pose a potential risk to humans and other organisms if chlorpheniramine is not effectively treated.

Over the last decades, a great deal of efforts have been made to develop and improve approaches to remove pharmaceuticals and personal care products (PPCPs) from contaminated waters and soils [10,11]. However, researches on chlorpheniramine are still very limited [12–15]. Some researchers [12–14] used Ca-montmorillonite, kaolinite or birnessite to adsorb chlorpheniramine in water, and found a higher chlorpheniramine adsorption was achieved under neutral to weak alkaline conditions. However, adsorption can only transfer chlorpheniramine from one phase to another phase without destructing it. Furthermore, chlorpheniramine is difficult to be biodegraded due to its recalcitrant characteristics. In general, advanced oxidation processes (AOPs) are effective in degrading the trace and recalcitrant PPCPs residuals [10]. Ozone, UV and Fenton are the most widely used oxidants. Our recent study investigated the ozonation of chlorpheniramine, and indicated that ozone was effective in removing chlorpheniramine when the ozone dose was higher than 16 mg/min [15]. Although no study was conducted to degrade chlorpheniramine using UV, Sedlak et al. [16] reported that the cost of UV treatment was considerable for removing other PPCPs. Compared with ozone and UV treatments, Fenton oxidation has attracted much more attention due to its strong oxidative capacity under mild reaction conditions [17]. Although the degradation of PPCPs by Fenton's reagent is promising, the homogeneous catalyst is usually added as ferrous salt which is rapidly consumed, resulting in incompletely removal of PPCPs. In order to achieve a higher removal efficiency, usually a significant quantity of ferrous salt is needed, which leads to a large amount of iron in the effluent and sludge [11,18]. A heterogeneous Fenton-like system using iron supported catalysts (e.g., zero-valent iron (Fe^0), goethite (α-FeOOH), Fe_3O_4 and Fe^0/Fe_3O_4) provides an alternative to the homogeneous Fenton process [19–21]. The iron supported catalyst can serve as a slow-releasing source of ferrous ion, which would activate hydrogen peroxide (H_2O_2) to produce hydroxyl radicals ($^{\text{rad}}$OH) constantly. Nevertheless, these approaches usually require UV, visible light irradiation or ultrasound to accelerate the degradation rate [18,22]. Recently, nanoscale zero-valent iron (nZVI) has been increasingly used in the heterogeneous Fenton system, due to its large specific surface area and high reactivity [11,17,23–25]. It is reported that the removal of contaminants in the nZVI induced heterogeneous Fenton system involves two steps [26–28]: (1) H_2O_2 decomposes on or near the nZVI surface to form Fe^{2+} (Eq. (1)); (2) then, Fenton reaction occurs, Fe^{2+} reacts with H_2O_2 to produce $^{\cdot}OH$ (Eq. (2)), and contaminants are degraded. Meanwhile, the produced Fe^{3+} is further reduced to Fe^{2+} (Eq. (3)).

$$Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O \quad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^- \quad (2)$$

$$2Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+} \quad (3)$$

A few reports have employed nZVI induced heterogeneous Fenton processes for the oxidative degradation of refractory organic compounds, such as amoxicillin [11], trichloroethylene [17], 4-chloro-3-methyl phenol [18], *p*-chloronitrobenzene [29], polychlorinated biphenyls [30], monochlorobenzene [31], carbamazepine [32] and 2,4-dichlorophenol [33]. These refractory organic compounds were almost completely removed after nZVI/H_2O_2 oxidation. Based on the similar chlorobenzene moiety in these chemicals, we speculated chlorpheniramine can also be degraded by the nZVI Fenton process.

Besides during chloramination or chlorination, NDMA was also found to be generated from PPCPs containing dimethylamine (DMA) functional group during the AOPs. Nevertheless, most related researches focused on the ozonation process [15,34,35]. Generation of NDMA was observed during chlorpheniramine ozonation in our previous study [15]. However, NDMA formation during other AOPs has not been reported yet. Thus, it is also necessary to investigate the NDMA formation when exploring the degradation of chlorpheniramine in the nZVI/H_2O_2 system.

The main objective of this study was to investigate the removal of chlorpheniramine in a nZVI induced heterogeneous Fenton system. The effects of initial chlorpheniramine concentration, initial pH, H_2O_2 concentration and nZVI dose were assessed. The reaction kinetics was studied. Furthermore, degradation intermediates of chlorpheniramine were analyzed, and a tentative degradation pathway was proposed. In addition, as a potential NDMA precursor, the formation of NDMA and NDMA formation potential (NDMA FP) during the degradation of chlorpheniramine were also evaluated.

2. Materials and methods

2.1. Chemicals

Chlorpheniramine was obtained from Sigma–Aldrich (>98%, Milwaukee, WI, USA). NDMA and DMA were bought from Chem Service Inc. (West Chester, PA, USA). Phenyl isothiocyanate was purchased from Sigma–Aldrich (Milwaukee, WI, USA), and it was used as derivatization reagent with DMA. NDMA-d_6 was purchased from Chem Service Inc. (West Chester, PA, USA), and it was used as an isotope-labeled surrogate standard. Sodium hypochlorite was bought from Alfa Aesar (Ward Hill, MA, USA). Methylene dichloride, acetonitrile and tert-butyl alcohol (TBA) were obtained from Sigma Chemical Co. (St. Louis, MO, USA). Ultrapure water was prepared using a Gradient A10 water purification system (Millipore, Bedford, MA). Commercial reductive nZVI powder (>99.9%, 50 ± 20 nm) was obtained from Aladdin Industrial Co. (Los Angeles, SC, USA) and stored in an anaerobic chamber. Other reagents including H_2O_2 (30%, w/w) were of analytical grade and were supplied by Sinopharm Chemical Reagent Co. (Shanghai, China).

2.2. Experimental procedures

2.2.1. Factors influencing chlorpheniramine degradation

Experiments for chlorpheniramine degradation by nZVI/H_2O_2 were carried out in 500 mL Erlenmeyer flasks. The working volume was 300 mL. After addition of chlorpheniramine solution, nZVI and H_2O_2 sequentially in an anaerobic chamber, the flasks were capped and placed on a rotary shaker (ZD-85, Jintan Jinda Instrument Manufacturing Co. LTD, China) under dark conditions. The temperature and rotary speed were controlled at 25 °C and 200 rpm, respectively. Experiments evaluating the effects of initial chlorpheniramine concentration (5–30 mg/L), initial pH (2.0–5.0), H_2O_2 concentration (0.01–0.2 mM) and nZVI dose (11.2–28.0 mg/L) were