



Removal of multiple nitrosamines from aqueous solution by nanoscale zero-valent iron supported on granular activated carbon: Influencing factors and reaction mechanism

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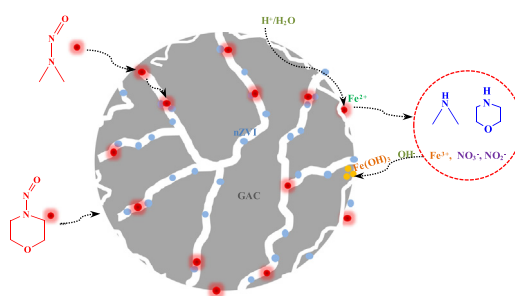
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HIGHLIGHTS

- Nitrosamines could be degraded effectively with the pseudo-second-order kinetics.
- The removal efficiencies of the linear nitrosamines correlated with the properties
- Coexistent substances exhibited a negative effect in the removal of nitrosamines.
- Adsorption and reduction impacted on the removal of nitrosamines simultaneously

GRAPHICAL ABSTRACT



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ABSTRACT

Due to their significant absorption and reduction abilities, nanoscale zero-valent iron (nZVI)/granular activated carbon (GAC) composites are very effective for the degradation of organic contaminants and heavy metals. However, to date, there is no systematic study on the applicability of nZVI/GAC for the removal of multiple highly toxic nitrosamines from water supplies. For this study, nZVI/GAC was synthesized and applied to the degradation of multiple nitrosamines. The effects of initial nitrosamine concentration, composite dosage, contact duration, competition with coexistent elements, and reaction mechanisms during the nitrosamine removal process from aqueous solutions were investigated. Compared with bare nZVI and GAC, the removal rates of six nitrosamines via nZVI/GAC were initially very rapid. The highest removal ratios of the six nitrosamines were 76.1% (*N*-nitrosodimethylamine, NDMA), 84.7% (*N*-nitrosomethylethylamine, NMEA), 89.8% (*N*-nitrosodiethylamine, NDEA), 93.5% (*N*-nitrosodi-*n*-propylamine, NDPA), 95.7% (*N*-nitrosodi-*n*-butylamine, NDPA), and 80.4% (*N*-nitrosomorpholine, NMor). The nitrosamine degradation kinetics data agreed well with the pseudo-second-order model ($R_2^2 > 0.99$), the rate constant k_2 for nitrosamine (200 ng/L) removal by nZVI/GAC increased in the order of NDPA (0.3675) > NDPA (0.0254) > NMEA (0.0109) > NDEA (0.0105) > NDMA (0.0101) > NMor (0.0077). In the presence of cations, anions, and humic acid (HA) the removal of the six nitrosamines was inhibited at each concentration. Furthermore, the removal ratios and K_2 of the five linear nitrosamines by nZVI/GAC partially scaled with structure, $\text{Log}K_{ow}$, and Henry's constant, particularly between K_2 and these properties ($R^2 > 0.80$). The reaction mechanism revealed that nitrosamines were adsorbed by GAC and then reduced by Fe^0 , where the reductive products were primarily secondary amines, nitrate, and nitrite. This study serves to improve our understanding, and further characterizes the removal of multiple nitrosamines by nZVI/GAC.

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1. Introduction

Due to their suspected carcinogenicity, mutagenicity, and extensive occurrence in water supplies, nitrosamines, as the industrial byproducts and disinfection byproducts of chlorination, chloramination, and ozonation, have raised great concerns (USEPA, 2007; Krauss et al., 2009; Wang et al., 2016). As the dominant species of nitrosamines that are frequently detected in source water and drinking water in many countries (Asami et al., 2009; Zhao et al., 2008; Wang et al., 2011, 2016), the concentrations of *N*-nitrosodimethylamine (NDMA) and *N*-nitrosodiethylamine (NDEA), as low as 0.7 and 0.2 ng/L, are estimated to be associated with a 10^{-6} lifetime cancer risk (USEPA, 2007). The International Agency for Research on Cancer (IARC) has classified these two nitrosamines as probable carcinogens in humans (Group 2A), whereas several other nitrosamines were classified as possible carcinogens to humans (Group 2B) (IARC, 1978). In several developing countries, shallow contaminated groundwater is the primary source of drinking water in many rural areas due to the lack of safe drinking water and water treatment systems (Dudeja et al., 2011; Shahid and Hazarika, 2010; Ma et al., 2012). Therefore, high water solubility and negligible soil adsorption facilitate the transfer of nitrosamines from surface water to shallow groundwater (Drewes et al., 2006).

To reduce the presence of nitrosamines in source water, drinking water, and the effluents of wastewater treatment plant, advanced oxidation processes (AOP, e.g., UV/H₂O₂, O₃/H₂O₂) (Liang, 2002; Huang et al., 2010) and reverse osmosis (RO) (Plumlee et al., 2008) have been employed. However, the efficacy of nitrosamine removal is quite limited in widespread rudimentary water treatment facilities, due to the high operating costs and complexity of the methods mentioned above. (Lee et al., 2007; Huang et al., 2010). Further, the biodegradation (Hatzinger et al., 2011; Carissa and Jonathan, 2013; Wang et al., 2015) of nitrosamines is not considered due to its extended treatment period and the marginalized utility of degrading bacteria. For practical water supply operations, green and contaminant-free technologies that have the capacity to remove multiple nitrosamines from ambient waterways and potable water are urgently required.

Nanoscale zerovalent iron (nZVI) is among the most widely applied nanomaterials for the reduction of various organic and inorganic contaminants (e.g., halogenated hydrocarbons, nitroaromatic compounds, azo dyes, flame retardants, antibiotics, perchlorate, heavy metal ions, and radionuclides), due to its large specific surface area and high reactivity (Zhan et al., 2011; Choi et al., 2008; Shu et al., 2010; Fu et al., 2013; Raychoudhury et al., 2014; Tang and Lo, 2013; Zhao et al., 2016). No reports exist as yet regarding the removal of multiple nitrosamines by nZVI. Gui et al. (2000) and Odziemkowski et al. (2000) clarified the pathways and kinetics for the reduction of NDMA with granular iron and nickel-enhanced iron throughout laboratory batch and column tests. The NDMA transformation mechanism via Fe and Ni/Fe was postulated to be catalytic hydrogenation, which resulted in the breakdown of N—N bonds to form dimethylamine (DMA) and ammonium as final products. The NDMA transformation process appeared to follow pseudo-first-order kinetics. However, the disadvantages of nZVI, which easy oxidation and aggregation, limit its practical application (Phenrat et al., 2006). The immobilization of nZVI onto a supporting material, such as granular activated carbon (GAC), offers a promising strategy to resolve the issues described above (Ling et al., 2012). Moreover, Fe⁰ and GAC may form a Fe⁰/GAC microelectrolysis system (Kallel et al., 2009). It has been reported that C≡N can be degraded by radicals and oxidants, such as the free hydrogen [H] and O· that is generated via electrode action (Lai et al., 2013). In previous studies, several reports have shown that activated carbon (AC) (e.g., from coconut shell) could absorb a limited quantity of NDMA (Fleming et al., 1996; Dai et al., 2009, 2010); the reason being that AC is a hydrophobic material, which repels the hydrophilic NDMA in aqueous media. The adsorption capacity of AC may be significantly improved by heat treatment and doping with TiO₂ nanoparticles (Dai et al., 2009). Further, modified

5ZnAC may remove 73% of tobacco specific nitrosamines from aqueous solutions (Sun et al., 2014). He and Cheng (2016) also reported that the microporous mineral adsorbent dealuminated ZSM-5, coupled with microwave-induced degradation had the capacity to simultaneously remove NDMA and its precursor DMA, and ultimately facilitated their full mineralization. Up to now, the removal of multiple nitrosamines by nZVI/GAC has not been studied. In terms of the reduction of Fe⁰ and the microelectrolysis system, the N=O bonds of nitrosamine should be reduced and subsequently transformed to inorganic ions, and so on. Hence, investigations are required to clearly elucidate and characterize nitrosamine removal by nZVI/GAC, including the reaction conditions, influencing factors, kinetics, and degradation mechanisms.

To better control the health and safety risks of drinking water associated with multiple nitrosamines, this study explored the characterization of nitrosamine removal using nZVI/GAC composites. The objectives of the present study were to 1) study the nitrosamine degradation efficiency and kinetics with nZVI/GAC, 2) evaluate the influences of coexistent substances during nitrosamine removal, and 3) elucidate the potential degradation mechanisms of nitrosamines by nZVI/GAC. To the best of our knowledge, this is the first report to describe the use of nZVI/GAC composites to systematically treat multiple nitrosamines in aqueous solutions.

2. Material and methods

2.1. Chemicals and materials

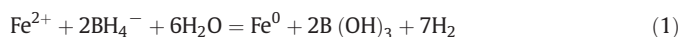
Commercial granular coconut shell based activated carbon (GAC, 4–8 mesh) was obtained from Sigma-Aldrich (Netherlands). Ferrous sulfate heptahydrate (FeSO₄·7H₂O, ≥99%), sodium borohydride (NaBH₄, ≥98.0%), polyethylene glycol-4000 (PEG-4000), and absolute alcohol (≥99.7%) (Sinopharm Group Chemical Reagent, China) were from the Sinopharm Group Chemical Reagent (China) and used for the synthesis of the nZVI.

A standard solution containing 1000 mg/L each of NDMA, *N*-nitrosomethylethylamine (NMEA), NDEA, *N*-nitrosodi-*n*-propylamine (NDPA), *N*-nitrosodi-*n*-butylamine (NDBA), and *N*-nitrosomorpholine (NMor) was purchased from Supelco (USA). The internal standard [²H₆] *N*-nitrosodimethylamine (NDMA-d₆) was obtained from Cambridge Isotope Laboratories (Andover, MA, USA). Resprep EPA Method 521 cartridges (6 mL/2 g) were purchased from Restek (Milford, MA, USA), and glass fiber pads (GF/F, 0.7 μm) were obtained from Whatman International Ltd. (Maidstone, UK). All other chemicals used in this study were of HPLC or GR grade. Stock solutions for all standard substances were stored at −20 °C.

2.2. Synthesis of nZVI/GAC

The GAC was initially subjected to boiling water for 30 min, rinsed thoroughly with distilled water until the pH of the solution was stabilized (pH = 7.0), and then dried at 105 °C for 24 h.

The nZVI particles were synthesized via a traditional liquid phase reduction method (Zhu et al., 2009), where 4.0 g of FeSO₄·7H₂O was dissolved in 200 mL of an ethanol-water solution (ethanol/water = 4/6, v/v), with the addition of PEG-4000 (0.25 g) as a dispersant to reduce nZVI aggregation in the ferrous sulfate solution. Following the dropwise addition of 100 mL of 0.6 mol/L NaBH₄, the mixture was continuously stirred at 300 r/min for 30 min. The reaction could be represented as Eq. (1):



The formed metal nanoparticles were settled and separated from the liquid phase by vacuum filtration using filter papers. The solids were then rinsed with water and ethanol several times and finally dried at 60 °C in a water-bath. To prevent the oxygen passivation of the synthesized nZVI, the preparation process was conducted under a nitrogen

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