Catalytic debromination of tetrabromobisphenol A by Ni/nZVI bimetallic particles

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HIGHLIGHTS

- nZVI/Ni particles before and after the reaction are characterized and compared.
- The debromination processes follows a pseudo first-order reaction kinetic.
- Higher nZVI/Ni dosage and lower TBBPA concentration accelerates the reaction.
- Slightly acidic pH favors complete and rapid debromination of TBBPA.
- More acidic and alkaline pH retards the reaction and di-BBPA is dominant product.

ARTICLE INFO

ABSTRACT

In this paper, nickel/nanoscale zero-valent iron (Ni/nZVI) bimetallic particles were explored for TBBPA degradation under ambient condition. Various factors such as Ni/nZVI loading (0.5, 1.0, 1.5, 2.0, and 3.0 g L^{-1}), initial TBBPA concentration (5, 10, 15, 20, and 30 mg L^{-1}), and initial solution pH (3.0, 5.0, 6.0, 7.0, 9.0, and 11.0) were tested in order to find the optimum conditions for rapid and complete degradation of TBBPA. The results showed that TBBPA could be degraded via pseudo first-order kinetics with respect to the Ni/nZVI loading and that the observed pseudo first-order rate constant (k_{obs}) was found to decrease with the increasing of initial TBBPA concentration at constant Ni/nZVI loading. At initial concentration of 10 mg L^{-1}, nearly 100% TBBPA could be degraded within 120 min by 2.0 g L^{-1} Ni/nZVI with k_{obs} reached up to 5.35×10^{-2} min^{-1} at acidic to neutral pH. pH plays an important role during TBBPA debromination processes inherent to iron corrosion. Slightly acidic pH (5.0–6.0) was favorable for the complete debromination of TBBPA, with over 93% bisphenol A (BPA) formed during the experiment. Whereas under acidic (pH 3.0) or alkaline conditions (pH 9.0 and 11.0), the reaction kinetics were slower and partial debromination product dibromobisphenol A (di-BBPA) was dominant. This study suggested that under optimized conditions, Ni/nZVI could be effectively applied for rapid and complete debromination of TBBPA in handling of wastewater treatment.

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1. Introduction

Brominated flame retardants (BFRs) are commonly used to improve the fire resistance in plastics, textiles, and circuit boards

[1]. As one of the most widely applied BFRs, tetrabromobisphenol A (TBBPA) accounts for 59% of the BFRs in the world market and 76% in Asia [2,3]. Due to its widespread use and its relatively high persistence in the environment, TBBPA has been detected not only in environmental media including air, sediment and soil, but also in living organisms such as fish, human blood, and even breast milk [3–5]. Since TBBPA has a chemical structure similar to thyroid hormones, it is regarded as a potential endocrine disruptor. Proper containment and treatment of TBBPA during disposal of electronic

wastes are necessary in order to decrease possible environmental risk.

Current technologies for treatment of TBBPA include processes based on biodegradation, pyrolysis, adsorption, and physico-chemical transformation [6–10]. Prior studies showed that biodegradation was efficient when a sequential anaerobic–aerobic process was employed, but it took months to completely degrade the chemical [6]. Pyrolysis can rapidly decompose TBBPA, but the process usually requires stringent conditions and is energy intensive [7]. Formation of brominated dioxins is another major concern for the pyrolytic treatment of e-waste-bound TBBPA. Adsorption process based on multiwall carbon nanotubes/iron oxides ($MWCNTs/Fe_3O_4$, $MWCNTs/Fe_3O_4–NH_2$) is also efficient for removal of TBBPA from aqueous phase [8], but further disposal strategy is necessary. Advanced oxidation processes such as Fenton [9] and photocatalytic degradation [11] have also been investigated. However, Fenton reagent generates large amount of iron sludge, photocatalytic degradation requires UV light, which limit their applications in environment remediation. It appears that exploration of cost-effective technologies are still necessary for TBBPA removal.

Over the past decades, nanoscale zero-valent iron (nZVI) and its bimetallic particles have been successfully applied for groundwater remediation due to its high reactivity with a broad spectrum of organic and inorganic pollutants [12–14]. So far, nZVI-based technologies have been implemented for treating halogenated organic compounds (trichloroethylene, polychlorinated biphenyls, lindane, etc.) [15–17], and inorganic pollutants (chromium, arsenic, nitrate and perchlorate, etc.) [13,18–20]. To achieve even higher reactivity and more complete degradation, a second metal (Pd, Ni, Ag, Ir, Co, etc.) is often doped at nZVI surface [14,15,17,21,22]. The addition of the third metal shows even higher reactivity compared to the bimetallic system [23]. It is believed that the addition of these metals promotes electron transfer between Fe^0 and target contaminants through a galvanic mechanism or promotes the reaction through a secondary redox processes within the oxide film on Fe^0 (electron from Fe(II) or H/H_2) [15,17,21,22,24]. In addition, Pd and Ni as catalysts can transform H^+ or H_2 into highly activated hydrogen atom (H^*) (Eqs. (1)–(4)), which attacks the organic contaminant double bond via electrophilic hydrogen [15,22,25].

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2 \qquad (1)$$

$$H_2 \xrightarrow{Ni} 2H^* \qquad (2)$$

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \qquad (3)$$

$$2H^+ + 2e^- \xrightarrow{Ni} 2H^* \qquad (4)$$
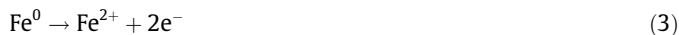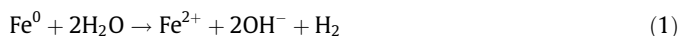
Recently, nZVI and Ag/nZVI were also applied for the degradation of TBBPA [22,26,27]. 80% of TBBPA ($C_0 = 2$ mg L^{-1}) could be removal by 3.0 g L^{-1} nZVI within 16 h at pH 7.5 [26]. With the assistance of ultrasound radiation, 0.4 g L^{-1} Ag/nZVI could remove over 99% of TBBPA ($C_0 = 2$ mg L^{-1}) within 30 min at pH 6.0 [22]. Nonetheless, the results show the great potential of nZVI, especially its bimetallic particles for the degradation of TBBPA. On the other hand, the addition of ultrasound increases the total cost and complexity for engineering degradation of TBBPA. Therefore, more cost effective nZVI technology need to be developed for TBBPA debromination at ambient environment.

Because of its relatively low price and known catalytic hydrogenation effect as mentioned above [21,25,28], nickel was often used as the doping metal at nZVI surface and has been proved to be very effective for the treatment of environmental pollutants [18,21,25,28,29]. In an effort to develop cost-effective method,

Ni/nZVI was chosen in this study for the debromination of TBBPA. The focus of the study was to find the optimal conditions under ambient condition for rapid and complete debromination of TBBPA by Ni/nZVI. The varied conditions included Ni/nZVI loading, TBBPA-to-nanoparticle ratio, and initial solution pH. The evolution of the intermediates and final products of the TBBPA reaction was also monitored and the reaction condition that yielded BPA as the final product was targeted. The study provided an alternative method for rapidly converting TBBPA to BPA.

2. Experimental

2.1. Materials

TBBPA (>98.0%) and bisphenol A (BPA, $\geqslant$99.0%) were purchased from Tokyo Chemical Industry Co., Ltd (Tokyo, Japan) and Aldrich (Milwaukee, WI) respectively. Sodium borohydride ($NaBH_4$, $\geqslant$97%) was obtained from Chengdu Kelong Chemical Reagent Company (Chengdu, China). Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, $\geqslant$99.0%) and nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, $\geqslant$98%) were supplied by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and Xilong Chemistry Co., Ltd (Shantou, China), respectively. All chemicals were used as received without further purification. Deionized water was purged with N_2 for 15 min to remove dissolved O_2 prior to use.

2.2. Synthesis of Ni/nZVI

nZVI was prepared according to the method described by Li et al. [12]. Briefly, it was synthesized by dropwise adding 0.25 M $NaBH_4$ into 0.045 M $FeCl_3$ solution at final 1:1 volumetric ratio. Ferric iron was reduced to nZVI according to the following reaction:

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 \downarrow + 3H_2BO_3^- + 12H^+ + 6H_2 \uparrow \qquad (5)$$
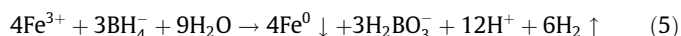
The synthesized nZVI particles were collected via vacuum filtration. The particles were rinsed with deionized water followed by ethanol, and the wet particles were then stored at 4 °C before usage. The moisture content of the collected nZVI was 70–80% as measured by a moisture analyzer (MX-50, A&D, Japan).

Ni/nZVI bimetallic particles were synthesized by coating Ni on the freshly prepared nZVI particles in an ethanol–water mixture. In brief, 2.0 g of nZVI particles were first dispersed in an Erlenmeyer flask filled with 300 mL ethanol, followed by adding 0.50 mL of $NiCl_2$ solution (20 g L^{-1} in ethanol), the mixture was then stirred for 15 min at 300 rpm to allow the deposition of Ni at nZVI surface:

$$Fe^0 + Ni^{2+} \rightarrow Fe^{2+} + Ni^0 \downarrow \qquad (6)$$

The content of the flask was purged continuously with nitrogen gas to avoid particle oxidation by minimizing exposure of the particles to the atmosphere. The prepared Ni/nZVI particles were collected and stored following the same procedures as for the nZVI particles. The nickel content on the bimetallic particles was about 0.5 wt% based on a mass balance calculation.

2.3. Characterization of Ni/nZVI

The physicochemical properties of the prepared bimetallic particles were characterized with several state-of-the-art instruments. Scanning electron microscope (SEM) images of the prepared particles were obtained through LEO 1530VP (LEO, Germany). Energy-dispersive spectroscopy (EDS) was performed on the particles by the same microscope equipped with Inca 300 (Oxford,