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Treatment of halogenated phenolic compounds by sequential tri-metal reduction and laccase-catalytic oxidation

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ABSTRACT

Halogenated phenolic compounds (HPCs) are exerting negative effects on human beings and ecological health. Zero-valence metal reduction can dehalogenate HPCs rapidly but cannot mineralize them. Enzymatic catalysis can oxidize phenolic compounds but fails to dehalogenate efficiently, and sometimes even produces more toxic products. In this study, [Fe|Ni|Cu] tri-metallic reduction (TMR) and laccase-catalytic oxidation (LCO) processes were combined to sequentially remove HPCs, including triclosan, tetrabromobisphenol A, and 2-bromo-4-fluorophenol in water. The kinetics, pH and temperature dependences of TMR and LCO were obtained. The detailed TMR, LCO, and TMR-LCO transformation pathways of three HPCs were well described based on the identification of intermediate products and frontier molecular orbitals (FMOs) theory. The results showed that the two-stage process worked synergically: TMR that reductively dehalogenated HPCs followed by LCO that completely removed dehalogenated products. TMR was proven to not only improve biodegradability of HPCs but also reduce the yield of potential carcinogenic by-products. Furthermore, a TMR-LCO flow reactor was assembled and launched for 256 h, during which >95% HPCs and >75% TOC were removed. Meanwhile, monitored by microorganism indicators, 83.2%–92.7% acute toxicity of HPCs was eliminated, and the genotoxicity, produced by LCO, was also avoided by using TMR as pretreatment process.

1. Introduction

Halogenated phenolic compounds (HPCs) are an important class of manufactured chemicals widely used as herbicides, pesticides, biocides, flame retardants and wood preservatives. Many HPCs are suspected carcinogens, therefore their discharge into the aquatic environment with wastewater poses a serious threat to the ecological and human health (Montaño et al., 2013). Recently, some new emerging HPCs

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have drawn much research attention. Triclosan (5-chloro-2-(2,4-dichloro-benyl)-phenol, TCS) is a popular antimicrobial (Gautam et al., 2014). Upon exposure to water environment, TCS kills microorganisms, weakens the ecological environment, and it may even be transformed into highly carcinogenic dioxins under sunlight irradiation (Sanchez-Prado et al., 2006). Tetrabromobisphenol A (2,6-dibromo-4-[1-(3,5-dibromo- 4-hydroxy-phenyl)-1-methyl-ethyl]-phenol, TBBPA) belongs to the reactive brominated flame retardant, which was widely detected in the aquatic environment, biota, and human tissues (Luo et al., 2011; Meerts et al., 2000). TBBPA can act as thyroid hormone and estrogen agonist at high concentration, leading to neurotoxicity effects on mammals (Chu and Letcher, 2013). 2-Bromo-4-fluorophenol (BFP) is a kind of HPC containing two types of halogen atoms. Due to its persistence and bioaccumulation (Duque et al., 2012), it is difficult to be removed from environment. Fluorophenols have caused negative biological effects as an enzyme inhibitor and modifier of cell–cell communication (Koerts et al., 1997). Besides, because the solubility of BFP in water is relatively high, they can easily migrate within different aqueous environments and contaminate groundwater. These HPCs and their derivatives are still contaminating the aquatic environment due to the irregular disposal. Therefore, efficient techniques and definite mechanisms for the removal of HPCs from water are highly desirable.

HPCs can be decomposed by oxidation process, including aerobic microorganisms (Lee et al., 2012), enzyme-catalysis (Feng et al., 2013), ozonation (Huang et al., 2004), and photocatalytic oxidation (Son et al., 2009), etc. However, the biodegradation efficiency of HPCs was limited due to the high toxicity and poor biodegradability of HPCs. For other chemical oxidation techniques, their removal efficiencies for HPCs also decreased obviously as the increase of halogen atom number, suggesting that high-halogenated HPCs are stubbornly resistant to oxidation (Wang et al., 2014). Furthermore, these oxidation processes of HPCs might produce more toxic and hazardous products (e.g., dioxin, tetrachlorobenzoquinone, and tetrabromo-p-benzoquinone) depending on the operating conditions (Jeong and Swenberg, 2005; Sanchez-Prado et al., 2006). Thus, there is a need for developing cost-effective solutions to overcome the above drawbacks of oxidation treatment.

Various dehalogenation techniques have been considered as the pretreatment processes to reduce the chemical stability and bio-resistance of HPCs. For example, Munoz et al. (Munoz et al., 2013) employed hydrodechlorination to achieve the complete dechlorination of chlorophenols and suppress the formation of highly toxic chlorinated by-products during the wet peroxidation of chlorophenols. Bokare et al. (2010) treated TCS with zero-valent iron to generate 2-phenoxyphenol which was then degraded biologically. In our previous study, a mixture of 2,4-dichlorophenol and pentachlorophenol was dechlorinated by photocatalytic reduction firstly, and then treated by enzyme catalytic oxidation (Yin et al., 2010).

In the present study, we attempted to remove HPCs from water with [Fe|Ni|Cu] tri-metallic reduction (TMR) for the dehalogenation of HPCs and subsequent laccase-catalytic oxidation (LCO) for the dehalogenated products. Herein, laccase is a phenoloxidase which is highly specific to phenolic compounds. LCO is effective for destroying phenolic compounds, however, is less active when facing HPCs, especially highly halogenated HPCs (Yin et al., 2010). The "TMR" is an improvement of dimetallic [Ni|Cu] reduction which has proved to be highly efficient for dechlorination of chlorophenols in our previous study (Yin et al., 2012). By adding the Fe^0, the major technical obstacles of [Ni|Cu], the release of Ni^{2+}, has been avoided in the practical application. Therefore, we selected TMR as the pretreatment of LCO to reinforce the removal of HPCs in present study. In some similar cases, bimetallic reduction technology has been adopted to enhance biological treatment of industrial wastewater, and applied to the full-scale wastewater treatment plant (Ma and Zhang, 2008), indicating that tri-metallic reduction technology might have a good potential in practical treatment of HPCs wastewater. The objective of this study was to reveal the reaction kinetics, decomposition pathway, toxicity changes of several typical HPCs during the two-stage (TMR-LCO) process. These HPCs included TCS, TBBPA, and BFP, as representatives of chloro-, bromo-, and fluoro-bromo-HPC. Furthermore, we hoped to clarify the reaction mechanism and application prospect of TMR-LCO process for the removal of HPCs with a long-term operation.

2. Materials and methods

2.1. Chemicals

TCS (>98.5%), TBBPA (>95.0%), BFP (>99.5%), sodium borohydride ($NaBH_4$), ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), nickel chloride ($NiCl_2$), copper chloride dihydrate ($CuCl_2 \cdot 2H_2O$), sodium acetate (NaAc), hydrochloric acid, sodium hydroxide (NaOH), acetic acid (HAc), citric acid and dipotassium phosphate were bought from Sinopharm, CHN. Laccase (EC 1.10.3.2, from *Trametes versicolor*) was supplied by Sigma with an activity of 22.6 U mg^{-1}. Deionized water (18.2 MΩ from Milli-Q system) was used throughout the experiments. Other inorganic salts and chromatographic standards were obtained from Fisher Scientific. Stock solutions of the halogenated phenolic compounds (HPCs) were prepared in methanol.

2.2. Preparation and characterization of [Fe|Ni|Cu] nanoparticles

[Fe|Ni|Cu] nanoparticles were synthesized using liquid-phase reduction with $NaBH_4$ as a reductant. Firstly, $FeCl_3 \cdot 6H_2O$ (13.51 g), $NiCl_2$ (0.13 g), and $CuCl_2 \cdot 2H_2O$ (0.17 g) were distributed in 100 mL of citric acid solution (0.05 mol L^{-1}) at pH 3.0. The mixture was stirred under nitrogen for 10 min, and then 1.0 mol L^{-1} $NaBH_4$ solution (100 mL) was added dropwise with vigorous stirring. The reductive reactions are described as:

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0\downarrow + 3H_2BO_3^- + 12H^+ + 6H_2\uparrow \quad (1)$$

$$2Ni^{2+} + BH_4^- + 3H_2O \rightarrow 2Ni^0\downarrow + H_2BO_3^- + 4H^+ + 2H_2\uparrow \quad (2)$$

$$2Cu^{2+} + BH_4^- + 3H_2O \rightarrow 2Cu^0\downarrow + H_2BO_3^- + 4H^+ + 2H_2\uparrow \quad (3)$$

$$Cu^{2+} + Fe^0 \rightarrow Cu^0\downarrow + Fe^{2+} \quad (4)$$