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Targeted removal of trichlorophenol in water by oleic acid-coated nanoscale palladium/zero-valent iron alginate beads[1]

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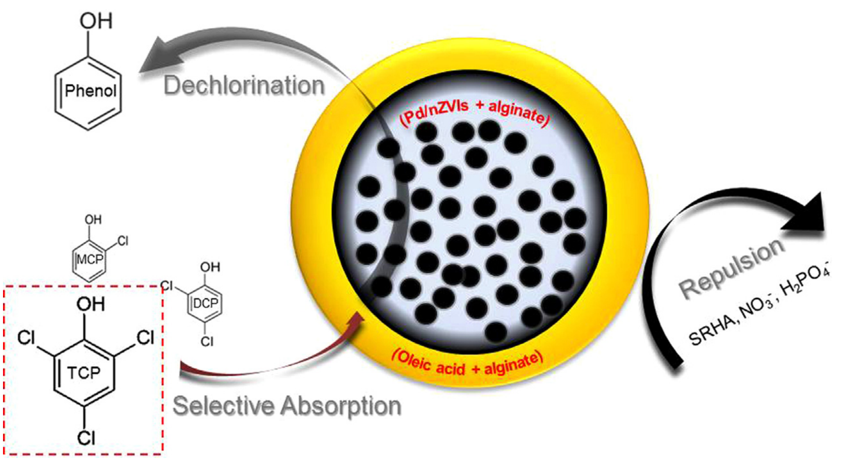
HIGHLIGHTS

- Alginate beads with nanoscale palladium/zero-valent iron were coated with oleic acid.
- The Pd/nZVI-A-O was applied for the targeted reduction of trichlorophenol (TCP).
- The beads reduced TCP selectively in the presence of other chlorophenols.
- TCP removal was not affected by other organic or inorganic substances.
- Selectivity was attributed to the hydrophobicity of the oleic acid coating.

GRAPHICAL ABSTRACT



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ABSTRACT

A new material was developed and evaluated for the targeted removal of trichlorophenol (TCP) from among potential interferents which are known to degrade removal activity. To achieve TCP-targeted activity, an alginate bead containing nanoscale palladium/zero-valent iron (Pd/nZVI) was coated with a highly hydrophobic oleic acid layer. The new material (Pd/nZVI-A-O) preferentially sorbed TCP from a mixture of chlorinated phenols into the oleic acid cover layer and subsequently dechlorinated it to phenol. The removal efficacy of TCP by Pd/nZVI-A-O was not affected by co-existing organic substances such as Suwannee River humic acid (SRHA), whereas the material without the oleic acid layer (Pd/nZVI-A) became less effective with increasing SRHA concentration. The inorganic substances nitrate and phosphate significantly reduced the reactivity of Pd/nZVI-A, however, Pd/nZVI-A-O showed similar TCP removal efficacies regardless of the initial inorganic ion concentrations. The influence of bicarbonate on the TCP removal efficacies of both Pd/nZVI-A and Pd/nZVI-A-O was not significant. The findings from this study

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[1] Abbreviations: CP – chlorophenol; DCP – dichlorophenol; MCP – monochlorophenol; n-ZVI – nanoscale zero-valent iron; Pd/nZVI – nanoscale palladium zero-valent iron; Pd/nZVI-A – nanoscale palladium zero-valent iron alginate beads; Pd/nZVI-A-O – oleic acid-coated nanoscale palladium zero-valent iron alginate beads; SRHA – Suwannee River humic acid; TCP – trichlorophenol.

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suggest that Pd/nZVI-A-O, with its targeted, constant reactivity for TCP, would be effective for treating this contaminant in surface water or groundwater containing various competitive substrates.

1. Introduction

Chlorophenols (CPs) have been extensively used as source chemicals in various commercial products including dyes, herbicides, paints, and wood preservatives [1–5]. However, due to their high toxicity and environmental persistence, concerns over their possible release into the ecosystem are justifiably valid. A recent study reported notable concentrations of CPs in riverine environments near industrial complexes [6–8], and highlighted the need for preparing effective countermeasures to control CP levels. One of the strategies for treating aqueous CPs is to reduce their toxicity and persistence by reductive dechlorination [9–11], although a post-treatment process such as biodegradation should follow to remove the phenolic reaction byproducts [12,13]. In previous studies, a bimetallic material, nanoscale zero-valent iron (nZVI) combined with palladium (Pd/nZVI), was suggested as an effective candidate for the abiotic dechlorination of CPs. Zhou et al. reported that Pd/nZVI nanoparticles showed significantly higher reduction rates for 4-monochlorophenol (4-MCP), 2,4-dichlorophenol (2,4-DCP), and 2,4,6-trichlorophenol (2,4,6-TCP) than nZVIs combined with platinum (Pt/nZVI), nickel (Ni/nZVI), copper (Cu/nZVI), or cobalt (Co/nZVI) [10]. Wei et al. demonstrated that a higher Pd loading on nZVIs could enhance the dechlorination rate of 2,4-DCP [14].

However, several drawbacks may limit the application of Pd/nZVI in practice, including aggregation of the material under typical water chemistry conditions [15,16], the necessity for an additional process to separate the nanoparticles from the treated water, and the rapid decrease of its reactivity due to co-existing organic and inorganic substances in the water system [17–20]. The immobilization of the nanoparticles in a separable structure is known to resolve the material aggregation and post-separation issues [15,21,22]. For instance, Ca-alginate has been recognized as a promising agent for immobilizing nZVIs in a porous structure [15,23]. Alginate beads containing nZVIs have been successfully applied for treating redox-sensitive nitrate and trichloroethylene contaminants, with reduction rates comparable to those of nZVIs in the free phase [15,21,23,24]. However, a reactivity decrease due to co-existing organic and inorganic substances is inevitable, even in the nZVI-embedded alginate beads. For example, non-targeted chlorinated compounds might compete with the contaminant of interest for the limited dechlorination capacity of the nZVIs, resulting in a decrease in the removal efficacy for the target. Organic substances such as humic acid can interrupt the direct contact between the nZVIs and the contaminants by adsorbing onto the nZVI surfaces or combining with the organic pollutants, which would reduce the material's reactivity toward the contaminants [17,18]. Inorganic anions including nitrate, phosphate, and bicarbonate have also been reported to reduce dechlorination efficacy, by co-opting the reduction capacity of the nZVI reagent or deactivating it by forming surface precipitates with ferrous ions (Fe^{2+}, nZVI oxidation products) that block electron transfer from the nZVIs to the contaminant [19,20].

In this study, we proposed and evaluated a new material which enables the preferential dechlorination of the targeted CP and retains its original reactivity toward the contaminant even in the presence of organic or inorganic substances. Among the CPs, trichlorophenol (TCP) with three covalently bound chlorine atoms was selected as the target contaminant because of its environmental significance [25–27]. TCP has a high octanol-water partition coefficient ($K_{ow} = 3.69$) and low bioavailability, implying its environmental persistence in case of release. Moreover, it is regarded as a human carcinogen and can cause chronic bronchitis upon respiratory system exposure [28,29]. The new material has a core-shell structure: a Pd/nZVI-containing alginate bead capable of TCP dechlorination is encapsulated by a highly hydrophobic oleic acid layer that allows selective absorption of the targeted organic contaminant for subsequent reduction. Selective dechlorination of the material was evaluated with a mixture of TCP and mono-CPs. The influence of co-existing substances on the reactivity of the new beads was investigated using Suwanee River humic acid (SRHA) as a surrogate for natural organic matter, and nitrate, phosphate, and bicarbonate ions as representative inorganic species.

2. Materials and methods

2.1. Chemicals

All chemicals in this study were reagent grade and used without further purification. Iron(II) sulfate heptahydrate ($FeSO_4\ 7H_2O$), sodium borohydride ($NaBH_4$), palladium(II) acetate ($Pd(OCOCH_3)_2$), calcium chloride hexahydrate ($CaCl_2\ 6H_2O$), phenol, 2-monochlorophenol (2-MCP), 4-monochlorophenol (4-MCP), 2,4-dichlorophenol (2,4-DCP), 2,6-dichlorophenol (2,6-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), sodium bicarbonate ($NaHCO_3$), potassium phosphate monobasic (KH_2PO_4), and acetone were purchased from Sigma–Aldrich. Suwannee River humic acid (SRHA, International Humic Substances Society), sodium alginate (Showa), oleic acid (Fisher Scientific), and potassium nitrate (Kanto) were used as received. Deionized (DI) water (18 MΩ·cm), obtained from a Millipore system (Milli-Q Plus, USA), was used to prepare all solutions.

2.2. Preparation of Pd/nZVI alginate beads with oleic acid layer (Pd/nZVI-A-O)

Pd/nZVI was synthesized as described previously [14,30]. Briefly, aqueous $NaBH_4$ (1.37×10^2 mmol L^{-1}, 50 mL) was added dropwise to aqueous $FeSO_4$ (0.69×10^2 mmol L^{-1}, 1 L), resulting in a black suspension of nZVI. Then, $Pd(OCOCH_3)_2$ solution (0.25 mmol L^{-1}, 50 mL) was added dropwise to the nZVI suspension to produce Pd/nZVI. The bimetallic nanoparticles were separated from the solution using a magnet, rinsed with DI water and acetone, and dried in an anaerobic chamber.

To prepare the Pd/nZVI-containing alginate beads (Pd/nZVI-A), the Pd/nZVI (0.2 g) was mixed with 1% (w/v) sodium alginate solution (20 mL) while applying sonication to minimize nanoparticle aggregation. Using a pipette, the mixture was added dropwise into 3% (w/v) $CaCl_2$ solution and gently stirred with a magnetic stirrer for 1 h, resulting in black beads. These were rinsed with DI water and acetone, and dried in an anaerobic chamber.

The Pd/nZVI-A was encapsulated by an oleic acid layer by mixing the oleic acid with 1% sodium alginate solution (1:1 by weight). Oleic acid was chosen because of its low environmental toxicity [31], and was supposed to preferentially sorb a highly-hydrophobic compound among contaminant mixtures in water. The transparent alginate solution was transformed into a light gray emulsion upon mixing with oleic acid. Dried Pd/nZVI-A beads were immersed in the emulsion for 3 min and collected using tweezers. The oleic acid-coated beads were soaked in 3% $CaCl_2$ solution to solidify the