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Adsorption and dechlorination of 2,4-dichlorophenol (2,4-DCP) on a multi-functional organo-smectite templated zero-valent iron composite

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ABSTRACT

Controlling the reactivity of nano-scale zero-valent iron (nZVI) remains a challenge for its practical application. In the present study, smectite-templated nZVI is hydrophobized by adding N,N,N-trimethyl-1-dodecanaminium salt (DTA$^+$) to yield organo-smectite-ZVI. The obtained material was characterized by XRD, TEM and FTIR. Its reactivity was evaluated for the aqueous removal of 2,4-DCP. Results show that (i) nanosized ZVI clusters of <5 nm are intercalated into the clay interlayers; (ii) hydrophobization of smectite surfaces occurs after binding of DTA$^+$ to the clay minerals; (iii) aqueous 2,4-DCP could be rapidly accumulated in the vicinity of the solid phase; (iv) accumulated 2,4-DCP is then gradually dechlorinated. This demonstrates that hydrophobic conditions in clay interlayer facilitate the 2,4-DCP adsorption. In a 2,4-DCP successive addition systems, dechlorination can be maintained even after five cycles for organo-smectite-ZVI, but just two cycles for smectite-ZVI. This indicates that the hydrophobization of smectite-ZVI could significantly sustain its reactivity and inhibit the rapid consumption of ZVI in the Fe^0/H_2O system. This statement is supported by XPS analysis. Furthermore, organo-smectite-ZVI provides strong adsorptive affinity to 2,4-DCP and its reaction products. This is beneficial for the long-term stability of removed contaminants.

1. Introduction

Nanosized zero-valent iron (nZVI) has been successfully synthesized and utilized as a removing agent to treat contaminants, such as nitroaromatic compounds, halogenated hydrocarbons, and trace metals in subsurface water for over a decade [1–7]. An attractive property for ZVI particle size getting into nano region is that the ratio of surface to volume is substantially increased, thus facilitating the removal of recalcitrant contaminants and offering the possibility of subsurface employment via injection [2,3,5,7]. However, a few drawbacks remain in its synthesis and practical application. Firstly, the high reactivity of nZVI induces its quick consumption during synthesis, storage and application, resulting in the depletion of reducing agents (such as Fe(II), H and H_2) in short time [6–8]. This chemical instability has been considered as a main reason for the observed low efficiency of nZVI systems compared with that of μm- and mm-ZVI [6,7]. Secondly, expansive corrosion is a universal property of metals (such as nZVI). Under oxic conditions, this corrosion could be accelerated and resultant products are larger in volume ($V_{Fe3O4}/V_{Fe} = 2.1$, V_{oxide}/V_{Fe} up to 6.4) [9], which is detrimental to successful mass transfer of removal agent to contaminants from bulk media [3,6]. Thirdly, reaction products retaining on the ZVI surface will decrease the number of available surface active sites, resulting in lower activity. Thus, the removal of products and prevention of surface deactivation are necessary for practical application of ZVI [10,11]. In addition, the organic contaminants are generally not completely mineralized by nZVI, thus their products are released into bulk solution and some of them will induce secondary pollution. For in situ field applications, it is thereby desirable to remove contaminants and their subsequent products completely.

Surface-modification has been applied for stabilizing nZVI particles and efficiently sustaining their reactivity. Typical agents such as carboxymethyl cellulose, polyvinylpyrrolidone, starch, polyelectrolyte membranes, and guar gum have been employed in an effort to enhance the suspension stability and therefore particle mobility of nZVI during preparation and utilization [12–16]. These stabilizations are achieved by enhancing the steric or electrostatic repulsions between the particles to inhibit nZVI aggregation and hence to increase the stability. In addition, introduction of low reactive material such as sand or natural minerals into ZVI is an effective tool to prevent compaction and delay clogging, which increases the removal efficiency of contaminants by nZVI [10,11]. In this context, smectite has been employed as a supporting matrix to synthesize stabilized ZVI in the interlayer [17,18]. Smectite clay layers generally consist of a center octahedral Al—O sheet sandwiched

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between two tetrahedral Si—O sheets. The planar aluminosilicate layers typically exist in stacked assemblages. Negative charges are embedded in the individual layers (due to isomorphic substitution) in a fixed but isolated distribution, and commonly neutralized by exchangeable inorganic cations that reside at or near the negatively charged sites. Smectite clay usually features with an interlayer distance (between two clay sheets) ranging from ~0.1 to 0.8 nm. This structural arrangement creates an ideal template to host ZVI clusters formed by reduction of exchangeable Fe(III) [17,18]. In this approach, smectite clay functions as a layered template that constrains the size of the ZVI formed at the nanoscale, and directs a fixed distribution of isolated regions of the ZVI clusters, which enhances the stability of the ZVI due to the readily dispersion property of smectite clay [17].

Based on our previous work [17,18], hydrophobic composite system benefits the adsorption of target organic compounds and products, and also potentially acts as a retardant against rapid consumption of nZVI by water and dissolved O_2, thus to increase its efficiency and to inhibit volumetric expansion [7]. Organic modification of smectite interlayer has been proven to be an effective strategy to enhance the interlayer hydrophobization and adsorption capacity by organic cations for ion exchange [19,20]. From this prospect, organic modified smectite-templated nZVI composites are developed for effective removal of persistent organic pollutants (such as 2,4-DCP, which is persistent to nature degradation and abundance in environmental media) in the present work. Furthermore, the combined adsorption–dechlorination property and involved mechanism of as-synthesized composite are studied in detail, including the efficacy of nZVI loaded into organic modified interlayer environment and the adsorption properties of organo-smectite-ZVI for products.

2. Experimental

2.1. Chemicals

Sodium borohydride ($NaBH_4$, >98%), 2,4-dichlorophenol (>99.5%), 2-chlorophenol (>99.5%), 4-chlorophenol (>97%), phenol (>99%), anhydrous ferric chloride ($FeCl_3$), hydrochloride acid (HCl, 36–38%), hydrofluoric acid (HF, 48%), perchloric acid ($HClO_4$, 70%), nitric acid (HNO_3, 68–70%), acetic acid ($C_2H_4O_2$, 98%) and N,N,N-trimethyl-1-dodecanaminium salt (DTA^+, 98%) were obtained from China National Medicines Corporation Ltd. Acetonitrile (HPLC-grade solvent) were purchased from Sigma–Aldrich. All the chemicals were used as received.

Smectite clay (montmorillonite) was obtained from Zhejiang FengHong clay chemicals Co. LTD. The cation exchange capacity (CEC) of the smectite clay is 90 cmol/kg.

2.2. Synthesis of organo-smectite templated ZVI

As shown in Scheme 1, the synthesis of organo-smectite templated ZVI was proceeded via three essential steps: (1) saturating the clay mineral cation exchange sites with Fe(III), (2) reducing the Fe(III) species to Fe^0 using $NaBH_4$, and (3) substituting the inorganic cations (i.e., Na^+) with organic ammonium cations (i.e., DTA^+) in the clay interlayer via ion exchange. Specifically, the purified smectite clay and 0.1 M $FeCl_3$ solution were mixed and shaken for 8 h. After centrifugation at 4500 rpm for 20 min, the supernatant was removed and replenished with the same amount of $FeCl_3$ solution. This procedure was repeated four times to assure that cation exchange sites of clay minerals were fully compensated with Fe(III) species. The Fe(III)-saturated smectite clay was washed using deionized water (All water used in the experiment was deoxygenated by purging with N_2 for 1 h) until free of chloride as indicated by a negative test with $AgNO_3$.

Before reduction by $NaBH_4$, the pH of the Fe(III)-smectite slurry was adjusted to 2 using 1 M HCl to depolymerize $[Fe(OH)_{1-4}]_n^{-1-2+}$ [17,21]. Then, a 3 mL of Fe(III)-smectite suspension containing ~3.3% (wt/vol) of clay was mixed with a 2 mL of 0.36 M $NaBH_4$ aqueous solution. Upon addition of the $NaBH_4$ solution, the clay in suspension turned black immediately, indicating that Fe(III) on the clay was reduced to ZVI via the following reaction:

$$Fe(H_2O)_6{}^{3+} + 3BH_4{}^- + 3H_2O \rightarrow Fe^0 + 3B(OH)_3 + 10.5H_2 \tag{1}$$

The reduced clay suspensions were centrifuged immediately and washed two times using deionized water to remove any excessive $NaBH_4$ in the clay suspensions. The obtained smectite-supported ZVI was denoted as smectite-ZVI. Organo-smectite supported ZVI was synthesized by adding DTA^+ solution in an amount matched to the cation-exchange capacity of clay into the smectite-ZVI suspension, then the suspension was mixed and shaken at 60 °C for 2 h. After that, the suspension was centrifuged at 4500 rpm for 20 min, and the supernatant was removed and washed two times using deionized water. Organo-smectite supported ZVI were thus obtained and denoted as organo-smectite-ZVI. All procedures for synthesis of smectite-ZVI and organo-smectite ZVI were performed under oxygen free condition.

The clay samples before Fe(III) saturation and after organic modification were digested by the mixture of hydrofluoric acid, nitric acid and perchloric acid at 250 °C for 90 min, and Fe contents were determined using an inductively coupled plasma atomic emission spectrometer (VISTA-PRO CCD Simultaneous ICP-OES).

2.3. Adsorption of 2,4-DCP by Na^+-smectite and organo-smectite

Organo-smectite was prepared by adding DTA^+ solution into the Na^+-smectite suspension, then the suspension was mixed and shaken at 60 °C for 2 h. After that, the suspension was centrifuged and washed using deionized water. Batch experiments were conducted to test the adsorption capabilities of Na^+-smectite and organo-smectite. The reaction was initiated by adding a 20 μL of 2,4-DCP stock methanol solution into a 10.0 mL of the Na^+-smectite suspension or organo-smectite suspension in a 15 mL reaction vial to obtain an initial 2,4-DCP concentration of 0.123 mmol L^{-1}. The concentration of smectite or organo-smectite was at 15 g/L. Then the mixture was agitated using a shaker at 40 rpm as suggested by Noubactep [22]. At pre-selected reaction intervals, samples were taken and sacrificed for 2,4-DCP analysis in solid and liquid phases.

2.4. Dechlorination of 2,4-DCP by organo-smectite-ZVI

Time evolution of sacrificial batch reactions were designed without real-world complexities to test dechlorination reaction kinetics. In an anaerobic chamber, a 20 μL of 2,4-DCP stock methanol solution was added to a 10.0 mL of the synthesized organo-smectite-ZVI suspension to obtain an initial 2,4-DCP concentration of 0.123 mmol L^{-1}. The concentration of organo-smectite-ZVI was kept at 15 g/L. After adding the 2,4-DCP stock solution, the mixtures were placed on a rotary shaker shaking with a rate of 40 rpm. At pre-selected reaction intervals, the samples were taken and sacrificed for HPLC analysis of 2,4-DCP and its daughter products in solid and liquid phases.

2.5. Recycling experiments for 2,4-DCP dechlorination by organo-smectite-ZVI and smectite-ZVI

The recycling experiments were conducted with 15 g/L organo-smectite-ZVI or smectite-ZVI suspensions under anaerobic conditions, and the initial concentration of 2,4-DCP was