



# Enhanced reduction of chlorophenols by nanoscale zerovalent iron supported on organobentonite



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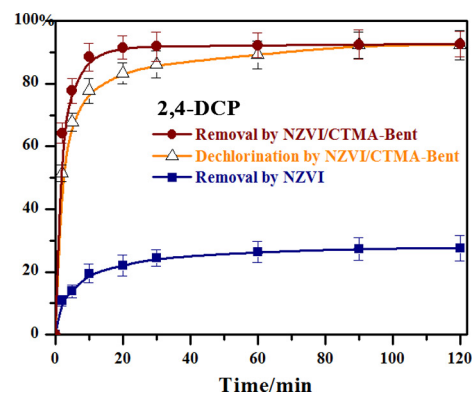
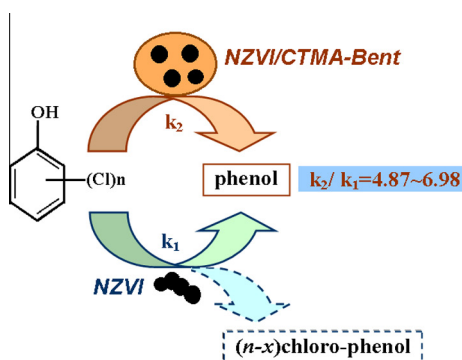
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## HIGHLIGHTS

- ▶ CMTA-Bent enriched chlorophenol(CP)s on NZVI surface and enhanced the reduction.
- ▶ The enhancement on reduction rate is positively related to CPs' hydrophobicity.
- ▶ NZVI/CTMA-Bent showed good reusability due to fewer precipitates on iron surface.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The reactivity of nanoscale zerovalent iron (NZVI) on removing chlorophenols (2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol) was remarkably enhanced by using a hydrophobic support of organobentonite (CTMA-Bent), namely the bentonite modified with organic cetyltrimethylammonium (CTMA) cations. The complete dechlorination of chlorophenols and total conversion into phenol using this novel NZVI/CTMA-Bent combination was observed in batch experiments. The kinetic studies suggested that the reduction of chlorophenols by NZVI was accelerated due to the enhanced adsorption onto CTMA-Bent, which facilitated the mass transfer of chlorophenols from aqueous to iron surface. The enhanced reduction rate by NZVI/CTMA-Bent was positively related to the hydrophobicity of chlorophenols, and an increasing linear relationship was obtained between the relative enhancement on reaction rate constants ( $k_2/k_1$ ) and  $\log K_{ow}$  values of chlorophenols. XPS results suggested there were fewer precipitates of ferric (hydro)xides formed on the surface of NZVI/CTMA-Bent, which may also lead to the improved reactivity and repetitive usability of NZVI/CTMA-Bent on removing chlorophenols.

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## 1. Introduction

Zerovalent iron (ZVI) has been suggested as a promising candidate for the removal of a wide range of organic contaminants

(Gillham and O'Hannesin, 1994; Cao et al., 1999; Dries et al., 2004; Yoon et al., 2011; Habekost and Aristov, 2012). However, its reaction rate with chlorinated aromatics is slow, with half-lives of days or longer calculated by a pseudo-first-order kinetics (Sayles et al., 1997; Feng and Lim, 2005). The slow reduction may result in the accumulation of toxic byproducts from partial dechlorination (Liu et al., 2005), and introduce new contaminants in the environment. As the reduction of contaminants by ZVI is surface mediated, the reaction rate is positively related to the concentration of

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contaminants around the iron surface (Loraine, 2001; Wu and Ritchie, 2006), which could be increased by improving hydrophobicity of iron surface. For example, modification of ZVI with cationic surfactants enhanced the reduction rate for perchloroethylene (PCE) by an order of magnitude (Alessi and Li, 2001). In such a system, the sorbed cationic surfactants on ZVI served as hydrophobic mosaics for PCE partitioning, and increased PCE concentration on reactive sites of iron and thus enhanced the reduction rate. Combining surfactant-modified zeolite (SMZ) with ZVI in a palletized form also showed dramatic enhancement on PCE removal (Li et al., 1999). It was speculated that concentration of chlorinated contaminants in the vicinity of iron surface was increased by the sorption of SMZ, and then the mass transfer was enhanced (Zhang et al., 2002; Cho and Park, 2006).

Nanoscale zerovalent iron (NZVI) with larger specific surface area is another choice for enhancing the reactivity of iron on removing contaminants (Wang and Zhang, 1997). The reduction rate of chlorinated organics was dramatically enhanced, and fewer chlorinated byproducts were observed using nanoscale iron particles (Wei et al., 2006; Cho and Choi, 2010). In addition, NZVI particles have potential for in situ remediation (Choe et al., 2001; Elliott and Zhang, 2001), because they may be directly injected as a slurry into contaminated subsurface zones. However, NZVI particles exhibit strong tendency to agglomerate into larger ones due to the high surface energy and intrinsic magnetic interaction. This results in adverse effect on both effective surface area and removal performance (Zheng et al., 2008). Besides, the separation and recycling of bare nanoscale particles from aqueous phase is extremely difficult (Wang et al., 2008a,b). To overcome these drawbacks, several solid have been developed serving as supporting materials of NZVI (Ponder et al., 2000). For example, cellulose derivatives (Wu and Ritchie, 2006; Cho and Choi, 2010) and silica (Zheng et al., 2008; Saad et al., 2010) could help to inhibit the aggregation of NZVI particles. Cation exchange resin, as the carrier of NZVI, promoted the removal efficiency to decabrominated diphenyl ether and water-soluble azo dyes (Li et al., 2007). However, some of these immobilization methods are complex, while some supporting materials are not hydrophobic enough, and they did not perform well on enriching organic contaminants due to their limited adsorption to organic compounds.

Modified bentonites, as good sorbents prepared from cheap bentonite by simple cation exchange reactions, have been investigated on the removal of various contaminants in the past decades (Zhu et al., 1997; Ma and Zhu, 2007). Both inorganic and organic cations containing various functional groups have been used in the bentonite modifications, and the dose of cations for exchange reaction is adjustable. Therefore, the structure and properties (e.g. hydrophobicity) of modified bentonites can be designed to achieve high adsorption to target contaminants. When the modified bentonites are used together with ZVI, its reactivity with target contaminants will be enhanced because of the enrichment of contaminants to the solid iron surface (Cho et al., 2005; Li et al., 2010).

The objective of this work is to enhance the reactivity of NZVI to chlorinated aromatics by using a support of organobentonite (CTMA-Bent), a modified bentonite prepared by cation exchange reaction with organic cetyltrimethylammonium cations. The organic phase in this support will improve the hydrophobicity of iron surface and have organic contaminants enriched around the reactive sites, so an enhanced reactivity on removing contaminants is expected. For this purpose, a series of chlorophenols (CPs) were employed as the target contaminants, including 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP). The reaction kinetics of CPs with NZVI/CTMA-Bent will be investigated by Langmuir–Hinshelwood (L–H) model, and compared with that by NZVI, so as to discuss the role of CTMA-Bent in the combined reduction system.

Furthermore, X-ray photoelectron spectroscopy (XPS) is employed for surface element investigation to determine the distribution and valence state of iron on the surface of NZVI or NZVI/CTMA-Bent samples.

## 2. Materials and methods

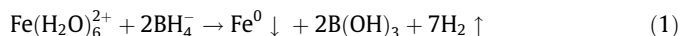
### 2.1. Materials

The original bentonite composed primarily of Na<sup>+</sup>-montmorillonite (Na-Bent) was purchased from Inner Mongolia, China. Its cation exchange capacity (CEC) is 115 cmol kg<sup>-1</sup>. Commercial iron powder (100 mesh, Fe<sup>0</sup>) and other chemicals of analytical grade were purchased from Shanghai Chemical Co., China: ferrous sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O), sodium borohydride (NaBH<sub>4</sub>), cetyltrimethylammonium bromide (CTMA), sodium hydroxide (NaOH), 2-CP (C<sub>6</sub>H<sub>5</sub>ClO), 2,4-DCP (C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>O), 2,4,6-TCP (C<sub>6</sub>H<sub>3</sub>Cl<sub>3</sub>O) and PCP (C<sub>6</sub>HCl<sub>5</sub>O).

### 2.2. Synthesis and characterization of organobentonite and NZVI samples

The organobentonite was prepared by a cation exchange process (Li et al., 2008). CTMA was added to a 1% (w/w) aqueous suspension of 20.0 g of Na-Bent under continuous stirring for 120 min in a water bath at 70 °C. The molar amount of CTMA added was equal to the CEC of Na-Bent, and then, the suspension was centrifuged, washed and dried to a constant weight. Finally, the solid was mechanically ground to less than 0.15 mm in size and heated at 115 °C for 120 min before use. The final product was denoted as CTMA-Bent.

NZVI particles were obtained through reduction of FeSO<sub>4</sub>·7H<sub>2</sub>O by dropwise addition of an excessive amount of NaBH<sub>4</sub> under stirring (Phenrat et al., 2007). The reaction could be represented as



The solution was stirred for another 30 min under room temperature. The metal particles formed were settled and filtered. Then the solid was washed with ethanol for several times, and finally vacuum-dried. The preparation was operated under a nitrogen atmosphere. The final product was labeled as NZVI. The immobilized NZVI was prepared by a similar procedure as described above, except that CTMA-Bent was soaking in FeSO<sub>4</sub>·7H<sub>2</sub>O solution under continuous stirring overnight before the addition of NaBH<sub>4</sub> solution (Li et al., 2011). The final product was labeled as NZVI/CTMA-Bent.

The X-ray diffraction (XRD) measurement of NZVI and NZVI/CTMA-Bent has confirmed the formation of iron in its zerovalent state with its major reflection at  $2\theta = 44.8^\circ$ . BET specific surface areas were determined to be 33.5 m<sup>2</sup> g<sup>-1</sup> for NZVI, and 29.5 m<sup>2</sup> g<sup>-1</sup> for NZVI/CTMA-Bent. Their iron contents were measured to be 75.3% and 16.8%, respectively.

### 2.3. Batch experiments for the removal of CPs

The removal of CPs was conducted in conical flask containing 100 mL of CP solution (pH = 5.5) of 0.500 mM ([CP]<sub>0</sub>) under stirring. Iron samples including NZVI (0.0797 g) and NZVI/CTMA-Bent (0.357 g) were added respectively in the CP solutions. In these treatments, the two iron samples were used at the same dose of iron of 0.600 g L<sup>-1</sup>. The CP solutions were deoxygenated by N<sub>2</sub> stream for 10 min before adding iron samples, and kept sealed with a stopper during the reaction. The experiments were carried out by putting the flask in a thermostatic shaker bath at 25 ± 0.1 °C, with a rotation speed of 150 rpm. At given time

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