

Bimetallic nZVI nanoparticles for chlorinated volatile organic compounds degradation.

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Degradation of chlorinated volatile organic compounds (CVOC) using nZVI has attracted significant attention over the past few years. Despite several advantages offered by nZVI, it is associated with drawbacks like agglomeration and passivation. Doping nZVI with traces of other metals has been found to overcome this drawback. In this study, we doped nZVI with Palladium (nZVI/Pd), nickel (nZVI/Ni), silver (nZVI/Ag) and copper (nZVI/Cu) and compared their efficiency in the degradation of vinyl chloride (VC), 1,2-dichloroethene (DCE), trichloroethene (TCE) and perchloroethene (PCE) in different media including synthetic contaminated water and groundwater procured from a contaminated site in Novy Bydzov. The doped nanoparticles demonstrated better degradation efficiencies than their undoped counterpart.

Keywords: zero-valent iron nanoparticles, bimetallic nanoparticles, water remediation, dechlorination.

Introduction

Chlorinated volatile organic compounds (CVOC) are a class of recalcitrant compounds that pose a great risk to the environment. Owing to the extensive use of these compounds in daily use products, CVOC like vinyl chloride (VC), 1,2-dichloroethene (DCE), trichloroethylene (TCE) and perchloroethylene (PCE) are ubiquitous in air, soil, rivers, lakes and even in groundwater[1]. In the last few decades degradation of CVOC using nZVI has attracted the attention of researchers[2]. Despite the high reactivity and the ability to degrade a wide range of pollutants, nZVI suffers from certain drawbacks like rapid passivation, non-selective nature and tendency for agglomeration. Doping nZVI with traces of other metals can overcome these drawbacks[3]. Traces of metals including silver (Ag), copper (Cu), nickel (Ni) and palladium (Pd) can improve the efficiency of nZVI in pollutant degradation. Hence, these metals were chosen to dope nZVI to obtain bimetallic nanoparticles for CVOC degradation. Herein, we doped nZVI with Palladium (nZVI/Pd), nickel (nZVI/Ni), silver (nZVI/Ag) and copper (nZVI/Cu) and compared their efficiency in the degradation of vinyl chloride (VC), 1,2-dichloroethene (DCE), trichloroethene (TCE) and perchloroethene (PCE) in different media including synthetic contaminated water and groundwater procured from a contaminated site in Novy Bydzov.

Materials and methods

1.1 Reagent and solution

Iron (III) chloride hexahydrate, Sodium borohydride (98%), Silver nitrate ($\geq 99\%$), Nickel(II) chloride (98%), Potassium tetrachloropalladate(II) (98%), Copper(II) chloride (97%), trichloroethylene (TCE), 1,2 dichloro ethene (DCE), and perchloroethene (PCE) were purchased from the Sigma–Aldrich.

1.2 Analytical

SEM (UHR FE-SEM Carl Zeiss ULTRA Plus, Germany) operating at an acceleration voltage 0.5–2.5 kV was used to study the composition and morphology of the nZVI nanoparticles, energy–dispersive X–ray spectroscopy (EDX) analysis was conducted using an EDX system (Oxford Instruments, AZtec) with X–Max detector attached to a Scanning Electron Microscope.

GC/ion trap MS instrument (Varian Saturn 3800) with VF-624ms column was used in full scan mode to qualitatively measure VOCs. Helium acted as the carrier gas (flow rate of 1 ml/min). WTW pH-meter equipped with SenTix pH electrodes (TMultiLine® Multi 3430 IDS) was used to measure the pH.

1.3 Nanoparticles synthesis

nZVI was prepared by reducing 0.2 M of iron(III) chloride hexahydrate solution using 0.5 M sodium borohydride solution added using a peristaltic pump

at a rate of 1.5 mL/min under nitrogen atmosphere under stirring for 10 min. The synthesized nanoparticles were washed three times with ethanol and then freeze dried for further use.

Bimetallic nZVI (nZVI/X) was prepared by activating nZVI by 1M HCl for 20 seconds, followed by the addition of 1% Pd/Ni/Ag/Cu metal precursors under stirring for 10 min. The prepared nanoparticles were washed three times with distilled water.

1.4 CVOC degradation test

CVOC reduction by nZVI was performed in batch setup in 250 mL glass vials without any headspace. The degradation tests were performed in synthetic CVOC mixture prepared in lab as well as real contaminated ground water procured from Nový Bydžov. All tests were performed at room temperature for 24 h at pH of 7 under stirring (200 rpm).

Results and discussion

The morphology and the composition the nanoparticles were analyzed by SEM and EDX analysis. Nanoparticles displayed chain-like structures typical of nZVI, while EDX shows the presence of doped metals on the nZVI surface.

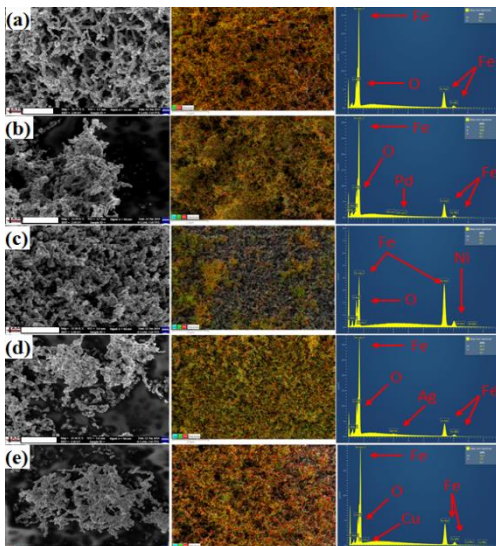


Figure 1 . Images of SEM (left, scale bar 1 μ m), EDS mapping (centre) and EDS (right) of (a) nZVI, (b) nZVI/Pd, (c) nZVI/Ni, (d) nZVI/Ag and (e) nZVI/Cu. In EDS mapping, Red colour denotes iron, green for oxygen and turquoise for the dopant metal.

The effect of doping on the degradation efficiency of the nZVI was evaluated in synthetic contaminated

water and real contaminated ground water. In the synthetic media (fig 2), complete degradation of all CVOC within 60 min was observed in case of nZVI/Pd. nZVI/Ni degraded TCE and DCE completely within 4 h while complete degradation of PCE was observed at 24 h mark. Even though nZVI/Cu and nZVI/Ag demonstrated better results than pristine nZVI, except for PCE with nZVI/Ag, no complete degradation of CVOC was observed.

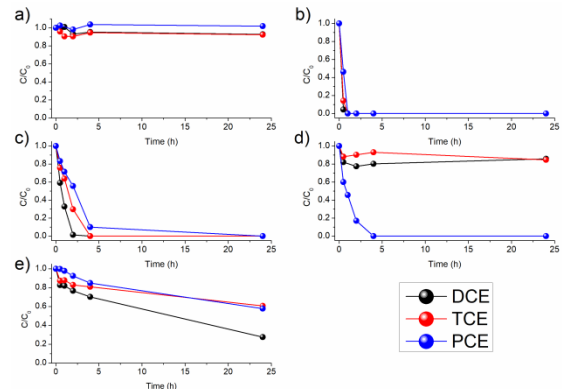


Figure 2. Degradation of CVOC mixtures in synthetic contaminated water by a) nZVI, b) nZVI/Pd, c) nZVI/Ni, d) nZVI/Ag and e) nZVI/Cu (nZVI/X 1 g/L, sum of CVOC 25 mg/L)

In case of real ground water from Novy Bydžov (fig 3), nZVI/Pd and nZVI/Ni completely degraded VC, DCE and TCE within 2 h while complete degradation of PCE was observed at 24 h mark. nZVI/Cu and nZVI/Ag demonstrated only a marginal improvement in the degradation efficiency of CVOC.

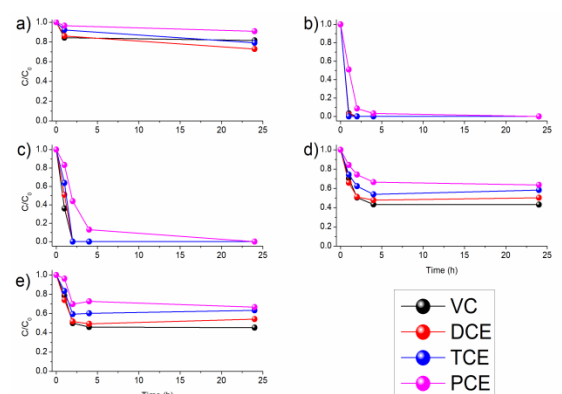


Figure 3. Degradation of CVOC in contaminated groundwater procured from Novy Bydžov by a) nZVI, b) nZVI/Pd, c) nZVI/Ni, d) nZVI/Ag and e) nZVI/Cu, (nZVI/X 1 g/L)

Conclusions

The present work focuses on the synthesis of doped nZVI bimetallic nanoparticles and evaluating their efficiency in the degradation of CVOC. Successful doping of nZVI was confirmed by EDS mapping while SEM revealed typical nZVI morphology. The resultant doped nZVI particles showed better results compared to their undoped counterpart. nZVI/X could overcome the passivation problem associated with nZVI particles as observed by their significant improvement in the degradation of CVOC. nZVI/Pd and nZVI/Ni demonstrated the best results in both synthetic and real waste-waters with complete degradation of the contaminants while marginal improvements were observed for nZVI/Ag and nZVI/Cu.

Acknowledgment

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Reference

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