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Adsorption–dechlorination of 2,4-dichlorophenol using two specified MWCNTs-stabilized Pd/Fe nanocomposites

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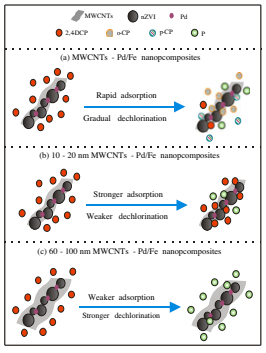
HIGHLIGHTS

- Two MWCNTs-Pd/Fe nanocomposites were synthesized to inhibit iron aggregation.
- Two MWCNTs-Pd/Fe nanocomposites used remove 2.4-DCP was investigated.
- MWCNTs had a selective adsorption capacity as follows: 2,4-DCP > p-CP, o-CP > P.
- Stronger dechlorination and weaker adsorption was found by 60–100 nm MWCNTs-Pd/Fe.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study a systematic investigation of two specified MWCNTs-Pd/Fe nanocomposites to remove 2,4-dichlorophenol (2,4-DCP) is presented. Two specified Multi-Walled Carbon Nanotubes (MWCNTs), i.e., 60–100 nm and 10–20 nm were introduced in nZVI synthesis in order to improve its adsorption–dechlorination efficiency. Both MWCNTs-Pd/Fe nanocomposites showed excellent adsorption efficiencies for phenols and followed the sequential order; 2,4-DCP > p-CP > o-CP > P. Batch sorption experiments including kinetics and isotherm were also intensively investigated. Significantly high 2,4-DCP removal was observed after 1 min when it reached to 49.7% and 53.2%, then continuously increased up to 95.2% and 77.7% after 5 h at 0.20 wt.% Pd loading by 60–100 nm and 10–20 nm MWCNTs-Pd/Fe nanocomposites, respectively. However, stronger dechlorination and weaker adsorption was found in 60–100 nm MWCNTs-Pd/Fe nanocomposites. Moreover, an integrated approach of physical adsorption by 60–100 nm MWCNTs and chemical reduction by Pd/Fe nanoparticles to remove 2,4-DCP was successfully achieved. The property of quick adsorption of targeted pollutants and steady release of dechlorination products enhance the applicability of this process for an in situ pollution remediation measures.

1. Introduction

Chlorinated phenols are commonly applied in agricultural and industrial sectors and result of growing ecological and environmental concerns [1], although their use have been strictly restrained in recent years due to carcinogenic properties. In general, Chlorinated phenols concentrations in contaminated soils range 0.1–10 mg kg^{-1}, but in highly contaminated areas, like

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abandoned site near Bitterfeld in Germany, concentrations up to 50 mg L^{-1} have been recorded in the groundwater aquifer [2].

In recent years, nanoscale zero-valent iron (nZVI) has been extensively studied to remove various wastewater contaminants including nitrate [3], chlorinated compounds [4], heavy metals [5], and so on. Furthermore, in order to improve the efficiency of dechlorination by nZVI, another noble metal (i.e., Pd) was introduced as a catalyst on nZVI surface. Primarily, the catalytic metal is not consumed in the reaction like the base metal (nZVI), has been proved to be an ideal bimetallic system for the rapid dechlorination of various chlorinated organic compounds [4,6]. However, one of the major concerns for nZVI particles is to inhibit its aggregation or improve its stability during synthesis and application [7]. According to conventional DLVO theory, aggregation of nZVI particles is greatly associated with van der Waals attraction and electrostatic double layers repulsion–interaction. Besides water chemistry in nZVI surrounding environment, other factors including ionic strength, presence of natural organic matters and the coexisting colloids also greatly affects the stability of nZVI particles. Thus, addition of surfactants (i.e., starch [8], carboxymethyl cellulose [9], Tween-20 [10], guar gum [11], chitosan [12], Vitamin B_{12} [13], and polyvinylpyrrolidone (PVP) [14]) would usually improve the stability of nZVI in aqueous systems. Stabilizers have been used to modify the surface of nZVI particles during (adding of pre-synthesis stabilizer) and following (adding of post-synthesis stabilizer) iron nanoparticles synthesis. What so ever, in each synthesis method, stabilizers either enhance suspension viscosity and stability, or strongly attach to the iron nanoparticles surface, preventing particle agglomeration. Some stabilizers have other special functions as well. Particularly, a variety of functional groups (hydroxyl, carboxyl, amino, sulfonic group, etc.) usually exist for binding the inner surface of porous supports including silica [15], and polymeric resins [16]. Starch and carboxymethyl cellulose are environment friendly materials and that can be utilized by microorganisms as a carbon source.

Since their discovery by Iijima in 1991, carbon nanotubes (CNTs) are considered to be superior adsorbents of pollutants due to their unique properties and relatively high reactivity [17]. Their high adsorption capacities of toxic organic chemicals removal have been profoundly discussed [18,19]. Since CNTs are good adsorbent and nZVI is a strong reductant, so the combination is worth considering for pollutants remediation. In this paper, Pd/Fe nanoparticles were supported on multi-walled carbon nanotubes (MWCNTs), hence both physical adsorption by MWCNTs and chemical reduction by Pd/Fe nanoparticles took place to remove 2,4-DCP. The objective of this study was to compare the removal efficiency and mechanism of the adsorption–dechlorination of 2,4-DCP in two specified MWCNTs-Pd/Fe systems. Special attentions were given to: (i) adsorption behaviors of four contaminants including phenol (P), 2-chlorophenol (o-CP), 4-chlorophenol (p-CP) and 2,4-DCP, (ii) dechlorination at different Pd loading (wt.%), and (iii) mechanism and kinetics of adsorption–dechlorination. Moreover, in this study CP was used as an abbreviated form of chlorophenol (i.e., o-CP and p-CP). The carbon mass balance of all the phenols in the aqueous phase was considered and calculated as 2,4-DCP (mg L^{-1}) in mass balance equation.

2. Experimental section

2.1. Materials

Chemicals including 2,4-DCP (CP grade), o-CP (CP grade), p-CP (CP grade), phenol (CP grade) and other reagents were purchased from the Sinopharm Group Chemical Reagent Co., Ltd., China. All chemicals were used as received without further treatment. Potassium hexachloropalladate (K_2PdCl_6, 99%) was obtained from Sigma–Aldrich. MWCNTs with 60–100 nm and 10–20 nm pore diameter were obtained from Nanotech Port Co., Shengzhen, China. 2,4-DCP stock solution was prepared by dissolving it in deionized water and stored at 4 °C. MWCNTs-Pd/Fe nanocomposites were synthesized immediately before use.

2.2. Preparation of MWCNTs-Pd/Fe nanocomposites

The MWCNTs-Pd/Fe nanocomposites were prepared from the original MWCNTs by intercalation with nZVI and Pd particles in a 1000 mL three-necked flask under nitrogen atmosphere. Firstly, MWCNTs and $FeSO_4{\cdot}7H_2O$ were mixed through stirring at 500 rpm and ultrasound at 40 kHz for 2 h. Then MWCNTs-nZVI was prepared by dropwise addition of a stoichiometric amount of $NaBH_4$ aqueous solution according to the following reaction [20]:

$$\mathrm{MWCNTs} + \mathrm{Fe(H_2O)_6^{2+}} + 2\mathrm{BH_4^-} \rightarrow \mathrm{MWCNTs - Fe^0} + 2\mathrm{B(OH)_3} + 7\mathrm{H_2} \quad (1)$$

Subsequently, MWCNTs-Pd/Fe nanocomposites were synthesized by mixing the wet MWCNTs-nZVI with K_2PdCl_6 aqueous solution under stirring. Reduction and deposition of Pd occurred on nZVI surface according to the the following reaction:

$$2\mathrm{Fe^0} + \mathrm{Pd^{4+}} \rightarrow 2\mathrm{Fe^{2+}} + \mathrm{Pd^0} \quad (2)$$

The resulting composites were then rinsed with copious amount of deionized water to remove excess SO_4^{2-}, Cl^-, Na^+, and K^+ ions, and a thin discontinuous layer of the noble metal was formed on top of the Fe^0.

2.3. Batch experiments

Equilibrium adsorption experiments were performed in 100 mL flask as a batch reactor system, which was mechanically shaken for 24 h in a thermostated rotary shaker at temperature of 303 ± 1 K. The supernatant solution was then analyzed by HPLC. The initial concentrations of each phenol were 5 mg L^{-1} in the competitive adsorption experiments. And in following experiments, all the initial concentrations of 2,4-DCP were 20 mg L^{-1}.

The batch adsorption–dechlorinations of 2,4-DCP were carried out in three-necked flask containing freshly prepared MWCNTs-Pd/Fe nanocomposites. The reaction was carried out through stirring under nitrogen flow. Aliquots of samples were periodically collected with glass syringes and the reaction was quenched by passing through 0.45 μm filter membrane.

2.4. Method of analysis

Organic compounds such as 2,4-DCP, p-CP, o-CP and P were analyzed by SHIMADZU HPLC 2010-AT. SHIMADZU ODS-SP Column, 150 × 4.6 mm. Mobile phase: MeOH/H_2O (60/40, v/v), flow rate: 1.0 mL min^{-1}, detector: UV at 280 nm, and sample size: 50 μL.

Field emission scanning electron microscopy (SEM, Hitachi S-4800, operated at 20 kV) and transmission electron microscopy (TEM, JEOL 2010, operated at 200 kV voltage) were used to characterize the morphology of the particles. X-ray powder diffraction (XRD) was performed using Siemens D 500 diffractometer with Cu Kα radiation at 1.54 Å. The surface functional groups on the MWCNTs were studied by Fourier transform infrared analysis (Nexus670 FTIR spectrometer, acquired in the 4000–1000 cm^{-1} wavenumber).