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Catalytic degradation of PNP and stabilization/solidification of Cd simultaneously in soil using microwave-assisted Fe-bearing attapulgite

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HIGHLIGHTS

- Fe/ATP can catalytically oxidize PNP and stabilized Cd in soil under MW induction.
- Cd is mineral-integrated with Fe/ATP and MW irradiation promotes Cd solidification.
- The formation of ferrite and vitrification promote the long-term stability of Cd.
- Active species are generated from the redox of Fe^{2+}–Fe^{3+} species in Fe/ATP.
- ·OH is the predominant radicals and $\cdot O_2^-$ plays a minor role in PNP degradation.

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ABSTRACT

A novel Fe-bearing attapulgite (Fe/ATP) as microwave (MW) absorber, cadmium (Cd) stabilizer and active catalyst to simultaneously stabilize/solidify Cd and oxidize p-nitrophenol (PNP) in soil was reported. The toxicity characteristic leaching procedure tests showed 80% of Cd was successfully stabilized in soil with Fe/ATP addition, whereas Cd stabilization efficiency of 99.3% was successfully achieved in MW-assisted Fe/ATP system. In addition, the long-term stabilization efficiency of Cd (180-day of curing) increased about 2-fold in MW-assisted Fe/ATP system compared with Fe/ATP system. XRD, FTIR, and XPS studies showed that Cd was more mineral-integrated than surface-bound with Fe/ATP, and a part of the stabilized Cd in Fe/ATP transformed into ferrite or encapsulated in vitrification with MW irradiation. Fe/ATP also showed extremely high catalytic performance for PNP oxidation, achieving complete PNP removal from soil within 20 min of MW irradiation. The enhancements of Cd stabilization and PNP removal were attributed to the "hot spots" effect on the Fe/ATP surface with MW excitation. In addition, active species (holes, ·OH, and $\cdot O_2^-$) generated from the redox of Fe^{2+}–Fe^{3+} species were responsible for the PNP degradation. The use of Fe/ATP to catalytic oxidize PNP and stabilize/solidify Cd under MW irradiation was demonstrated to be an effective method for rapid remediation of organic-heavy metal co-contaminated soil.

1. Introduction

Cadmium (Cd), one of the major toxic heavy metal contaminants that can accumulate in human bodies and cause softening of bones and kidney failure, generates great threat to both environmental ecology and human health [1]. p-Nitrophenol (PNP) as a priority pollutant is listed by the US Environmental Protection Agency due to its significant environmental and public health risk [2]. PNP and Cd contaminants are released to soil as fugitive emissions from organophosphate pesticides and phosphate fertilizers production, respectively [1,3]. In China, there are more than hundreds of abandoned organophosphate pesticide and phosphate fertilizers chemical industrial parks and most of those have large quantities of nitrobenzenes-heavy metal (Cd, Zn, Cu, etc) co-contaminated soils without proper treatment. The leachability of nitrobenzenes and heavy metal from contaminated sites has

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caused serious contamination of soil and groundwater. In addition, these contaminated sites need to be tackled to meet the increasing strictness of environmental standards for further development and reuse.

PNP-contaminated soil is traditionally tackled with advanced oxidation processes [4,5], and Cd-contaminated soil is normally tackled by chemical washing [6] and stabilization [7]. However, technologies listed above are mostly targeted for Cd or PNP and not applicable for PNP-Cd co-contaminated soil. Microwave (MW) technology has drawn great attention due to its capability to stabilize/solidify heavy metals in soil [8–10] or decompose and co-evaporate organic contaminates from soil [11–13]. MW performs the thermal or nonthermal effect [14] and has rapid heating compared with conventional thermal treatment [8]. MW catalytic oxidation is also widely used to degrade organic compounds in aqueous solution [15–18]. These studies show that the strong MW absorption of the catalyst, such as iron and/or oxide, is in favor of their catalytic efficiency due to the dramatical increase of "hot spots" and active species on the catalyst surface [15,16,19]. However, nano-sized iron oxides aggregate easily and hence limit their catalytic activity [20,21]. Attapulgite (ATP) with high surface area and good mechanical/thermal stability, is widely used as catalyst support and can significantly enhance the catalytic efficiency of iron by ensuring better dispersion of iron oxide and increasing desired active sites [22,23]. And what is more, iron-bearing ATP (Fe/ATP) catalysts facilitate the sorption of organic compounds due to their strong cationic-π-tractions [24,25], which might be followed by further transformation processes including redox and pyrolysis. However, relevant researches are mostly focused on wastewater treatment [24,26,27] and little has been reported on soil remediation.

Besides the promotion of catalytic activity and adsorption capability of organic compounds with Fe/ATP, it is expected that great adsorption capability of Cd on Fe/ATP could also be achieved. Muehe et al. found that Cd was more mineral-integrated than surface-bound to the iron oxide, thus Cd could be hardly retrieved from the iron oxide [28]. Compared with iron oxide, Cd is bonded to ATP mainly in the form of exchangeable fraction through co-precipitation, ion exchange and surface complexes, and is easily detached and released to the environment again under the exposure of minor environment disturbance, although ATP shows more adsorption capacity for Cd than iron oxides [29,30]. Waseem et al. observed that the sorption capacity of Cd^{2+} ion on Fe-bearing silica was greater than iron oxide or silica itself in aqueous phase [31]. In sharp contrast to silica, ATP is a family of fibrous clay with three-dimensional structure, many functional end-groups, empty internal cavities, and high local densities of active groups which are able to connect Cd or encapsulate it in tetrahedral and octahedral lattices [29]. Thus, Fe/ATP was supposed to improve both the adsorption capacity and the binding energy of Cd. Moreover, due to the strong MW absorption performance of iron, MW-assisted Fe/ATP in soil remediation to support the long-term stability of Cd in theory was available. However, Fe/ATP as stabilizer in Cd-contaminated soil remediation has not been investigated, and the long-term stability of Cd with MW treatment in soil has not been verified. The stabilization/solidification mechanism of Cd in soil using Fe/ATP with MW irradiation is still unclear.

In this work, Fe/ATP was used as catalyst, MW absorber, and Cd stabilizer in MW system for remediation of PNP-Cd co-contaminated soil. The toxicity characteristic leaching procedure (TCLP) for total Cd was used to evaluate the effectiveness of MW-assisted Fe/ATP treatment from a leaching perspective. Catalytic oxidation mechanism of PNP and stabilization/solidification mechanisms of Cd in soil were studied. Possible pathways of PNP removal and Cd stabilization/solidification in the MW catalytic system were also proposed.

2. Materials and methods

2.1. Materials

ATP (chemically pure) was supplied from R&D Center of Xuyi Attapulgite Applied Technology, Lanzhou Institute of Chemical Physics, China. PNP (guaranteed reagent) was obtained from Acros organics, Belgium. Other chemical information was provided in S1 of the supplementary material (SM).

2.2. Soil sample preparation

The soils used in this study were including the artificially PNP-Cd co-contaminated soil and the actual PNP-Cd co-contaminated soil. For the artificially PNP-Cd co-contaminated soil, the soil was obtained from an uncontaminated site in Huazhong University campus, China, and grinded to pass a 50 mesh standard sieve. The details of soil characterization analyses, such as pH, cation exchange capacity, size distribution, organic matter content were described in S2 of SM. To close to the content levels of the actual PNP-Cd co-contaminated soil, 500 g of the campus soil sample was added to 600 mL $CdCl_2$ solution (400 mg L^{-1}), homogenized, and then 700 mL PNP acetone solution (400 mg L^{-1}) was added with vigorously homogenization. The artificially contaminated soil sample was placed in a fume hood until acetone evaporated completely. It was then air-dried and aged for over six months before use. The extraction method of PNP in soil was according to the Chinese hazardous waste identification standard method (GB 5085.3-2007). In brief, soil was ultrasonically extracted using acetonitrile as extractant, and separated, combined, concentrated by pressure blowing concentrator and finally filtrated for determination with high performance liquid chromatography-mass spectrometry (HPLC/MS, HP1100/MSD, Agilent Co., USA), shown in S3 of SM. The extraction procedure of the total Cd content in soil was hot digested with a HCl-HNO_3-$HClO_4$-HF solution according to the Chinese standard protocol (GBT17140-1997) and detected with inductively coupled plasma-atomic emission spectrometry (ICP-OES, Optima 8300, PerkinElmer, USA), shown in S4 of SM. The TCLP test (HJ/T299-2007, Chinese solid waste-extraction procedure for leaching toxicity) was performed to evaluate the mobility of stabilized Cd in soil. In brief, 10 g of soil was extracted with the mixed H_2SO_4 and HNO_3 solution of pH 3.2 ± 0.05 at a liquid/solid mass ratio of 10 for 18 h (30 rpm, 25 °C). The details of the leaching procedure were described in S5 of SM.

For the actual PNP-Cd co-contaminated soil, soil sample was collected from an abandoned organophosphate pesticide and phosphate fertilizer industry park in Wuhan, China. The soil sample was air-dried, disaggregated, and sieved to a 50 mesh. The details of soil characterizations were described in Table S2 of SM. Total concentrations of Cd, Pb, Zn, etc., were determined by the Chinese standard method (GBT17140-1997), shown in S4 of SM. The TCLP test was conducted to estimate the quantity of available heavy metals in soil (S5 of SM). Extraction and analysis methods of organic contaminate, including nitrobenzene and organophosphate pesticides in soil were described in S3 and S6 of SM, respectively.

2.3. Synthesis of Fe/ATP

The Fe/ATP sample was synthesized by a chemical co-precipitation method. 50 g ATP were activated by 200 mL HCl (1 M) for 2 h to remove metal ions and residual carbon in the crystal backbone of ATP, and thus improve the adsorption capability. After exhaustive washing with deionized water and ethanol, the activated ATP was dried for 24 h at 80 °C under vacuum. The acti-