



Microwave-enhanced catalytic degradation of p-nitrophenol in soil using MgFe_2O_4



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HIGHLIGHTS

- MgFe_2O_4 induced with MW showed a good removal for PNP in soil.
- Both $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ were participate in the catalytic process.
- Water, oxygen, and the surface hydroxyl groups serve as reactive species donors.
- Thermal desorption, catalytic oxidation, and thermal stabilization were occurred.

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ABSTRACT

The application of MgFe_2O_4 as microwave (MW) absorber and catalyst to removal p-nitrophenol (PNP) in soil has been investigated, including the catalytic performance, removal route, and reaction mechanisms. Five types of MgFe_2O_4 nanoparticles were synthesized with chemical co-precipitation (M_1 , M_{1-1} , and M_{1-2}), gel combustion (M_2), and reverse micelle (M_3) methods, respectively, and characterized by FTIR, XRD, and SEM technologies. The results showed that the chemical co-precipitation of MgFe_2O_4 (M_1 , calcined at 600 °C for 2 h) with higher O–H and H–O–H contents and higher $\text{Mg}^{2+}/\text{Fe}^{3+}$ occupying tetrahedral sites had the highest catalytic performance for PNP degradation. The enhancement of MW catalytic performance was attributed to the significant increased and hypodispersion of “hot spots” on MgFe_2O_4 surface (>1000 °C) and the generation of various active species ($\cdot\text{OH}$ and $\cdot\text{O}_2^-$). Water and oxygen molecular as active species donors played an important role in the catalytic process. The main degradation products were phenol, hydroquinone, 1,2,4-trihydroxybenzene, and dihydroxynitrobenzene. Three stages were occurred in the MW catalytic process. A part of PNP was firstly thermal desorbed from soil with soil temperature increasing, and PNP was further catalytically oxidized by $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ species from the disassociation of water and oxygen. Parts of PNP and its decomposed products were directly encapsulated in soil by thermal stabilization.

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1. Introduction

p-Nitrophenol (PNP), as a priority pollutant listed by the US EPA due to its toxicity and potential risk to human health, has been used widely as raw material in industries for manufacturing many pesticides, herbicides, synthetic dyes and pharmaceuticals [1,2]. PNP contaminated sites that were former chemical factories were being identified. These sites often sited extensively in the populated areas [2]. Effective and rapid remedial alternatives were

warranted to make the lands available for new development and to minimize the adverse environment impact.

Recently, use of microwaves (MW) for soil remediation has been recognized as a cost effective, time saving, and environmental friendly remediation technology [3–7]. However, MW energy is often insufficient to cleave the chemical bonds of PNP. Comparably, MW-induced catalytic oxidation is a promising technology, coupled with appropriate MW absorbent catalysts, such as, carbon materials [8,9] metals and metal oxides [6,10,11]. Ferrites (MFe_2O_4 , M=Mg, Cu, Ni, Mn, etc.) have been the subject of increasing research endeavors due to their strong MW absorption ability, good thermal stability, and remarkable catalytic ability [12–14]. Under MW irradiation, the dipoles of spinel ferrites align and flip

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around. Subsequently, the “hot spots” and active species ($\cdot\text{OH}$ and $\cdot\text{O}_2^-$) are generated, which are responsible for the degradation of organic pollutants [12]. Due to their excellent properties, spinel ferrites have been employed in many MW-assisted aqueous protocols [15–17]. In a previous study, magnesium ferrite (MgFe_2O_4) exhibited the largest increase in temperature under MW irradiation from all the ferrites examined ($\text{M}=\text{Cu}, \text{Fe}, \text{Mn}, \text{Ni}, \text{Sr}, \text{Co}$) [18]. MgFe_2O_4 was consequently selected as the MW absorber and catalytic material to catalytically decompose PNP in soil in this study. To the best of our knowledge, this is the first report of the catalytic degradation of PNP in soil under MW irradiation using MgFe_2O_4 . Higher temperatures in soil could be obtained than those for aqueous phase, which could result in different reaction route of organic pollutants. However, the removal route of organic compounds during the process of MW reaction has not been provided yet in detail. In addition, the catalytic property of ferrite is strongly depend on the distribution of the cations and the amount of metal incorporated in the structure [15]. The crystalline structure and compositions of ferrites are significantly affected by the synthesis processes, which determine the activity of the final materials [19,20]. Therefore, it is important and desirable to control the synthesis procedures to achieve nanomaterials with a high catalytic activity. However, only calcination temperature was evaluated as an influence factor of catalytic activity while the effects of different synthesis methods were out of consideration.

In this study, MgFe_2O_4 nanopowders were prepared not only under different calcination temperatures, but also by three different wet chemistry routes, namely co-precipitation, citrate gel and reverse micelle. The morphologies and structures of five spinel-type magnesium ferrite nanopowders were characterized. Furthermore, the influence of catalytic properties of the magnesium ferrites on the removal of PNP in soil under MW irradiation conditions was discussed. The effects of preparation methods, reaction temperatures and soil to water ratios on the removal of PNP in soil were also studied. Possible reaction routes were proposed.

2. Experimental

2.1. Materials

PNP (AR) was obtained from Acros organics, Belgium. Kaolin (Reagent grade, Tianjin Kermel Chemical Reagent Development Center, China) was used as the model soil. The other chemicals were supplied in the Supporting information (S1). The soil was grinded to pass a 50-mesh sieve. The carbon content of the clay soil was ~ 0.3 wt%. Further details of PNP and soil physical–chemical properties were described in the Supporting information (Fig. S1 and Table S1). PNP contaminated soil was prepared by adding PNP methanol solution into kaolin, mixed evenly, vibrated vigorously for 24 h in 25 °C thermostat water bath, dried in air to evaporate the methanol thoroughly and grinded to sieve through 100 mesh. Then the soil was stored in brown bottle and aged for over six month before use. The initial PNP concentration in the soil was 492 mg kg^{-1} detected with UV–vis spectrophotometer. The details of extraction and analysis of PNP were described in the Supporting information (S2).

2.2. Preparation of MgFe_2O_4 nanoparticles

Five MgFe_2O_4 nanopowders were prepared via three different methods (co-precipitation with different combustion temperature and time, gel combustion and reverse micelle). During the modified synthesis process of previously described MW assisted chemical co-precipitation method [17], $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Fe

$(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ salts with a molar ratio of 1:2 were dissolved in deionized water. 2.5 mol L^{-1} NaOH was then added dropwise to the solution until pH around 11 with magnetic-stirring. The mixed solution was irradiated under MW (230 W) for 10 min. The precipitations were filtered, washed with deionized water and ethanol, respectively, and then dried in an oven at 110 °C for 24 h. The prepared MgFe_2O_4 materials were then calcined at 600 °C for 2 h, 500 °C for 3 h, and 600 °C for 3 h, respectively (labeled as M_1 , M_{1-1} and M_{1-2} , respectively). For the gel combustion method [19], $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ with a molar ratio of 1:2:3 were dissolved in 200 mL deionized water. The solution was continuously stirred and kept at 60 °C until it turned into a brownish sol. The stabilized nitrate–citrate sol was rapidly heated to 80 °C for 2 h. Finally, the prepared precursors were calcined at 600 °C for 2 h (labeled as M_2). In the reverse micelle route [19], $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in distilled water to a molar ratio of 1:2. The yellow microemulsion solution was prepared by mixing 80 mL of poly(oxyethylene) nonylphenyl ether (a nonionic surfactant, Igepal CO-520), 200 mL of heptane and 39 mL of mixed aqueous salt solution. The microemulsion was mixed and 18 mL of $\text{NH}_3 \cdot \text{OH}$ was added dropwise into the microemulsion. The precipitations were then subjected to several cycles of washing with ethanol and finally dried at 80 °C for 24 h and calcined at 600 °C for 2 h (labeled as M_3).

2.3. Characterization

The morphologies of MgFe_2O_4 nanoparticles were characterized by SEM (Nova Nano SEM 450, FEI, Netherlands). The crystalline structure was measured with XRD (RINT 2500, XRD-Rigaku Corporation, Japan) employing Cu-K α radiation in the range of 2θ from 10° to 80°. The surface chemistry of MgFe_2O_4 before and after MW was investigated using FTIR spectrometry (VERTEX 70, Bruker, Germany). The generation of $\cdot\text{OH}$ radicals in the MW-assisted catalyst suspension was monitored by measuring the fluorescence of the coumarin-OH adduct (7-hydroxycoumarin). The fluorescence emission intensity of 7-hydroxycoumarin was measured at 467 nm using monochromatic light with a wavelength of 332 nm as the excitation source on a spectrofluorometer (JASCO FP-6200, Japan).

2.4. Catalytic experiments

MW experiments were conducted in a quartz reactor with a controllable MW oven (WD750B, Guangdong Galanz Company, China). As shown in Fig. S2, the reactor consists of a MW oven, quartz reactor, gas inlet system, and effluent collecting system. Soil samples (20 g) were weighted into self-made quartz reactor followed by the addition of 2 g MgFe_2O_4 and 6 mL deionized water. The soil was stirred as slurry. Air was sparged into the quartz reactor during the entire experiment. Water-free experiment was conducted to study the influence of water on the removal of PNP in soil. A sheltered type-K thermocouple probe was used to record the temperature profile of the soil surface during MW radiation. The quartz reactor was not insulated; hence, there were heat losses to the surrounding air inside the MW chamber. Although the conditions of the experiment did not allow for an accurate mass balance, comparison of the experimental temperatures for various conditions could be performed. NaOH and methanol solution were used as the first and the second gas absorbing solutions, respectively. Triplicate runs for each experiment were performed and the errors were within 5%. PNP and its decomposition intermediates in the gas absorbing solutions and soil were detected with high performance liquid chromatography (HPLC). The details of extraction and analysis of PNP and its degradation were described in S2 of the Supporting information.

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