



Removal of trichloroethylene by biochar supported nanoscale zero-valent iron in aqueous solution



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ABSTRACT

Nanoscale zero-valent iron (NZVI) has been widely used for the degradation of trichloroethylene (TCE) in contaminated water, however, it is suffering from being easy to aggregate and having low adsorption capacity for TCE. In order to overcome the shortcomings of NZVI, modified NZVI particles with biochar (NZVI/BC) were applied in this study for removal and degradation of TCE, given the high stability and adsorption capacity of BC. The effects of pyrolysis temperature of BC, mass ratio of NZVI/BC and solution pH on the removal and degradation efficiency of TCE were studied. The different pyrolysis temperatures of BC resulted in the differences on the surface areas, aromaticity and noncarbonized fractions, which determined the sorption capacity of TCE. Compared with pure NZVI, the NZVI/BC at different mass ratios could increase the removal efficiency of TCE to 99%, which was attributed to the higher adsorption capacity of BC for TCE. Besides, the yield of final products (ethane, ethylene and acetylene) differed at different mass ratios of NZVI/BC. Generally, the main product was ethylene in all reactions and the yield of acetylene and ethane were relatively low. Solution pH had little effect on the total removal of TCE but significantly influenced the yield of final products. The yield of ethylene decreased with the increasing pH. The results indicate that solution pH could not affect the sorption of TCE but influenced the degradation rate of TCE by NZVI/BC.

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1. Introduction

In recent years, increasing numbers of chlorinated hydrocarbons have been released into soil and groundwater, owing to their common use in industrial production [1,2]. The chlorinated hydrocarbons often have the following characters: non-aqueous phase liquid, higher density than water, and low solubility in water [3], thus they may serve as contamination sources of groundwater and soil [4–6], and pose threats to the health and safety of the environment [7].

Trichloroethylene (TCE), as a representative of chlorinated hydrocarbons, has attracted wide attention since it was firstly detected in the environment in late 1970s [8]. For the remediation of contaminated soil or groundwater with TCE, biotic and abiotic methods have been employed [1,9]. While biotic methods utilize microorganisms to dechlorinate TCE completely or into less chlorinated by-products under aerobic or anaerobic conditions [10,11], abiotic methods generally include physical adsorption [12] and

chemical oxidation [13] or reduction [14] of TCE. Among these methods, nanoscale zero-valent iron (NZVI) has been widely used in TCE dechlorination in groundwater because of its simplicity, low cost and environmental friendliness [15–18]. However, there are still many challenges regarding the removal of TCE with NZVI, one of which is the agglomeration of NZVI particles [19–21]. Due to the high surface energy and magnetic interaction, NZVI particles can easily attach to each other and form large-sized aggregates, resulting in declined reactivity [19–21]. In order to hinder the aggregation of NZVI, researchers have employed different materials as the support for NZVI to provide better distribution, which include bentonite [22], mesoporous silica [23], activated carbon [24] and biochar [25]. Among these materials, biochar has been regarded as one of the best adsorbents because of its high adsorption capacity [26] and low cost [27]. Biochar has been used as an adsorbent to remove organic pollutants such as TCE [28]. However, biochar does not decompose TCE into other harmless products. Therefore, modifying NZVI particles with biochar could compensate the deficiencies of them in removing TCE.

In recent years, there are many studies about removing TCE by biochars or NZVI, but far fewer about combining biochars and NZVI [18,29]. Therefore, this study investigated the feasibility and

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mechanisms of degradation of TCE by NZVI supported by biochar. The specific objectives of this study were (1) to investigate the effects of pyrolysis temperature, the ratio of NZVI to biochar and the solution pH on the removal of TCE, (2) to examine the differences in quantity and species of reaction products under different conditions, and (3) to probe into the reaction mechanisms of removing TCE by the biochar supported NZVI (NZVI/BC).

2. Materials and methods

2.1. Reagents

The cornstalk was purchased from a local agricultural field at Lianyungang City, Jiangsu Province, China. NaBH_4 (98%), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Analytical Reagent) and methanol (Analytical Reagent) were purchased from Sinopharm Chemical Reagent Co., Ltd. TCE (Analytical Reagent) was purchased from Huihong reagent co., Ltd, Hunan province, China. Hexane (HPLC) was purchased from Tianjin chemical reagent research institute co., LTD, China, and was used as extractant for TCE detection. Gaseous alkene standards (3.11% ethane, 12.3% ethylene and 8.1% acetylene) were obtained from Huategas Co., Ltd, Guangdong province, China.

2.2. Preparation of biochar, NZVI, and biochar-modified NZVI

The cornstalk was used as raw feedstocks to produce biochar. The feedstocks were dried in an air-forced oven at 60 °C for a day and ground to less than 150 μm (100 mesh sieve). The grounded feedstocks were placed in a quartz porcelain boat and pyrolyzed in a tube furnace at 7 °C min^{-1} under a limited oxygen condition (via purging nitrogen). The different peak temperatures, i.e. 500, 600 and 700 °C, were adapted to carbonize each feedstock, where they were held for 2 h followed by being cooled to room temperature inside the furnace [30]. Then the biochar was washed with 1 M HCl (1/20, v/v) for demineralization of cations such as K^+ , Na^+ , Ca^{2+} and Mg^{2+} , and was purified by using ultrapure water until the solution pH achieved stability before being dried at 60 °C in an air-forced oven [30]. The developed biochars (BC) at different pyrolysis temperatures (i.e., 500, 600 and 700 °C) were saved in air-tight containers, and referred to as BC500, BC600 and BC700, respectively.

NZVI particles were synthesized via the method as described in previous studies [15,31]. In the synthesis of NZVI/BC composites with different mass ratios of NZVI/BC at 1:1, 1:3 and 1:5 (referred to as NZVI/BC_(1:1), NZVI/BC_(1:3), NZVI/BC_(1:5)), ferric chloride solution ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 0.05 M) was mixed with BC of different amounts (0.28 g, 0.84 g and 1.4 g, respectively) for one night. All solvents were purged with N_2 for more than 60 min prior to use and the whole synthesis process was under N_2 atmosphere. The FeCl_3 -BC solution was added in a 3-mouth container with mechanical stirring at least an hour. An equal volume of 0.2 M potassium borohydride (KBH_4) was dropwisely added into the 3-mouth container. Another 30 min was needed for the generation of Fe^0 and uniformly attached to the surface of the biochar. Afterwards, the composite was separated with refrigerated centrifuge, and washed with ethanol. The NZVI/BC slurry was finally dried in a vacuum drying oven at 60 °C for 8 h. The synthesized NZVI/BC powders were stored in vacuum bag and used in batch experiments within 2 days.

2.3. Characterizations

The surface morphologies of BC and NZVI/BC were examined by using a field emission scanning electron microscope (FE-SEM) (JSM-6700F, JEOL, Japan) equipped with an energy dispersive spec-

troscopy (Oxford Inca EDS). X-ray diffractometer (XRD, Philips Electronic Instruments) was used to determine oxidation state of Fe on the surface of BC. The specific surface areas of BC were analyzed by an ASAP 2020 N_2 -Brunauer-Emmett-Teller (BET) -surface area analyzer (Micromeritics, USA). The spectral properties of BC pyrolyzed at different temperatures were measured by Fourier transform infrared spectroscopy (FTIR), and spectra was obtained in a wavelength range of 450–4000 cm^{-1} .

2.4. Adsorption and dechlorination experiments

Batch experiment was conducted in 40-mL glass vials under anoxic conditions. The ultra-pure water was purged with Helium (He) for 30 min (dissolved oxygen <0.2 mg/L). 100 mg pure NZVI or NZVI/BC were added into the vials, followed by adding 20 mL anaerobic ultrapure water. Then 50 μL of 12 g/L TCE solution (diluted from the analytical reagent TCE with acetone) was added, which made the initial TCE concentration come to 30 mg/L. The vials were capped and transferred to a horizontal shaker at 250 rpm at room temperature.

Liquid sample was taken from the glass vials, and extracted through 0.45 μm needle filter to remove the solid impurities. Then, the remaining TCE in the aqueous phase was extracted with n-hexane. The mixture was analyzed by the means of common GC method for TCE (Rtx-5MS chromatographic column 30 mm \times 0.25 mm \times 0.25 μm , MS detection). Gas sample was taken from the headspace over the reaction solution and analyzed using the same method as described above for the determination of ethane, ethylene and acetylene.

3. Results and discussion

3.1. Characterization of biochar and NZVI/BC

3.1.1. SEM-EDS

The morphologies of NZVI and NZVI/BC were observed by using FE-SEM as shown in Fig. 1. SEM images show that biochar had abundant porous structure and NZVI particles were distributed on the porous structure as well as the surface of biochar. To verify the successful synthesis of NZVI/BC, the EDS mapping and XRD spectrum of the synthesized composites were presented in Fig. 2. The elemental mapping as illustrated in Fig. 2(B and C) showed the uniform distribution of C and Fe. XRD analysis (Fig. 2D) further demonstrated that the Fe existed in the form of Fe^0 . The results reveal that NZVI particles were successfully synthesized and uniformly dispersed on the surface of biochar.

3.1.2. BET

The BET surface area, pore volume and pore size of the derived biochars at 500 °C(BC500), 600 °C(BC600) and 700 °C(BC700) and NZVI/BC were presented in Table 1. The BET surface area of biochar increased with the increase of the pyrolysis temperatures. As shown in Table 1, compared with BC500 and BC600 (28.5 $\text{m}^2 \text{g}^{-1}$ and 31.2 $\text{m}^2 \text{g}^{-1}$ for BC500 and BC600, respectively), BC700 had a larger BET surface area (64.8 $\text{m}^2 \text{g}^{-1}$). The previous research has shown that the pyrolysis temperature in the biochar production process is closely related to the biochar structure [32]. During the thermal decomposition of biomass, coal tar would be produced, which forms pores on the surface of the biochar and increases the related specific surface area. At a higher pyrolyzed temperature, more pores are easily produced because of volatilization of the biomass components [32]. Therefore, the pore volume of the biochar is also closely related to the BET surface area [33]. As shown in Table 1, the data of pore volume displayed an upward trend with the increasing pyrolyzed temperature (0.023, 0.0241 and

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