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Removal of 2-ClBP from soil–water system using activated carbon supported nanoscale zerovalent iron

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ABSTRACT

We explored the feasibility and removal mechanism of removing 2-chlorobiphenyl (2-ClBP) from soil–water system using granular activated carbon (GAC) impregnated with nanoscale zerovalent iron (reactive activated carbon or RAC). The RAC samples were successfully synthesized by the liquid precipitation method. The mesoporous GAC based RAC with low iron content (1.32%) exhibited higher 2-ClBP removal efficiency (54.6%) in the water phase. The result of Langmuir–Hinshelwood kinetic model implied that the different molecular structures between 2-ClBP and trichloroethylene (TCE) resulted in more difference in dechlorination reaction rates on RAC than adsorption capacities. Compared to removing 2-ClBP in the water phase, RAC removed the 2-ClBP more slowly in the soil phase due to the significant external mass transfer resistance. However, in the soil phase, a better removal capacity of RAC was observed than its base GAC because the chemical dechlorination played a more important role in total removal process for 2-ClBP. This important result verified the effectiveness of RAC for removing 2-ClBP in the soil phase. Although reducing the total RAC removal rate of 2-ClBP, soil organic matter (SOM), especially the soft carbon, also served as an electron transfer medium to promote the dechlorination of 2-ClBP in the long term.

Introduction

Polychlorinated biphenyls (PCBs) are a group of semi-volatile organic compounds, which have high toxicity, environmental persistence, bioaccumulation, and long-range transport characteristics. More than one million tons of PCBs have been produced and used in electrical transformers, heat exchangers, and hydraulic systems in the world. About one-third of them have been distributed in our environment, most of which are attached on soil and river sediment. Once adsorbed on soil particles, PCBs have a half-life of up to several decade years due to their extremely stable chemical and biological nature. Therefore, PCBs are still being constantly detected in environmental samples although the manufacture of PCBs had ceased in 1977 under the Toxic Substances Control Act (Samara et al., 2006; Ren et al., 2007). Between 1965 and 1974, about 10 million kg PCBs were produced in China (He et al., 2009). Most of them were used in electrical transformers, many of which have been abandoned. The irrational disposal of these appliances containing PCBs has caused serious soil pollution in some regions in China. Recent reports indicated that the concentration of PCBs in the soil sample in China was up to 5789.5 μg/kg, which was about two hundred times that of the control group (Tang et al., 2010).

Recently, nanoscale zerovalent iron (nZVI) technology has attracted great attention due to its high dechlorination

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efficiency for PCBs and the relatively cheap price (Fu et al., 2014). However, nZVI has its own disadvantages: firstly, nZVI particles tend to agglomerate and lose its chemical dechlorination efficiency in the soil environment; secondly, nanoparticles also have some environmental health risks and need to be controlled (Auffan et al., 2009; Huang et al., 2008). Therefore, in recent years, nZVI immobilization methods have attracted great research attention and many materials, such as alginate (Kim et al., 2010) and polyelectrolyte multilayers (Huang et al., 2008), have been considered as the support material for nZVI. Granular activated carbon (GAC) adsorption technology has been proven as a reliable technology and widely used to remove organic pollutants, especially hydrophobic organic compounds, in soil and groundwater. Actually, several studies have focused on the nZVI/GAC (reactive activated carbon, RAC) materials synthesis methods and RAC's capacity for removing chlorinated compounds including PCBs. However, as to our knowledge, RAC was considered as the possible material for covering cap on PCB contaminated sediment in most published papers, and these prior studies were performed to investigate the PCB removal behavior in the water phase using RAC (Zhuang et al., 2011; Choi et al., 2009a, 2009b, 2009c, Choi and Al-Abed, 2010). However, RAC's capacity for PCBs in the soil phase has not yet been fully investigated. The adsorption capacity of GAC for PCBs is much higher than soil organic matter (SOM) where most PCBs in the soil phase were adsorbed (Jonker and Koelmans, 2002). Therefore, directly mixed with GAC, PCBs can be removed from contaminated soil/sediments, and migrate onto GAC particles. Even a low dose of GAC may change the thermodynamic partitioning equilibrium in sediment significantly (Werner et al., 2006). Thus, RAC has a great potential to reduce the overall concentration of PCBs in soil/sediments, and thereby strengthen the remediation effect (Werner et al., 2005). In the soil phase, the removal kinetics and dechlorination reaction mechanisms of PCBs would be much different from those in the water phase due to the effect of SOM and common ions in soil and need to be deeply investigated.

Besides the mechanism study in the soil phase, several questions about the RAC properties also need to be further investigated: (1) The influence of the pore structure of base GAC on RAC's capacity for PCBs needs to be clarified. GAC pores are classified as micropores (pore diameter <2 nm), mesopores (2–50 nm), and macropores (>50 nm). The pore structures of different GACs are dependent on the raw material and the activation process (Zhang et al., 2007; Ying et al., 2006). The different pore distributions of the base GAC may result in the different morphologies of nZVI in RAC and also influence the pore diffusion rates and adsorption capacities of PCBs in RAC. (2) The contribution of adsorption and chemical dechlorination to RAC's capacity for chlorinated compounds of different molecular structures also needs to be investigated. Langmuir–Hinshelwood (LH) kinetic model can be used to describe the removal kinetics of the heterogeneous reaction process and identify the contribution of adsorption and chemical reaction during PCBs and other chlorinated compound removal using RAC (Kumar et al., 2008).

The main objectives of this article are: (1) to compare the capacities for the typical PCBs (2-chlorobiphenyl, 2-ClBP) of RAC with different GAC pore structures; (2) to analyze contribution of adsorption and chemical reaction on RAC while treating 2-ClBP and trichloroethylene (TCE) with LH kinetic model; (3) to evaluate the kinetic and removal mechanism of 2-ClBP removal in the soil phase and compare it with that in the water phase; and 4) to investigate the effect of NOM in the soil phase on the 2-ClBP removal efficiency.

1. Experimental

1.1. Synthesis of RAC

The RAC particles were synthesized by the liquid precipitation method. The GAC samples were sieved (10–40 meshes, 0.45–2 mm), washed by ultrapure water and dried at 105°C overnight. The desired amount of $FeSO_4 \cdot 7H_2O$ and 1.25 g polyethylene glycol (PEG4000) were dissolved with 100 mL ethanol/water (40/60, *V/V*) and then adjusted the pH (>6.5) using 1 mol/L NaOH solution. Ten grams of GAC was added to the ethanol/water solution with stirring. Then, 1.690 g $NaBH_4$ dissolved in 20 mL water was added to reduce Fe^{2+} to nZVI on the surface of the GAC samples. And the mixture slurry was allowed to stir until no gas bubble (H_2) can be observed. After being washed by oxygen-free water for 3 times and ethyl alcohol for 1 time, RAC particles were dried at 700°C for 0.5 hr under nitrogen gas and stored in an anaerobic chamber prior to use.

To assess the influence of the pore structure of GAC on the removal capacity of RAC for PCBs, mesoporous GAC HD (HD 3000, Norit Americas Inc., USA) and microporous GAC F (F 400, Calgon Carbon Inc., USA) were selected as the nZVI support materials and the prepared RAC were named as RAC HD and RAC F, respectively.

1.2. Characterization of RAC

The surface morphology of GAC and RAC was investigated using scanning electron microscope (JSM 6360LV, JEOL, Japan). The Brunauer–Emmett–Teller (BET) surface area and total pore volume were determined using an ASAP 2020 specific surface area and porosity analyzer (Micromeritics Instrument Corp., USA). The elemental iron content of RAC was determined by inductively coupled plasma-atomic emission spectrometer (Varian 710, Varian Inc., USA) after digestion with nitromurlatic acid. A D/max-RB XRD diffractometer (Rigaku, Japan) with a CuKa radiation source ($\lambda = 1.5406$ Å) was used for X-ray diffraction (XRD) analysis. A generator voltage of 40 kV and tube current of 200 mA were used for all acquisitions.

1.3. Batch experiments

Among PCB congeners, 2-ClBP was selected as a model PCB in this study because it has the highest solubility in water (up to 5.9 mg/L) and is the most persistent among mono PCB congeners for dechlorination due to the ortho positional chlorine (Fig. 1) (Choi et al., 2009a).

The water phase batch experiments were conducted as follows: 5 mg/L 2-ClBP (99%, AccuStandard, Apollo Scientific Ltd., UK) aqueous solution was added into 24 mL glass vials containing 0.12 g RAC or GAC without headspace. The vials were rolled using a homemade tumbling barrel at 5 r/min and