The impact of solution chemistry of electrolyte on the sorption of pentachlorophenol and phenanthrene by natural hematite nanoparticles

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HIGHLIGHTS

- Hematite NPs was tested for PCP/PHE sorption under environmentally relevant conditions.
- Sorption of PCP/PHE on hematite NPs depended on pH and ionic strength of electrolyte.
- Natural NPs would be more competitive and efficient than engineered NPs for PCP/PHE sorption.
- This finding increases our knowledge of natural NPs for OC remediation.

ARTICLE INFO

ABSTRACT

Hematite nanoparticles (NPs) were studied as a sorbent for hydrophobic organic contaminants (OCs) under natural ambient conditions through specially designed contrasting solution chemistry of electrolyte. Ionizable pentachlorophenol (PCP) and non-ionizable phenanthrene (PHE) were selected as representative OCs. The sorption capacities of PCP and PHE were pH-dependent, and a larger amount of PCP was sorbed at pH values below its pK_a (4.75). However, the PHE sorption capacity was higher at relatively high or low pHs (e.g. below 4.0 and above 10.0), possibly due to the larger available surface area of the hematite NPs, caused by the higher values of net charges and charge density. Changes in pH might thus affect the sorption of OCs by hematite NPs, through modification of the surface characteristics of the sorbent and the electronic properties of the sorbate molecules. The influence of different ionic strengths indicated that the amounts of PCP and PHE sorbed by hematite NPs decreased as a concentration function of different types of ions (e.g. Na^+, K^+, Mg^{2+} and Ca^{2+}), with the underlying mechanism possibly being due to four interactions i.e. hydrogen-bonding, competitive sorption by ions in the ambient solution, screening effects and aggregation effects. The results confirmed that the surface chemistry of hematite NPs, the chemical properties of PCP and PHE, and solution chemistry (e.g. pH and ionic strength) of the electrolyte all played an important role in PCP and PHE sorption by hematite NPs. By comparison of both sorption capacity and ecologic advantages, our results suggested that natural hematite NPs would be more competitive and efficient for PCP and PHE sorption than engineered NPs. This finding increases our knowledge regarding the environmental function of natural NPs (such as hematite NPs) for OC remediation through manipulating their interfacial behavior.

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1. Introduction

Remarkable progress has been made in the area of nanotechnology with the use of engineered nanoparticles (NPs) (e.g., metal and metal oxide, carbon nanotubes, and fullerenes) increasing in commercial products, including pigments, coatings, photocatalysts, sunscreens, and semiconductors (Dunphy-Guzman et al., 2006; Liu, 2006; Wilson et al., 2008; Zhang et al., 2008). Because of their widespread use and possible release to the environment, potential harmful impacts of these NPs on humans and the environment are attracting increasing research and public attention (Li et al., 2013a, 2013b; Muller et al., 2005;

Wang et al., 2009, 2011; Zhao et al., 2012). Previous toxicological studies indicate that NPs may enter the body and be toxic to animals (Tang et al., 2008), plants (Stampoulis et al., 2009), and bacteria (Choi and Hu, 2008). Due to the perceived environmental risks of engineered NPs, recent researches have increasingly focused on natural NPs (Li et al., 2012; Tsao et al., 2011). Natural NPs, in their natural form and their environmentally-occurring concentrations, have been involved in the evolutionary process; thus, they are compatible with the local environment, or more precisely, with the organisms present there (Pan and Xing, 2012).

Natural NPs have large sorption capacities for metals and organic contaminants (OCs) (Hochella et al., 2008; Li et al., 2013c; Waychunas et al., 2005), and play an important role in geocatalysis because of their large surface area (Wilson et al., 2008). Therefore, sorption of

OCs by natural NPs is an important process affecting their fate, transport and toxicity. Well-known examples of natural NPs in soil are alumino-silicate (clay) minerals; oxides and hydroxides of Al, Fe, and Mn; enzymes; humic substances; viruses; and mobile colloids (Kretzschmar and Schäfer, 2005). Because of the special physicochemical performance of large surface area (25–54 $m^2 g^{-1}$), highly reactive surface sites and high in-situ reactivity (Theron et al., 2008), there has been a growing interest in the application of Fe oxide NPs for environmental remediation, such as groundwater treatment. The potential applications of magnetite NPs for the removal of chlorotetracycline and neutral red dye from aqueous solution have been investigated (Iram et al., 2010; Zhang et al., 2011). Among the Fe oxide NPs, hematite, with its high thermodynamic stability, is the most common species in the soil (Theng and Yuan, 2008). Our previous research proved that hematite NPs are one of the main components of natural soil NPs (Li et al., 2012). Once released to the environment, the hematite NPs might also play an important role in the retention of OCs, possibly with more efficiency than other engineered NPs. An improved understanding of the capability of hematite NPs as special sorbent for OC removal and the mechanisms involved is required, in order to provide improved knowledge of useful applications of environmentally-friendly hematite NPs in polluted water treatment and environmental remediation.

The main objectives of this study were to investigate the capability of hematite NPs for the sorption of typical environmental OCs in aqueous solution. This was done by conducting sorption experiments under natural ambient conditions using the contrasting solution chemistry of electrolytic pH and ionic strength. Ionizable pentachlorophenol (PCP) and non-ionizable phenanthrene (PHE) were selected as representative OCs. It was hypothesized that variations in electrolytic solution chemistry would induce changes in available functional adsorption sites for OC sorption within, or on the surface of, hematite NPs, which may be interactively influenced by the solution chemistry-dependent dissociation characteristics of OCs, This may then result in contrasting values of hematite NPs for OC removal in the natural aquatic environment.

2. Materials and methods

2.1. Sorbates and sorbents

PCP (C_6Cl_5OH) and PHE ($C_{14}H_{10}$) that have been widely distributed and persistent in the environment (Ge et al., 2007; He et al., 2007; Li et al., 2009; Wang et al., 2013), were used as sorbates. PCP is a highly chlorinated ionizable hydrophobic OC and a weak acid with pK_a of 4.75, the ionizing pH depending on whether it is either phenol or the phenolate anion over the environmental pH (4–8) range (He et al., 2006a, 2006b). Non-ionizable hydrophobic PHE, a polycyclic aromatic hydrocarbon with three benzene rings, was selected because of its common association with aquatic and subsurface contamination resulting

from past petroleum and coal production (Li et al., 2013d). Selected physicochemical properties and structures of the sorbates are presented in Table 1. All chemicals used were of analytical grade or above. PCP and PHE, with a purity of >98%, were purchased from Aldrich Chemical Co.

Since organic colloids in soil are largely associated with their inorganic counterparts or form coatings on mineral surfaces (Theng and Yuan, 2008), the extraction yields of individual hematite NPs in soil are generally low. Consequently, commercial hematite NPs (α-Fe_2O_3, with 38.45 $m^2 g^{-1}$ BET surface area, purity >99.5% and particle size <30 nm) were selected as the sorbent and purchased from Aladdin Reagent Co. (Shanghai, China). It was used without any further treatment. The surface area of the sorbent was determined by N_2 sorption isotherms with a multi-point BET method using a Surface Area and Porosimetry Analyzer (Tristar 3020, Tulane, USA) after the sample was out-gassed at 60 °C for 24 h.
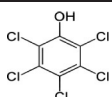
2.2. Sorption experiments

To obtain the appropriate sorption equilibrium time and NP concentrations, sorption experiments with PCP and PHE were carried out in two ways by: (1) maintaining constant NP concentrations (50 mg) but varying sorption times with a total of 9 time points from 0 h to 96 h, and (2) using one identical sorption time (appropriate sorption equilibrium time obtained by the first approach) but with 7 NP concentrations from 5 mg to 200 mg. The spiked concentrations were 10 mg L^{-1} for PCP and 1000 μg L^{-1} for PHE, respectively. The concentration differences were chosen because of their solubility differences. Subsequently, 10 mL of PCP or PHE containing solution was added to 40-mL polytetrafluoroethylene-lined screw cap glass vials and the tubes were tightly closed. This solution was prepared in advance by transferring a precise volume of PCP or PHE methanol stock solution into aqueous solution containing 200 mg L^{-1} NaN_3 (bio-inhibitor), 0.111 mg L^{-1} $CaCl_2$, 0.0095 mg L^{-1} $MgCl_2$ and 0.1907 mg L^{-1} $Na_2B_4O_7 \cdot 10H_2O$ (background solution A) for PCP, and 200 mg L^{-1} NaN_3 and 1.1098 mg L^{-1} $CaCl_2$ (background solution B) for PHE. The experiments were carried out at the native pH of background solution (with the pH value of 8.87 for PCP and 6.64 for PHE, respectively). To minimize cosolvent effects, the volume of methanol added in each vial did not exceed 0.1% (v/v) of the total aqueous phase. Duplicates were studied at each time point and NP concentrations. One series of control experiments using PCP or PHE in solution without hematite NPs was conducted. The resulting solutions were mixed by end-over-end rotation in the dark, at 200 rpm and a temperature of 25 ± 1 °C to reach each equilibrium time. After centrifugation at 3000 rpm for 20 min, the concentrations of sorbates in the supernatant were measured by high performance liquid chromatography (HPLC) with a UV detector for PCP and a fluorescence detector for PHE, respectively.

A sorption isotherm experiment was further conducted using a batch equilibration technique following the above preliminary test confirming the optimum equilibrium time and NPs concentration. By consideration of both the solubility difference and the detection threshold of analysis method, initial concentrations ranging from 0.2 to 40 mg L^{-1} for PCP, and from 10 to 1000 μg L^{-1} for PHE, respectively, were prepared. Subsequently, 10 mL of PCP or PHE solutions containing solution was added to 40-mL polytetrafluoroethylene-lined screw cap glass vials containing 10 mg hematite NPs, respectively. Due to the special acid–base ionizable behavior of PCP (a weak acid with pK_a of 4.75), a separate set of experiments with PCP was conducted with the pH of background solution A adjusted to 4.75. The resulting solutions were mixed by end-over-end rotation in the dark, at 200 rpm and 25 ± 1 °C for 48 h for PCP and 24 h for PHE separately to reach the apparent equilibrium. Other procedures were conducted in the same way as described above, in duplicate, with one series of control experiments.

The concentrations of PCP and PHE in the supernatant were analyzed by HPLC according to the method of He et al. (2006a) and the modified method of Wang et al. (2013), respectively. Briefly, HPLC

Table 1
Selected physicochemical properties of PCP and PHE.

Compound[a]	Structure	Molecular formula	Molecular weight (g mol^{-1})	Water solubility S_w (mg L^{-1})	$LogK_{ow}$	pK_a
PCP		C_6Cl_5OH	266.34	3[b]	4.4[b]	4.75[c]
PHE		$C_{14}H_{10}$	178.23	1.29[d]	4.57[d]	

[a] PCP and PHE are abbreviations of pentachlorophenol and phenanthrene, respectively.
[b] From Chen et al. (2004).
[c] From Ferro et al. (1994).
[d] From Iorio et al. (2008).