



Natural soil mineral nanoparticles are novel sorbents for pentachlorophenol and phenanthrene removal



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ABSTRACT

Natural soil montmorillonite and kaolinite nanoparticles (NPs) were tested as efficient sorbents for organic contaminant (OC) removal through mimicking their natural environmental dispersive states. Sorption of both mineral NPs decreased with increasing pH with ionizable pentachlorophenol (PCP), but increased with pH with non-ionizable phenanthrene (PHE), within the pH range of 4–10. In contrast, sorption decreased consistently for both PCP and PHE, as a function of increasing ion concentration (0.001–0.1 mol L⁻¹). Sorption differences were likely caused by the electrolytic conditions dependent upon surface chemistry of OCs and mineral NPs. The results confirmed that the highly dispersive soil mineral NPs would prevail over both engineered NPs and their regular μm-sized colloids for OC removal, due to their ecological advantages and higher sorption properties. This finding provided a realistic assessment of the environmental function of soil natural minerals in water once they are released from soil into OC polluted aqueous systems.

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1. Introduction

A large number of nanoparticles (NPs) with novel chemical and physical properties are being discharged into the environment as a result of the development of nanotechnology (Dunphy Guzman et al., 2006; Wilson et al., 2008). The wide spread use of these NPs has triggered some concerns about their potentially adverse effects on both environmental and human health (Muller et al., 2005; Wang et al., 2009; Zhao et al., 2012). The major toxicological concern is that some of the engineered NPs are redox active (Colvin, 2003), and others are transported across cell membranes, especially into mitochondria (Foley et al., 2002). Due to the perceived environmental risks of engineered NPs, recent research has increasingly focused on natural NPs (Foley et al., 2002; Tsao et al., 2011; Li et al., 2012, 2013; Zeng et al., 2014). Natural geochemical and biological processes each produce natural NPs, which are ubiquitously distributed in various environmental media worldwide, e.g. soils, sediments, volcanic dust and ash, ice cores, ocean surface microlayers, freshwater and other natural waters. They are mainly composed of clay minerals, metal oxides or

hydroxides, carbonates and humic substances (Kretzschmar and Schäfer, 2005). With huge surface areas and strong catalytic abilities, natural NPs play an important role in regulating the fate, transport and toxicity of organic contaminants (OCs), usually through sorption (Hochella et al., 2008; Li et al., 2013; Zeng et al., 2014).

NPs are always undergoing a dynamic equilibrium of aggregation and dispersion. Aggregation usually enlarges, while dispersion reduces, the size of the particles (Zhang et al., 2008; Mashayekhi et al., 2012). This inevitably produces changes in the surface area of the NPs, and thereby modifies their properties as sorbents (Ghosh et al., 2008). A few studies suggest that adsorptive capacity can be improved when the initial aggregates are broken into smaller masses. For example, Zhang et al. (2012) observed that sonication broke down aggregated carbon nanotubes and increased pyrene adsorption by up to 1.4 orders of magnitude. Gai et al. (2011) also proposed that aqueous dispersions of fullerenes led to increased available sites and, consequently, enhanced the sorption of atrazine on fullerenes. Therefore, a realistic investigation of the sorption ability of NPs should be based upon the premise that the NPs are highly dispersive avoided aggregation, so as to guarantee their particle size within the nano scale.

Montmorillonite is a typical clay mineral in soil with substantial isomorphous substitution properties. Exchangeable cations in the 2:1

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layers balance the negative charges generated by isomorphic substitution. Montmorillonite plays an important role in the environment by acting as a natural scavenger of pollutants by taking up cations and anions either through ion exchange or adsorption or both (Abollino et al., 2003; He et al., 2006b), and this mineral is largely formed by rock weathering (Hochella et al., 2008; Theng and Yuan, 2008). In contrast to montmorillonite, kaolinite is one of the very common low cost natural clay adsorbents with ionic crystalline structures. Kaolinite is a 1:1 aluminosilicate with a chemical composition of 46.54% SiO₂, 39.50% Al₂O₃ and 13.96% H₂O (Wang et al., 2009). A large number of previous sorption studies have used these clay minerals as sorbents for OCs removal, and their sorption ability has been well testified at the μm scale colloids for typical environmental OCs, such as PCP and basic dyes (e.g. methylene blue and malachite green) (He et al., 2006b; Nandi et al., 2009). However so far, the key information is missing regarding their sorption ability at the nano scale, which is also within the size of the natural forms of these clay minerals. As two of the major components of natural soil NPs (Li et al., 2012), the natural nano-montmorillonite and nano-kaolinite, once released into the environment, might also play an important role in the retention of OCs. Possibly, they may be even more efficient in OC retention compared with aggregated montmorillonite and kaolinites at conventional μm sizes. This warrants further investigation.

The aim of the present work was to investigate the capability of natural nano-montmorillonite and nano-kaolinite for the sorption of typical environmental OCs. Special efforts were made to mimic the naturally occurring state of both mineral NPs during sorption through use of the aqueous suspension of montmorillonite and kaolinite at the nano scale. Ionizable pentachlorophenol (PCP) and non-ionizable phenanthrene (PHE) that have been widely distributed and persistent in the environment (Wang et al., 2013; Zeng et al., 2014), were selected as representative OCs for sorbates. PCP is a highly chlorinated hydrophobic ionizable organic compounds and a weak acid with pK_a of 4.75, ionizing pH dependently and existing as either phenol or the phenolate anion over the range of environmental pHs (Ferro et al., 1994; He et al., 2006a). PHE, as a representative polycyclic aromatic hydrocarbon, was selected because of its common association with aquatic and subsurface contamination resulting from past petroleum and coal production (Zeng et al., 2014). It was hypothesized that the interfacial interaction between mineral NPs and OCs would be modified differentially under contrasting electrolytic conditions of pH and ionic strength, thereby resulting in the contrasting ability of mineral NPs for OC removal in the natural aquatic environment.

2. Materials and methods

2.1. Preparation for the aqueous suspension of mineral NPs

The aqueous suspensions of montmorillonite and kaolinite at the nano scale were selected as the sorbents. Two steps were included for preparation: dispersion of the mineral samples in an aqueous phase, and separation of the nano-sized fractions from the matrix, according to the method of Li et al. (2012). The mineral samples of montmorillonite (purity >98% and size <2 μm) and kaolinite (purity >98% and size <3.5 μm) were purchased from Aladdin Reagent Co. (Shanghai, China).

After ultrasonic preparation of dispersion of mineral NPs, the aqueous suspensions were passed through a 50- μm sieve to remove any larger particles. The suspension was then centrifuged at 3500 g for 24 min to obtain the desired particles with size less than 100 nm according to Stokes' Law (Tang et al., 2009). The above separation process was further conducted two more times to collect sufficient amounts of aqueous suspension of mineral NPs. The

supernatants were then combined, collected in a 100-mL glass bottle and stored at 4 °C for further study, with their concentrations for mineral NPs determined by a standard gravimetric method. The pH, hydrodynamic size and zeta potentials of minerals NPs were further analyzed. All results are the mean of three replicates. Details for preparation, separation and analyses of concentration, pH, hydrodynamic size and zeta potentials of minerals NPs in aqueous suspension can be found in the [Supplementary information \(SI\)](#).

To guarantee the particle size of minerals used for sorbents within the nano scale range (less than 100 nm), differences in loading amounts of montmorillonite samples were considered for comparison. Six loading amounts (50 mg, 100 mg, 200 mg, 500 mg, 1000 mg, and 2000 mg) were used for the preparation of the suspension of montmorillonite NPs; while the amount used for preparation of the suspension of kaolinite NPs was standardized to 1000 mg, based on the empirical analysis with respect to montmorillonite.

2.2. Sorption experiments

PCP and PHE were purchased from Aldrich Chemical Co. with a purity of >98%. The total water solubility is 3.0 mg L⁻¹ for PCP (Chen et al., 2004) and 1.29 mg L⁻¹ for PHE (lorio et al., 2008), respectively.

The sorption experiments were conducted using a batch equilibration technique. Ten milliliter aliquots of aqueous suspensions of nano-montmorillonite and nano-kaolinite were taken from the stock flask into 40-mL polytetrafluoroethylene-lined screw cap glass vials (Reason for choosing 40-mL vials can be found in the SI), making sorbent concentrations of 0.464 g L⁻¹ and 0.353 g L⁻¹, respectively. Then, sorption was initiated by adding a pre-determined amount of PCP and PHE stock solution (dissolved in methanol). The volume of injected methanol was less than 0.1% (v/v) to avoid cosolvent effects. By consideration of both the solubility difference and the detection threshold of the analytical method, the initial concentrations of sorbates ranged from 0.4 to 40 mg L⁻¹ for PCP and from 50 to 1000 μg L⁻¹ for PHE, respectively. To investigate the influence of pH on sorption of PCP and PHE by mineral NPs, the initial pH of the suspensions was adjusted to 4, 6, and 10 using HCl or NaOH, both at 0.1 mol L⁻¹, respectively. Additionally, the impact of ionic strength (0.001, 0.01, 0.1 mol L⁻¹) was tested by adding NaCl and CaCl₂ solution at pH 6.5, respectively. One series of control experiments using PCP or PHE in solution without mineral NPs was conducted. The resulting solutions were mixed by end-over-end rotation in the dark, at 200 rpm at 25 ± 1 °C for 24 h. Preliminary tests indicated that 24 h was sufficient to reach the apparent equilibrium. After reaching the apparent equilibrium, both the size and zeta potential of the mineral NPs were measured. Then, after centrifugation at 13,000 rpm (equal to 16,200 g) with Teflon tubes for 30 min at 25 °C (Gai et al., 2011) (Details for the removal efficiency of NPs from solution and the relevant discussion can be found in the SI), the concentrations of sorbates in the supernatant were measured by high performance liquid chromatography (Zeng et al., 2014). The amounts of PCP and PHE sorbed by mineral NPs were determined by the difference in mass between the initial and the equilibrium solutions.

2.3. Characterization of mineral NPs before and after sorption, and sorption data analysis

Both minerals NPs before and after sorption (at the largest PCP/PHE sorption conditions) were further characterized by powder X-ray diffraction (XRD) analyses. All sorption data were analyzed for sorption partition coefficient (K_d , L kg⁻¹). Only sorption data at different initial solution pH were analyzed for Freundlich sorption parameter (K_f [(μg g⁻¹) (mg L⁻¹)^{-N}] and N). Details are in the SI.

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