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Interactions between biogenic selenium nanoparticles and goethite colloids and consequence for remediation of elemental mercury contaminated groundwater

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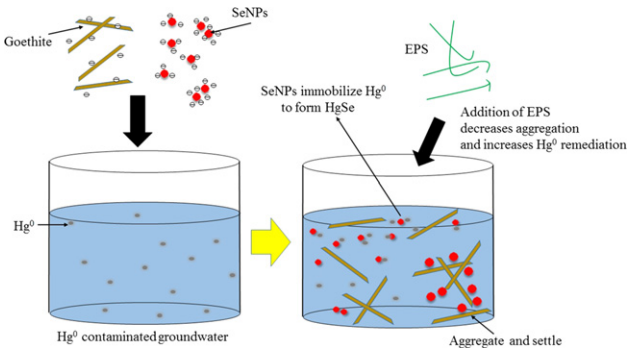
HIGHLIGHTS

- SeNPs have a strong tendency to heteroaggregation with goethite
- Bacterial EPS can effectively decrease the heteroaggregation
- Goethite coated sand retains more selenium nanoparticles than uncoated sand
- Goethite inhibits Hg^0 remediation and EPS can significantly mitigate this inhibition

GRAPHICAL ABSTRACT



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ABSTRACT

Ubiquitous colloidal minerals such as goethite can have a significant impact on the performance of nanoparticles-based groundwater remediation due to aggregation. Heteroaggregation and retention of Se nanoparticles (SeNPs) by goethite in groundwater, and its impact on Hg^0 remediation by SeNPs were investigated in this study. In order to mitigate the adverse effects of aggregation, the effects of bacterial extracellular polymeric substances (EPS) on the stability of SeNPs and Hg^0 sequestration using SeNPs were also evaluated. Heteroaggregation of SeNPs with goethite in groundwater was stronger than homoaggregation of SeNPs or goethite. Addition of EPS could slightly decrease homoaggregation of SeNPs and significantly reduce heteroaggregation. Column transport experiments showed that goethite coated quartz sand could retain 1.36 times a higher amount of SeNPs than uncoated quartz sand. Hg^0 remediation by SeNPs was significantly inhibited by heteroaggregation of SeNPs with goethite and EPS could effectively mitigate this inhibitory effect. The Hg^0 removal efficiency decreased to 71.6% and 66.9%, respectively in the presence of 20 and 100 mg L^{-1} goethite. When 200 mg L^{-1} EPS was added together with 100 mg L^{-1} goethite, 81.2% of the supplied Hg^0 was removed from the groundwater. This study demonstrates that the widespread presence of goethite could significantly reduce the remediation efficiency of Hg^0 contaminated groundwater and that

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EPS is a promising amendment for mitigating the adverse effects of heteroaggregation. This research also contributes to a further understanding of the environmental behaviour of nanoparticles.

1. Introduction

Selenium nanoparticles (SeNPs) are receiving increasing attention as a new functional material due to their special properties such as high photoconductivity, non-linear optical responses, thermoelectric responses, and anisotropy of thermal-conductivity (Berger, 1996; Zhang et al., 2011). Because Se^0 is prone to react with Hg^0 to form mercuric selenide (HgSe) (ΔG^0 −38.1 kJ mol^{-1}), the most stable inorganic mercury compound with a K_{sp} of 1.0×10^{-59}, SeNPs have been applied to remediation of elemental mercury (Hg^0) contamination of air (Ralston, 2008; Johnson et al., 2008; Lee et al., 2009; Fellowes et al., 2011) and soil (Wang et al., 2017). However, remediation of soil and groundwater using nanoparticles can be severely limited because of widespread aggregation of nanoparticles in the soil solution and groundwater. Nanoparticles have a strong tendency to attach to each other and to other surfaces present in the environment and form aggregates up to microparticles scales. Nanoparticle aggregation takes place when nanoparticles undergo collision, mediated by Brownian motion and/or external forces, e.g. hydrodynamic shear and gravitational force leading to particle-particle attachment (Shen et al., 2014). There are two types of aggregation, homoaggregation and heteroaggregation. Aggregation between the same type of particles in a suspension is called homoaggregation. Alternatively, aggregation between dissimilar particles is termed heteroaggregation. Generally, heteroaggregation is likely to play a more significant role than homoaggregation in governing the stability and transportation of nanoparticles (Chen et al., 2010). A binary system of two different kinds of nanoparticles is more complex than a single particle kind system. Aggregation of nanoparticles can influence their stability, transport and toxicity in the natural environment.

Soil contains a diversity of mineral colloids which play an important role in controlling the fate of nanoparticles and their remediation efficiency. Mineral colloids which have a very high surface area to volume ratio, are widespread in natural waters and soil solutions (Zhou et al., 2012). Such ubiquitous mineral colloids may have a significant impact on the stability and reactivity of nanoparticles which are introduced into soil or groundwater. (McCarthy and Zachara, 1989). Therefore, it is essential to consider the impact of mineral colloids when a contaminated environment is remediated using engineered nanoparticles (Buffle and Leppard, 1995; Lin et al., 2010). Goethite (α-FeOOH) is a common iron oxide colloid which exists in all types of soils and sediments. Little research on the impacts of goethite on the behaviour of SeNPs has been reported and any effects on Hg immobilization using SeNPs is completely unclear.

The objective of this study was to investigate homoaggregation and heteroaggregation of SeNPs with goethite in groundwater and its subsequent impact on remediation of Hg^0 contaminated groundwater using SeNPs. Because the transport of nanoparticles in an aquifer is also an important factor that can significantly affect remediation, the effect of goethite on transport of SeNPs through quartz sand was examined by column transport experiments. In an attempt to mitigate the adverse effects of aggregation, the effects of bacterial extracellular polymeric substances (EPS) on the stability and Hg^0 sequestration properties of SeNPs were also evaluated.

2. Materials and methods

2.1. SeNPs, goethite, EPS and groundwater

SeNPs were produced by reduction of Na_2SeO_3 (1 mM) using the selenite-reducing bacterium *Citrobacter freundii* Y9 (Wang et al., 2017). Biogenic SeNPs precipitates were collected by centrifugation (10,000 g × 10 min, 4 °C). The precipitate was washed twice with Tris-HCl (10 mM, pH 7.4) and re-suspended in 2% (*w*/*v*) sodium dodecyl sulfate and 0.2 M NaOH. The precipitate suspension was then sonicated using an ultrasonic cell disruptor (Scientz Biotechnology, Ningbo, China) at 120 W for 10 min in an ice bath, centrifuged (10,000 g × 10 min, 4 °C), and washed with Milli-Q water at least three times (Cui et al., 2016). Finally, precipitated SeNPs was freeze-dried in a vacuum freeze dryer (Labconco, Kansas, USA). The synthesized SeNPs were characterized by SEM-EDS, XRD and TEM (see Wang et al., 2017).

Goethite (α-FeOOH) was synthesized as follows (Schwertmann and Comell, 2000). Solutions of 1-M $Fe(NO_3)_3$ and 5-M KOH were thoroughly mixed and then heated at 70 °C for 60 h. The yellow precipitate was collected, washed with Milli-Q water, oven-dried at 70 °C to constant weight, and then ground to pass through a 300-mesh sieve. The produced goethite was characterized by scanning electron microscopy with energy-dispersive X-ray spectrometry (SEM-EDS) and X-ray diffraction (XRD). Samples were coated with gold with a sputter coater (Emitech K575, Ashford Kent, UK) for SEM analysis (Zeiss Super 55VP, Oberkochen, Germany). Elemental analysis was carried out by energy-dispersive X-ray spectrometry (Bruker XFlash 5010, Berlin, Germany). XRD spectra from 5 to 80° 2θ were obtained using a X-ray diffractometer (Bruker D8, Karlsruhe, Germany) with a Cu anode (40 kV and 30 mA).

The zeta potential of SeNPs and goethite particles as a function of pH over the range pH 3–10 in groundwater was measured using a Zetasizer Nano (Malvern Zetasizer Nano ZS90, Malvern, Worcestershire, UK) and calculated based on the Smoluchowski approximation. The pH of water was adjusted with 0.1 M HCl or 0.1 M NaOH. Samples were equilibrated for 120 s for determination of the zeta potential. Measurements for each sample were repeated in triplicate. The zeta potential of 50 mg L^{-1} SeNPs in the absence and presence of 200 mg L^{-1} EPS was also measured.

All the experiments were carried out in groundwater, which was collected from Urumqi, Xinjiang, China, The groundwater sample was filtered through 0.45 μm pore size mixed cellulose ester membranes (Shanghai Xinya Purification Equipment Co., Ltd., Shanghai, China) and kept at 4 °C. The properties of groundwater were characterized as follows. Electric conductivity was determined using a DDSJ-308A conductivity meter (REX Instrument Factory, Shanghai, China) and the pH measured using a Mettler Seven Easy pH meter (Mettler Toledo, Greifensee, Switzerland). Concentrations of K^+, Ca^{2+}, Na^+ and Mg^{2+} were quantified by ICP-OES (735-ES, Agilent Technologies, Tokyo, Japan). Concentrations of Cl^- and SO_4^{2-} were analyzed by ion chromatography (IC) (Dionex ICS 5000, Thermo Fisher Scientific, Waltham, USA), CO_3^{2-} and HCO_3^- were assessed using a Mettler-Toledo G20 automatic titrator (Mettler Toledo, Greifensee, Switzerland).

EPS from *Citrobacter freundii* Y9 was extracted by centrifugation. The cell suspension was centrifuged at (3320 g × 10 min, 4 °C) (Anke GL-20G-II, Shanghai, China). Harvested biomass was re-suspended in Milli-Q water and the suspension was recentrifuged (16,600 g × 20 min, 4 °C). The supernatant was filtered through 0.45 μm pore size mixed cellulose ester membranes (Shanghai Xinya Purification Equipment Co., ltd., Shanghai, China) and then purified using dialysis membranes (3500 Da) at 4 °C for 24 h (Adav and Lee, 2008; Pan et al., 2010). Finally, EPS was collected by centrifugation (16,600 g × 20 min, 4 °C) and freeze-dried.

2.2. Aggregation experiments

The homoaggregation kinetics of SeNPs/goethite and the heteroaggregation kinetics of SeNPs with goethite in the absence and