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Metal removal from soil leachates using DTPA-functionalised maghemite nanoparticles, a potential soil washing technology

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HIGHLIGHTS

- DTPA-functionalised magnetic nanoparticles can remove Cd, Co and Cu from solution at a range of pHs.
- Ca and Mg have far lower removal efficiencies.
- Metal extraction from soil leachates is similar or reduced compared to single metal solutions.
- The nanoparticles have potential for remediating metal-contaminated water and solutions generated by soil washing.

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ABSTRACT

There is significant current interest in the application of magnetic (magnetite or maghemite) nanoparticles functionalised with chelating agents for the environmental remediation of metal contaminated waters and solutions. Whilst there is a body of knowledge about the potential remediation efficacy of such engineered nanoparticles from studies involving synthetic solutions of single metals, there is relatively little data involving mixed-metal solutions and virtually no studies about nanoparticle performance in chemically complex environmental solutions representing those to which a scaled-up nanoremediation process might eventually be applied. Therefore, we investigated the ability of diethylenetriaminepentaacetic acid (DTPA)-functionalised, silica-coated maghemite nanoparticles to extract potentially toxic (Cd, Co, Cu) and "non-toxic" (Ca, Mg) metals from solution (initial [metal] = 10 mg L^{-1}; pH range: 2–8) and to extract a wider range of elements (As, Ca, Cd, Co, Cr, Cu, Mg, Na, Pb, Zn) from leachate obtained from 10 different contaminated soils with variable initial pH, (semi-)metal and dissolved organic carbon (DOC) concentrations. The functionalised nanoparticles could extract the potentially toxic metals with high efficiency (in general >70%) from single metal solutions and with efficiencies that were either unaffected or reduced from the soil leachates. K_d values remained high (>500 L kg^{-1}), even for the soil leachate extractions. Our findings show that DOC and relatively high concentrations of non-toxic elements do not necessarily reduce the efficiency of metal contaminant removal by DTPA-functionalised magnetic nanoparticles and thus demonstrate the remediation potential of such particles when added to chemically complex soil-derived contaminated solutions.

1. Introduction

The contamination of soils with toxic metals can potentially lead to significant health effects in humans, flora and fauna (Siegel, 2002). This occurs if a pathway of exposure to toxic metals is established. Toxic metals are present in many different phases in the soil including being bound to organic matter, iron or manganese hydroxides and being incorporated within the structure of

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mineral grains (Sahuquillo et al., 1999; Lei et al., 2010). However the most important fraction with regards to potential risk is the water soluble fraction as the metals within this fraction are both mobile and bioavailable (Seguin et al., 2004). This means they can be taken up by organisms and leach into rivers, lakes and groundwater thereby providing a pathway for plant, animal and human exposure. When metal contamination of soils poses a risk to the surrounding ecosystem and human health, remediation schemes are often instigated. Soil washing is an established technology used for removing toxic metals from soils, and aminocarboxylate chelating agents such as DTPA and EDTA are often used to enhance metal removal (Lestan et al., 2008). Whilst using chelating agents improves the effectiveness of metal removal, the techniques currently used for removing the chelating agents from solution after use, such as membrane separation, electrochemical treatment or precipitation via the addition of ferric chloride or calcium hydroxide can often add to remediation costs as they require inputs of energy or chemical reagents (Lo and Zhang, 2005; Finzgar and Lestan, 2008; Pociecha and Lestan, 2009).

The nanoparticle revolution has impacted on many areas of modern life. In the field of remediation perhaps most practical applications of nanotechnology have focussed on the use of zero valent iron as a treatment of organic contaminants in ground water (e.g. Li et al., 2006; Varanasi et al., 2007; Kim et al., 2017; Zhang et al., 2009; Crane and Scott, 2012; Fu et al., 2014). However, a challenge with the use of zero valent iron is the concern regarding the environmental fate of nanoparticles post injection into aquifers (Oughton et al., 2017). Another promising application of nanotechnology in the field of remediation focusses on the use of magnetic nanoparticles as there is the potential for recovery of the nanoparticles using magnets following deployment. Many studies have now investigated the use of magnetic nanoparticles, typically magnetite or maghemite, which are then functionalised with chelating agents to enable the particles to adsorb metal contaminants in a highly efficient way. The majority of these studies have currently been conducted in the laboratory using ideal solutions of single (Liu et al., 2009; Wang et al., 2011, 2015; Zhang et al., 2011; Figueira et al., 2011; Koehler et al., 2009; Afsar et al., 2014; Yen et al., 2017; Chung et al., 2012; Chen et al., 2014, 2016; Pan et al., 2016) or far less frequently, multiple (Zhang et al., 2011; Liu et al., 2008; Zeng et al., 2012; Hughes et al., 2017; Shan et al., 2015) potentially toxic metals. To increase levels of realism some studies have considered the impact of dissolved organic matter (DOM) on the efficiencies of metal removal by such nanoparticles, either through additions of organic acids to metal solutions (Zhang et al., 2012; Hughes et al., 2017) through the use of metal-amended natural waters (Figueira et al., 2011; Liu et al., 2008) or, rarely, the use of actual metal contaminated environmental solutions (Bao et al., 2016).

In our previous study we described a synthetic method for preparing DTPA-functionalised maghemite nanoparticles and tested the efficiency of the nanoparticles for Pb and Zn removal from solution for both single and binary metal solutions and in the presence and absence of fulvic acid as a model form of DOM. Metal-bearing solutions arising from soil washing will contain a wider range of metals (both contaminant and non-contaminant) and a more diverse range of forms of DOM. Therefore, the aims of the current study were to consider the effectiveness of our nanoparticles for 1) adsorption of a wider range of metals (Ca, Cd, Co, Cu and Mg) from solution and 2) extraction of metals from leachate obtained from metal contaminated soils. Our study is novel in the following respects. Firstly, it uses DTPA functionalised nanoparticles; despite the established chelating capacity of DTPA there are hardly any reports of the synthesis and use of DTPA-functionalised magnetic nanoparticles (Koehler et al., 2009; Zhao et al., 2015; Zhang et al., 2016; Hughes et al., 2017 to date that we are aware of). Secondly, and from the perspective of assessing the practical applications of this emerging technology more importantly, it uses soil leachate from metal contaminated soils resulting in mixed metal solutions with relatively high DOM contents and the presence of “non-toxic” metals such as Ca and Mg.

2. Methods

2.1. *DTPA-functionalised maghemite nanoparticles*

DTPA-functionalised maghemite nanoparticles were synthesised as previously described (Hughes et al., 2017). In brief, the maghemite nanoparticles were synthesised by the reaction of Fe^{2+} and Fe^{3+} ions present in $FeCl_2$ and $FeCl_3$ solutions in a 1:2 M ratio in the presence of 2 M NaOH as a base. The nanoparticles were given a silica coating by reacting them in tetraethyl orthosilicate (TEOS) and an amine linker added to the surface via reaction with 3-aminopropyltriethoxysilane (APTES). The nanoparticles were washed in dimethylformamide (DMF) and the diethylenetriaminepentaacetic acid (DTPA) added to the amine linker by reaction with triethylamine (TEA) and DTPA dianhydride to give the final composite nanoparticle (Fig. 1). Finally the nanoparticles were washed four times in methanol and stored in deionised water. The average diameter of the resulting particles was 47 ± 6.9 nm (according to TEM). Full details of particle characterization are given in Hughes et al. (2017).

2.2. *Extraction tests*

The extraction tests (for both single metal solutions and soil leachates) followed the same basic protocol detailed in Hughes et al. (2017). 2 mL of an aqueous suspension of DTPA-functionalised nanoparticles (10 mg in total) were added to 8 mL of either a test solution containing a background electrolyte of 0.1 M $NaNO_3$, to maintain a constant ionic strength in the extraction solutions (Yang et al., 2006) or a soil leachate. For fixed pH experiments the pH of the suspensions were adjusted by dropwise addition of 0.01 M HCl and 0.1 M NaOH. pH was measured using a Jenway 3310 pH meter with a Fisherbrand FB68793 glass electrode. The pH meter was calibrated using pH 4 and pH 7 buffers. Calibration was conducted at the start of analysis and after every 10 samples. Following addition of the nanoparticles, each solution was shaken for 18 h on an end-over-end shaker at constant temperature (20 °C). The nanoparticles were then removed from solution using a neodymium permanent magnet and the solution analysed for the metal(s) of interest by either a Perkin Elmer 100B Atomic absorption spectrometer (AAS) or a Perkin Elmer OPTIMA 3000 inductively coupled plasma optimal emission spectrometer (ICP-OES). In the single metal experiments, to check for nanoparticle stability and/or remnant nanoparticles in suspension, Fe in solution was also analysed by AAS or ICP-OES. In all cases Fe was below detection in solution indicating that the nanoparticles were stable and removal of at least 99.99% of the added nanoparticles (Hughes et al., 2017). Nanoparticle free controls were also run. All experiments were performed in triplicate. Metal extraction efficiency was calculated as the difference in concentration between the test and a control solution expressed as a percentage of the control solution concentration. Partition coefficients (K_d) were calculated as the ratio of metal concentration on the nanoparticles to the metal concentration remaining in solution.

2.2.1. *Single metal solutions*

In the first set of experiments, solutions containing 10 mg L^{-1} of either Ca, Cd, Co, Cu or Mg were used (though note that results are expressed in terms of moles to allow comparison between