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Article

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

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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

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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 potential of this process when applied to chemically complex soil-derived contaminated solutions.

Keywords: metals; soil; DTPA; adsorption; remediation; nanoparticles

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 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; Pochieca 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; Zhang et al., 2011; Figueira et al., 2011; Koehler et al., 2009; Afsar et al., 2014; Yen et al., 2017; Chung et al., 2012; Wang et al., 2015l Chen et al., 2014; Chen et al., 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.

Methods

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 molar 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).

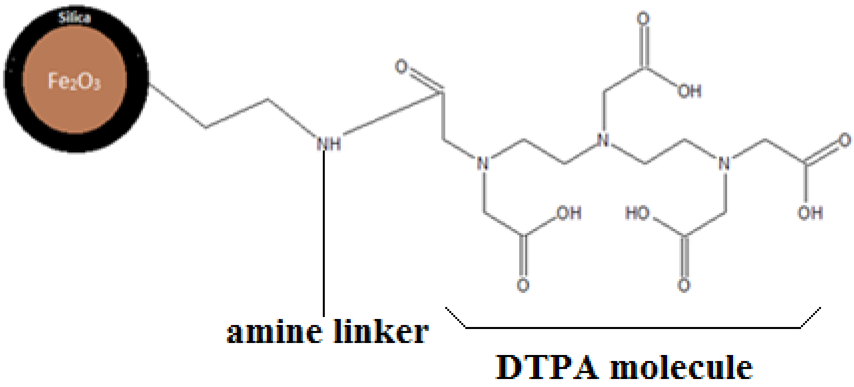

Fig. 1. Theoretical structure of the silica coated DTPA-functionalised maghemite nanoparticle.

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 0.1M $NaNO_3$, 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 0.01M HCl and 0.1M 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 hours 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.

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 elements). The metals were introduced as nitrate salts and the pH was adjusted to pH 2, 3, 4, 5, 6, 7 and 8. Metal concentrations were analysed by AAS. Detection limits were 0.02 mg L^{-1} (Ca), 0.01 mg L^{-1} (Cd), 0.007 mg L^{-1} (Cu), 0.009 mg L^{-1} (Co), 0.001 mg L^{-1} (Fe), 0.001 mg L^{-1} (Mg), 0.008 mg L^{-1} (Pb) and 0.01 mg L^{-1} (Zn), whilst precision was 3.16% (Ca), 4.62% (Cd), 2.99% (Cu), 3.71% (Co), 2.66% (Fe), 3.40% (Mg), 3.52% (Pb) and 3.08% (Zn). Accuracy was 98% (Ca), 97% (Cd), 98% (Cu), 95% (Co) and 96% (Mg).

Soil leachates

For a second set of experiments, soils were collected from metal contaminated sites: Avonmouth (ST 532 803) a former Pb/Zn smelter, which was operational until 2003 (Nahmani et al. 2007); Barney Beck (SD 992 998), an episodically flooded pasture located near a small tributary of the River Swale in North Yorkshire, an area that was extensively mined for Pb from the Roman era up until the late 19th Century when the mine was abandoned (Dennis, 2005); Cwmystwyth (SN 804 747) a former Pb/Zn mine site located in

Ceredigion, central Wales that was mined from the beginning of the Roman era to 1950 (Hughes, 1981); Devon Great Consols (DGC) (SX 728 964) an abandoned Cu and As mine which operated between 1844 and 1930 (Richardson, 1991); Graig Goch (SN 802 741) an abandoned Pb mine located in Ceredigion, central Wales and a part of the central Wales orefield (Palumbo-Roe, 2013); Redruth (SW 724 397) the former Tresavean Cu and Sn mine site, which ceased operating in 1928 (Dines, 1956); Rookhope (NY 894 441) a former Pb and fluorspar mine (Sizmur et al. 2011); Scunthorpe (SE 893 108) the site of the Buckingham allotments which have elevated soil As concentrations due to the underlying geology of the area which consists of arsenic rich Jurassic ironstone (Palumbo-Roe et al. 2005); Shipham (ST 448 573) a former Zn mining site, active in the 18th and 19th centuries in Somerset (Kiekens, 1995); and, Wisley (TQ 065 592) an uncontaminated sandy loam soil that was spiked with lead nitrate, copper sulphate and zinc sulphate in 2005 (Alexander et al. 2006). These soils were used to generate leachates that were in turn used to investigate the ability of the DTPA-functionalised nanoparticles to remove metals from mixed-metal solutions that also contained natural dissolved organic matter. This allowed an assessment of the potential use of the nanoparticles as a component of soil washing remedial treatments or to remediate metal-contaminated water courses. The soil leachates were prepared by adding 2.5 g of soil (air dried, 2mm sieved) to 50 mL of ultrapure H_2O. This ratio was based on the 1:20 to 1:40 range of optimal ratios for extraction of metals from soil washing solutions using EDTA (Papassiopi et al., 1999). The suspension was shaken on an end over end shaker for 24 hours then centrifuged for 20 minutes at 3500 rpm. The supernatant was decanted off, producing the final soil leachate. The pH of the leachate was measured and then 10 mg of nanoparticles in 2mL of ultrapure water were added to 8 mL of leachate. After removal of the nanoparticles, solutions were syringe filtered using 0.45µm cellulose nitrate filters before being analysed for a range of metals by ICP-OES (As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Na, Ni, P, Pb, Zn). Detection limits and precision were as follows: As (1.3×10^{-3} mg L^{-1}, 3.1 %), Ca (1.3×10^{-3} mg L^{-1}, 2.6%), Cd (8.9×10^{-5} mg L^{-1}, 2.9 %), Co (1.6×10^{-3} mg L^{-1}, 4.2%), Cr (3.2×10^{-4} mg L^{-1}, 3.9%), Cu (1.3×10^{-3} mg L^{-1}, 2.6 %), Fe (2.1×10^{-3} mg L^{-1}, 4.5

%), Mg (1.6×10^{-4} mg L^{-1}, 2.5%), Na (9.2×10^{-4} mg L^{-1}, 3.1 %), Ni (3.3×10^{-3} mg L^{-1}, 2.7%), P (3.3×10^{-2} mg L^{-1}, 2.7 %), Pb (1.2×10^{-2} mg L^{-1}, 3.3 %), Zn (8.5×10^{-4} mg L^{-1}, 3.6 %). Dissolved organic carbon (DOC) was measured using a Shimadzu TOC-L total carbon analyser equipped with a non-dispersive infra-red (NDIR) detector. The detection limit for the DOC was 1.31×10^{-4} mg L^{-1} and the precision value for the 12 samples measured in duplicate was ± 2.4 %.

Statistical analysis

Data were analysed using SigmaPlot 12 for Windows.

Results and Discussion

Single metal studies

Metal concentrations in the control and nanoparticle-treated mono-metallic solutions are presented in Table 1 and calculated extraction efficiencies in Table 2. The decrease in control solution concentrations with increasing pH for Cu and, to a lesser extent Cd and Co, indicate that some precipitation occurred at higher pH values for these metals. However, differences in concentration between the control and nanoparticle-treated solution concentrations at a given pH are indicative of adsorption as the metal removal process. K_d values were calculated as the ratio of the concentration of metal on the nanoparticles at equilibrium concentrations (mmol kg^{-1}) and the concentration of metal in solution at equilibrium (mmol L^{-1}) for the extractions and are presented in Table 3.

Table 1. Concentrations (mmol L^{-1}) of metals in solution in control and nanoparticle treated solutions. Values are mean ± standard deviations (n = 3).

	Ca		Cd		Co		Cu		Mg	
pH	Control	NP	Control	NP	Control	NP	Control	NP	Control	NP
2	0.232 ±0.004	0.223 ± 0.001	0.086 ± 0.001	0.032 ± 0.003	0.173 ± 0.002	0.033 ± 0.013	0.163 ± 0.002	0.022 ± 0.00	0.406 ± 0.002	0.402 ± 0.006
3	0.233 ± 0.003	0.161 ± 0.032	0.085 ± 0.001	0.010 ± 0.000	0.171 ± 0.002	0.018 ± 0.002	0.158 ± 0.001	0.017 ± 0.000	0.416 ± 0.004	0.348 ± 0.031
4	0.237 ± 0.003	0.090 ± 0.008	0.080 ± 0.000	0.006 ± 0.002	0.168 ± 0.001	0.017 ± 0.001	0.150 ± 0.007	0.026 ± 0.002	0.407 ± 0.004	0.337 ± 0.026
5	0.227 ± 0.001	0.079 ± 0.012	0.065 ± 0.001	0.006 ± 0.002	0.169 ± 0.001	0.020 ± 0.002	0.154 ± 0.003	0.032 ± 0.000	0.410 ± 0.002	0.336 ± 0.031
6	0.236 ± 0.001	0.080 ± 0.004	0.077 ± 0.000	0.007 ± 0.002	0.168 ± 0.001	0.019 ± 0.001	0.150 ± 0.002	0.026 ± 0.000	0.413 ± 0.005	0.339 ± 0.016
7	0.228 ± 0.002	0.059 ± 0.005	0.077 ± 0.003	0.006 ± 0.001	0.152 ± 0.001	0.019 ± 0.000	0.067 ± 0.004	0.017 ± 0.001	0.410 ± 0.002	0.354 ± 0.014
8	0.231 ± 0.000	0.057 ± 0.007	0.079 ± 0.000	0.006 ± 0.000	0.152 ± 0.003	0.020 ± 0.000	0.058 ± 0.011	0.012 ± 0.002	0.402 ± 0.016	0.391 ± 0.008

Table 2. Percentage extraction efficiencies of Ca, Cd, Co, Cu, Mg, Pb and Zn from aqueous solution by nanoparticles at pH 2 to 8. Values are mean ± standard deviation, n = 3. Pb and Zn data from Hughes et al. (2017).

pH Metal	2	3	4	5	6	7	8
Ca	3.6 ± 0.54	31 ± 14	62 ± 3.3	65 ± 5.3	66 ± 1.9	74 ± 2.1	75 ± 3.0
Cd	62 ± 3.7	89 ± 0.57	92 ± 2.0	91 ± 2.8	91 ± 3.1	92 ± 1.4	92 ± 0.13
Co	81 ± 7.5	90 ± 1.2	90 ± 0.53	88 ± 1.2	89 ± 0.66	87 ± 0.23	87 ± 0.40
Cu	86 ± 0.17	90 ± 0.10	82 ± 1.5	79 ± 0.18	82 ± 0.060	75 ± 1.8	79 ± 3.2
Mg	1.0 ± 1.5	16 ± 7.4	17 ± 6.3	18 ± 7.6	18 ± 3.8	14 ± 3.5	2.7 ± 2.0
Pb	91 ± 2.8	97 ± 0.32	94 ± 0.78	95 ± 0.92	94 ± 1.6	62 ± 9.4	71 ± 8.1
Zn	76 ± 10	92 ± 2.6	92 ± 1.8	91 ± 1.4	91 ± 1.7	91 ± 0.53	88 ± 0.26

Table 3. Metal partition coefficients (K_d / L kg^{-1}) for Cd, Co, Cu, Pb, Zn, Ca and Mg extraction by nanoparticles between pH 2 and 8. Values are mean ± standard deviation (n = 3). Pb and Zn values taken from Hughes et al (2017).

pH	Cd	Co	Cu	Pb	Zn	Ca	Mg
2	1680±250	5140±3190	6270±88.1	10800±4400	4050±2850	37.3±5.80	10.4±15.9
3	7780±441	8750±1070	8580±91.2	32800±3440	12000±3560	486±329	200±112
4	12100±2950	8630±483	4700±494	17300±2780	12000±2660	1650±222	212±95.6
5	11000±3290	7570±836	3810±40.9	18900±3760	10000±1720	1990±425	228±120
6	11100±3570	7870±520	4670±19.4	16000±4240	10900±2440	1960±171	220±57.5
7	11400±1950	6820±141	3060±281	1760±747	10100±636	2880±324	160±47.8
8	12300±234	6800±242	3890±706	2670±1140	7560±189	3120±499	28.4±21.7

Of the potentially toxic metals, extraction efficiency of Cd, Co and Cu is in the same range as that of Pb and Zn in our previous experiments (Hughes et al., 2017) and as reported for a range of functionalised nanoparticles (e.g. Afsar et al., 2014; Liu et al., 2008; Liu et al., 2009; Koehler et al., 2009; Zhang et al., 2011; the review of Lofrano et al., 2016; Table S1 in the Supplementary Information). In depth comparison of extraction efficiencies found here and in other studies is compromised by differences in initial solution composition and solid/liquid ratios. Two way Analysis of Variance (ANOVA) indicates that significant ($p \leq 0.01$) differences are present between metals and between pH for both extraction efficiencies and K_d values and that there are significant interaction terms between the two. Extraction efficiency is greater for Cd, Co, Cu, Pb and Zn than it is for Ca and Mg at all pH levels except at pH 7 and 8 when extraction efficiency of Ca increases; relative to the other "toxic" metals Cd shows reduced extraction efficiency at pH 2 and Cu at pHs 4 – 6. Pb extraction efficiency decreases at pH 7 and 8. In general K_ds of ≥ 500 L kg^{-1} are considered acceptable and > 5000 mg/L very good (Fryxell et al., 2005). Thus the K_ds determined for our nanoparticles across a range of potentially toxic metals are suggestive of them being a useful adsorbent. Ca and Mg always have the lowest K_ds. Similar results are reported in other studies using functionalised nanoparticles.

The iso-electric point of the nanoparticles is 6.74 (Hughes et al., 2017). Thus whilst our previous data suggest that adsorption of the metals is most likely dominated by chelation with the nitrogen atoms in the DTPA (Hughes et al., 2017) for pH ≤ 6 ion exchange with protons on the protonated functional groups of the DTPA and for pH ≥ 7 electrostatic adsorption to deprotonated functional groups of the DTPA is also likely to occur. The differences in efficiencies and K_ds between the different metals are due in part to the metal-DTPA complexation stability constants for the potentially toxic metals tested being higher than those for Ca and Mg (e.g. Lindsay et al., 1979; Dojino, 2017; Liu et al., 2008). However, in addition, as initial concentrations in solutions for the single metal tests were equal for all metals on a mg L^{-1} basis the different atomic masses of the elements result in differing molar concentrations which may also have an impact. For example, both Ca and Mg have lower atomic masses than the toxic metals and therefore their molar concentrations are higher. Adsorption sites on the nanoparticles are potentially closer to saturation in the Ca and Mg extraction tests which may reduce extraction efficiency.

The reduced extraction efficiency of Cd at pH 2 compared to Cu and Pb (Hughes et al., 2017) is consistent with previous studies using EDTA-functionalised nanoparticles (Koehler et al., 2009; Zhang et al., 2011) and is due to the lowering of the pH-dependent complex formation constant (Anderegg et al., 1959). Reduced extraction efficiency of Cu relative to Cd and Pb at similar concentrations to those used in our experiment has been previously observed at pH 6 (Koehler et al., 2009) and pH 5 (Zhang et al. 2011) and attributed to the lower molar concentration of Cd and Pb solutions relative to Cu for solutions of the same concentration by mass leading to increased saturation levels of adsorption sites for the Cu. The high extraction efficiency and K_d values for Pb at pH 2 – 6 are consistent with a number of other studies using a variety of functionalised nanoparticles (Koehler et al., 2009; Zhang et al., 2011; Liu et al, 2009; Liu et al., 2008) and are related to high stability constants and the low molar concentration of Pb in the test solution relative to the other metals. We have discussed the reduced extraction efficiency and K_d values of Pb at pH 7 and 8 previously (Hughes et al., 2017); it is consistent with previous studies on a variety of functionalised nanoparticles and is attributed to changes in speciation at these pH values (Hughes et al., 2017; Wang et al., 2015; Weng, 2004; Liu et al., 2009).

Similar to other studies on a variety of chelating agent functionalised magnetic nanoparticles (e.g. Chen et al., 2016; Liu et al., 2008; Liu et al., 2009; Shi et al., 2016; Zhang et al., 2012, Zhang et al., 2011; Table S1 in Supporting Information) our single metal extraction experiments show that our functionalised nanoparticles can extract a range of contaminant metals. This is to be expected as the chelating agents used to functionalise the nanoparticles are not specific for a single metal. This is encouraging for use of functionalised nanoparticles in real world situations where mixed metal contamination is more likely than single metal contamination. However, although previous studies have shown the capacity of functionalised nanoparticles to maintain high extraction efficiencies in mixed metal solutions often containing high concentrations of nontoxic elements such as Ca and Mg (e.g. Hughes et al., 2017; Liu et al., 2008; Shan et al., 2015; Zhang et al., 2012) extraction efficiency can be reduced relative to single metal solutions (e.g. Hughes et al., 2017; Liu et al., 2008; Zhang et al., 2011). Ca and Mg often occur at high concentrations in soils (Ca =1-200 g kg^{-1}; Mg = 0.1-28.6 g kg^{-1}) (Bolan et al. 2004) and solutions and leachates from soil could therefore contain higher concentrations of such elements than concentrations considered in experiments to date. Similarly although previous studies have shown high levels of metal extraction in the presence of DOC (Hughes et al., 2017; Liu et al., 2008; Shan et al., 2015; Zhang et al. 2012) our previous experiments (Hughes et al., 2017) also showed significant reductions in extraction efficiency at concentrations of 2.1 mg L^{-1} and 21 mg L^{-1} DOC. Metal-rich extracts obtained by leaching soils with water may contain higher concentrations of DOC than this which could potentially have an impact on the extraction efficiency of toxic metals from such soils. Therefore to investigate further the potential use of our DTPA-functionalised nanoparticles for removal of metal from the aqueous leachates of contaminated soils, we determined extraction efficiencies using leachates from soils containing a mixture of inorganic contaminants and variable, native concentrations of DOC.

Soil extractions

The chemistry of the soil leachates in control and nanoparticle-present treatments is presented in Tables 4 and 5. All the leachates were filtered to 0.45 μm prior to use. Operationally we have assumed that this filtration step results in the production of a pure solution and that differences between control and nanoparticle-present treatments are therefore due to interactions between ions in solution and the added nanoparticles. We did not analyse our filtered solutions for the presence of colloids but these may be present and have an impact on our results. However, from a practical perspective the aim of our investigation was to determine whether our nanoparticles were effective at removing metals from leachates obtained from metal contaminated soils regardless of whether colloidal particles play a role or not. The leachates contain relatively low concentrations of metals despite samples being taken from former mine sites with soils that have high total metal concentrations reported in the literature; this reflects the speciation of the metals in the soils and highlights the important difference between concentrations of “total” metals compared to other fractions such as “bioavailable”, “bioaccessible” and “mobile”. The Scunthorpe soil is a good example of this. Palumbo-Roe et al (2005) report elevated As concentrations in soils taken from this sample locality but also that the majority of this As is not bio-accessible. Further the pH of the leachate (c. neutral) lies in the range where As sorption to Fe oxides is high which reduces the likelihood of As passing into solution (Dixit and Hering, 2003; Partey et al. 2008). However, in this study we are not concerned with the issue of bioavailability of metals in soils. Rather, the contaminated soils were used to generate leachates containing metals which could be used to determine the ability of the DTPA-functionalised nanoparticles to remove metals from mixed metal solutions that also contained dissolved organic matter. This allowed us to assess the potential use of the nanoparticles as a stage in soil washing remedial treatments and / or for remediating metal-contaminated natural waters.

The total concentration of “non toxic” elements (Ca, Mg, Na) in the control leachate was significantly greater ($p \leq 0.05$, Kruskal-Wallis analysis of variance on ranks) than that of the total concentration of potentially toxic elements (As, Cd, Co, Cr, Cu, Pb, Zn). Despite this the nanoparticles removed significantly more toxic than non-toxic (either Ca+Mg or Ca+Mg+Na) elements from solution ($p \leq 0.05$, Kruskal-Wallis analysis of variance on ranks). Out of the 10 soils studied, where there are significant differences ($p \leq 0.05$; t-tests) between the concentrations in the nanoparticle-present and control treatments (As – 4 soils, Cd – 4 soils, Cu – 4 soils, Pb – 5 soils, Zn – 6 soils), the nanoparticle-present treatments contain lower concentrations of potentially toxic metals than the controls. Cd, Cu, Pb and Zn would be present as cations under the solution conditions whereas As would be present as an oxyanion. As with the single element extractions, adsorption of the cations is most likely dominated by chelation but will also involve, depending on pH, ion exchange or electrostatic adsorption whilst adsorption of the As is most likely due to non-specific adsorption between the As oxyanion and the protonated nanoparticle surface.

With respect to the effect of the nanoparticle treatment on concentrations of the major, non-toxic elements, Na usually has significantly higher concentrations in the nanoparticle-present treatments (7 out of 8 soils) whereas Mg was lower in the nanoparticle-present leachates for two soils (Avonmouth and Cwmystwyth) and Ca showed no consistent trend in the two soils (Avonmouth and Barney Beck) where there were significant differences. The production of the nanoparticles involves precipitation of Fe oxide in 2 M NaOH. Despite subsequent washing stages, the most obvious explanation for the increase in Na in solution on addition of the nanoparticles to the leachates is that residual Na^+ is still present associated with the nanoparticles.

Table 4. Mean concentrations (μmol L^{-1}) of metals in control (cont) and nanoparticle (NP)-treated soil leachate. Values are mean ± standard deviations (n = 3). BDL indicates concentration below detection limit. ***Bold italics indicate a significant difference ($p \leq 0.05$; t-test) between control and nanoparticle present solution element concentrations.*** For statistical analysis of solutions where concentrations were below detection limits, concentrations were fixed at the detection limit. Avon = Avonmouth, Barn = Barney Beck, Cwm = Cwmystwyth, DGC = Devon Great Consols, Graig= Graig Goch, Red – Red Ruth, Rook = Rookhope, Scun = Scunthorpe, Ship = Shipham, Wis = Wisley.

Soil	Treatment	As	Ca	Cd	Co	Cr	Cu	Mg	Na	Pb	Zn
Avon	cont	***0.241 ± 0.075***	***415 ± 10.8***	***8.46 ± 0.380***	0.167 ± 0.00348	0.151 ± 0.116	***9.01 ± 0.997***	***145 ± 22.2***	***82.4 ± 11.1***	***7.89 ± 2.11***	***579 ± 22.8***
	NP	***BDL***	***376 ± 15.7***	***6.48 ± 0.271***	0.142 ± 0.0145	0.00900 ± 0.00417	***1.19 ± 0.213***	***1.70 ±2.30***	***119 ± 3.05***	***BDL***	***473 ± 19.9***
Barn	cont	BDL	***118 ± 2.25***	***0.00226 ± 0.000111***	BDL	0.0615 ± 0.0271	0.0197 ± 0.00143	16.4 ± 2.06	47.1 ± 0.415	***0.686 ± 0.183***	0.701 ± 0.204
	NP	BDL	***130 ± 5.39***	***BDL***	BDL	0.0621 ± 0.0137	0.0241 ± 0.00388	17.3 ± 1.91	104 ± 8.08	***0.143 ± 0.0826***	0.270 ± 0.213
Cwm	cont	BDL	14.7 ± 4.65	0.0150 ± 0.0000489	0.0293 ± 0.00361	0.0210 ± 0.0193	0.132 ± 0.0470	***10.2 ± 0.554***	***31.4 ± 2.54***	***1.53 ± 0.618***	***11.3 ± 0.704***
	NP	BDL	10.2 ± 2.39	BDL	BDL	0.00822 ± 0.00359	0.0663 ± 0.00695	***7.42 ± 1.00***	***78.5 ± 2.62***	***0.075 ± 0.000503***	***2.07 ± 1.45***
DGC	cont	***2.27 ± 0.101***	107 ± 11.9	BDL	0.0755 ± 0.00810	BDL	***11.7 ± 1.73***	16.2 ± 2.17	***15.9 ± 1.20***	BDL	1.44 ± 0.508
	NP	***1.129 ± 0.0449***	111 ± 1.42	BDL	0.0633 ± 0.00713	BDL	***0.247 ± 0.146***	16.5 ± 0.304	***66.1 ± 2.54***	BDL	0.626 ± 0.285
Graig	cont	BDL	16.2 ± 0.683	***0.157 ± 0.00535***	0.109 ± 0.0183	0.00676 ± 0.00105	***0.383 ± 0.00204***	12.4 ± 0.656	***28.3 ± 12.0***	***41.4 ± 0.591***	***75.9 ± 1.83***
	NP	BDL	18.0 ± 0.909	***0.0946 ± 0.0107***	0.0904 ± 0.00569	0.00635 ± 0.000342	***0.0787 ± 0.0236***	11.4 ± 0.293	***71.3 ± 3.15***	***0.228 ± 0.145***	***51.0 ± 7.39***
Red	cont	BDL	636 ± 47.5	BDL	BDL	BDL	0.0384 ± 0.00696	14.9 ± 0.842	***90.4 ± 3.25***	BDL	***0.459 ± 0.212***
	NP	BDL	681 ± 47.4	BDL	BDL	0.0330 ±	0.0325 ± 0.0112	18.8 ± 2.75	***35.4 ± 1.96***	BDL	***0.0404 ± 0.00485***
Rook	cont	***0.0764 ± 0.0124***	308 ± 26.4	***0.0181 ± 0.000750***	0.166 ± 0.0701	0.0600 ± 0.0476	0.0429 ± 0.0293	53.4 ± 2.72	***38.5 ± 2.54***	3.38 ± 1.46	***8.59 ± 0.966***
	NP	***0.0400 ± 0.00467***	301 ± 3.37	***BDL***	0.126 ± 0.0141	0.0200 ± 0.00547	0.024 ± 0.0118	49.6 ± 0.820	***85.7 ± 5.68***	0.952 ± 0.0782	***1.50 ± 0.532***
Scun	cont	0.181 ± 0.157	549 ± 403	0.00671 ± 0.00519	0.119 ± 0.0259	0.214 ± 0.250	0.135 ± 0.187	72.1 ± 34.3	140 ± 72.2	BDL	0.718 ± 0.525
	NP	0.230 ± 0.0552	335 ± 35.8	0.00792 ± 0.00413	0.150 ± 0.0470	0.278 ± 0.0890	0.0255 ± 0.00346	73.5 ± 11.9	129 ± 12.2	BDL	0.600 ± 0.101
Ship	cont	0.546 ± 0.0948	337 ± 3.71	0.787 ± 0.0366	0.119 ± 0.0555	0.0407 ± 0.0212	0.0314 ± 0.00786	144 ± 4.93	***61.9 ± 9.30***	0.839 ± 0.284	***177 ± 3.71***
	NP	0.400 ± 0.0501	343 ± 9.01	0.521 ± 0.0247	0.210 ± 0.0595	0.0126 ± 0.00593	0.0357 ± 0.00168	146 ± 3.83	***111 ± 3.34***	0.263 ± 0.288	***148 ± 5.95***
Wis	cont	***0.0666 ± 0.00387***	417 ± 14.3	0.00435 ± 0.00125	0.166 ± 0.0266	0.0181 ± 0.00358	***1.05 ± 0.0368***	51.9 ± 1.31	***35.6 ± 2.18***	***0.145 ± 0.0187***	2.04 ± 0.0316
	NP	***0.0409 ± 0.00306***	424 ± 2.57	0.00292 ± 0.00195	0.137 ± 0.0279	0.00839 ± 0.00388	***0.828 ± 0.0336***	50.6 ± 1.21	***101 ± 3.33***	***BDL***	1.24 ± 0.517
Detection Limit		0.0174	0.0324	0.0008	0.0272	0.0062	0.0205	0.0066	0.04	0.0579	0.013

Table 5. Leachate pH and dissolved organic carbon content / mg L^{-1} in control (cont) and nanoparticle (NP)-treated soil leachate. Soil names are as specified in the legend for Table 4. Values are means ± standard deviation (n = 3).

Soil	Treatment	pH	Dissolved organic carbon
Avon	cont	5.32 ± 0.20	9.16 ± 1.73
	NP	5.17 ± 0.07	10.0 ± 0.375
Barn	cont	6.94 ± 0.40	22.1 ± 23.1[1]
	NP	6.78 ± 0.09	23.6 ± 24.5[2]
Cwm	cont	5.44 ± 0.05	15.5 ± 0.633
	NP	5.43 ± 0.13	18.7 ± 0.522
DGC	cont	4.48 ± 0.12	1.85 ± 0.233
	NP	4.38 ± 0.05	2.66 ± 0.206
Graig	cont	4.41 ± 0.32	9.69 ± 0.600
	NP	4.44 ± 0.18	10.8 ± 0.510
Red	cont	7.70 ± 0.21	11.2 ± 0.576
	NP	7.51 ± 0.29	15.6 ± 2.25
Rook	cont	6.30 ± 0.11	10.7 ± 0.924
	NP	5.90 ± 0.06	11.5 ± 0.454
Scun	cont	7.74 ± 0.38	7.11 ± 3.63
	NP	7.71 ± 0.31	7.56 ± 2.09
Ship	cont	5.79 ± 0.06	30.9 ± 2.42
	NP	5.53 ± 0.12	30.9 ± 5.13
Wis	cont	6.98 ± 0.33	19.2 ± 6.14
	NP	6.52 ± 0.23	20.9 ± 6.17

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[1] individual values were 48.8, 9.7 and 7.9 mg L^{-1}. The initial value is likely to be an error which would give a mean composition of 8.8 ± 1.3 mg L^{-1}

[2] individual values were 51.9, 10.4 and 8.6 mg L^{-1}. The initial value is likely to be an error which would give a mean composition of 9.5 ± 1.3 mg L^{-1}

The lower concentrations of Mg in the nanoparticle-present treatments seems most likely to be due to adsorption of Mg, despite the relatively low Mg-DTPA complexation stability constants (e.g. Lindsay et al., 979; Dojino, 2017; Liu et al., 2008) and adsorption efficiencies measured in our single metal experiments.

Extraction efficiencies (Table 6) were calculated for the metals that showed significant reductions in concentration between the controls and the nanoparticle treatments.

Table 6. Percentage extraction efficiencies from soil solutions by nanoparticles where nanoparticles cause a significant decrease in solution concentration. Values are mean ± standard deviations (n = 3). Soil names are as specified in the legend for Table 4.

Metal Soil	As	Cd	Cu	Pb	Zn
Avon	93 ± 0	23 ± 3.2	87 ± 2.4	97 ± 4.8	18 ± 3.4
Barn	-	62 ± 4.8	-	79 ± 12	-
Cwm	-	-	-	95 ± 0.033	82 ± 13
DGC	37 ± 16	-	97 ± 0.70	-	-
Graig	-	40 ± 6.8	79 ± 6.1	99 ± 0.35	33 ± 9.7
Red	-	-	-	-	91 ± 1.1
Rook	48 ± 6.1	91 ± 8.1	-	-	83 ± 6.2
Scun	-	-	-	-	-
Ship	-	-	-	-	16 ± 3.4
Wis	39 ± 4.6	-	21 ± 3.2	60 ± 0	39 ± 25

Extraction efficiencies are variable between soils (no significant differences for As, ANOVA on Ranks; significant differences for Cd and Cu between all soils, ANOVA and Holm-Sidak multiple comparisons; between Graig Goch and Wisley for Pb and between Redruth and Shipham for Zn, ANOVA on ranks and Tukey test multiple comparisons) and are similar or lower to those obtained from the single metal solutions (Table 2). These results are consistent with previous findings in which extraction efficiencies of metals from mixtures are high and either unaffected or reduced by the presence of multiple metals, presumably due to competition for adsorption sites and preferential adsorption (Zhang et al., 2012; Liu et al., 2008; Zhang et al., 2011, Hughes et al., 2017; Shan et al., 2015) with precise trends depending on a range of variables including the metal concentration, pH and nanoparticle concentration. Additionally there will be competition for metal binding between the adsorption sites on the nanoparticles and complexation sites on the dissolved organic matter present in solution. In our study Zn extraction efficiencies in particular appear to be depressed compared to the typical range (70 – 90%) found in single metal extraction experiments which is consistent with our previous findings from mixed Pb-Zn solutions (Hughes et al., 2017). Pb extraction efficiencies remain high except for from the Wisley soil which has a relatively high pH. Reduced Pb extraction at high pH is consistent with our previous findings on the effect of pH on Pb extraction (Hughes et al., 2017). Considering individual replicates rather than mean values the DOC content of the control leachate was in the range 2 – 49 mg L^{-1} with no significant differences (two-way ANOVA, $p \geq 0.05$) between the DOC content of the control and treated leachates. The maximum DOC values are higher than those in previous studies (e.g. Zhang et al., 2012; Liu et al., 2008; Shan et al., 2015; Hughes et al., 2017) where extraction efficiencies have been found to remain high but have been reduced by the presence of the DOC. Thus our results indicate that even in the presence of dissolved organic matter, the nanoparticles could be used to remove metals from solution. There were insufficient data to perform meaningful multiple regression analysis to determine any controlling variables for extraction efficiency. Correlation analysis between the extraction efficiency of individual metals and the pH, DOC, individual metal concentration and total metal concentration in controls for As, Cd, Cu, Pb and Zn only gave a significant correlation for % Pb extraction and pH ($r = -0.89$, $p \leq 0.05$).

K_d values were calculated for metals that showed a significant decrease in concentration between the controls and nanoparticle treatments (Table 7). The K_d for specific metals largely show no significant differences between soils. The K_d values for individual elements determined from the soil samples were usually either significantly lower (16 out of 40 values) or had no significant difference (21 out of 40 values) compared to the K_d values obtained on single metal solutions at similar pH values. The lower K_d values relative to those obtained from single metal solutions are consistent with the reduced extraction efficiencies observed and again, reflect competition for adsorption sites and competition between adsorption on the nanoparticles and complexation with the dissolved organic matter. Despite the reductions in K_d values, they are still typically > 500 L kg^{-1} and many are > 5000 L kg^{-1} indicating the potential for the nanoparticles to be used as adsorbents (Fryxell et al., 2005). As with the extraction efficiency data, there were insufficient data to carry out multiple linear regression to determine controlling variables on the K_d values. There were no correlations between the K_d for a particular metal and the pH, DOC, individual metal concentration and total metal concentration in the controls. The reduction in K_d values compared to single-metal solutions and the lack of extraction of some elements from the leachates despite the presence of those elements in solution indicates the importance for more studies such as this one in which real, rather than synthetic, metal-bearing solutions are used to test the potential of novel sorbents for remediation.

Due to the significant variation between the different soil leachates used in our study in terms of pH, metal concentration, DOC and also the variations between this study and others in the literature (again pH, metal concentration, DOC but also the nature of the chelating agent added to the magnetic nanoparticles), together with the paucity of multi-element studies using real solutions in the literature it is difficult to make comparisons that are other than rather general as above. However, this study further demonstrates the potential for chelating agent functionalised magnetic nanoparticles to remove a range of metal contaminants from contaminated solutions and indicates that dissolved organic carbon and relatively high concentrations of non-toxic elements should not necessarily reduce the efficiency of the process.

Although not considered in our study, an important consideration in the viability of adsorbents for metal removal is their potential for reuse. There are various studies in the literature where solutions including HCl, HNO_3, CH_3COOH, NaOH, EDTA and water are used to desorb metals from sorbents including those that present DTPA, EDTA and other chelating agents at their surface (e.g. Huang et al., 2018; Alizadeh et al., 2018; Ma et al., 2017; Yuan et al., 2016; Zhao et al., 2015; Liu et al., 2009; Zhang et al., 2011; Yang and Hodson, In press; Kaur et al., 2013; Venkateswarlu and Yoon, 2015, Zhang et al. 2016 (and references therein)and thus we are confident that reuse of the DTPA functionalised magnetic nanoparticles should be possible. Whilst that should be confirmed in laboratory studies, more important requirements for future studies are further investigations using “real” rather than synthetic test solutions and also the large scale application of this potential remediation technology. Larger scale trials would address issues concerned with potential mixing of nanoparticles in larger volumes of solution and also removal efficiencies of the nanoparticles when, depending on the design of reactor vessels, the nanoparticles may be further from the magnets required to collect the nanoparticles.

Table 7. Metal partition coefficients (K_d / L kg^{-1}) for As, Cd, Cu, Pb and Zn extraction by nanoparticles from different soil leachates. Values are means ± standard error (n = 3). Where solution concentrations were below detection limits these were set at the detection limits for the purposes of calculation. For each element, values with an alphabetic superscript in common are not significantly different ($p \geq 0.05$) between soils as assessed by analysis of variance (ANOVA) and Holm Sidak pair wise comparisons (As) or ANOVA on ranks and Tukey tests (Cd, Cu, Pb, Zn). $^{<lo/hi}$ indicates significantly lower and $^{>lo/hi}$ significantly higher values than the K_d determined on a single metal solution at the nearest pH below (lo) or above (hi) that of the soil experiment, $^{=lo/hi}$ indicates no significant difference (Analysis of variance and Holm-Sidak pair wise comparisons except for Avon and DGC Cu and Avon, Barn, Graig and Wis Pb which were analysed by ANOVA on ranks and Tukey tests). Soil names are as specified in the legend for Table 4.

Soil	As	Cd	Cu	Pb	Zn
Avon	12900 ± 0.00^{a}	$308\pm55.1^{a<lo<hi}$	$6750\pm1500^{ab>lo=hi}$	$93500\pm72200^{ab=lo=hi}$	$227\pm50.5^{ab<lo<hi}$
Barn		$1670\pm313^{ab<lo<hi}$		$4950\pm3086^{ab=lo=hi}$	
Cwm				$19400\pm137^{ab=lo=hi}$	$6680\pm5230^{ab=lo=hi}$
DGC	1010 ± 81.7^{b}		$57100\pm27700^{a=lo>hi}$		
Graig		$674\pm202^{ab<lo<hi}$	$4140\pm1390^{ab=lo=hi}$	$233000\pm128000^{a=lo=hi}$	$511\pm236^{ab<lo<hi}$
Red					$10500\pm1470^{a>hi=lo}$
Rook	927 ± 230^{bc}	$16090\pm10090^{b=lo=hi}$			$5420\pm2870^{ab=lo=hi}$
Scun					
Ship					$198\pm47.3^{b<lo<hi}$
Wis	633 ± 118^{c}		$264\pm51.7^{b<lo<hi}$	$1500\pm0^{b=lo=hi}$	$852\pm778^{ab<lo<hi}$

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