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Adsorption of Pb and Zn from binary metal solutions and in the presence of dissolved organic carbon by DTPA-functionalised, silica-coated magnetic nanoparticles

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Abstract

The ability of diethylenetriaminepentaacetic acid (DTPA)-functionalised, silica-coated magnetic nanoparticles to adsorb Pb and Zn from single and bi-metallic metal solutions and

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from solutions containing dissolved organic carbon was assessed. In all experiments 10 mL solutions containing 10 mg of nanoparticles were used. For single metal solutions (10 mg L^{-1} Pb or Zn) at pH 2 to 8, extraction efficiencies were typically >70%. In bi-metallic experiments, examining the effect of a background of either Zn or Pb (0.025 mmol L^{-1}) on the adsorption of variable concentrations (0 - 0.045 mmol L^{-1}) of the other metal (Pb or Zn, respectively) adsorption was well modelled by linear isotherms (R^2>0.60; p≤0.001) and Pb was preferentially adsorbed relative to Zn. In dissolved organic carbon experiments, the presence of fulvic acid (0, 2.1 and 21 mg DOC L^{-1}) reduced Pb and Zn adsorption from 0.01, 0.1 and 1.0 mmol L^{-1} solutions. However, even at 21 mg DOC L^{-1} fulvic acid, extraction efficiencies from 0.01 and 0.1 mmol L^{-1} solutions remained >80% (Pb) and > 50% (Zn). Decreases in extraction efficiency were significant between initial metal concentrations of 0.1 and 1.0 mmol L^{-1} indicating that at metal loadings between c. 100 mg kg^{-1} and 300 mg kg^{-1} occupancy of adsorption sites began to limit further adsorption. The nanoparticles have the potential to perform effectively as metal adsorbents in systems containing more than one metal and dissolved organic carbon at a range of pH values.

Keywords: soil washing; nanoparticles; heavy metals; magnetic; remediation

1. Introduction

Contamination of water and soils by potentially toxic metals is a global concern. Metals such as Pb, Zn and Cd have been demonstrated to be a hazard to human health (Pais and Benton Jones, 1997). For example Pb can reduce mental function in exposed populations, particularly amongst children (Lanphear et al., 2005) and can also cause damage to the central nervous system and liver (IPCS, 1995). It has been estimated that in the year 2004, Pb was responsible for 143,000 deaths globally (WHO, 2010).

The severe consequences of the release of potentially toxic metals to the environment mean that removal of these metals from contaminated waters and soils is of great importance. Due to their high specific surface area and ease of removal from solution via an external permanent magnet, magnetic iron oxide nanoparticles have garnered increasing attention as a possible adsorbent of potentially toxic metals from contaminated waters (Afsar et al., 2014; Auffan et al., 2007; Koehler et al., 2009; Liu et al., 2008a; Liu et al. 2008b; Zhang et al., 2011, 2012). Nanoparticles can also be engineered with a surface coating to reduce agglomeration and with functional groups which have a high affinity for toxic metals, with the aim of further increasing their adsorption potential. Investigations into the ability of engineered iron oxide nanoparticles to remove metals from solution have included functionalising nanoparticles with chitosan (Liu et al., 2008a), humic acid (Liu et al, 2008b), dithiocarbamate groups (Figueira et al., 2011) and a range of chelating agents (Koehler et al, 2009; Wang et al., 2011; Zhang et al., 2011).

It has been observed by numerous studies on an array of different materials that competition for surface sites by different metals can lead to preferential adsorption of one metal species over another (Corami et al, 2008; Depci et al., 2012; Heidmann et al., 2005; Trivedi et al., 2001). In environmental systems contaminants are rarely found in isolation and therefore it is important to determine how the interaction between metals affects their adsorption. Additionally, in contaminated natural systems, dissolved organic matter is almost always present. Dissolved organic matter can interact with the surface of adsorbents (Tsang et al., 2012) and also complex metals in solution, reducing their adsorption to solids (Brown et al., 1999; Christl et al., 2005; Kerndorff and Schnitzer, 1980; Sekaly et al., 1999; Tipping, 2002).

The aims of this study were therefore to 1) synthesise novel magnetic nanoparticles functionalised with diethylenetriaminepentaacetic acid (DTPA); 2) determine the sorption capacity of these nanoparticles for two common metal contaminants, Pb and Zn, both in single and binary metal solutions and, 3) determine how the presence of dissolved organic carbon impacted on the extraction efficiency of the nanoparticles.

2. Materials and Methods

2.1 DTPA functionalised magnetic nanoparticles

Magnetic nanoparticles with a silica coating to reduce agglomeration and a DTPA-functionalised surface were synthesised (See Supplementary Material). The composition of the particles was confirmed by X-ray diffraction and Fourier transform infrared (FTIR) spectroscopy. The mean diameter of the nanoparticles, as assessed by analysis of images obtained using a Philips CM20 transmission electron microscope was 47 $\pm$ 7 nm (n = 100, $\pm$ standard error) with 81% of the diameters measured lying in the range 30 – 60 nm. The iso-electric point of the nanoparticles as measured using a Malvern Zetasizer Nano was pH 6.74. Details of the synthesis methods and characterisation are given in the Supplementary material.

2.2 Metal Extraction Tests

Extraction tests were conducted with single metals (Pb or Zn), binary mixtures of Pb and Zn and also with either Pb or Zn in the presence of dissolved organic carbon. For all extraction tests, metal solutions were produced by dissolving $Pb(NO_3)_2$ and / or $Zn(NO_3)_2 \cdot 6H_2O$ in deionised water. DTPA-functionalised magnetic nanoparticles (10 mg) suspended in 2 mL of ultrapure water were added to 8 mL of the metal solution. The pH was then adjusted by drop-wise addition of 0.01M HCl or 0.1M NaOH. Each solution was shaken for 18 hours on an end-over-end shaker at constant temperature (20ºC). The nanoparticles were then removed from solution using a magnet and the solution analysed for the metal(s) of interest together with Fe (as a measure of either dissolution of the nanoparticles and / or presence of residual nanoparticles after removal by magnets) by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) using a Perkin Elmer OPTIMA 3000. Accuracy of

analysis, as assessed by analysis of a known in-house standard of 0.5 mg L^{-1} concentration was 99% for Pb and 97% for Zn. Precision as assessed by measurement of paired samples and expressed as the coefficient of variation (Gill and Ramsey, 1997) was 3% for Fe, 9% for Pb and 3% for Zn. Detection limits, calculated from the mean plus six times the standard deviation of blank analyses (Walsh, 1997) were 0.001 mg L^{-1}, 0.008 mg L^{-1} and 0.018 mg L^{-1} for Fe, Pb and Zn respectively. Using the average particle diameter of our nanoparticles and the density of maghemite we calculate that 10 mg of nanoparticles contains c. 4.78 x 10^{12} individual particles. An Fe detection limit of 0.001 mg L^{-1} means that the minimum number of nanoparticles we could detect would be 4.78 x 10^{6} particles.

All experiments were carried out in triplicate with nanoparticle-free controls. Iron was below detection in all the experiments indicating that use of the magnet to remove nanoparticles from solution removed at least 99.99% of the nanoparticles initially added. In all our experiments, Pb and Zn concentrations in nanoparticle-free control solutions showed no significant difference between the initial and final solutions ($p = 0.43$) indicating that any differences in Pb and Zn concentrations between the control and nanoparticle-present solutions were due to adsorption by the nanoparticles. To control for any decrease in concentration due to precipitation, extraction efficiency was calculated as the percentage decrease in metal concentration relative to the appropriate nanoparticle-free control at the end of the experiment. Partition coefficients (K_d) were calculated as the ratio of the equilibrium concentrations of metal adsorbed to the nanoparticles to the concentration of metal in solution.

Single metal extraction experiments used solutions initially containing 10 mg L^{-1} of Pb or Zn at pH values ranging between pH 2 and pH 8. Binary metal extraction experiments were carried out to investigate the impact of co-contaminants. Extraction efficiencies were

calculated and the fit of adsorption data to linear, Langmuir and Freundlich isotherms was determined. One set of binary metal experiments investigated Pb extraction for a range of initial Pb concentrations (0.000, 0.015, 0.020, 0.025, 0.030, 0.035, 0.040 and 0.045 mmol L^{-1}) against a background Zn concentration of either 0 or 0.025 mmol L^{-1} Zn at pH 2, pH 4 and pH 6. A second set of experiments used a range of Zn concentrations (0.000, 0.015, 0.020, 0.025, 0.030, 0.035, 0.040 and 0.045 mmol L^{-1}) against a background Pb concentration of either 0 or 0.025 mmol L^{-1} at pH 2, pH 4 or pH 6.

Extraction experiments investigating the impact of dissolved organic carbon used solutions containing 0.01, 0.1 and 1 mmol L^{-1} Pb or Zn and either 0, 2.1 or 21 mg L^{-1} dissolved organic carbon at pH 4 and pH 6. The choice of dissolved organic carbon concentrations was informed by typical soil solution and stream water concentrations in temperate regions (e.g. Herbirch et al. 2017; Lee and Lajtha, 2016; Seifert et al., 2016; Ledesma et al., 2016; Neal et al., 2004; Van den Berg et al., 2012). As with the binary metal experiments extraction efficiencies were calculated. Dissolved organic carbon solutions were produced by dissolving Elliott soil fulvic acid IV (4S102F) obtained from the International Humic Substances Society in deionised water. Dissolved organic and inorganic carbon contents of the extraction solutions were measured using a Shimadzu TOC-L total carbon analyser equipped with a non-dispersive infra-red (NDIR) detector. CO_2 free air was used as the carrier gas at a flow rate of 150 mL min^{-1}. Measured concentrations of dissolved organic carbon were on average within 3% of target values. For convenience, for both the binary metal and dissolved organic carbon experiments, target concentrations are referred to in the text but measured values were used for all calculations.

Statistical tests were conducted using SigmaPlot 12 for Windows. For the single metal experiments one way analysis of variance (ANOVA) on ranks and ANOVA was used to determine whether pH affected % extraction and K_d respectively. For the binary metal experiments a three way ANOVA was used to determine whether adsorption of metals,

expressed as % extraction was significantly affected by pH, the initial Zn or Pb concentration and the presence of a background metal species. Three-way ANOVA was also used to determine whether extraction efficiencies were significantly affected by pH, fulvic acid concentration and initial metal concentration.

3. Results

3.1. Single metal extraction in the pH range 2 - 8

For the single metal solutions Pb (Fig. 1a) and Zn (Fig. 2a) extraction efficiency was generally greater than 70% and was significantly affected by pH ($p \leq 0.001$ for each element). Lead extraction at pH 7 and 8 and Zn extraction at pH 2 was significantly lower than at all other pH values. K_d values were in the range 1760 – 32800 L kg^{-1} for Pb and 4050 – 12000 L kg^{-1} for Zn (Table 1) and were significantly affected by pH ($p \leq 0.001$).

Table 1

Mean K_d values (L kg^{-1}) for Pb and Zn adsorption by nanoparticles between pH 2 and 8 (n = 3, ± standard deviation).

pH	Pb	Zn
2	10800 ± 4400	4050 ± 2850
3	32800 ± 3440	12000 ± 3560
4	17300 ± 2780	12000 ± 2660
5	18900 ± 3760	10000 ± 1720
6	16000 ± 4240	10900 ± 2440
7	1760 ± 747	10100 ± 636
8	2670 ± 1140	7560 ± 189

3.2 Binary metal solutions

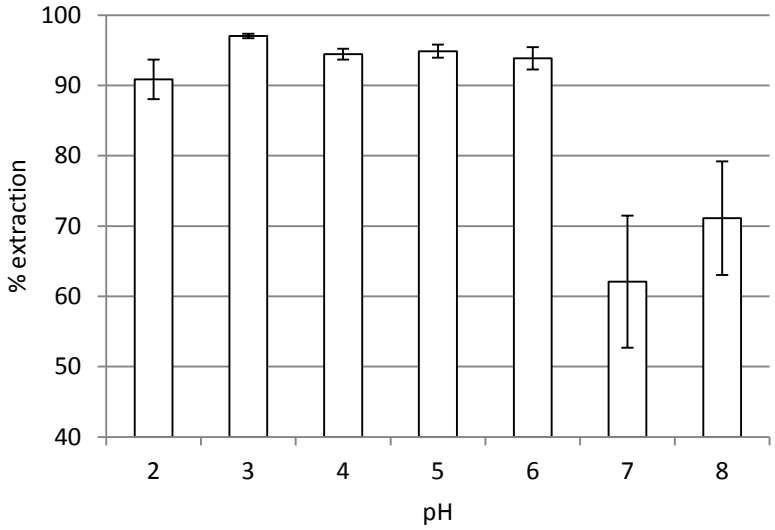
3.2.1 Pb extraction against a Zn background

The effect of Zn at a concentration of 0.025 mmol L^{-1} on the extraction efficiency of Pb from solution by the nanoparticles over a range of initial Pb concentrations and solution pH values is shown in Fig. 1b-d. The Pb extraction efficiencies were significantly higher at pH 4 and 6

171 (89 – 93%) than at pH 2 (82 - 88%) ($p \leq 0.001$). The extraction efficiencies of Pb from
172 solutions containing a Zn background were not significantly different to the efficiencies
173 measured in the Pb-only solutions at all pH values ($p > 0.05$). However, when the removal of
174 the Zn background was also considered, extraction efficiencies decreased significantly ($p \leq$
175 0.001) although the total number of moles removed of Pb and Zn combined was significantly
176 greater in the presence of Zn ($p \leq 0.001$).
177

178 The data were fitted to linear, Langmuir and Freundlich isotherms. Statistcally, the data were
179 equally well described by all three isotherms, but the fits to the Langmuir equation resulted in
180 negative values for the maximum binding capacity and many of the fits to the Freundlich
181 isotherms resulted in a power term in the Freundlich equation of > 1 suggesting upward
182 curvature of the isotherm. Fits to the Langmuir and Freundlich isotherms are presented in
183 the Supplementary material. Fits to the linear isotherms are reported in Table 2 and the
184 isotherms themselves are presented in the Supplementary material. There is no indication of
185 decreasing Pb adsorption with increasing site occupancy. In the Pb-only solutions the 95%
186 confidence intervals of the pH 2 and 4 K_d values and the pH 4 and 6 K_d values overlap
187 between pH treatments suggesting that the values are not significantly different. There is
188 also overlap for the Pb K_d values between the Pb-only and the Zn background solutions at
189 each pH. Inclusion of both Pb and Zn in the isotherm calculations generally results in lower
190 K_d values.

191 Fig. 1a.



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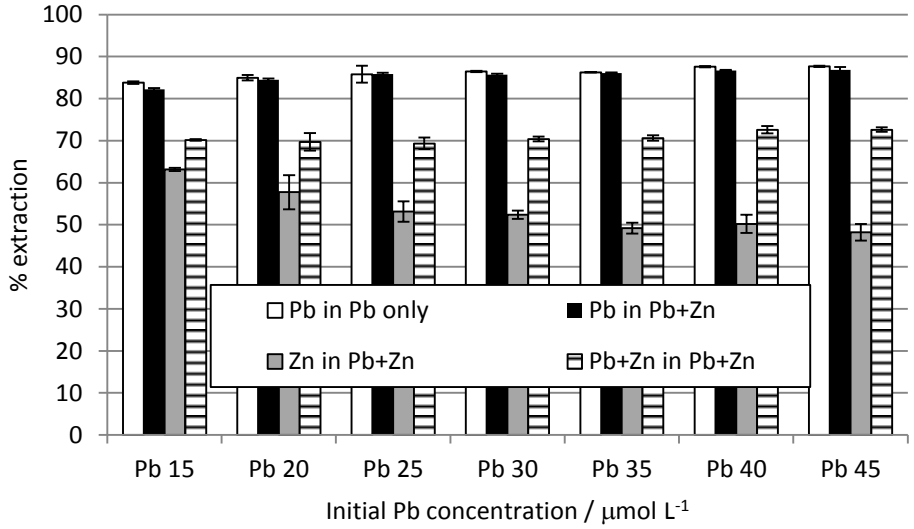
193 Fig. 1b.



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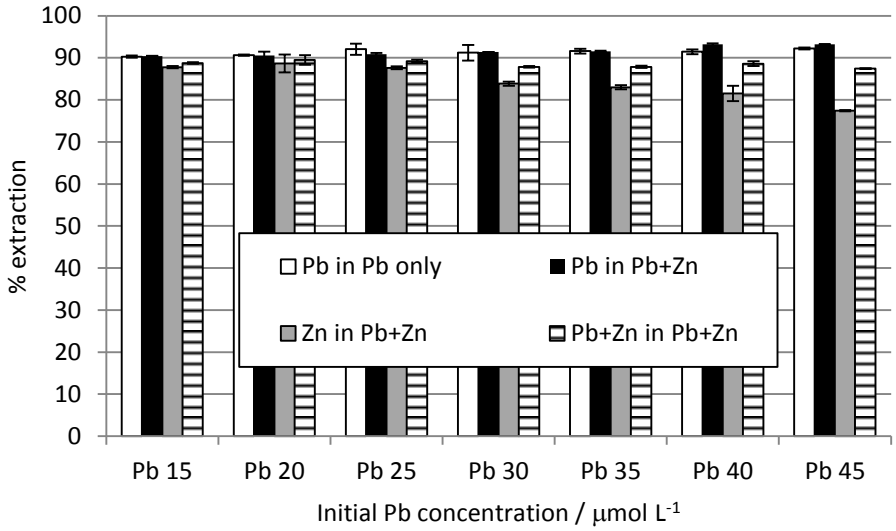
196 Fig. 1c.



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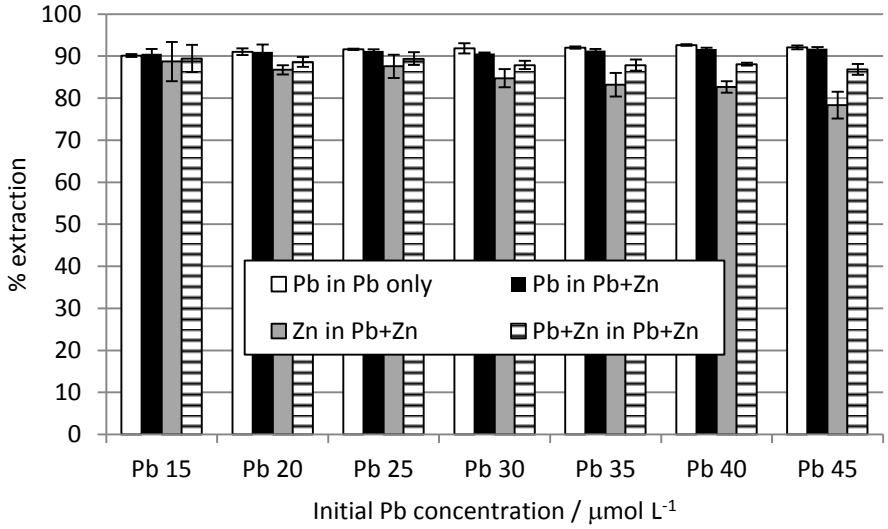
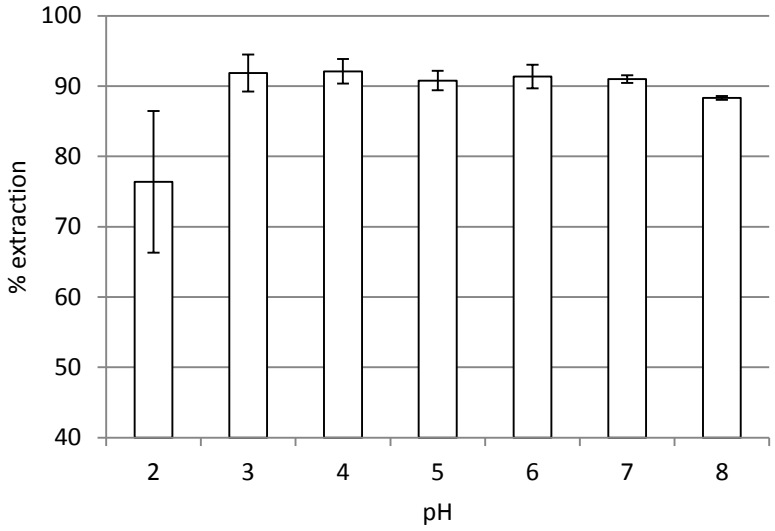
199 Fig. 1d.



200

201 **Fig. 1. a)** Extraction efficiency of Pb from 10 mL of single metal solutions after the addition of
202 10 mg of Fe_2O_3@SiO_2-$(CH_2)_3$-NH-DTPA nanoparticles at a range of pH values. **b – d)** Effect
203 of the presence of Zn (0.025 mmol L^{-1}) on the extraction efficiency of Pb by 10 mg of
204 Fe_2O_3@SiO_2-$(CH_2)_3$-NH_2-DTPA from 10 mL solutions with initial Pb concentrations between
205 0.015 and 0.045 mmol$L^{-1}$and an initial pH of b) pH 2, c) pH 4 and d) pH 6. The extraction
206 efficiency of the background of Zn and of Pb and Zn in the binary mixture are also shown.
207 Error bars represent standard deviation (n = 3).

208 Fig. 2a.



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210 Fig. 2b.

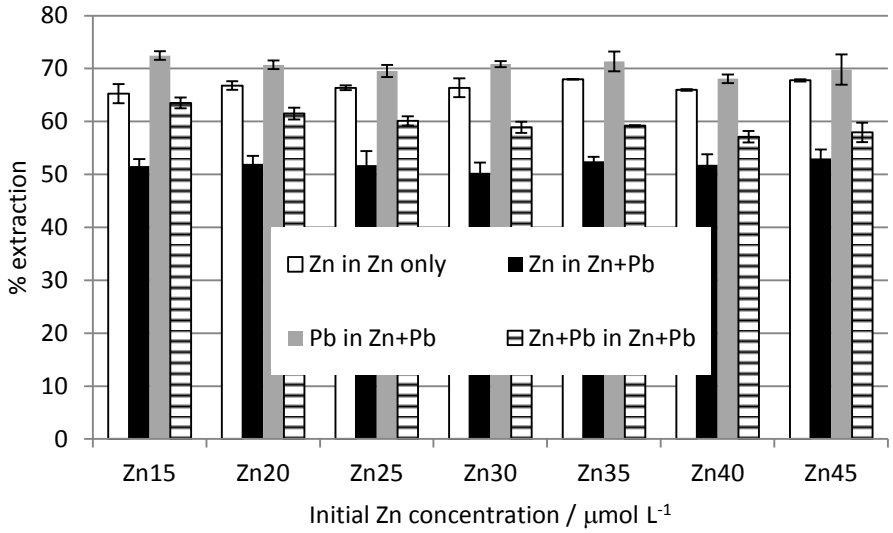

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Fig. 2c.

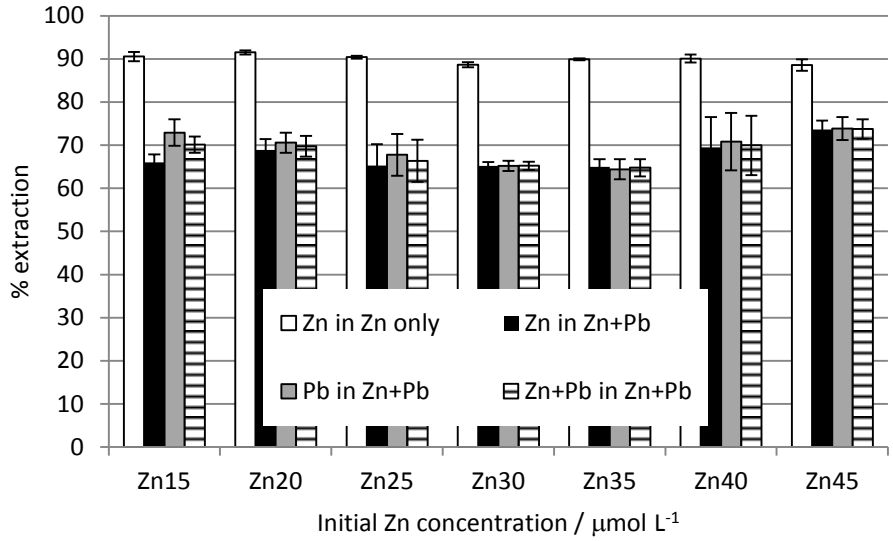


Fig. 2d.

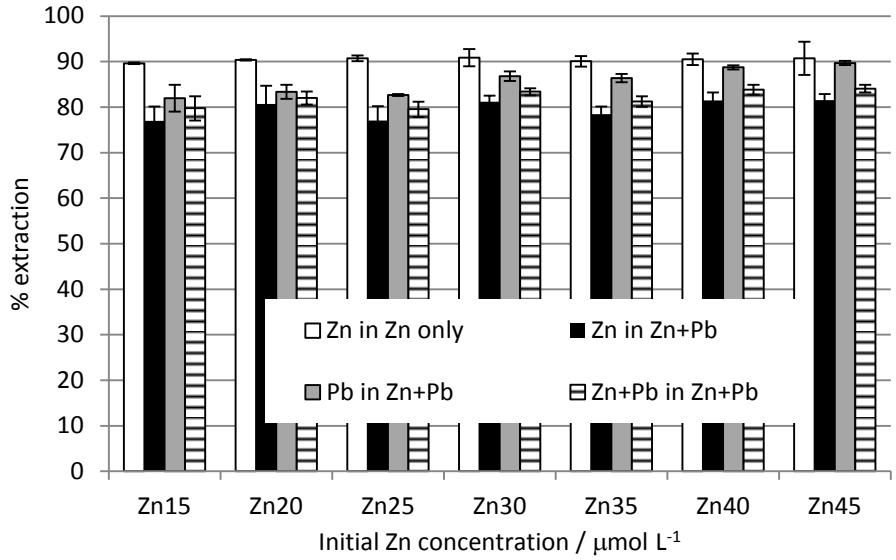


Fig. 2a). Extraction efficiency of Zn from 10 mL of single metal solutions after the addition of 10 mg of Fe_2O_3@SiO_2-$(CH_2)_3$-NH-DTPA nanoparticles at a range of pH values **b-d)** Effect of the presence of Pb (0.025 mmol L^{-1}) on the extraction efficiency of Zn by 10 mg of Fe_2O_3@SiO_2-$(CH_2)_3$-NH_2-DTPA from 10 mL solutions with initial Zn concentrations between 0.015 and 0.045 mmol L^{-1} and an initial pH of a) pH 2, b) pH 4 and c) pH 6. The extraction efficiency of the background of Pb and of Zn and Pb in the binary mixture are also shown. Error bars represent standard deviations (n = 3).

227 **Table 2**

228 Linear isotherm parameters and 95**% confidence intervals (n = 3) for adsorption of Pb in Pb-only and**
229 **Zn-background solutions and Pb+Zn in Zn-background solutions (initial Zn background = 0.025 mmol L^{-1})**
230 **and Zn in** Zn-only and Pb-background and Zn+Pb in Pb background solutions (initial Pb
231 background = 0.025 mmol L^{-1}) **pH values 2, 4 and 6.**

232

Test Solution	Pb K_d / L kg^{-1}	R^2	p	Zn K_d / L kg^{-1}	R^2	p
	Pb-only solution			Zn-only solution		
pH 2	8453 (7589-9317)	0.95	≤ 0.001	2120 (1981-2260)	0.99	≤ 0.001
pH 4	11223 (9054-13393)	0.85	≤ 0.001	6742 (5756-7727)	0.91	≤ 0.001
pH 6	13314 (11542-15085)	0.92	≤ 0.001	6769 (4392-9145)	0.63	≤ 0.001
	Pb removal from Zn-background solution			Zn removal from Pb-background solution		
pH 2	7954 (7429-8479)	0.98	≤ 0.001	1114 (997-1231)	0.95	≤ 0.001
pH 4	16679 (13372-19985)	0.85	≤ 0.001	2062 (1286-2838)	0.60	≤ 0.001
pH 6	11406 (10013-12800)	0.94	≤ 0.001	3968 (2891-5046)	0.74	≤ 0.001
	Pb+Zn removal from Zn-background solution			Pb removal from Pb-background solution		
pH 2	3066 (2512-3619)	0.87	≤ 0.001	922 (801 – 1042)	0.93	≤ 0.001
pH 4	5491 (4723-6259)	0.92	≤ 0.001	1272 (337-2207)	0.26	≤ 0.001
pH 6	4240 (3123-5356)	0.76	≤ 0.001	4307 (2228-6386)	0.47	≤ 0.001

233

234

3.2.2 Zn extraction against a Pb background

The effect of Pb at a concentration of 0.025 mmol L^{-1} on the extraction efficiency of Zn from solution by the nanoparticles over a range of initial Pb concentrations and solution pH values is shown in Fig. 2b - d. The Zn extraction efficiencies decreased significantly in the order pH 6 > pH 4 > pH 2 ($p \leq 0.001$). Extraction efficiencies for Zn were greater in the absence of Pb than in the presence of Pb (63 – 68% vs 48 – 55%; 87 – 92% vs 62 – 76%; 87 – 95% *vs* 74 – 84% for pH 2, 4 and 6 respectively, $p \leq 0.001$). This trend was also observed when extraction of both the Zn and the Pb background were considered. As was observed with the Zn background extraction however, when total number of moles removed was considered, extraction efficiency was significantly greater in the presence of the Pb background ($p \leq 0.001$).

As with the Pb data, generally, the data are well described statistically by linear, Langmuir and Freundlich isotherms but some fits to the Langmuir equation resulted in negative values for the maximum binding capacity and several of the power terms in the fits to the Freundlich equation were greater than 1 when 95 % confidence limits were considered and therefore the Langmuir and Freundlich parameters are only reported in the Supplementary material. K_d values are reported in Table 2 and linear isotherms presented in the Supplementary material. In the Zn-only solutions the 95% confidence intervals of the pH 4 and 6 K_d values overlap between pH treatments. K_d values are lower for Zn in the Pb background solution than in the Zn-only solution. The K_d values at pH 2 and 4 overlap when calculated for both Zn and Pb in the Pb-background solution.

257
258
259 *3.3 Dissolved organic carbon*

260 The effect of dissolved organic carbon (added as fulvic acid) on Pb and Zn extraction by the
261 nanoparticles is shown in Figs. 3 and 4. Adsorption data for both metals (Fig. 3) suggest that
262 between initial metal solution concentrations of 0.1 mmol L^{-1} and 1.0 mmol L^{-1} occupancy of
263 adsorption sites begins to influence adsorption.

264

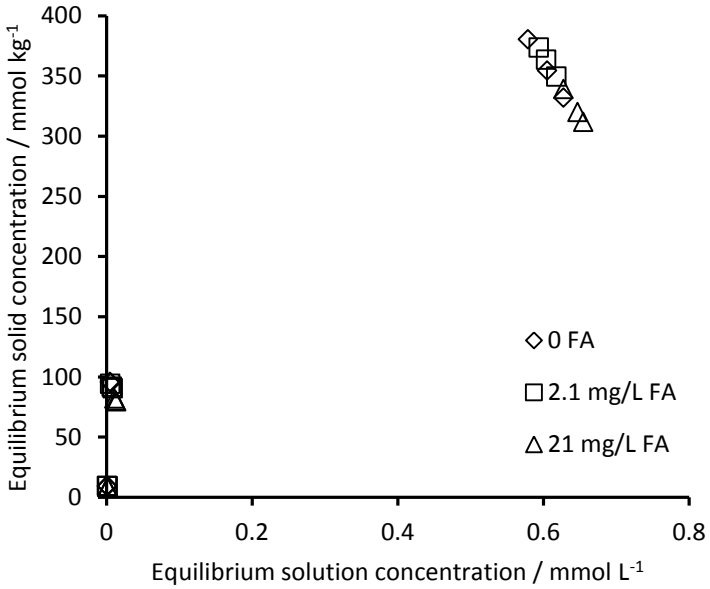
265 Extraction efficiencies did not significantly differ with pH for Pb ($p > 0.05$) but they did vary
266 significantly ($p \leq 0.001$) with initial molarity (78-91% at 0.01 mmol L^{-1} Pb, 87-95% at 0.1
267 mmol L^{-1} Pb and 27-40% at 1 mmol L^{-1} Pb). Extraction efficiency at 0 and 2.1 mg L^{-1}
268 dissolved organic carbon (35-95% and 36-95% respectively) differed significantly ($p \leq 0.001$)
269 from that at 21 mg L^{-1} dissolved organic carbon (27-90%).

270

271 Zinc extraction efficiency varied significantly with pH ($p \leq 0.001$) and was in the range 35 –
272 88% at pH 4 and 41 – 93% at pH 6. Extraction efficiencies varied significantly between Zn
273 molarities for all dissolved organic carbon treatments (0, 2.1, 21 mg L^{-1}) ($p \leq 0.001$) with the
274 exception of the difference between extraction efficiency at 0.01 mmol L^{-1} Zn and 0.1 mmol
275 L^{-1} Zn for 0 mg L^{-1} dissolved organic carbon ($p > 0.05$). Extraction efficiencies varied
276 between all dissolved organic carbon concentrations at 0.01 mmol L^{-1} Zn ($p \leq 0.01$), between
277 21 mg L^{-1} compared to 0 and 2.1 mg L^{-1} at 0.1 mmol L^{-1} Zn ($p \leq 0.01$) but showed no
278 significant variation with dissolved organic carbon concentration at 1.0 mmol L^{-1} Zn.

279

280 Fig. 3a.



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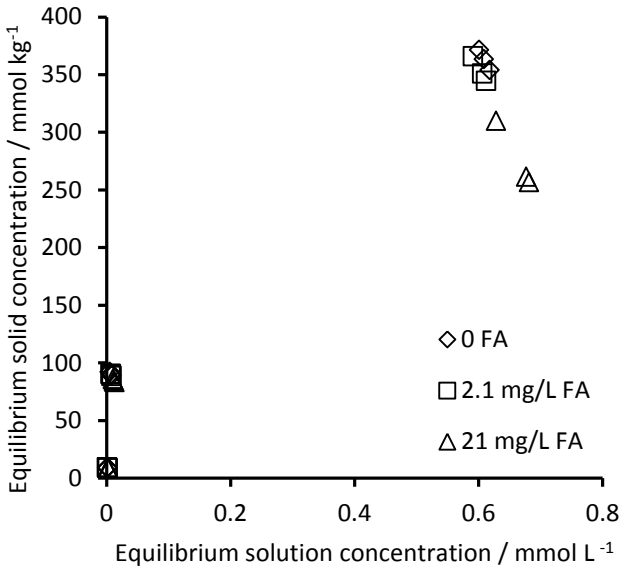
283 Fig. 3b.



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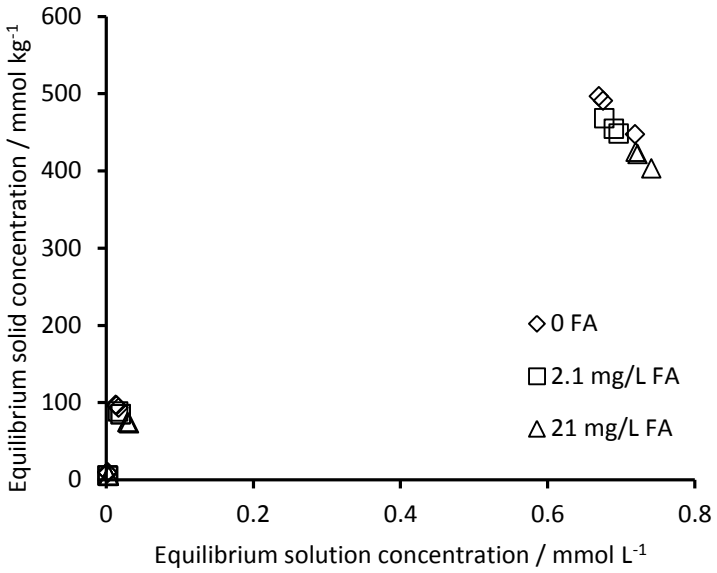
285 Fig. 3c.



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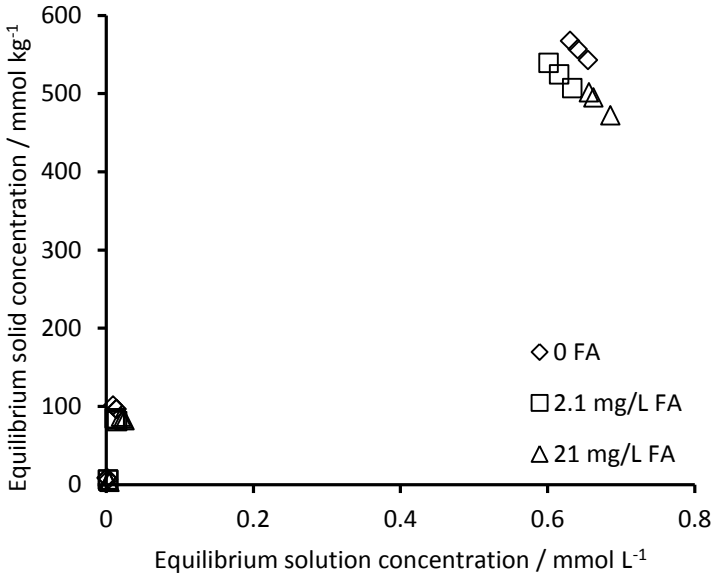
287

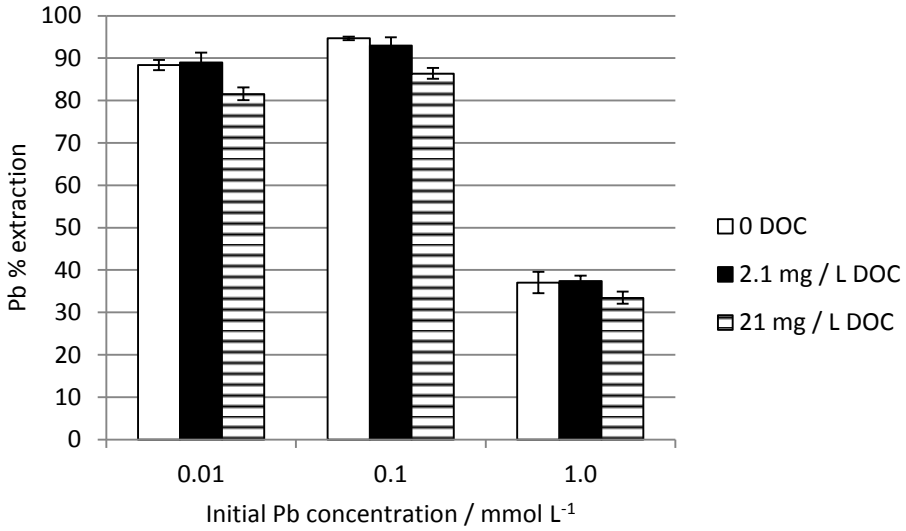
288 Fig. 3d.



289

290 Fig. 3. Adsorption isotherms at a), c) pH 4 and b), d) pH 6 for a), b) Pb and c), d) Zn in the
291 presence of 0 – 21 mg L^{-1} fulvic acid.

292 Fig. 4a.



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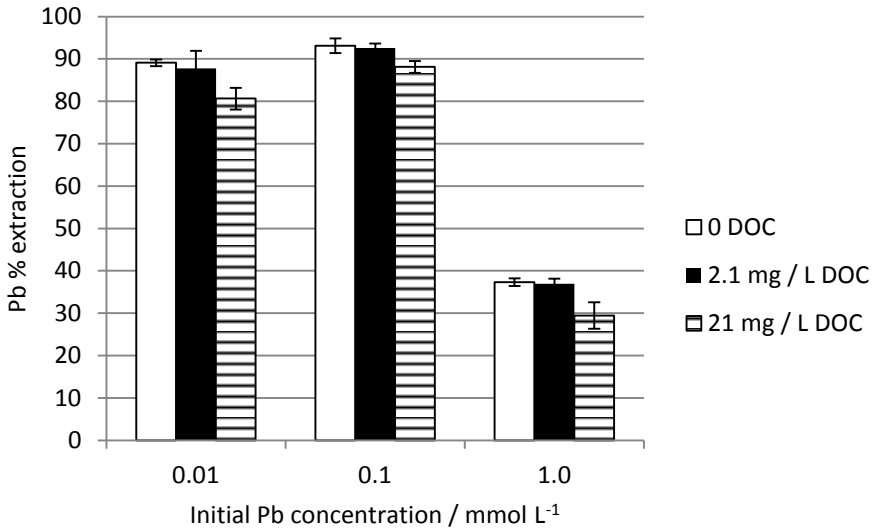
294 Fig. 4b.



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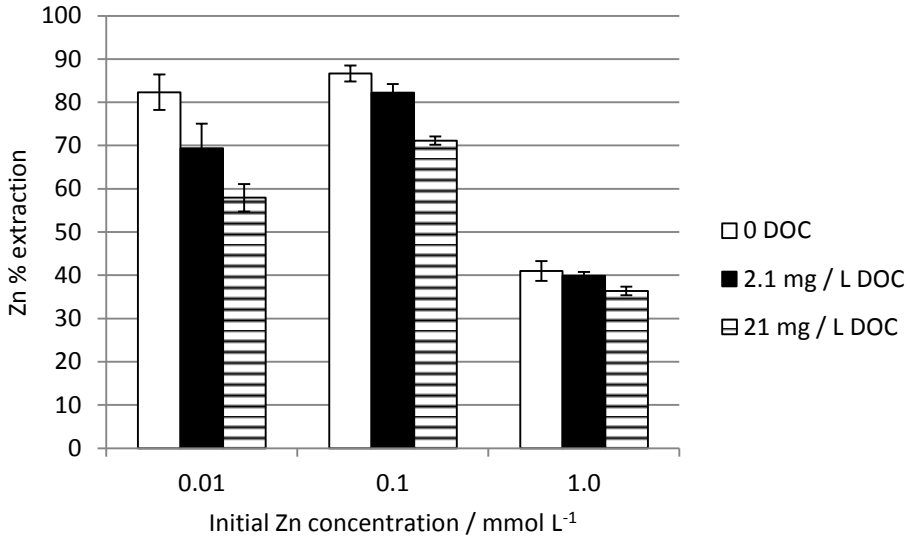
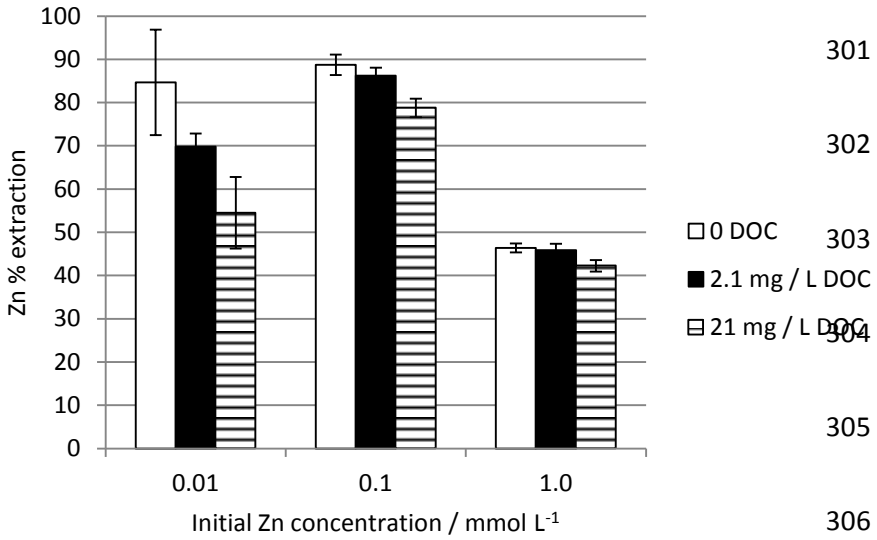
298 Fig. 4c.



299

300 Fig. 4d.



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307 **Fig. 4.** Effect of the presence of dissolved organic carbon added as fulvic acid (no added
308 fulvic acid, 2.1, 21 mg L^{-1}) on the extraction of (a, b) Pb and (c, d) Zn by 10 mg of
309 Fe_2O_3@SiO_2-$(CH_2)_3$-NH-DTPA nanoparticles from 10 mL solutions with initial metal
310 concentrations of 0.01, 0.1 and 1 mmol L^{-1} and an initial pH of (a, c) pH 4 and (b, d) pH 6.
311 Error bars represent standard deviations (n = 3).

312

4. Discussion

The DTPA-functionalised nanoparticles were able to remove Pb and Zn from solution in the presence of competing ions (Pb and Zn; Figs. 1 and 2) and in the presence of dissolved organic carbon (Fig. 4) at a range of pH and metal concentrations. Removal of the nanoparticles from the solutions by the use of the external magnet was very efficient (> 99.99% based on lack of detection of Fe in solutions post-extraction). The good fit to a linear isotherm of the data from the 0.015 – 0.045 mmol L^{-1} experiments indicate that at these concentrations adsorption sites were not saturated and that increasing adsorption site occupancy did not influence adsorption. The decrease in extraction efficiency between initial concentrations of 0.1 and 1.0 mmol L^{-1} Pb and Zn in the dissolved organic carbon experiments indicate that at these concentrations adsorption site occupancy began to have an influence on adsorption. Maximum sorption of Pb (Depci et al, 2012; Kalmykova et al, 2008; Dong et al., 2010; Gerçel and Gerçel, 2007; Li et al., 2005; Gharaibeh et al., 1998; Qin et al., 2006; Goel et al., 2005)] and Zn (Depci et al, 2012, Baraka et al., 2007; Kalmykova et al, 2008; Kaya and Ören, 2005; Levya et al., 2002) determined for a range of sorbents reported in the literature is similar or less than the adsorption measured in the dissolved organic carbon experiments. Thus our results suggest that DTPA-functionalised nanoparticles could potentially be used to remove metals from contaminated waters. Such solutions may occur due to drainage from metal contaminated sites but may also be generated by soil washing, a remedial process in which contaminated soils are treated both physically and chemically resulting in contaminants being concentrated in either a specific solid fraction or a wash solution (e.g. CL:AIRE, 2007; Griffiths, 1995; Semer and Reddy, 1996). The chemistry of the wash solution is highly variable and can include acids, alkalis, complexing agents, surfactants and dispersants depending on the target contaminants. Such wash solutions are cleaned up for reuse, typically using sand filters, exchange resins, activated carbon or precipitation. Our results suggest that magnetic nanoparticles could also

be considered as a means of cleaning up these wash solutions though efficiencies will be a function of the precise composition of the wash solutions.

Baraka *et al*. (2007) postulated that two methods of adsorption can occur for the DTPA ligand: (i) coordinate bonds form between the metal and the lone pair electrons of N or O atoms in the DTPA and (ii) ion exchange. The iso-electric point of the nanoparticles, as determined by measurement of zeta potential, was 6.74. Thus in the majority of experiments reported here the nanoparticles would have a net positive charge and it is proposed that the majority of the bound DTPA will be protonated. This suggests that chelation with the lone pairs of the three nitrogen atoms present in the DTPA molecule will likely be the dominant adsorption mechanism though ion exchange involving the metals and the H^+ ions on the protonated functional groups will also occur. At higher pH the carboxylic acid group on the DTPA will be negatively charged and so will take part in adsorbing cations from solution.

Extraction efficiency in the single metal treatments varied with pH ($p \leq 0.001$). There was a significant decrease in extraction efficiency for Pb at pH 7 and 8 in the single metal treatments (Fig. 1a.) despite these pH values being greater than the nanoparticles' iso-electric point suggesting that the nanoparticles would develop a negatively charged surface. Below pH 6 Pb^{2+} dominates in solution whilst above pH 6 $Pb(OH)^+$ is the dominant species (e.g. Depci et al., 2012; Berber-Mendoza et al., 2006). The decrease in extraction efficiency may therefore reflect reduced interaction between the $Pb(OH)^+$ ions and the chelation sites on the DTPA compared to that of the Pb^{2+} ions. Extraction efficiency of Zn is significantly reduced at pH 2; although the decrease is not significant, this trend is also seen for Pb. This decrease probably reflects protonation of the DTPA at this pH (Chauhan et al., 2015).

Preferential adsorption of Pb over Zn in mixed metal systems has been reported previously for activated carbon, (Depci et al., 2012), tourmaline (Jiang et al., 2006) and basic oxygen

366 furnace slag (Xue et al., 2009). In this investigation the presence of a Pb background
367 reduced the Zn extraction efficiency and K_d values suggesting preferential adsorption of the
368 Pb relative to Zn despite the similarity in DTPA-Pb and DTPA-Zn stability constants
369 (Lindsay, 1979). Selectivity coefficients (K_s) calculated using Equation (1) all have values <
370 1.0 consistent with preferential Pb adsorption (0.45 $\pm$ 0.25 for Pb adsorption with a Zn
371 background, 0.68 $\pm$ 0.23 for Pb adsorption in the variable Zn with a Pb background
372 experiment, n = 63 for each value).
373
374 $\text{nanoparticle} - Pb_{(s)} + Zn^{2+}_{(aq)} \Leftrightarrow \text{nanoparticle-}Zn_{(s)} + Pb^{2+}_{(aq)}$ (1a)
375 $K_s = [\text{nanoparticle-Zn}] \,.\, [Pb^{2+}] / [\text{nanoparticle-Pb}] \,.\, [Zn^{2+}]$ (1b)
376
377 Where K_s = selectivity coefficient
378 [X] = concentration
379
380 The preferential adsorption of Pb over Zn is likely a function of the greater electronegativity
381 of the Pb (McBride, 1994) and its electronic configuration. Kalmykova *et al*. (2008)
382 suggested that Pb may have a greater affinity for forming inner sphere complexes than Zn
383 because Pb has 2 electrons on the 6s orbital which can be easily divided by a ligand in a
384 complex. In a similar fashion to the single metal experiments, greater extraction efficiencies
385 were observed at pH values 4 and 6 relative to pH 2 in both the variable Pb-constant Zn
386 (Fig. 1b – d) and constant Pb-variable Zn (Fig. 2b – d) experiments. This most likely reflects
387 increasing deprotonation of the carboxylic acid functional groups on the DTPA ligand with
388 increased pH (Chauhan et al., 2015).
389
390 Decreases in extraction efficiency (but increases in moles of metal removed) with increased
391 metal molarity observed in the dissolved organic carbon experiments reflect increased
392 saturation of adsorption sites on the nanoparticles in the 1 mmol L^{-1} treatments. Extraction

efficiencies decreased with increasing dissolved organic carbon though these remained relatively high due to the stability constants for Pb-DTPA and Zn-DTPA complexes (typically of the order 18 – 19, e.g. Lindsay, 1979; Dojindo, 2017) being much higher than their respective complexes with fulvic acid (typically of the order 2.6 – 10 for Pb, e.g. Castetbon et al., 1986; Grzybowski, 2000; Saar and Weber, 1980;; Sterritt and Lester, 1984 and of the order 2.7 – 7.8 for Zn, e.g. Hirata, 1981; Prasad and Sinha, 1980; Ram and Raman, 1984; Sterritt and Lester, 1984). The decreases in extraction efficiency seen with increases in dissolved organic acid concentration reflect increasing competition between the nanoparticles and the fulvic acid for complexation of the metals. This is consistent with Dong *et al*. (2010) who reported similar results for sorption of Pb to hydroxyapatite/magnetite in the presence of humic acid.

The greater decreases in extraction efficiency observed for Zn compared to Pb for increased dissolved organic carbon concentrations most likely reflects the differences in the relative affinities of Pb and Zn to the different functional groups present on the DTPA molecules and the fulvic acid. Whilst DTPA and fulvic acid both contain carboxyl and hydroxyl groups, the lone pair N atoms present in DTPA are not present in the chemical structures for fulvic acid postulated by Buffle *et al*. (1977) and Leenheer *et al*. (1995). The Pb has a greater affinity for the lone pair of N atoms than Zn due to its greater electronegativity. Electronegativity was combined with ionic radii by Nieboer and Richardson (1989) to define the covalent index. Metal with a higher covalent index may be referred to as “soft” lewis acids and have a stronger attraction to corresponding “soft” ligand atoms such as N or S. Lead has a much higher covalent index value (6.41) compared to Zn (2.04) thus Pb will be more likely to bind to the lone pair of N atoms in the DTPA than Zn. Conversely, the lower covalent index value of Zn means it will behave as a hard acid and will be more attracted to the O-containing functional groups which are present in both DTPA and fulvic acid compounds.

5. Conclusions

Our experiments demonstrate the potential for DTPA-functionalised nanoparticles to be used as a remedial technology for both metal-contaminated water and solutions generated by soil washing. Magnets were effective at removing > 99.9% of nanoparticles from solution; an important consideration given ongoing concerns about the introduction of engineered nanoparticles into the environment. The nanoparticles can remove metals from binary solutions with a high level of efficiency and this is maintained in the presence of environmentally relevant concentrations of dissolved organic carbon. Further work is now required to consider more realistic solutions containing a greater range of ions.

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