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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1 Adsorption of Pb and Zn from binary metal solutions and in the presence of dissolved

2   organic carbon by DTPA-functionalised, silica-coated magnetic nanoparticles

3

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6

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11

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14

15 **Abstract**

16 The ability of diethylenetriaminepentaacetic acid (DTPA)-functionalised, silica-coated

17 magnetic nanoparticles to adsorb Pb and Zn from single and bi-metallic metal solutions and

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18   from solutions containing dissolved organic carbon was assessed. In all experiments 10 mL

19   solutions containing 10 mg of nanoparticles were used. For single metal solutions (10 mg L^{-1}

20   Pb or Zn) at pH 2 to 8, extraction efficiencies were typically >70%. In bi-metallic

21   experiments, examining the effect of a background of either Zn or Pb (0.025 mmol L^{-1}) on

22   the adsorption of variable concentrations (0 - 0.045 mmol L^{-1}) of the other metal (Pb or Zn,

23   respectively) adsorption was well modelled by linear isotherms (R^2>0.60; p≤0.001) and Pb

24   was preferentially adsorbed relative to Zn. In dissolved organic carbon experiments, the

25   presence of fulvic acid (0, 2.1 and 21 mg DOC L^{-1}) reduced Pb and Zn adsorption from 0.01,

26   0.1 and 1.0 mmol L^{-1} solutions. However, even at 21 mg DOC L^{-1} fulvic acid, extraction

27   efficiencies from 0.01 and 0.1 mmol L^{-1} solutions remained >80% (Pb) and > 50% (Zn).

28   Decreases in extraction efficiency were significant between initial metal concentrations of 0.1

29   and 1.0 mmol L^{-1} indicating that at metal loadings between c. 100 mg kg^{-1} and 300 mg kg^{-1}

30   occupancy of adsorption sites began to limit further adsorption. The nanoparticles have the

31   potential to perform effectively as metal adsorbents in systems containing more than one

32   metal and dissolved organic carbon at a range of pH values.

33

35

36   **1. Introduction**

37   Contamination of water and soils by potentially toxic metals is a global concern. Metals such

38   as Pb, Zn and Cd have been demonstrated to be a hazard to human health (Pais and

39   Benton Jones, 1997). For example Pb can reduce mental function in exposed populations,

40   particularly amongst children (Lanphear et al., 2005) and can also cause damage to the

41   central nervous system and liver (IPCS, 1995). It has been estimated that in the year 2004,

42   Pb was responsible for 143,000 deaths globally (WHO, 2010).

43   The severe consequences of the release of potentially toxic metals to the environment mean

44   that removal of these metals from contaminated waters and soils is of great importance. Due

45   to their high specific surface area and ease of removal from solution via an external

46   permanent magnet, magnetic iron oxide nanoparticles have garnered increasing attention as

47   a possible adsorbent of potentially toxic metals from contaminated waters (Afsar et al., 2014;

48   Auffan et al., 2007; Koehler et al., 2009; Liu et al., 2008a; Liu et al. 2008b; Zhang et al.,

49   2011, 2012). Nanoparticles can also be engineered with a surface coating to reduce

50   agglomeration and with functional groups which have a high affinity for toxic metals, with the

51   aim of further increasing their adsorption potential. Investigations into the ability of

52   engineered iron oxide nanoparticles to remove metals from solution have included

53   functionalising nanoparticles with chitosan (Liu et al., 2008a), humic acid (Liu et al, 2008b),

54   dithiocarbamate groups (Figueira et al., 2011) and a range of chelating agents (Koehler et al,

55   2009; Wang et al., 2011; Zhang et al., 2011).

56   It has been observed by numerous studies on an array of different materials that competition

57   for surface sites by different metals can lead to preferential adsorption of one metal species

58   over another (Corami et al, 2008; Depci et al., 2012; Heidmann et al., 2005; Trivedi et al.,

59   2001). In environmental systems contaminants are rarely found in isolation and therefore it is

60   important to determine how the interaction between metals affects their adsorption.

61   Additionally, in contaminated natural systems, dissolved organic matter is almost always

62   present. Dissolved organic matter can interact with the surface of adsorbents (Tsang et al.,

63   2012) and also complex metals in solution, reducing their adsorption to solids (Brown et al.,

64   1999; Christl et al., 2005; Kerndorff and Schnitzer, 1980; Sekaly et al., 1999; Tipping, 2002).

65   The aims of this study were therefore to 1) synthesise novel magnetic nanoparticles

66   functionalised with diethylenetriaminepentaacetic acid (DTPA); 2) determine the sorption

67   capacity of these nanoparticles for two common metal contaminants, Pb and Zn, both in

68   single and binary metal solutions and, 3) determine how the presence of dissolved organic

69   carbon impacted on the extraction efficiency of the nanoparticles.

70

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 ± 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.

82

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 (20^oC). 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

95   analysis, as assessed by analysis of a known in-house standard of 0.5 mg L^{-1} concentration

96   was 99% for Pb and 97% for Zn. Precision as assessed by measurement of paired samples

97   and expressed as the coefficient of variation (Gill and Ramsey, 1997) was 3% for Fe, 9% for

98   Pb and 3% for Zn. Detection limits, calculated from the mean plus six times the standard

99   deviation of blank analyses (Walsh, 1997) were 0.001 mg L^{-1}, 0.008 mg L^{-1} and 0.018 mg L^{-1}

100   for Fe, Pb and Zn respectively. Using the average particle diameter of our nanoparticles and

101   the density of maghemite we calculate that 10 mg of nanoparticles contains c. 4.78×10^{12}

102   individual particles. An Fe detection limit of 0.001 mg L^{-1} means that the minimum number of

103   nanoparticles we could detect would be 4.78×10^{6} particles.

104

105   All experiments were carried out in triplicate with nanoparticle-free controls. Iron was below

106   detection in all the experiments indicating that use of the magnet to remove nanoparticles

107   from solution removed at least 99.99% of the nanoparticles initially added. In all our

108   experiments, Pb and Zn concentrations in nanoparticle-free control solutions showed no

109   significant difference between the initial and final solutions (p = 0.43) indicating that any

110   differences in Pb and Zn concentrations between the control and nanoparticle-present

111   solutions were due to adsorption by the nanoparticles. To control for any decrease in

112   concentration due to precipitation, extraction efficiency was calculated as the percentage

113   decrease in metal concentration relative to the appropriate nanoparticle-free control at the

114   end of the experiment. Partition coefficients (K_d) were calculated as the ratio of the

115   equilibrium concentrations of metal adsorbed to the nanoparticles to the concentration of

116   metal in solution.

117

118   Single metal extraction experiments used solutions initially containing 10 mg L^{-1} of Pb or Zn

119   at pH values ranging between pH 2 and pH 8. Binary metal extraction experiments were

120   carried out to investigate the impact of co-contaminants. Extraction efficiencies were

121 calculated and the fit of adsorption data to linear, Langmuir and Freundlich isotherms was

122 determined. One set of binary metal experiments investigated Pb extraction for a range of

123 initial Pb concentrations (0.000, 0.015, 0.020, 0.025, 0.030, 0.035, 0.040 and 0.045 mmol L^{-1}

124) against a background Zn concentration of either 0 or 0.025 mmol L^{-1} Zn at pH 2, pH 4 and

125 pH 6. A second set of experiments used a range of Zn concentrations (0.000, 0.015, 0.020,

126 0.025, 0.030, 0.035, 0.040 and 0.045 mmol L^{-1}) against a background Pb concentration of

127 either 0 or 0.025 mmol L^{-1} at pH 2, pH 4 or pH 6.

128

129 Extraction experiments investigating the impact of dissolved organic carbon used solutions

130 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

131 carbon at pH 4 and pH 6. The choice of dissolved organic carbon concentrations was

132 informed by typical soil solution and stream water concentrations in temperate regions (e.g.

133 Herbirch et al. 2017; Lee and Lajtha, 2016; Seifert et al., 2016; Ledesma et al., 2016; Neal et

134 al., 2004; Van den Berg et al., 2012). As with the binary metal experiments extraction

135 efficiencies were calculated. Dissolved organic carbon solutions were produced by

136 dissolving Elliott soil fulvic acid IV (4S102F) obtained from the International Humic

137 Substances Society in deionised water. Dissolved organic and inorganic carbon contents of

138 the extraction solutions were measured using a Shimadzu TOC-L total carbon analyser

139 equipped with a non-dispersive infra-red (NDIR) detector. CO_2 free air was used as the

140 carrier gas at a flow rate of 150 mL min^{-1}. Measured concentrations of dissolved organic

141 carbon were on average within 3% of target values. For convenience, for both the binary

142 metal and dissolved organic carbon experiments, target concentrations are referred to in the

143 text but measured values were used for all calculations.

144

145 Statistical tests were conducted using SigmaPlot 12 for Windows. For the single metal

146 experiments one way analysis of variance (ANOVA) on ranks and ANOVA was used to

147 determine whether pH affected % extraction and K_d respectively. For the binary metal

148 experiments a three way ANOVA was used to determine whether adsorption of metals,

149   expressed as % extraction was significantly affected by pH, the initial Zn or Pb concentration

150   and the presence of a background metal species. Three-way ANOVA was also used to

151   determine whether extraction efficiencies were significantly affected by pH, fulvic acid

152   concentration and initial metal concentration.

153

154   **3. Results**

155   *3.1. Single metal extraction in the pH range 2 - 8*

156   For the single metal solutions Pb (Fig. 1a) and Zn (Fig. 2a) extraction efficiency was

157   generally greater than 70% and was significantly affected by pH ($p \leq 0.001$ for each

158   element). Lead extraction at pH 7 and 8 and Zn extraction at pH 2 was significantly lower

159   than at all other pH values. K_d values were in the range 1760 – 32800 L kg^{-1} for Pb and 4050

160   – 12000 L kg^{-1} for Zn (Table 1) and were significantly affected by pH ($p \leq 0.001$).

161

162   **Table 1**

163   Mean K_d values (L kg^{-1}) for Pb and Zn adsorption by nanoparticles between pH 2 and 8 (n =
164   3, $\pm$ standard deviation).

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

165

166   *3.2 Binary metal solutions*

167   *3.2.1 Pb extraction against a Zn background*

168   The effect of Zn at a concentration of 0.025 mmol L^{-1} on the extraction efficiency of Pb from

169   solution by the nanoparticles over a range of initial Pb concentrations and solution pH values

170   is shown in Fig. 1b-d. The Pb extraction efficiencies were significantly higher at pH 4 and 6

7

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
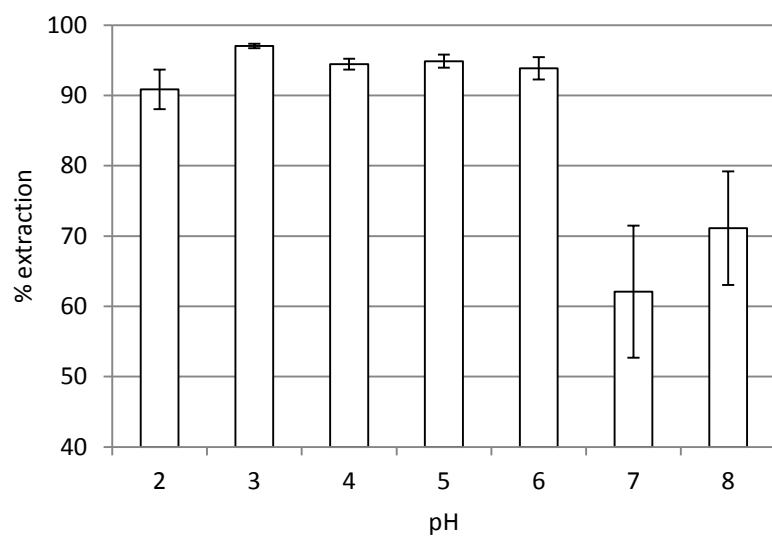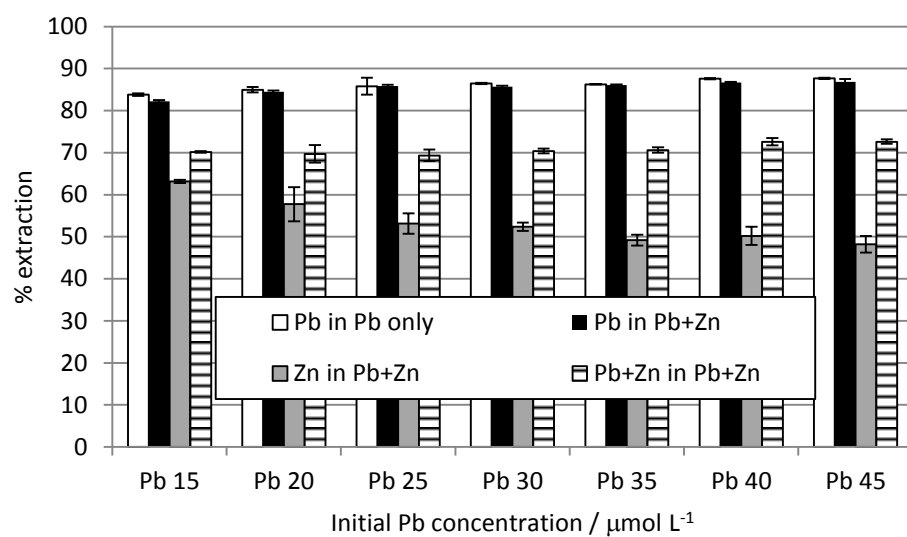
190 K_d values.

191   Fig. 1a.

192

193   Fig. 1b.

194

195

196   Fig. 1c.

197

198

199   Fig. 1d.

200

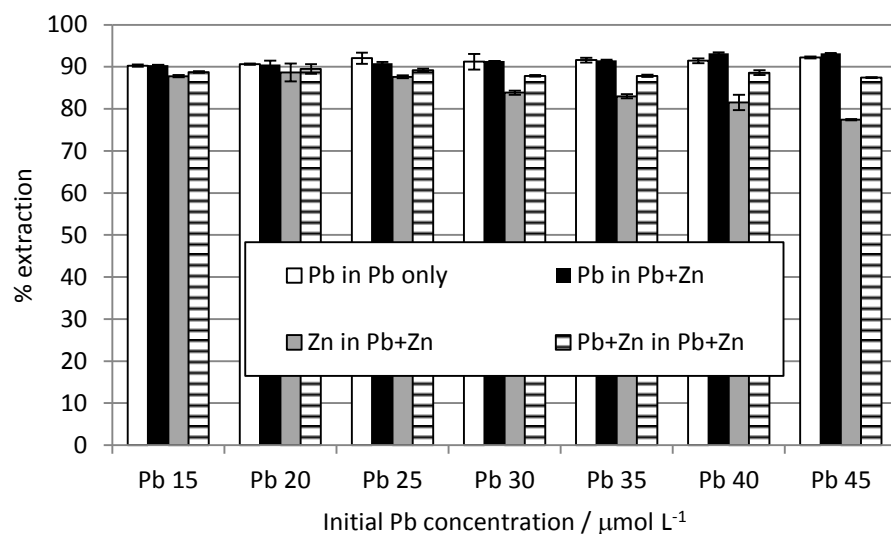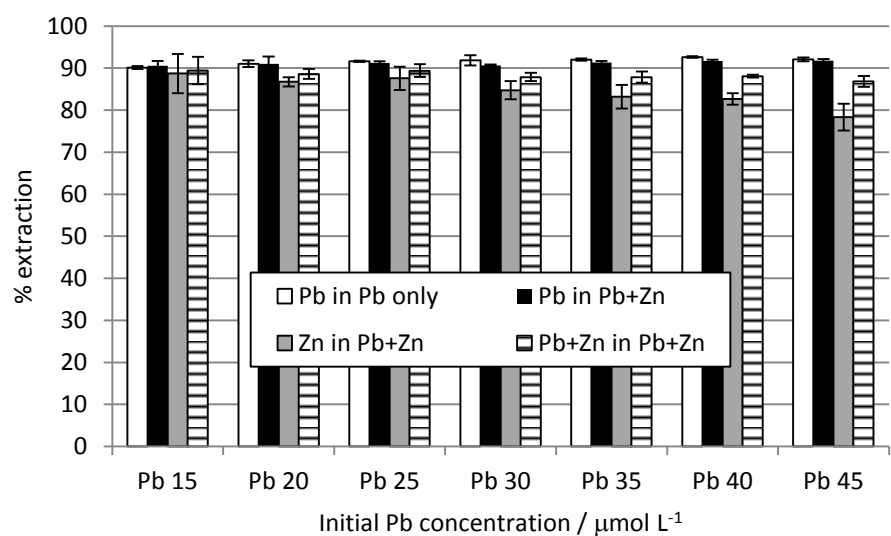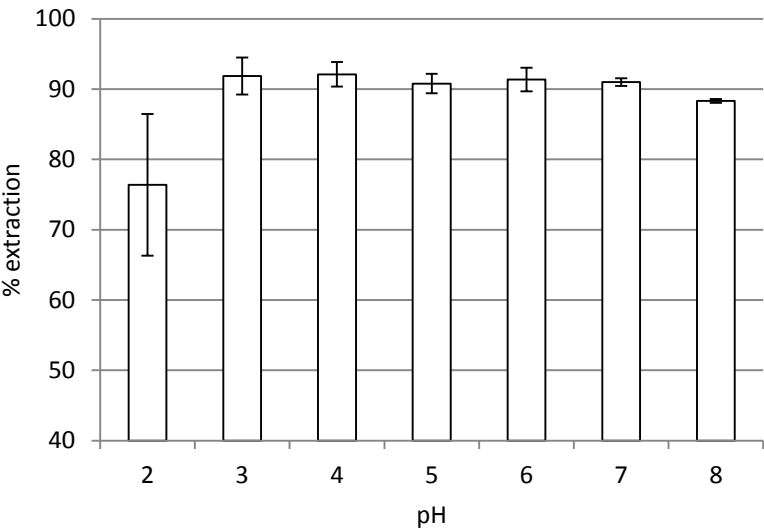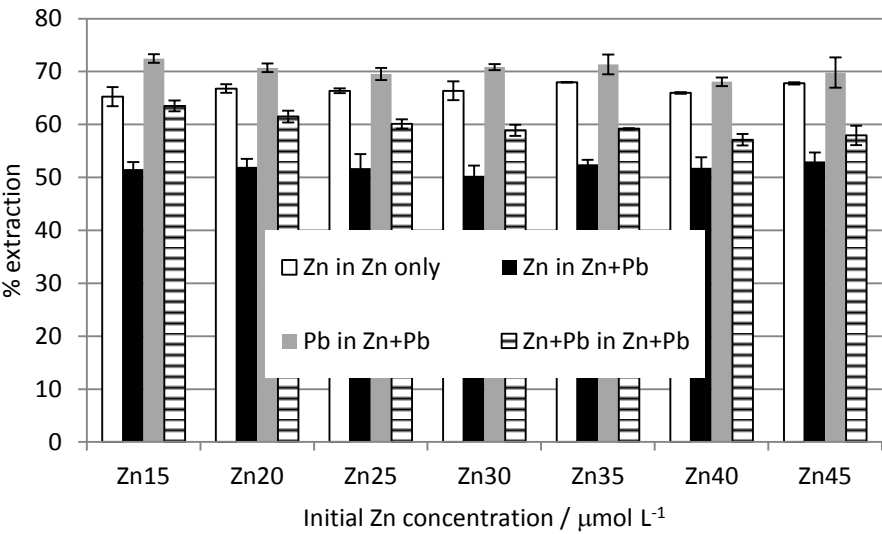201   **Fig. 1. a)** Extraction efficiency of Pb from 10 mL of single metal solutions after the addition of
202   10 mg of Fe_2O_3@SiO_2-$(CH_2)_3$-NH-DTPA nanoparticles at a range of pH values. **b – d)** Effect
203   of the presence of Zn (0.025 mmol L^{-1}) on the extraction efficiency of Pb by 10 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 mmolL^{-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).

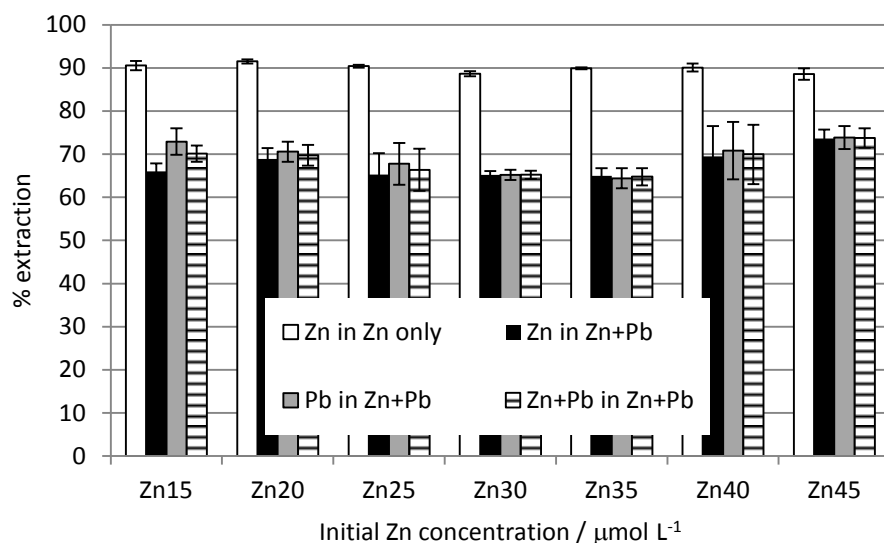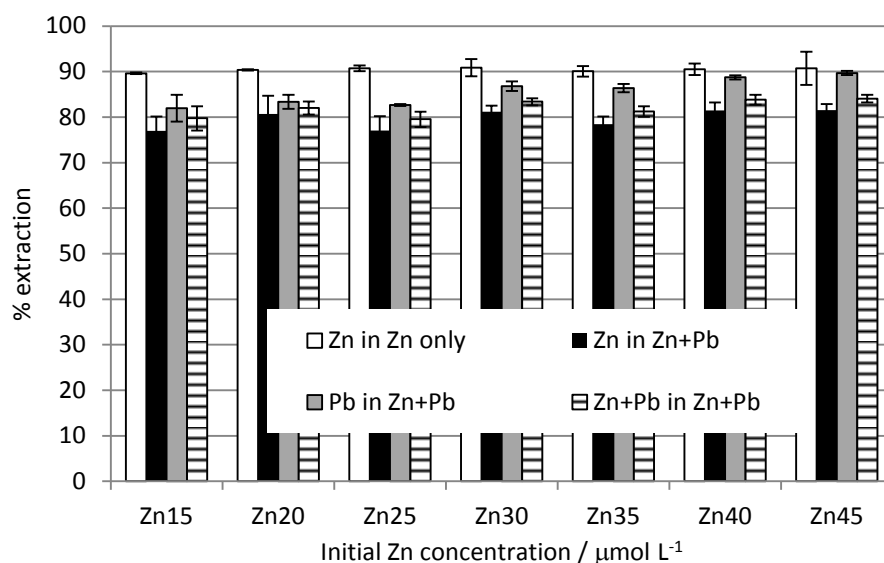208   Fig. 2a.

209

210   Fig. 2b.

211

212

213

214   Fig. 2c.

215

216

217   Fig. 2d.

218

219   **Fig. 2a)**. Extraction efficiency of Zn from 10 mL of single metal solutions after the addition of

220   10 mg of $Fe_2O_3@SiO_2-(CH_2)_3-NH-DTPA$ nanoparticles at a range of pH values **b-d)** Effect of

221   the presence of Pb (0.025 mmol L^{-1}) on the extraction efficiency of Zn by 10 mg of

222    $Fe_2O_3@SiO_2-(CH_2)_3-NH_2-DTPA$ from 10 mL solutions with initial Zn concentrations between

223   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

224   efficiency of the background of Pb and of Zn and Pb in the binary mixture are also shown.

225   Error bars represent standard deviations (n = 3).

226

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

233

234

235 *3.2.2 Zn extraction against a Pb background*

236 The effect of Pb at a concentration of 0.025 mmol L^{-1} on the extraction efficiency of Zn from

237 solution by the nanoparticles over a range of initial Pb concentrations and solution pH values

238 is shown in Fig. 2b - d. The Zn extraction efficiencies decreased significantly in the order pH

239 6 > pH 4 > pH 2 ($p \leq 0.001$). Extraction efficiencies for Zn were greater in the absence of Pb

240 than in the presence of Pb (63 – 68% vs 48 – 55%; 87 – 92% vs 62 – 76%; 87 – 95% *vs* 74

241 – 84% for pH 2, 4 and 6 respectively, $p \leq 0.001$). This trend was also observed when

242 extraction of both the Zn and the Pb background were considered. As was observed with the

243 Zn background extraction however, when total number of moles removed was considered,

244 extraction efficiency was significantly greater in the presence of the Pb background ($p \leq$

245 0.001).

246

247 As with the Pb data, generally, the data are well described statistically by linear, Langmuir

248 and Freundlich isotherms but some fits to the Langmuir equation resulted in negative values

249 for the maximum binding capacity and several of the power terms in the fits to the Freundlich

250 equation were greater than 1 when 95 % confidence limits were considered and therefore

251 the Langmuir and Freundlich parameters are only reported in the Supplementary material.

252 K_d values are reported in Table 2 and linear isotherms presented in the Supplementary

253 material. In the Zn-only solutions the 95% confidence intervals of the pH 4 and 6 K_d values

254 overlap between pH treatments. K_d values are lower for Zn in the Pb background solution

255 than in the Zn-only solution. The K_d values at pH 2 and 4 overlap when calculated for both

256 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
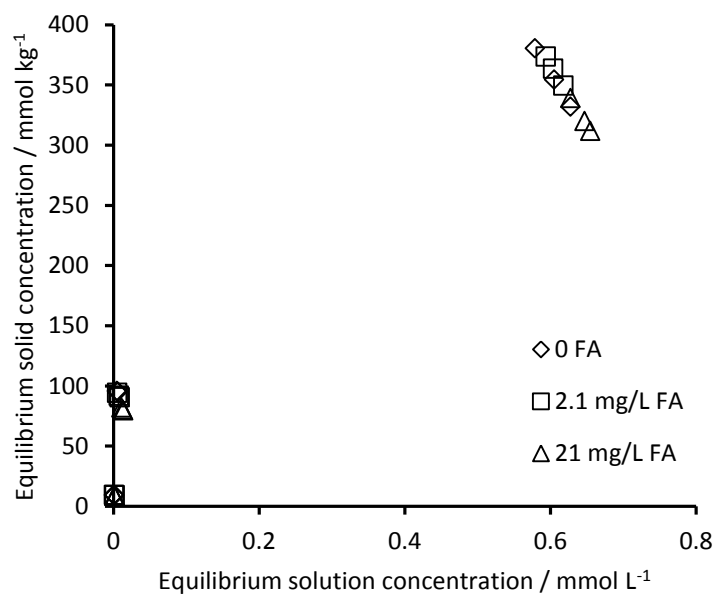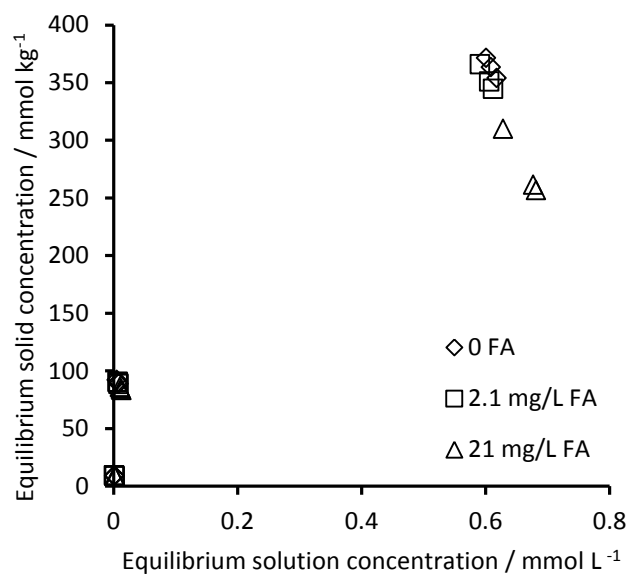
280   Fig. 3a.
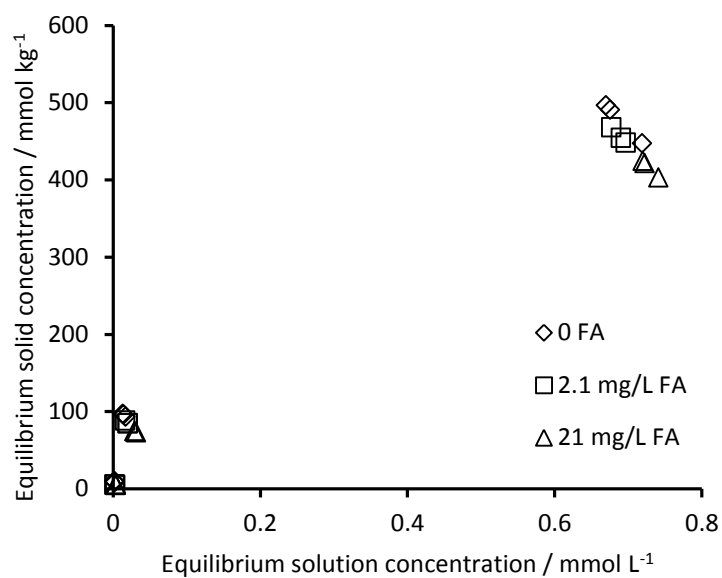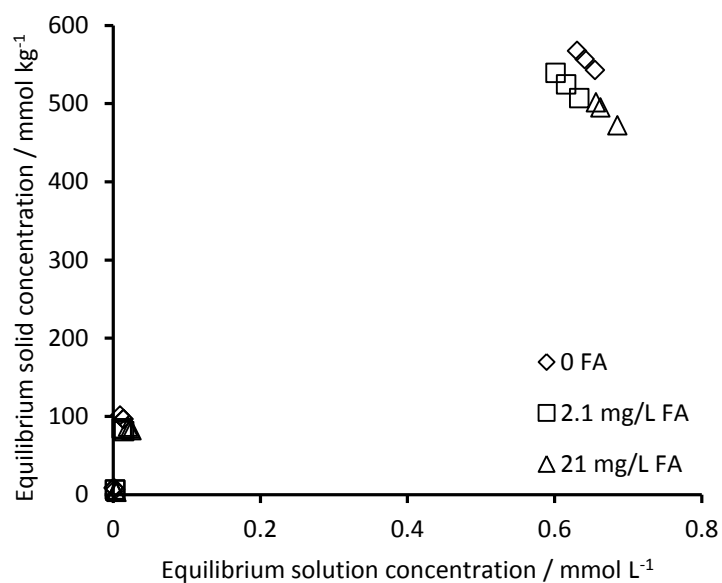

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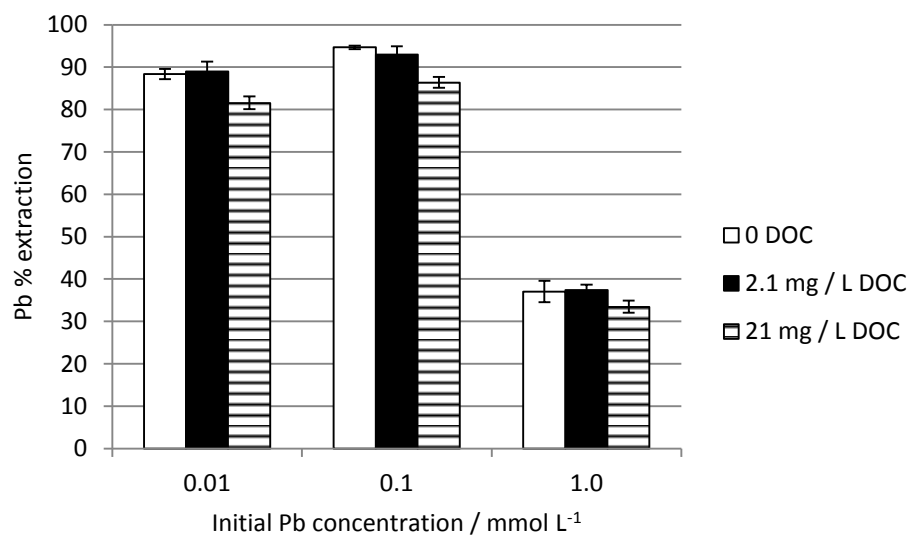283   Fig. 3b.

284

285 Fig. 3c.
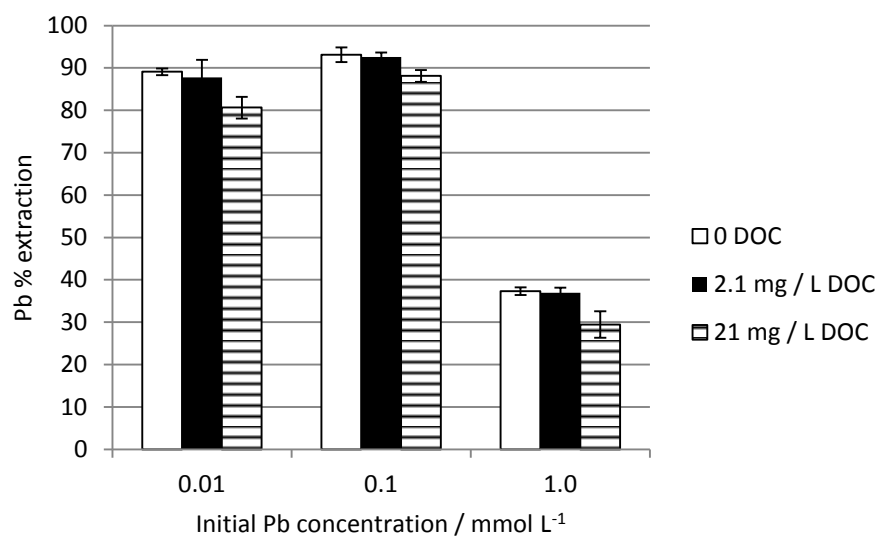

286

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.

293

294   Fig. 4b.

295

296

297

298 Fig. 4c.

299

300 Fig. 4d.

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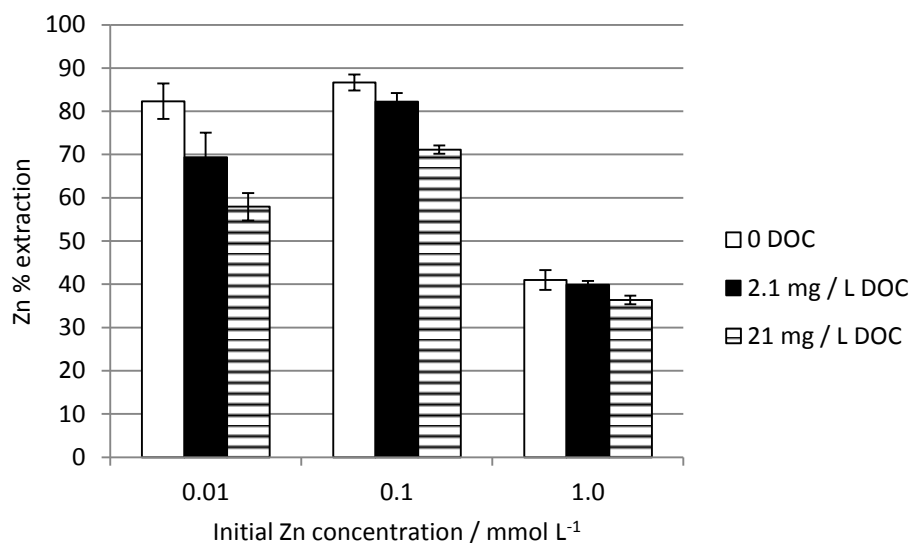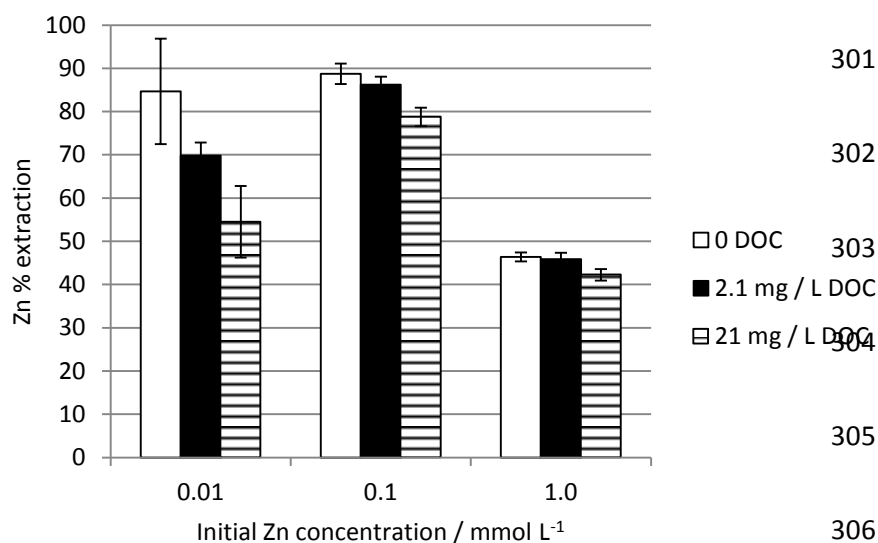
307 **Fig. 4.** Effect of the presence of dissolved organic carbon added as fulvic acid (no added

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

339   be considered as a means of cleaning up these wash solutions though efficiencies will be a

340   function of the precise composition of the wash solutions.

341

342   Baraka *et al.* (2007) postulated that two methods of adsorption can occur for the DTPA

343   ligand: (i) coordinate bonds form between the metal and the lone pair electrons of N or O

344   atoms in the DTPA and (ii) ion exchange. The iso-electric point of the nanoparticles, as

345   determined by measurement of zeta potential, was 6.74. Thus in the majority of experiments

346   reported here the nanoparticles would have a net positive charge and it is proposed that the

347   majority of the bound DTPA will be protonated. This suggests that chelation with the lone

348   pairs of the three nitrogen atoms present in the DTPA molecule will likely be the dominant

349   adsorption mechanism though ion exchange involving the metals and the H^+ ions on the

350   protonated functional groups will also occur. At higher pH the carboxylic acid group on the

351   DTPA will be negatively charged and so will take part in adsorbing cations from solution.

352

353   Extraction efficiency in the single metal treatments varied with pH ($p \leq 0.001$). There was a

354   significant decrease in extraction efficiency for Pb at pH 7 and 8 in the single metal

355   treatments (Fig. 1a.) despite these pH values being greater than the nanoparticles' iso-

356   electric point suggesting that the nanoparticles would develop a negatively charged surface.

357   Below pH 6 Pb^{2+} dominates in solution whilst above pH 6 $Pb(OH)^+$ is the dominant species

358   (e.g. Depci et al., 2012; Berber-Mendoza et al., 2006). The decrease in extraction efficiency

359   may therefore reflect reduced interaction between the $Pb(OH)^+$ ions and the chelation sites

360   on the DTPA compared to that of the Pb^{2+} ions. Extraction efficiency of Zn is significantly

361   reduced at pH 2; although the decrease is not significant, this trend is also seen for Pb. This

362   decrease probably reflects protonation of the DTPA at this pH (Chauhan et al., 2015).

363

364   Preferential adsorption of Pb over Zn in mixed metal systems has been reported previously

365   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   nanoparticle – $Pb_{(s)}$ + $Zn^{2+}_{(aq)}$ $\Leftrightarrow$ nanoparticle-$Zn_{(s)}$ + $Pb^{2+}_{(aq)}$ (1a)

375   K_s = [nanoparticle-Zn] . [Pb^{2+}] / [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

393   efficiencies decreased with increasing dissolved organic carbon though these remained

394   relatively high due to the stability constants for Pb-DTPA and Zn-DTPA complexes (typically

395   of the order 18 – 19, e.g. Lindsay, 1979; Dojindo, 2017) being much higher than their

396   respective complexes with fulvic acid (typically of the order 2.6 – 10 for Pb, e.g. Castetbon et

397   al., 1986; Grzybowski, 2000; Saar and Weber, 1980;; Sterritt and Lester, 1984 and of the

398   order 2.7 – 7.8 for Zn, e.g. Hirata, 1981; Prasad and Sinha, 1980; Ram and Raman, 1984;

399   Sterritt and Lester, 1984). The decreases in extraction efficiency seen with increases in

400   dissolved organic acid concentration reflect increasing competition between the

401   nanoparticles and the fulvic acid for complexation of the metals. This is consistent with Dong

402   *et al.* (2010) who reported similar results for sorption of Pb to hydroxyapatite/magnetite in the

403   presence of humic acid.

404

405   The greater decreases in extraction efficiency observed for Zn compared to Pb for increased

406   dissolved organic carbon concentrations most likely reflects the differences in the relative

407   affinities of Pb and Zn to the different functional groups present on the DTPA molecules and

408   the fulvic acid. Whilst DTPA and fulvic acid both contain carboxyl and hydroxyl groups, the

409   lone pair N atoms present in DTPA are not present in the chemical structures for fulvic acid

410   postulated by Buffle *et al.* (1977) and Leenheer *et al.* (1995). The Pb has a greater affinity for

411   the lone pair of N atoms than Zn due to its greater electronegativity. Electronegativity was

412   combined with ionic radii by Nieboer and Richardson (1989) to define the covalent index.

413   Metal with a higher covalent index may be referred to as "soft" lewis acids and have a

414   stronger attraction to corresponding "soft" ligand atoms such as N or S. Lead has a much

415   higher covalent index value (6.41) compared to Zn (2.04) thus Pb will be more likely to bind

416   to the lone pair of N atoms in the DTPA than Zn. Conversely, the lower covalent index value

417   of Zn means it will behave as a hard acid and will be more attracted to the O-containing

418   functional groups which are present in both DTPA and fulvic acid compounds.

419

5. Conclusions

421 Our experiments demonstrate the potential for DTPA-functionalised nanoparticles to be used

422 as a remedial technology for both metal-contaminated water and solutions generated by soil

423 washing. Magnets were effective at removing > 99.9% of nanoparticles from solution; an

424 important consideration given ongoing concerns about the introduction of engineered

425 nanoparticles into the environment. The nanoparticles can remove metals from binary

426 solutions with a high level of efficiency and this is maintained in the presence of

427 environmentally relevant concentrations of dissolved organic carbon. Further work is now

428 required to consider more realistic solutions containing a greater range of ions.

429

443

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