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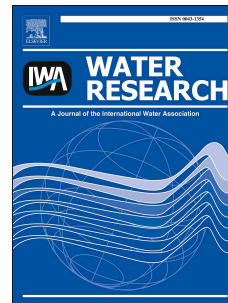


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Ion exchange removal of Cu(II), Fe(II), Pb(II) and Zn(II) from acid extracted sewage sludge – Resin screening in weak acid media

James P. Bezzina, Laura R. Ruder, Robert Dawson, Mark D. Ogden



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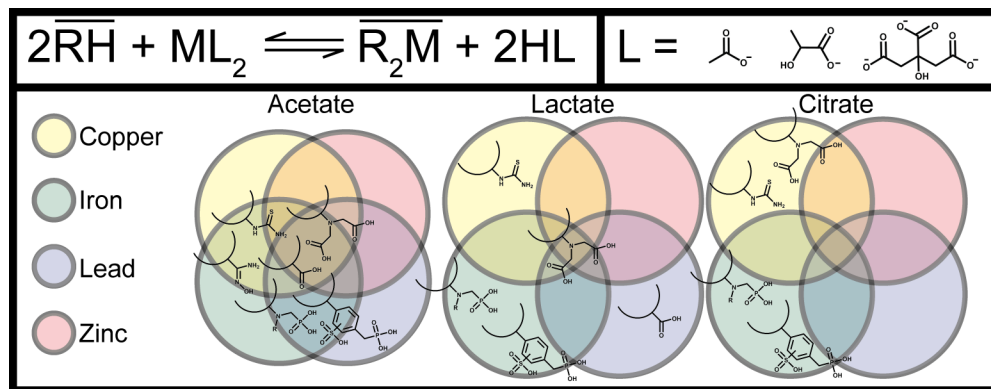
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1 **Ion Exchange Removal of Cu(II), Fe(II), Pb(II) and Zn(II) from**
2 **Acid Extracted Sewage Sludge – Resin screening in weak acid**
3 **media**

4 James P. Bezzina¹, Laura R. Ruder¹, Robert Dawson², Mark D. Ogden¹

5 ¹Separation and Nuclear Chemical Engineering Research (SNUCER), Department of Chemical and
6 Biological Engineering, University of Sheffield, Sir Robert Hadfield Building, Sheffield, S1 3JD,
7 United Kingdom

8 ²Department of Chemistry, University of Sheffield, Western Bank, Sheffield, S10 2TN, United
9 Kingdom

10 Corresponding author: jpbazzino1@sheffield.ac.uk

11 ***Abstract***

12 A shortage of phosphate rock resources has led to a focus on the use of sewage sludge as a fertiliser.
13 One factor preventing the unlimited application of sewage sludge in agriculture is the heavy metal
14 content. This work looks at a process where weak acid leaching of sewage sludge would be coupled to
15 ion exchange (IX) for heavy metal ion removal. IX offers an effective method for the recovery of
16 these metals from a leachate. This study presents the pH performance of six selected IX resins in
17 extracting Cu²⁺, Fe²⁺, Pb²⁺ and Zn²⁺ from acetic, lactic and citric acid media simulated weak acid
18 leachate. Acetic acid media displayed limited suppression of metal extraction, whilst lactic and citric
19 acid media rendered MTS9100 ineffective. Lactic acid media when combined with C107E resin
20 allows for the targeted extraction of lead. Both MTS9570 and MTS9501 display high ferrous
21 extraction in all media at all pH values, although citric acid hinders extraction by both resins at higher
22 pH values. TP214 is selective for copper over all other metal ions in all weak acid media. MTS9301 is
23 the most effective at extracting all metals from all media solutions, with separation of copper
24 becoming more apparent when transitioning to citric acid.

25 **Keywords;** transition metals, weak acid, ion exchange resin, remediation, extraction.

26 1 Introduction

27 Projected phosphate fertiliser demand has increased exponentially as a result of a predicted global
28 population increase from 7.4 billion in 2016 to approximately 10 billion by 2050 (United Nations,
29 2013). This increase in population combined with depletion and poor recycling of phosphate reserves
30 (a limited resource) could lead to a potential global food security crisis (FAO, 2015; Fytili and
31 Zabaniotou, 2008; Spångberg, *et al.*, 2014). Treatment of municipal waste water leaves a solid waste
32 product (sewage sludge) which is dense in phosphates and nitrogen compounds (up to 44% and 28%
33 of that found in commercially available fertiliser, respectively (Spångberg, *et al.*, 2014)). The
34 combination of road run off and domestic and industrial waste water into municipal effluent systems
35 leaves the sewage contaminated with toxic heavy metals (Fytili and Zabaniotou, 2008; Vriens, *et al.*,
36 2017; Westerhoff, *et al.*, 2015). Sewage sludge application in agriculture is already undertaken but
37 concentrations of copper, lead and zinc, along with biological contaminants, prevent its unrestricted
38 use on crops as the metals can exceed limits allowed by the Department of Environment, Food and
39 Rural Affairs (DEFRA) and the European Council (EC) (DEFRA, 2006; European Commission, 1986;
40 Fytili and Zabaniotou, 2008) for fertiliser use. Reuse of sewage sludge as a fertiliser has attracted
41 research into struvite precipitation (Maurer and Schwegler, 2003; Ueno and Fujii, 2001), phosphate
42 recovery circuits (Weigand, *et al.*, 2013), incineration (Adam, *et al.*, 2007) or metallic immobilisation
43 within the sludge (Fu and Wang, 2011). Whilst these technologies are economically viable, they do
44 little to address the remaining heavy metals. These metals may be discharged back into water systems
45 or potentially leach into the environment at a later time. It can therefore be surmised that the largest
46 barrier to the unlimited application of sewage sludge fertiliser is the design and implementation of an
47 economically viable technology for the separation and removal of heavy metals (Westerhoff, *et al.*,
48 2015). Attempts to remove metals from sludges have utilised technologies such as membrane
49 filtration (Fu and Wang, 2011) and electro-kinetic technologies at the laboratory scale (Filho, *et al.*,
50 2014), with the caveat of these technologies being that metals are required to be within a mobile
51 phase.

52 Previous research into the mobilisation of metals from sewage sludge has involved strong acid
53 leaching (Stylianou, *et al.*, 2007) or bioleaching (Gu, *et al.*, 2018). Both methods incur increased
54 neutralisation costs with the latter being potentially less economical on scale-up (Sreekishnan and
55 Tyagi, 1996). Weak acid lixivants present a less toxic and lower acidity approach to leaching sewage
56 sludge (del Mundo Dacera and Babel, 2006). The complex forming nature of carboxylic weak acids
57 (such as acetic acid, lactic acid and citric acid) may aid the leaching process and present lower
58 neutralisation costs. Weak complexing acids stabilise metal ions in solution but can actively compete
59 against extraction by ion exchange (IX) (Bezzina, *et al.*, 2018b). Whilst IX from strong acid media is
60 well studied (Dąbrowski, *et al.*, 2004), the use of IX resins within complexing weak acid media is
61 sparsely understood. Ionic strength, aqueous media and pH have all been altered to optimise the
62 extraction capabilities of IX resins (Bezzina, *et al.*, 2018a; Bezzina, *et al.*, 2018b; Riley, *et al.*, 2018).
63 Currently there is a paucity of information upon which a weak acid media extraction process can be
64 based. The focus of this study is on the ability of complexing acid systems to alter metal ion
65 extraction and separation characteristics of IX resins. The work presented in this paper brings a
66 comprehensive resin functionality screening within three different weak acid media, including an in-
67 depth solution phase speciation analysis, for simulated leachate solutions of weak acid leached
68 sewage sludge. The most promising resins discovered within this study will be continued through
69 further characterisation within future research.

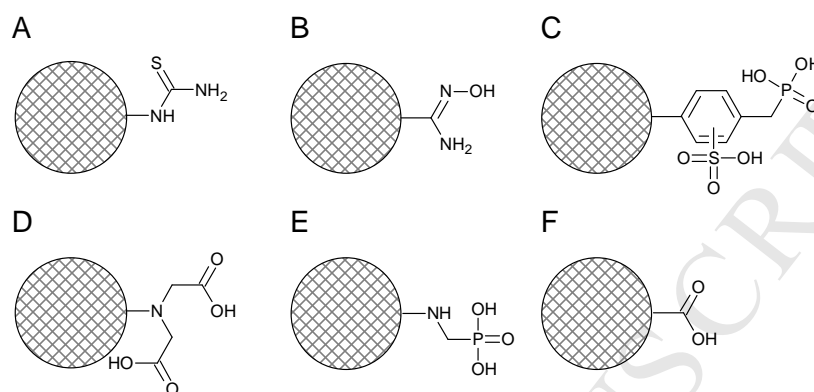
70 **2 Materials and Methods**

71 **2.1 Reagents and stock solutions**

72 The functionalities of the resins tested are given in Figure 1. All IX resins were supplied by Purolite,
73 except Lewatit MonoPlus TP214, which was provided by Lanxess. Calcium chloride was purchased
74 from Fisher Scientific, lactic acid (80%) was purchased from Scientific Laboratory Supplies and
75 glacial acetic acid was purchased from VWR. All other chemicals were purchased from Sigma-
76 Aldrich as analytical grade or better unless otherwise specified. All IX resins were preconditioned by

77 treatment with 1 M H₂SO₄ (10 bed volumes) for 24 h, prior to washing with 50 bed volumes of
 78 deionised water. The characteristics of the IX resins are given in supplemental Table S1.

79



80

81 Figure 1: Chemical structure of the functionalities of the IX resins tested throughout this study (A =
 82 TP214 (thiourea), B = MTS9100 (amidoxime), C = MTS9570 (phosphonic/sulphonic acid
 83 combination), D = MTS9301 (iminodiacetic acid), E = MTS9501 (aminophosphonic acid), F = C107E
 84 (carboxylic acid); crosshatch circles represent the polymer matrix).

85 2.2 Batch extractions from buffered media

86 Batch extractions were carried out by contacting 2 mL of wet settled resin (WSR) with 50mL of
 87 mixed metal solution and agitating on an orbital shaker for 24 h at room temperature, after which
 88 samples were taken for metal concentration and pH analysis. Mixed metal solutions contained
 89 chloride salts of Ca²⁺, Cu²⁺, Fe²⁺ and Zn²⁺ (100ppm), in addition to Pb(NO₃)₂ (100ppm Pb²⁺), NaCl
 90 (0.5 M) and weak acid (0.5 M, acetic acid and lactic acid). While Ca²⁺ concentration was not analysed,
 91 a resin:solution ratio was maintained so that the total metal concentration was far below the saturation
 92 of resin functional sites. Acidity was adjusted to a range ± 1 pH unit either side of the corresponding
 93 weak acid's pK_a (pH 4.76 for acetic acid and pH 3.86 for lactic acid), the approximate buffering
 94 region of the acid, using either NaOH or HCl.

95 Metal extraction was determined by difference using equation (1), where V_{aq} is the volume of aqueous
96 solution, m is the mass of resin used in each experiment, C_i is the concentration of the solution pre-
97 contact and C_e is the concentration of the solution at equilibrium.

$$98 \quad K_d = \frac{(C_i - C_e)}{C_e} \times \frac{V_{aq}}{m} \quad (1)$$

99 Error was calculated through triplicate sampling and analysis of aqueous solutions prior to contact
100 with exchange resins. Samples were diluted with 1% nitric acid (1:10 dilution) and metals analysis
101 was conducted using a Perkin Elmer Atomic Absorption Spectrometer AAnalyst 400. pH
102 measurements were conducted using a Ag/AgCl electrode, calibrated using a four-point calibration
103 with commercially available pH calibration buffers. Citric acid data from the publication Bezzina *et*
104 *al.* (2018b) has been reanalysed to produce K_d values, for comparison. This data was obtained using
105 the exact same methodology as used for acetic acid and lactic acid, with the pH being adjusted across
106 the three distinct pK_a values of citric acid.

107 **2.3 Speciation Modelling**

108 To support understanding into the extraction mechanism of metals from weak acid leaching,
109 speciation modelling was carried out using the HySS2008 software suite (Gans, *et al.*, 2009). All
110 complex stability constants attained for the modelling were sourced from the NIST database (Martell,
111 *et al.*, 2009) where possible and all hydrolysis product stability constants were sourced from Brown
112 and Ekberg (2016). Iron-lactate stability constants were sourced from Gorman and Clydesdale (1984)
113 and copper and iron-citrate stability constants were obtained from Field *et al.* (1974). Tabulation of
114 the stability constants can be found in the supplementary information (Table S20 – S28) with
115 speciation diagrams (Supplementary Figures S1, S2 and S3) for acetate, lactate and citrate media,
116 respectively. Stability constants are displayed as $\log \beta$ values, with all reported literature conditions
117 being 25°C and consistent ionic strength.

118 Iron oxidation state modelling has been conducted using the Aqion software suite (Kalka, 2015). This
119 modelling software is a GUI for the Phreeqc software, and the results are presented in Table S29.

120 3 Results

121 3.1 Extraction from acetic acid media

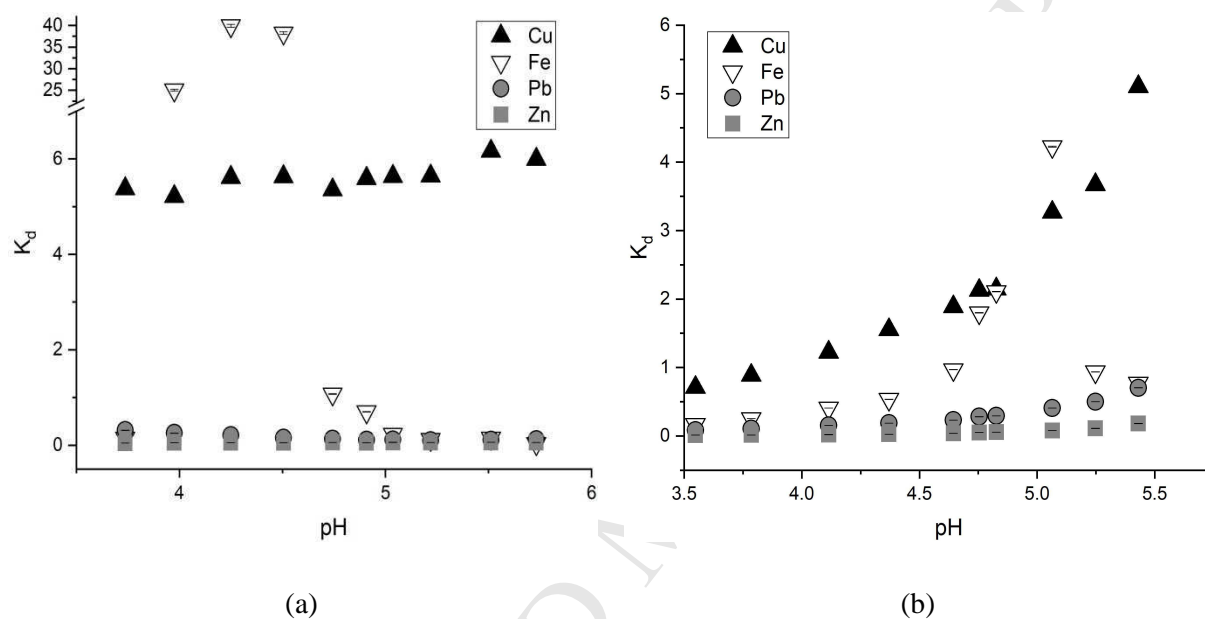
122 Initially, the distribution coefficients (K_d) of metal ions from acetic acid by all six resins were
123 screened (Figures 2-4). While the distribution of iron onto TP214 (Fig. 1A) reaches >40 , the high
124 distribution value is only maintained between pH 3.97 and 4.51, outside of this region the K_d decrease
125 to ≤ 1 (Figure 2a). Copper is extracted to $\sim 100\%$, with the K_d remaining between 5 and 6 throughout
126 the entire pH range studied. Both zinc and lead maintain distribution values <0.5 . Between the pH
127 region of 3.97 and 4.51, the affinity series remains $Fe \gg Cu > Pb > Zn$, however outside of this region
128 the affinity series becomes $Cu > Fe > Pb > Zn$.

129 Data for amidoxime functionalised Purolite MTS9100 (Fig. 1B) are shown in Figure 2b. Results again
130 show a high affinity for copper from acetate media throughout the studied pH range, with the K_d
131 increasing exponentially from ~ 1 as pH increases. Zinc and lead show increasing extraction with
132 increasing pH (although K_d remaining <1). The K_d of iron increases exponentially to a peak of 4.2 at
133 pH 5 before dropping to <1 beyond this. The observed affinity series for MTS9100 towards the
134 studied metals in acetic acid is $Cu > Fe > Pb > Zn$ between pH 3.55 and 4.83 and \geq pH 5.25, with iron
135 having the highest affinity at pH 5.06.

136 Figure 3a shows the extraction of metal ions from acetate media by MTS9570 (Fig. 1C). The K_d of
137 iron increases to a peak of 14 at pH 3.75, before dropping to 8 towards the higher pH values. Lead
138 distribution coefficients remained at ~ 2 throughout the entire pH range, while zinc values continue to
139 increase until the highest pH studied. The K_d of copper remained <0.3 between the studied pH values.
140 At $pH \geq 3.71$ the observed affinity series is $Fe \gg Pb > Zn > Cu$, with $Zn = Cu$ at pH 2.84. Figure 3b
141 presents the extraction of copper, iron, lead and zinc ions from acetate media by iminodiacetic acid
142 (IDA) MTS9301 (Fig. 1D) as a function of pH. This resin shows a high affinity toward copper ions,
143 with K_d values reaching beyond 10. The IDA functionality shows moderately high affinity for the
144 other metals studied, with the K_d of all metals >1 towards higher pH values, iron peaking at ~ 6
145 between pH 4.25 and 4.50 and zinc peaking at almost 10 at pH 5.2. At lower pH values, the resin is

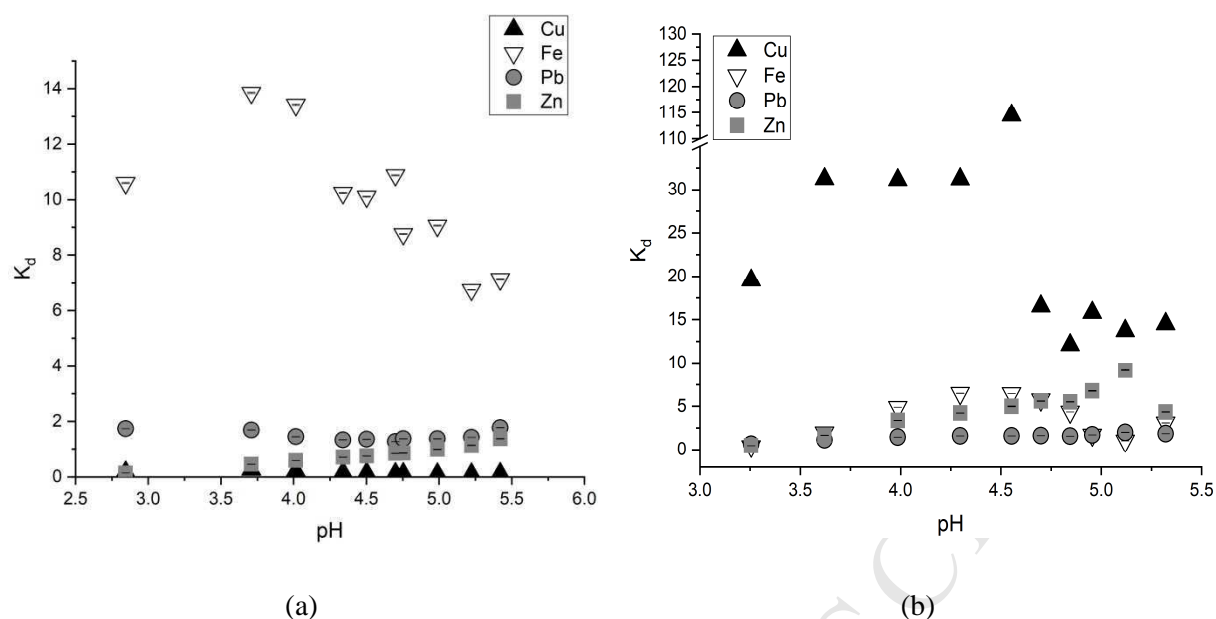
146 selective towards copper, with extraction of other metals suppressed. The affinity series at a $\text{pH} \leq 3.62$
 147 is $\text{Cu} \gg \text{Zn} = \text{Pb} = \text{Fe}$. The separation between lead, zinc and iron, changes at $\text{pH} 5.32$ leading to an
 148 affinity series of $\text{Cu} \gg \text{Zn} > \text{Fe} > \text{Pb}$. However, between $\text{pH} 3.99$ and 4.70 iron has more of an affinity
 149 than zinc, and at $\text{pH} 5.12$ lead has greater affinity than iron.

150



151 Figure 2. The distribution of metal ions from acetic acid media by (a) TP214 and (b) MTS9100 as a
 152 function of pH at $20\text{ }^{\circ}\text{C}$ after 24hr of contact time

153



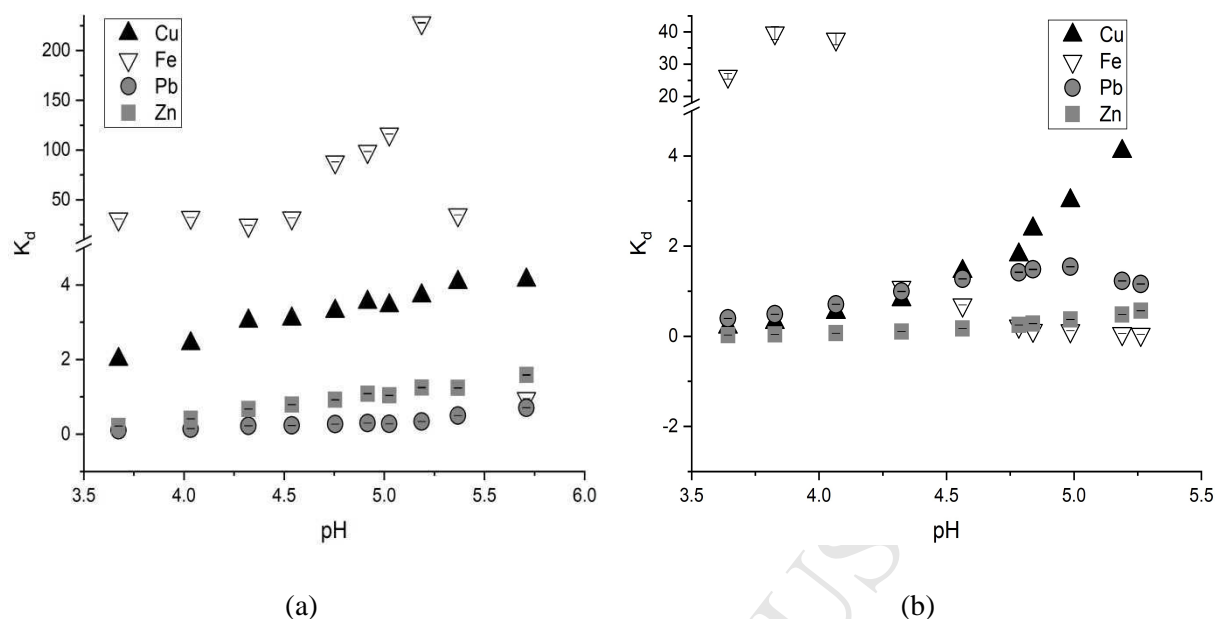
154 Figure 3. The distribution of metal ions from acetic acid media by (a) MTS9570 and (b) MTS9301 as
 155 a function of pH at 20 °C after 24hr of contact time

156

157 Distribution coefficients of metals on the aminophosphonic acid functionalised resin MTS9501 (Fig.
 158 1E) from acetate media are shown in Figure 4a. Copper recovery is constant from acetate media,
 159 remaining between 2 and 4. Iron is recovered very effectively from acetate media with this resin, with
 160 K_d values reaching beyond 200, however the K_d drops below 1 beyond pH 5.5. Lead and zinc affinity
 161 increases with pH, with zinc showing a higher affinity than lead for the resin. The Observed affinity at
 162 pH <5.5 is Fe >>Cu >>Zn >Pb, however, at the highest pH value tested (5.75) the separation of each
 163 metal decreases and the order of extraction becomes Cu >>Zn >Fe >Pb.

164 Figure 4b shows the pH dependence of metal distribution onto carboxylic acid functionalised C107E
 165 (Fig. 1F) from an acetate media. At pH <4 in acetate media the observed affinity series for C107E is
 166 Fe >>Pb >Cu >>Zn. As pH increases, iron extraction is suppressed, whereas copper, lead and zinc
 167 K_d values increase with increasing pH. At pH ~ 4.5 the affinity of C107E for iron, lead and copper
 168 become roughly similar, with the affinity for zinc overtaking the affinity for iron at pH ~ 4.8. Above
 169 pH 4.8 the affinity of C107E for metals is in the order Cu >Pb >Zn >Fe.

170



171 Figure 4: The distribution of metal ions from acetic acid media by (a) MTS9501 and (b) C107E as a
 172 function of pH at 20 °C after 24hr of contact time

173

174 3.2 Extraction from Lactic acid media

175 Similarly to the results from acetate media TP214 also has a high affinity for copper in lactate media
 176 (Figure 5a), in this case with K_d values above 50 throughout all pH values. Lead showed highest
 177 distribution at lower lactic acid pH values, with this decreasing as pH increases to around 1 at pH
 178 >4.0. Zinc and iron K_d remained below 0.05 throughout the measured pH range by TP214 in lactate
 179 media. The observed affinity series for TP214 within this media was $\text{Cu} \gg \text{Pb} > \text{Fe} = \text{Zn}$. MTS9100,
 180 was not as effective within lactate media (Figure 5b). The only metal to show K_d values >0.1 from
 181 lactate media was lead.

182 Observed metal extraction behaviour of MTS9570 from lactate media is similar to that observed from
 183 acetate media, with the same general trend in affinity $\text{Fe} > \text{Pb} > \text{Zn} > \text{Cu}$ (Figure 6a). Iron K_d decreased
 184 as pH increased, plateauing at pH ~ 4.2. The lead K_d values increase to a maximum of 1 at pH 4.0.

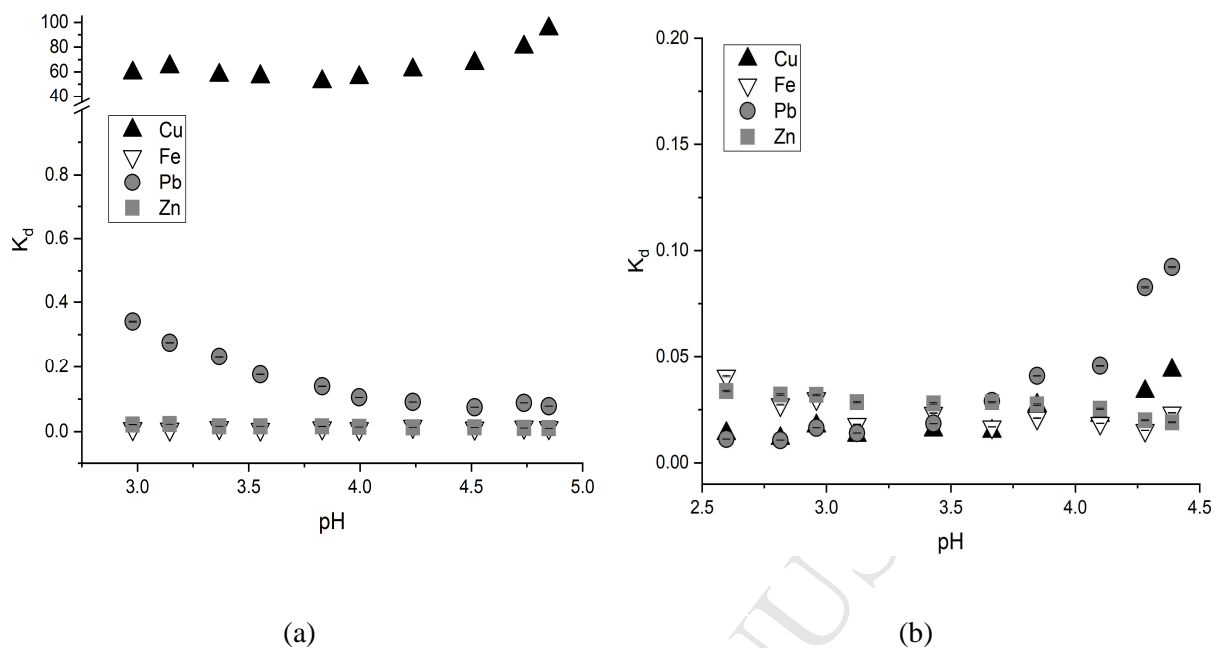
185 Copper and zinc extraction within lactate was suppressed with respect to MTS9570, as shown by the

186 low K_d of both metals. The observed trend in affinity is $\text{Fe} \gg \text{Pb} > \text{Zn} > \text{Cu}$, throughout the entire pH
187 range studied

188

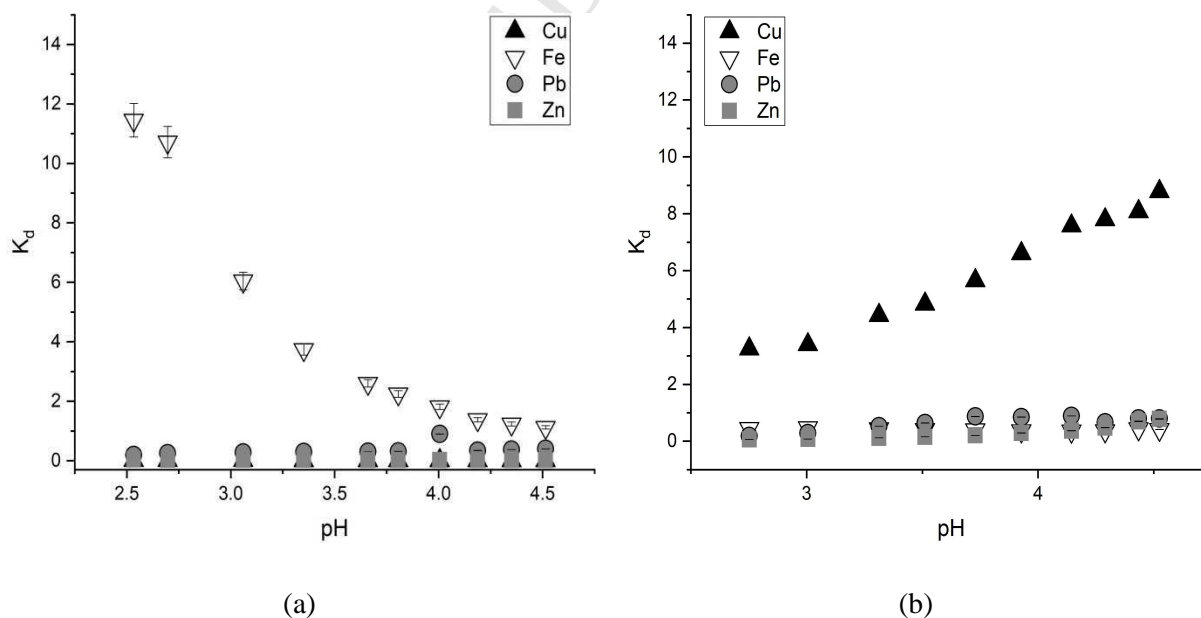
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190 Figure 5: The distribution of metal ions from lactic acid by (a) TP214 and (b) MTS9100 as a function
 191 of pH at 20 °C after 24hr of contact time

192



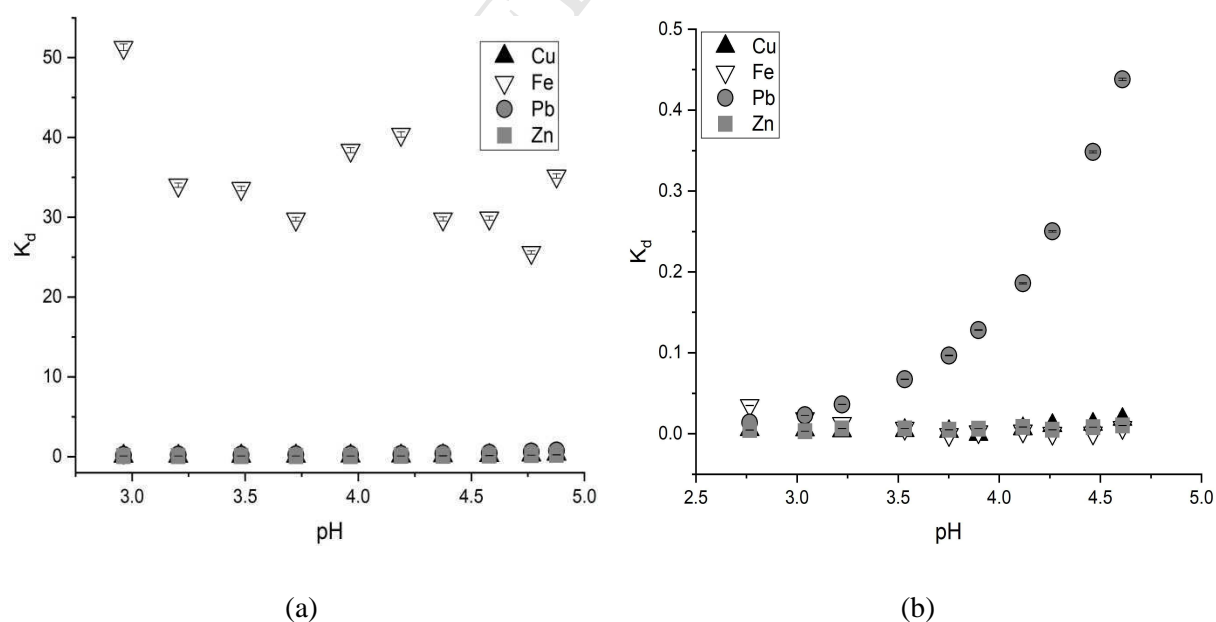
193 Figure 6: The distribution of metal ions from lactic acid by (a) MTS9570, (b) MTS9301 as a function
 194 of pH at 20 °C after 24hr of contact time

195

196 The lactate media displays suppression of metal uptake by MTS9301 in comparison to acetate media,
 197 with the copper reaching a K_d of ~ 10 , while all other metals remain below 1 (Figure 6b). The K_d of
 198 lead reaches 0.89, peaking at a pH of 4.14, while zinc peaks at a pH of 4.52 with a K_d of 0.78. The K_d
 199 of iron remains at ~ 0.4 throughout the entire pH range. While towards the lowest pH values studied
 200 (pH <3.31) the trend in affinity was Cu >>Fe >Pb >Zn, at pH 4.52 the trend in affinity was Cu >>Pb
 201 >Zn >Fe.

202 Changing weak acid medium from acetate to lactate increases selectivity of MTS9501 (Figure 7a).
 203 Iron K_d values remain between 25 and 50, while copper, lead and zinc remain below 1. As pH
 204 increases, copper, lead and zinc K_d values increase 0.30, 0.73 and 0.24, and an affinity series
 205 throughout the entire range studied of Fe >>Pb >Cu = Zn. The weak acid resin, C107E, showed a
 206 high affinity and separation for lead within lactic acid media (Figure 7b). K_d values of lead from this
 207 media increased to 0.4, while all other metal K_d values remained below 0.02.

208



209 Figure 7: The distribution of metal ions from lactic acid by (a) MTS9501 and (b) C107E as a function
 210 of pH at 20 °C after 24hr of contact time

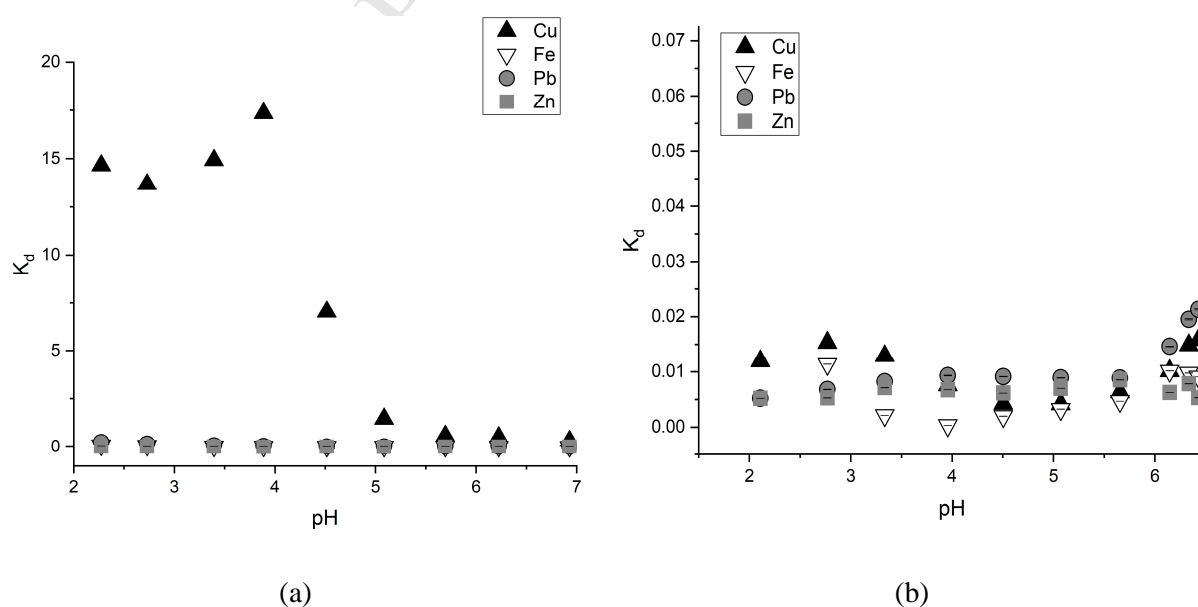
211

212 **3.3 Extraction from citric acid media**

213 The pH dependence of the K_d of the metals from citric acid media, reported as extraction percentage
 214 in Bezzina (2018b), is displayed for each resin studied in Figures 8-10. Figure 8a shows the copper K_d
 215 values for TP214 within citric acid reached a maximum of 17 before decreasing past a pH of 3.88. All
 216 other metals studied show K_d values below 0.02. The affinity trend for TP214 within citrate is Cu
 217 \gg Pb $>$ Fe $>$ Zn at pH \leq 3.9, with lead, iron and zinc reducing the difference in extraction as pH
 218 increases. In Figure 8b, the plot of K_d vs pH for MTS9100 in citric acid media shows that there was no
 219 appreciable extraction of metal ions by the amidoxime functionality.

220 The K_d of metals extracted by MTS9570 as a function of pH within citric acid media is displayed in
 221 Figure 9a. The initial pH (1.8) shows the resin has a high iron affinity, after which the K_d
 222 exponentially decreases with increasing pH. Copper and zinc show little interaction with MTS9570 in
 223 citric acid, with K_d values remaining below 0.01 for copper and 0.03 for zinc. A maximum K_d of 0.1
 224 for lead is observed at a pH of 2.5. The affinity trend for extraction of these metals from citrate media
 225 is observed to be Fe \gg Pb $>$ Zn $>$ Cu at pH \leq 3.8, before becoming Pb $>$ Zn $>$ Fe $>$ Cu at pH \geq 4.4.

226

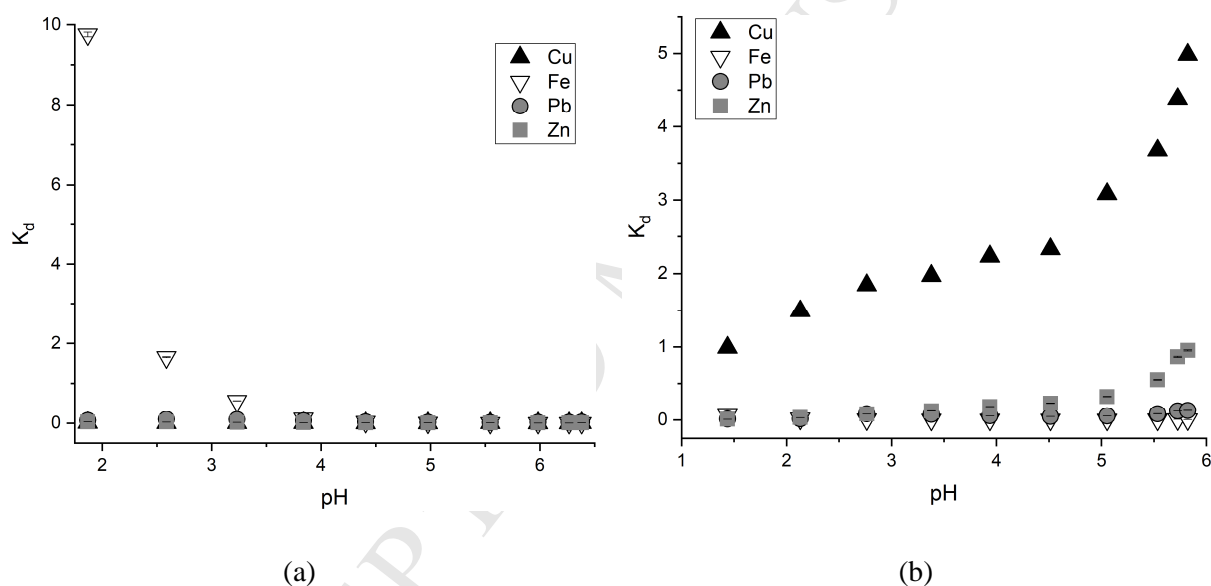


227 Figure 8: The distribution of metal ions from citric acid by (a) TP214 and (b) MTS9100 as a function
 228 of pH at 20 °C after 24hr of contact time

229

230 The K_d for copper extraction from citric acid media by MTS9301 (Figure 9b) reached a maximum of
 231 5 from a minimum of 1, increasing with respect to pH. All other metals maintain K_d values at or below
 232 0.1, apart from zinc, which reached a K_d of ~ 1 by pH 5.8. The trend in affinity at a higher pH (pH \geq
 233 4) can be described as Cu \gg Zn $>$ Pb $>$ Fe.

234



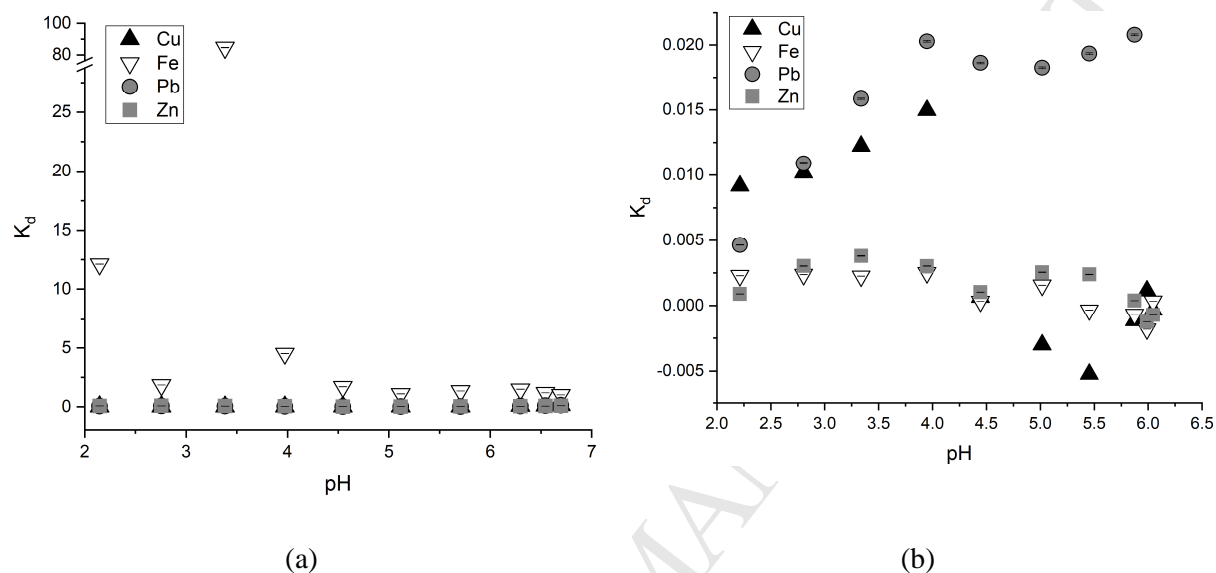
235 Figure 9: The distribution of metal ions from citric acid by (a) MTS9570 and (b) MTS9301 as a
 236 function of pH at 20 °C after 24hr of contact time

237

238 Figure 10a displays the pH dependence of the distribution coefficients of copper, iron, lead and zinc
 239 from a citric acid media. At a lower pH there was much higher extraction of iron, with distribution
 240 coefficients beginning at 12.5 and peaking at 80, before dropping to < 1.5 . The higher pH values (pH
 241 ≥ 6.7) affinity trend was Fe $>$ Zn = Pb = Cu, with separation from copper becoming more apparent as
 242 pH decreases to displayed a trend showing Fe \gg Zn = Pb $>$ Cu. All other metals within this media

243 display relatively negligible distribution coefficients (<0.15). C107E within the citric acid media
 244 (Figure 10b) displayed very low distribution coefficients ($K_d \sim 0.02$), however the extraction of
 245 lead, and copper until pH 4.5, showed a relatively large separation from the other metals.

246

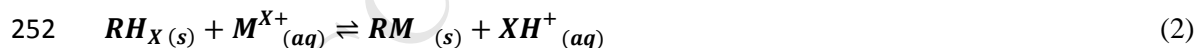


247 Figure 10: The distribution coefficients of metal ions from citric acid by (a) MTS9501 and (b) C107E
 248 as a function of pH at 20 °C after 24hr of contact time

249

250 4 Discussion

251 The general IX equation for extraction of metals from solution is given by equation (2);



253 where a metal (M^{X+}) is exchanged for X protons (H^+) on the functional group (R). A simplistic
 254 interpretation to metal uptake trends could be made by comparing solution speciation in weak acid
 255 media with the overall stability constants ($\log\beta$) for a metal binding the aqueous analogue of each
 256 functional group. The caveat to this is that no consideration is given to hydrophobic matrix effects of
 257 the ion exchange resin.

258 As the comparison of divalent metal ions within this study includes iron(II), there is likelihood for the
259 oxidation of iron(II) to iron(III). Modelling within studied region displays little concentration of
260 iron(III), however there is precipitation of iron at higher pH within acetate and lactate media (Table
261 S29), to minimise the effect, fresh solutions were made prior to each experiment.

262 4.1 Performance of TP214 in weak acid media

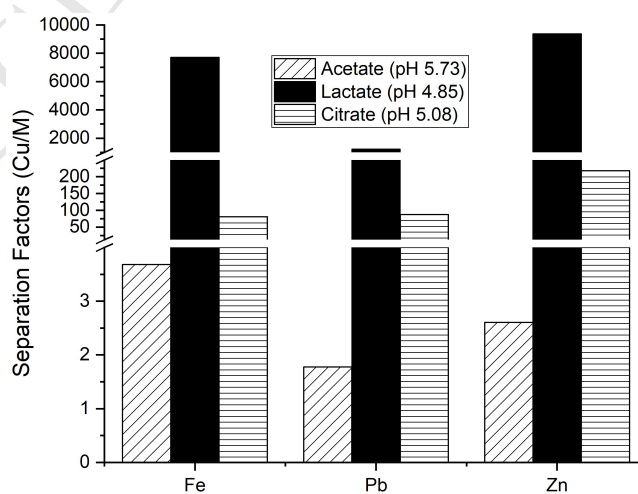
263 Thiourea functionalised TP214 has been previously used for precious metal removal and could be
264 useful in the valorisation of some sewage sludges (Aktas and Morcali, 2011; Hubicki, *et al.*, 2007;
265 Morcali, *et al.*, 2013). However, the moiety displays affinity for copper (Kołodynska and Hubicki,
266 2009; Hubicki, *et al.*, 2007) potentially reducing effective extraction of precious metals. If
267 complexing weak acids suppress the extraction of copper it could lead to a potential selective removal
268 of precious metals from sewage sludge. The observed strong extraction of copper is due to the
269 generation of copper (I) by the thiourea functional group on TP214 (Doona and Stanbury, 1996;
270 Kołodynska and Hubicki, 2009; Krzewska, 1980; Hubicki, *et al.*, 2007; Morcali, *et al.*, 2013). The
271 extraction is independent of speciation in acetate (Figure S1a) and lactate media (Figure S2a), while
272 copper(I) displays high affinities for the thiourea group, above those of the carboxylic acid groups
273 (Martell, *et al.*, 2009). The observed extraction decrease, below pH 4.5, in citrate media correlates to a
274 transition from a charge neutral CuHCit (MHL) species to a negatively charged dimer (M_2L_2) and a
275 hydrolysis product (MH_1L) complex of copper citrate as pH increases (Figure S3a).

276 The high extraction of Fe^{2+} observed in acetate media is not recorded for lactate and citrate. Within
277 acetic acid we see an initial uptake suppression by proton competition, followed by a transition of the
278 iron species to FeAc^+ (Figure S1b) preventing uptake at $\text{pH} > 4.5$, the extraction of iron(II) at lower
279 pH values could be explained by the observation of a thiourea complex $(\text{Fe}(\text{thiourea})_4\text{Cl}_2)$ within
280 chloride media, however little to no data exists on the stability of this complex (Rosenheim and
281 Meyer, 1906). The extraction suppression of Fe^{2+} in citrate is due to screening in solution by
282 complexation (Figures S3b), while the reduction of copper could be causing oxidation of iron and also
283 leading to stabilisation by complexation in lactate media (Figure S2b).

284 Lead complexation with lactate is weaker than acetate for the dominant species (ML^+ and ML_2)
 285 (Tables S25 and S24, respectively), explaining the higher extraction in lactate, however both decrease
 286 in extraction with increasing neutral bis- and negative tris- complexation ($PbLac_3^-$ being a stronger
 287 binding species than $PbAc_3^-$) (Figure S1c and S2c, acetate and lactate, respectively). The complete
 288 suppression of extraction in citrate is due to the formation of stable multidentate complexes in
 289 solution (Figure S3c). Zinc extraction is low within all three media. The free Zn^{2+} remains close to
 290 10%, even towards the higher pH in acetic acid, while this is zero in lactate (Figure S2d) and citrate
 291 (Figure S3d), explaining the higher extraction in acetate.

292 The high stability of copper(I)-thiourea complexes ($\log\beta$ of 12.3 for ML species, increasing for ML_2
 293 and ML_3) supports the assumption of copper(II) reduction. Little to no data on iron(II)/(III) stability
 294 exists, however a comparison of copper(I) with lead and zinc suggest an affinity for low charge
 295 densities (Martell, *et al.*, 2009), leaving copper(I) as the only species displaying higher stability bound
 296 to the surface than in solution. The separation factors of copper from other metals ($Cu K_d/M K_d$) at the
 297 pH of maximum separation is displayed within Figure 11 (other separation factors have been
 298 tabulated in supporting information Table S2, S8 and S14 for acetic, lactic and citric acid,
 299 respectively) with lactic acid providing the largest separation factors. The proposed surface redox
 300 reaction of copper is a concern regarding resin regeneration.

301



302

303 Figure 11: TP214 separation factors of copper from iron, lead and zinc extracted from acetate, lactate
304 and citrate media at 20 °C after 24hr of contact time.

305

306 **4.2 Performance of MTS9100 in weak acid media**

307 Within acetic acid, the amidoxime functionalised MTS9100 extraction can be assumed to be dictated
308 by proton concentration mainly. Copper continues the increase in extraction observed from pH 2 in
309 sulphate media (Riley, *et al.*, 2018), with extraction at pH 2.5 being ~30%, then 75% at pH 3.5 in this
310 study. Fe²⁺ is the only ion observably affected by speciation beyond pH 5, where a large proportion is
311 FeAc⁺ in solution (Figure S1b), relating to a decrease in extraction. There is limited information on
312 solution phase iron-amidoxime species, alluding to a stronger binding of the carboxylic species
313 (Martell, *et al.*, 2009).

314 The distribution of lead and zinc increase with pH, however they do not exceed 0.7 and 0.2,
315 respectively in all media. The extraction of all metals from lactic and citric acid by MTS9100 is
316 greatly hindered, with these media rendering this functionality incapable of effective metals
317 extraction. Neither metal (lead nor zinc) is effectively removed, until higher pH in the case of acetate,
318 from any media.

319

320 **4.3 Performance of MTS9570 in weak acid media**

321 The phosphonic/sulphonic combined functionality of MTS9570 has been proposed in previous
322 research for the removal of ferric ions from electrolyte copper solutions (Mckevitt and Dreisinger,
323 2009). This copper rejection is also demonstrated within the weak acid media, where the maximum
324 distribution coefficient of all media was 0.25. As with other sources (Riley, *et al.*, 2018) and similarly
325 to Diphonix™ (Chiariza, *et al.*, 1997), an increase in pH within acetate displayed an increase in
326 extraction, until a peak recorded at pH ~3.75. This peak correlates to a transition between Cu²⁺ and

327 CuAc^+ before suppression by the neutral CuAc_2 and negatively charged CuAc_3^- species (Figure S1a)
328 within solution. Within both lactic and citric acid, almost complete rejection of copper is observed.

329 The speciation of iron within acetate solution has no effect on the extraction (Figure S1b), while both
330 lactic acid and citric acid display decreasing K_d with increasing pH. In citric acid media, this relates to
331 a transition from free iron species to negatively charged FeCit^- for iron(II) at pH 3 (Figure S3b), which
332 is when there is a perceived drop in K_d , and in lactic acid this relates to the small increase in FeLac^+
333 from free iron species (Figure S2b), as this decrease in extraction is only ~5% (roughly the same
334 value as the concentration of the FeLac^+ species).

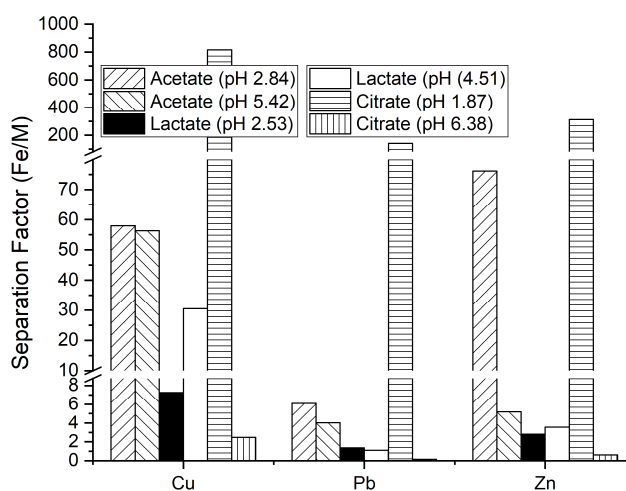
335 Lead complexes with lactic acid slightly stronger than acetic acid, reducing distribution coefficients
336 from ~ 2 throughout all pH ranges for acetic acid, to a maximum of 0.9 within lactic acid, where the
337 major species is the charge neutral PbLac_2 (Figure S2c). Citric acid, on the other hand, reaches a K_d of
338 0.1 at a pH of 2.58, decreasing as both negatively charged PbCit^- and PbCit_2^{4-} species increase in
339 relative concentration (Figure S3c).

340 Transitioning from acetic to lactic to citric acid the maximum K_d reached for zinc is 1.37, 0.03 and
341 0.03, respectively. Within acetic acid, this maximum extraction is observed at the highest pH studied,
342 when the most abundant species is that of cationic ZnAc^+ (Figure S1d), however within lactate and
343 citrate media, the transition to either a neutral ZnLac_2 species or ZnHCit species occurs at much lower
344 pH values (Figure S2d and S3d, respectively). While sulphate media sees ~100% extraction of zinc at
345 pH >1 (Riley, *et al.*, 2018) and the Diphonix resin sees high extraction of zinc at pH >2 within nitric
346 acid media (Chiariza, *et al.*, 1997).

347 Figure 12 displays the maximum observed separation factors of iron from copper, lead and zinc from
348 within acetate, lactate and citrate media. The drop in iron extraction from citrate media at the higher
349 pH range studied becomes extremely apparent, with separation factors from all metals dropping
350 substantially from the initially large values; especially true for copper. The separation factors of iron
351 from lead and zinc are less pronounced than copper (Table S4, S10 and S16, for acetate, lactate and
352 citrate media, respectively), with similarly functionalised resins displaying large extraction capability

353 for zinc in other studies (Chiariza, *et al.*, 1997; Riley, *et al.*, 2018) and the phosphonic acid group
 354 previously displaying effective extraction of lead (Dąbrowski, *et al.*, 2004; Rao, *et al.*, 2005).

355



356

357 Figure 12: MTS9570 separation factors of iron from copper, lead and zinc extracted from acetate,
 358 lactate and citrate media at 20 °C after 24hr of contact time.

359

360 4.4 Performance of MTS9301 in weak acid media

361 IDA functionalised resins are generally efficient at the extraction of copper, and can also show high
 362 affinity toward zinc (Edebali and Pehlivan, 2016; Pesavento, *et al.*, 1993; Riley, *et al.*, 2018;
 363 Soldatov, *et al.*, 2011). This functionality could have had the potential to extract high concentrations
 364 of copper and zinc that are common within modern sewage treatment plants (Fytily and Zabaniotou,
 365 2008). In accordance with the high affinity of the IDA resin for copper, the ML_2 stability constant
 366 trend follows 4 coordinate Z/IR with $Cu^{2+} > Zn^{2+} > Fe^{2+} > Pb^{2+}$, with all of the focus IDA-metal
 367 stability constants outcompeting predicted carboxylic acid complexes (Tables S22, S25 and S27)
 368 (Martell, *et al.*, 2009).

369 Copper extraction within acetate media maintains K_d values between 30 and 10, (one outlier at ~ 110 ,
 370 or an extraction difference of 0.2%), lactic and citric acid media increases from relatively low K_d

371 values (~ 2 and 1 , respectively) to ~ 9 and 5 , respectively. Literature sources show that the extraction
372 of copper by this functionality is generally hindered by competition between copper and protons,
373 which is often found to dramatically reduce extraction after pH 1 (Edebali and Pehlivan, 2016;
374 Pesavento, *et al.*, 1993; Riley, *et al.*, 2018; Soldatov, *et al.*, 2011), therefore the increase in copper
375 extraction, irrespective of the neutral and anionic solution phase species, is likely due to the lower
376 competition of protons.

377 Within lactate the extraction of iron remains consistent throughout all pH values, as does the solution
378 speciation (Figure S2b). The acetate behaviour can be rationalised by a decrease in the competition
379 between iron in solution and protons to a peak extraction at pH 4.5 , before a transition between Fe^{2+}
380 and FeAc^+ (Figure S1b) suppressing extraction, alluding to a bidentate binding mechanism ($\text{ML}_2 \gg$
381 ML). In both acetate and lactate media, the extraction of iron(II) was $>85\%$, showing a similarly high
382 affinity for iron as within strong acid media, with high proton concentration being detrimental to
383 extraction (Pesavento, *et al.*, 1993; Riley, *et al.*, 2018). This high affinity is not observed within citric
384 acid, where the K_d decreases from a low 0.06 to 0.007 as the speciation transitions to 100% iron citrate
385 complexes (Figure S3b).

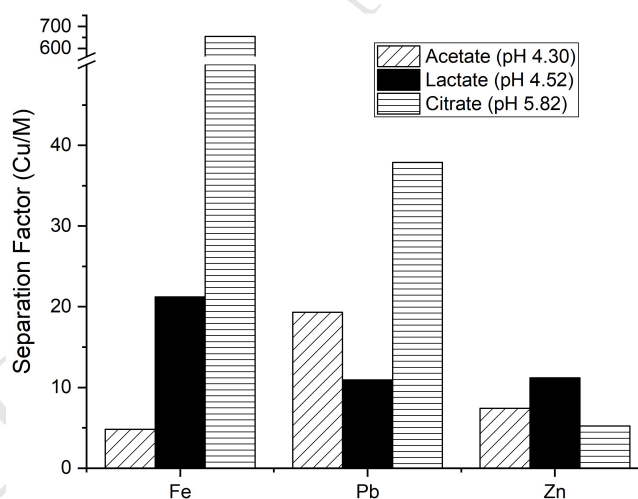
386 Lead reaches a maximum by pH ~ 3.25 in acetate and lactate media, with extraction irrespective of
387 the speciation (Figures S1c, and S2c, respectively), a similar pH to that observed by an iminodiacetic
388 acid and carboxylic acid co-functionalised resin (Soldatov, *et al.*, 2011). Citrate media, however,
389 shows a peak at pH ~ 3 leading to extraction suppression, corresponding to a peak in anionic PbCit^-
390 concentration (Figure S3c), before extraction again increases beyond the studied region, with an
391 increase in anionic $\text{Pb}_2\text{Cit}_2^{2-}$ abundance (Figure S3c).

392 Acetic acid sees maximum zinc extraction by pH ~ 4 , with $98-99\%$ extraction (K_d of $\sim 3.5 - \sim 9$), similar
393 to Chelex 100 in nitrate media (Pesavento, *et al.*, 1993). Within either acetic acid or lactic acid, zinc
394 extraction seems to be irrespective of speciation changes (Figures S1d and S2d, respectively), with the
395 aqueous IDA-zinc complexes being more stable (Martell, *et al.*, 2009). The formation of ZnLac_2 and
396 ZnLac_3^- complexes reduces the recorded distribution coefficients from ~ 5 at pH 4.5 in acetate media

397 to ~0.8 in lactate media (translating to a decrease from 99% to 92% extraction). In citric acid zinc
 398 maintains a ZnHCit complex (Figure S3d), further suppressing the extraction of zinc, to ~0.2 at pH
 399 ~4.5 and a maximum of ~1 at pH 5.8, where the anionic ZnCit_2^{4-} species becomes apparent.

400 At higher pH (>2), the iminodiacetic acid functionality is known to be a great extractor of metals, it is
 401 one of the best chelating resins for the extraction of copper and lead from waste water streams
 402 (Dąbrowski, *et al.*, 2004; Riley, *et al.*, 2018). The selectivity of this resin towards copper becomes
 403 apparent when looking at the separation factors for citric acid (Table S17), in comparison to those of
 404 lactate and acetate media (Table S11 and S5, respectively), where the resin is far less selective (Figure
 405 13). From all media, this resin is shown to be the most selective towards the target metals (copper,
 406 lead and zinc) over iron, from lactate and citrate media. Of all the resins tested, this was, overall, the
 407 most effective at extraction of metals from solution, maintaining relatively high extraction of all
 408 metals from solution from all media tested.

409



410

411 Figure 13: MTS9301 separation factors of copper from iron, lead and zinc extracted from acetate,

412 lactate and citrate media at 20 °C after 24hr of contact time.

413

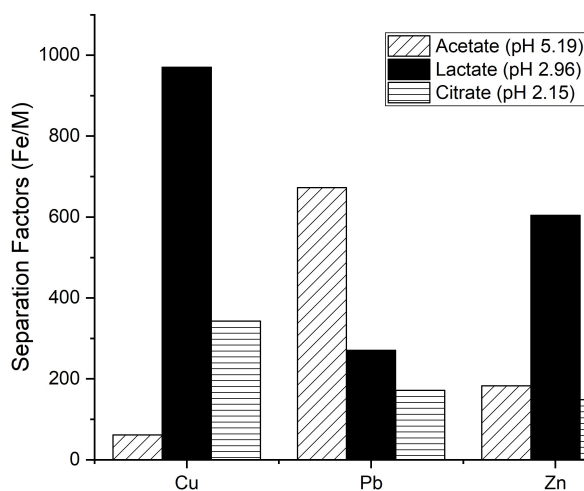
414 4.5 Performance of MTS9501 in weak acid media

415 The aminophosphonic acid functionalised MTS9501 has been shown to have a high affinity for
416 iron(III) towards a H^+ concentration through to $\sim 4M$ (Riley, *et al.*, 2018), while towards higher pH
417 values, the aminophosphonic acid functional group has a high affinity for all of the focus metals in
418 this study (copper, iron, lead and zinc) (Dąbrowski, *et al.*, 2004). Despite this experimental data, there
419 is little information for iron(II)/(III) or lead complexes, however, the high stability constants of
420 aqueous copper and zinc complexes allude to extraction of both hard and soft species (Martell, *et al.*,
421 2009).

422 The separation factors (Figure 14, Table S6, S12 and S18, for acetate, lactate and citrate, respectively)
423 show that the MTS9501 has a high selectivity for iron. Neither lactate media nor acetate media are a
424 substantial hindrance of the extraction of iron by this functionality. The citrate media, however, was
425 able to reduce the K_d values to < 12.5 (still relatively high), with an outlier at pH 3.4 of 85, with these
426 values decreasing to remain at ~ 1 towards the higher studied pH range, which still translates to an
427 extraction of $> 90\%$. The extraction efficiency of iron(III) by the industrial equivalent Duolite ES 467
428 has been shown to decrease beyond pH 2 (Rao, *et al.*, 2005), which is contrary to what is observed
429 with iron(II) in this study. However, the use of complexing species within this study could be, to a
430 certain extent, preventing hydrolysis of the iron, and therefore preventing precipitation.

431 $> 99\%$ of copper is removed from solution by the MTS9501 resin functionality within acetate media,
432 displaying K_d values between 2 and 4, with the extraction increasing with pH. The extraction of
433 copper from lactate media however, is hindered to produce K_d values < 0.5 (the presence of neutral
434 $CuLac_2$ or anionic $CuLac_3^-$ assumed to be the major contributing factor), while within citrate media
435 the extraction is restricted even more with a max K_d of 0.13 (with either neutral $CuHCit$ or anionic
436 $Cu_2Cit_2^{2-}$ and $CuOHCit^{2-}$ stabilising copper in solution). While remaining low, the copper recovery
437 within lactate media increases with an increasing pH, this increase in extraction with a decrease in
438 proton competition has also been observed within strong acid media (Cortina, *et al.*, 1996; Riley, *et*
439 *al.*, 2018), which is similar case to lead and zinc. While the complexation with the acid has hindered
440 extraction of metals by the aminophosphonic functionality, the competition for binding sites between
441 metals and protons has remained one of the driving factors in removal of metals from solution.

442



443

444 Figure 14: MTS9501 separation factors of copper from iron, lead and zinc extracted from acetate,
 445 lactate and citrate media at 20 °C after 24hr of contact time.

446

447 4.6 Performance of C107E in weak acid media

448 The weak acid resin functionality is a similar structure to the complexing acids, and therefore is
 449 assumed to have similar affinities towards the metals. This similarity should allow for a tailored
 450 approach to the extraction of the metals, manipulating pH either side of both resin functionality and
 451 weak acid species in order to gain the desired extraction. The binding affinity of copper, lead and zinc
 452 for the weak acid functionality seem to be higher than for the solution phase acetate, as their
 453 extraction increases beyond the approximate pK_a of the weak acid resin (assumed to be similar to
 454 formic acid, 3.75). While small values, and therefore a very speculative statement, the extraction of
 455 copper from citric acid is dictated highly by the complexation (Figure S3a) in a similar fashion to the
 456 thiourea based resin, with the extraction dropping substantially in conjunction with the speciation
 457 change of solution phase copper.

458 Within acetic acid, changing the pH seems to allow for either the selective extraction or rejection of
 459 iron, by shifting the pH either side of the acetate pK_a , this could possibly be due to the higher
 460 presence of the $FeAc^+$ species beyond a pH of 4; in this case, the decrease in concentration is observed

461 beyond the pH where Fe^{2+} complexes with acetate (Figure S1b). This is also contrary to what had been
462 observed for ferric ions within a similar media where no Fe^{3+} had been taken up by the weak acid
463 resin throughout the same pH range (Bezzina, *et al.*, 2018a).

464 Within lactic acid, all metals are stabilised within the solution, apart from lead, potentially due to the
465 higher ionic radius; allowing the Pb^{2+} ions to interact with more functional groups on the resin surface.
466 This stabilisation leads to large separation factors for lead from copper, iron and zinc for this media,
467 exceeding 50 (Table S13). If lead were to be the target metal, a higher pH within lactate media would
468 allow for very selective extraction (assuming low concentrations of metals unstudied).

469 Linking the functional group to formic acid, once again, the stability constants of these metals with
470 this functional group are relatively low when compared to the largest constants of the other resins
471 (Martell, *et al.*, 2009). The available data shows increasing stability constants with increasing ionic
472 radii (with the exception of copper as the strongest bound species) (Martel, *et al.*, 2009), with zinc
473 displaying the least stable complex of the studied metals. Within both acetate and lactate media, the
474 metals are bound in similar fashion to both the functional group and the complexing acid, as the
475 singular carboxylic acid unit is present in both. The lactic acid moieties have far higher binding
476 strength than the acetic acid moieties possibly due to a conjugation effect between the β hydroxy
477 group and lactate being a stronger binding ligand, this effect must not be present within the functional
478 groups bound to the resin surface, leaving lactic acid as a far stronger binding species. Again, citric
479 acid being a stronger binding agent than lactic acid (due to the three protonation sites), it has been
480 observed to restrict extraction by this functionality even more than lactic acid.

481 **5 Conclusions**

482 The removal of metals from simulated weak acid sewage sludge leachates have been studied, with
483 promising results. The complexing nature of carboxylic weak acids stabilise metal ions in solutions
484 generating broader functional pH regions for metal extraction. Depending on the metals present in
485 solution, a variety of different combinations of acids and resin functionalities could be used for
486 selective separation processes. While lactate complexes are more stable in solution than acetate,

487 neither of these ligands compared to the stability of citrate complexes. The increased stability in
488 solution could render extraction processes more expensive, as more solid phase extraction stages
489 would be required for removal of the target metals. TP214 has a high affinity for copper, as well as
490 iron in acetate media, and must be taken out prior to a precious metals recovery stage. The amidoxime
491 functionalised resin MTS9100 is rendered ineffective in lactate and citrate media. MTS9570
492 maintained a high affinity for iron within all media, while decreasing extraction efficiency of copper,
493 lead and zinc within lactate and citrate media. The phosphonic acid functionalised resin MTS9501 is
494 extremely efficient at extracting copper and iron in acetate media, while only iron extraction is
495 maintained in lactate, lead extraction displays little response to the change of buffer. The weak acid
496 functionalised resin selectivity for lead was significantly increased within lactic acid media, with
497 speciation dependent extraction in acetate media. The MTS9301 IDA functionalised resin displayed
498 the best performance for metals in all media. This resin was especially effective at the removal of
499 metals from an acetic acid media, with high separation of copper. Further investigation is required to
500 understand the kinetics, as well as capacity of the MTS9301 resin within these weak acid systems.

501

502

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1 **Highlights**

- 2 • MTS9301 is effective at extracting selected metal ions from all tested media
- 3 • Citrate media is effective at hindrance of metal adsorption
- 4 • TP214 can selectively extract copper from high complexing solutions
- 5 • C107E can selectively extract lead from lactate media

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: