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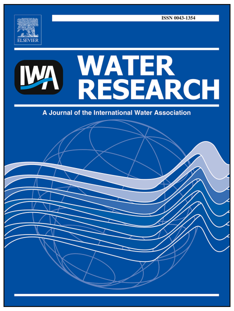

Ion exchange removal of Cu(II), Fe(II), Pb(II) and Zn(II) from acid extracted sewage sludge – Resin screening in weak acid media

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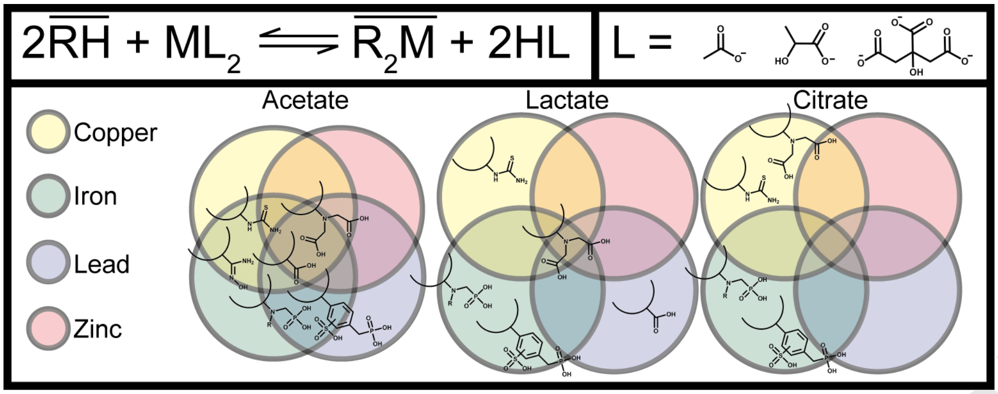
2RH + ML2 ⇌ R2M + 2HL
L =
Acetate
Lactate
Citrate
Copper
Iron
Lead
Zinc

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

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Abstract

A shortage of phosphate rock resources has led to a focus on the use of sewage sludge as a fertiliser. One factor preventing the unlimited application of sewage sludge in agriculture is the heavy metal content. This work looks at a process where weak acid leaching of sewage sludge would be coupled to ion exchange (IX) for heavy metal ion removal. IX offers an effective method for the recovery of these metals from a leachate. This study presents the pH performance of six selected IX resins in extracting Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} from acetic, lactic and citric acid media simulated weak acid leachate. Acetic acid media displayed limited suppression of metal extraction, whilst lactic and citric acid media rendered MTS9100 ineffective. Lactic acid media when combined with C107E resin allows for the targeted extraction of lead. Both MTS9570 and MTS9501 display high ferrous extraction in all media at all pH values, although citric acid hinders extraction by both resins at higher pH values. TP214 is selective for copper over all other metal ions in all weak acid media. MTS9301 is the most effective at extracting all metals from all media solutions, with separation of copper becoming more apparent when transitioning to citric acid.

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

1 Introduction

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

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

2 Materials and Methods

2.1 Reagents and stock solutions

The functionalities of the resins tested are given in Figure 1. All IX resins were supplied by Purolite, except Lewatit MonoPlus TP214, which was provided by Lanxess. Calcium chloride was purchased from Fisher Scientific, lactic acid (80%) was purchased from Scientific Laboratory Supplies and glacial acetic acid was purchased from VWR. All other chemicals were purchased from Sigma-Aldrich as analytical grade or better unless otherwise specified. All IX resins were preconditioned by treatment with 1 M H_2SO_4 (10 bed volumes) for 24 h, prior to washing with 50 bed volumes of deionised water. The characteristics of the IX resins are given in supplemental Table S1.

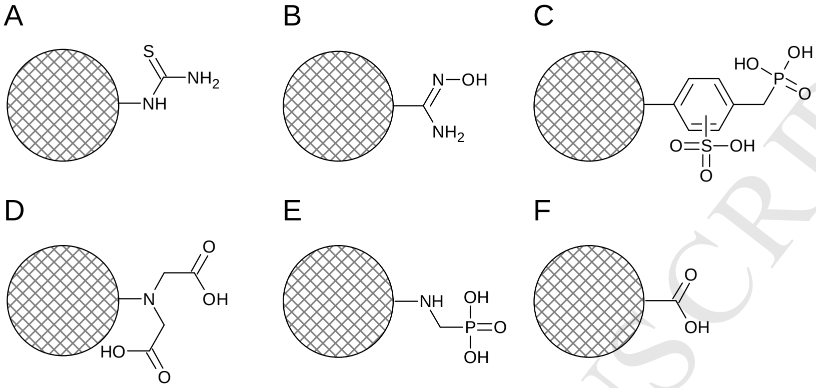


Figure 1: Chemical structure of the functionalities of the IX resins tested throughout this study (A = TP214 (thiourea), B = MTS9100 (amidoxime), C = MTS9570 (phosphonic/sulphonic acid combination), D = MTS9301 (iminodiacetic acid), E = MTS9501 (aminophosphonic acid), F = C107E (carboxylic acid); crosshatch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

2.2 Batch extractions from buffered media

Batch extractions were carried out by contacting 2 mL of wet settled resin (WSR) with 50mL of mixed metal solution and agitating on an orbital shaker for 24 h at room temperature, after which samples were taken for metal concentration and pH analysis. Mixed metal solutions contained chloride salts of Ca^{2+}, Cu^{2+}, Fe^{2+} and Zn^{2+} (100ppm), in addition to $Pb(NO_3)_2$ (100ppm Pb^{2+}), NaCl (0.5 M) and weak acid (0.5 M, acetic acid and lactic acid). While Ca^{2+} concentration was not analysed, a resin:solution ratio was maintained so that the total metal concentration was far below the saturation of resin functional sites. Acidity was adjusted to a range ± 1 pH unit either side of the corresponding weak acid's pK_a (pH 4.76 for acetic acid and pH 3.86 for lactic acid), the approximate buffering region of the acid, using either NaOH or HCl.

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

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

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

2.3 Speciation Modelling

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

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

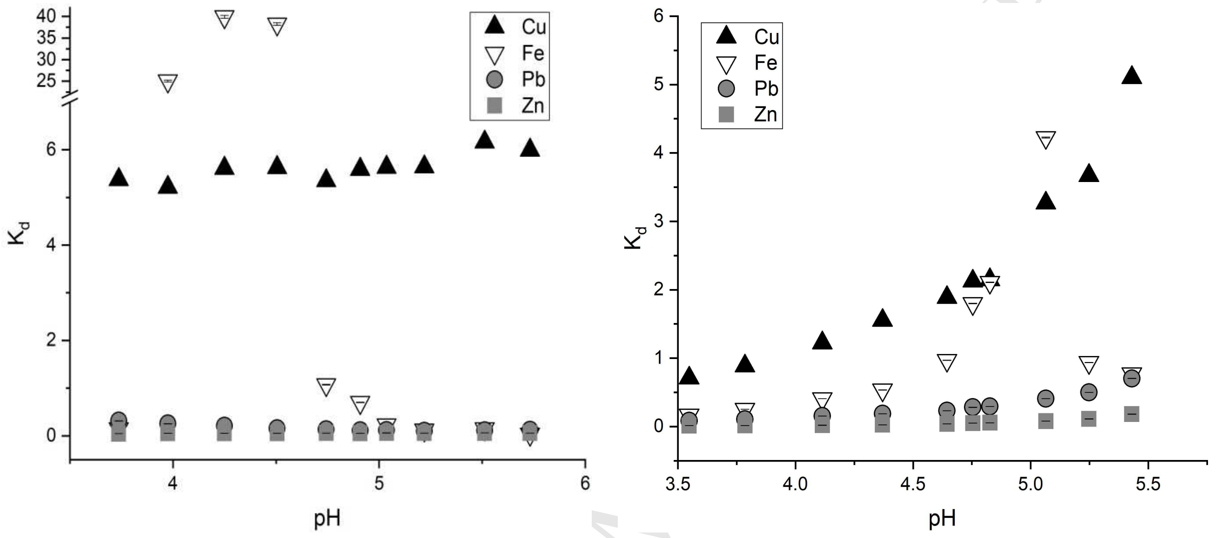
3 Results

3.1 Extraction from acetic acid media

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

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

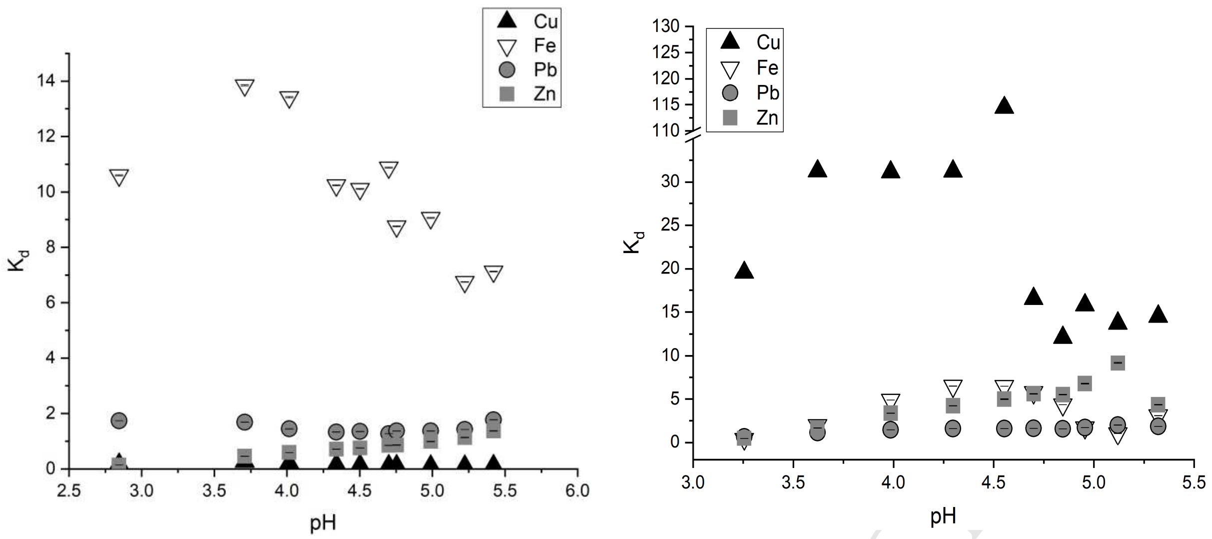
Figure 3a shows the extraction of metal ions from acetate media by MTS9570 (Fig. 1C). The K_d of iron increases to a peak of 14 at pH 3.75, before dropping to 8 towards the higher pH values. Lead distribution coefficients remained at ~ 2 throughout the entire pH range, while zinc values continue to increase until the highest pH studied. The K_d of copper remained <0.3 between the studied pH values. At pH ≥ 3.71 the observed affinity series is Fe >>Pb >Zn >Cu, with Zn = Cu at pH 2.84. Figure 3b presents the extraction of copper, iron, lead and zinc ions from acetate media by iminodiacetic acid (IDA) MTS9301 (Fig. 1D) as a function of pH. This resin shows a high affinity toward copper ions, with K_d values reaching beyond 10. The IDA functionality shows moderately high affinity for the other metals studied, with the K_d of all metals >1 towards higher pH values, iron peaking at ~ 6 between pH 4.25 and 4.50 and zinc peaking at almost 10 at pH 5.2. At lower pH values, the resin is selective towards copper, with extraction of other metals suppressed. The affinity series at a pH ≤ 3.62 is Cu >>Zn = Pb = Fe. The separation between lead, zinc and iron, changes at pH 5.32 leading to an affinity series of Cu >>Zn >Fe >Pb. However, between pH 3.99 and 4.70 iron has more of an affinity than zinc, and at pH 5.12 lead has greater affinity than iron.



(a)

(b)

Figure 2. The distribution of metal ions from acetic acid media by (a) TP214 and (b) MTS9100 as a function of pH at 20 °C after 24hr of contact time

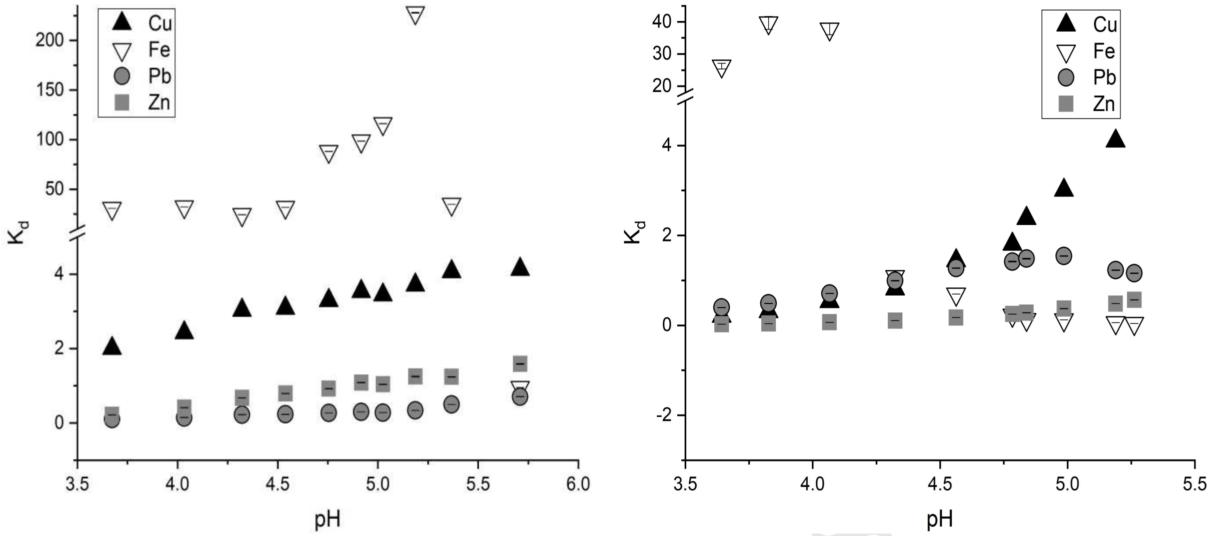


(a) (b)

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

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

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



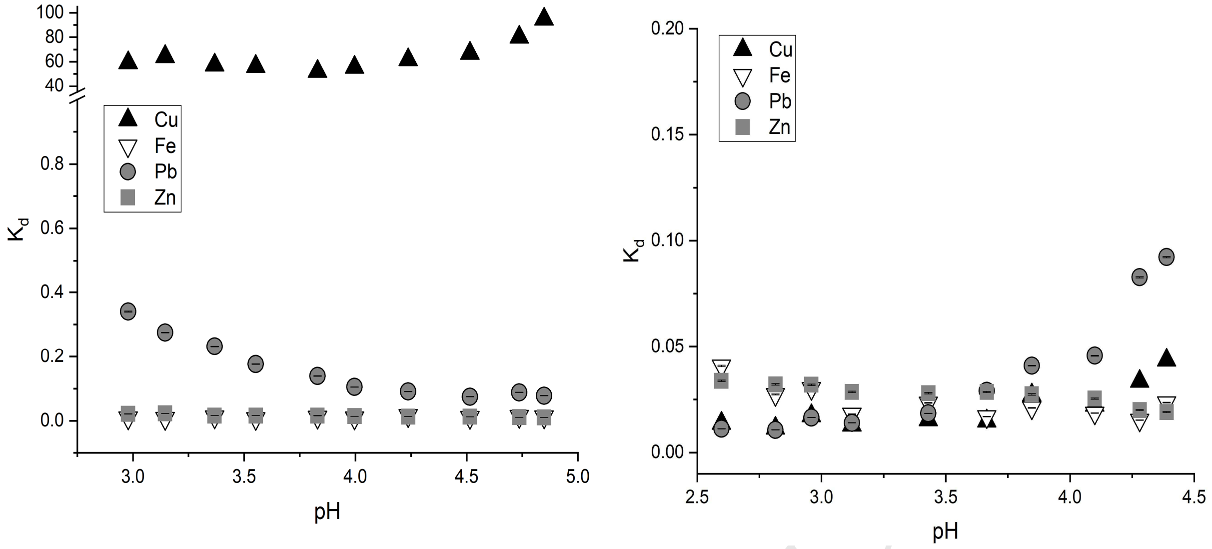
(a) (b)

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

3.2 Extraction from Lactic acid media

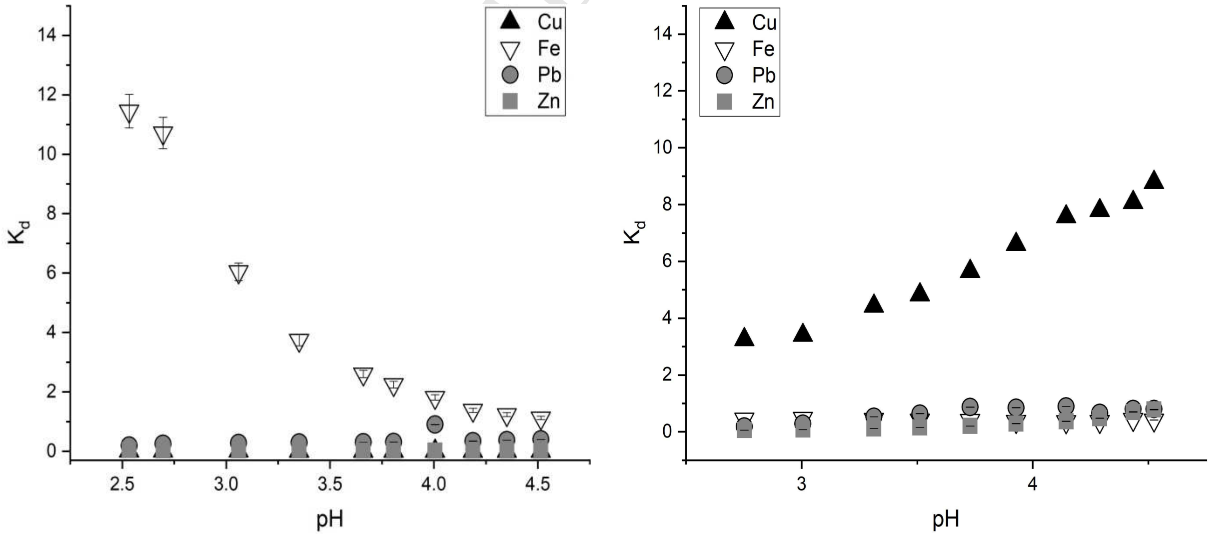
Similarly to the results from acetate media TP214 also has a high affinity for copper in lactate media (Figure 5a), in this case with K_d values above 50 throughout all pH values. Lead showed highest distribution at lower lactic acid pH values, with this decreasing as pH increases to around 1 at pH >4.0.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

Observed metal extraction behaviour of MTS9570 from lactate media is similar to that observed from acetate media, with the same general trend in affinity Fe >Pb >Zn >Cu (Figure 6a). Iron K_d decreased as pH increased, plateauing at pH ~ 4.2. The lead K_d values increase to a maximum of 1 at pH 4.0. Copper and zinc extraction within lactate was suppressed with respect to MTS9570, as shown by the low K_d of both metals. The observed trend in affinity is Fe >>Pb >Zn >Cu, throughout the entire pH range studied



(a) (b)

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

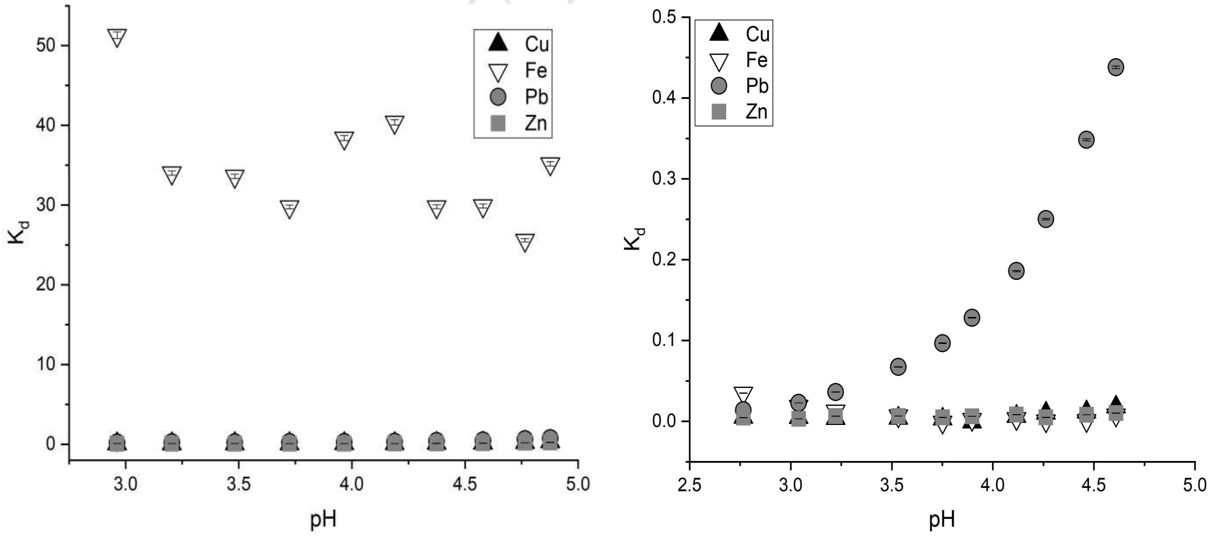


(a) (b)

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

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

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



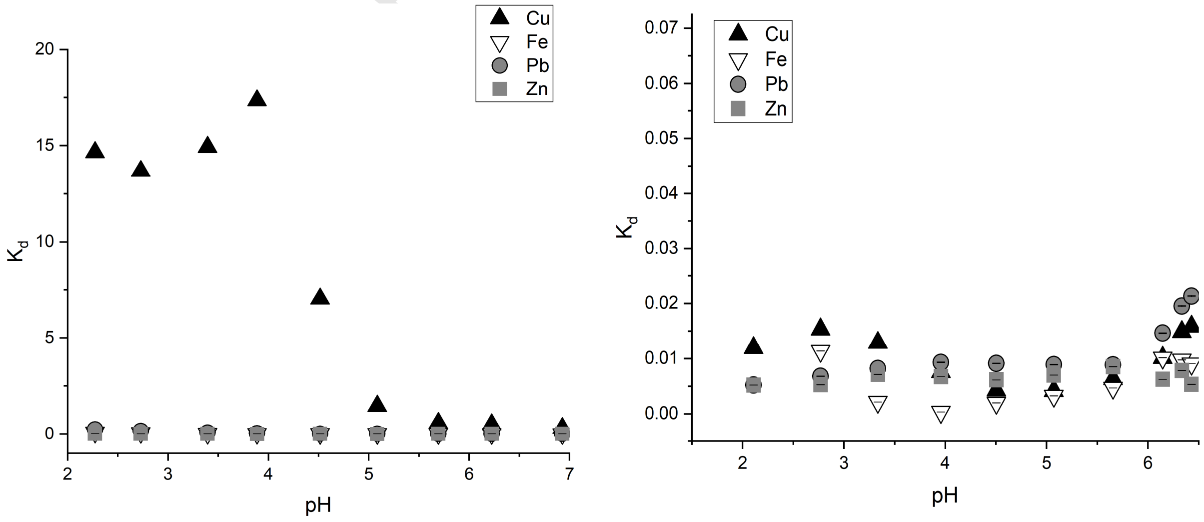
(a) (b)

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

3.3 Extraction from citric acid media

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

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

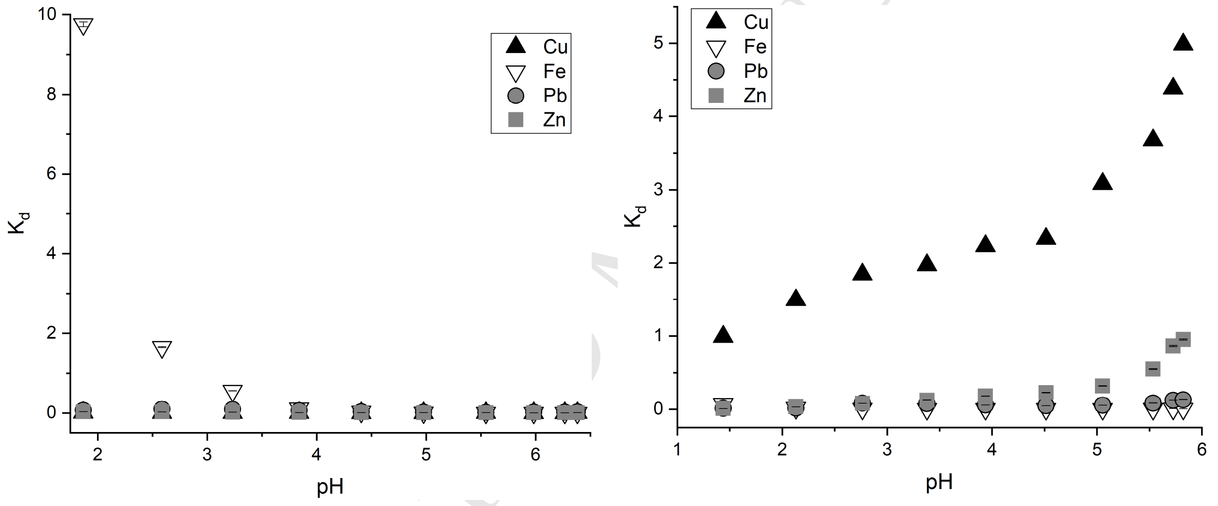


(a)

(b)

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

The K_d for copper extraction from citric acid media by MTS9301 (Figure 9b) reached a maximum of 5 from a minimum of 1, increasing with respect to pH. All other metals maintain K_d values at or below 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 ≥ 4) can be described as Cu >>Zn >Pb >Fe.



(a) (b)

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

Figure 10a displays the pH dependence of the distribution coefficients of copper, iron, lead and zinc from a citric acid media. At a lower pH there was much higher extraction of iron, with distribution coefficients beginning at 12.5 and peaking at 80, before dropping to <1.5. The higher pH values (pH ≥ 6.7) affinity trend was Fe >Zn = Pb = Cu, with separation from copper becoming more apparent as pH decreases to displayed a trend showing Fe >>Zn = Pb >Cu. All other metals within this media display relatively negligible distribution coefficients (<0.15). C107E within the citric acid media (Figure 10b) displayed very low distribution coefficients (K_d <~ 0.02), however the extraction of lead, and copper until pH 4.5, showed a relatively large separation from the other metals.

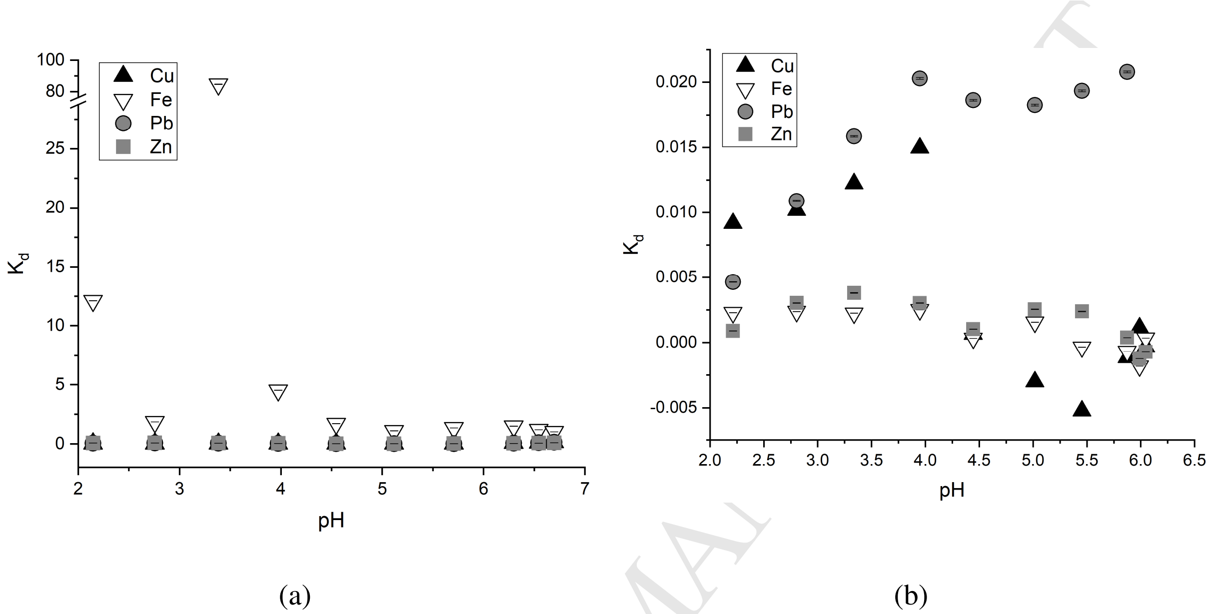


Figure 10: The distribution coefficients of metal ions from citric acid by (a) MTS9501 and (b) C107E as a function of pH at 20 °C after 24hr of contact time

4 Discussion

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

$$RH_{X\,(s)} + M^{X+}{}_{(aq)} \rightleftharpoons RM\ {}_{(s)} + XH^{+}{}_{(aq)} \qquad (2)$$

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

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

4.1 Performance of TP214 in weak acid media

Thiourea functionalised TP214 has been previously used for precious metal removal and could be useful in the valorisation of some sewage sludges (Aktas and Morcali, 2011; Hubicki, *et al.*, 2007; Morcali, *et al.*, 2013). However, the moiety displays affinity for copper (Kołodynska and Hubicki, 2009; Hubicki, *et al.*, 2007) potentially reducing effective extraction of precious metals. If complexing weak acids suppress the extraction of copper it could lead to a potential selective removal of precious metals from sewage sludge. The observed strong extraction of copper is due to the generation of copper (I) by the thiourea functional group on TP214 (Doona and Stanbury, 1996; Kołodynska and Hubicki, 2009; Krzewska, 1980; Hubicki, *et al.*, 2007; Morcali, *et al.*, 2013). The extraction is independent of speciation in acetate (Figure S1a) and lactate media (Figure S2a), while copper(I) displays high affinities for the thiourea group, above those of the carboxylic acid groups (Martell, *et al.*, 2009). The observed extraction decrease, below pH 4.5, in citrate media correlates to a transition from a charge neutral CuHCit (MHL) species to a negatively charged dimer (M_2L_2) and a hydrolysis product ($MH_{-1}L$) complex of copper citrate as pH increases (Figure S3a).

The high extraction of Fe^{2+} observed in acetate media is not recorded for lactate and citrate. Within acetic acid we see an initial uptake suppression by proton competition, followed by a transition of the iron species to $FeAc^+$ (Figure S1b) preventing uptake at pH >4.5, the extraction of iron(II) at lower pH values could be explained by the observation of a thiourea complex ($Fe(thiourea)_4Cl_2$) within chloride media, however little to no data exists on the stability of this complex (Rosenheim and Meyer, 1906). The extraction suppression of Fe^{2+} in citrate is due to screening in solution by complexation (Figures S3b), while the reduction of copper could be causing oxidation of iron and also leading to stabilisation by complexation in lactate media (Figure S2b).

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

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

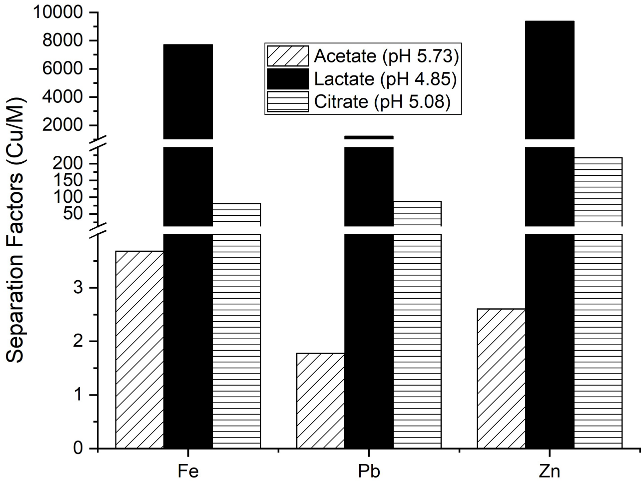


Figure 11: TP214 separation factors of copper from iron, lead and zinc extracted from acetate, lactate and citrate media at 20 °C after 24hr of contact time.

4.2 Performance of MTS9100 in weak acid media

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

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

4.3 Performance of MTS9570 in weak acid media

The phosphonic/sulphonic combined functionality of MTS9570 has been proposed in previous research for the removal of ferric ions from electrolyte copper solutions (Mckevitt and Dreisinger, 2009). This copper rejection is also demonstrated within the weak acid media, where the maximum distribution coefficient of all media was 0.25. As with other sources (Riley, *et al.*, 2018) and similarly to Diphonix™ (Chiariza, *et al.*, 1997), an increase in pH within acetate displayed an increase in extraction, until a peak recorded at pH ~3.75. This peak correlates to a transition between Cu^{2+} and

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

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

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

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

Figure 12 displays the maximum observed separation factors of iron from copper, lead and zinc from within acetate, lactate and citrate media. The drop in iron extraction from citrate media at the higher pH range studied becomes extremely apparent, with separation factors from all metals dropping substantially from the initially large values; especially true for copper. The separation factors of iron from lead and zinc are less pronounced than copper (Table S4, S10 and S16, for acetate, lactate and citrate media, respectively), with similarly functionalised resins displaying large extraction capability for zinc in other studies (Chiariza, *et al.*, 1997; Riley, *et al.*, 2018) and the phosphonic acid group previously displaying effective extraction of lead (Dąbrowski, *et al.*, 2004; Rao, *et al.*, 2005).

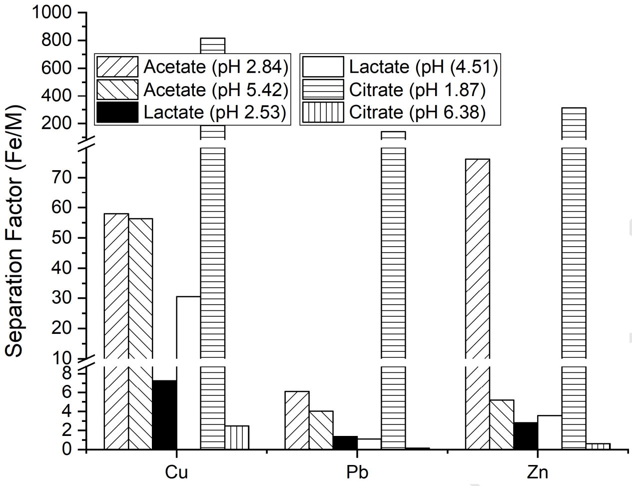


Figure 12: MTS9570 separation factors of iron from copper, lead and zinc extracted from acetate, lactate and citrate media at 20 °C after 24hr of contact time.

4.4 Performance of MTS9301 in weak acid media

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

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

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

Within lactate the extraction of iron remains consistent throughout all pH values, as does the solution speciation (Figure S2b). The acetate behaviour can be rationalised by a decrease in the competition between iron in solution and protons to a peak extraction at pH 4.5, before a transition between Fe^{2+} and $FeAc^{+}$ (Figure S1b) supressing extraction, alluding to a bidentate binding mechanism (ML_2 >> ML). In both acetate and lactate media, the extraction of iron(II) was >85%, showing a similarly high affinity for iron as within strong acid media, with high proton concentration being detrimental to extraction (Pesavento, *et al.*, 1993; Riley, *et al.*, 2018). This high affinity is not observed within citric acid, where the K_d decreases from a low 0.06 to 0.007 as the speciation transitions to 100% iron citrate complexes (Figure S3b).

Lead reaches a maximum by pH ~ 3.25 in acetate and lactate media, with extraction irrespective of the speciation (Figures S1c, and S2c, respectively), a similar pH to that observed by an iminodiacetic acid and carboxylic acid co-functionalised resin (Soldatov, *et al.*, 2011). Citrate media, however, shows a peak at pH ~3 leading to extraction suppression, corresponding to a peak in anionic $PbCit^{-}$ concentration (Figure S3c), before extraction again increases beyond the studied region, with an increase in anionic $Pb_2Cit_2^{2-}$ abundance (Figure S3c).

Acetic acid sees maximum zinc extraction by pH ~4, with 98-99% extraction (K_d of~3.5 – ~9), similar to Chelex 100 in nitrate media (Pesavento, *et al.*, 1993). Within either acetic acid or lactic acid, zinc extraction seems to be irrespective of speciation changes (Figures S1d and S2d, respectively), with the aqueous IDA-zinc complexes being more stable (Martell, *et al.*, 2009). The formation of $ZnLac_2$ and $ZnLac_3^{-}$ complexes reduces the recorded distribution coefficients from ~5 at pH 4.5 in acetate media to ~0.8 in lactate media (translating to a decrease from 99% to 92% extraction). In citric acid zinc maintains a ZnHCit complex (Figure S3d), further supressing the extraction of zinc, to ~0.2 at pH ~4.5 and a maximum of ~1 at pH 5.8, where the anionic $ZnCit_2^{4-}$ species becomes apparent.

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

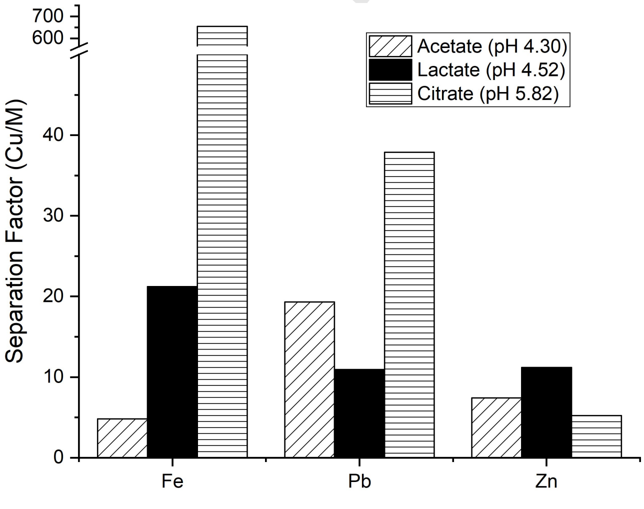


Figure 13: MTS9301 separation factors of copper from iron, lead and zinc extracted from acetate, lactate and citrate media at 20 °C after 24hr of contact time.

4.5 Performance of MTS9501 in weak acid media

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

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

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

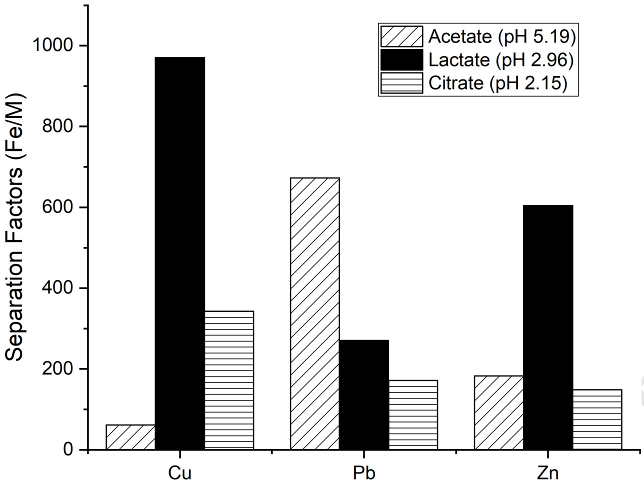


Figure 14: MTS9501 separation factors of copper from iron, lead and zinc extracted from acetate, lactate and citrate media at 20 °C after 24hr of contact time.

4.6 Performance of C107E in weak acid media

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

Within acetic acid, changing the pH seems to allow for either the selective extraction or rejection of iron, by shifting the pH either side of the acetate pK_a, this could possibly be due to the higher presence of the $FeAc^+$ species beyond a pH of 4; in this case, the decrease in concentration is observed beyond the pH where Fe^{2+} complexes with acetate (Figure S1b). This is also contrary to what had been observed for ferric ions within a similar media where no Fe^{3+} had been taken up by the weak acid resin throughout the same pH range (Bezzina, *et al.*, 2018a).

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

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

5 Conclusions

The removal of metals from simulated weak acid sewage sludge leachates have been studied, with promising results. The complexing nature of carboxylic weak acids stabilise metal ions in solutions generating broader functional pH regions for metal extraction. Depending on the metals present in solution, a variety of different combinations of acids and resin functionalities could be used for selective separation processes. While lactate complexes are more stable in solution than acetate, neither of these ligands compared to the stability of citrate complexes. The increased stability in solution could render extraction processes more expensive, as more solid phase extraction stages would be required for removal of the target metals. TP214 has a high affinity for copper, as well as iron in acetate media, and must be taken out prior to a precious metals recovery stage. The amidoxime functionalised resin MTS9100 is rendered ineffective in lactate and citrate media. MTS9570 maintained a high affinity for iron within all media, while decreasing extraction efficiency of copper, lead and zinc within lactate and citrate media. The phosphonic acid functionalised resin MTS9501 is extremely efficient at extracting copper and iron in acetate media, while only iron extraction is maintained in lactate, lead extraction displays little response to the change of buffer. The weak acid functionalised resin selectivity for lead was significantly increased within lactic acid media, with speciation dependent extraction in acetate media The MTS9301 IDA functionalised resin displayed the best performance for metals in all media. This resin was especially effective at the removal of metals from an acetic acid media, with high separation of copper. Further investigation is required to understand the kinetics, as well as capacity of the MTS9301 resin within these weak acid systems.

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References

Adam, C., Kley, G., and Simon, F.G., 2007, "Thermal Treatment of Municipal Sewage Sludge Aiming at Marketable P-Fertilisers," Mater. Trans.; 12(48), 3056–3061.

Aktas, S. and Morcali, M.H., 2011, "Gold uptake from dilute chloride solutions by a Lewatit TP 214 and activated rice husk," Int. J. Miner. Process., 101(1-4), 63–70.

Bezzina, J.P., Ogden, M.D., Moon, E.M., and Soldenhoff, K.L., 2018a, "REE behavior and sorption on weak acid resins from buffered media," J. Ind. Eng. Chem., 59, 440–455.

Bezzina, J.P., Amphlett, J.T.M., and Ogden, M.D., 2018b, "Extraction of Heavy Metals from Simulant Citrate Leachate of Sewage Sludge by Ion Exchange," Journal of Ion Exchange, 29(3), 1–7.

Brown, P.L. and Ekberg, C., 2016, Hydrolysis of Metal Ions. Wiley-VCH.

Chiariza, R., Horwitz, E.P., Alexandrators, S.D., and Gula, M.J., 1997, "Diphonix® Resin: A Review of Its Properties and Applications," Sep. Sci. Technol., 32(1-4), 1–35.

Cortina, J.L., Miralles, N., Aguilar, M., and Sastre, A.M., 1996, "Distribution studies of Zn (II), Cu (II) and Cd (II) with Levextrel resins containing 'Lewatit TP807'," Hydrometallurgy, 40(94), 195–206.

Dabrowski, A., Hubicki, Z., Podkoscielny, P., and Robens, E., 2004, "Selective removal of the heavy´ metal ions from waters and industrial wastewaters by ion-exchange method," Chemosphere, 56(2), 91–106.

Department for Enivironment, Food and Rural Agriculture (DEFRA), 2006, "Code of Practice for Agriculture Use of Sewage Sludge".

Doona, C.J., and Stanbury, D.M., 1996, “Equilibrium and Redox Kinetics of Copper(II)-Thiourea Complexes,” Inorg. Chem., 35(11), 3210–3216.

Edebalim, S., and Pehlivan, E., 2016, “Evaluation of chelate and cation exchange resins to remove copper ions,” Powder Technol., 301, 520–525.

European Commision, 1986, Council Directive on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture [82/278/EEC]. The Council of the European Communities.

FAO, 2015, “World fertilizer trends and outlook to 2019,” tech. report.

Field, T.B., McCourt, J.L., and McBryde, W.A.E., 1974, “Composition and Stability of Iron and Copper Citrate Complexes in Aqueous-Solution,” Can. J. Chem., 52(17), 1974, 3119–3124.

Filho, S., Castagno, P.J., and Elicker, K.R.L., 2014, “Electroremediation of heavy metals in sewage sludge,” ABEQ, 31(2), 365–371.

Fytili, D., and Zabaniotou, A., 2008, “Utilization of sewage sludge in EU application of old and new methods – A review,” Renew Sustain Energy Rev, 12(1), 116-140.

Fu, F., and Wang, Q., 2011, “Removal of heavy metal ions from wastewaters: A review,” J. Environ. Manage., 92(2), 407–418.

Gans, P., Sabatini, A., and Vacca, A., 2009, “Hyperquad Simulation and Speciation”.

Gorman, J.E., and Clydesdale, F.M., 1984, “Thermodynamic and Kinetic Stability Constants of Selected Carboxylic Acids and Iron,” J. Food Sci., 49, 500–503.

Gu, T., Rastegar, S.O., Mousavi, S.M., Li, M., and Zhou, M., 2018, “Advances in bioleaching for the recovery of metals and bioremediation of fuel ash and sewage sludge,” Bioresource Technol., 261, 428–440

Hubicki, Z., Leszczynska, M., Łodyga, B., and Łodyga, A., 2007, “Recovery of palladium(II) from chloride and chloride-nitrate solutions using ion-exchange resins with S-donor atoms,” Desalination, 207(1-3) 80–86.

Kalka, H., 2015, “Aqion: Manual (selected topics)”, http://www.aqion.de/site/98?

Kołodynska, D., and Hubicki, Z., 2009, “FT-IR / PAS Studies of Cu (II)– EDTA Complexes Sorption on´ the Chelating Ion Exchangers,” Ind. Eng. Chem. Res, 116(3), 340–343.

Krzewska, S., Podsiadły, H., and Pajdowski, L., 1980, “Studies on the reaction of copper(II) with thiourea—III,” J. Inorg. Nucl. Chem., 42(1), 89–94.

Martell, A.E., Smith, R.M., and Motekaitis, R.J., 2009, “Database 46: NIST Critically Selected Stability Constants of Metal Complexes”.

Maurer, M., and Schwegler, P., 2003, “Nutrients in urine: energetic aspects of removal and recovery,” Water Sci. Technol., 48(1), 37–46.

McKevitt, B., and Dreisinger, D., 2009, “A comparison of various ion exchange resins for the removal of ferric ions from copper electrowinning electrolyte solutions Part I: Electrolytes Containing No Other Impurities,” Hydrometallurgy, 98(1-2), 116.

Mendes, F.D., and Martins, A.H., 2016, “Selective sorption of nickel and cobalt from sulphate solutions using chelating resins,” Int. J. Miner. Process, 74(1-4), 359–371.

Morcali, M.H., Zeytuncu, B., and Yucel, O., 2013, “Comparison of the adsorption by rice hulls and Lewatit TP 214 of platinum from chloroplatinic solution,” J. Serb. Chem. Soc., 78(6), 811–826.

del Mundo Dacera, D., and Babel, S., 2006, “Use of citric acid for heavy metals extraction from contaminated sewage sludge for land application,” Water Sci. Technol., 54(9), 129–135.

Naoto TAKENO, 2005, “Atlas of Eh-pH diagrams - Intercomparison of thermodynamic databases,” tech. report, National Institute of Advanced Industrial Science and Technology.

Pesavento, M., Biesuz, R., Gallorini, M., and Profumo, A., 1993, “Sorption mechanism of Trace Amounts of Divalent Metal ions on a Chelating Resin Containing Iminodiacetate Groups,” Anal. Chem., 65(18), 2522–2527.

Rao, K.S., Dash, P.K., Sarangi, D., Chaudhury, G.R., and Misra, V.N., 2005, “Treatment of wastewater containing Pb and Fe using ion-exchange techniques,” J. Chem. Technol. Biot., 80(8), 892–898.

Riley, A.L., Pepper, S.E., Canner, A.J., Brown, S.F., and Ogden, M.D., 2018, “Metal recovery from jarosite waste–A resin screening study,” Separ. Sci. Technol., 53(1) 22–35.

Rosenheim, A. and Meyer, V.J., 1906, “Über die Thiokarbamidverbindungen zweiwertiger Metallsalze,” Z. Anorg. Chem. 34(62) 13–27

Soldatov, V.S., Zelenkovskii, V.M., and Orlovskaya, L.A., 2011, “Sorption of bivalent ions by a fibrous chelating ion exchanger and the structure of sorption complexes,” React. Funct. Polym., 71(1), 49–61.

Spangberg, J., Tidaker, P., and Jonsson, H., 2014, “Environmental impact of recycling nutrients in human excreta to agriculture compared with enhanced wastewater treatment,” Sci. Total Environ., 493, 209-219.

Sreekrishnan, T.R. and Tyagi, R.D., 1996, “A comparative study of the cost of leaching out heavy metals from sewage sludges,” Process Biochem., 31(1) 31–41.

Stylianou, M., Kollia, D., Haralambous, K.J., Inglezakis, V., Moustakas, K., and Loizidou, M., 2007, “Effect of acid treatment on the removal of heavy metals from sewage sludge,” Desalination, 216(1-3) 73–81.

United Nations, 2013, “World Population Prospects: The 2012 Revision. Highlights and Advance Tables,” Population and development review, 36, 775–801.

Vriens, B., Voegelin, A., Hug, S., Kaegi, R., Winkel, L., Buser, A., and Berg, M., 2017, “Quantification of Element Fluxes in Wastewaters: A Nationwide Survey in Switzerland,” Environ. Sci. Technol., 51, 10943–10953.

Weigand, H., Bertau, M., Hubner, W., Bohndick, F., and Bruckert, A., 2013, “RecoPhos: Full-scale fertilizer production from sewage sludge ash,” Waste Manage., 33(3), 540–544.

Westerhoff, P., Lee, S., Yang, Y., Gordon, G.W., Hristovski, K., Halden, R.U., and Herckes, P., 2015, “Characterization, Recovery Opportunities, and Valuation of Metals in Municipal Sludges from U.S. Wastewater Treatment Plants Nationwide,” Environ. Sci. Technol., 49(16), 9479–9488.

Ueno, Y., and Fujii, M., 2001, “Three Years’ Experience of Operating and Selling Recovered Struvite from Full-Scale Plant,” Environ. Technol., 22(11), 1373–1381.

Highlights

- MTS9301 is effective at extracting selected metal ions from all tested media
- Citrate media is effective at hindrance of metal adsorption
- TP214 can selectively extract copper from high complexing solutions
- 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: