Extraction of Heavy Metals from Simulant Citrate Leachate of Sewage Sludge by Ion Exchange

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(Manuscript received March 30, 2018; accepted June 5, 2018)

Abstract

A shortage of natural resources has led to a focus towards the use of sewage sludge as a fertiliser source due to its high phosphate content. One of the main issues with the use of sewage sludge as a fertiliser source is the concentration of heavy metals, particularly copper, lead and zinc. Economical alternatives to regular lixiviants (sulphuric acid, nitric acid, etc.) for the leaching of heavy metals from solids are weak complexing acids. Ion exchange technology offers an effective method for the recovery of these metals from the leachate. This study presents the pH dependence of Cu, Fe, Pb and Zn recovery from citrate media by the ion exchange resins TP214, MTS9100, MTS9570, MTS9301, MTS9501 and C107E. Copper recovery was found to be maximised by the use of either TP214 at a pH of 5 or MTS9301 at a pH of 2. The phosphonic acid functionality containing resins, MTS9570 and MTS9501 were found to be the most effective for the removal of iron at a pH of 2 and 5, respectively. TP214 and MTS9570 show promising results for the recovery of lead, with the caveat of large copper and iron recovery, respectively and MTS9301 shows high affinity towards zinc at high pH, although poor separation from copper.

Keywords: Citric acid media, Sewage sludge, Metal recovery, Sustainability

1. Introduction

As the global population increases towards ten billion¹ and pressure on natural phosphate reserves for fertiliser production increases³, the reuse of waste as a phosphate source is becoming more prevalent²⁴⁶. Sewage sludge is a high volume waste that is high in phosphate content, up to 44% of the concentration of commercial fertilisers³. It sees little use as a fertiliser, though it has great potential, with the additional benefit of increasing proportionately to population. One of the major issues pertaining to the use of sewage sludge as a fertiliser source is the inherent concentration of heavy metals.

Relatively high concentrations of heavy metals are common within waste from municipal wastewater treatment plants, ending within the solid waste product, which becomes problematic in the reuse of the sludge material. The inclusion of industrial discharge and road water run-off to these plants can lead to a large influx of toxic and precious metals, exacerbating the issue⁶⁻¹². Studies on the metals content of sewage sludge within Switzerland¹² and America¹⁹ have found appreciable concentrations of many precious metals. Remote outliers of Swiss water treatment plants were found to contain up to 40 mg.kg⁻¹ gold and silver¹², potentially generating a source of value.

For the current study, however, a focus has been placed upon the removal of metals for the reuse of sludge as a phosphate source. Throughout European waste water treatment plants, median values of dangerous heavy metals have been found to be over that of the guideline for use on agricultural crops⁶,¹³ (a comparison of these values and the guidelines is displayed in Fig. 1). This article will therefore be focused upon the recovery copper, lead and zinc from a synthetic sewage sludge PLS.

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Fig. 1 Comparison of the E.U. guideline limits for the agricultural use of sewage sludge\textsuperscript{10} and median values of heavy metals within E.U. sewage sludge\textsuperscript{6}.

While bioleaching has been extensively researched with regards to the treatment of sewage sludge\textsuperscript{14-16}, it has been found that acid leaches become more cost-effective with larger capacity processes\textsuperscript{17}. Further complicating the matter of leaching is the lixiviants chosen for the leach. Traditional leaching acids, such as sulphuric acid, phosphoric acid and nitric acid have been reported as suitable candidates for the removal of metals from sewage sludge\textsuperscript{18-20}, however it is postulated that weak organic acids provide a cheaper, environmentally safe alternative\textsuperscript{19, 21}.

Currently, the removal of metals from sewage sludge can render the process non-profitable\textsuperscript{22}. Removal of metals from the immobile phases by the use of weak organic acid could counteract this price barrier\textsuperscript{21}. Utilising a weak organic acid as the lixiviant for leaching can reduce the amount of acid required to be added due to complexation, therefore reduce the need for neutralisation of the raffinate, which will be used, in this case, as fertiliser. The low concentrations of these metals (when compared to traditional resources such as metal ores), coupled with the high concentration of potential sorbents within sludge\textsuperscript{23}), however, can also mean that extraction of metals is inefficient. An issue that may be circumvented by the combination of a leaching process with solid-phase extraction in a resin-in-leach or resin-in-pulp style process.

With the high concentrations of iron in comparison to more valuable metals within the sewage sludge waste, it may be necessary to utilise multiple resins in order to derive value from the solid\textsuperscript{23}. The use of a complexing weak acid as the lixiviant can allow for the higher separation of metals by adsorption, especially when considering metallic ions that have been traditionally difficult to separate (such as rare earth elements)\textsuperscript{23}.

Currently, there is a paucity of data in the literature surrounding the adsorption of metals from weak acid media. Industrial processes tend to focus on extraction from industrial solutions of strong acid media (e.g. HCl, H\textsubscript{2}SO\textsubscript{4} and HNO\textsubscript{3})\textsuperscript{24-29}. This paper will focus on the extraction of problematic heavy metals (zinc, lead and copper) from buffering regions of weak organic acids utilising ion exchange resins.

This paper presents the screening of multiple resins of differing functionalities and the affect pH has on the extraction of metal ions from citric acid buffered media.

### 2. Experimental

#### 2.1. Reagents and stock solutions

All chemicals used were of analytical grade or higher and purchased from Sigma-Aldrich unless otherwise specified. Citric acid monohydrate and calcium chloride were purchased

| Name           | Functionality          | Matrix    | Ionic form as shipped | Physical form | Capacity | Size (µm) | Water retention (wt. %) | Specific Gravity |
|----------------|------------------------|-----------|-----------------------|---------------|----------|-----------|------------------------|-----------------|
| Lewatit MonoPlus TP214 | Thiourea | PS-DVB | Free base | Spherical beads | 1.0 eq/L | 550 | 43 - 48 | 1.1 |
| Purolite MTS9100 | Amidoxime | PA-DVB | Free base | Spherical beads | 40 g/L Cu\textsuperscript{2+} | 300 - 1200 | 52 - 60 | 1.19 |
| Purolite MTS9501 | Phosphonic + sulphonic | PA-DVB | H\textsuperscript{+} | Spherical beads | 18 g/L Fe\textsuperscript{3+} | 550 - 750 | 55 - 70 | 1.19 |
| Purolite MTS9301 | Iminodiacetic | PS-DVB | Na\textsuperscript{+} | Spherical beads | 50 g/L Cu\textsuperscript{2+} | 425 - 1000 | 52 - 60 | 1.18 |
| Purolite MTS9501 | Aminophosphonic | PS-DVB | Na\textsuperscript{+} | Spherical beads | 24 g/L Ca\textsuperscript{2+} | 425 - 850 | 55 - 65 | 1.13 |
| Purolite C107E | Carboxylic | PA-DVB | H\textsuperscript{+} | Spherical beads | 3.6 eq/L | 300 - 1600 | 53 - 58 | 1.17 |
from Fisher Scientific. Lewatit MonoPlus TP214 was supplied by Lanxess and all other ion exchange resins were supplied by Purolite. Resin characteristics are outlined within Table 1 and functional groups of the resins screened are given in Fig. 2. Resins were preconditioned with 10 bed volumes 1 M H2SO4 on an orbital shaker overnight, then washed 5 times with 10 bed volumes of deionised water, then stored in deionised water.

![Chemical structure of the functionalities of the ion exchange resins tested throughout this study (A = TP 214, B = MTS9100, C = MTS9570, D = MTS9301, E = MTS9501, F = C107E; semicircles represent the matrix).](image)

Ca(II), Cu(II), Fe(II), Pb(II) and Zn(II) were added by dissolution of the respective chloride salt (Pb2+ was generated using the nitrate salt due to the solubility) into deionised water (18 MΩ). Metal concentrations were measured utilising a Perkin Elmer Atomic Absorption Spectrometer AAnalyst 400. Calibration of the instrument was performed by standard solutions diluted with 1% nitric acid.

2.2. Batch extractions from buffered media

Pre-contact solutions were adjusted to pH 1 below pKa1 and pH 1 above pKa3 of citric acid, displayed in Fig. 3.

Metal containing solutions (50 mL, 100 ppm M2+, 0.5 M Cl−, 0.5 M Citric acid) where contacted with resins (2 mL) overnight with agitation by orbital shaker. Metal uptake by the resin was determined by a difference between post- and pre-contact solution concentrations. The extraction percentage (E%) was calculated using the equation:

\[ E\% = \frac{C_i - C_e}{C_i} \times 100 \]  

where \( C_i \) is the concentration of the solution pre-contact and \( C_e \) is the concentration of the solution at equilibrium.

Measurements of pH were conducted using a Ag/AgCl reference electrode calibrated from pH 2-10 using standard buffer solutions. Error margins were calculated by triplicate measurement of the initial working solutions prior to pH adjustment.

![Reaction schematics of the three deprotonations of citric acid.](image)

3. Results

The extraction of common problematic heavy metals from solutions buffered by citric acid was measured at a pH range spanning over the buffering region of the acid. Figure 2 displays the extraction of copper, iron, lead and zinc from citric acid solutions by TP214 (Fig. 4), MTS9100 (Fig. 5), MTS9570 (Fig. 6), MTS9301 (Fig. 7), MTS9501 (Fig. 8) and C107E (Fig. 9) as a function of pH. Generally copper or iron were observed to be extracted most effectively over the pH range studied.

![Extraction of metal ions by TP214 as a function of pH. Cu = ▲, Fe = ▽, Pb = ◦, Zn = □.](image)
The extraction of metal ions from citric acid media by the thiourea functionalised resin TP214 as a function of pH is displayed in Fig. 4. Copper is extracted very effectively, however extraction percentage is reduced as pH increased above 4.5. Lead, iron and zinc extraction decreases with increasing pH. Throughout the pH range examined, the order of affinity of this resin may be defined as Cu >> Pb > Fe > Zn.

Figure 5 displays the pH dependence of the extraction of Cu$^{2+}$, Fe$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ by MTS9100 from citric acid media. While at pH ~2.0 the extraction of iron is ~50%, this decreases dramatically as pH increases. Extraction of remains under ~20-30% for all other metals across the pH range studied. Extraction of both copper and lead increases towards a pH of 6.5, reaching ~30%.

The pH dependence of the extraction of metals by MTS9570 in citrate media is displayed in Fig. 6. At lower pH (<3), MTS9570 displays a high affinity for iron, extracting almost 100% from solution, followed by lead, with ~60% extraction. The extraction of these metals decreases with increasing pH, however, iron, zinc and copper display a negligible extraction above pH 5.5. Conversely, lead displays an increasing trend in extraction beyond pH 5.5. At the lower pH range examined the order of affinity of metals is Fe >> Pb > Zn > Cu, with this becoming Pb >> Zn > Fe > Cu at higher pH.

Figure 7 shows the extraction of metals by MTS9301 from citric acid media as a function of pH. The iminodiacetic acid functionality of MTS9301 shows a high affinity toward copper throughout the pH range studied. At lower pH, iron shows peak extraction at ~50%, this decreasing with an increase in pH, which is the opposite to that of zinc. Lead begins with a low extraction, then increases to ~55% at a pH of ~2.75, this then decreases to a trough at pH 4.5 before increasing again to ~65% at pH ~6. MTS9301 is, by far, the best extractant for zinc, with around 95% extracted towards the higher pH examined. The low pH affinity of this resin is Cu >> Fe >> Zn = Pb, which becomes Cu > Zn >> Pb >> Fe towards the higher pH of the range tested.

Fig. 5  Extraction of metal ions by MTS9100 as a function of pH. Cu = ▲, Fe = ▽, Pb = ●, Zn = ■.

Fig. 6  Extraction of metal ions by MTS9570 as a function of pH. Cu = ▲, Fe = ▽, Pb = ●, Zn = ■.

Fig. 7  Extraction of metal ions by MTS9301 as a function of pH. Cu = ▲, Fe = ▽, Pb = ●, Zn = ■.
4. Discussion

4.1 Extraction of copper

In the present study copper is taken up most efficiently by thiourea and iminodiacetic acid functionalities. The thiourea functionalised resin shows suppression of copper recovery above pH 5, which aligns with pKa2 of citric acid (pH 4.75). This decrease in copper extraction towards the higher pH studied can be explained by the higher complexation of copper-citrate between pH 5 and 6\(^{29}\), stabilising copper within solution.

The iminodiacetic acid functionality binds to copper consistently across all tested pH within citric acid with a slight dip in extraction towards lower pH. The affinity for copper by MTS9301 has also been reported elsewhere at pH < 2\(^{24}\), however within the previous studies iron is extracted in comparable amounts. The high selectivity of iminodiacetic acid functionalities for copper has also been reported by Mendes and Martins\(^{26}\) as well as Edebali and Pehlivan\(^{29}\), who also reports a high selectivity of bis-picolyamine functionalities for copper.

Both functionalities display similar separations from metals at their optimum pH values for Cu\(^{2+}\) recovery (5 and 2 respectively for TP214 and MTS9301), displayed in Fig. 10. Both the separation of Fe and Pb are almost identical for both MTS9301 and TP214. The rejection of Zn by TP214 is far more prominent, with a separation factor over four times that of the iminodiacetic functionalised resin.

4.2 Extraction of iron

Both MTS9570 and MTS9501 are efficient extractors of iron, being due to both having phosphonic acid functionalities attached to the resin. (See Fig. 11.) Riley et al. has also reported the affinity of phosphonic acid functionalised resins towards iron\(^{24}\). This previous study, however, measured extraction in sulphuric acid media at a maximum pH of 2.

The composite functionality of MTS9570 does not compete with a dissociated citrate anion for metal binding, while the pure aminophosphonic functionalised resin, MTS9501 maintains the high iron affinity.
The highest extraction for iron over all other metals studied by MTS9570 is at a pH of ~1.75, which is also where the affinity of other metals is at the peak. The high extraction of iron by MTS9501 throughout all pH values screened allows for selective separation of iron as the extraction of other metals is suppressed to a maximum of <25% at a pH of ~5.

4.3 Extraction of lead

The observed general trend for lead recovery is that it is extracted less effectively than copper and iron. This being the case, however, TP214 and MTS9570 do show promising pH dependant recovery of lead. These resins show lead as the metal with the second highest extraction affinity.

While alone there may not be effective separation of lead from other metals, there is the potential to utilise resins sequentially to minimise co-extraction of iron and copper by selectively removing them from solution first. Both TP214 and MTS9570 are reported to have a peak lead extraction at pH ~2.5. The separation factors of lead from other metals by TP214, is much higher at this pH, while MTS9570 maintains a high affinity for iron (represented in the separation factors presented in Fig. 12.

With an increased pH, MTS9570 is able to successfully reject other metals and increase extraction of lead (to a maximum of ~35% extraction at pH ~6.5). The iminodiacetic acid functionality is also able to extract lead to a high degree. At a pH of ~5.5, ~60% of the lead has been extracted, however at this same pH ~95% of the copper and ~90% of the zinc is extracted as well.

Octylamino pyridine ligands have been used to successfully and selectively extract lead from an aqueous succinate solution containing multiple other heavy metal contaminants. This study had reported that lead extraction increases from ~20% to almost 100% beyond a pH of ~8, which could potentially describe the increase in lead extraction towards the higher pH range examined within this study. While no entirely selective functionality was determined throughout this screening study, perhaps an aromatic nitrogen, and aliphatic chain functionality could potentially increase selectivity towards lead.

4.4 Extraction of zinc

Of the resins examined, only MTS9301 seems suitable for the extraction of zinc. Towards pH 6, MTS9301 reaches zinc extractions of ~90%. With a lower concentration of copper within solution of citrate media, MTS9301 could be an effective extractant for zinc. While MTS9501 is the next most effective, the maximum extraction of zinc is only ~50%, having far less of a recovery than iron in solution. This high affinity of zinc to iminodiacetic acid and amino/amino-acetic acid groups has been observed previously, along with the removal from a highly concentrated solution, lacking dissolved iron species.

4.5 Summary

From the results obtained it is clear that the amidoxime and the carboxylic acid functionalised resins are not well suited for extraction of the selected metals from citric acid media. While above pK\textsubscript{a3} of citric acid, the extraction of lead begins to increase, beyond this point there is possibility for precipitation of the metals. Aqueous Cu, Fe, Pb and Zn citrate complexes are more stable than those formed by the functionalities on each resin, therefore recoveries are low.

At pH values below the pK\textsubscript{a1} of citric acid, the extraction of lead, copper and zinc by MTS9501 decreases. These extractions then increase beyond the pK\textsubscript{a2} of citric acid, suggesting a benefit to the complexation of these metals upon extraction by phosphoric acid groups. The extraction of copper, lead and zinc from solution by MTS9570 is likely due to the presence of the phosphonic functional as this behaves similarly to MTS9501.

The iminodiacetic acid functionalised resin displayed a high affinity at copper throughout lower pH values, with the selectivity for lead and zinc increasing with pH. Lead displays a higher affinity for the resin functionality as the citrate ion is deprotonated further, however there is less of an affinity as the citrate ion reaches pK\textsubscript{a3}, with extraction again increasing beyond this pH.

5. Conclusion

A pH screening study of the extraction of metals from a
simulated citric acid sewage sludge PLS utilising a selection of ion exchange functionalities has been reported. Carboxylic acid and amidoxime functionised ion exchange resins were found inappropriate for the extraction of Cu, Fe, Pb and Zn from citrate media, across pH ~1.5-6.5. No resin was capable of effectively removing lead or zinc without also extracting large amounts of either copper or iron. While no singular resin functionality was found capable of extracting all of the focus metals, a combination of resins utilised in series could allow for separation of metals and valorisation of this material\(^\text{[20]}\). The process that one could envision being created using highest concentration (within sewage sludge) and separation factors of metals obtained within this study would be conducted sequentially from iron, copper, zinc then lead. Future work within this research will include determination of the competition between metals for binding to the resin surface through column breakthrough experiments.

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