# Valorisation of Sewage Sludge by Removal of Heavy Metals

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## Introduction

The high projected increase in global population (UNDESA, 2013) has generated concerns surrounding food security (WFP, 2017) and increases pressure on the current global phosphate reserves. This creates a need for more common-place use of sewage sludge as an alternative agricultural nutrient sources, which is plagued by relatively high concentration of heavy metals (in particular copper, lead and zinc) (Fytili and Zabaniotou, 2008). Overcoming the issue of heavy metals within sewage sludge, for unrestricted use as fertiliser, will require economically favourable and inoffensive removal processes (Westerhoff *et al.*, 2015).

Removal of metals from the immobile phase requires alternatives to the acid and neutralisation intensive approaches of strong acid leaching. The use of complex forming weak organic acids could allow for higher pH leaches, requiring less acid for mobilisation of metals and less neutralisation costs for the fertiliser slurry (del Mundo Dacera and Babel, 2006; Wang, 2009). The combination of weak acid leaching with ion exchange, resin-in-pulp (RIP), could lead to the removal of trace heavy metals from sewage sludge (Mubarok and Irianto, 2016), allowing for less restrictions on the use of this valuable resource for crop production.

This work explores the extraction of heavy metals from a simulant sewage sludge using resin-in-pulp methodology. A resin screening study from previous work will be briefly presented, followed by the exploration of weak acid leaching of the metals from a simulated sewage sludge. The final exploration of this study will be the combination of these two processes to understand the feasibility of the RIP process on sewage sludge. This work will present novel work towards a RIP process for the heavy metal removal from a simulant sewage sludge.

## **Experimental Methods**

Resin screening studies were conducted in previous studies (Bezzina *et al.*, 2018; Bezzina *et al.*, 2019), and will be presented in brief to discuss the justification of resin and lixiviants pH choice. Preliminary leaching media studies were produced by contact of copper, lead and zinc oxide powders with 50 mL of 0.5 M acid (citric acid, acetic acid and lactic acid) at optimal pH within buffering region, agitated by orbital shaker (250 RPM) at 20°C. Leaches were performed by overhead agitation (300 RPM, 20°C) of a modified simulant faecal matter (Wignarajah and Litwiller, 2006) with the addition of metal oxides, pH was adjusted after acid addition. RIP studies were conducted by 24-hour contact of a resin with a 10-day leach.

#### **Results and Discussion**

From the preliminary leaching results of a metal oxide mixture (oxides and acid) it can be deduced that copper is the most difficult species to solubilise from their respective oxides Figure 1. While both lead and zinc reach >90% dissolution, regardless of media and pH, copper is leached to <20%, with maximum extraction reached by either citric or lactic acid at pH 3.00, reaching 15.4 and 16.6% respectively. From these results, and the resin screening study (Bezzina *et al.*, 2018; Bezzina *et al.*, 2019), the lixiviant of choice was determined to be acetic acid.



Figure 1. Percentage of copper, lead and zinc oxide dissolved with citric acid (pH 3, 4.5 and 6), acetic acid (pH 3.5, 4 and 4.5) and lactic acid media (pH 3, 4 and 4.5) (200 ppm metals; 24-hour contact; 20°C; 0.5 M acids).

The results of the leaching from simulant sewage sludge, displayed in Figure 2, show that the dissolution of zinc occurs rapidly, once the acid is added. Due to adsorption processes within the organic matter of the

simulant, leaching recovery of lead and copper has an observable decrease. Zinc is leached to a maximum of ~90% within both pH 4.0 and 3.5 leaching experiments, while this is reduced to ~70% at pH 4.5. Neither lead nor copper reach >10% extraction across the 10 days of leaching. Lead reaches an equilibrium in <6 hours at pH 3.5 and 4.0, with no appreciable gain in concentration after this mark. The concentration of copper in solution increases substantially from the 20-hour mark, without reaching equilibrium, leading to the assumption of an activation energy barrier.



Figure 2. Leaching kinetics of copper, lead and zinc by acetic acid at pH 3.5 (A), pH 4.0 (B) and pH 4.5 (C) (100 ppm metals; 20°C; 0.5 M acids).

The difficulty of dewatering sewage sludge generates a difficulty for the removal of mobile metals from the slurry, as filtered slurry is exceedingly difficult. When comparing the results obtained from the simulant sludge leach comparted to the oxide dissolution tests, it is also observed that the leaching process may suffer from adsorption of mobile metals to organic material within the sludge, known as preg-robbing. Resin-in-pulp systems can potentially negate both of these issues, as the resin beads are easily screened from slurries, and the parallel leaching and preferential adsorption to a resin surface can avoid the issues with preg-robbing (Mubarok and Irianto, 2016). Preliminary studies of resin within RIP (MTS9301) have shown that resin functionalities are still effective within the leach slurry. MTS9301 is capable of uptake of >90% of both copper and zinc that is leached after a 10-day period, while only 75% of the lead is up-taken. Current research work is continuing to explore the RIP process in further detail.

## Conclusions

Weak, carboxylic acids have been used for the dissolution of metal oxides, and their leaching from a simulant sewage sludge. Extraction was decreased substantially when leached from a simulant sewage sludge, however MTS9301 has been used within a preliminary RIP study, and shown that it is still effective for the extraction of mobile metals from a leach slurry. This creates the potential for the resin to increase the effectiveness of the weak acid leaches towards the engineering of a process for the removal of metals from sewage sludge.

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