

JYU DISSERTATIONS 486

Sini Reuna

Development of a Method for Phosphorus Recovery from Wastewaters



UNIVERSITY OF JYVÄSKYLÄ
FACULTY OF MATHEMATICS
AND SCIENCE

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Esitetään Jyväskylän yliopiston matemaattis-luonnontieteellisen tiedekunnan suostumuksella
julkisesti tarkastettavaksi tammikuun 28. päivänä 2022 kello 12.

Academic dissertation to be publicly discussed, by permission of
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JYVÄSKYLÄN YLIOPISTO
UNIVERSITY OF JYVÄSKYLÄ

JYVÄSKYLÄ 2022

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ISBN 978-951-39-8997-2 (PDF)

URN:ISBN:978-951-39-8997-0

ISSN 2489-9003

Permanent link to this publication: <http://urn.fi/URN:ISBN:978-951-39-8997-2>

ABSTRACT

Reuna, Sini

Development of a method for phosphorus recovery from wastewaters

Jyväskylä: University of Jyväskylä, 2022, 67 p.

(JYU Dissertations

ISSN 2489-9003; 486)

ISBN 978-951-39-8997-2 (PDF)

As an irreplaceable element for all life on Earth, the supply of phosphorus (P) needs to be preserved. Since the natural inorganic resources are slowly depleting, one gazes upon secondary sources for P such as sewage sludge. By developing recovery processes for phosphorus from secondary sources we can respond to the ever-increasing consumption of phosphate fertilizers and ensure that future generations will have a secure food supply.

In this thesis, a method for P recovery from post-precipitated sewage sludge is presented. The research has been part of the development of Helsinki Region Environmental Services' RAVITA -process. The literature review describes the already existing technologies for P recovery and the general principles of the techniques used in the method development such as the design of experiments (DOE) and solvent extraction. The experimental section briefly defines the experimental procedures used in the original publications.

In the results section first, the results from elemental analysis of the post-precipitated sludge are shown. The main components in the sludge are phosphorus and the metal used in precipitation in the production of the sludge. Trace metal concentrations in the post-precipitated sludge are below the average trace metal content of the sewage sludge in the EU. Then the findings from the optimization of the leaching procedure for post-precipitated sewage sludge are presented. Phosphoric acid was selected as leaching acid and the optimization was systematically implemented with the design of experiments procedure. Last the purification procedure for the obtained phosphoric acid solution was investigated. The precipitation metal is recovered from the phosphoric acid solution with solvent extraction.

Keywords: phosphorus, municipal sewage sludge, solvent extraction, recovery, wastewater

TIIVISTELMÄ

Reuna, Sini

Menetelmän kehittäminen fosforin talteenottamiseksi jätevesistä

Jyväskylä: Jyväskylän yliopisto, 2022, 67 p.

(JYU Dissertations

ISSN 2489-9003; 486)

ISBN 978-951-39-8997-2 (PDF)

Fosfori on kaikelle maapallon elämälle korvaamaton alkuaine ja on ehdottoman tärkeää, että sitä on saatavilla myös tulevaisuudessa. Luonnollisten fosforivarantojen hiljalleen vähetessä, katse kiinnittyy vaihtoehtoisiin fosforin lähteisiin, kuten jätevesiin ja -lietteisiin. Kehittämällä fosforin talteenottoprosesseja toissijaisista lähteistä, voidaan tulevaisuudessa vastata kasvavaan fosfaattilannoitteiden kulutukseen ja varmistaa ruoan riittävyys myös tuleville sukupolville.

Tässä väitöskirjassa esitetään menetelmä fosforin talteen ottamiseksi jälkisaostetusta jätevesilietteestä. Tutkimus on osa Helsingin seudun ympäristöpalvelujen kehittämää RAVITA™ -prosessia, joka on suunniteltu ottamaan talteen fosforia ja tyypeä jätevedestä. Kirjallisuuskatsauksessa perehdytään jo olemassa oleviin fosforin talteenottotekniikoihin sekä tutustutaan prosessin kehityksessä käytettyihin menetelmiin, kuten tilastolliseen koesuunnitteluun (DOE) ja neste-neste uuttoon. Kokeellinen osa esittelee lyhyesti alkuperäisissä julkaisuissa käytetyt kokeelliset menetelmät.

Tulososiossa käsitellään ensimmäiseksi jälkisaostetun lietteen alkuaineanalyysin tulokset. Lietteiden pääkomponentit ovat fosfori ja lietteiden saostuksessa käytetty metalli. Raskasmetallipitoisuudet jälkisaostetussa lietteessä ovat selkeästi matalammat kuin muiden EU-maiden keskimääräiset raskasmetallipitoisuudet lietteessä. Seuraavaksi esitetään jälkisaostetun jätevesilietteen liuotusprosessin optimoinnin tulokset. Liuotus päätettiin toteuttaa fosforihapolla ja optimointi toteutettiin tilastollisella koesuunnittelulla. Lopuksi väitöskirjassa on tutkittu liuotuksessa tuotetun fosforihappoliuoksen jatkokäsittelyä. Saostusmetallin talteen ottamiseksi fosforihappoliuos käsitellään neste-neste uutolla, jolloin saostusmetalli saadaan erilleen fosforihaposta. Tämän jälkeen metalli on mahdollista kierrättää takaisin saostukseen.

Avainsanat: fosfori, yhdyskuntajätevesiliete, neste-neste uutto, talteenotto, jätevesi

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PREFACE

This doctoral thesis work was done in the Department of Chemistry at the University of Jyväskylä during 2016-2020. The research has been funded by the Helsinki Region Environmental Services Authority HSY and the Department of Chemistry, University of Jyväskylä.

As with many others, my journey into doctoral thesis work started with my master's thesis. In 2015, I researched for HSY whether phosphorus could be post-precipitated from wastewater. Although I did not know it at the time, that research would set me on a path that has taught me enormously and grown me into an actual scientist.

I would like to thank my supervisor Prof. Ari Väisänen for his guidance and support during this thesis work. I would also like to thank Docent Päivi Kinnunen and Dr. Saija Rasi for the pre-examination of my dissertation thesis.

My warmest thanks to the former and present members of Team Väisänen and other colleagues at the Department of Chemistry. It was a pleasure to get to know you all and I surely miss our insightful coffee break talks.

My gratitude goes also to the people at HSY who were or are involved in the development of the RAVITA™ -process. I can honestly say this thesis would not exist without your contribution. I also feel privileged and thankful for the opportunity to continue the development of the recovery process beyond this doctoral thesis at HSY.

Finally, I want to say thanks to my family and friends. You have been there to lift my spirits when the thesis work has felt overwhelming, patiently listened to my endless talks about it, and showered me with support. For that, I am grateful.

Kerava 10.1.2022
Sini Reuna

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following original publications, referred to in the text by Roman numerals (**I-III**).

- I** S. Reuna and A. Väisänen, Optimizing the H₃PO₄ leaching conditions of post-precipitated sewage sludge using response surface methodology. *Journal of Environmental Management*, **2018**, 226, 70-75.

- II** S. Reuna and A. Väisänen, To incinerate or not? -Effects of incineration on leaching and heavy metal concentrations of post-precipitated sewage sludge (RAVITA™). *Waste Management*, **2020**, 118, 241-246.

- III** S. Reuna and A. Väisänen, Purification of recovered phosphoric acid by extracting aluminum with di-2-ethylhexyl phosphoric acid. *Chemical Papers*, **2021**

Author's contribution

In papers **I-III**, the author has the main role in the planning and the execution of the experimental work, ICP-OES and ICP-MS measurements, interpreting the results, and writing the manuscripts.

Related publications

- iv** L. Rossi, S. Reuna, T. Fred, & M. Heinonen, RAVITA Technology—new innovation for combined phosphorus and nitrogen recovery. *Water Science and Technology*, **2018** 78(12), 2511-2517.

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PREFACE

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ABBREVIATIONS

ACP	Amorphous calcium phosphate
Adj MS	Adjusted mean squares
Adj SS	Adjusted sum of squares
ANOVA	Analysis of variance
AO	Aqueous to organic phase ratio
CCC	Central composite circumscribed design
CCD	Central composite design
CCF	Central composite face-centered design
CCI	Central composite inscribed design
CHP	Calcium hydrogen phosphate
CP	Calcium phosphate
D	Distribution ratio
DF	Degrees of freedom
d.w.	Dry weight
DCP	Dicalcium phosphate
DEHPA	Di-2-ethylhexyl phosphoric acid
DOE	Design of experiments
EBPR	Enhanced biological phosphorus removal
F-Value	Test statistic
HAP	Hydroxyapatite
HSY	Helsinki Region Environmental Services Authority
ICP-MS	Inductively coupled plasma mass spectrometer
ICP-OES	Inductively coupled plasma optical emission spectrometer
ISSA	Incinerated sewage sludge ash
LOQ	Limit of quantification
L/S	Liquid to solid ratio
MAP	Magnesium ammonium phosphate hexahydrate
MDL	Method detection limit
OCP	Octacalcium phosphate
OVAT	One variable at a time
PAO	Polyphosphate accumulating organism
PE	People equivalent
PHA	Polyhydroxyalkanoate
ppm	Parts per million
PPS	Post-precipitated sewage sludge
PPA	Post-precipitated sewage sludge ash
P-Value	Probability that measures the evidence against the null hypothesis
R ²	R-squared
RSM	Response surface methodology
s.e.m	Standard error of the mean
SS	Sewage sludge
SSA	Sewage sludge ash
SX	Solvent extraction
TBP	Tri- <i>n</i> -butyl phosphate
TS	Total solids
TSS	Total suspended solids
VFA	Volatile fatty acids
vs	Versus
w-%	Weight percentage
WSP	Wastewater stabilization pond
WWTP	Wastewater treatment plant

1 INTRODUCTION

In 2014 European Commission listed phosphate rock (PO_4^{3-}) as a critical raw material.¹ The list was updated in 2017 and the elemental phosphorus (P) was added among the other critical raw materials.² Both materials stayed on the list when the latest update was published in 2020.³ This is no surprise when one considers the fact that P is a vital ingredient for all cell protoplasm, nervous tissue, and bones⁴ and fertilizers need phosphorus for enhanced crop production.⁵

On the other hand, wastewater treatment plants (WWTPs) in Europe are required to remove the phosphorus in wastewater by the directive of the European Commission Council (91/271/EEC).⁶ This requirement is based on the fact that excess phosphorus in the natural water systems causes eutrophication.⁷

On that note, depending on the point of view phosphorus can be seen as either a valuable raw material or a waste that is produced during the treatment of sewage water. This perception of phosphorus in sewage sludge as waste has changed as depleting virgin phosphorus resources force one to seek secondary sources for P. The first country in Europe to acknowledge sewage sludge phosphorus as a potential resource was Switzerland. They made phosphorus recovery and recycling from sewage sludge and slaughterhouse waste obligatory in January 2016.⁸ In May 2017 Germany, as the first EU member state, legislated phosphorus recycling obligatory from sewage sludge.⁹ Nevertheless, with long transition periods (10 to 15 years) it will take some time before the recovery of phosphorus is implemented in the wastewater treatment plants.^{8,9}

Because of the legislation and increasing awareness of phosphorus depletion, the research for phosphorus recovery methods from wastewater has increased in the past years.¹⁰ Most of the methods focus solely on P recovery, but other valuable nutrients such as nitrogen are also present in the wastewater streams.¹¹ Also, the possibility to recycle the reagent used to precipitate the phosphorus from wastewater has been unheeded so far. The ability to recycle precipitation chemicals would decrease the overall costs of phosphorus recovery thus enabling the WWTPs to recover phosphorus without

compromising the discharge requirements of P from wastewater. After all, the obligations of wastewater treatment according to EU regulations remain as the core purpose of WWTPs.¹² In addition, the enhanced recycling of P would ensure the availability of fertilizer in the European Union. Currently, the EU imports annually 1 million tons of phosphate fertilizers, since it has only one igneous mine at operation in Finland.^{13,14}

2 AIM OF THE STUDY

This study aimed to develop a recovery process for phosphorus from post-precipitated sewage sludge. As the virginal sources of phosphorus are diminishing at the same time, eutrophication is accelerating in the Baltic Sea. This compels the EU to tighten the limits of phosphorus discharge from wastewater. Because of the stricter limits, wastewater treatment plants all over Europe are required to improve their infrastructure. If a method for phosphorus recovery from wastewater as a high-value product would be developed, it would ease the cost of infrastructure update and conserve the virginal sources of phosphorus. This object included the following aspects:

- Selecting the leaching agent and optimizing the sludge leaching process
- Studying the methods for the recovery of phosphorus from the leach solution
- Characterization of elements in post-precipitated sewage sludge and post-precipitated sewage sludge ash
- Investigating recirculation of leaching agent

3 LITERATURE REVIEW

3.1 Optimization and experimental design

3.1.1 Response surface methodology

Response surface methodology (RSM) is a multivariate statistical analysis technique.¹⁵⁻¹⁷ It was developed in the 1950s by Box and his collaborators. With RSM, it is possible to model and analyze problems in which a response of interest is impacted by numerous independent factors. Typically, the aim is to find suitable factor levels that produce the best response. Depending on the experiment, the best response is either maximum or minimum.

The utilization of the response surface can be divided up into six steps. First, the factors for the experiment are selected. The selection can be based on the screening tests, the aim of the research, or the previous knowledge of the researcher. When the factors, that have a major effect on the studied response, have been chosen, then the experimental design with the appropriate model equation is selected. Usually, a linear first-order model is an initial type to be tested. The equation for the first-order model in k variables is conveyed as follows:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \epsilon, \quad (1)$$

where Y is the response, k is the number of factors, β_0 is a constant coefficient, β_i is the linear effect, x_i represents the factors, and ϵ is the error observed in the response. The experimental designs that utilize linear models are two-level factorial designs. However, if the response shows curvature, a second-order model is needed for modeling. The generalized second-order model equation in the response surface analysis can be expressed as follows:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum \sum_{i < j}^k \beta_{ij} x_i x_j + \varepsilon, \quad (2)$$

where β_{ii} is the quadratic effect and β_{ij} is the interaction effect. The designs that apply second-order equations are three-level factorial designs, Box-Behnken designs, and central composite designs. Out of these three, the central composite design and its variations are the most prevalent in chemometrics.¹⁸

Once the data has been collected, the third step is to analyze it and fit the polynomial equation.¹⁶ This is usually done with the same software that was used to produce the experimental design. When the model has been acquired the fourth step is to estimate its fitness and ensure that assumptions regarding the model are met. The assumption checks are done with a visual inspection of residual graphs. The residuals will be normally distributed if the model fits well. The fifth step is only necessary if the optimal conditions are not found in the experimental region. Then the experimental region is shifted towards the optimal area based on the obtained responses and the process started anew. However, this can only be done if no inhibiting physical or instrumental reasons exist. The final step is to attain the optimal levels for factors based on the obtained model. This can be done via the software or with a visual inspection of the surface response plot.

Central composite designs

For fitting the second-order model, the central composite design (CCD) is the most popular. It consists of a full (or fractional) factorial design (2^k) with n factorial runs, $2k$ axial runs, and c_p central points.¹⁵ CCD has three different varieties depending on the location of star points.¹⁹ Circumscribed designs (CCC) are the original form of the CCDs. The star points are at a distance a from the center. The distance a is determined based on the properties of the design and the number of factors. The face-centered design (CCF) is formed when the distance a is ± 1 from the design center for the star points. The inscribed design (CCI) is utilized when specific factor settings cannot be exceeded. The factor values are set as star points and a factorial design is generated within. **Figure 1** illustrates the star point locations of each variety. The utilization of these experimental design types in natural sciences is steadily increasing and their usage is encouraged.¹⁷

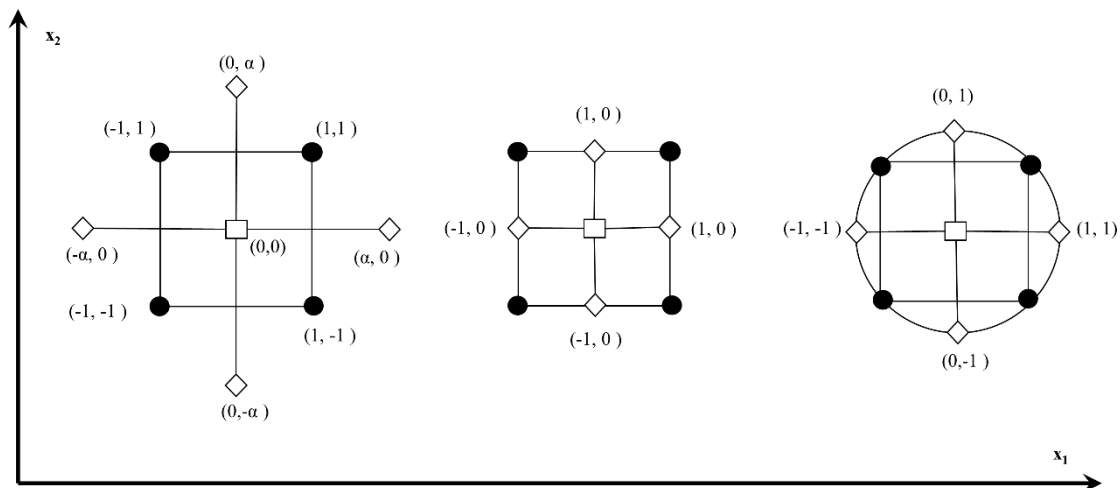


FIGURE 1. Star point (white) and factor level (black) locations in circumscribed (left), face-centered (middle), and inscribed (right) central composite designs

3.2 Recovery methods for phosphorus from wastewater

Methods for P recovery from wastewater can be divided into three categories: recovery directly from wastewater or recovery from sewage sludge (SS) or sewage sludge ashes (SSA) after incineration.^{20,21} Direct recovery from wastewater is done via crystallization, precipitation, or via the application of biological methods such as algae and micro-organisms. Recovery techniques from solid sludge or ash utilize more typically wet chemical or thermochemical approaches.

3.2.1 Crystallization/precipitation methods

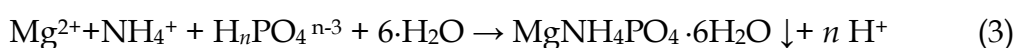
The most conventional method to remove P from wastewater is chemical precipitation by metal salts, such as iron or aluminum sulfates or chlorides.²² However, chemical precipitation is designed to reduce the dissolved P discharge to natural waters and not to recover it. Therefore, the salts formed in chemical precipitation are not as such usable for the phosphate industry and require further processing.

The most feasible compounds that can be directly crystallized/precipitated from wastewater are magnesium ammonium phosphate hexahydrate (MAP, $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$), known as struvite, and a group of calcium orthophosphates (Ca-P), such as hydroxyapatite (HAP, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$).²³ Both types of compounds can be used as slowly solubilizing fertilizers in agriculture. In addition, some of the calcium phosphates can be utilized by other phosphate industries, for example in the production of household products such as detergents.

3.2.1.1 Struvite formation

The formation of struvite from wastewater may either be spontaneous or can be stimulated with seed crystals and optimal process conditions.²⁴ Spontaneous struvite formation often occurs in wastewater treatment plants that use enhanced biological phosphorus removal (EBPR). In EBPR-process at the anaerobic digesters, the parameters that promote the struvite formation, such as pH, degree of supersaturation, temperature, and the concentrations of magnesium, ammonium, and phosphate ions are at an optimal level. The uncontrolled struvite formation often causes blockages in the pipelines and thus is considered a hindrance rather than a P-recovery method.²⁵

The controlled struvite crystallization is based on the addition of magnesium at an equal molar ratio with P and N, and increasing the pH to be slightly alkaline (7.5-9.0).^{26,27} Then, in the presence of seed material, struvite crystals begin to form as presented in **Equation 3**. The pH influences the struvite solubility, the degree of supersaturation, and crystal growth. The optimal pH value is dependent on wastewater type and a high dosage of alkaline chemical may be required to achieve the optimal level of pH, thus increasing the production costs. The optimum value for pH is often a trade-off between low chemical cost, product purity, and P removal efficiency. The type of wastewater also affects the optimal magnesium dosage. Magnesium is the restricting agent in precipitation reaction and to ensure its stoichiometric concentration, it should be added to the process in the form of MgCl₂, Mg(OH)₂, or MgO.²⁸ In addition, the P concentration in influent liquor must be considerable (over 100 mg L⁻¹) for the struvite crystallization to work. Despite the various challenges in struvite crystallization, it has been utilized successfully at the commercial level in Japan and the Netherlands with fluidized bed reactors.^{29,30}



3.2.1.2 Ca-P precipitation/crystallization

Like struvite formation, the crystallization of calcium phosphates depends highly on pH.^{21,31,32} In varying pH levels different Ca-P compounds start to precipitate depending on the concentrations of Ca²⁺ and PO₄³⁻ ions. Compounds such as amorphous calcium phosphate (Ca₃(PO₄)₂ · nH₂O, ACP), calcium hydrogen phosphate (CaHPO₄ · 2H₂O, CHP), calcium phosphate (Ca₃(PO₄)₂, CP), octacalcium phosphate (Ca₈H(PO₄)₆, OCP) and HAP are precipitated. Some of the other Ca-P compounds serve as precursors for HAP, which is partly formed via recrystallization of these precursors.

The straight precipitation reaction for HAP is presented in **Equation 4**. Yin et al.³² propose that the optimum pH for HAP precipitation is 9 to 10. At higher pH levels the probability of calcium carbonate co-precipitation increases hence diminishing the P content in the precipitate.³³ However, Vasenko and Qu³⁴ reported that as long as pH is higher than 6.3, HAP will be the main product in

calcium orthophosphate crystallization. As can be seen from **Equation 4** the theoretical Ca:P molar ratio for HAP precipitation is 1.67. Nevertheless, Duan et al.³⁵ deduced that molar ratio of 2 in HAP crystallization ensures the best removal efficiency for P. The HAP crystallization process in Crystalactor® pellet reactor has operated at full-scale in the Netherland.³⁶



3.2.2 Biological methods

In the biological methods polyphosphate accumulating organisms (PAOs), microalgae or macrophytes are exploited in P recovery. The PAOs are the core of the EBPR-process, collecting the excess of phosphorus beyond their normal metabolic requirements.^{37,38} This phenomenon is achieved by circling the PAOs between anaerobic and aerobic conditions. In the anaerobic settings, PAOs take up carbon sources such as volatile fatty acids (VFAs) and store them as polyhydroxyalkanoates (PHA). To gain the energy to do this they degrade the polyphosphate and as a follow-up release orthophosphate. In the following aerobic conditions, the PAOs oxidize PHAs to produce energy for cell growth and orthophosphate uptake. Since the orthophosphate intake is greater than the amount released in anaerobic conditions, phosphorus is accumulated in the biomass. In the EBPR-process P can be recovered from anaerobic side streams via struvite crystallization or the formed biomass can be applied to the soil after dewatering.^{39,40} The EBPR-process was developed in the 1970s; but several factors can still inhibit its stability and reliability, like wastewater quality, operating temperature, and shock loadings, thus making it challenging to operate.⁴¹

The P recovery with microalgae is based on their symbiotic relationship with bacteria.⁴² The heterotrophic bacteria metabolize carbon and nutrients into oxidized forms (CO_2 , NH_4^+ and PO_4^{3-}), which microalgae utilize for growth. Microalgae then produce oxygen to support bacterial activity. The microalgae can storage over 1 % P dry weight (d.w.) within the biomass, depending on nutrient concentrations, amount of light, temperature, and pH in waste stabilization ponds (WSP) where microalgae are cultivated.⁴³ The harvesting can be done with different methods like filtration, sedimentation, or a pilot-scale harvester.⁴⁴ The collected microalgae can be used as raw material for biofuels and biogas.

Aquatic macrophytes, i.e., large aquatic plants, are also used for wastewater treatment in WSPs. In P recovery, macrophyte systems assimilate phosphorus biologically into biomass, absorb it physically, cause its precipitation via pH upsurge or provide a surface area for heterotrophic bacteria to uptake P.⁴⁵ Especially duckweed has been named as the most promising macrophyte to recover nutrients from dairy wastewater.⁴⁶ After harvesting, duckweed can be processed to animal feed or digest anaerobically for biogas production.

3.2.3 Wet chemical methods for SS and SSA

The phosphate in sewage sludge, produced via chemical precipitation, is tightly bound with the metal, hence not available for plant uptake at regular soil pH.⁴⁷ For that reason, it needs to be chemically treated.

Thermal treatment via incineration is widely used as a disposal method for sewage sludge in European countries. In 2018, about 27 percent of the produced sewage sludge in Europe was thermally treated, making the utilization of incinerated sewage sludge ash (ISSA) in P recovery highly alluring.⁴⁸ However, in the Nordic countries, less than 5 % of total sludge was disposed of via incineration in 2018. For that reason, it is beneficial to develop a method to recover P directly from the sewage sludge.

3.2.3.1 Acidic and alkaline leaching

Several mineral and organic acids have been investigated for leaching of P from sewage sludge or ash. Hydrochloric acid, (HCl) sulfuric acid (H₂SO₄), nitric acid (HNO₃), and organic acids like oxalic acid (C₂H₂O₄) have so far been the most applied ones.⁴⁹⁻⁵⁴ Phosphoric acid (H₃PO₄) as a leaching agent has been investigated in treating the SSA but not with SS.^{55,56} The usage of H₃PO₄ would eliminate the need to remove excess sulfate, chloride or nitrate ions from the leachate solution.⁵⁷ On alkaline leaching the research has focused furthestmost on the utilization of sodium hydroxide (NaOH).^{58,59}

A couple of recovery techniques based on wet-chemical methods that have reached industrial or full-scale are Gifhorn, EcoPhos®, and RecoPhos®.⁶⁰ In the Gifhorn process the SS is leached with sulfuric acid followed by sulfidic precipitation to remove heavy metals.⁶¹ The nutrients are recovered as struvite by adjusting the pH and adding magnesium to the process flow.

EcoPhos® produces phosphoric acid by implementing SSA in their leaching process as a raw material.^{62,63} The SSA is leached in acidic conditions thus releasing most of P. From the leachate, the P can be precipitated as dicalcium phosphate (DCP) if HCl was used as leach solution or P can be recovered via ion exchange if H₃PO₄ was used.

RecoPhos® also implements phosphoric acid in their leaching.⁶⁴ This increases the plant availability of the SSA phosphates as the minerals in SSA are transformed into soluble calcium and magnesium phosphate. However, this requires SSA with low toxic trace metal concentrations because the process lacks a purification step.

3.2.3.2 RAVITA™

RAVITA™ -process is designed to recover nutrients (P and N) and recycle the metal used in P post-precipitation.^{11,65} The post-precipitated sewage sludge (PPS) is leached with dilute phosphoric acid and the obtained solution is purified with solvent extraction. During the solvent extraction process, the metal used in the precipitation of P is recovered and the purified phosphorus acid with elevated P concentration is the final product. The nitrogen (N) is

recovered from the rejected water formed in the dewatering process of the SS. The nitrogen is stripped from reject water to form ammonium phosphate. **Figure 2** presents the simplified process design for phosphorus recovery with RAVITA™. The process is currently being piloted.

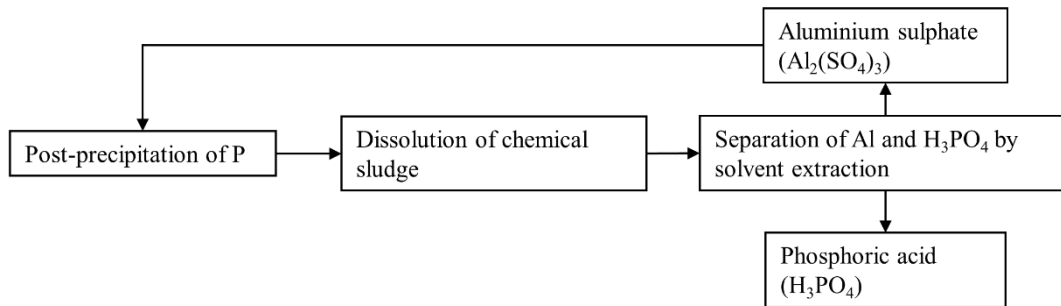


FIGURE 2. Simplified schematic for phosphorus recovery design with RAVITA™

3.2.4 Thermochemical methods for SS and SSA

Among the thermochemical methods for P recovery Outotec's AshDec® - process has reached the industrial scale.^{66,67} It is based on feeding hot SSA into a rotating reactor at temperatures over 900 °C. SSA is mixed with a reducing agent (Na_2SO_4) and sodium or potassium additives. The cations replace calcium ions in phosphates producing more plant-available Ca-K/Na PO_4 compounds. The toxic trace metals are volatilized during the thermal treatment due to the reducing atmosphere. The produced compounds are then processed into fertilizers in a mixed-granulator system. The simplified process schematic is presented in **Figure 3**.

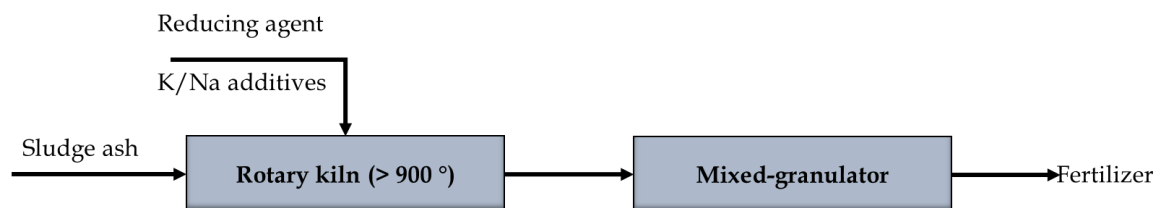


FIGURE 3. Simplified schematic of Outotec's AshDec® -process⁶⁶

Another thermochemical process, Mephrec®, utilizes both sewage sludge and sewage sludge ash.^{68,69} First SS is dried 80 % d.w., and after that, the SS is mixed with SSA and pressed into briquettes. The briquettes serve as input to the melting-gasifier, wherein in the presence of coke (< 1450 °C), the P is transformed into silicophosphates. The formed P-rich slag is then cooled and

granulated in a water bath. During the gasification, the volatile harmful elements (As, Cd, Hg, Pb, Zn) are evaporated, and non-volatile elements (Fe, Ni, Cu, Cr) are separated as liquid metal form. The Mephrec® -process has been tested on a pilot-plant scale in Freiberg (Germany) in 2008.

3.2.5 Summary of recovery techniques

So far none of the existing nutrient recovery methods have been able to contest production costs against the mined phosphate rock.⁷⁰ However, as the high-quality phosphate reserves are slowly diminishing, the alternative phosphorus recovery methods will come more competitive. **Table 1** displays some of the assets and limitations of the recovery methods presented. In summary, the recovery rate of influent P from wastewater is estimated to be 40-50 % and with SS and SSA a recovery rate of 90 % is possible to be achieved.⁷¹ However, even if 100 % recycling efficiency could be accomplished, this would compensate only 16 % (4,6 Mt) or less of the annual anthropogenic phosphorus consumption, since only that amount ends up in wastewater.^{28,72-77}

TABLE 1. Advantages and disadvantages of different phosphorus recovery methods

		Pros	Cons	Refs.
Crystallization methods	Struvite formation	<ul style="list-style-type: none"> • Can be directly applied as fertilizer • Removes nitrogen 	<ul style="list-style-type: none"> • Requires high P concentration ($> 100 \text{ mg L}^{-1}$) • Compels EBPR-system 	[24-26]
	HAP crystallization	<ul style="list-style-type: none"> • Recovery directly from the wastewater stream 	<ul style="list-style-type: none"> • High degree of crystallinity depends upon long process times 	[29]
Biological methods	EBPR	<ul style="list-style-type: none"> • Formed biomass can be applied to the soil 	<ul style="list-style-type: none"> • Sensitive to shock loadings • Spontaneous struvite formation may ensue \rightarrow pipe fouling 	[38,39]
	Microalgae and macrophytes	<ul style="list-style-type: none"> • Produces raw material for biogas and biofuel production 	<ul style="list-style-type: none"> • Products cannot be utilized in the fertilizer industry 	[40-43]
Wet-chemical methods	Gifhorn	<ul style="list-style-type: none"> • P recovered as struvite 	<ul style="list-style-type: none"> • High reagent consumption 	[59]
	EcoPhos®	<ul style="list-style-type: none"> • Versatile process design can produce either DCP or phosphoric acid 	<ul style="list-style-type: none"> • Ion exchange resins require regeneration 	[60,61]
	RecoPhos®	<ul style="list-style-type: none"> • Products are plant-available 	<ul style="list-style-type: none"> • No purification steps \rightarrow SSA needs to be free from toxic trace metals 	[62]
Thermo-chemical methods	AshDec®	<ul style="list-style-type: none"> • Produces fertilizers 	<ul style="list-style-type: none"> • High energy consumption 	[64,65]
	Mephrec®	<ul style="list-style-type: none"> • Utilizes both SS and SSA 	<ul style="list-style-type: none"> • Consumes heat for SS drying 	[66,67]

3.3 Leaching of elements

In general, leaching is the process of extracting a desired element or compound from a solid material by using a solvent.^{78,79} The actual extraction is divided into three parts: first, the metal dissolves in the solvent, secondly, the metal diffuses from the inside of the particle to the surface, and finally the metal transfers to the main bulk of the solution. The rate of this procedure depends on four factors, which are particle size, nature of the solvent, temperature, and agitation of the fluid. Smaller particle size increases the interfacial area between solid and particle, thus escalating the extraction rate. However, too small particle size hinders the separation of liquid and solid residue. The second influencing factor, the solvent, should be chosen in a manner so it is selective towards the desired element and possesses the lowest possible viscosity. The third factor, the temperature, typically increases the solubility and extraction rate at higher levels. Agitation, as the last factor, increases mass transfer and hinders the sedimentation of fine particles, therefore preventing the decrease of the interfacial surface.

3.4 Solvent extraction for separation of dissolved metals

Solvent extraction (SX), also known as liquid-liquid extraction, is a way to transfer a dissolved metal from one phase to another.^{80,81} It consists of two immiscible phases, organic and aqueous. The two phases are assumed non-soluble with each other, but there is a small loss of organic phase in the aqueous phase. The organic phase classically consists of organic extractant and solvent known as diluent. The purpose of diluent is to lower the viscosity of the organic phase and aid to dispense the extractant more efficiently in organic phase droplets. It is also typical to add a so-called phase modifier in the organic phase to enhance the phase separation.

During the separation of metal, the organic phase is contacted with an aqueous phase containing the dissolved metal, and the metal is partitioned between phases. The partition in equilibrium can be expressed as distribution ratio D and it is defined as

$$D = \frac{[M]_o}{[M]_{aq}}, \quad (5)$$

where D is the distribution ratio, $[M]_o$ is a total concentration of metal in the organic phase, and $[M]_{aq}$ is a total concentration of metal in the aqueous phase. The higher the D is, the better the extraction is.

Usually, a percentage value E % is a more informative way to express the extraction efficiency. It is calculated as follows:⁸²

$$E \% = \frac{C_0 - C_e}{C_0} \cdot 100 \% , \quad (6)$$

where E % is the extraction efficiency in percentage, C_0 is the initial concentration of metal and C_e is the metal concentration in the aqueous phase after extraction.

Following the extraction stage, the organic phase can be washed or scrubbed and possibly formed crud is removed. The simplified process scheme containing all possible stages in solvent extraction is presented in **Figure 4**. In the washing stage, the entrained aqueous phase is removed by contacting the organic with pure water and bleed electrolyte. The scrubbing is done to remove the co-extracted impurities, which are not wanted in the stripping solution with the extracted metal. Water, weak acids and bases, or metal salt solutions are used as an aqueous phase in the scrubbing. The crud removal and formation are discussed in detail in the following chapter 3.4.4. The organic phase is then moved to the stripping stage where the extracted metal is stripped back to the aqueous phase. If acidic extractant is used in the extraction phase, then acid is used as a stripping solution to force the equilibrium to shift toward the aqueous phase. The stripped organic phase is then returned to the extraction stage and the metal is in stripping solution.

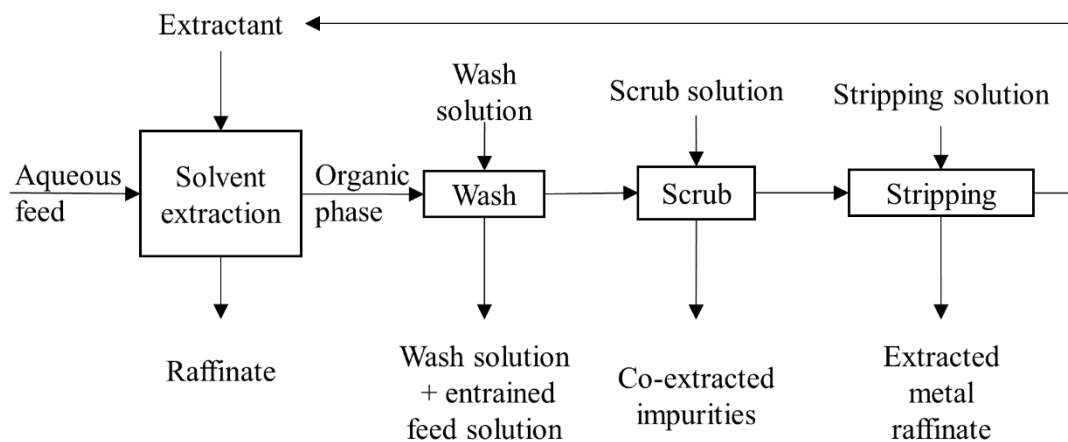


FIGURE 4. Process scheme for solvent extraction

3.4.1 Extraction reaction mechanisms

Three basic types of solvent extraction mechanisms exist ion exchange, solvation, and coordination mechanism.⁸¹ For extraction to happen, all three types require two main steps, dehydration and charge neutralization. Hydrated metal ions will not transfer in the organic phase; hence the dehydration needs

to happen. Charge neutralization is needed because the non-polar organic phase cannot accommodate the charged ions.

In metal recovery and separation processes, the extractants based on ion exchange are typically used.⁸² A wide range of different kinds of ion-exchange extractants exists. Among them are carboxylates, sulfonates, and organophosphorus extractants, which all are acidic. The basic extractants typically are primary, secondary, tertiary, or quaternary amines. A generalized equation for extraction reaction with cation exchangers can be expressed in the following manner:⁸¹



where M is the metal, RH represents extractant and n is the charge. The overbar denotes the organic phase. The concentration-based equilibrium constant K_c can be expressed:

$$K_c = \frac{[\overline{MR}_n][H^+]^n}{[M^{n+}][RH]^n}. \quad (8)$$

From **Equation 8** we can substitute the distribution ratio in **Equation 5**:

$$K_c = D \cdot \frac{[H^+]^n}{[RH]^n}. \quad (9)$$

By taking logarithmic and reorganizing **Equation 9** we get

$$\log D = \log K_c + n(\log[RH] - \log[H^+]), \quad (10)$$

where $-\log[H^+]$ is pH. The equilibrium constant K_c can be determined by plotting the $\log D$ versus $n(\log[RH] + \text{pH})$.

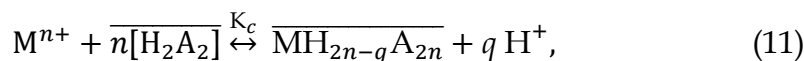
3.4.2 Extractants for metal extraction

Aliquat 336 is a quaternary ammonium salt extractant that consists of tri-*n*-alkylammonium chlorides.⁸³ It is produced by the methylation of mixed tri-octyl/decyl ammonium chloride.⁸⁴ **Table 2** presents the characteristics and structure of Aliquat 336. It is used to extract cobalt and nickel, especially from aqueous halide media with an anion exchange reaction.

Tri-butyl phosphate (TBP) is an organophosphorus extractant that extracts metals via the solvating mechanism.⁸⁵ It is used as an extractant in the Purex - process which is designed to recover plutonium and uranium from spent nuclear fuels.⁸⁶ Its characteristic are shown in **Table 2**.

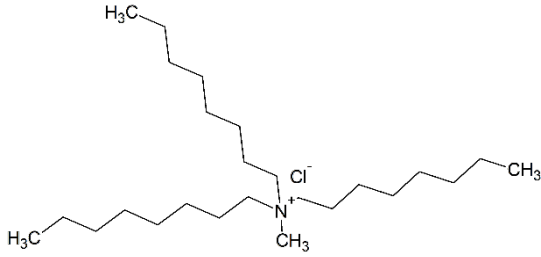
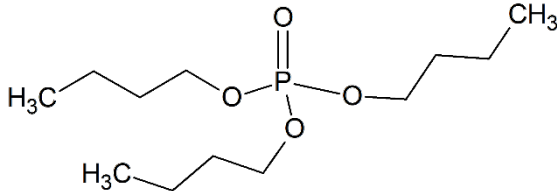
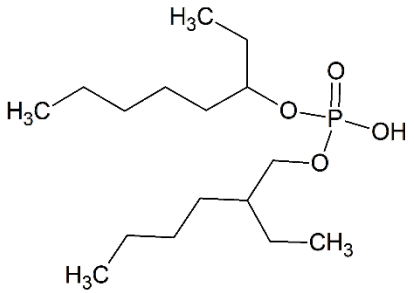
Di-2-ethylhexyl phosphoric acid (DEHPA) is an organophosphorus extractant that appears as an odorless yellow liquid. The characteristics and structure of DEHPA are presented in **Table 2**.⁸⁷ DEHPA was first used in the 1950s to extract uranium from wet phosphoric acid.⁸⁸ Since then, due to low

price, fast kinetics, and low aqueous solubility, its usage has expanded to the recovery of alkali metals, rare earth elements, and transition metals.⁸⁹⁻⁹¹ In kerosene DEHPA reacts with metal via a cation exchange reaction and can be expressed as follows:⁹²



where M is the metal, n is the charge, K_c is the reaction equilibrium coefficient and $[H_2A_2]$ denotes the dimeric form of the extractant, since in nonpolar aliphatic solvents DEHPA exists mostly as a dimer.⁹¹

TABLE 2. Characteristics of Aliquat 336, TBP and DEHPA^{4,93,94}

		Properties	
	Aliquat 336:		
	Molecular formula		C ₂₅ H ₅₄ ClN
	Molar mass (g mol ⁻¹)		404.2
	Boiling point (°C)		225
	Density (g cm ⁻³)		0.844
	TBP:		
	Molecular formula		C ₁₂ H ₂₇ O ₄ P
	Molar mass (g mol ⁻¹)		266.31
	Boiling point (°C)		289
	Density (g cm ⁻³)		0.978
	DEHPA:		
	Molecular formula		C ₁₆ H ₃₅ O ₄ P
	Molar mass (g mol ⁻¹)		322.42
	Boiling point (°C)		155/0.015
	Density (g cm ⁻³)		mmHg 0.975

3.4.3 Graphical analyses

3.4.3.1 Slope analysis

The classical way to study the stoichiometry of extracted species is slope analysis.⁸² It is based on the plots of $\log D$ versus pH at constant extraction concentration and $\log D$ versus extractant concentration at constant pH. To get precise results with the slope analysis several simplifying assumptions need to be done. First, no polymeric species should form in either phase. With organophosphorus extractants, this can be challenging to achieve. For instance, DEHPA dimerizes in kerosene as presented in **Equation 11**.⁹² By ensuring that the extraction reaction depicts this behavior, the problem is resolved. The second assumption is that activities are constant so that the equilibrium constant based on concentration can be utilized. This is easily ensured by using constant ionic strength and relatively low metal concentrations. The third assumption is that only uncharged species are extracted. This is always valid since the non-polar organic phase cannot put up charged species. A fourth assumption is that no intermediate non-extractable complexes are formed in during extraction. If this is not the case, then either of the plots could be curved. Fifth assumption is that no adduct formation takes place and the sixth is that hydrolysis reactions are irrelevant. If either of them is not met, then the $\log D$ values change. This causes a shift in the slope thus resulting in non-linearity. Because of the challenges to meet all the assumptions, the computer-aided methods have replaced the graphical methods in hydrometallurgical process development.⁹⁵

3.4.3.2 McCabe and Thiele diagram

McCabe-Thiele diagram is a graphical method to present the distribution isotherms in solvent extraction and evaluate the number of necessary extraction stages.⁸¹ An example of the McCabe-Thiele diagram is presented in **Figure 5**. The data $[MR_n]$ versus $[M^{n+}]$ is plotted to obtain a distribution curve in different volume ratios of the aqueous and organic phases. An operating line, which models the steady-state mass-balance limit for extraction i.e., aqueous to organic phase ratio, is drawn. In industrial-scale processes, the operating line is drawn based on flow rates of aqueous and organic feed. In addition, the operation is assumed to be in steady-state and to flow in counter-current. The needed stages for extraction can be determined if the metal concentration in the aqueous feed solution is known.

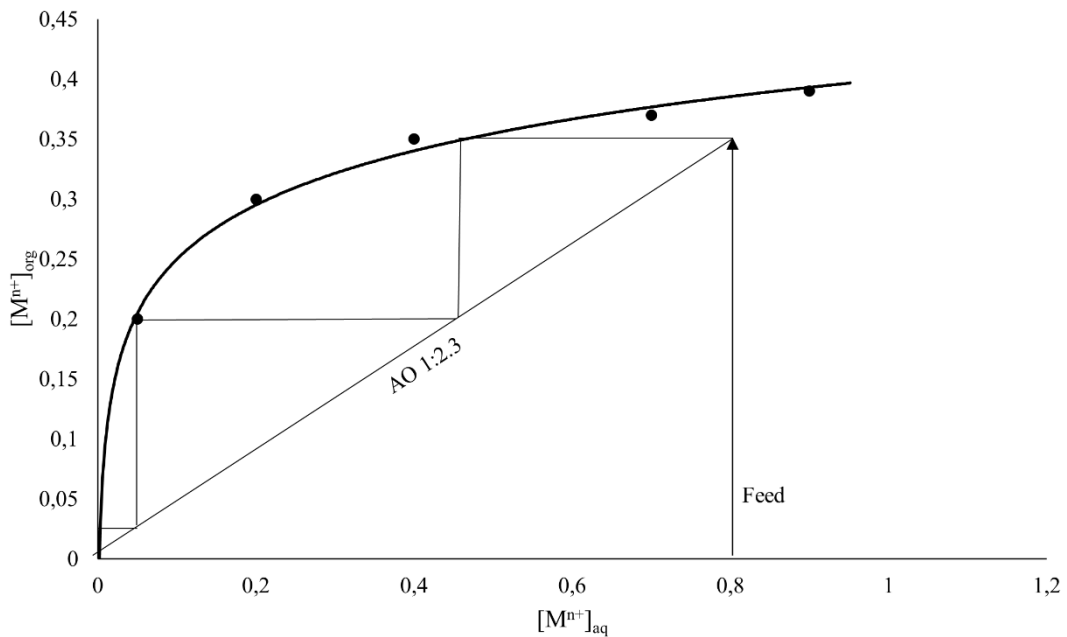


FIGURE 5. Example of McCabe-Thiele diagram.

3.4.4 Crud in solvent extraction

3.4.4.1 Description of crud

The crud is an emulsion mixed with fine particles, which is formed during mixing in solvent extraction.^{81,96} Its chemical and physical composition varies depending on extraction processes, but common constituents in crud are silicon, aluminum, iron, phosphorus, and sulfate. The composition of crud usually reflects on the composition of the aqueous feed solution.

Several factors affect its formation and each situation where crud is formed is unique. The main possible factors to cause crud are the structure of the feed solution or the solvent, the operation parameters, such as agitation, dispersion type, physical-chemical properties of the phases, and the equipment selection.

In the feed solution, especially the solids cause a crud formation. For that reason, it is important to clarify or filter the feed solution before the extraction step. Ritcey⁹⁶ suggests that the feed solution should contain no more than 10 mg L⁻¹ of suspended solids. In addition, other compounds, like surfactants from the leaching step can create crud. Usually, the formation of crud can be diminished if the compound is removed from the solution before the extraction. For instance, in uranium recovery from phosphoric acid solutions, the coagulation of humates by flocculation agents followed by filtration reduces the crud formation.⁹⁷ For phosphorus acid, there is also a patented method for pretreatment to minimize the crud formation in an actual extraction step of

uranium.⁹⁸ It consists of solvent extraction with hydrocarbon, which extracts the crud causing elements. The hydrocarbon, typically kerosene, is then regenerated with dilute sodium hydroxide.

A second possible source of crud is solvent degradation, or that solvents loading capacity is attained. This is avoided by the right choice of solvent and that the extraction is operated below loading capacity. For example, Liu et al.⁹⁹ concluded that crud formation in solvent extraction of copper decreases when the organic to aqueous phase ratio rises, thus increasing the loading capacity.

The method of crud prevention depends highly on the extraction process.⁹⁶ Hence, no “one size fits all” kind of solution can be given for its prevention. In each process, the right method for crud handling is found out by trial and error.

3.4.4.2 The mechanisms of crud forming

In leaching solutions silica often occurs in the form of suspended colloidal silica or as silicic acid.¹⁰⁰ Both compounds are most stable in pH 2 and can form aggregates in the pH range of 2-5. One way in which colloidal silica interferes with SX is called the protective colloid effect.¹⁰¹ The small silica particles form a supporting network under the other larger particles and thus prevent them from settling (see **Figure 6**). This increases the amount of total suspended solids (TSS) in the leach solution which then causes the crud formation during the SX process. This is prevented by using a coagulant that binds colloidal silica. The coagulation increases their particle size which allows them to be flocculated and removed.

The suspended solids, that generate crud in the leaching solution, are typically small particles of size below 1 μm .^{102,103} During mixing these particles end up into the interface between the aqueous and organic phases. In the interface, the particles are adsorbed between the disperse phase and the continuous phase. The adsorption stabilizes the disperse phase causing it to emulsify and form crud. Depending on the surface behavior of the solid particles and the continuous phase, the formed crud can be either the oil-in-water type if the particles have hydrophilic surface behavior or the water-in-oil type if the particles have hydrophobic surface behavior.

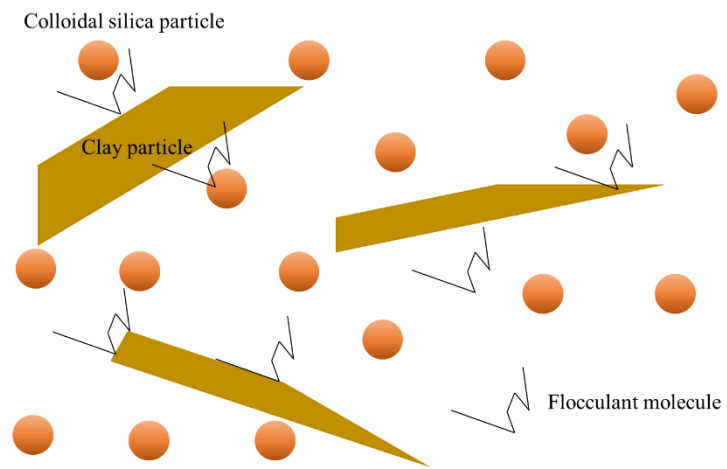


FIGURE 6. The protective colloid effect that hinders clarification in leach solutions¹⁰¹

4 EXPERIMENTAL

4.1 Samples

Aluminum-containing and iron-containing post-precipitated sewage sludge (PPS) samples used in this study were produced in the RAVITA™ pilot plant (PE 1,000) located in Viikinmäki wastewater treatment plant, Helsinki (**Figure 7**).¹¹ In the pilot plant the Viikinmäki WWTP's effluent water (average suspended solids value of 4.9 mg L⁻¹ and average concentration of P 0.221 mg L⁻¹) has been used as an inlet. Monopotassium phosphate solution (KH₂PO₄) was added to the pilot influent to adjust the P concentration higher (3-5 mg L⁻¹). In precipitation, both aluminum-based and iron-based coagulants have been used along with cationic and anionic polymers. Disc filter (Veolia, Hydrotec HSF1708/1-1F, 2.7 m/h) was used to separate formed precipitate. Batches of post-precipitated sewage sludge (1-20 liters) were collected and used in this research.

For elemental analysis part of the batches were air-dried for at least 72 h. In addition, to examine the effect of incineration on the leaching process, a part of the samples were incinerated at 550 °C according to Finnish Standards Association's standard SFS 3008.¹⁰⁴ Ash-samples are separated from PPS-samples with acronym PPA.



FIGURE 7. RAVITA™ pilot plant for P precipitation (HSY/Tuomas Uusiheimo)

4.2 Elemental analysis II

4.2.1 Microwave-assisted digestion

Sludge and ash samples, along with reference materials *Trace Metals-Sewage sludge* CRM029 LRAB1332 and SRM 1663c *Trace Metals in Coal Fly Ash*, were digested in CEM Mars6 -microwave, using nitric acid (HNO₃), hydrochloric acid (HCl), and hydrogen fluoride acid (HF). The digestion program was based on the US EPA 3052 method. Samples were held at 180 °C for 15 minutes. After cooling, boric acid (H₃BO₃, 5 wt.-%) was added and a separate HF neutralization program was performed where samples were held at 170 °C for 15 minutes.

4.2.2 Instrumentation

4.2.2.1 ICP-OES

The concentrations of the major elements were quantified with inductively coupled plasma optical emission spectrometers (ICP-OES) PerkinElmer Avio 500 and PerkinElmer Optima 8300. For sample introduction, the GemCone low flow -nebulizer with a glass or HF resistant (Tracey) cyclonic spray chamber was used. The measurement parameters for all measurements are presented in Table 3. I-III

TABLE 3. Operating parameters for PerkinElmer Avio 500 and PerkinElmer Optima 8300 ICP-spectrometers.^{I-III}

Argon gas flow (L min ⁻¹)	8
Nebulizer gas flow (L min ⁻¹)	0.6-0.7
Auxiliary gas flow (L min ⁻¹)	0.2
Sample flow rate (mL min ⁻¹)	1.5
RF power (W)	1500

4.2.2.2 ICP-MS

The quantification of trace element concentrations was done with PerkinElmer NexION 350D inductively coupled plasma mass spectrometer (ICP-MS). The ICP-MS measurement settings are shown in **Table 4**. Before analysis, the samples were diluted by a factor of 200 or 50 with ESI Prep-Fast.^{II}

TABLE 4. Operating parameters for PerkinElmer Nexion 350d ICP-MS.^{II}

Spray chamber	Cyclonic
Nebulizer	PFA-ST
RF power (W)	1600
Ar nebulizer gas flow (L min ⁻¹)	0.90-0.93
Scan mode	Peak hopping
Readings/replicate	1
Dwell time (ms)	50
Sweeps/reading	24
Integration time (ms)	1200
Replicates	3
Isotopes	⁷⁵ As, ⁵³ Cr, ¹¹⁴ Cd, ⁶⁵ Cu, ⁵⁸ Ni, ²⁰⁸ Pb, ¹²³ Sb, ⁸² Se, ¹¹⁸ Sn, ¹²⁶ Te, ⁶⁸ Zn

4.3 Optimization of leaching^I

The face-centered composite design was utilized in the optimization of leaching. Phosphoric acid concentration, solution volume, temperature, and leaching time were chosen as factors. **Table 5** presents the levels of each factor. The optimization was done on both dried sludge and sludge with a total solid content of 3-4 %.

TABLE 5. The factor levels used in CCF design in the optimization of leaching the aluminum-based PPS

	Levels		
	-1	0	+1
H ₃ PO ₄ concentration (M)	0.5	1.25	2.0
Acid volume (mL)	5	10	15
Temperature (°C)	20	40	60
Leaching time (h)	2	4	6

4.4 Solvent extraction^{III}

Central composite face-centered design, with three independent variables: the extractant concentration ([DEHPA]), the ratio of aqueous to the organic (AO), and pH (pH) at three levels ($\pm 1, 0$), was utilized to investigate the extraction of aluminum from phosphoric acid solution to DEHPA. Throughout the experiments, kerosene was utilized as a diluent. To study the extraction isotherms, tests with different aqueous to organic phase ratios (4:1 - 1:4) were done. A McCabe-Thiele diagram was plotted based on the obtained results.

In the stripping tests, the sulfuric acid concentration and the stripping isotherms were investigated. The experiments were done in a one-variable-at-time (OVAT) -manner. Each of the stripping experiments was done at 50 degrees of Celsius in a water bath.

5 RESULTS AND DISCUSSION

In this chapter summarized findings from papers **I-III**, are presented in logical order.

5.1 Elemental analysis^{II}

Table 6 shows the major and trace element concentrations by weight percentages (w-%) for major elements and mg kg⁻¹ for trace elements in PPS and PPA.^{II} The obtained results were compared with different SS and ISSA samples collected from Chinese WWTP. Liang et al.,¹⁰⁵ analyzed the P concentration in raw sludge to be 29.4 g kg⁻¹ and 52.1 g kg⁻¹ in ISSA. From **Table 6** we can conclude that PPS and PPA have greater concentrations of phosphorus irrespective of the metal used in post-precipitation. A similar tendency applies to all elements as can be seen from **Table 6**. For instance, aluminum is present at three-fold higher concentrations in Al-PPA than in ISSA (109.7 g kg⁻¹) that Liang et al., have analyzed. The increase of the concentrations of major elements occurs because the post-precipitation ensues after the removal of biological solids.

The trace element concentrations are increased by a factor of 1.3 after incineration in both sludge types. Still, even after incineration, most trace element concentrations are substantially lower than the average trace element content of the sewage sludge in the EU and Finland.^{106,107} As well, Finland's limit values for trace elements in sludge for agricultural usage, present almost no issue at all.¹⁰⁸ This is illustrated in **Figure 8a** for aluminum-based sludge and ash and **Figure 8b** for iron-based sludge and ash. The single aberration is cadmium in iron-based sludge since its average concentration is over Finland's limit value. However, the cadmium volatilizes at elevated temperatures so it will not concentrate on ash residue.¹⁰⁹ Instead, Cd could concentrate on combustion residues like fly ash.¹¹⁰

Franz¹¹¹ studied sewage sludge ash produced in fluidized-bed incinerators from Switzerland. Compared to those values, PPA contains far lower concentrations of trace elements. For instance, the concentration of zinc is three times lower in PPA than in traditionally produced sewage ash (1850 mg kg⁻¹ d.w.). Usually, the usage of ash in landfilling is prohibited because of the high concentration of Zn. The same trend applies to ISSA produced from Chinese sewage sludge. Liang et al.¹⁰⁵ incinerated raw sewage sludge samples at 600 °C resulting in a copper concentration of 423 mg kg⁻¹. The concentration is five times higher than what aluminum-based PPA contains.

Also, the tin and antimony concentrations in iron-based PPA are only a fraction of concentrations presented in the study of Cyr et al.¹¹² They determined the chemical composition of ISSA to study its technical behavior in cement-based materials. In that analysis, the antimony and tin concentrations were 73 and 283 mg kg⁻¹, respectively.

The acquired findings prove the point that by using the post-precipitation of phosphorus the trace element concentrations are substantially smaller in the sewage sludge. This eases the recovery process as there is no necessity to purify the toxic trace elements from the phosphorus solution product.

TABLE 6. Major and trace element concentrations of PPS and PPA (mean \pm standard error of the mean (s.e.m)).^{II}

	Unit	n	Aluminum-based		Iron-based	
			sludge	ash	sludge	ash
			6	9	6	5
Al	(w-%)		18.3 \pm 0.3	29.1 \pm 0.3	0.221 \pm 0.01	0.351 \pm 0.009
Ca	(w-%)		1.14 \pm 0.01	1.53 \pm 0.03	1.97 \pm 0.02	2.39 \pm 0.02
Fe	(w-%)		1.03 \pm 0.01	1.62 \pm 0.02	36.8 \pm 0.2	43.5 \pm 0.4
Mg	(w-%)		0.075 \pm 0.002	0.114 \pm 0.01	–	0.144 \pm 0.002
P	(w-%)		10.0 \pm 0.2	14.85 \pm 0.15	8.1 \pm 0.08	9.52 \pm 0.12
Cu	(mg kg ⁻¹)		52.6 \pm 0.8	85 \pm 3	37.7 \pm 0.9	49.8 \pm 0.5 [†]
Zn	(mg kg ⁻¹)		219 \pm 4	360 \pm 7	470 \pm 13	587 \pm 7 [†]
Sn	(mg kg ⁻¹)		187 \pm 0.09	3.1 \pm 0.2	1.512 \pm 0.014	1.79 \pm 0.03 [†]
Pb	(mg kg ⁻¹)		0.66 \pm 0.04	1.01 \pm 0.05	–	0.481 \pm 0.015 [†]
Ni	(mg kg ⁻¹)		10.6 \pm 0.6	18 \pm 3	–	–
Sb	(mg kg ⁻¹)		–	–	1.09 \pm 0.04	1.31 \pm 0.02 [†]
Cd	(mg kg ⁻¹)		–	–	3 \pm 0.4	–

– Below LOQ/MDL

[†]n= 6

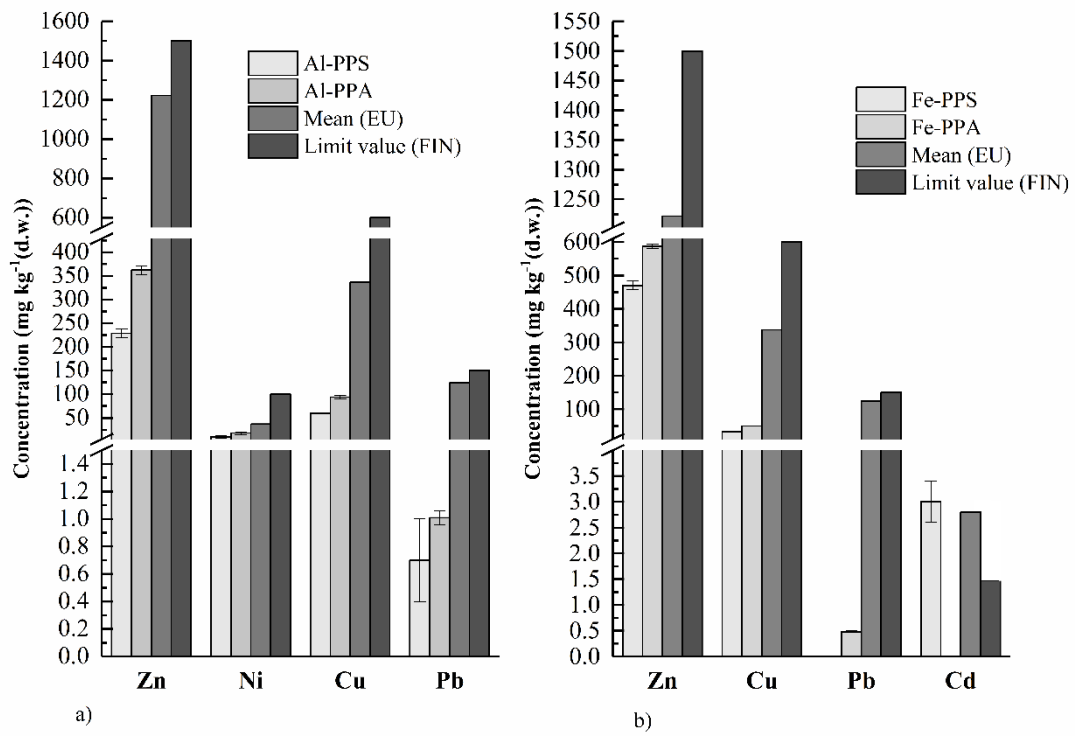


FIGURE 8. Trace element concentrations for PPS and PPA (mean \pm standard error of the mean (s.e.m)), mean EU concentrations and sludge limit values for agricultural use in Finland, (a) Al-PPS and Al-PPA and (b) Fe-PPS and Fe-PPA.^{II}

5.2 Leaching^I

5.2.1 Fitting of the second-order model^I

After the collection of experimental data, the second-order model was first fitted as per **Equation 2** for aluminum-based PPS. The insignificant terms were removed in Minitab 18 software using backward elimination. The resulting ANOVA (analysis of variance) data for the reduced quadratic models are presented in **Tables 7** and **8** for leaching of moist and dry sludge, respectively. The significant terms, for the model of the moist sludge, are acid volume (B), the quadratic effect of volume (B²), the two-level interactions of volume and time (B*D), and the two-level interactions of temperature and time (C*D). Additional insignificant terms left in the model are there to preserve the hierarchy.

The significant terms for the model of dried sludge are the concentration of acid (A), the acid volume (B), the quadratic effect of volume (B²), the quadratic effect of temperature (C²), and the two-level interactions of acid concentration and acid volume (A*B). In both models the adjusted R²-value and the predicted R²-value are over 90 %, meaning that the models fit the data.

Below are presented the regression equations for the leaching models in uncoded units:

Moist sludge:

$$Y = 4004 - 393.1B - 7.21C - 2.1D + 14.00B^2 - 6.17B*D + 1.76C*D \quad (12)$$

Dried sludge:

$$Y = -19488 + 18361A + 5949B - 711C - 259.8 B^2 + 8.36C^2 - 795A*B, \quad (13)$$

where Y is the aluminum concentration in acid after leaching, A is acid concentration, B is the volume of acid, C is temperature and D is leaching time.

TABLE 7. ANOVA table for the reduced quadratic model of moist sludge leaching.¹

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	6	9552419	1592070	155.10	0.000
Volume of acid (B)	1	8526540	8526540	830.66	0.000
Temperature (C)	1	45	45	0.00	0.948
Time (D)	1	3111	3111	0.30	0.587
(B ²)	1	882558	882558	85.98	0.000
(B*D)	1	60865	60865	5.93	0.023
(C*D)	1	79298	79298	7.73	0.011
Error	23	236090	10265		
Lack-of-Fit	20	170898	8545	0.39	0.915
Pure Error	3	65192	21731		
Total	29	9788508			
Model Summary:	R ²	R ² (adj)	R ² (pred)		
	97.59 %	96.96 %	95.89 %		

TABLE 8. ANOVA table for the reduced quadratic model of dried sludge leaching.¹

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	6	1436763871	239460645	41.14	0.000
Concentration (A)	1	1097519032	1097519032	188.53	0.000
Volume of acid (B)	1	26026670	26026670	4.47	0.046
Temperature (C)	1	12670746	12670746	2.18	0.154
(B ²)	1	145294521	145294521	24.96	0.000
(C ²)	1	38511436	38511436	6.62	0.017
(A*B)	1	142190719	142190719	24.43	0.000
Error	23	133890714	5821335		
Lack-of-Fit	20	108523781	5426189	0.64	0.769
Pure Error	3	25366933	8455644		
Total	29	1570654585			
Model Summary:	R ²	R ² (adj)	R ² (pred)		
	91.48 %	89.25 %	85.48 %		

5.2.2 The effect of the four variables on aluminum concentration¹

To study the effects of four variables (concentration of acid, the acid volume, temperature, and time) on the aluminum concentration, response surface plots were made. **Figures 9** and **10** present the 3D response surface plots for moist and dry sludge, respectively. In both cases, one variable showed to be insignificant and was deleted from the model. The effects of variables are briefly discussed here. A more detailed analysis can be found on paper I.

Figure 9 supports visually the ANOVA analysis statement that neither temperature nor time has a significant main effect on the leaching of moist sludge. Nevertheless, the time and temperature have a synergetic influence as a two-level interaction term (C*D) and therefore can not be disregarded when contemplating optimum settings for variable levels. Only the volume of acid has the main effect and is, therefore, the governing process variable. The acid concentration was entirely excluded from the model indicating that the concentration of H⁺ in 0.5 M phosphoric acid can dissolve the aluminum and phosphorus.

As for the dried sludge, it is evident from **Figure 10** and from **Table 8** to see that acid concentration has a major effect on aluminum concentration. On the account of the variable ranges, it cannot be said if a stronger concentration than 2 M phosphoric acid could enhance the leaching efficiency. However, due to the common ion effect, increased acid concentration could cause the re-precipitation of aluminum phosphate and is thus not a viable option. With this model, the leaching time was an irrelevant variable which signifies that diffusion rates are not enhanced by other variables when pulverized sludge is leached.

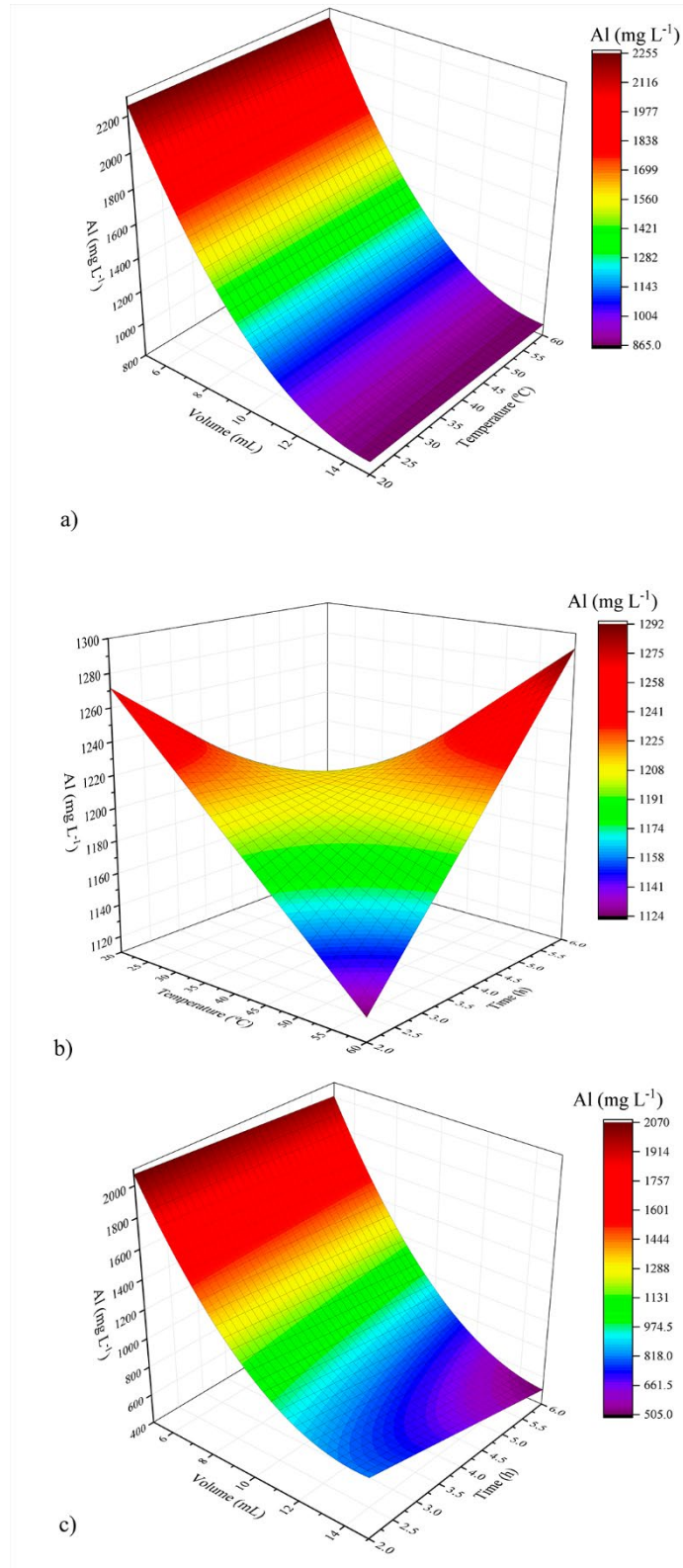


FIGURE 9. Variations in aluminum concentration (Al mg L^{-1}) as moist sludge is leached with phosphoric acid at different variable settings: a) temperature ($^{\circ}\text{C}$) and acid volume (mL), b) time (h) and temperature ($^{\circ}\text{C}$), c) time (h) and acid volume (mL).¹

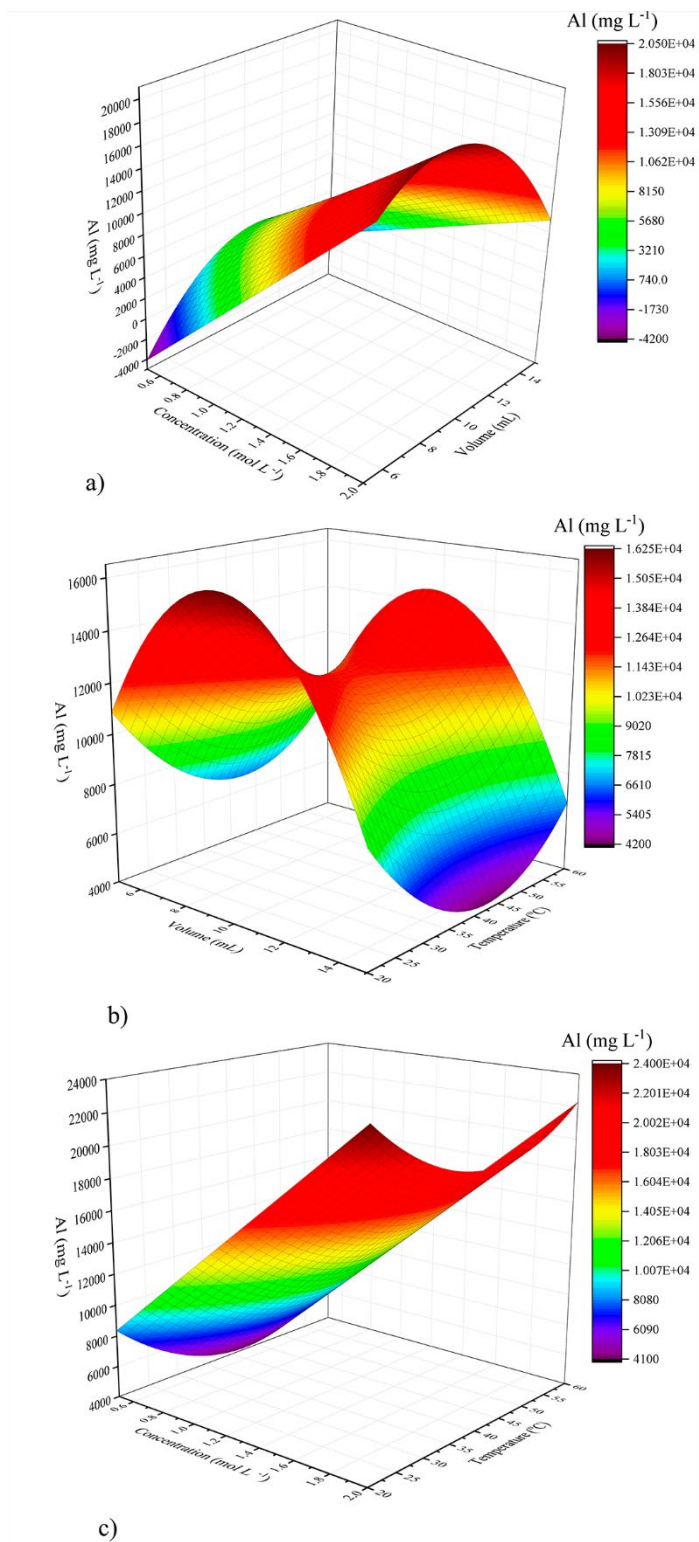


FIGURE 10. Variations in aluminum concentration (Al mg L^{-1}) as dried sludge is leached at different variable settings: a) acid concentration (M) and acid volume (mL), b) acid volume (mL) and temperature ($^{\circ}\text{C}$), c) acid concentration (M), and temperature ($^{\circ}\text{C}$).¹

5.2.3 Optimized leaching conditions¹

Table 9 presents the verification test results for optimized conditions with both sludge types. The difference between the obtained and the predicted values are small, so it can be presumed that the obtained regression models are precise.

TABLE 9. Optimum leaching settings and acquired values (n=3 (mean \pm std. error)) from the verification test.¹

	Factors					Predicted c(Al) (mg L ⁻¹)	Obtained c(Al) (mg L ⁻¹)	Differ- ence (%)
	Sam- ple mass (g)	Acid concen- tration (M)	Vol- ume of acid (mL)	Tempera- ture (°C)	Time of leach- ing (h)			
Moist ^a	2	0.5*	5	60	6	2400	2210 \pm 130	-7.9
Dry ^b	1	2	8.4	20	2*	24650	21030 \pm 800	-14.7

^a Total solids (TS) content 3-4 %

^b dewatered in 105 °C for 16 h

*Insignificant factor

The liquid to solid ratios L/S (mL/g) found here with optimized conditions are 2.5 and 8.4 for moist and dry sludge, respectively. This is a considerably smaller ratio than what Donatello et al.⁵¹ and Fang et al.⁴⁹ achieved when optimizing ISSA leaching with sulfuric acid (L/S ratio 20), though Donatello proposes that by using the optimal stirring equipment as low as L/S ratio of 2 could be attained. Franz¹¹¹ also agrees that the L/S ratio 2 is most favorable, but, the acid concentration in that experiment was high (2.5 M), whereas Donatello determined that 0.19 M sulfuric acid is adequate. Levlin and Hultman¹¹³ succeeded in efficiently leaching P from sewage sludge with only 0.25 M hydrochloric acid (HCL). Since H₃PO₄ is a weak acid, a higher concentration is needed when using it for leaching. Up to a concentration of 2 M of H₃PO₄, no complications with precipitation were detected as contrary to Ottesen et al.⁵⁷ studies with ISSA, where sulfuric acid leaching generated precipitation of gypsum in ash residue.

With moist sludge, it is possible to leach 2.6 times more aluminum than Levlin and Hultman¹¹³ managed to with 0.25 molar HCl in their two-step leaching process for ISSA (836 mg L⁻¹). The time required for the leaching of dry sludge is equivalent to Donatello's results. Franz, however, reported that only 10 minutes of contact time resulted in a 90 % recovery of phosphorous. Biswas et al.,¹¹⁴ likewise examined the impact of time and temperature on H₂SO₄ leaching of ISSA and stated 4 hours and 30 °C as optimal. Those values are similar to 60 °C and 6 hours that are required for moist sludge. Elevated temperature produces the necessary energy to break down the chemical bonds of the metal compounds in the sludge.¹¹⁵

5.2.4 Effect of incineration on leaching^{II}

Figure 11 depicts the impact of the incineration of the sludge on leaching with dilute phosphoric acid. The effectiveness of leaching aluminum is higher with the post-precipitated sewage sludge ash than leaching the post-precipitated sewage sludge. Two reasons for the better leaching efficiency of ash exists. First, the ratio of H^+ /metal increases after incineration because organic matter does not any longer compete with metals. The next reason is the reduced particle size in PPA which creates a higher surface area. After grinding PPS samples resulted in the size range 45 - 1000 μm and PPA samples were 32 - 500 μm without any manual grinding. This eases the leaching of metals from the ash.^{116,117} However, it should be mentioned that the incineration temperature used in this study does not reflect actual temperatures used in incineration processes.

While the leaching of metal is better with ash, the effect of increasing metal concentrations must be considered on the entire recovery process. As aluminum is the main component to produce the crud in SX-settlers, the aluminum concentration of $4.60 \pm 0.03 \text{ g L}^{-1}$ in leach solution after leaching might set a challenge.⁹⁶

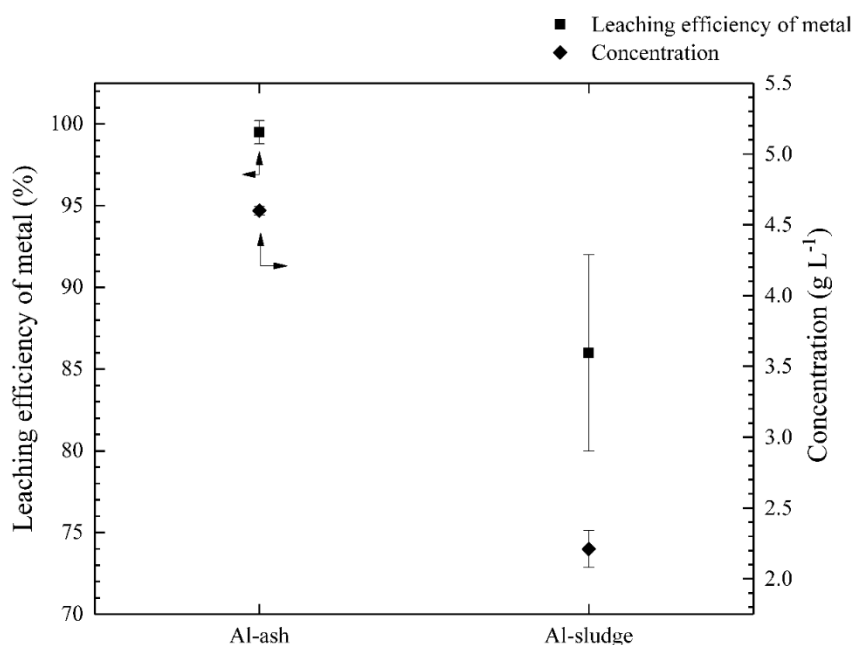


FIGURE 11. Leaching efficiency (square, left axis) of aluminum-based PPS and PPA in dilute phosphoric acid ($n=3$, mean \pm standard deviation). The concentration of Al in phosphoric acid after leaching (rhombus, right axis) ($n=3$, mean \pm standard deviation).^{II}

5.3 Solvent extraction^{III}

5.3.1 Extraction

Based on the experimental data the reduced quadratic model of extraction was fitted and its ANOVA table is presented in **Table 10**. First-order terms have a P-value below 0.05, indicating that all three factors influence the extraction. The lack-of-fit test results in a P-value of 0.373, which means it is insignificant. The goodness-of-fit value for the model is excellent as the coefficient of determination (R^2 -value) is high, 90.32 %, indicating that simply 9.68% of the total sample variation is not described by the model. The adjusted R^2 -value of 85.85 % shows that all the factors involved in the model influence the response variable.

The regression equation is expressed as follows:

$$Y = -207.9 + 176.5\text{pH} + 50.7[\text{DEHPA}] - 5.80\text{AO} - 35.4\text{pH}^2 + 6.54\text{AO}^2 - 16.7([\text{DEHPA}] \cdot \text{AO}), \quad (14)$$

where Y is the efficiency of extraction (%), $[\text{DEHPA}]$ is extractant concentration (M) and AO is the ratio of the volume of the aqueous phase to the volume of the organic phase. Since the R^2 -values are high, it is possible to calculate the efficiency of aluminum extraction within the factor limits.

TABLE 10. ANOVA table for aluminum extraction with DEHPA.^{III}

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	6	3789.40	631.57	20.22	0.000
Linear	3	3587.50	1195.83	38.28	0.000
pH	1	1241.00	1241.00	39.73	0.000
[DEHPA]	1	577.60	577.60	18.49	0.001
AO	1	1768.90	1768.90	56.63	0.000
Square	2	151.90	75.95	2.43	0.127
pH*pH	1	102.60	102.60	3.28	0.093
AO*AO	1	136.76	136.76	4.38	0.057
2-Way Interaction	1	50.00	50.00	1.60	0.228
[DEHPA]*AO	1	50.00	50.00	1.60	0.228
Error	13	406.06	31.24		
Lack-of-Fit	9	312.56	34.73	1.49	0.373
Pure Error	4	93.50	23.38		
Total	19	4195.46			
Model Summary:	R^2 (%)	R^2_{adj} (%)	R^2_{pred} (%)		
	90.32	85.85	74.32		

5.3.1.1 Impact of the variables on extraction efficiency

To analyze the impact of variables (extractant concentration, AO ratio, and pH) on extraction efficiency, response surface plots were illustrated based on **Equation 14**. The plots are presented in **Figure 12**.

Merely one interaction term (extractant concentration versus AO) appears in the reduced quadratic model for aluminum extraction. Then again, variables AO and pH have a quadratic effect. **Figure 12a** displays that the interaction between the extractant concentration and the AO ratio creates a plane with a curved slope. No maximum value is found within the factor levels, but the best result (59.6%) is attained when the molar ratio of DEHPA and Al is at maximum. If an organic phase with a higher concentration of DEHPA were to be applied to get an even higher molar ratio, a phase modifier would be needed to improve the separation of different phases.

Figures 12b-c depict interaction terms that are not contained within the model. In both instances, the best efficiencies are achieved when pH and extractant concentration are at the maximum variable value and the volume ratio of aqueous to organic is 1:2.

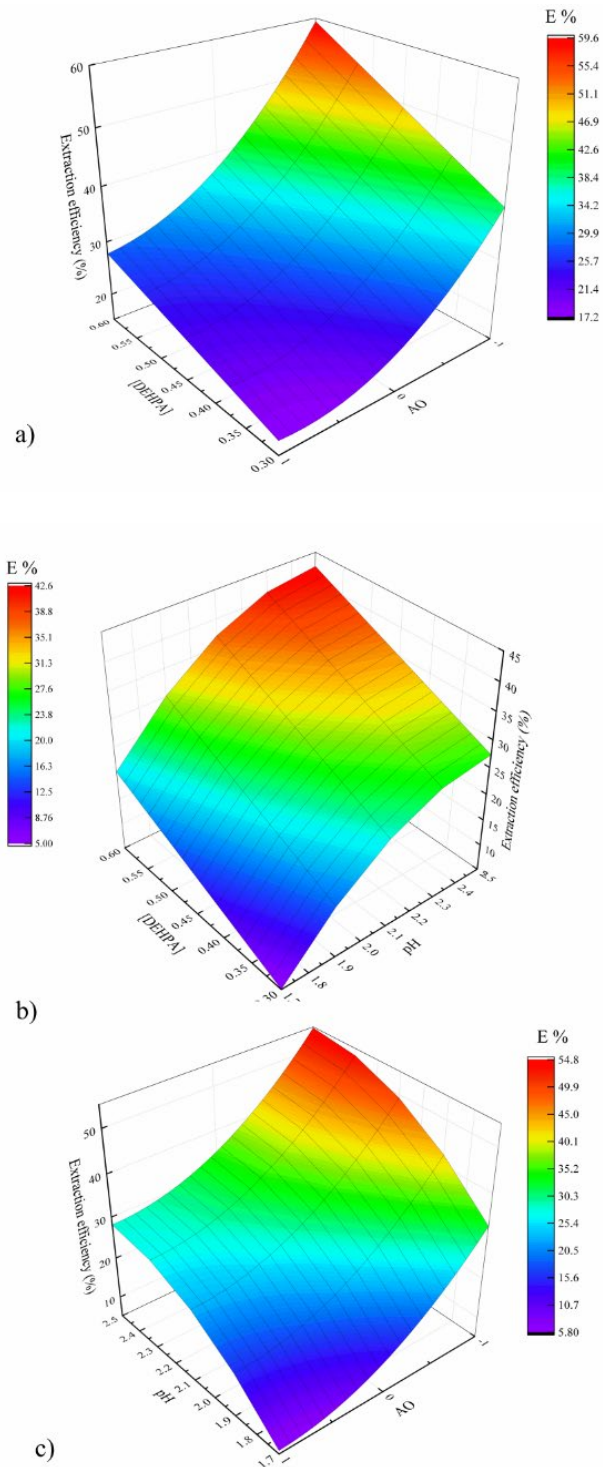


FIGURE 12. Variations in extraction efficiency of aluminum at different variable settings: a) AO ratio vs concentration of DEHPA (M) b) pH vs concentration of DEHPA (M) and c) AO ratio vs pH.^{III}

5.3.1.2 Optimization and extraction reaction

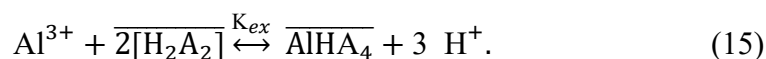
The predicted value for maximum aluminum extraction efficiency was determined based on **Equation 14** using the variable values of 2.5 for pH and 0.6 M for extractant concentration. For the AO ratio, the smallest level of 1:2 was used. By using these variable settings, the predicted extraction efficiency value of 64.9 % with a 95 % confidence interval of 56.1-73.7 % was attained.

The model was checked by contacting the dilute phosphoric acid solution containing aluminum 2.4 g L⁻¹, with organic phase using the maximum variable levels for aqueous phase pH (2.5) and extractant concentration (0.6 M) and the lowest level for the AO ratio (1:2). The check test resulted in extraction efficiency of 69 ± 5 % for aluminum. This indicates that the regression model developed is precise for calculating the aluminum extraction efficiency at different variable settings.

The DEHPA concentration of 0.6 M is greater than that of Mohapatra et al.¹¹⁸ used while studying aluminum recovery with DEHPA from diversified sulfate solutions. According to their findings, just 0.3 M of Na-DEHPA was enough to extract aluminum. Nevertheless, the phosphoric acid solution holds numerous metallic contaminants, such as Fe, Ca, and Mg, which contend with aluminum in the cation exchange reaction. Additionally, Mohapatra et al.¹¹⁸ had a less acidic equilibrium pH. Nonetheless, the pH cannot be raised in the phosphoric acid solution because of the precipitation of the aluminum phosphate at above pH 2.5.¹¹³

The number of released protons (q) was determined, by extracting the aqueous phase (0.5 molar H₃PO₄ containing aluminum 2.4 g L⁻¹) with 0.6 M DEHPA in kerosene as the volume ratio was kept at 1. The pH of the aqueous phase was adjusted beforehand. To keep the ionic strength constant in the aqueous phase, a NaCl solution of 1 molar was added. The distribution factor as a function of equilibrium pH is displayed in **Figure 13** as a log-log graph. The slope of 2.95 ± 0.3 is showing that three protons are exchanged for one aluminum ion during extraction. The graph can be concluded to be a satisfactory fit, as Pearson's correlation coefficient for the linear fitting is 0.984.

Mashimo et al. determined the number of extractant molecules (n) that form a complex with aluminum.¹¹⁹ They proved that with dimeric DEHPA two molecules are required for the aluminum equilibrium reaction in sulfuric acid media. Wu et al.¹²⁰ came to a similar deduction with rare earth elements, which normally exist as trivalent cations similar to aluminum. With this knowledge, the cation exchange reaction is written as presented below:



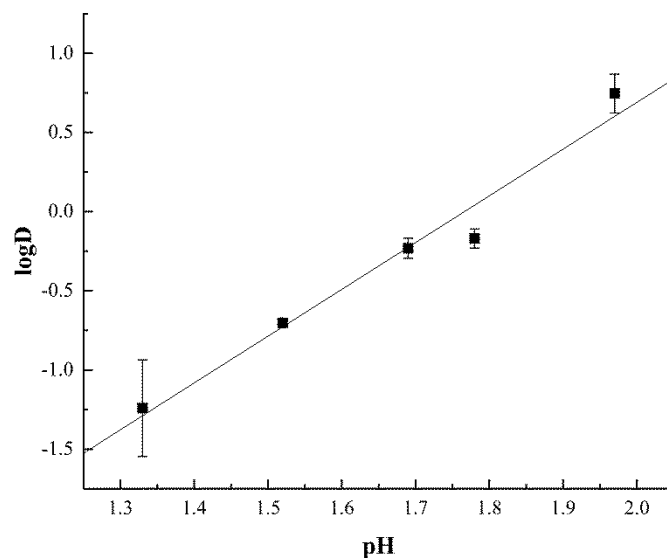


FIGURE 13. Influence of pH on the distribution factor of aluminum.^{III}

5.3.1.3 McCabe and Thiele diagram for extraction

The extraction isotherms were defined by contacting the aqueous phase having an aluminum concentration of 2.0 g L^{-1} with 0.6 M DEHPA at various AO ratios from 0.25 to 4. **Figure 14** illustrates the acquired extraction isotherms. An excellent polynomial fitting for the extraction isotherms was reached as the R^2 - value was 97.6 %. Based on the McCabe-Thiele graph, three theoretical stages are needed for the comprehensive extraction of Al^{3+} , when the AO ratio is 1:2. More often than not, one extra stage is necessary for complete extraction.⁸⁵ This was tested by batch extraction in which the dilute phosphoric acid solution containing 2.2 g L^{-1} of aluminum and having a pH of 2.5, was contacted four times with a new organic phase consisting of 0.6 M DEHPA in kerosene. The experiment yielded an extraction efficiency of $99.0 \pm 0.3 \%$ for aluminum, validating the necessity of four stages.

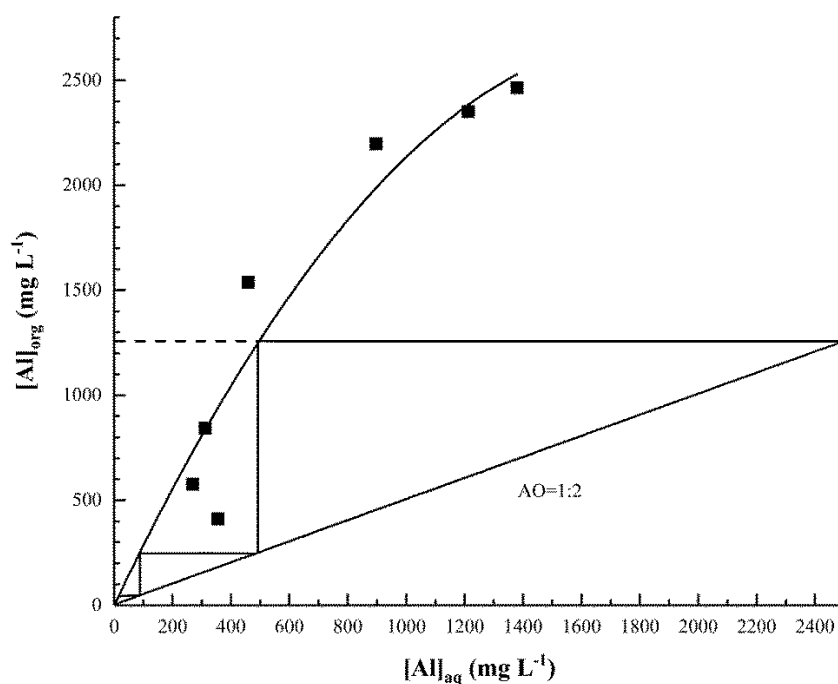


FIGURE 14. McCabe-Thiele graph of aluminum extraction.^{III}

5.3.2 Stripping

The necessary stripping stages for the comprehensive recovery of aluminum from the organic solution of 0.6 M DEHPA in kerosene, were defined by contacting the 0.9 M sulfuric acid with loaded DEHPA at various AO phase ratios ranging from 0.16 to 1. **Figure 15** portrays the acquired extraction isotherms for the stripping of aluminum. An agreeable R^2 -value of 82.4 % was achieved for polynomial fitting. To quantitatively strip aluminum by using a volume ratio of 1:2 and 0.9 M sulfuric acid, two stages are needed. Mohapatra et al.,¹¹⁸ managed to strip aluminum with only one stage (0.3 M Na-DEHPA, Al 2.4 g L⁻¹) as they utilized faintly greater acid concentration (1 M) and a volume ratio of 1:1.

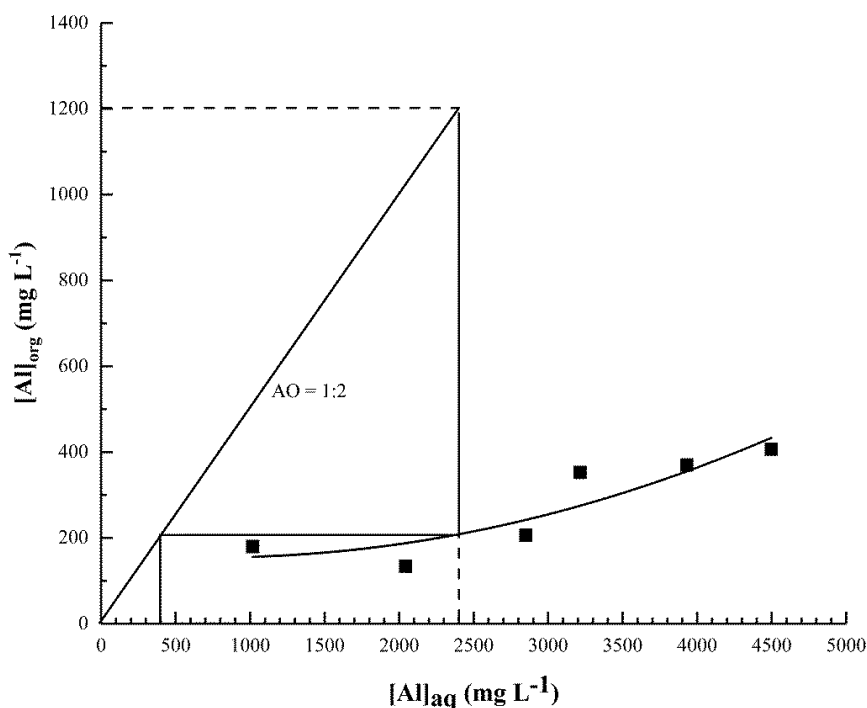


FIGURE 15. McCabe-Thiele graph for stripping of aluminum.^{III}

Figure 16 shows the stripping efficiency of aluminum and the concentration of aluminum at different AO ratios. It is clear from **Figure 16** that the stripping efficiency starts to diminish after the AO ratio of 1:2 even as the aluminum concentration improves through each phase ratio. The drop in efficiency is explicated by the reduction of the H^+ vs. metal molar ratio. With smaller phase ratios more aluminum is available than the sulfuric acid can strip. It is possible to concentrate Al on stripping solution with a lower AO ratio, but this would radically reduce the effectiveness of one step.

If the AO ratio of 1:2 is used then the aluminum is concentrated by a factor of 1.85 resulting in an aluminum concentration of $2.04 \pm 0.04 \text{ g L}^{-1}$. When this kind of stripping was conducted, the P concentration was measured to be $0.25 \pm 0.05 \text{ g L}^{-1}$ in the aqueous phase. This shows that no more than 1.5 % of P is co-extracted with aluminum during the extraction.

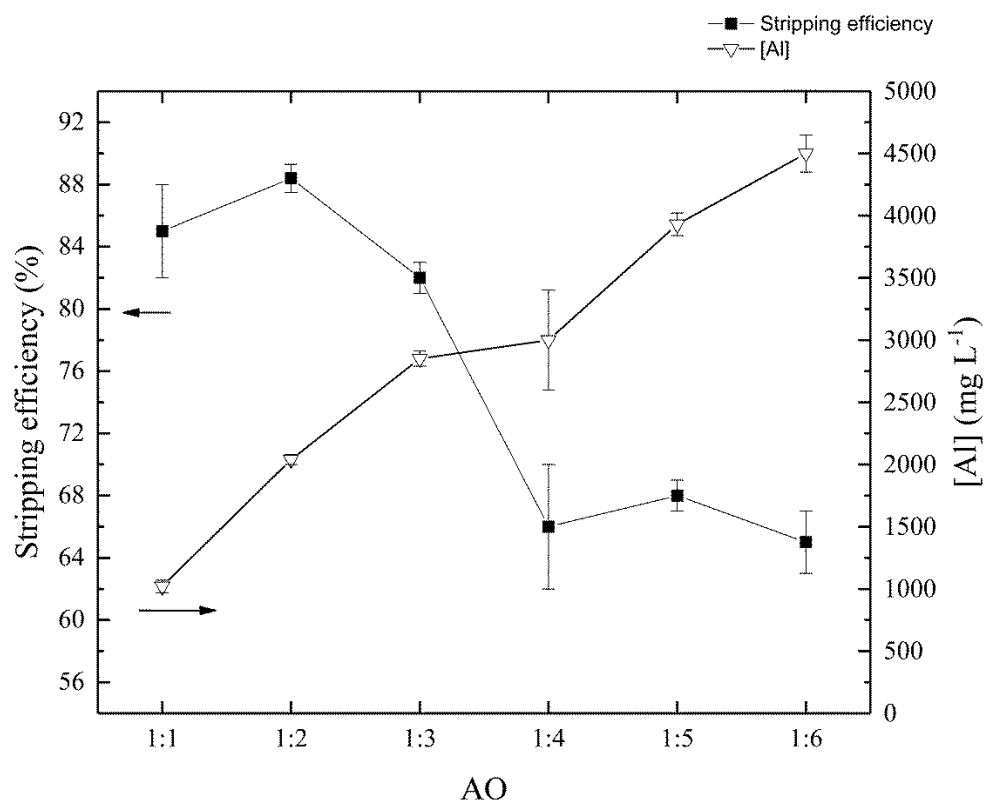


FIGURE 16. Efficiency percentages for aluminum stripping and concentration of aluminum in 0.9 M sulfuric acid solution after stripping.^{III}

6 CONCLUDING REMARKS

There is no single solution to achieving a phosphorus-secure future.

– Dana Cordell *et al.*¹²¹

This research has been a part of the Helsinki Region Environmental Service Agency's RAVITA-project, which aims to develop a nutrient recovery process fitting for WWTPs of different sizes. The focus of this study was to develop a method for P recovery from post-precipitated sewage sludge.

The major element and trace element concentrations were determined from both aluminum- and iron-based PPS and PPA. Due to the lower content of biological matter, the major element concentrations in PPS resulted in higher concentrations than in traditionally produced SS. A 1.5-fold increase in the major element concentrations could be seen after incineration. However, the incineration temperature (550 °C) used in this study is not comparable to industrial-scale incineration, which typically utilizes temperatures above 850 °C. Hence, no extensive conclusions regarding the effect of incineration on PPS should be drawn. The trace element concentrations were lower in both types of PPS than the average concentrations of toxic trace metals in SS in the EU region. This indicates that no separate procedure for trace element removal is needed when processing PPS.

The leaching of Al-PPS with dilute phosphoric acid was optimized to achieve the highest possible leaching efficiency for Al. The central composite face-centered design was utilized in the optimization tests and a validated model was separately achieved for the moist sludge (3-4 % TS) and the dry sludge. No clear maximum could be seen in the response surface plots drawn from the models, but the optimal conditions were found within the experimental region. The leaching in optimized conditions produced the maximum recovery of 85 % for aluminum.

Solvent extraction was chosen as the method to recover the aluminum from the leach solution and at the same time purify the obtained phosphoric

acid solution. The extraction with DEHPA diluted in kerosene was investigated with a central composite face-centered design. At the optimal conditions, an aluminum extraction efficiency of 64 % in one extraction step was attained. However, the formation of crud during the extraction indicates that either the AO ratio is too small, leading to the overloading of DEHPA or that the total suspended solids (TSS) concentration in the aqueous phase is too high instigating the fine particles to emulsify during the mixing. The causes of the crud formation and the techniques to avoid it are issues that need to be investigated further. The stripping was concluded with sulfuric acid resulting in stripping efficiency of 98 % in one step, thus concentrating aluminum from the organic phase by a factor of 1.85.

The results presented in this dissertation show that phosphorus can be leached from the PPS. By treating the formed sludge directly, instead of the ash residue, the costs of building an incineration plant can be avoided. Since the post-precipitation can easily be adjusted into existing WWTPs of all sizes, it is a viable method to be used in Finland. Provided that challenges with crud formation in solvent extraction can be overcome, it is a suitable method for the purification of recovered phosphoric acid, thus also enabling the recycling of the precipitation metal.

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ORIGINAL PAPERS

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OPTIMIZING THE H_3PO_4 LEACHING CONDITIONS OF POST- PRECIPITATED SEWAGE SLUDGE USING RESPONSE SURFACE METHODOLOGY

by

Sini Reuna & Ari Väisänen 2018

Journal of Environmental Management vol. 226, 70-75

DOI: 10.1016/j.jenvman.2018.08.004

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Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Optimizing the H₃PO₄ leaching conditions of post-precipitated sewage sludge using response surface methodology

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ARTICLE INFO

Keywords:

Post-precipitation
Sewage sludge
Phosphorus recovery
Central composite design

ABSTRACT

The leaching procedure of post-precipitated aluminium phosphate sludge with dilute phosphoric acid was developed. The leaching offers a route to recover both critical phosphorous from sewage sludge and the metal used in precipitation. Using phosphoric acid as leaching solution makes it possible to continue the recovery process without the need to remove chloride or sulfate anions. The optimization of the leaching was based on experimental three-level-four-variable central composite face-centered design. The four variables included were acid concentration, volume of acid, temperature and time of leaching. The leaching was conducted for dewatered and water-containing sludge (total solid content 3–4%) and for both second-order regression models were obtained. For water-containing sludge optimal conditions for leaching are solid to liquid ratio (S/L) 400 gL⁻¹, a temperature of 60 °C and a leaching time of 6 h. For the dewatered sludge, optimal leaching is attained when S/L ratio 119 gL⁻¹ with 2 M acid is used at a temperature of 20 °C. The obtained results enable the developing of full-scale process where phosphate in the sludge is refined to phosphorous acid and metal used in sludge production recycled back to precipitation.

1. Introduction

High phosphorus content in water systems accelerates eutrophication (Morse et al., 1998) and because of that its removal from wastewaters is required by the directive of European Commission Council (91/271/EEC). However at the same time, phosphorus is an irreplaceable element for food production as it is used in fertilizers (Cordell et al., 2009). The current phosphate rock deposits being depleted and for that reason European Commission listed it as a critical raw material in 2014 (European Commission, 2014). In 2017 the critical raw material listing was updated and elemental phosphorus was added to the list (European Commission, 2017). This encourages research on the possibility to recover vital phosphorus from secondary sources, like sewage sludge, and process it to a valuable product, for instance phosphorous acid.

Phosphorus is most often removed from wastewaters by chemical precipitation as a phosphate or via enhanced biological treatment (Bashar et al., 2018; Pratt et al., 2012). The sludge formation in chemical precipitation is high and currently the most common ways to process the sludge is incineration, using it in landfilling or agricultural use (Kacprzak et al., 2017). However the agricultural use of the sludge is restricted in some European countries because of the heavy metals, pathogens and micropollutants in the sludge (Kelessidis and Stasinakis,

2012; Veeken, 1999). Incinerating sewage sludge is widely used in European countries, but it is energy-consuming process and the heavy metals are enriched in the ash (Franz, 2008; Kelessidis and Stasinakis, 2012). The problem with heavy metals can be overcome with chemical post-precipitation where phosphorus is precipitated with aluminum or iron as phosphate salt in the end of wastewater process while still achieving the required removal efficiency of phosphorus (Eklund et al., 1991). Formed sludge can then be processed without the need to consider the possibility of heavy metals contaminating the end-product.

Leaching in alkaline or acidic conditions is one of the most widely investigated methods for recovery of phosphorus from sewage sludge, but most studies focus on incinerated sewage sludge ash (ISSA) (Donatello et al., 2010; Donatello and Cheeseman, 2013; Franz, 2008). Few studies concentrating on the leaching of the sludge has been reported, but these are focused on the sludge formed in conventional chemical precipitation (Levlin et al., 2002). Typically the leaching solutions investigated have been ones within lower price range such as inorganic sulfuric acid H₂SO₄, and nitric acid HNO₃, and organic acids like oxalic acid C₂H₂O₄ (Fang et al., 2018; Li et al., 2018). However, the problem with these is that excess sulfate or chloride need to be removed from leaching solution (Ottosen et al., 2013) which adds another process step in the recovery process. Leaching with dilute phosphoric acid (H₃PO₄) would make it possible to continue the processing without the

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<https://doi.org/10.1016/j.jenvman.2018.08.004>

Received 17 April 2018; Received in revised form 29 June 2018; Accepted 1 August 2018

Available online 13 August 2018

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need to remove chloride or sulfate anions. Phosphorus is recovered as phosphoric acid due the low pH (Levlin and Hultman, 2004) and the metal used in precipitation step can be circulated back to the precipitation via ion exchange or solvent extraction (Levlin et al., 2004; Mohapatra et al., 2007).

The aim of this study is to optimize the leaching of moist or dried post-precipitated aluminium phosphate sludge with dilute phosphoric acid. To achieve this goal regression equations for both types of sludge are created with response surface methodology (RSM). The methodology is commonly used in natural sciences for optimization purposes (He et al., 2018; Sen et al., 2017). The obtained results serve as a first step in developing the phosphorous recovery process where not only phosphorous is recovered but also the metal used in precipitation step can be recycled.

2. Experimental

2.1. Materials and chemicals

The batch of post-precipitated aluminium phosphate sludge was received from RAVITA pilot plant located in Viikinmäki wastewater treatment plant, Helsinki. Before use the sludge was filtrated (Whatman no. 41 filtration paper). This resulted in sludge with solid content of about 3–4%. A part of the filtrated sludge was held at 105 °C for 16 h in order to dewater it and then manually ground in a mortar.

All chemicals were of analytical grade and were used as purchased without further purification. The standard stock solutions of elements (1000 mg L⁻¹) were supplied by PerkinElmer. Phosphoric acid (85 wt. %) was obtained from VWR International. Nitric acid (65–68 wt. %) and hydrochloric acid (37–39 wt. %) were purchased from Sigma-Aldrich. High-purity water produced by a Purelab Ultra water purification system supplied by Elga (Buckinghamshire, U.K.) was used throughout the experiments.

2.2. Methods

2.2.1. Digestion of sludge

A sludge sample (250 mg for moist and 100 mg for dry sludge) was accurately weighed into a 50 mL centrifuge tube (Sarstedt) and 10 mL of aqua regia (HCl + HNO₃) was added. The bottle was closed and placed into a 750 W, 37 kHz, Elmasonic P ultrasonic water bath supplied by Elma Schmidbauer GmbH. The ultrasound-assisted extraction was carried out at a temperature of 60 °C. The sonication was conducted in the series of 8 × 3 min. After each sonification step the samples were shaken by hand. After cooling, the sample solution was filtered (Whatman no. 41 filter paper) into a 50 mL volumetric flask. The residue was washed three times with a few milliliters of water and diluted with high purity water to a volume of 50 mL.

2.2.2. Leaching of sludge

The leaching was conducted in a water bath with manual temperature control. A sludge sample (2 g for moist and 1 g for dry sludge) was accurately weighed into a 50 mL centrifuge tube and the volume of phosphoric acid depending on the experimental design was added. Samples were placed in water bath and were stirred with magnetic stirrer with the speed of 250 rpm (rounds per minute). After leaching samples were centrifuged for 10 min with speed 3500 rcf (relative centrifugal force) with Heraeus Labofuge 400 centrifuge supplied by Thermo Scientific and filtrated (Whatman no. 41 filtration paper).

Because the pH during leaching is below 2.2 (Levlin and Hultman, 2004) the dissolution reaction is as follows:



The equation (1) proves that with high leaching efficiency of aluminium also phosphorus is leached simultaneously.

Table 1

Coded and actual levels of variables in the experimental design.

Factors	Levels		
	Lowest	Center	Highest
	-1	0	+1
Acid concentration (M)	0.5	1.25	2.0
Volume of acid (mL)	5	10	15
Temperature (°C)	20	40	60
Time of leaching (h)	2	4	6

2.2.3. Experimental design

Central composite face-centered design with four independent variables (acid concentration (A), volume of acid (B), temperature (C) and time of leaching (D)) and three levels ($\pm 1, 0$), including six replicates at the center point, was used to design the experiments. The variables and their values are shown in Table 1. The experimental runs were randomized in order to reduce bias from extraneous or uncontrollable conditions. The response variable measured was the concentration of aluminium in acid after leaching (Y). The concentration of phosphorus cannot be used as a response because phosphoric acid is used as leaching solution. The design was generated with Minitab 18 software. The experimental plan and the results are presented in supplementary data (Table S1).

2.2.4. Statistical analysis

The response surface analysis of the Minitab 18 software was used to analyze the experimental data (Table S1) and to produce the response surface plots. The experimental data were fitted to a second-order polynomial model and regression coefficients obtained. The generalized second-order response surface model used in the response surface analysis was as follows:

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i < j}^k \beta_{ij} x_i x_j + \varepsilon, \quad (2)$$

where y is the response (aluminium concentration), β_0 is constant coefficient, β_i is the linear effect, β_{ii} is the quadratic effect, β_{ij} is the interaction effect and ε is the error observed in response (Montgomery, 2009). After analysis Minitab 18 software's response optimizer feature was used to achieve maximum value for aluminium concentration within the range of factor levels.

2.2.5. ICP-OES measurements

The element concentrations were determined with a PerkinElmer ICP-OES (inductively coupled plasma-optical emission spectrometer) Optima 8300 –spectrometer. The GemCone low flow –nebulizer with cyclonic spray chamber was used for sample introduction. The measurement parameters for all measurements were argon gas flow of 8 L min⁻¹, nebulizer gas flow of 0.6 L min⁻¹, auxiliary gas flow of 0.2 L min⁻¹, sample flow rate of 1.5 L min⁻¹ and the radio frequency power of 1500 W. The wavelengths, calibration ranges and the method detection limits are presented for each element in supplementary data (Table S2). The method detection limits were determined according to U.S. Environmental Protection Agency method 2007 (U. S. Environmental Protection Agency, 2001).

3. Results

3.1. Analysis

The total concentration of aluminium and phosphorus in post-precipitated sludge was analyzed. The concentrations (mean \pm standard error) extracted by ultrasound-assisted digestion method and determined by ICP-OES are shown in Table 2. Other analyzed elements

Table 2
Determined element concentrations (mg kg⁻¹) of post-precipitated phosphorus sludge (n = 3).

	moist sludge ^a	dry sludge ^b
Al (mg kg ⁻¹)	6500 ± 400	188400 ± 800
P (mg kg ⁻¹)	1580 ± 80	44900 ± 300

^a Solid content 3–4%.

^b Dried in 105 °C for 16 h.

are presented in supplementary data [Table S3](#).

3.2. ANOVA analysis and fitting of second-order model

The second-order model was first fitted according to equation (2), but in order to achieve an improved model for the leaching conditions, insignificant model terms were removed. A backward elimination process with Minitab 18 software was chosen to automatically remove the insignificant terms. The resulting ANOVA (analysis of variance) data for the reduced quadratic models of moist and dried sludge leaching are given in [Tables 3 and 4](#), respectively. It can be seen from [Table 3](#) that the F-value for the model of reduced quadratic model of moist sludge leaching is 155.1 and the corresponding P-value is less than 0.0001. This means that the model is significant and can be used for optimization of leaching. The significant terms in this model are volume of acid (B), the quadratic effect of volume (B²), the two-level interactions of volume and time (B*D) and the two-level interactions of temperature and time (C*D). Other insignificant terms remaining in the model are there to support hierarchy. The P-value for the lack-of-fit is 0.915, which indicates that it is not significant. The goodness-of-fit of the model can be checked from the coefficient of determination (R²). The R²-value is high, 97.59%, which means that only 2.41% of the total sample variation cannot be explained by the model. The adjusted R²-value of 96.96% indicates that all the factors included in the model are significant and affect the response variable. High predicted R²-value 95.89% proves that this model can predict proper responses for new observations.

From [Table 4](#) can be seen that F-value for the reduced quadratic model, where dried sludge is used for leaching, is 41.14 and the corresponding P-value is less than 0.0001. This model is also significant and can be used for optimization of leaching. The significant terms are acid concentration (A), volume of acid (B), the quadratic effect of volume (B²), the quadratic effect of temperature (C²) and the two-level interactions of acid concentration and volume of the acid (A*B). Other insignificant terms remaining in the model are there to support hierarchy. The P-value for the lack-of-fit is 0.769, which indicates that it is not significant. The R²-value is high, 91.48%, which means that only 8.52% of the total sample variation cannot be explained by the model. The adjusted R²-value (89.25%) and the predicted R²-value (85.48%)

Table 3
ANOVA table for reduced quadratic model of moist sludge leaching (response: concentration of aluminium (mg L⁻¹)).

Source	DF	Adj SS	Adj MS	F-Value	P-Value	Remarks
Model	6	9552419	1592070	155.10	0.000	Significant
Volume of acid (B)	1	8526540	8526540	830.66	0.000	
Temperature (C)	1	45	45	0.00	0.948	
Time (D)	1	3111	3111	0.30	0.587	
Volume of acid*Volume of acid (B ²)	1	882558	882558	85.98	0.000	
Volume of acid*Time (B*D)	1	60865	60865	5.93	0.023	
Temperature*Time (C*D)	1	79298	79298	7.73	0.011	
Error	23	236090	10265			
Lack-of-Fit	20	170898	8545	0.39	0.915	Not significant
Pure Error	3	65192	21731			
Total	29	9788508				
Model Summary:	R ²	R ² (adj)	R ² (pred)			
	97.59%	96.96%	95.89%			

are both relatively high, meaning that the model fits to the data.

The regression equations for the leaching of moist and dried phosphorus sludge in uncoded units were obtained as follows:

Moist sludge:

$$Y = 4004 - 393.1 B - 7.21 C - 2.1 D + 14.00B^2 - 6.17B*D + 1.76C*D \quad (3)$$

Dried sludge:

$$Y = -19488 + 18361 A + 5949 B - 711 C - 259.8 B^2 + 8.36C^2 - 795 A*B \quad (4)$$

where Y is the concentration of the aluminium in acid after leaching, A concentration of the acid, B acid volume, C temperature and D leaching time. The regression equations obtained can be used to predict aluminium concentration in acid after leaching within the limits of the experimental factors. The model assumption checks are presented in supplementary data along with main effects plots.

3.3. Effect of the four variables on aluminium concentration in leaching acid

Based on the second-order models created in the previous section, response surface plots were made to investigate the effects of four variables (acid concentration, volume of acid, temperature and time of leaching), on the aluminium concentration in acid after leaching of moist or dried sludge. In both models one factor proved to be insignificant and was removed from the model. Hence, only three variables remained and in each surface plot one variable is kept at the central level (0), while considering the other two variables.

3.3.1. Factor effects when leaching the water containing sludge

In the reduced quadratic model for leaching of moist sludge only two interaction terms are present volume of acid*time and temperature*time. Those interactions can be investigated by drawing the 3D response plots ([Fig. 1a–c](#)). In [Fig. 1a](#), where the effects of temperature and acid volume to the aluminium concentration form a plane with a curving slope, an increase in aluminium concentration when volume decreases can be seen. Because concentration proved to be insignificant factor it can be deduced that H⁺ concentration in 0.5 M phosphoric acid is sufficient to leach the aluminium and along with the phosphorus from the moist sludge. In that case, the volume becomes the regulating factor for aluminium concentration and any increase in volume decreases the aluminium concentration. A slight increase in the aluminium concentration is also obtained when leaching time is increased from 2 to 6 h, but according to ANOVA analysis the change is so minor that temperature on its own does not enhance the leaching. The maximum value of 2250 mg L⁻¹ for aluminium concentration is achieved when acid S/L ratio is 400 g L⁻¹ and temperature is 60 °C. [Fig. 1b](#) displays the effects of temperature and time on the aluminium concentration. When both factors are increased, temperature from 20 to

Table 4
ANOVA table for reduced quadratic model of dried sludge leaching (response: concentration of aluminium (mg L^{-1})).

Source	DF	Adj SS	Adj MS	F-Value	P-Value	Remarks
Model	6	1436763871	239460645	41.14	0.000	Significant
Concentration (A)	1	1097519032	1097519032	188.53	0.000	
Volume of acid (B)	1	26026670	26026670	4.47	0.046	
Temperature (C)	1	12670746	12670746	2.18	0.154	
Volume of acid*Volume of acid (B^2)	1	145294521	145294521	24.96	0.000	
Temperature*Temperature (C^2)	1	38511436	38511436	6.62	0.017	
Concentration*Volume of acid ($A*B$)	1	142190719	142190719	24.43	0.000	
Error	23	133890714	5821335			
Lack-of-Fit	20	108523781	5426189	0.64	0.769	Not significant
Pure Error	3	25366933	8455644			
Total	29	1570654585				
Model Summary:	R^2	R^2 (adj)	R^2 (pred)			
	91.48%	89.25%	85.48%			

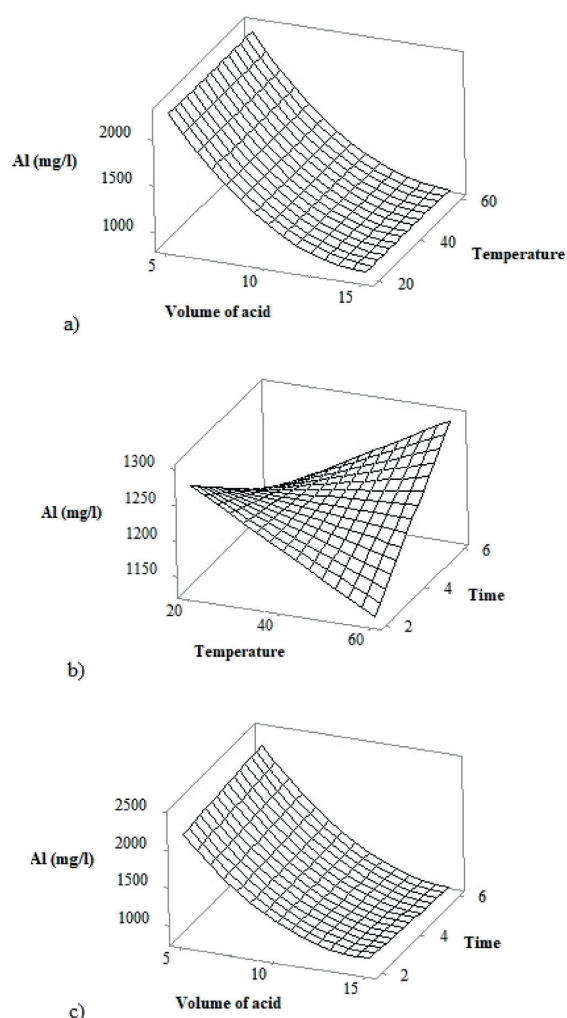


Fig. 1. Changes in aluminium concentration (Al mg/l) with respect to: a) volume of acid (mL) and temperature ($^{\circ}\text{C}$), b) temperature ($^{\circ}\text{C}$) and time (h), c) acid volume (mL) and time (h) when leaching the moist sludge ($m = 2\text{ g}$).

60°C and time from 2 to 6 h, a maximum aluminium concentration is attained. The interaction between these two factors enhances the leaching, but only when both factors are at higher level. Aluminium concentration is at maximum 1300 mg L^{-1} when temperature is 60°C and leaching time is 6 h. Fig. 1c shows the effect of acid volume and leaching time to the aluminum concentration. The plot confirms the ANOVA analysis determination that the leaching time has no significant effect in sludge leaching, even though a small increase in aluminium concentration is seen when leaching time increases. Aluminium concentration is at maximum 2330 mg L^{-1} when S/L ratio is 400 g L^{-1} and leaching time is 6 h.

At the current factor value ranges, the volume of acid is the dominant process variable. However, the leaching time and temperature have a synergistic effect and therefore cannot be discarded when considering optimal conditions for leaching process.

3.3.2. Factor effects when leaching the dewatered sludge

There is only one interaction term present in the reduced quadratic model for leaching of dewatered sludge, but both temperature and acid volume have significant quadratic effects in the model. In Fig. 2a can be seen that higher acid concentration increases the amount of leached aluminium. The rising ridge surface indicates that 2 M phosphoric acid is needed to maximize the leached aluminium. Due to the factor ranges it cannot be said if higher H^{+} concentration is needed for better leaching efficiency. However, this would mean increasing the phosphate concentration in the leaching solution. This will cause re-precipitation of aluminium phosphate due to common ion effect and it is not for that reason a viable option. Within the factor levels a maximum aluminium concentration of 20.5 g L^{-1} is achieved when acid concentration is 2 M and S/L ratio is 100 g L^{-1} . Fig. 2b shows the effects of temperature and volume of acid on the aluminium concentration. Due to the quadratic effects of both factors a saddle is formed. The highest aluminium concentration, 16.2 g L^{-1} , is reached at a low temperature (20°C) and S/L ratio 102 g L^{-1} . Fig. 2c displays effects of acid concentration and temperature on the aluminium concentration. Again the substantial effect of the leaching acid concentration on aluminium concentration is seen, while temperature has no influence. The highest value for aluminium concentration 24.0 g L^{-1} is achieved when acid concentration is 2 M and temperature is 20°C .

According to ANOVA analysis acid concentration is the dominant process variable, but due to the significance of quadratic and interaction terms of the other two factors they must be taken into account when considering optimal conditions for leaching process. Leaching time proved to be insignificant factor which means that diffusion rates are not affected by the other factors when leaching pulverized sludge.

3.4. Optimization and verification of the models

In both models no clear maximum could be found within the range

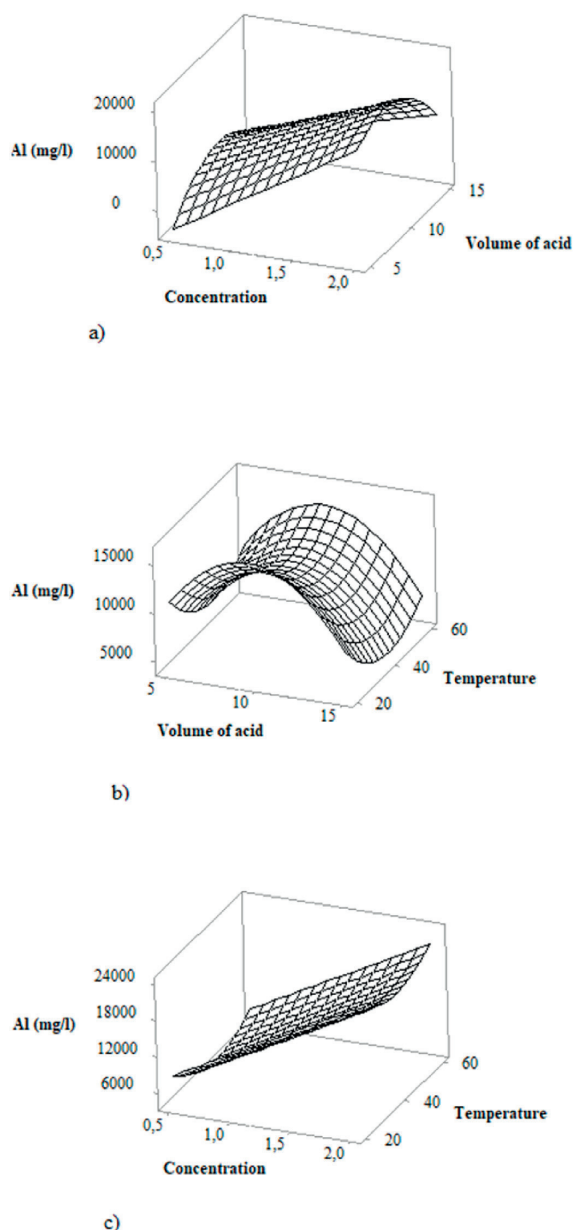


Fig. 2. Changes in aluminium concentration (Al mg/l) with respect to: a) concentration (M) and volume of acid (mL), b) volume of acid (mL) and temperature (°C), c) concentration (M) and temperature (°C) when leaching dried sludge ($m = 1$ g).

of variable values. However, moving further from factor levels displayed in this study would mean increasing the costs of leaching. In addition, an increase in phosphorous acid concentration would mean higher phosphate content in leaching solution. This would lead to re-precipitation of aluminum phosphate. For that reason optimization of leaching with both sludge types was conducted within the limits of factor values. For the factors that were removed from the reduced second-order models, the lowest factorial level was chosen. Predicted

values for moist sludge and dried sludge leaching were calculated according to equations (3) and (4), respectively. Table 5 presents the optimized conditions for leaching, predicted and obtained results for these settings and the percentage errors between the actual and predicted values. With both sludge types the values obtained are smaller than predicted values, resulting in error percentages of -7.9% for moist sludge and -14.7% for dried sludge. The analyzed aluminium content of the sludge (Table 2) estimates that in two grams of moist sludge the aluminium amount is 13 mg and for dry sludge one gram contains 188 mg. If all of those amounts would be leached in optimized conditions, the concentration of aluminium should be 2.6 and 22.4 g L^{-1} with moist and dry sludge, respectively. If the obtained results and these values are compared the difference between values is -15% for moist sludge and -4.8% for dry sludge. Considering the heterogeneous nature of sewage sludge, it can be concluded that the regression models acquired are realistically accurate for predicting the amount of aluminium in leach solution after leaching under optimized conditions.

4. Discussion

In optimized conditions, the liquid to solid ratio L/S (mL/g) is 2.5 and 8.4 for moist and dry sludge, respectively. This is significantly lower ratio than what Donatello et al., 2010 and Fang et al., 2018 reached when optimizing ISSA leaching with sulfuric acid (L/S ratio 20) although Donatello suggests that as low as 2 could be achieved with right stirring equipment. Franz 2008 also concludes that L/S ratio 2 to be optimal, however the acid concentration in that study was high (2.5 M) while Donatello concluded that 0.19 M sulfuric acid to be sufficient. Levlin and Hultman, 2004 managed to efficiently leach P from sewage sludge with just 0.25 M hydrochloric acid. Higher acid concentration is needed with H_3PO_4 due to it being a weak acid. Even at concentration of 2 M of H_3PO_4 no precipitation problems were observed as opposed to Ottosen et al., 2013 study with ISSA where usage of sulfuric acid lead to a formation of gypsum crystals in ash residue.

In their two-step leaching process of ISSA Levlin and Hultman 2004 managed to leach 836 mg L^{-1} aluminium with hydrochloric acid (0.25 M) while the optimized conditions in this process manages to leach 2.6 times more even with moist sludge. If we assume that equation (1) goes to full length obtained P concentration would be 2.5 g L^{-1} which is 2.2 times higher than what Levlin & Hultmann (1.134 g L^{-1}) achieved. The leaching time for dry sludge is similar to Donatello results while Franz reported that as short as 10 min lead to 90% recovery of phosphorous. Biswas et al. (2009) also investigated the effect of time and temperature on H_2SO_4 leaching of ISSA and reported 4 h and 30°C as optimal, which is comparable to 60°C and 6 h that are needed for moist sludge. High temperature in this case offers the required energy to break the chemical bonds of the metal compounds in the sludge (Naoum et al., 2001).

5. Conclusions

The optimized leaching conditions with low liquid to solid ratio (2.5) and (8.4) for moist and dried post-precipitated sludge were established, respectively. With optimized leaching conditions, phosphorus and aluminium can effectively be recovered (aluminium recovery 85 %) from post-precipitated sewage sludge. For moist sludge optimal leaching conditions are: S/L ratio 400 g L^{-1} , temperature 60°C and leaching time of 6 h; while for dried sludge optimal leaching conditions are: acid concentration 2 M, S/L ratio 119 g L^{-1} , temperature 20°C and leaching time of 2 h. The method presented has significant potential to be used in wastewater treatment for the recovery of phosphorus in industrial applications. The possibility to recycle aluminium back to the precipitation process is pioneering feature that has not yet been presented. In the future work, the separation process of aluminium from the phosphoric acid solution is developed.

Table 5
Optimized leaching conditions and obtained values (n = 3 (mean ± std. deviation)) from verifications runs.

	Factors				Predicted (Al mg L ⁻¹)	Obtained (Al mg L ⁻¹)	Difference (%)
	Acid concentration (M)	Volume of acid (mL)	Temperature (°C)	Time of leaching (h)			
Moist ^a sludge	0.5 ^c	5	60	6	2400	2210 ± 130	-7.9
Dry ^b sludge	2	8.4	20	2 ^c	24650	21030 ± 800	-14.7

^a Solid content 3–4%.

^b dewatered in 105 °C for 16 h.

^c Not significant factor.

Declaration of interest

The funder Helsinki Region Environmental Services Authority has applied for a patent (Patent application no. 17162458.8–1371) based on the results presented in this paper and the corresponding author S.R. has been nominated as one of the inventors.

Role of the funding source

The funders had no role in research design or in the collection, analysis and interpretation of the data or in the writing of the report. Nor did they have any role in the decision to submit the paper for publication.

Acknowledgements

This research has received funding from the RAKI Programme of Ministry of the Environment of Finland. In addition, the financial support of Helsinki Region Environmental Services Authority and Department of Chemistry of University of Jyväskylä is gratefully acknowledged. Also, the author S.R. thankfully acknowledges the financial support provided through a Finnish Concordia Fund grant.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.jenvman.2018.08.004>.

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II

TO INCINERATE OR NOT? : EFFECTS OF INCINERATION ON THE CONCENTRATIONS OF HEAVY METALS AND LEACHING EFFICIENCY OF POST-PRECIPIATED SEWAGE SLUDGE (RAVITA™)

by

Sini Reuna & Ari Väisänen 2020

Journal of Waste Management vol. 118, 241-246

DOI: 10.1016/j.wasman.2020.08.022

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Waste Management

journal homepage: www.elsevier.com/locate/wasman

To incinerate or not? – Effects of incineration on the concentrations of heavy metals and leaching efficiency of post-precipitated sewage sludge (RAVITA™)



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ARTICLE INFO

Article history:

Received 17 February 2020

Revised 13 August 2020

Accepted 16 August 2020

Available online 8 September 2020

Keywords:

Phosphorus recovery

Sewage sludge ash

Characterization

Thermal treatment

ABSTRACT

The major element and heavy metal concentrations of post-precipitated sewage sludge (PPS) and its ash residue (PPA) were determined using microwave digestion followed by inductively coupled plasma optical emission spectrometry (ICP-OES) and mass spectrometry (ICP-MS). To the best of our knowledge, this has not been previously done. In both PPS and PPA the heavy metal concentrations were clearly below the average concentrations than those encountered in sewage sludge in Europe. The leaching efficiency of the metal (Al/ Fe) used as a precipitation agent from post-precipitated sludge and its ash residue with phosphoric acid was also investigated with previously optimized leaching conditions. Tests resulted in leaching efficiencies for Al of $85 \pm 1\%$ and $99.5 \pm 0.7\%$ for PPS and PPA, respectively which were produced with aluminum as precipitation agent for phosphorus. Sludge, which was produced using iron as a precipitation agent, had a leaching efficiency of $36.6 \pm 0.9\%$ and $68.0 \pm 1.1\%$, for PPS and PPA, respectively. The leaching efficiency for P was $94 \pm 3\%$ and $96 \pm 5\%$ for Al-PPA and Fe-PPA, respectively.

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1. Introduction

Since the European Commission listed phosphate rock as a critical raw material in 2014, the development of methods to recover phosphorus (P) from secondary sources has been increasing steadily (European Commission, 2014; Scopus, 2019). One of the main secondary sources can be the sewage sludge produced in wastewater treatment plants. It is estimated that 90% of the P in wastewater end up in sewage sludge (SS) (Liang et al., 2019).

Currently, the three main applications for SS are landfilling, use in agriculture, and incineration (Kacprzak et al., 2017). In 2016, 35% of sewage sludge was incinerated in the European countries producing thousands of tonnes of ash (EUROSTAT, 2019). For that reason, many of the wet chemical methods developed for phosphorus recovery utilize the incinerated sewage sludge ash (ISSA). The problem is that incineration concentrates the harmful heavy metals in ash causing challenges in the development of the phosphorus recovery processes (Franz, 2008).

The usual first step in P recovery is the leaching of ISSA with either inorganic or organic acids. This extracts P from the ash along with metals and metalloids (Fang et al., 2018). The purification process for heavy metal separation can be done with solvent

extraction, ion exchange resins or membranes before the leachate is utilized for the recovery of P (Biswas et al., 2009; Donatello et al., 2010; Guedes et al., 2014; Paltrinieri et al., 2019; Shiba and Ntuli, 2017). Another method for separation of P from heavy metals is the pretreatment of ISSA. For instance, a chelating agent EDTA (ethylenediaminetetraacetic acid) has been successfully tested as a pre-leaching agent for reducing the metals before P leaching (Fang et al., 2018). This however produces a waste fraction containing EDTA and leached metals, which must be processed. Several studies have also investigated the possibilities to directly transform P from the acidic leachate into a plant-available form. Biochars derived from waste materials (peanut shells, sewage sludge) have been successfully used for P-adsorption and then used as fertilizer (Fang et al., 2020a, 2020b). Direct precipitation with calcium silicate hydrates has also been implemented resulting in a leaching efficiency of 55% for P (Lee et al., 2018).

One way to prevent heavy metals from contaminating the phosphorus-rich sludge, without extra process steps, is so-called post-precipitation (PP) (Eklund et al., 1991). In PP the precipitation agent, typically aluminum or iron salt, is added into effluent wastewater after other wastewater treatment procedures, such as primary treatment and biological treatment.

Post-precipitation of P is utilized by RAVITA™-process. It is a process developed and patented by the Helsinki Region Environmental Services Authority to recover phosphorus and nitrogen

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from municipal wastewater (Fred et al., 2019, 2018; Rossi et al., 2018). In RAVITA™ the PP produces a chemical sludge that mainly consists of aluminum or iron phosphate depending on the used precipitation agent. The chemical sludge is separated from effluent wastewater by disc filtration. This results in an extremely low total P concentration of 0.1 mg L⁻¹ in effluent wastewater (Rossi, 2014). Formed chemical sludge is leached with dilute phosphoric acid. Next, the leachate is processed to separate the precipitation metal and phosphorus from each other. Currently, the purification of phosphoric acid with solvent extraction is researched. The purified phosphoric acid solution is partly used in nitrogen recovery from the rejects waters of drying of the biological sludge to produce ammonium phosphate. The excess phosphoric acid can be utilized in the fertilizer industry. The separated metal is recycled back to the wastewater treatment process to be used as a precipitation agent again. The recycling of the precipitation agent is not utilized in any other P recovery process.

RAVITA™ will utilize only the chemical sludge formed in PP. The biosludge that is formed during biological treatment will contain an estimated 30–35% of the P that comes with incoming wastewater and it is digested (FCG Suunnittelu ja Tekniikka, 2015). Because of the lower P content, the biological sludge has a better nutrient ratio and greater amounts can be used in agriculture. Also, when P is not chemically bound with iron or aluminum its bioavailability for plants increases. The heavy metal concentrations of the biological sludge depend on industries that produce wastewater (Persson et al., 2015). However, the concentration levels of heavy metals in biological sludge are controlled at the EU level by The Sewage Sludge Directive 86/278/EEC (The Council of the European Communities, 1986). The final treatment for biological sludge varies between the EU member states (Raheem et al., 2018). After digestion and composting the sludge can be utilized in green building or it can be incinerated.

Previously for RAVITA™-process, we have optimized the leaching procedure for aluminum-based post-precipitated sewage sludge (Al-PPS) with dilute phosphoric acid (Reuna and Väisänen, 2018). The optimized leaching conditions for iron-based post-precipitated sewage sludge (Fe-PPS) have not been previously published. Phosphoric acid was chosen as a leaching solution instead of sulfuric acid or hydrochloric acid in order to avoid the removal of sulfate or chloride ions from the leachate. (Ottosen et al., 2013). In this study, we have studied if the incineration of PPS enhances the leaching process and determined the concentrations of heavy metals (HMs) in the sludge (PPS) and ash residue (PPA). To our knowledge, the HM concentrations have not been previously determined from PPS and PPA. Nor has the leaching of PPA from the post-precipitation of P with dilute phosphoric acid previously been tested.

2. Experimental

2.1. Materials and chemicals

The standard stock solutions of the elements (1000 mg L⁻¹, analytical grade) were supplied by PerkinElmer. Boric acid (H₃BO₃, 99.99%, AlfaAesar) and phosphoric acid (85 wt%) were obtained from VWR International. Analytical grade nitric acid (65–68 wt%) and hydrochloric acid (37–39 wt%) were purchased from Merck. Analytical grade hydrofluoric acid (40%) was procured from Merck. Ultra-pure hydrochloric and nitric acid were purchased from ANA-LYTIKA, spol. s.r.o. (34–37%, Prague, Czech Republic). Certified reference materials CRM029 *Heavy Metals – Sewage Sludge 2* (Lot LRB1332) and SRM 1663c *Heavy Metals in Coal Fly Ash* were used for method validation. All the chemicals were used as obtained without further purification. High-purity water produced by the

Elga Purelab Ultra water purification system was used throughout the experiments.

The batch of post-precipitated aluminum phosphate (Al-PPS) and iron phosphate sludge (Fe-PPS) were received from the RAVITA™ pilot plant located in the Viikinmäki wastewater treatment plant, Helsinki. Post-precipitated sewage sludge (PPS) batches were dried in a fume cupboard for 72 h and ground manually before sample treatment. Parts of the batches were incinerated (550 °C, 2 h) to produce post-precipitated sewage sludge ash (PPA).

2.2. The procedure of sample treatment

2.2.1. Dry matter determination, incineration, and particle size determination

The dry matter content of sludge samples and reference materials were determined according to the Finnish Standards Association's standard SFS 3008 (SYKE, 2011). Samples of 500 mg were weighed and kept 16 h at 120 °C. After cooling the weight was measured and dry weight and moisture content were calculated. The particle size range was determined with the Retch AS200 sample sieve. The results are presented in [supplementary data \(Table S1\)](#).

2.2.2. Microwave-assisted digestion

Sewage sludge samples (200 mg, dry weight content 81.8% for aluminum-based sludge and 70.1% for iron-based sludge) and ash residue samples (200 mg) were weighed in digestion vessels and 9 mL nitric acid (HNO₃, 65%), 3 mL hydrochloric acid (HCl, 35%) and 1 mL hydrofluoric acid (HF, 40%) was added. Vessels were closed and a digestion program based on EPA 3052 method was performed with CEM Mars6 –microwave oven. After cool down 10 ml of boric acid (H₃BO₃, 5 wt-%) was added and the HF neutralization program was executed. Temperature profiles of digestion programs are presented in [supplementary data \(Table S2\)](#). Digested samples were filtered (filter paper Whatman 41) and diluted to a volume of 40 ml with high-purity water. Also, samples from certified reference materials *Heavy metals-Sewage sludge CRM029-50G* (250 mg, dry weight content 89.8%), *SRM 1663c Heavy Metals in Coal Fly Ash* (200 mg, dry weight content 99.73%) were digested similarly.

2.2.3. Leaching

Leaching of Al-PPS and Al-PPA was done according to optimized leaching conditions (Reuna and Väisänen, 2018): solid to liquid ratio S/L of 15.9 g dry weight (d.w.) L⁻¹, the phosphoric acid concentration of 0.5 M and leaching time of 360 min. The Fe-PPS and Fe-PPA were leached in the following matter: S/L 121 g (d.w.) L⁻¹, the phosphoric acid concentration of 2 M and leaching time of 60 min. The PPS was used in the leaching test as received. The properties of PPS and PPA are listed in [Table S1 in the supplementary data](#). The specific compounds of metals in the solution after leaching with phosphoric acid is discussed in the [supplementary data](#).

2.3. ICP-OES measurements

The concentrations of the major elements Al, Ca, Fe, and Mg were determined with PerkinElmer ICP-OES Avio 500 –spectrometer for Fe-PPS and Fe-PPS and with PerkinElmer Optima 8300 for Al-PPS and Al-PPA. The GemCone low flow –nebulizer with Tracey spray chamber (HF resistant) was used for sample introduction. The parameters for all measurements are presented in [supplementary data \(Table S3\)](#). The wavelengths, calibration ranges, and the limits of quantification (LOQ) are presented for each element in [supplementary data \(Table S4\)](#).

2.4. ICP-MS measurements

The heavy metals analyzed were As, Cd, Cr, Cu, Ni, Pb, Sb, Se, Sn, and Zn. The element concentrations were determined with PerkinElmer NexION 350D inductively coupled plasma mass spectrometer (ICP-MS). The ICP-MS operating conditions are shown in [supplementary data \(Table S5\)](#). Before measurement, the samples were diluted by a factor of 200 or 50 with ESI Prep-Fast. Method detection limits (MDL) were determined from method blanks ($n = 9$) for each element according to US EPA Method 200.7 (U.S. Environmental Protection Agency, 2001) and are presented along with calibration ranges and internal standards used for analytes in [supplementary data \(Table S6\)](#). Validation of ICP-OES and ICP-MS measurements is presented in the [supplementary data \(Tables S7–S8\)](#).

3. Results and discussion

3.1. Determination of element concentrations of PPS and PPA

[Table 1](#) presents the major and heavy metal concentrations by weight percentages (w-%) for main elements and mg kg^{-1} for heavy metals in PPS and PPA. Concentrations for As, Se, and Cr are not presented since they resulted in concentrations lower than MDLs in all sample types. To see if the heavy metal concentrations are lower in the PPS than in traditionally produced sewage sludge the values were compared to existing literature. [Liang et al. \(2019\)](#) determined the elemental concentrations of raw waste activated sludge and ISSA and the results are presented in [Table 1](#) along with data from this study. [Liang et al. \(2019\)](#) determined that the concentrations of P in raw sludge and ISSA were 29.4 g kg^{-1} and 52.1 g kg^{-1} , respectively. From [Table 1](#) we can see that PPS and PPA contain higher concentrations of phosphorus regardless of the metal used in post-precipitation. The same trend applies to all concentrations of the main elements. For instance, aluminum is present almost thrice as high in concentration in Al-PPA than in ISSA (109.7 g kg^{-1}) that [Liang et al. \(2019\)](#) have researched. The high Al content is a consequence of using the Al-based precipitation agent. This increase in element concentrations is expected since the precipitation in PP happens after the removal of biological solids.

In both sludge types, the heavy metal concentration is increased by a factor of 1.3 after incineration. However, even after incineration, most heavy metal concentrations are considerably below the

average heavy metal content of the sewage sludge in the EU and Finland (Helsinki Region Environmental Services Authority, 2018; [Inglezakis et al., 2014](#)). Likewise, Finland's limit values for heavy metals in sludge for use in agriculture are straightforwardly passed ([Ministry of the Environment, 1994](#)). This is illustrated in [Fig. 1a](#) for Al-PPS/PPA and [Fig. 1b](#) for Fe-PPS/PPA. The only exception is cadmium which average concentration in Fe-PPS is the same as Finland's limit value for Cd in sludge for use in agriculture. However, the cadmium will not concentrate on PPA, since it volatilizes at elevated temperature ([Shi et al., 2014](#); [Zhang et al., 2008](#)). Instead, at a full-scale process of incineration, Cd would concentrate on combustion residues (CRs) such as fly ash ([Xiao et al., 2015](#)). This could affect the end-use of the CRs, which have been reported to be utilized in construction material production and for agricultural land ([Ning et al., 2013](#)). [Xiao et al., 2015](#) studied the mobility and phyto-accessibility of some heavy metal from SS after combustion. They concluded that Cd in fly ash had little bioavailability or eco-toxicity for plants. Thus, incineration could be a viable step in RAVITA™-process despite the Cd content in Fe-PPS.

Typically, the high concentration of Zn is the reason, which prevents the usage of ash in landfilling or other purposes ([Franz, 2008](#)). This will not be the issue with PPA since the concentrations of Zn are 2 times lower than the mean value in Europe. These HM concentrations determined in this study indicate that in a full-scale process most of the HMs in wastewater will be bound in the biological sludge. However, since this has not been piloted, it is too soon to evaluate the possible concentrations in the biological sludge. The obtained results confirm the fact that by using the post-precipitation of phosphorus the heavy metal concentrations are significantly lower in the produced sewage sludge. This simplifies the recovery process of P and the precipitation agent since there is no longer a need to purify the phosphorus product from heavy metals.

3.2. The effect of incineration on leaching of Al, Fe, and P

[Table 2](#) presents the determined concentrations of Al, Fe, and P from the leachates and the pH of the solution after leaching. The concentration of P in the leachate for PPA was determined by subtracting the theoretical P concentration of the phosphoric acid from the measured value. When leaching the PPS, due to the water content, it is not possible to accurately determine the extra P content in leachate. For that reason, those values are not presented.

Table 1

Major and heavy metal concentrations of PPS and PPA (mean \pm standard error of the mean (s.e.m)) determined with ICP-OES/MS. Sample size: $n(\text{Al/Fe-PPS}) = 6$, $n(\text{Fe-PPA}) = 5$ and $n(\text{Al-PPA}) = 9$. Elemental concentrations of waste activated sludge (WAS) and ISSA incinerated at $600 \text{ }^\circ\text{C}$ determined by [Liang et al. \(2019\)](#).

Unit	n	Al		Fe		Liang et al. (2019)	
		PPS 6	PPA 9	PPS 6	PPA 5	WAS	ISSA
Al (w-%)		18.3 ± 0.3	29.1 ± 0.3	0.221 ± 0.01	0.351 ± 0.009	5.43 ± 0.03	10.97 ± 0.02
Ca (w-%)		1.14 ± 0.01	1.53 ± 0.03	1.97 ± 0.02	2.39 ± 0.02	1.69 ± 0.05	3.19 ± 0.05
Fe (w-%)		1.03 ± 0.01	1.62 ± 0.02	36.8 ± 0.2	43.5 ± 0.4	2.64 ± 0.09	5.14 ± 0.06
Mg (w-%)		0.075 ± 0.002	0.114 ± 0.01	–	0.144 ± 0.002	0.67 ± 0.03	1.3 ± 0.02
P (w-%)		10.0 ± 0.2	14.85 ± 0.15	8.1 ± 0.08	9.52 ± 0.12	2.84 ± 0.09	5.5 ± 0.07
Cu (mg kg^{-1})		52.6 ± 0.8	85 ± 3	37.7 ± 0.9	49.8 ± 0.5^a	90 ± 1	423 ± 10
Zn (mg kg^{-1})		219 ± 4	360 ± 7	470 ± 13	587 ± 7^a	225 ± 12	895 ± 49
Sn (mg kg^{-1})		1.87 ± 0.09	3.1 ± 0.2	1.512 ± 0.014	1.79 ± 0.03^a	nd ^b	nd
Pb (mg kg^{-1})		0.66 ± 0.04	1.01 ± 0.05	–	0.481 ± 0.015^a	nd	460 ± 5
Ni (mg kg^{-1})		10.6 ± 0.6	18 ± 3	–	–	nd	209 ± 1
Sb (mg kg^{-1})		–	–	1.09 ± 0.04	1.31 ± 0.02^a	nd	nd
Cd (mg kg^{-1})		–	–	3 ± 0.4	–	nd	126 ± 3

– Below LOQ/MDL.

^a $n = 6$.

^b Not detected.

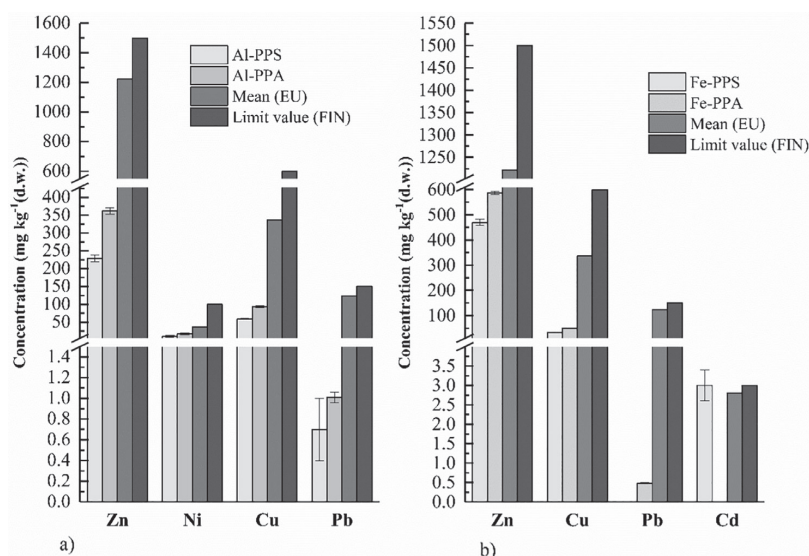


Fig. 1. Heavy metal concentrations for PPS and PPA (mean \pm standard error of the mean (s.e.m)), average EU concentrations and sludge limit values for agricultural use in Finland, (a) Al-PPS and Al-PPA and (b) Fe-PPS and Fe-PPA.

Table 2

The determined concentrations of Al, Fe, and P (mean \pm s.d, $n = 3$.) from the leachate, when the leaching solution is 0.5 M H_3PO_4 for Al-PPS/PPA and 2 M H_3PO_4 for Fe-PPS/PPA.

	Al		Fe	
	PPS	PPA	PPS	PPA
Al ($g L^{-1}$)	2.46 ± 0.05	4.60 ± 0.03	0.08 ± 0.01	0.40 ± 0.05
Fe ($g L^{-1}$)	0.151 ± 0.008	0.25 ± 0.1	16.4 ± 0.3	36 ± 2
P ^a ($g L^{-1}$)	—	2.24 ± 0.03	—	11.1 ± 0.6
pH _{after leaching}	1.5	1.9	1.6	1.2

^a P concentration determined by subtracting the theoretical P concentration of H_3PO_4 from the measured value.

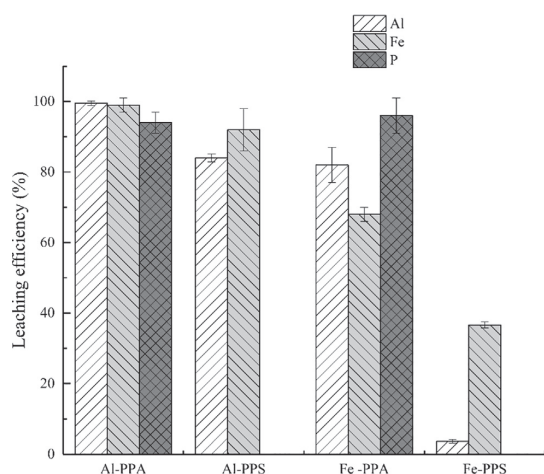


Fig. 2. Leaching efficiency of Al, Fe, and P after leaching Al-PPS/PPA and Fe-PPS/PPA with dilute phosphoric acid ($n = 3$, mean \pm s.d.).

Fig. 2 portrays the effect of incineration on leaching efficiency when dilute phosphoric acid is used. Since the leaching efficiency for Al and Fe seems to be higher with PPA, the Student's t -test

(one-tail) was performed to determine if there is a statistically significant difference between the main metal concentration in leachate after leaching with either PPS or PPA. The t -test results for both types of sludge are presented in the [supplementary data](#) (Table S9). In both cases, the absolute value for t_{stat} exceeds the critical t -value. This indicates that the leaching efficiency of the main metal from PPA is higher than from PPS.

There are two reasons for the higher leaching efficiency of ash. First, the organic material does not anymore compete with metals. Hence, the ratio of H^+ /metal increases even though metal concentrations rise in 1.5-fold after incineration. The higher H^+ / metal ratio enhances the leaching efficiency. The second reason is the smaller particle size in PPA (see Table S1) resulting in higher surface area, which makes the metals easier to be leached (Hong et al., 2005; Stark et al., 2006).

Even though the leaching efficiency of metal is higher with ash, the effect of increasing concentration must be considered on the whole recovery process. The aluminum concentration ($4.60 \pm 0.03 g L^{-1}$) in leachate after leaching with Al-PPA seems reasonable, but the leachate containing iron ($36 \pm 2 g L^{-1}$) could be problematic. For instance, if the solvent extraction (SX) is contemplated as a purification method for leachate it should be taken into account that aluminum and iron are the main components to cause the formation of crud in SX-settlers (Ritcey, 1980). Thus, too high iron concentration in the leachate would increase the possibility of crud formation during solvent extraction. A higher concentration of iron in the aqueous phase also means that the SX-process

requires more steps and steeper aqueous to organic phase ratios. Besides, the predominant compound of the Fe in the leaching solution is $\text{FeH}_2\text{PO}_4^{2+}$ (see Fig. S1). Since the goal is to recover both P and the precipitation agent (Al/Fe) in different fractions, it is not possible to achieve if iron forms a compound with phosphate anion. For these reasons, other purification methods for leachates that are produced from Fe-PPS/PPA need to be investigated.

For P, high recovery in leaching is achieved after incineration, $94 \pm 3\%$, and $96 \pm 5\%$ for Al-PPA and Fe-PPA, respectively. These results are consistent with the results Donatello et al. (2010) obtained when leaching ISSA with sulfuric acid. Their investigation resulted in P recoveries between 72% and 91%. This supports incineration as a pretreatment method before leaching with H_3PO_4 as it removes the organic matter, thus improving the leaching of the main metal. Lee et al. (2018) achieved 55% P recovery when leaching SS with sulfuric acid, but due to the water content in PPS, it is not possible to accurately determine the excess P amount in phosphoric acid solution. However, since the pH remains below 2 after leaching it can be estimated that most of the P will be leached from PPS (Monea et al., 2020).

4. Conclusions

The major elements and heavy metal concentrations of PPS and PPA were determined. Also, the effect of incineration on the leaching efficiency of the metal used in the P post-precipitation was investigated. A 1.5-fold increase in element concentrations can be observed when comparing the PPA to the PPS. Nevertheless, all heavy metal concentrations were clearly below the average of heavy metal concentrations in sewage sludge in the European Union. This indicates that PP is a valid method to prevent heavy metals to accumulate in sewage sludge hence easing the development of recovery processes for phosphorus.

The leaching efficiency of the metal was discovered to increase when PPA was used as raw material instead of PPS. With Al-PPS and Al-PPA, this resulted in a leaching efficiency of $84.0 \pm 1.1\%$ and $99.5 \pm 0.7\%$ for aluminum, respectively. However, the concentrations of iron in leachate after leaching of Fe-PPS or PPA are significantly higher but the efficiency is lower, resulting in a leaching efficiency of $45 \pm 4\%$ for Fe-PPS and $68.0 \pm 1.1\%$ for Fe-PPA. Because of the predominant compound of the Fe in the leaching solution is $\text{FeH}_2\text{PO}_4^{2+}$ other purification methods than solvent extraction needs to be studied for leachate produced from Fe-PPA. With both sludge types incineration yields high P recovery, $94 \pm 3\%$, and $96 \pm 5\%$ for Al-PPA and Fe-PPA, respectively. Hence, it can be concluded that incineration is a viable pretreatment method before leaching with dilute H_3PO_4 . In further work, the purification method for the separation of P and Al/Fe will be investigated. The choice of purification method will greatly influence the overall recovery value of P.

Declaration of Competing Interest

We are reporting that Helsinki Region Environmental Services Authority has registered patents for phosphorus recovery (European Patent no. 3222587 and US Patent No.: US 10,351,428 B2). The corresponding author S.R. has been nominated as one of the inventors in these patents.

Acknowledgments

The authors acknowledge project-engineer Laura Rossi from Helsinki Region Environmental Services Authority who kindly manufactured the original RAVITA™ sludge. The authors would also like to thank FM Virva Kinnunen for guidance in ICP-MS measurements. Also, our warmest thanks to laboratorian trainees Essi

Pyykkö and Kaisa Lampinen who assisted with the microwave digestions and ICP-OES/MS measurements.

Funding sources

This research did not receive any specific grants from funding agencies in the public, commercial, or not-for-profit sectors.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wasman.2020.08.022>.

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III

PURIFICATION OF RECOVERED PHOSPHORIC ACID BY EXTRACTING ALUMINIUM WITH DI-2-ETHYLHEXYL PHOSPHORIC ACID

by

Sini Reuna & Ari Väisänen 2021

Journal of Chemical Papers

DOI: 10.1007/s11696-021-01848-9

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Purification of recovered phosphoric acid by extracting aluminium with di-2-ethylhexyl phosphoric acid

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Received: 14 February 2021 / Accepted: 30 August 2021
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Abstract

The extraction of aluminium from dilute phosphoric acid with di-2-ethylhexyl phosphoric acid (DEHPA) was optimized using response surface methodology. The optimization was based on the experimental three-level central composite face-centred design (CCF) and was conducted on real-life samples. The three variables included were pH, extractant concentration and aqueous to organic phase ratio (AO). Under the optimized conditions (pH 2.5, 0.6 M DEHPA and AO ratio 1:2), extraction efficiency of 99% for aluminium in four extraction stages is achieved. The purified phosphoric acid solution can then be utilized by the fertilizing industry. Stripping tests for organic phase loaded with aluminium were conducted with sulphuric acid. Extremely high stripping efficiency was obtained with 0.9 M sulphuric acid resulting in the recovery rate of 88% in one stage. After stripping, the aluminium sulphate solution can be reused as a precipitation agent for phosphorus in the wastewater treatment process.

Keywords Response surface methodology · Optimization · Sewage sludge · Wastewater · Precipitation agent · Solvent extraction

Introduction

In 2008, the price of phosphate rock skyrocketed, causing a shortage of P fertilizer, especially in developing countries (Cordell and Neset 2014; Mew 2016). Since then, the development of phosphorus recovery methods from secondary sources has been exponentially increasing (Scopus 2019). One alluring source is sewage sludge, which can contain phosphorus (P) between 0.6 and 6.7 wt.% (Milieu Ltd et al. 2008). The even higher concentration is found in sewage sludge ash (SSA) which can contain P up to 8 wt.% (Biswas et al. 2009). For that reason, several leaching methods with acid or alkaline have been presented for SSA (Donatello et al. 2010; Franz 2008; Petzet et al. 2012). However, for instance, in the Nordic countries, less than 5% of sewage sludge was incinerated in 2016 (EUROSTAT 2019). Thus, it is important to research methods to recover P straight from sewage sludge. Hence, in this study, we present the results,

which assisted the Helsinki Region Environmental Services Authority to patent and develop a process called RAVITA™ (Fred et al. 2019, 2018).

The RAVITA™ is a process designed to recover phosphorus and nitrogen from municipal wastewater (Rossi et al. 2018). The first step is phosphorus post-precipitation as phosphate salt with aluminium or iron at the end of the wastewater treatment process. This ensures a purer fraction, which contains fewer heavy metals than the sludge formed in conventional chemical precipitation (Eklund et al. 1991). The post-precipitated sludge is then leached with dilute phosphoric acid (H_3PO_4) and a leaching solution containing aluminium in moderate concentration is obtained (Reuna and Väisänen 2018). Dilute phosphoric acid simplifies the process since there is no need to remove chloride or sulphate ions. This would be the case if hydrochloric acid or sulphuric acid were used as a leaching solution. After leaching, the separation of aluminium with solvent extraction enables it to be recycled to the precipitation step while the purified phosphoric acid with an elevated concentration of P is a valuable product. A simplified process schematic for phosphorus recovery with RAVITA™ is presented in Fig. 1. A detailed description of how RAVITA™ can be added to the conventional

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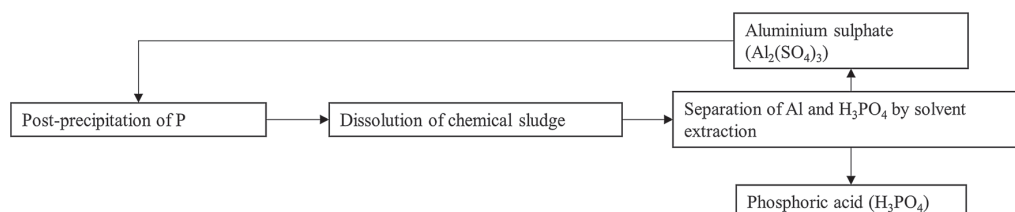
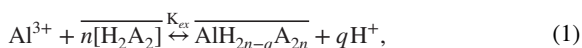


Fig. 1 Process schematic for RAVITA™

wastewater treatment process to recover both nitrogen and phosphorus is presented in Rossi et al. 2018.

The recovery of aluminium can be performed with di-2-ethylhexyl phosphoric acid (DEHPA). DEHPA is a commercially available acidic organophosphorus extractant that is widely used for uranium recovery from wet processed phosphoric acid and rare earth elements recovery from aqueous solutions (Awad et al. 2014; Wang et al. 2013; Xie et al. 2014). Mohapatra et al. (Mohapatra et al. 2007) have also used it for the recovery of aluminium from sulphate solutions. In kerosene, DEHPA exists as a dimer and its cation exchange reaction with aluminium can be generally expressed as follows (Mellah and Benachour 2006):



where K_{ex} is the reaction equilibrium coefficient and $[\text{H}_2\text{A}_2]$ denotes the dimeric form of the extractant. Overbar denotes species present in the organic phase.

This study aims to investigate the effects of pH, aqueous and organic ratio (AO) and concentration of DEHPA to achieve the optimum conditions for aluminium extraction from dilute phosphoric acid solution that is produced from leaching of post-precipitated sewage sludge. The sludge is produced in RAVITA™-pilot plant located in the Viikinmäki wastewater treatment plant in Helsinki. For the analysis of optimum conditions, the response surface methodology was utilized. The stripping of aluminium from the organic phase is carried out with sulphuric acid, and the parameters AO ratio and concentration of stripping acid are inspected. Sulphuric acid was chosen as the stripping solution because stripping then yields an aluminium sulphate solution, which can be used directly for phosphorus precipitation in the wastewater treatment process. The ability to recirculate aluminium back to precipitation makes the overall process more cost-efficient at a larger scale. The study of recovering and reusing the precipitation reagents in a process is a step towards circular economy and slowly becoming a more common part of process development (Abdel-Ghafar et al. 2019). The obtained results in this work are used as preliminary

data for bench-scale and pilot-scale testing of the solvent extraction process.

Experimental

Materials and chemicals

All the chemicals used were of analytical grade and used as obtained without further purification. The DEHPA (97%) extractant was provided from Sigma-Aldrich. The kerosene, which was used as a diluent, was purchased from Honeywell, Riedel-de Haën. The standard stock solutions of elements (1000 mg L^{-1}) were supplied by PerkinElmer. Phosphoric acid (85 wt.%), ammonia (40 wt.%) and NaCl (99.99%) were obtained from VWR International. Nitric acid (65–68 wt.%), hydrochloric acid (37–39 wt.%) and sulphuric acid (37–39 wt.%) were purchased from Sigma-Aldrich. High-purity water produced by the Elga Purelab Ultra water purification system (Buckinghamshire, U.K.) was used throughout the experiments.

Experimental design

Central composite face-centred design with three independent variables: pH (pH), the concentration of the extractant ($[\text{DEHPA}]$) and the aqueous to the organic ratio (AO) at three levels ($\pm 1, 0$), including six replicate at the centre point, was used to design the experiments. The variables and their values are shown in Table 1. The experimental runs were randomized to reduce bias from extraneous or uncontrollable conditions. The design was generated with Minitab 18 software. The response variable (Y) was the extraction efficiency ($E\%$) of aluminium into the organic phase, which is calculated as follows:

$$E\% = \frac{[C_o] - [C_e]}{[C_o]} \cdot 100\%, \quad (2)$$

where C_o is the initial concentration of aluminium and C_e is the aluminium concentration in the aqueous phase after

Table 1 Coded and actual levels of variables in the experimental design

Factors	Coded term	Levels		
		Lowest -1	Centre 0	Highest +1
pH	pH	1.7	2.1	2.5
Concentration of extractant/M	[DEHPA]	0.3	0.45	0.6
Aqueous to organic ratio	AO	1:2	1:1	2:1

extraction. The experimental design and individual results are presented in supplementary data (Table S1).

Statistical analysis

The response surface analysis of the Minitab 18 software was used to analyse the experimental data and to produce the response surface plot. The experimental data were fitted to a second-order polynomial model and regression coefficients were obtained. The generalized second-order response surface model used in the response surface analysis was as follows:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i < j}^k \beta_{ij} x_i x_j + \epsilon, \quad (3)$$

where Y is the response (aluminium extraction efficiency), β_0 is a constant coefficient, β_i is the linear effect, β_{ii} is the quadratic effect, β_{ij} is the interaction effect and ϵ is the error observed in response (Montgomery 2009).

The procedure of extraction and stripping

The extraction experiments were carried out in separating funnels by using Stuart SF1 -flask shaker (600 osc/min). The organic and aqueous phases were allowed to separate, and samples were prepared from the aqueous phase. Aluminium concentrations in organic phases were calculated based on mass balance. The experiments were conducted at temperatures of 21–23 °C. The phase contact time of 10 min was used and the volume ratios of organic and aqueous phases varied between 4:1 and 1:4. The pH was adjusted with 5 M ammonia. Stripping was performed in a water bath at 50 °C. Phases were stirred with a blade mixer and a contact time of 30 min was applied. The organic and aqueous phases were allowed to separate, and samples were prepared from the aqueous phase. The volume ratios of aqueous and organic phases between 1:1 and 1:6 were tested. Any changes to these parameters are reported in the text.

The aqueous phase was produced according to the optimum leaching conditions for moist post-precipitated sludge presented in Reuna and Väisänen (2018). This resulted in an aqueous phase, which contained aluminium in a range of 2.0–2.5 g L⁻¹ in 0.5 M phosphoric acid and had an initial pH of 1.7. The variation of aluminium concentration is due

to a fact that we used actual post-precipitated sewage sludge (PPS) to produce the leachate. For stripping experiments, the loaded organic phase was prepared by extracting the aqueous phase (pH 2.5) with 0.6 M DEHPA diluted in kerosene with AO ratio of 1:1.

The ICP-OES measurements

The aluminium concentrations in aqueous phases were determined with a PerkinElmer inductively coupled plasma-optical emission spectrometer (ICP-OES) Optima 8300. The GemCone low flow nebulizer with a cyclonic spray chamber was used for sample introduction. The measurement parameters for all measurements were as follows: argon gas flow of 8 L min⁻¹, nebulizer gas flow of 0.6 L min⁻¹, auxiliary gas flow of 0.2 L min⁻¹, sample flow rate of 1.5 L min⁻¹ and the radio frequency power of 1500 W. The measured wavelength in radial view was 396.153 nm and the calibration range was 5–50 mg L⁻¹. The method detection limit for aluminium was determined according to the U.S. Environmental Protection Agency method 200.7 (U. S. Environmental Protection Agency 2001) and it was calculated to be 30 µg L⁻¹.

Results and discussion

Extraction

Analysis of variance and fitting of the second-order model

The second-order model was first fitted according to Eq. (3). To achieve an improved model, insignificant model terms were removed by the backward elimination technique. The resulting analysis of variance (ANOVA) data for the reduced quadratic model of extraction is presented in Table 2. The calculated F -value for this model was 20.22 and the corresponding P -value is less than 0.0001. Thus the model is significant and can be used for optimization. All first-order terms are significant meaning that all three parameters affect the extraction. The P -value for the lack-of-fit is 0.373, which indicates that it is not significant. The goodness-of-fit of the model can be checked from the coefficient of determination (R^2). The R^2 -value is high, 90.32%, which means that only 9.68% of the total sample variation cannot be explained by the model. The adjusted R^2 -value of 85.85% indicates

Table 2 Analysis of variance table for aluminium extraction with DEHPA

Source	DF	Adj SS	Adj MS	F-value	P-value	Remarks
Model	6	3789.40	631.57	20.22	0.000	
Linear	3	3587.50	1195.83	38.28	0.000	Signif
pH	1	1241.00	1241.00	39.73	0.000	
[DEHPA]	1	577.60	577.60	18.49	0.001	
AO	1	1768.90	1768.90	56.63	0.000	
Square	2	151.90	75.95	2.43	0.127	
pH*pH	1	102.60	102.60	3.28	0.093	
AO*AO	1	136.76	136.76	4.38	0.057	
2-Way interaction	1	50.00	50.00	1.60	0.228	
[DEHPA]*AO	1	50.00	50.00	1.60	0.228	
Error	13	406.06	31.24			
Lack-of-fit	9	312.56	34.73	1.49	0.373	Not signif
Pure error	4	93.50	23.38			
Total	19	4195.46				
Model summary:	R^2 (%)	R^2_{adj} (%)	R^2_{pred} (%)			
	90.32	85.85	74.32			

that all the factors included in the model affect the response variable.

The regression equation for the model in uncoded units was obtained as follows:

$$Y = -207.9 + 176.5 \cdot \text{pH} + 50.7 \cdot [\text{DEHPA}] - 5.80 \cdot \text{AO} - 35.4 \cdot \text{pH}^2 + 6.54 \cdot \text{AO}^2 - 16.7([\text{DEHPA}] \cdot \text{AO}), \quad (4)$$

where Y is the extraction efficiency of aluminium (%), [DEHPA] is extractant concentration (M) and AO is the aqueous to organic ratio. The regression equation can be used to estimate the extraction efficiency of aluminium from the phosphoric acid solution within the factor limits. To verify the model assumptions, the residual plots were analysed in supplementary data (Fig. S1).

Effect of variables on extraction efficiency

Response surface plots were defined based on Eq. (4), to examine the effects of variables (pH, extractant concentration and AO ratio) on extraction efficiency (Fig. 2). In each plot, one variable is kept constant at level 0.

Only extractant concentration vs AO interaction term is present in the reduced quadratic model for aluminium extraction efficiency. However, two quadratic effects, pH and AO, are present. Figure 2a shows that the interaction between the extractant concentration and the aqueous to organic ratio forms a plane with a curving slope. No clear maximum can be found in Fig. 2a, but the highest result (59.6%) is obtained when the molar ratio of extractant and aluminium is at its highest point. At that point, extractant concentration is at the highest level and volume of the

organic phase is at maximum. A more concentrated DEHPA concentration could be used for solvent extraction. However, this would require the use of a modifier in the organic phase to enhance the phase separation. Figures 2b-c depict interaction terms that are not included in the model. In both cases, a plane with a bent slope is formed and the highest efficiencies are reached when extractant concentration and pH are at the highest level and AO ratio is on the lowest level (1:2). The same phenomenon can be seen from the main effect plots, which are presented in supplementary data (Fig. S2).

Optimization and verification of the model

To find the highest extraction efficiency of aluminium within the factor limits, the predicted value for aluminium extraction was calculated based on Eq. (4) using the highest factor levels for pH and extractant concentration and the lowest level for the AO ratio. This resulted in the predicted extraction efficiency value of 64.9% with a 95% confidence interval of 56.1–73.7%.

The model was verified by performing a test with three replicates where aqueous phase (Al 2.4 g L⁻¹) was contacted with organic phase using the highest factor levels for pH (2.5) and extractant concentration (0.6 M) and the lowest level for the AO ratio (1:2). The verification test resulted in an extraction efficiency of 69 ± 5% for aluminium. The result is slightly higher than what the model predicted, resulting in an error percentage of +4.1%. It can be concluded that the regression model acquired is realistically accurate for predicting aluminium extraction.

The obtained result from the verification test is also supported by experimental data. Experimentally, the highest obtained extraction efficiency was 64% (Table S1 in

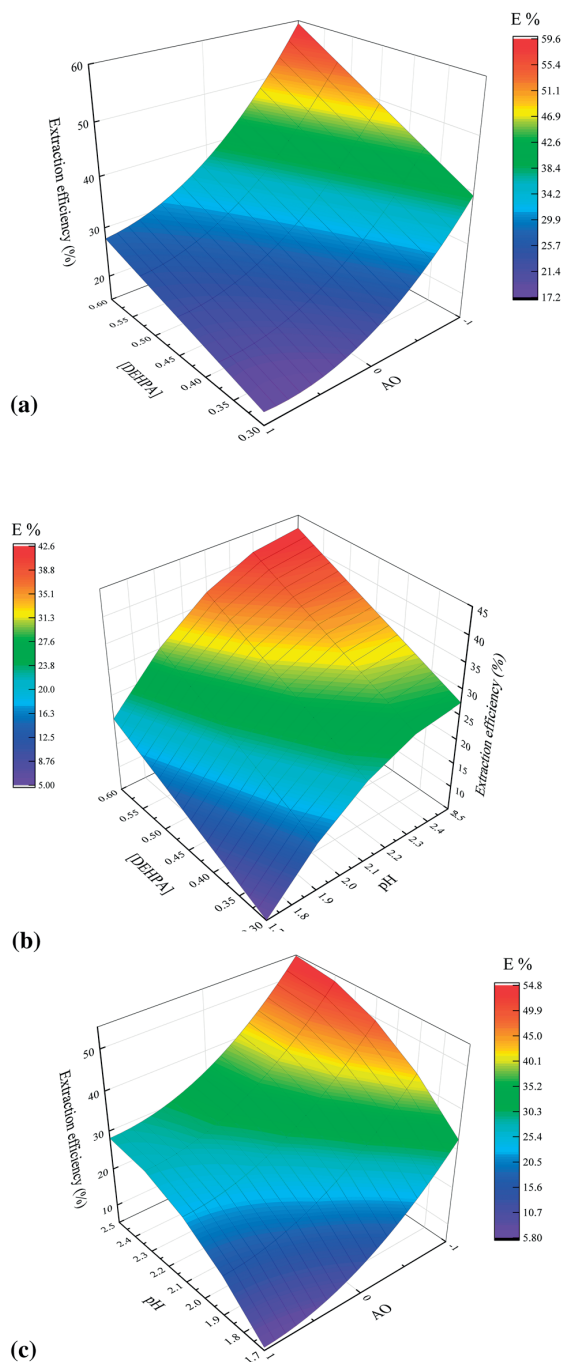


Fig. 2 Changes in extraction efficiency of aluminium concerning **a** extractant concentration (M) and AO ratio, **b** extractant concentration (M) and pH, and **c** pH and AO ratio

supplementary data) and it was achieved when pH and extractant concentration are at the highest level, 2.5 and 0.6 M, respectively, and the AO ratio is at the lowest level (1:2). The extractant concentration of 0.6 M is higher than that of Mohapatra et al. (2007) discovered as they investigated aluminium recovery with DEHPA from mixed sulphate solutions. Their results indicated that only 0.3 M of Na-DEHPA was sufficient to extract aluminium. However, they only had nickel and cobalt as competing elements while the phosphoric acid solution contains several metallic impurities (Fe, Ca, and Mg) that compete with aluminium in the cation exchange reaction (Reuna and Väisänen 2020). Also, Mohapatra et al. (2007) had a higher equilibrium pH. Nevertheless, the pH cannot be increased with the phosphoric acid solution because the aluminium phosphate precipitates at a pH above 2.5 (Levlin and Hultman 2004).

Distribution ratio and extraction equilibrium

The distribution ratio (D) is defined as the ratio of metal concentration in the organic phase to the aqueous phase at equilibrium (Harris 2010). It is expressed as follows:

$$D = \frac{[C_{\text{org}}]_{\text{total}}}{[C_{\text{aq}}]_{\text{total}}}, \quad (5)$$

where C_{aq} and C_{org} are the total concentrations of the element in the aqueous and organic phases, respectively. Knowing the cation exchange reaction of DEHPA with aluminium (Eq. 1) the distribution ratio can be expressed as follows:

$$D = \frac{[AlH_{2n-q}A_{2n}]_{\text{org}}}{[Al^{q+}]_{\text{aq}}} \quad (6)$$

then the reaction equilibrium coefficient is as follows:

$$K_{\text{ex}} = \frac{D \cdot [H^+]^q}{[[H_2A_2]]^n} \quad (7)$$

Taking the logarithm of Eq. (7) and rearranging, the equation can be reduced to (Mohapatra et al. 2007; Sarangi et al. 1999):

$$\log K_{\text{ex}} = \log D + q \log [H^+] - n \log [[H_2A_2]] \quad (8)$$

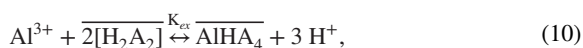
$$\log D = \log K_{\text{ex}} - q \log [H^+] + n \log [[H_2A_2]] \quad (9)$$

By plotting the log–log graph of the distribution ratio as a function of equilibrium pH or the concentration of extractant, it is possible to determine the number of released protons to one aluminium ion (q) or the number of extractant molecules complexed with aluminium (n) from the slope of the graph.

However, this requires that the other parameters and ionic strength are constant.

To determine the number of released protons (q), the aqueous phase ($2.4 \text{ g L}^{-1} \text{ Al } 0.5 \text{ M H}_3\text{PO}_4$) with adjusted pH was extracted with 0.6 M DEHPA in kerosene in AO ratio 1:1. To maintain constant ionic strength, 1 molar concentration of NaCl was added to the aqueous phase. Figure 3 shows the log–log graph of the distribution ratio as a function of equilibrium pH. The slope of 2.95 ± 0.3 is indicating that three protons are released during extraction. Pearson's correlation coefficient for the linear fitting resulted in 0.984 , which shows adequate fitting.

The number of extractant molecules complexed with aluminium (n) was determined by Mahimo et al. (Mahimo et al. 1997). When investigating the aluminium equilibrium reaction with DEHPA in sulphuric acid media, they deduced that two molecules of dimeric DEHPA are needed for the reaction. Wu et al. (Wu et al. 2018) came to the same conclusion with rare earth elements, which typically occur as trivalent cations like aluminium. Using the information above, the cation exchange reaction can be written:



McCabe and Thiele graph for extraction

The extraction stages required for the full recovery of aluminium from phosphoric acid were determined by contacting the aqueous phase ($2.0 \text{ g L}^{-1} \text{ Al}$, pH 2.5) with 0.6 M DEHPA at different phase ratios from 0.25 to 4. Figure 4

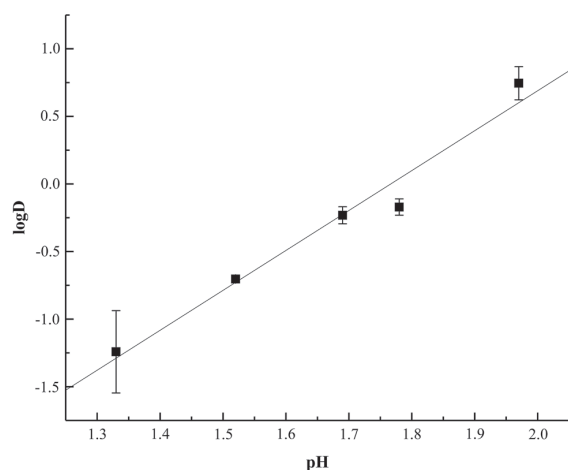


Fig. 3 Effect of pH on the distribution coefficient of aluminium. Aqueous phase: $\text{Al } 2.4 \text{ g L}^{-1} 0.5 \text{ M H}_3\text{PO}_4$, AO ratio of 1:1, contact time 30 min (Data points: mean \pm standard error of the mean (SEM), $n=3$)

depicts the obtained extraction isotherms, where each data point is the mean of three replicate tests for each phase ratio. A satisfactory R^2 -value of 97.6% was attained for polynomial fitting. With the AO ratio of 1:2, three theoretical stages are required for the quantitative extraction of aluminium(III). Typically one additional stage is required for complete extraction (Rydberg et al. 2004). This was verified by batch extraction in which the aqueous phase ($2.2 \pm 0.1 \text{ g L}^{-1} \text{ Al}$, pH 2.5) was extracted four times with the fresh organic phase. The test resulted in the extraction efficiency of $99.0 \pm 0.3\%$ for aluminium confirming the need for four steps.

Crud formation

During some of the tests, a formation of crud was observed. This is a common problem in solvent extraction and several factors can be attributed to crud formation (Ritcey, 1980). For instance, with DEHPA the saturation loading should not be exceeded. Since aluminium is one of the main components causing crud formation, the current concentration of aluminium may be too high. However, crud formation can be avoided by changing the AO ratio of extraction. This was proved in McCabe and Thiele's extraction test where no crud was observed with an AO ratio of 1:4. Another prevention method is also a pre-treatment of the aqueous phase with kerosene (Smith et al. 1980). This way crud forming agents are transported into kerosene which can be regenerated with sodium hydroxide. Further, remedies for reducing the crud formation are investigated in forthcoming research.

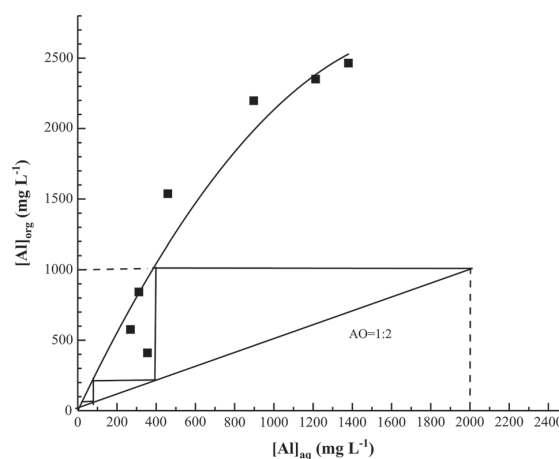


Fig. 4 McCabe–Thiele plot for Al(III) extraction. Organic phase: 0.6 M DEHPA in kerosene. Aqueous phase: $\text{Al } 2.0 \pm 0.1 \text{ g L}^{-1} 0.5 \text{ M H}_3\text{PO}_4$ ($n=3$)

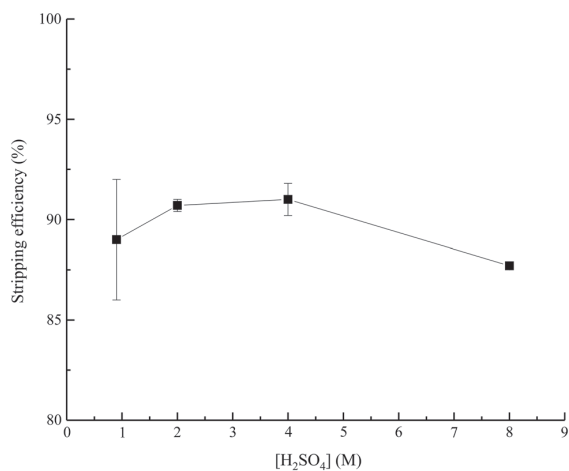


Fig. 5 Effect of stripping acid concentration on the stripping percentage of aluminium (mean \pm SEM, $n=3$). Organic phase: 0.6 M DEHPA in kerosene Al 1.1 ± 0.1 g L⁻¹, $t=30$ min, AO ratio 1:1

Stripping of aluminium from loaded DEHPA

The aluminium loaded DEHPA was stripped with sulphuric acid in varying concentrations (0.9–8 M). Figure 5 presents the stripping percentage of aluminium from the organic phase with different sulphuric acid concentrations. Table 3 presents the single factor analysis of variance for stripping efficiency of aluminium. ANOVA does not reveal a statistically significant difference between sulphuric acid concentrations since the critical F -value (4.066) is higher than the calculated F -value of 1.786. Besides, the acidity of stripping solution containing aluminium should not be unnecessarily elevated. Otherwise, the pH of the solution should be adjusted before the aluminium is recycled to the precipitation process. For those reasons, 0.9 M concentration was chosen for further testing.

Table 3 Analysis of variance table for stripping of aluminium from loaded DEHPA with sulphuric acid in different concentrations

SUMMARY						
Groups	Count	Sum	Average	Variance		
0.9 M	3	3052.47	1017.49	1986.853		
2 M	3	3123.195	1041.065	17.11923		
4 M	3	3132.849	1044.283	245.8064		
8 M	3	3019.318	1006.439	10.85741		
ANOVA						
Source of variation	SS	df	MS	F	P -value	F_{crit}
Between Groups	3027.935	3	1009.312	1.78589	0.22757	4.06618
Within Groups	4521.271	8	565.1589			
Total	7549.207	11				

McCabe and Thiele graph for stripping

The required stripping stages for the complete recovery of aluminium from the organic phase were determined by contacting the aqueous phase with loaded DEHPA at various AO phase ratios from 1:1 to 1:6. Figure 6 depicts the obtained extraction isotherms. An acceptable R^2 -value of 82.4% was attained for polynomial fitting. With an AO ratio of 1:2, two stages are required for quantitative stripping of Al(III) with 0.9 M sulphuric acid. In the studies of Mohapatra et al. (2007), only one stage was required for aluminium stripping from the organic phase (0.3 M Na-DEHPA, Al 2.4 g L⁻¹) because they used slightly higher acid concentration (1 M) and AO ratio 1:1.

Figure 7 illustrates the extraction efficiency of aluminium and the final concentration of Al at each AO ratio. As can be seen from Fig. 7, the stripping efficiency starts to diminish after AO ratio of 1:2 while the aluminium concentration increases throughout the experiment. The decline in efficiency is explained by the decrease of acid versus metal molar ratio. At lower AO ratios, more aluminium is available than sulphuric acid is capable to strip. With a lower AO ratio, it is possible to concentrate Al in stripping solution, but this would drastically lower the efficiency of one step.

In this study, by using the AO ratio of 1:2, the aluminium is concentrated by a factor of 1.85 resulting in the aluminium concentration of 2.04 ± 0.04 g L⁻¹. This is accomplished without sacrificing high stripping efficiency. The P concentration of stripping solution was determined to be 0.25 ± 0.05 g L⁻¹ after one stripping stage at AO 1:2. This indicates that less than 1.5% of P is co-extracted with aluminium in the extraction process.

Conclusions

The extraction of aluminium from dilute phosphoric acid was investigated using di-2-ethylhexyl phosphoric acid (DEHPA) in kerosene. The response surface method

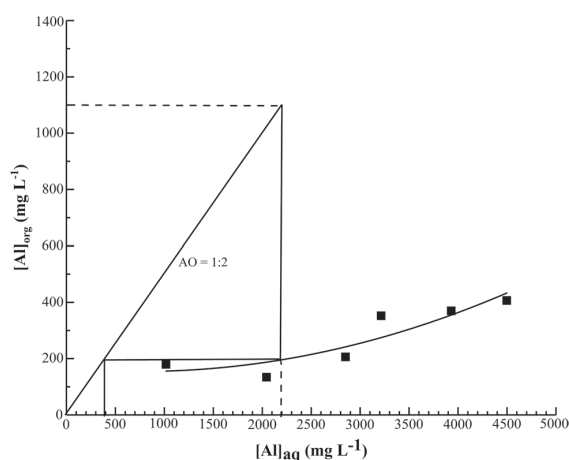


Fig. 6 McCabe–Thiele plot for Al^{3+} stripping. Organic phase: 0.6 M DEHPA in kerosene $\text{Al } 1.1 \pm 0.1 \text{ g L}^{-1}$ Aqueous phase: 0.9 M H_2SO_4 , $t = 30 \text{ min}$ ($n = 3$)

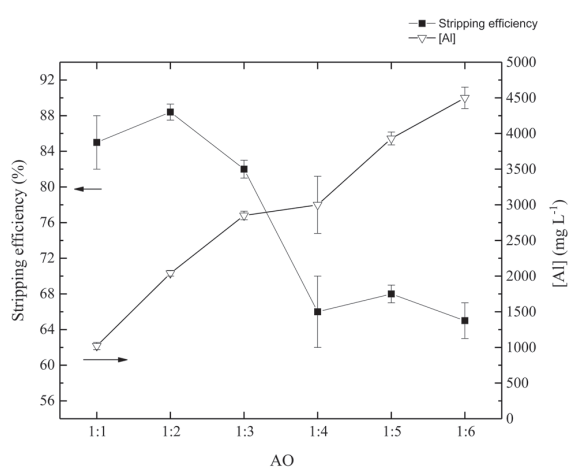


Fig. 7 Stripping efficiencies of aluminium and concentration of Al in stripping solution. Organic phase: 0.6 M DEHPA in kerosene $\text{Al } 1.1 \pm 0.1 \text{ g L}^{-1}$ Aqueous phase: 0.9 M H_2SO_4 , contact time 30 min (mean \pm SEM, $n = 3$)

was used to determine the optimal conditions for solvent extraction at the selected factor levels. To achieve the highest extraction efficiency, the pH of the aqueous phase and the extractant concentration must be at the highest level, 2.5 and 0.6 M, respectively. The aqueous to organic phase ratio must be at the lowest level (1:2) meaning that the molar ratio of extractant and aluminium is at the highest point. The theoretical stages for extraction were deduced with McCabe and Thiele's graph resulting in four steps required for the quantitative extraction of aluminium. This was verified with a batch test that resulted

in extraction efficiency of $99.0 \pm 0.3\%$. For the stripping, two stages are necessary when using the AO ratio of 1:2 and 0.9 M sulphuric acid for the complete recovery of Al. In one stripping step the efficiency is $88.4 \pm 1.4\%$.

The determined optimized conditions can now be implemented in the process design of the solvent extraction step and thus contribute to the overall development of the RAVITATM process, where phosphorus is recovered from wastewater and the precipitation agent (aluminium) is recycled to the precipitation stage. The recycling of the precipitation agent back to phosphorus precipitation is a ground-breaking feature that has not been presented in any other phosphorus recovery processes.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s11696-021-01848-9>.

Acknowledgements This research has received funding from the RAKI Programme of the Ministry of the Environment of Finland. Also, the financial support of Helsinki Region Environmental Services Authority and Department of Chemistry of the University of Jyväskylä is gratefully acknowledged. The corresponding author would also thank project engineer Laura Rossi who kindly manufactured the original RAVITATM sludge.

Authors' contributions SR: Conceptualization, Investigation, Formal analysis, Writing—Original Draft, Writing—Review & Editing, Visualization. AV: Supervision, Writing—review & editing.

Funding Open access funding provided by University of Jyväskylä (JYU). This research has received funding from the RAKI Programme of the Ministry of the Environment of Finland. Also, the financial support of Helsinki Region Environmental Services Authority is acknowledged.

Availability of data and material Data will be made available upon request.

Code availability Not applicable.

Declarations

Conflict of interest We are reporting that both the European Patent Office and U.S Patent Agency have granted a patent (European Patent no. 3222587 and US Patent No.: US 10,351,428 B2) for the funder Helsinki Region Environmental Services Authority based on the results presented in this paper. The corresponding author S.R. has been nominated as one of the inventors.

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