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# RAVITA Technology – new innovation for combined phosphorus and nitrogen recovery

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## ABSTRACT

Present phosphorus (P) recovery technologies mainly contain P recovery from sludge liquor or ash. These types of technologies are suitable for large wastewater treatment plants (WWTPs) with enhanced biological phosphorus removal (EBPR), digestion and/or incineration. In Finland and other Nordic countries, strict P discharge limits require chemical precipitation, thus EBPR alone is not sufficient. Ammonium recovery from wastewater, on the other hand, is not so often discussed. However, recovery from WWTP reject waters would decrease the energy demand of ammonium synthesis by Haber-Bosch technology and the energy demand of the WWTP's biological process. Helsinki Region Environmental Services Authority (HSY) has developed a new process called RAVITA whereby P and nitrogen recovery are combined in order to produce phosphoric acid ( $H_3PO_4$ ) and ammonium phosphate ( $(NH_4)_3PO_4$ ). Furthermore, in this process metal salt used in precipitation is recovered. The research was carried out on pilot (1,000 population equivalent) and laboratory scales. The objectives of this article are to explain the principles of the RAVITA process and give the first results of processing and production of chemical sludge.

**Key words** | chemical precipitation, hazardous substances, nutrient recovery, phosphorus removal, wastewater effluent

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## INTRODUCTION

Phosphorus (P) is a limited resource and essential for all life. Phosphorus fertilizers are needed for feeding the increasing human population but the main source of P, phosphate rock, has been declared as a critical raw material by the European Commission in 2014 (EC 2014). A potentially significant alternative source of P could be recycled from municipal wastewater and especially sewage sludge.

During the past decades, a vast number of new technologies have been developed for advanced P recovery from sewage sludge and sludge liquor streams as well as from sewage sludge ash. Only some of the technologies have been developed for P recovery from effluent wastewater as the concentration of P is low and the volume high. These technologies include ion exchange or the use of selective adsorbents (Egle *et al.* 2015; Sengupta *et al.* 2015; Drenkova-Tuhtan *et al.* 2017).

The recovery rates of P, removal and destruction of hazardous substances, economic efficiency as well as the fertilizing effects of end products vary a lot between the known technologies (Egle *et al.* 2016). According to the

comprehensive assessment study of Egle *et al.* (2016), there are significant tradeoffs between these factors in different technologies. In addition, the use of the analyzed technologies is limited to wastewater treatment plants (WWTPs) with either enhanced biological phosphorus removal (EBPR), digestion or sludge incineration. Thus, the potential of small and middle-sized plants is lost. In addition, extremely low effluent P concentrations with EBPR are hard to maintain without chemical additions (Morse *et al.* 1997).

Normally, nitrogen recovery has been discussed and studied apart from P recovery. Variation in nitrogen recovery technologies is much lower and the recovery technologies have mainly concentrated on stripping ammonium ( $NH_4$ ) from sludge liquor, as the  $NH_4$  concentration is high (Mehta *et al.* 2015). This is understandable due to the status of nitrogen as a raw material as well as its easy and free availability in the atmosphere. However, the  $CO_2$  footprint and energy consumption of produced  $NH_4$  by Haber-Bosch synthesis is large (Mehta *et al.* 2015). As the reject waters from sludge dewatering are high in  $NH_4$ , they can

impose over 20% of the WWTP's nitrogen load. This will also increase the energy consumption of the WWTP's biological treatment. If  $\text{NH}_4$  could be recovered from WWTPs' reject waters, it would decrease the energy consumption needed for biological treatment and for the Haber-Bosch synthesis.

## PRINCIPLES OF RAVITA PROCESS

The main idea in the RAVITA process is post-precipitation of P from the water phase at the end of the entire wastewater treatment process (Figure 1). The P recovery potential is high (>70% of inlet P) since only P required for the microbial metabolism is removed from the water before the RAVITA process.

The first process step is advanced post-precipitation of the high P content and the separation of formed chemical sludge. Mechanisms of post-precipitation are well known and the factors pertaining to it as well (Bratby 2006; Szabó et al. 2008). The separation step can be, for example, sedimentation, flotation or filtration. At Helsinki Region Environmental Services Authority (HSY), disc filtration has been studied extensively; therefore, it was considered as the first process to be tested (Rossi 2014).

The separated chemical sludge can be processed to increase the dry content of sludge and remove water from the product. The second process phase is dissolution of the formed chemical sludge with phosphoric acid ( $\text{H}_3\text{PO}_4$ ). In the acidic conditions, P and metal salt (aluminum, Al or iron, Fe) used in the coagulation are in a

dissolved state so they can be separated from each other. Separation can be done with ion exchange (Reuna 2015) or a solvent extraction, for example. When the metal salt is separated from the solution, it can be recycled back to the post-precipitation step, which increases the financial productivity rate potential of the process. The end product,  $\text{H}_3\text{PO}_4$ , is partly recycled back to the dissolution step. Surplus  $\text{H}_3\text{PO}_4$  can be used as a raw material in the fertilizer industry, for example, or in many other industries, so it is more exploitable compared to other recycled nutrients.

The RAVITA process can also be combined with nitrogen recovery from reject waters.  $\text{NH}_4$  is recovered using a stripping process, which is a well-known technology. The twist in the RAVITA process is that the  $\text{H}_3\text{PO}_4$  obtained in the P recovery part can be used in the air washer unit, in which case the formed product will be  $(\text{NH}_4)_3\text{PO}_4$ , which is an attractive fertilizer. Figure 1 depicts a traditional wastewater treatment process with addition of the RAVITA process in the end. It should be noted that no EBPR or coagulation metals are added to the process before the RAVITA process.

The significant advantages of the RAVITA process are that it fits nearly all kinds of WWTPs and there is no need for EBPR nor digestion as P is not integrated into the biological sludge. In addition, the process maximizes the P recovery rate potential and enables the circulation of precipitation metals. Furthermore, different process steps can be separated from each other, thus the P harvesting is also possible in small and mid-sized treatment plants and the further processing of the chemical sludge can be centralized in large units. The RAVITA process can also be

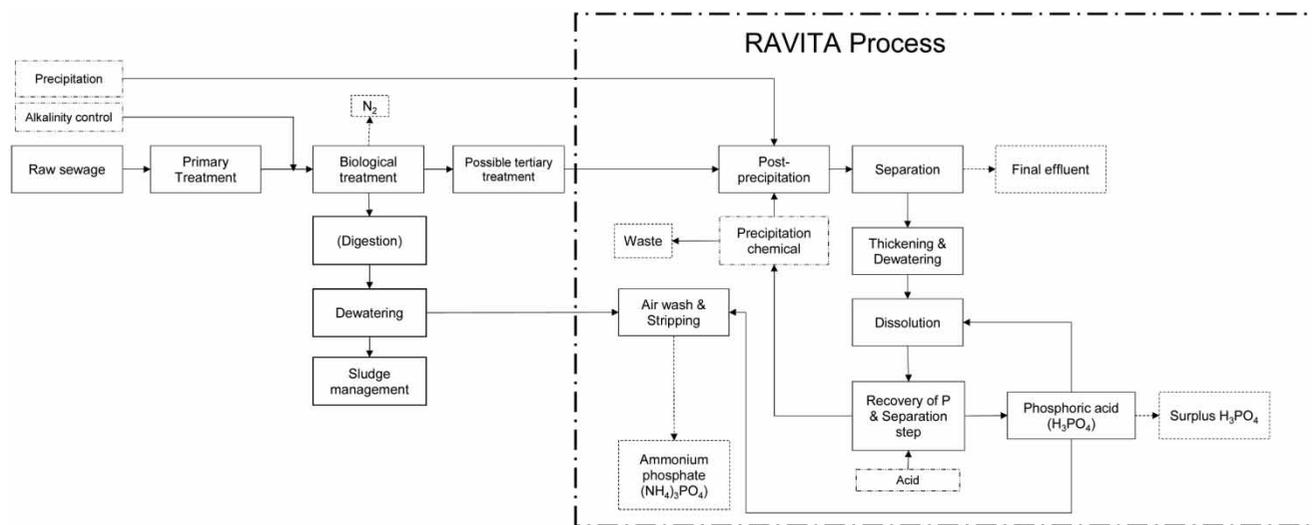


Figure 1 | RAVITA process added to a conventional wastewater treatment process.

combined with nitrogen recovery, which offers a totally new perspective for the recovery technology market.

## MATERIALS AND METHODS

The research was carried out both on the laboratory and large pilot scale (1,000 population equivalent, PE). Piloting is performed in the facilities of HSY's Viikinmäki WWTP (1.1 million PE) in Helsinki, and the objective is to optimize the precipitation process and find the most suitable processes for the chemical sludge treatment. The dissolution of chemical sludge and separation of metal salt are studied at the laboratory scale in this phase of piloting.

## PILOT SCALE

The RAVITA pilot plant was built at the Viikinmäki WWTP in 2016 and it is equivalent to 1,000 PE (Figure 2). The inlet of the pilot plant was the Viikinmäki WWTP's effluent water (suspended solids,  $SS_{\text{average}} = 4.9 \text{ mg/l}$  and  $P_{\text{average}} = 0.221 \text{ mg/l}$ ). To simulate the process without chemical coagulation or EBPR prior to RAVITA, the phosphorus concentration had to be increased to 3–5 mg/l. This was done by adding monopotassium phosphate solution (MKP,  $\text{KH}_2\text{PO}_4$ ) to the pilot influent. For precipitation, Al-based coagulant and anionic and cationic polymers were tested. Coagulation and flocculation comprised four basins with mixers (total volume  $0.94\text{--}1.5 \text{ m}^3$ ). Formed precipitates were separated by a disc filter (Veolia, Hydrotec HSF1708/1-1F, 2.7 m/h). The disc filter's reject water was first collected to a sludge sump (40  $\text{dm}^3$ ) and then pumped by a submerged pump to

the gravity thickener (0.115–0.42 m/h). The disc filter operation was evaluated by backwash percentage (BW%). Precipitation parameters such as coagulant and polymer concentrations, residence time, mixing intensity and sludge circulation were studied.

Figure 2 also depicts the RAVITA DEMO plant with chemical sludge processing units (dewatering, dissolution and separation). The RAVITA DEMO plant will be constructed in 2019.

## LABORATORY SCALE

In this phase of the project, chemical sludge processing has been studied only at the laboratory scale. The laboratory scale research was carried out in collaboration with the University of Jyväskylä.

Dissolution tests were performed with chemical sludge produced at the RAVITA pilot plant.

In dissolution studies, the solubility of chemical sludge in hydrochloric acid (HCl, 37 wt% and 0.7 M), sulfuric acid ( $\text{H}_2\text{SO}_4$ , 95 wt%), sodium hydroxide (NaOH, 50 wt%) (Reuna 2015) and  $\text{H}_3\text{PO}_4$  (0.1–2 M) were tested (Reuna & Väisänen 2018). Dissolution parameters such as acid volume, acid concentration, temperature, time and number of dissolution steps were studied. In addition, effects of dry solids content of the chemical sludge, storage temperature and time on solubility were studied. A factory analysis and Student's t-test were used to discover which parameters have statistical relevance for dissolution. In addition, response surface method and *factorial analysis* are used for the optimization of leaching conditions. (Reuna & Väisänen 2018).

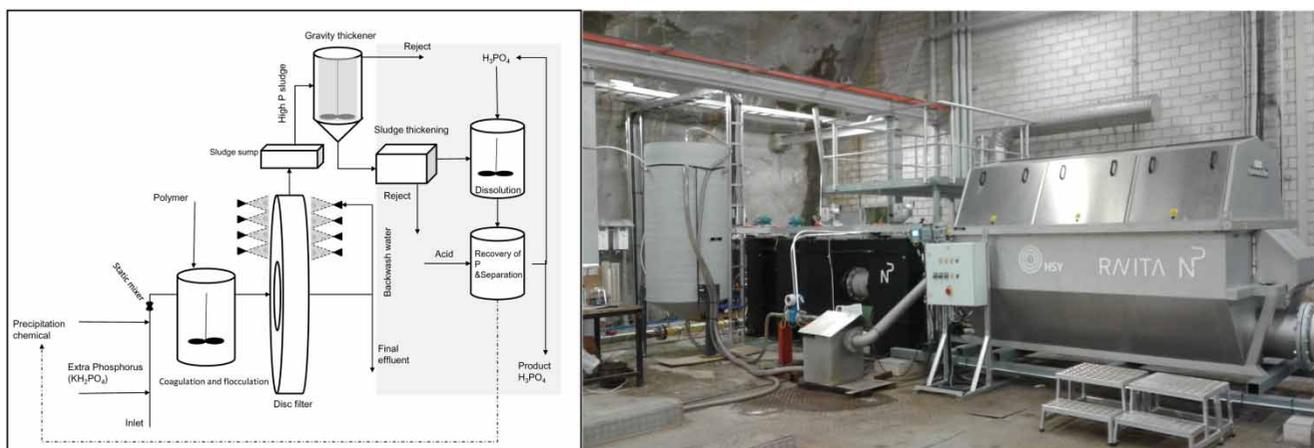


Figure 2 | On the left, flow scheme of RAVITA and RAVITA DEMO plant (grey colored) and on the right, the actual pilot plant in 2017.

For metal salt and P separation, ion exchange (Reuna 2015) and solvent extraction were studied. Tests were done both with synthetic and wastewater-based solutions. Synthetic solution was prepared by dissolving pure aluminum phosphate in pure water. A wastewater based solution was prepared by dissolving chemical sludge from the RAVITA pilot plant with  $\text{H}_3\text{PO}_4$ . The studied process parameters for solvent extraction are solvent type and concentration, the ratio between the aqueous and organic phase (A/O ratio), organic phase/Al ratio and number of extraction steps.

## RESULTS AND DISCUSSION

### Pilot scale studies

In post-precipitation, P removal is enhanced by increasing coagulant concentration, thus increasing the molar ratio between metal ions and P (Figure 3). The optimum molar ratio between Al and P was 2.6 mol:mol when the target concentration in the effluent was at least 0.5 mg TP/l. Similar results have been obtained by other studies (Szabó *et al.* 2008; Reuna 2015). Optimum polymer concentration was 1 mg/l and anionic polymer produced a better result than cationic. This is probably because flocs formed by metal hydroxides are positively charged under most conditions (Bratby 2006). Although it is possible to remove over 90% of the inlet P by a one-step precipitation, the process should be two-step to avoid the risk of high P concentrations in the effluent. Furthermore, it is not advantageous for the next process steps if the molar ratio between Al and P is too high in the chemical sludge.

In the pilot scale studies, it was observed that formed flocs tend to float on the surface of flocculation tanks and

form thick chemical sludge blankets. The floating sludge contained high concentrations of P and Al. Thus, it could be collected with surface scrapers and pumped straight to a gravity thickener. Alternatively, the sludge blanket could be avoided by a different tank design (Väänänen 2017). The flotation problem occurring in the pilot plant's flocculation tanks was solved by installing paddles on the top part of slowly-moving mixers. On the other hand, flotation could be an alternative separation process but then the energy demand of the process will increase due to fine bubble aeration.

During the pilot scale studies, it was observed that floc formation is the most critical step in order to achieve stable disc filter operation. If the formed flocs were too small or too high, the disc filter's capacity was decreased. Low SS concentration in the treated wastewater made the flocculation process difficult as there were not enough nuclei to work as a precipitation platform for new flocs. However, by circulating the disc filter's reject water to the precipitation step it might be possible to improve the flocculation and disc operation. It was also observed that the retention time (7 or 12 minutes) did not have much effect on the P removal but it had more effect on the disc filter operation because with longer residence time the flocs were larger. According to studies by Väänänen (2017), the suggestion for a minimum retention time for coagulation and flocculation is 5 minutes.

For chemical sludge thickening, it would be ideal if the SS concentration of the disc filter's reject water was as high as possible. The highest SS concentrations achieved were 1,300–1,600 mg/l. At the laboratory scale, the formed reject water tended to float, and it was observed that slow mixing enhanced settling. At the pilot scale, a similar kind of flotation in the gravity thickener was not observed because the submerged pumping probably induced mixing

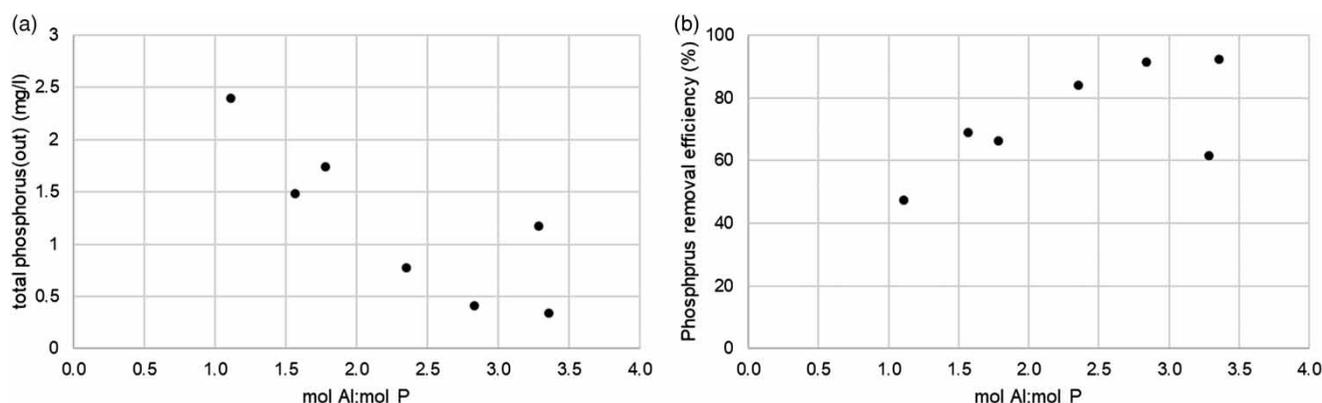


Figure 3 | Effect of molar ratio on the outlet P concentration (a) and P removal efficiency (b) with an Al-based coagulant.

and helped settling. It was also observed that chemical sludge does not settle very fast and an overly high pumping sequence to the gravity thickener was detrimental to settling. With 24 hours' settling time, it was possible to achieve SS concentrations of 3,000–9,000 mg/. Settling of the chemical sludge will be studied more thoroughly in the RAVITA DEMO plant. The goal is to achieve at least a thickness of 1% to make mechanical drying more feasible.

### Laboratory scale studies

At a laboratory scale, different chemicals and parameters for chemical sludge dissolution were studied (Reuna 2015; Reuna & Väisänen 2018). Ion exchange (Reuna 2015) and solvent extraction were studied for separation of P and metal salt.

All the acids and NaOH could dissolve wastewater-based precipitates (Reuna 2015; Reuna & Väisänen 2018).  $H_3PO_4$  was chosen for the dissolution acid as it could be recycled within the process. With the optimized conditions, it is possible to dissolve over 95% of the P and 85% of Al (Reuna & Väisänen 2018).

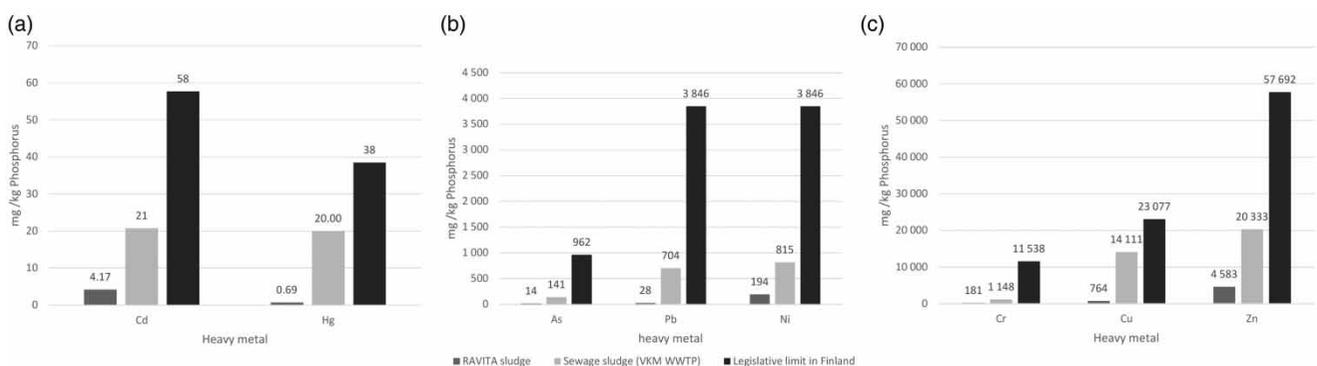
Preliminary ion exchange tests showed that it was possible to separate P and metal salt (either Al or Fe) from each other and use them as their own fraction. The recovery percentage was 44–66%, but it can be enhanced with optimized dissolution and ion exchange conditions (Reuna 2015). The drawback of ion exchange was that P was carried into the elution solution. This would make the use of elution solution as a coagulant more difficult. In addition, the pH of the elution solution is under 1, thus it must be increased before recycling the solution into the precipitation step. Rinsing of the ion exchange resin before elution could prevent the P transfer. However, this would make the eluent;

that is,  $H_3PO_4$ , more dilute and the product needs to be concentrated (Reuna 2015).

In addition to ion exchange, solvent extraction has been studied for metal salt and P separation. Laboratory tests have been done both with synthetic and pilot sludge. First results have revealed that using solvent extraction, it is possible to transfer 97% of Al to the organic phase. The organic phase is further processed so that Al can be used in the precipitation step. So far 91% of Al has been successfully stripped from the organic phase with sulfuric acid. This results in aluminum sulfate solution, which can be used as a coagulation chemical.

### Hazardous substances

One of the most concerning aspects with wastewater-based products is concentrations of heavy metals, micropollutants and microplastics. Preliminary studies have shown that the heavy metal content in the dewatered RAVITA sludge is low, which is extremely important for the potential partners and end users (Figure 4). Organic micropollutants such as bisphenol, perfluorooctanesulfonic acid, perfluorooctanoic acid and so on are not precipitated by metal salts, so it can be assumed that they are not found in the RAVITA product either. Of course, there is always a possibility of absorption on the precipitates, so micropollutants are also going to be analyzed from the chemical sludge and  $H_3PO_4$  product. Through the research done by Talvitie *et al.* (2017a), it was discovered that microplastics are already removed very effectively after the secondary treatment (99%). Thus, prior to the tertiary treatment the concentrations are very low. Microplastic removal in tertiary disc filtration was 40–98% (Talvitie *et al.* 2017b), hence the RAVITA sludge will also contain some microplastics. However, it is possible that processing of the sludge will influence



**Figure 4** | Heavy metal content of the RAVITA sludge compared to sewage sludge from Viikinmäki WWTP and Finland's legislative limit: (a) cadmium and mercury, (b) arsenic, lead and nickel, (c) chromium, copper and zinc.

the concentration. Analysis of the product will be done when the RAVITA DEMO plant is constructed.

## CONCLUSIONS

The decreasing amount of phosphate rock and its deposits have increased the development of P recovery technologies. However, the current P recovery technologies are mostly applicable to only certain types of WWTPs. RAVITA is an innovative process concept where P and nitrogen recoveries are combined, and it is applicable for many kinds of treatment plants. The RAVITA process is also modular, so it enables P harvesting from small and mid-sized WWTPs. Phosphorus is recovered from the water phase by post-precipitation and nitrogen from the sludge liquor by a stripping process. The end products are  $\text{H}_3\text{PO}_4$  and  $(\text{NH}_4)_3\text{PO}_4$  and the P recovery potential is high (>70% of inlet P).

Pilot scale studies showed that the critical point in post-precipitation is floc formation. However, with only one step precipitation, it is possible to transfer over 80% of the inlet P to the recovery part. By dissolving the produced chemical sludge, it is possible to recover over 95% of P and 85% of Al. The separation techniques investigated were ion exchange and solvent extraction. By ion exchange, the recovery rate was 44–64% and with solvent extraction it was possible to remove 97% of Al to the organic phase. Concentrations of hazardous substances are one of the most concerning aspects with recycled nutrients. The preliminary results from heavy metal analysis have shown that RAVITA sludge will fulfil the legislative limits.

In 2019, the RAVITA DEMO plant will be constructed and sludge processing (i.e. sludge dewatering, dissolution and solvent extraction) at the pilot scale will be studied. At laboratory scale the solvent extraction will be further studied and optimized. The quality of the sludge and recovered  $\text{H}_3\text{PO}_4$  will be analyzed. In addition, the combination of phosphorus and nitrogen recovery will be tested at the pilot scale.

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