NEW PROCESSES OF THE CIRCULAR ECONOMY IN WATER AND WASTEWATER TREATMENT

– WATERPRO PROJECT PUBLICATION –

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Abstract

This report presents results of research done in the WaterPro project *New processes of the circular economy in water and wastewater treatment*. In this project, water treatment solutions based on material streams produced as sidestreams or wastestreams of industrial processes or mining were researched and developed. These materials were modified for use as adsorbents or precipitation chemicals for water treatment solutions aiming to remove nutrients or metals. Materials such as paper mill sludge, slag, fly ash, jarosite, analcime, and brucite were used. Adsorption, chemical precipitation, and electrochemical precipitation were applied as water purification methods. Experiments were performed using model solutions and real wastewaters from different industries or other water resources. The components that were removed included nutrients (nitrogen and phosphate) and metals (zinc, copper, manganese, chromium, nickel, antimony, cobalt, and iron). Based on results, summarized in the report, metakaolin-based adsorbents were chosen for further experiments that will scale up from laboratory studies to small-scale and pilot experiments.

Tiivistelmä

Raportissa on esitetty *WaterPro - Kiertotalouden uudet prosessit veden ja jäteveden käsittelyssä* -projektissa saatuja tuloksia. Projektissa tutkittiin ja kehitettiin teollisuuden sivu- ja jätevirroista valmistettuja vedenpuhdistusratkaisuita. Saatavilla olevista materiaalivirroista valittiin sopivimmat ja materiaaleista muokattiin adsorbenttimateriaaleja tai saostuskemikaaleja ravinteiden tai metallien talteen ottamiseksi vedestä. Vedenpuhdistusmenetelminä käytettiin adsorptiota, kemiallista saostusta ja sähkökemiallista saostusta. Projektiin valittuja materiaaleja olivat esimerkiksi paperitehtaan liete, kuonat, lentotuhka, jarosiitti, analsiimi ja brusiitti. Valmistettuja vedenpuhdistusmateriaaleja testattiin malliliuoksilla ja aidoilla teollisuuden tai muulla yhteiskunnassa muodostuvilla vesillä. Vesistä poistettiin ravinteita (typpi ja fosfori) ja metalleja (sinkki, kupari, mangaani, kromi, nikkeli, antimoni, koboltti ja rauta). Saatujen tulosten perusteella metakaoliinipohjaiset geopolymeerit valittiin jatkotutkimuksiin, joissa kokeet suoritettiin laboratoriomittakaavaa suuremmalla mittakaavalla.

Foreword

Water pollution and lack of clean drinking water represent global challenges. Worldwide, one in three people does not have access to safe drinking water. Clean water and sanitation are also UN sustainable development goals. Industrial activities use massive amounts of fresh water and produce process waters and wastewaters. Therefore, there is a growing need to find cost-effective methods to purify wastewaters, utilize industrial waste materials, and recover valuable materials from wastewaters.

WATERPRO explored functional solutions to combine these three objectives in a cost-efficient way that provides new solutions and business to companies. The overall aim was the purification of wastewaters and the recovery of valuable materials through the identification of a novel solution, which would combine new methods and previously developed technologies into a hybrid method. Water purification with methods proposed in this project saves annual costs (water, energy, waste management, chemicals) due to the use of industrial by-products in water purification as precipitation chemicals or adsorbents. This project resulted in several scientific publications, presentations, and company meetings. More sustainable utilization of materials, economical water purification solutions, and an increase in the appreciation of Finnish know-how and the development of new knowledge were all observed. The project partners were from Central Ostrobothnia, North Ostrobothnia, and the area of Kainuu.

I express my deepest thanks to all project collaborators, companies, and stakeholders for their active collaboration and deep discussions related to the topic.

Kokkola, 29th November 2021

Ulla Lassi
Professor, Principal Investigator

Abbreviations

AAMs	Alkali-activated materials
AAS	Atomic absorption spectroscopy
ANAMMOX	Anaerobic ammonium oxidation
BEC	Batch electrocoagulation
BFS	Blast furnace slag
BFS-GP	Blast furnace slag-based geopolymer
BRU	Brucite
CEC	Continuous flow electrocoagulation
CP	Chemical precipitation
FA	Fly ash
FA F	Fly ash, class F
FA-GP	Fly ash-based geopolymer
FSHCa-GP	Geopolymer based on fiber sludge with high calcium content
FS MKGP	Fiber sludge metakaolin-based geopolymer
q_e	Equilibrium adsorption capacity
q_m	Maximal adsorption capacity
GP	Geopolymer
GR	Granules
HYD	Hydromagnesite
K-AAM	Potassium-based alkali-activated material
LD	Linz–Donawitz converter slag
LS	Ladle slag
Na-AAM	Sodium-based alkali-activated material
MK	Metakaolin
MKGP	Metakaolin-based geopolymer
LECA	Light expanded clay aggregate
LOI	Lost on ignition
PBS	Passive barrier filtration system
TMCA	Transmembrane chemical absorption
TDS	Total dissolved solids
WWTP	Wastewater treatment plant
XRD	X-ray diffraction method
XRF	X-ray fluorescence

Contents

1   Introduction

Pure water is essential for life. In Finnish households, approximately 150 liters of water per day [1] must be purified after use. This, combined with leakage waters from built-up areas, means annually approximately 500 million cubic meters of wastewater are treated in municipal wastewater treatment plants [2]. Additionally, wastewaters are formed in industry even though industrial plants have developed closed water cycle processes and industrial wastewater treatment plants to reduce components released into nature along with wastewater.

Regulations guiding emission-limit values of pollutants in water that is released into nature from industries and communities protect the environment. These limit values are defined for components that are considered the most contaminating substances and are set in the environmental permits of each industrial plant. Such substances include metals and their compounds, as well as compounds causing eutrophication, like nitrate and phosphate [3]. Metals can accumulate in water or the food chain and have toxic effects on the environment [4], while nutrients in natural bodies of water can cause eutrophication and decrease water quality, leading to a decrease in oxygen levels and a loss of biodiversity [5].

A large proportion of metals and nutrients contained in wastewater are lost during the water treatment process nowadays. In 2017, the wastewater treated in Finnish municipal wastewater plants contained 4,260 tons of phosphorous and 32,760 tons of nitrogen, of which 96.4% and 66.1% respectively were removed during the purification process [2]. Only approximately 70% of phosphorous and under 10% of nitrogen is utilized as sewage sludge in landscaping and agriculture [6]. Wastewater also contains metals that are described by Finnish government regulations as harmful to aquatic environments. Such metals include lead, mercury, nickel, and their compounds [7]. Wastewater can additionally contain metals like antimony, cobalt, chrome, copper, manganese, iron, and zinc. A portion of metals present in wastewater end up in sewage sludge and can limit the utilization of sludge for agricultural purposes. Cadmium, chrome, copper, mercury, nickel, lead, zinc, and arsenic are considered harmful metals in sewage sludge if used in agricultural lands [8].

However, these metals and nutrients from wastewater could replace some raw materials from primary resources like mines. For example, phosphorous is still mined for agricultural fertilizers from apatite deposits. Only 65% of phosphorous fertilizers are made from secondary resources like manure or recycled nutrients [9]. Current wastewater treatment processes are not designed to specifically recover nutrients or other compounds for recycling or further use. Phosphorous, for example, is precipitated with iron salt in municipal wastewater systems. Precipitated phosphorous is weakly soluble; thus, phosphorous in precipitate has a weaker fertilization effect than phosphorous in inorganic fertilizers [10, 11]. Industrial wastewaters have even greater potential for compound recycling. Recovery of metals or nutrients in industrial wastewater plants would enable either the return of material streams to the process to replace or complete primary raw material streams or their transfer to another process. These kinds of solutions would support the aims of a circular economy.

Besides wastewaters, solid (or moist) sidestreams and wastestreams are formed in industrial plants. In 2019, 86,743,000 tons of mineral waste were produced from mining, 338,000 tons of sludge waste and 242,000 tons of mineral waste from the paper, pulp, and printing industry, and 807,000 tons of wood waste from the sawn timber and wood product industry [12]. A portion of these material streams could potentially be modified to new products like water treatment materials.

The WaterPro project was designed to support this kind of material efficient solutions in water treatment. In this project, industrial sidestreams and other materials with the highest potential of being modified to adsorb or precipitate compounds from wastewaters were identified. Materials chosen for further research were:
- metakaolin-rich sludge from the paper industry,
- slag (blast furnace slag, ladle slag, and Linz-Donawitz converted slag) from metallurgical processes,
- jarosite, analcime, brucite, and hydromagnesite materials from the mining industry, and
- sawdust from the wood product industry.

The adsorbent properties of these materials were investigated and modifying processes of adsorbents were developed. Adsorption properties of materials for metals and nutrients were studied. The best adsorbent materials were characterized and additional adsorption experiments were performed. Regeneration properties of the chosen materials were studied and experiments were scaled up from laboratory to pilot scale. In addition to adsorption experiments, some sidestreams were used in electrochemical and chemical precipitation experiments. Struvite was precipitated from nutrient-rich waters and ettringite from sulfite-rich waters by electrochemical precipitation. Studies on chemical precipitation were also performed. Calcium-rich industrial sidestreams were used to precipitate hydroxylapatite, and dolomite and fly ash to precipitate struvite. Utilization of precipitate sludges as fertilizers was also studied.

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2 Utilization of sidestreams in production of adsorption materials

Adsorption is widely used in water treatment processes. The process is low-cost, highly efficient, and easy to operate [1]. Adsorption is a suitable process for treating reasonably small amounts of water with a low concentration of the contaminant, whereas precipitation is more suitable for water with a high concentration [2]. In the adsorption process, water is led through a solid adsorbent bed. Contaminants present in the water attach to the surface of the adsorbent, after which they can be cleaned, collected and utilized, or disposed of. Several solid materials can be used as adsorbents depending on their properties for adsorbing the specific contaminant and the final disposal of adsorption material. For example, activated carbon is a well-known adsorbent in water treatment solutions.

Some adsorbent materials can be regenerated. In regeneration, contaminants are removed from the adsorbent by changing process conditions, like temperature or pH, or by using a regeneration solution. By cycling adsorption-desorption steps, it is possible to recover contaminants to a regeneration solution. In the first step, contaminants are removed from the water to the adsorbent, and in the second step, contaminants are recovered from the adsorbent to the regeneration solution. These adsorption-desorption steps can be cycled so that the same adsorbent is reused and cleaned multiple times. However, the number of cycles possible depends on the adsorbent material, as some materials do not desorb contaminants. These cannot be used again and must be disposed of or utilized together with contaminants. Some materials release all or a portion of contaminants during the regeneration process and can be reused. If only some of a contaminant is desorbed, the adsorption properties of the adsorbent decrease after each cycle. When adsorption capacity decreases to an extent that the process is no longer profitable, the adsorbent is disposed of.

In some cases, the regeneration solution can be used several times to remove contaminants so that concentration of the contaminant increases in the solution after each cycle. The solution can then be utilized in another process or application or used to return compounds to the original process.

This WaterPro project identified waste and sidestream materials that can be modified for use as adsorbents. These materials and their properties were investigated for their ability to remove nutrients and metals from model solutions as well as from real waters originating from industries, mines, and other water resources. For example, adsorption properties, modifying process, availability, economical potential, suitability for the aim contaminants and wastewaters were considered when adsorbent materials were compared. The best materials were characterized more closely, and their regeneration properties were studied as well.

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2.1 Metakaolin

Metakaolin is produced from the clay mineral kaolinite by calcination. Kaolinite is a hydrated aluminum silicate, which is the dominant mineral in kaolin deposits. Due to the physical and chemical properties of kaolinite, it has a wide variety of applications. The paper industry, for example, uses kaolin as a paper filler and coater.

Metakaolin-based geopolymers can be used for ammonium removal [2]; thus, metakaolin-based adsorption materials were researched in the WaterPro project. For example, a paper mill sidestream containing both kaolinite and commercial metakaolin was used in this research. Removal of ammonium and metals were studied, as well as the regeneration of metakaolin-based geopolymers and the effect of different real waters.

2.1.1 Metakaolin-based geopolymers for ammonium removal

The paper mill sludge was preliminarily dried at room temperature for several days. The small fiber particles within the sludge were ignited and the remaining kaolinite calcined at 750 ^{o}C for three hours. Commercially available metakaolin was obtained from Aquaminerals Finland Oy.

The elemental composition of samples was measured semi-quantitatively with an X-ray fluorescence (XRF) spectrometer (PanAnalytical Minipal 4). The chemical compositions of raw material and prepared adsorbents are listed in Table I.

Table I   Chemical compositions of metakaolin recovered from paper mill sludge and prepared geopolymers.

Constituent (wt. %)	Calcined metakaolin, content (wt. %)	Geopolymer, activator content			
		6M	8M	10M	12M
Na_2O	–	6.42	6.55	7.47	8.60
Al_2O_3	27.7	28.5	27.3	24.6	23.9
SiO_2	32.9	39.4	40.2	32.8	30.6
SO_3	0.17	0.04	0.05	0.05	0.07
K_2O	0.14	0.13	0.12	0.11	0.10
CaO	6.39	4.35	3.75	3.99	3.77
Fe_2O_3	0.94	0.81	0.78	0.80	0.80
TiO_2	0.85	0.84	0.81	0.81	0.81

Aluminum oxide and calcium oxide were present in significant quantities, while titanium, potassium, and iron oxides were present as impurities. After geopolymerization, the content of Na, Si, and Al increased and loss of ignition (LOI, 950 ^{o}C) rose to 7.4% for the calcined metakaolin and up to 12.1 % for the geopolymers.

Diffractograms of geopolymers were obtained via the powder X-ray diffraction method (XRD, a PANnalytical X´Pert PRO MPD diffractometer, Co Kα radiations generated at 40 kV and 40 mA, step width of 0.02°, Highscore software 3.0). XRD patterns of the obtained FS MKGP and geopolymer prepared from commercially available metakaolin (Fig. 1 and 2) show the presence of both an amorphous and crystalline structure. The crystalline phase of FS MKGP is defined by the presence of aluminum and silicon oxide (quartz type). Gehlenite is also a substantial part of this phase since FS MKGP contains up to 3% Ca. To compare the structures of FS MKGP and geopolymer made from commercial metakaolin, a reference geopolymer was prepared in accordance with standard procedure [4]. The crystalline phase of the latter aligned with the literature, and characteristic peaks of muscovite, quartz, and albite were observed. In a series of 6–12M FS MKGP, a larger relative yield of amorphous phase was observed when activators with higher alkali molarity were used, while the crystalline phase composition and ratios of minor minerals were generally similar.
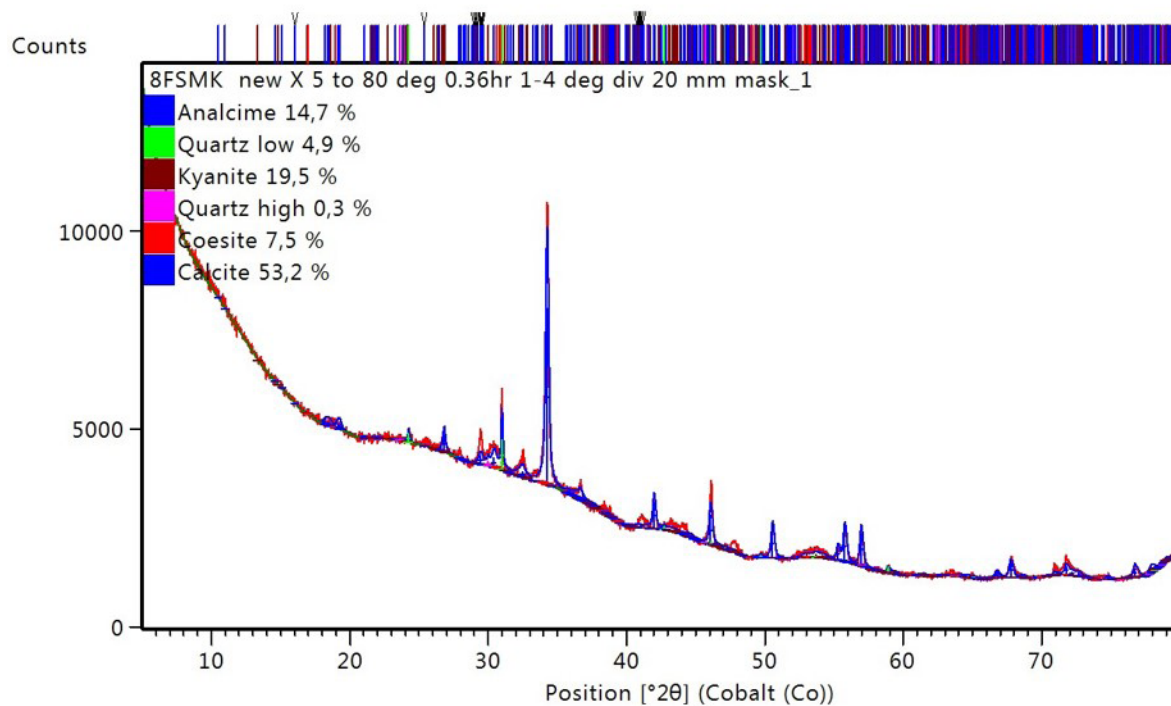

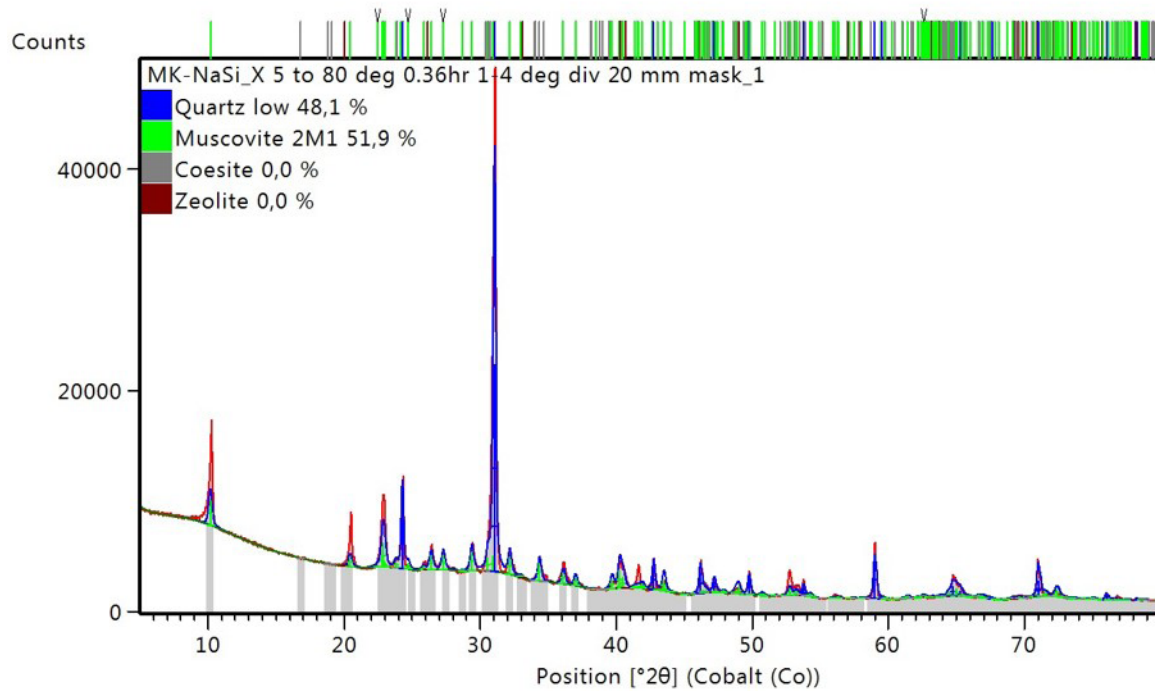**Figure 1**   XRD patterns of FS MKGP.

Figure 2   XRD patterns of MKGP.

2.1.1.1 Adsorption study on ammonium recovery

Adsorption experiments were performed using batch equilibration and fixed-bed methods. In the batch method, an adsorbent was agitated with a 200 mL solution containing nitrogen as ammonium at 30 rpm (overhead shaker) at room temperature for 24 h to reach equilibrium. The effect of adsorbent dosage on ammonium removal was studied by keeping other factors constant. Similar experiments were conducted to study the effects of initial adsorbate concentration, pH, and contact time. Continuous experiments were performed by pumping samples of synthetic or municipal wastewaters at a flow rate of 0.35 L/h through a column filled with 100 g of geopolymer granules. Wastewater effluents (before and after biological treatment), runoff waters, spiked lake water, and mine drainage effluents were objects of the research. The runoff and lake water samples had low amounts of total dissolved solids (TDS) and low ionic strength, while TDS values of mine effluents were high. Table II illustrates the content of major elements in mine water samples. Such a complex composition has a large effect on the adsorption process, leading to a significant decrease in removal rates (Table III).

Table II   Content of major elements and competitive ions in mine water samples.

Element	Point 1, mg/L	Point 2, mg/L
Na	163	100
Ca	614	302
Mg	14.2	96
K	130	16.1
Sr	1.4	2.7
Si	1.2	7.8
S	612	343
NH_4-N*	27.9	9.04

*target contaminant, as N mg/L.

Capacity and selectivity of the MKGP and FS MKGP were calculated and compared with three commercial zeolite samples (Table III). While a strong influence of the water matrix on capacity was observed for both geopolymers and zeolites, synthetic and natural materials could be successfully used for ammoniacal nitrogen removal from various wastewaters.

Table III   Removal rates of ammonium by commercial zeolites and proposed adsorbents from industrial effluents and natural waters (n = 3, P = 0.95, variability did not exceed 5.2% in all cases).

Sample Adsorbent[a]	Run-off[b]	Lake water[b]	Mine water		WWTP effluents	
			Point 1[c]	Point 2[d]	Before[e]	After[f]
MKGP	68%	64%	44%	45%	54%	52%
FS MKGP	92%	95%	69%	72%	82%	81%
Spanish zeolite	61%	58%	32%	38%	51%	56%
Chinese zeolite	55%	58%	17%	21%	57%	57%
Bulgarian zeolite	87%	84%	52%	60%	77%	78%

[a] adsorbent dose 10 g/L, grain size 63−125 μm, contact time 3h

[b] spiked with ammoniacal nitrogen 40 mg N/L

[c] ammoniacal nitrogen concentration 27.9 mg N/L

[d] ammoniacal nitrogen concentration 9.04 mg N/L

[e] ammoniacal nitrogen concentration 36.4 mg N/L

[f] ammoniacal nitrogen concentration 40.5 mg N/L

2.1.1.2 Regeneration

To estimate the regeneration and preconcentration ability of MKGP and FS MKGP, granules were fully saturated with ammonium nitrogen before desorption with various regeneration solutions. To obtain a saturated adsorbent, a solution containing 140 mg/L of ammonium was pumped through the adsorption column using flow rates of 1 L/h. Both potassium and sodium salts were used for regeneration experiments with at least five adsorption-desorption cycles. The ammonium concentration in effluents was determined at regular time intervals and the obtained breakthrough curves were used for results interpretation.

To optimize a regeneration procedure, the influence of several factors such as regenerant composition, competing ion concentration, and pH were studied. A solution containing sodium chloride and sulfate and a solution containing potassium chloride,

sulfate, and phosphate were studied as potential regeneration solutions (with sodium/ potassium concentration 1M). Each regeneration solution was pumped at a flow rate of 0.35 L/h and residence time was 5.5 min. The recovery rate for ammonium was estimated in accordance with the preloaded amount of nitrogen in the column. All variants were tested at neutral pH and at different alkalinity (0.1M, 0.25M, 0.5M as NaOH/KOH). Potassium salts and sulfate salts were chosen as regenerants to test the assumption that solutions post-desorption could be used directly as liquid fertilizers. In this light, potassium as an ion-exchange cation would be more beneficial than sodium, which could cause salinity and sodicity problems [1]. Chloride as an anion has the same limitations as sodium. Phosphorous and potassium are both essential elements for crop yield increase. Thus, a regeneration solution based on potassium phosphates could be a reasonable option for obtaining a value-added final product.

Under neutral conditions with sodium salts, recovery rates did not exceed 65% and 55% from MKGP and FS MKGP granules, respectively. Potassium salts as regenerants yielded up to 21% higher regenerated ammonium for both adsorbents. However, it was found that after regenerating FS MKGP with potassium salts, the efficient removal of ammonium decreased substantially. Only 55% of ammonium was adsorbed from a loading solution in a second adsorption cycle. Removal capability of the FS MKGP granules could be regained after 24h contact time with 5M sodium chloride, however.

The efficiency of the regeneration procedure based on different pH and salt concentrations in regeneration solution and was studied. Higher pH yielded higher recovery rates. Although a pH of 9 was sufficient for efficient regeneration of ammonium from the adsorbent, 0.1M solutions of alkaline were used in further experiments due to the substantial decrease of pH from 12.8 to 9.2 during the cyclic regeneration experiments. In all cases, cation concentration equaling 1M was preferable and yielded higher recovery rates than 0.5M or 0.25M solutions. The amount of salt and alkaline used not only influences the efficiency of regeneration but also defines the cost of treatment. Thus, various combinations of salt/alkaline were evaluated to find the most cost-effective option. To this end, cyclic adsorption-desorption tests were carried out.

The proposed adsorbents demonstrated entirely different behavior. In one case, the MKGP granules could be treated with the same regenerating solution several times, while for FS MKGP regeneration, ammonium had to be removed from the regenerant prior to a new cycle. Regeneration of MKGP with the same regenerant was carried out for five cycles without stripping ammonium out, yielding a final concentration of ammonium in the regeneration solution of 2.75 g/L. After the fifth cycle, the adsorption capacity of a column treated with an ammonium-laden regenerant decreased substantially, and the regenerant required cleaning and pH adjustment prior to the next desorption cycle. With FS MKGP, a regenerant could be used for only one cycle without ammonium stripping. If an ammonium-laden regenerant was used for the second cycle, readsorption of ammonium on FS MKGP was observed instead of desorption, leading to adsorbent saturation. To use this adsorbent multiple times, ammonia removal from the regenerant via air-stripping or membrane technology is recommended. Although the enhancement coefficient in a laboratory-scale layout did not exceed 7.5, even this preconcentration yet has potential for further stripping technologies.

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2.1.2 Metakaolin-based alkali-activated materials for metal removal

Metakaolin was used as a raw material for the preparation of sodium (Na)- and potassium (K)-based alkali-activated materials (AAMs). The aim was to produce stable and highly porous materials using two combinations of alkali solutions (NaOH/Na$_2$SiO$_3$ and KOH/K$_2$SiO$_3$). Metakaolin was prepared by calcinating commercial kaolin, after which it was mixed with a concentrated alkali solution. Results showed that the Na-AAM and K-AAM differed in viscosity of the pastes and that porosity of the AAMs was increased using foaming agents. The blank AAMs (foaming agent-free) demonstrated the highest strength values. The compressive strength of both materials decreased to below 1.0 MPa when concentration of the foaming agent was increased. These results improved the understanding of the development of porous structure for geopolymers/alkali-activated materials. Porosity typically improves adsorption capacity of materials.

The research procedure has been described in more detail in the following publication:

Christophliemk, M. P., Pikkarainen, A. T., Heponiemi, A., Tuomikoski, S., Runtti, H., Hu, T., Kantola, A. M., Lassi, U. Manufacture of sodium- and potassium- based alkali-activated materials (AAMs): comparison of physical properties (2021). Manuscript

Granular-shaped AAM blocks with a diameter of 10mm*5mm were manufactured in mold for adsorption tests with optimal molar ratios for the alkali solution. Metakaolin was used as raw material. The 24-hour column tests utilized a closed-loop system with a passthrough flow of 1200 mL per minute and were carried out using 50 grams of AAM granules in a base solution with a total volume of 5 liters. In this case, a closed-loop system means that solution goes through the same column several times. The base solution contained Mn(II), Zn(II), Cu(II), and Cr(VI), with a metal concentration of 100 mg/L. Metal removal rate was measured by taking samples from the base solution after certain periods, and metal concentration was determined by atomic absorption spectroscopy (AAS). Two types of adsorption tests were performed: the first employed acetic acid prewashed AAM granules, while the second employed regenerated AAM granules with NaCl solution after acetic acid prewashing. The results showed that regenerated granules prewashed with acetic acid were considerably more effective for the removal metals than granules which have been only prewashed with acetic acid. The best removal percent, around 76 % was obtained for the removal of copper. These experiments clarified the effect of mild acetic acid washing and NaCl treatment before adsorption as a way of improving adsorption capacity. Furthermore, the preparation method using a small mold was studied in this case, and results suggest that using a specific mold is one way to prepare geopolymers of uniform size.

Figure 3   a) Prepared AAM blocks; b) column tests as a closed-loop system.

An acid-activation route for geopolymer preparation was considered after literature review (Bachelor thesis, Miska Veijola), and some preliminary experiments were conducted. Metakaolin was used as raw material for producing acid-activated geopolymers. Preliminary experiments demonstrated that acid-activated geopolymers failed to remove Ni and Zn.

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2.2 Slags

Throughout different stages of metal processing, several slags (e.g., blast furnace slag (BFS), ladle slag (LD), and Linz-Donawitz converter slag (LD)) can be generated. BFS primarily consists of silicates, aluminosilicates, and calcium-alumina-silicates and is removed from the top of molten iron during its extraction from ore. LD is formed in a Linz-Donawitz converter in steel plants, and LS is generated during the ladle treatment process stage of smelting in steel plants. In this project, raw materials (BFS, LS, and LS) were obtained from an SSAB Europe production site located in Raahe, Finland and were used as raw materials for alkali activation.

Figure 4   Different slag materials.

2.2.1 Blast furnace slag-based geopolymers for nutrient removal

Although powdery adsorbents present large adsorption capacities due to their large surface areas, powdered forms create difficult separation and recovery processes, limiting their industrial application. Crushed monolith of GPs (e.g., shards with particle size 0.5–4 mm) are generally used in column experiments to overcome powder limitations [1]. Debris is sieved to a specific diameter to obtain adsorbents of irregular form and specific size.

Spherical granules with a diameter of 2–3 mm could be obtained by direct geopolymerization during granulation, through a suspension and solidification method [2], or by deposition of the geopolymer on inert support [3].

2.2.1.1 Supported adsorbents and composite structures

A new approach to manufacturing adsorbents is being applied to gain new properties (porosity, lightness, ability to float) and/or reduce production costs. An inert support was used as a carrying substrate for GP. The adsorbent design consisted of the following steps: (1) selection of an inert substrate; (2) identification of GP compositions for effective surface adhesion. The resulting adsorbents should have high capacity and selectivity towards nutrients as well as possess unique properties and ease of manufacturing.

Since a substrate could lend new valuable features for resulting adsorbents, several substances for passing down predetermined properties were examined:
- Light expanded clay aggregate (LECA)
- Cork waste
- Perlite

LECA has previously been investigated as adsorptive material for nutrient removal, but the efficiency and adsorption capacity of the raw material are low (< 0.1 mg P/g) [3]. Modification of the LECA surface with Fe or Al oxides enhanced the adsorption of P on LECA [4]. Obtained adsorptive materials were further tested as substrates for constructed wetlands. As the adsorption properties of granules are attributable mainly to surface area, light and porous LECA substrate provide the required support. LECA is non-toxic, environmentally friendly, and low in cost material, substantially reducing the price of adsorbent manufacturing. Techniques similar to conventional geopolymer preparation were applied to design floatable light granules for ammonium and phosphate removal, results of which are reported in more detail in the following publication [5]:

Samarina, T., Takaluoma, E., Kazmaganbetova, A. Geopolymers Supported on Inert Substrate for Phosphate Removal from Natural Waters. 6th World Congress on New Technologies, Virtual, Aug. 2020. DOI: 10.11159/icepr20.119.

Cork is composed of an aggregate of cells (about 42 M/cm^3) that provides the unique properties of this material and makes it one of the most versatile natural raw materials known. As a cellular material, its unique properties arise from its closed-cell structure. Cork is light in weight, elastic, flexible, impermeable to gases or liquids, imperishable, a good electric and thermal insulator, and a dielectric material, all of which render cork a suitable option for the designing of the supported adsorbents. Only 25% of the raw material is acceptable for cork stopper production (natural corks) [6]. Thus, new applications have been sought for utilizing waste cork as cork composites. In 2019, export of waste cork (crushed, granulated, or ground) by the top five producers exceeded 100 M tons [7].

Perlite is a natural, lightweight, inert, and fireproof rock. Expanded perlite is a major product on a perlite market since crude perlite has limited applications as casting sand or as a slag coagulant. Physical and chemical properties of expanded perlite include low heat conductivity, very low bulk density, resistance to high temperatures, chemical neutrality, and high physical stability.[8].

All three chosen supports were used to prepare core-shell structures. LECA, cork, or perlite provided support for functional material, while BFS-GP, FA-GP, or MKGP was used as a shell layer to improve or tune adsorption properties of composites.

The work in this part was supported by Maa- ja vesitekniikan tuki (no 13-8271-17).

2.2.1.2 Nutrient removal with BFS geopolymer

Due to high calcium content, BFS-GP was examined as a prospective adsorptive material for phosphate removal from diluted aqueous solution. To evaluate phosphate removal efficiency, batch and column adsorption experiments were performed. The effect of various operating conditions (e.g., initial pH, adsorbent dose, initial phosphate concentration, and adsorption time) has been studied. The adsorption process was relatively fast for BFS-GP and maximum removal rate was achieved at 5h. The adsorption capacity at a phosphate concentration of 100 mg L^{-1} was 26 mg g^{-1} . A removal ratio of over 98% was achieved with an adsorbent dose of 4 g L^{-1}. The ability of BFS-GP to remove phosphate ions increased with increasing pH values up to 9 and then decreased until a pH of 12.

Fixed-bed continuous column experiments were carried out with granulated forms to evaluate the influence of granule size, flow rate, and adsorptive layer length on operational conditions of the adsorption tower (Fig. 5). Two samples of water from field run-offs (Pyhäjärvi area) were treated in bench-scale application with a granulated form of BFS-GP. Both water samples showed removal rates of at least 95% for at least 125 bed volumes of the adsorption column at an initial concentration of 0.8−1.2 mg L^{-1} for the phosphate.

Figure 5   Adsorption columns filled with BFS-GP, FS MKGP, and MKGP adsorbents.

To remove both major nutrients presented in run-off waters simultaneously, composite materials with affinity to N and P were prepared and tested. Bulk geopolymers were prepared by mixing 100 g of solid material (BFS or its mixtures with MK) with an alkaline activator in a solid-to-liquid ratio (S/L) of 1:1. The alkaline activator contained 6−12 M sodium hydroxide and sodium silicate in a weight ratio of 1:2. The ability of the composites to adsorb phosphate and ammonium ions separately or from one solution was investigated.

In general, composites prepared using sodium hydroxide with a molarity of 8M and 10M had higher adsorption characteristics towards both nutrients. However, a tendency towards lower ammonium removal was observed when molarity of an activator increased from 6M to 12M. Based on preliminary results, the geopolymer composite containing 60 wt% BFS and 40 wt% MK (with 8M NaOH as an activator) was chosen for further bench-top tests. This composite was able to reduce phosphate-ion content by 60% and ammonium-ion content by 15% from an initial phosphate concentration of 10 mg/L and ammonium concentration of 50 mg/L. The effect of initial concentration of the target ions on adsorption characteristics was measured by varying the concentration of ammonium solution from 10 to 200 mg/L and phosphate solution from 10 to 100 mg/L at an initial pH of 7.1.

In the first step, solutions containing either only ammonium or phosphate ions were tested. In ammonium removal tests, 50 mg/L of ammonium was removed effectively with an adsorbent dose of 2 g/L, reaching 23% removal (4.3 mg/g) at a final pH of 7.9. By increasing adsorbent dose to 5 g/L, removal up to 38% could be achieved. A further increase in adsorbent dose is not reasonable due to technological obstacles. An 80-min contact time was sufficient for the geopolymer composite to reach saturation. According to Luukkonen et al. [2], geopolymer containing only metakaolin has an ammonium removal capacity of 6.5 mg/g at a 50 mg/L initial concentration of ammonium nitrogen. Thus, adsorption potential of the proposed composite towards ammonium ions is largely satisfactory. In phosphate removal tests, removal rate was 96% at an adsorbent dose of 2 g/L and phosphate concentration of 10 mg/L, decreasing to 68% at a phosphate concentration of 100 mg/L.

In a mixture solution containing both ammonium and phosphate, the ammonium adsorption capacity onto the tested geopolymer composite declined insignificantly with increasing phosphate concentration. The maximum phosphate adsorption capacity was enhanced in the presence of ammonium (Fig. 6). The maximum capacity towards phosphate in the presence of both ions amounted to 35 mg/g, while the maximum capacity in absence of ammonium was up to 25% lower.
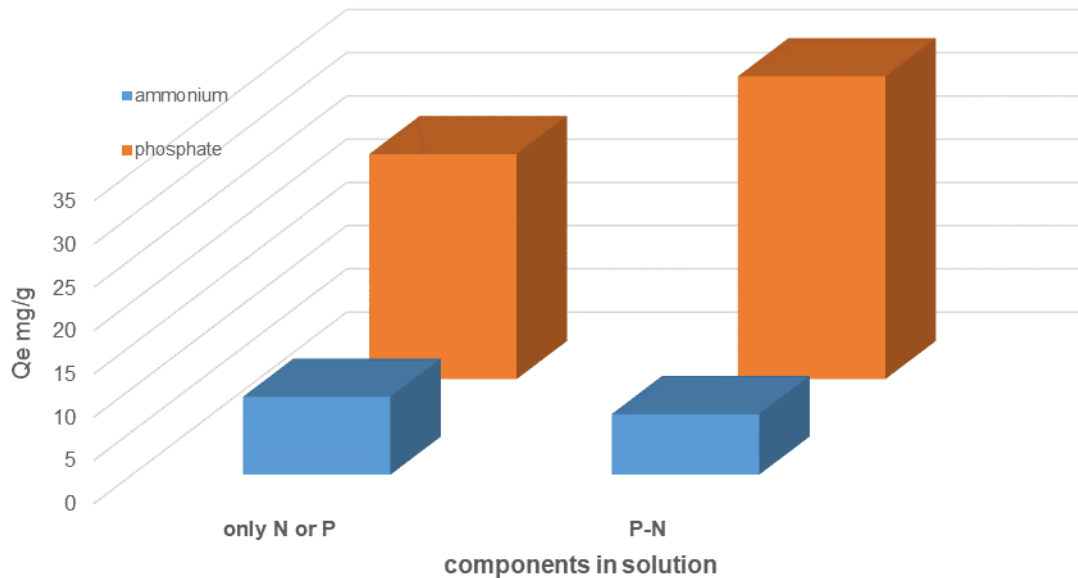

Figure 6   Adsorption capacity of the proposed adsorbents towards nutrients in mono- and multicomponent solutions.

2.2.1.3 Field experiment of alkali-activated blast furnace slag

Alkali-activated blast furnace slag (BFS) granules were prepared and characterized for composition, microstructure, and surface properties. Granules were used in a field experiment at Lake Kivijärvi in Finland, a lake that has been heavily affected by a mining accident. This work aimed to evaluate the performance of the amendment material for in situ remediation. Two mesocosms were placed in the lake and, after two weeks, both sediment and pore water samples were taken. Bioaccessibility of metals from sediments was assessed with a three-stage leaching procedure, which showed that the granules were effective in decreasing the mobility of Fe, Zn, Ni, and Cr in all leaching stages compared to unamended sediment.

This research procedure has been described in more detail in the following publication:
Laukkanen, J., Takaluoma, E., Runtti, H., Mäkinen, J., Kauppila, T., Hellsten, S., Luukkonen, T., Lassi, U. In situ remediation of metal(loid)-contaminated lake sediments with alkali-activated blast furnace slag granule amendment: A field experiment (2021). Manuscript

2.2.2 Blast furnace slag, ladle slag, and Linz–Donawitz converter slag-based adsorbents for nickel removal

Alkali-activated adsorbents were synthesized by mixing three different slags from the steel industry: blast furnace slag (BFS), ladle slag (LS), and Linz–Donawitz converter slag (LD). Before alkali activation, BFS, LS, and LD slags were sieved to a particle size of 1 mm. Prepared powdered slag-based geopolymers (GP) were used to remove nickel(II) from

aqueous model solutions in fixed-bed column studies. Experiments were conducted at a pH of 6 using a phosphate buffer with an initial nickel(II) concentration of 50 mg/L. Flow rate was 5 mL/min and samples were taken at time intervals ranging from 5 to 90 min. Used bed height was 0.5 cm and three adsorption-desorption cycles were implemented. Results showed that experimental adsorption capacity was 2.92 mg/g for GP (BFS, LS) and 1.34 for GP (LD, BFS, LS). This research has been described in further detail in the scientific publication published during the project. Of ultimate importance to the WaterPro project, this research demonstrated that non-traditional slags from the steel industry can also be used as raw material for geopolymer production and that material was regenerable for at least 3 adsorption-desorption cycles.

This research has been described in more detail in the following publication, published during the project:

Sudhararasu, E., Tuomikoski, S., Runtti, H., Hu, T., Varila, T., Kangas, T., Lassi, U. Alkali-Activated Adsorbents from Slags: Column Adsorption and Regeneration Study for Nickel(II) Removal. ChemEngineering, 5(13) (2021). DOI: 10.3390/chemengineering5010013.

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2.3 Fly ash

Fly ash (FA) is a prominent material used as an alkaline-activation binder. FAs comprise abundant yet complex materials, the composition of which is affected by co-incinerated material. During the combustion process, slag, bottom and fly ash are generated from

flue gas separation and air pollution control processes. Fly ash composition varies widely, as it is derived from various primary sources, including municipal waste/sludge co-incineration, various coal types, and subspecialized byproducts from industrial treatment plants (paper, forestry industry, or agriculture). The combustion and cooling processes impact the characteristics of FA (particle size, shape, surface area, uniformity, etc.), as well as its composition and impurity inclusions.

The combustion technology itself has an influence on the amount of FA produced. In a conventional grate firing process, FA comprises about 10–40% of total ash, while in fluidized bed boilers, FA can make up 80–90% of total ash. Considering the increasing number of fluidized bed boilers compared to grate boilers in the energy industry, larger amounts of generated fly ash can be anticipated in the future [1]. The Circhubs platform [2] reported the average annual amount of ash and slag generated in Finland as 378 Kt in 2017, about 75 Kt of which may be attributed to FAs [3]. According to Official Statistics of Finland [5], 116 Mt of industrial waste were generated in Finland in 2019. Excluding mineral waste (86.7 Mt), slightly less than 56% (5.7 Mt) of the waste gathered was recovered as heat and energy. More than half of the energy was obtained from 2.5 Mt of wood waste. Amount of waste generated and waste treatment methods have not undergone drastic changes since 2017, and average annual amount of FA in Finland can be estimated as 75–80 Kt.

Direct application or further recycling of FA depends on co-combustion materials. Bio-based ashes after pretreatment (self-hardening, granulation, or pelletizing) could be used in forestry or agriculture [6]. As ash from the industrial or the district heating sector is available for large-scale recycling, it is primarily used in different types of earth construction or production of construction materials. The recycling rate varied between 64–87% in different municipalities during the past 5 years. The price of FA as raw material in a local market includes pretreatment, transportation, and logistics and is currently nearing 70–130 €/t.

As with BFS, geopolymers produced from FA in the WaterPro project took three forms: powder, granules, and inert substrate-supported. Powder forms were investigated in order to characterize the resulting compositions, calculate maximal adsorption capacities, and find an optimal recipe for up-scale production (semi-industrial granulation). Bio-based FA (class F, according to ASTM C 618 specification) obtained from a Finnish district heating plant was used in all experiments. This FA was chosen due to the lower content of heavy metals compared with FA classes E and D, as well as for its higher content of calcium (59.2% CaO), a possible catching ion for phosphate. CaO content was 15.6% and 25.1% in FA classes E and D, respectively [4].

An adsorptive media, the geopolymer adsorbent Fly ash F (FAF-GP), was used for phosphate removal from diluted aqueous solution. To evaluate phosphate removal efficiency of FAF-GP, batch and column adsorption experiments were performed. The adsorption process was relatively fast for FAF-GP, with equilibrium reached at 1.5h contact time (Fig. 7), while for BFS-GP, maximum removal rate was achieved at 5h. Adsorption capacity of FAF-GP for diluted solutions at a phosphate concentration of 10 mg/L was 24.5 mg PO_4 /g with a removal rate of 96.9% (adsorbent dose 2 g/L, Fig. 8). However, maximum adsorption capacity could be as high as 256 mg PO_4/g under saturation conditions. Moreover, phosphate adsorption on the adsorbent surface was observed over multiple cycles. After the first adsorption cycle, the same portion of adsorbent was able to remove almost an equal amount of phosphate for another three cycles. This phenomenon requires further research for a correct interpretation. This behavior is especially beneficial for phosphate removal from diluted solutions and was used during the piloting of a passive filtration system.
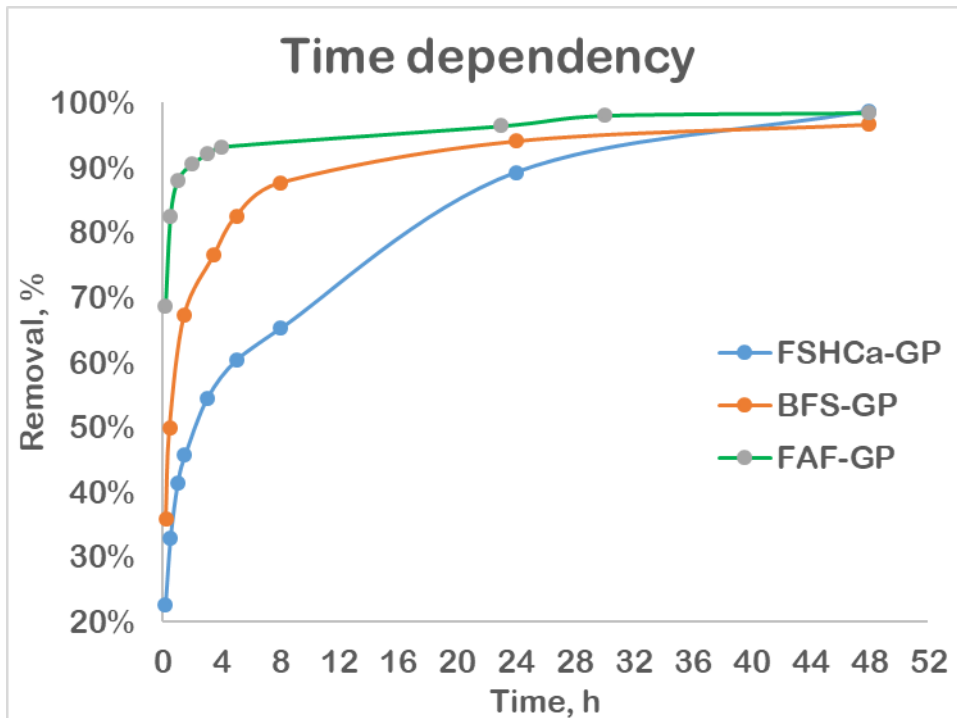
Figure 7   The influence of contact time on phosphate removal rates by proposed adsorbents.
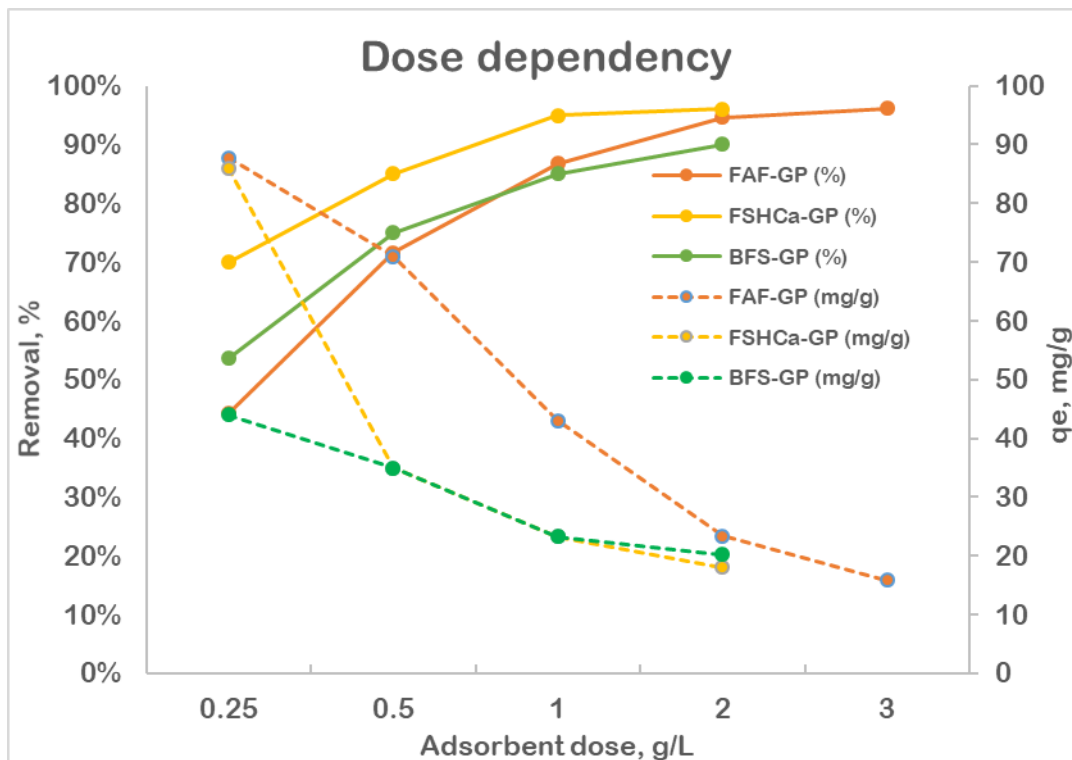

Figure 8   The influence of adsorbent dose on phosphate removal rates and equilibrium adsorption capacity (qe) by proposed adsorbents.

Fiber sludge with high calcium content (77.8% CaO) was another waste material chosen to prepare the geopolymers (FSHCa-GP) for phosphate removal to compare its properties with FAF-GP and BFS-GP. However, equilibrium and thus maximal removal rate with FSHCa-GP took much longer to achieve than with FAF-GP and BFS-GP. However,

removal rate with FSHCa-GP at a phosphate concentration of 10 mg/L was 98% at an adsorbent dose of 1 g/L, while maximal removal rate with FAF-GP or BFS-GP at the same adsorbent dosage did not exceed 87%.

Effective phosphate removal was demonstrated during laboratory-scale fixed-bed continuous column experiments with proposed geopolymers produced in granulated form. To evaluate the influence of granule size, flow rate, and adsorptive layer height on operational conditions, tap water spiked with 5 mg/L phosphate-ion was pumped through an adsorption tower filled with adsorptive material. The comparison of adsorbent properties was based on bed volume required for 85% removal of phosphate from the solution. Generally, retention time should be as long as possible, taking into consideration the low kinetic rates for these adsorbents. However, considering possible industrial applications, two reasonable flow rates were selected and tested.

Removal rate of the phosphate varied substantially between 0.5 L/h and 1 L/h. At a higher flow rate, a portion of unreacted phosphate could be observed from the beginning of adsorption, although the removal rate remained constant for a long time. At a lower flow rate, all three adsorbents demonstrated a 95% removal rate (less than 0.1 mg/L as P) from the beginning of the adsorption process. The effect of granule size was investigated for granules 1–2 mm and 2–4 mm (Fig. 9). A smaller granule size would substantially increase hydraulic resistance, causing a higher energy demand and cost of required equipment. A bigger granule size is unreasonable for use due to a drastic decrease of the surface area, which is responsible for phosphate removal. Smaller granule size lasted up to 1.5, 2.4, and 1.3 times longer before the established limit (removal rate 95%) was reached than larger granules for BFS-GP, FSHCa-GP, and FAF-GP, respectively. The higher adsorption layers removed higher amounts of phosphate, as expected. The 15-cm layer was able to remove 1.5, 1.8, and 1.3 times more phosphate than the 10-cm layer (Fig. 10) for BFS-GP, FSHCa-GP, and FAF-GP, respectively.
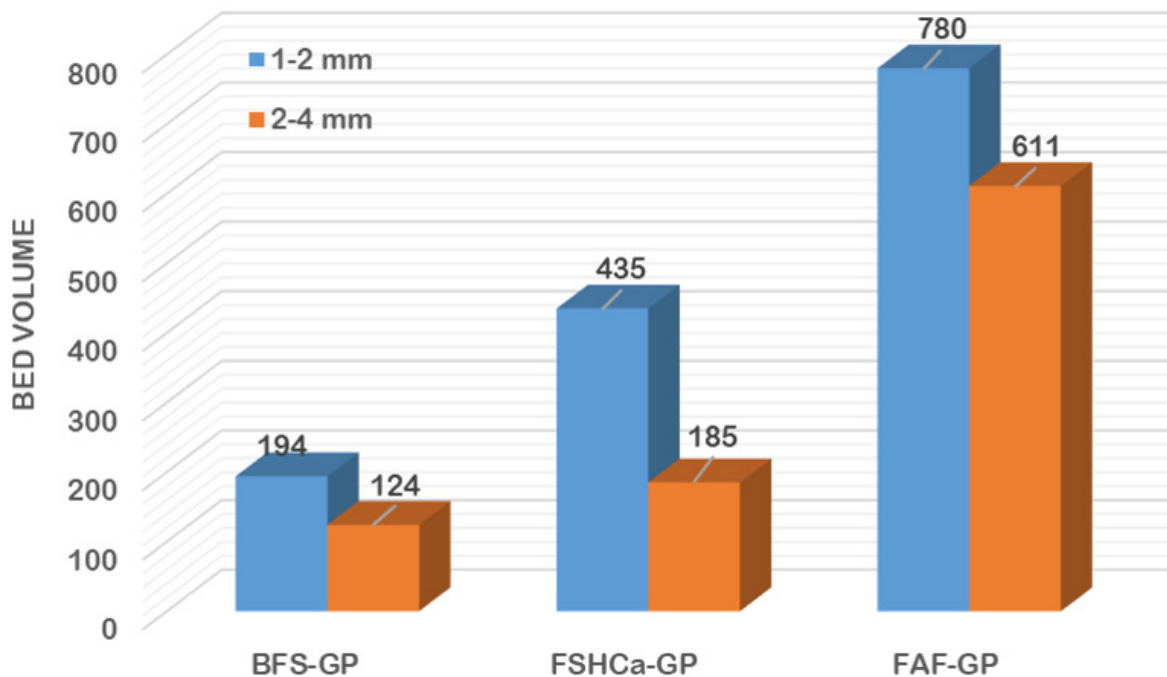

Figure 9   The effect of adsorbent granule size on removal ability of proposed adsorbents during continuous adsorption experiment.
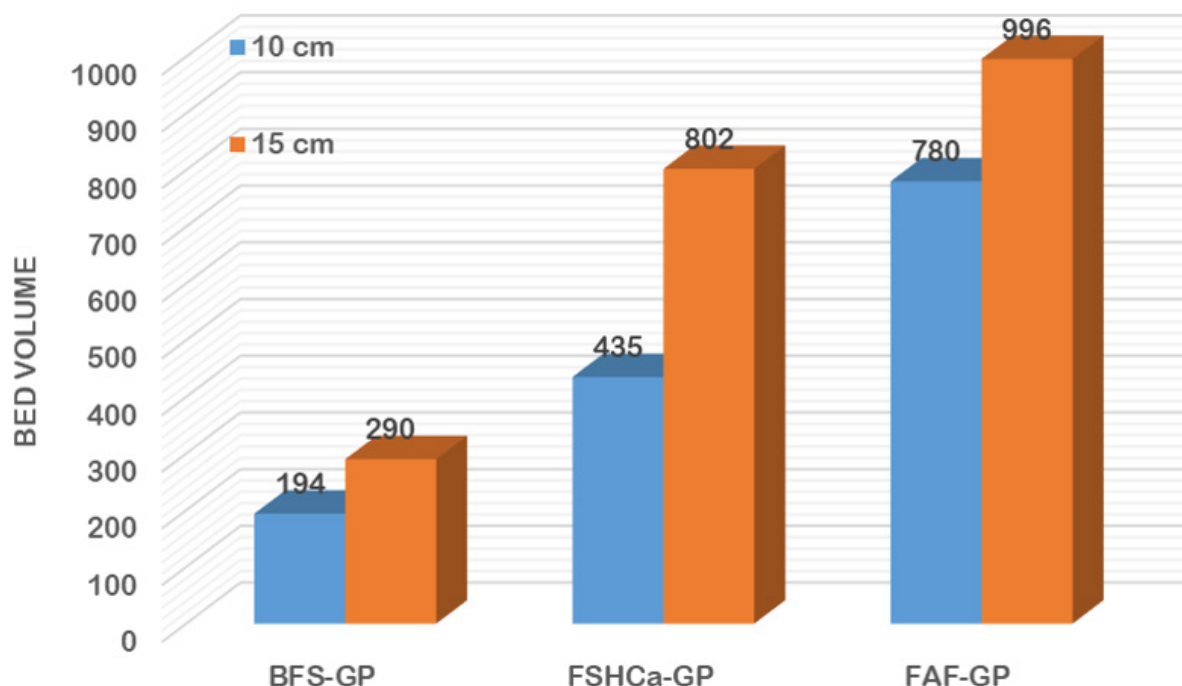
Effect of adsorbent layer height

Figure 10   The effect of adsorbent layer on removal ability of proposed adsorbents during continuous adsorption experiment.

Two field-collected samples (run-off water and lake water) were treated in bench-scale application with powder form. In both water samples, removal rates of at least 95% were observed. A biogas leachate was used to demonstrate phosphate removal from complex matrice by new adsorbent. . At a 10 g/L adsorbent dose, 47% of phosphate could be removed. (Table IV).

Table IV   Treatment of contaminated environmental and industrial samples by FAF-GP.

Sample	Initial C(P), mg/L	Conditions	Removal, %
Run-off water	1.2	pH 6.3, 1 g/L, 2 h	98
River water	0.3	pH 7.01, 1 g/L, 2 h	96
Biogas leachate	56	pH 4.3, 10 g/L, 5 h	47

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2.4 Jarosite

Jarosite is a sidestream of the zinc manufacturing industry. It is obtained during the extraction of zinc from its sulfide ore through a hydrometallurgical process, which consists of three main stages: roasting, leaching and purification, and electrolysis. Jarosite is obtained at the second stage, leaching and purification. The zinc ore concentrate is roasted at $900\,°C$ and is afterwards subjected to leaching with the help of hot acid, where jarosite is formed as a waste material [1], [2]. Jarosite can be expressed by the formula $MFe_3(SO_4)_2(OH)_6$, where M is a cation such as Na^+, K^+, Ag^+, Pb^{2+}, or NH_4^+, among others [3]. Hydrometallurgical sidestreams, including jarosite, are dangerous for both the environment and the health of humans and animals due to the elements in their composition [4]. Thus, a sustainable alternative is needed to use them safely and effectively. Jarosite used in this project was obtained from Norilsk Nickel.

During this project, the target was to prepare a stable geopolymer in which jarosite had been utilized as raw material. In practice, several geopolymers were synthesized using metakaolin, fly ash, and blast furnace slag as raw material sources of aluminosilicates. Jarosite was also included to analyze how it works in the geopolymerization process. Preliminary results showed that it is possible to produce chemically and physically stable geopolymers using jarosite as a raw material. Produced geopolymers were tested for the removal of ammonium and metals, and promising removal efficiency results were achieved. A stabilization study was also performed for the used, zinc-loaded jarosite geopolymer. Either 25% or 50% of metakaolin was replaced with the zinc-loaded jarosite geopolymer, and a mixture of sodium silicate and NaOH was used as the activator. Leaching of Zn was studied using water extraction. However, the leaching of Zn was not reduced after stabilization.

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2.5 Analcime

Analcime from the mining industry was studied for the uptake of NH_4^+ from synthetic wastewater and real agricultural slurry via adsorption. Analcime is a sidestream from lithium carbonate production and was received from a Finnish mining company. Analcime was pre-treated before use via drying in a hot air oven for 24–48 h at 105 ˚C. The goal was that after use, analcime could be utilized as a soil enhancer. Different adsorbent dosages and initial concentrations of NH_4^+ were used. Effects of adsorption time and temperature were also studied.

Effect of initial NH_4^+ concentration was studied using an analcime dose of 200 g/L with 4 h contact time at room temperature. Results showed that highest removal percentage (62.4%) was achieved when the initial NH_4^+ concentration was 150 mg/L. The lowest removal percentages (33.1–37.4%) were achieved when the initial concentration was 800–1000 mg/L. Sorption capacity (q) increased with increasing NH_4^+ concentration from 0.04 mg/g (25 mg/L) to 1.4 mg/g (1000 mg/L). Results from kinetic studies showed that removal percentage was around 40% during the first 20 minutes and settled there until 180 minutes (sorbent dose: 20 g/L, initial NH_4^+ concentration: 100 mg/L, room temperature). When analcime dose was increased, NH_4^+ uptake improved, and when initial NH_4^+ concentration increased above 150 mg/L, uptake decreased. Temperature had no clear impact on NH_4^+ removal when temperature increased up to 90 °C. However, when the temperature was 120 °C, NH_4^+ uptake increased considerably. In this case, NH_4^+ concentration in analcime was 2.85 %; this can be explained by the formation of ammonioleucite, which is identical with the $(SiAl)O_4$ framework of analcime, but NH_4^+ takes the place of crystal water in the analcime structure. The reason for this is that at high temperatures (above 100 °C), the inside diameter of the tunnel size in analcime is increased because of lattice vibration and an NH_4^+ ion can pass through the tunnel and replace the water molecule. However, at room temperature, the NH_4^+ is captured in the ammonioleucite structure and cannot be released for soil enhancer use [1]. NH_4^+ uptake was also tested with real agricultural slurry (initial NH_4^+ concentration: 176 mg/L), but NH_4^+ removal percentages were small. The best removal percentage, around 30%, was achieved with a sorbent dose of 500 g/L at room temperature. Sorption capacity was below 3 mg/g and it decreased as the sorbent dose increased. The release of NH_4^+ from analcime was studied using a 10-stage shaking test (distilled water (stages 1–2); 0.1 M NaCl solution (stages 3–10)). Release of NH_4^+ was around 315 mg/kg in the first stage, which was then reduced to less than 75 mg/kg in the second stage. With NaCl, release of NH_4^+ was at first 1200 mg/kg, decreased constantly in stages 4–7, and then settled around 70–100 mg/kg in stages 8–10. Results confirm that analcime releases NH_4^+ slowly over a long period of time. Given this, analcime could be mixed directly in soil, together with fertilizer containing NH_4^+, to reduce ammonia losses.

Hybrid experiments were also performed during the project. Industrial wastewater was first treated with precipitation, followed by adsorption. The target was to remove NH_4^+. Used adsorbents were analcime, jarosite, and slag-based geopolymers. Preliminary experiments showed that adsorption capacities were 2–4 mg/g and removal percentages 25–51% with analcime-based geopolymers when initial ammonium nitrogen concentration was ~40 mg/L and adsorbent dosage 5 g/L (initial pH: 2, shaking time: 2 h). In the case of jarosite and slag-based geopolymers, adsorption capacities were 4.3–6.2 mg/g and removal percentage between 8–12% when initial ammonium nitrogen concentration was ~220 mg/L and adsorbent dosage 5 g/L (initial pH: 4, shaking time: 2 h).

Figure 11 Analcime sample.

This research has been described in more detail in the following conference paper, published during the project:
Pesonen, J., Tuomikoski, S., Näppä, J., Prokkola, H., Hu, T., Lassi, U., Runtti, H., Ammonium uptake over analcime and its soil enhancer potential, 8th International Conference on Sustainable Solid Waste Management, 2021. http://uest.ntua.gr/thessaloniki2021/pdfs/THESSALONIKI_2021_Pesonen_et_al.pdf

2.5.1. Analcime geopolymers

Analcime, obtained from a Finnish mining company, was alkali-activated using five different treatment methods. Adsorbents were produced with silicate and/or NaOH to improve the adsorption properties of analcime. In some cases, metakaolin was used as a blending component. Before adsorption experiments, prepared materials were crushed and sieved to a particle size < 150 μm and washed with deionized water until pH was stable. Batch adsorption experiments were performed at room temperature with a model solution (initial pH adjusted to 2.5). The goal was to evaluate the effect of initial ammonium ion concentration (5–1000 mg/L), adsorbent dosage (1–20 g/L), and contact time (1 min–24 h) on adsorption. When the effect of initial NH_4^+ concentration was studied, results showed that removal percentages and adsorption capacities ranged from 40–75% and 7.2–29.8 mg/g, respectively (initial pH: 2.5, adsorbent dosage: 5 g/L, contact time: 24 h, room temperature). This study showed that analcime geopolymers are more effective for the removal of ammonium nitrogen than non-treated analcime. Prepared analcime geopolymers were also tested for the removal of ammonium nitrogen in column mode.

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2.6 Brucite and hydromagnesite

The naturally occurring, layered double hydroxide mineral brucite (BRU), hydromagnesite (HYD), and a commercial magnesium-rich mineral adsorbent (AQM PalPower M10) were tested for their ability to remove antimony (Sb) from synthetic and real wastewater samples. The BRU, HYD, and M10 were obtained from a Finnish

supplier. BRU and HYD samples were calcined at 500 °C and 700 °C, respectively. Afterwards, samples were washed with deionized water and dried at 105 °C. The M10 was used as received. Batch adsorption experiments were performed and the effects of initial pH (2–10), Sb concentration (5–25 mg/L), adsorbent dosage (0.5–5.0 g/L with synthetic solution and 0.1–15 g/L with mine effluent and textile wastewater), and contact time (1 min–48 h) were all studied. Antimony was removed from synthetic wastewater, mine effluent, and textile wastewater. Antimony (Sb) is a metalloid element existing primarily as Sb(III) or Sb(V) in the environment. Sb is present as soluble hydroxides (e.g., $Sb(OH)_6^-$) but can also form complexes with chloride, fluoride, or bromide [1] in aqueous environments. The aqueous concentration of Sb is < 1 µg/L in uncontaminated natural waters, mg/L in mining effluent, and > 1g/L in geothermal waters [2], [3]. Sb is toxic or even lethal at elevated intake levels and is on the EU's list of critical raw materials (European Commission, 2020; International Agency for Research on Cancer (IARC), 1989; World Health Organization (WHO), 2003). Safe Sb levels in drinking water were set at 5, 6, and 20 µg L−1 by the European Union (EU) (Directive, 1998), the United States Environmental Protection Agency (2009), and the WHO (2011), respectively. The highest removal percentage and adsorption capacity was achieved with BRU (27.6 mg/g). However, these parameters did not differ considerably from HYD (27.0 mg/g) and M10 (21.3 mg/g). Additionally, an efficient performance in the continuous removal of Sb from mine effluent in the column mode was demonstrated. Results also showed that regeneration was more effective under acidic conditions than under alkaline conditions.

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2.7 Sawdust

Lignocellulosic biomass is ubiquitous worldwide and is produced as a waste material (e.g., in sawmills). During the WaterPro project, sawdust was used as a raw material in the production of biomass-based activated carbon to be applied as an adsorbent for metal removal. Carbonization and activation of sawdust were performed in a single-step process by employing a temperature of 800 °C and using steam as a physical activation agent. Single-step production without any cooling steps between carbonization and activation is easier in larger-scale production and can additionally save costs. The adsorption capacity towards cobalt, nickel, and zinc was studied by using activated carbon produced from spruce sawdust and towards zinc by using activated carbon from birch sawdust.

Specific surface area was 860 m^2/g for birch carbon and 1,010 m^2/g for spruce carbon. During adsorption experiments, the effects of pH, initial metal concentration, adsorbent dosage, and adsorption time were studied. For birch carbon, the optimum adsorption conditions for zinc removal were a pH of 4, initial concentration of 75 mg/L, adsorbent dosage of 3 or 5 g/L, and adsorption time of 24 h. The maximum experimental adsorption capacity of zinc for birch carbon was 21.44 mg/g. For spruce carbon, the highest adsorption capacity was obtained by using a pH of 7, adsorbent dosage of 10 g/L, initial metal concentration of 30 mg/L (10 mg/L for each metal), and adsorption time of 24 h. The order of maximum adsorption capacity was zinc > nickel > cobalt. Experimental adsorption capacities when using spruce carbon were 17.2, 6.6, and 4.5 mg/g for zinc, nickel, and cobalt, respectively.

Desorption was achieved in the case of birch carbon by using 0.1 M HCl within one cycle and in the case of spruce carbon by using 0.1 M HCl, HNO_3, and H_2SO_4 within three cycles. All of these regeneration solutions were suitable for regeneration. Adsorption capacity remained the same across three adsorption-desorption cycles. It was noted during this project that regenerable activated carbon towards metals from lignocellulosic biomass was produced at laboratory-scale by using steam as a physical activating agent. Materials are suitable for mono- and multi-metal solutions with large flow and low initial metal concentrations. No harmful chemicals were used during the production of the carbon, and regeneration could also be performed using diluted acid solutions.

This research is described in more detail in the following two publications, published during the project:

Tuomikoski, S., Kupila, R., Romar, H., Bergna, D., Kangas, T., Runtti, H., Lassi, U. Zinc Adsorption by Activated Carbon Prepared from Lignocellulosic Waste Biomass, Applied sciences, 9 (21) (2019), 4583. DOI: 10.3390/app9214583.

Tuomikoski, S., Runtti, H., Romar, H., Lassi, U., Kangas, T. Multiple heavy metal removal simultaneously by a biomass-based porous carbon, Water Environ. Res. 93(8) (2021), 1303–1314. DOI: 10.1002/wer.1514.

3   Electrochemical and chemical precipitation

Electrochemical and chemical precipitation for different water types containing nutrients, sulfate, and metals were studied during the WaterPro project. In chemical precipitation, a precipitation agent is added as chemical salt to the solution, while in electrochemical precipitation, precipitating ions are dissolved from metal plates using electricity. Figure 12 presents the basic laboratory-scale electrochemical precipitation system. Precipitation agent creates flocs with impurities that easily settle out from the solution. A notable amount of sludge is formed during precipitation, and there is a growing need to find suitable utilization applications for this sludge. During the WaterPro project, the formed sludge was characterized and potential utilization applications (e.g., as a fertilizer) were studied.
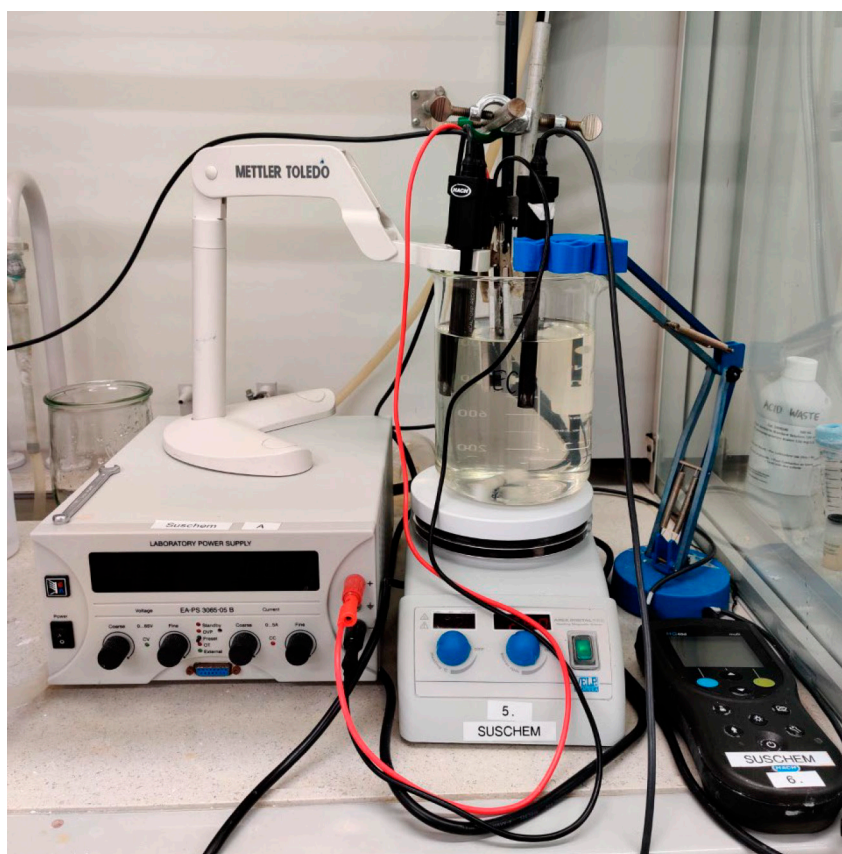

Figure 12   Setup of an electrochemical precipitation experiment.

3.1 Electrochemical precipitation case studies

In the WaterPro project, electrochemical precipitation of nutrients and metals was researched. Using this method, nitrogen and phosphate were precipitated as struvite, metals as hydroxides, and sulfate as gypsum. A survey of the utilization potential of formed sludges was also conducted.

3.1.1 Electrochemical precipitation of nutrients

In the WaterPro project, batch electrocoagulation (BEC) and continuous flow electrocoagulation (CEC) were studied for the precipitation of struvite ($MgNH_4PO_4*6H_2O$), during which nitrogen and phosphorus can be removed simultaneously. Struvite has potential use as a slow-release fertilizer because it contains nutrients, ammonium and phosphate, and magnesium at equal molar concentrations. In this case study, magnesium was dissolved electrochemically in the precipitation of ammonium and phosphate from synthetic and authentic waters from peat bog drainage. In the case of synthetic water, initial ammonium concentration was 200 mg/L, initial phosphate concentration was 1,053 mg/L, and humic acid concentration was 50 mg/L. In the case of authentic water, nutrient concentrations were adjusted to be the same as in synthetic water by using chemical salts to obtain a molar ratio of 1:1:1 for magnesium, ammonium, and phosphate. Results were compared to chemical precipitation (CP), in which MgO was used as a magnesium source. Struvite yield, phosphate and ammonium removal rates, and cost of treatment were compared with batch and continuous flow electrocoagulation and chemical precipitation.

Struvite yield was 1.72 in BEC, 0.61 in CEC, and 1.54 kg/m^3 in CP in the case of synthetic water. As a comparison, the same values for authentic water were 2.55, 3.04, and 2.47 kg/m^3. The costs of production of 1 kg struvite for BEC, CEC, and CP were 0.55, 0.55, and 0.11 €, respectively, for synthetic water and 0.35, 0.22, and 0.07 € for authentic water. Phosphate removal in the case of synthetic water was 93.6, 74.5, and 71.6% in BEC, CEC, and CP, respectively. For authentic water, phosphate removal rates were 89.7, 77.8, and 74.4%. Ammonium removal in the case of synthetic water in BEC, CEC, and CP was 79.4, 51.5, and 62.5%, respectively. For authentic water, rates were 56.1, 64.1, and 60.9%. Efficiency in CEC and BEC are equal in nutrient recovery for synthetic water, although energy efficiency was better in CEC. CP is cheaper than BEC and CEC. Electrochemical magnesium dosage is as effective as the chemical magnesium dosage as MgO for struvite formation.

Instead of electrochemical precipitation, the more traditional method for precipitating struvite is chemical precipitation with Mg-salts. Commercial Mg-salts are typically used for this purpose and represent the largest cost associated with struvite precipitation. Therefore, the industrial sidestreams, dolomite and fly ash, were studied during this project to provide a cheaper Mg source for struvite precipitation. This is presented in more detail in Section 3.5.

This research has been described in more detail in the following publication, published during the project:

Rajaniemi, K., Hu, T., Nurmesniemi, E.-T., Tuomikoski, S., Lassi, U. Phosphate and Ammonium Removal from Water through Electrochemical and Chemical Precipitation of Struvite, Processes 9(150) (2021). DOI: 10.3390/pr9010150.

3.1.2 Electrochemical precipitation of metals

Sulfate and metals can be precipitated chemically using lime. Metals precipitate as hydroxides, and part of sulfate precipitates as gypsum. However, the precipitation can be improved by using an aluminum addition when sulfate precipitates as an ettringite $(Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O)$. Solubility of ettringite is lower compared with precipitate formed during lime precipitation. In addition, ettringite can be further used as an adsorbent in arsenic removal.

During this project, electrochemical ettringite precipitation was used for precipitation of metals (iron, copper, zinc, and nickel). Based on the XRD results, formed precipitate was ettrigite, which has the potential to adsorb or co-precipitate metals. In addition, precipitate included minor amounts of other compounds like $CuFeS_2$. Removal rate was > 99% for iron, copper, and nickel and > 93–99% for zinc when initial metal concentrations were 50 mg/L. The pH was over 12 during the experiments, partially explaining the good removal rates.

During the WaterPro project, sidestream from the aluminum industry was used as an aluminum source in ettringite precipitation. Aluminum was dissolved successfully during experiments, but notable amounts of dissolved sulphate from the sidestream were also observed. Therefore, experiments were not continued. Electrochemical ettringite precipitation was performed by dissolving aluminum from metal plates electrochemically.

3.1.3 Utilization of sludge formed in electrochemical precipitation

Electrochemical precipitation has been widely studied for several impurities, including in the WaterPro project, and several case studies exist in the literature. Electrochemical precipitation processes generate sludge that is typically considered waste. Sludge handling also increases operational costs caused by sludge disposal. Depending on the electrodes used and the properties of purified water, sludge can contain valuables, such as metals and/or nutrients. Therefore, based on the principles of circular economy, it would be beneficial to identify suitable utilization applications for sludge formed during electrochemical precipitation.

During the WaterPro project, a literature review concerning sludge utilization potential was conducted. Generally, electrochemical precipitation produces less sludge compared to conventional chemical precipitation [1], [2]. Ilhan et al., for example, found that the volume of electrochemical precipitation sludge is less than 2% [3]. Sludge typically contains metal oxides, metal hydroxides, and metal oxyhydroxides. Flocs formed during electrochemical precipitation are larger compared to chemical precipitation sludge and contain less water. Sludge typically settles easily and is also stable [1], [4]. Sludge composition (e.g., crystal structure) depends on anode and cathode material, as well as on chemical compounds that have been precipitated.

Utilization potential of sludge must be considered on a case-by-case basis. Nutrient-containing sludge, particularly struvite, may be used as fertilizer. Struvite, also known as magnesium ammonium phosphate, contains nitrogen and phosphorous, valuable elements for fertilization [5]. Electrochemical precipitation sludge can also be used as an adsorbent or as a catalyst. Different sludges have been used for the removal of dyes [6], phosphate [7], and boron [8], [9]. Sludge with high iron concentration is suitable as catalyst material; photocatalysis can also be performed using this kind of sludge [10]. Iron-containing sludge has further potential for use as a pigment [11] or as construction material.

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3.2   Chemical precipitation case studies

Chemical precipitation was studied during the WaterPro project by conducting case studies. Calcium-rich industrial sidestreams were compared to lime as precipitants in the phosphorous removal process. In addition, removal of phosphorous as struvite via dolomite and fly ash was studied. One possible solution for utilizing struvite is to use it in fertilizers. In this project, the potential of chemically precipitated struvite as fertilizer was studied.

3.2.1 Chemical precipitation of phosphate

Phosphorus-rich waters were precipitated using calcium-rich precipitation chemicals (lime ($Ca(OH)_2$) and five calcium-rich industrial sidestreams) with the aim of precipitating hydroxylapatite, as presented in Figure 13. Model solutions and phosphorus acid plant process water were used. Sidestreams included lime 48–87%. Results demonstrated that hydroxylapatite can be precipitated from model solutions by using industrial sidestreams; furthermore, up to 72% phosphate removal was obtained by using a sidestream that was partially composed of burnt lime that had been stored outdoors. Up to 84% phosphate removal was obtained from phosphorus acid plant process water using the same sidestream. Similar results were obtained by using a sidestream that was partially composed of burnt lime that had been stored in a silo. Formed precipitates were 86% hydroxylapatite when using the model solution and 67% when using the phosphorus acid plant process water. Hydroxylapatite has potential for use as fertilizer.
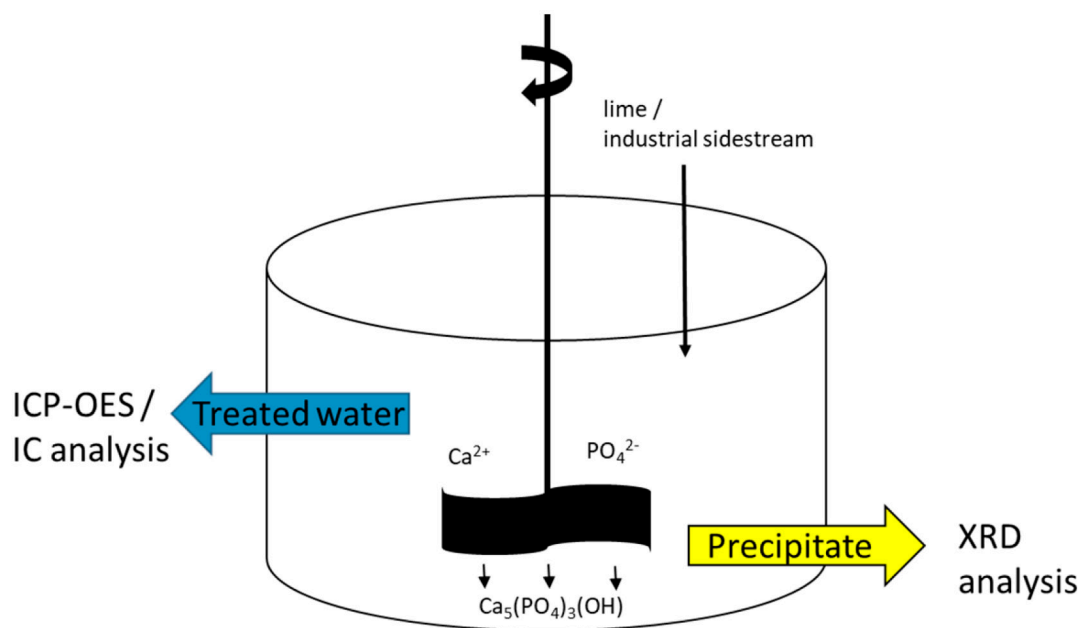

Figure 13   Schematic diagram of the precipitation experiments.

This research procedure has been described in more detail in the following conference presentation:
Nurmesniemi, E.-T., Tuomikoski, S., Pesonen, J., Huhta, M. and Lassi, U. (2020) Phosphate removal and recovery from wastewater with industrial sidestreams, IWA Nutrient removal and recovery conference, Espoo September 2020.

3.2.2 Dolomite and fly ash as chemical precipitants of phosphate

Commercial dolomite $CaMg(CO_3)_2$ from a Finnish lime quarry and fly ash from a Finnish power plant were used to precipitate ammonium-nitrogen and phosphate-phosphorus as struvite from model solutions and from authentic agricultural sludge. The dolomite was moist dolomite left over from the process where dolomite is sieved to desired size fractions. Demand for this type of dolomite is poor. Calcination of dolomite at different temperatures (650 °C, 750 °C, and 950 °C) was studied to enhance the solubility of magnesium. Since CaO easily precipitates phosphates as hydroxyapatite, lower CaO

concentrations favor struvite formation. For calcination, 750 °C was found to be the most optimal temperature since $MgCO_3$ was mostly decomposed to MgO, whereas $CaCO_3$ was still primarily carbonate. Up to 60% phosphate removal from the model solutions and 70% phosphate removal from the agricultural sludge was obtained after the dolomite was calcined at 750 °C. Precipitates were a mixture of struvite and $CaCO_3$.

The other possible route studied was to treat dolomite with sulfuric acid. In this case, calcium reacts with sulphate to form gypsum, which has low solubility and can be separated from solution by filtration. Magnesium sulphate is highly soluble and the remaining $MgSO_4$ solution can be used as a precipitation chemical. This treatment was also performed for fly ash samples. Over 90% phosphate removal was obtained with $MgSO_4$ solutions prepared from dolomite and over 80% removal with $MgSO_4$ solutions prepared from fly ash. In all cases, struvite precipitates exhibited high purity. Raw material, $MgSO_4$ solution and formed precipitate is presented in Figure 14. Experimental set-up for chemical precipitation is presented in Figure 15.
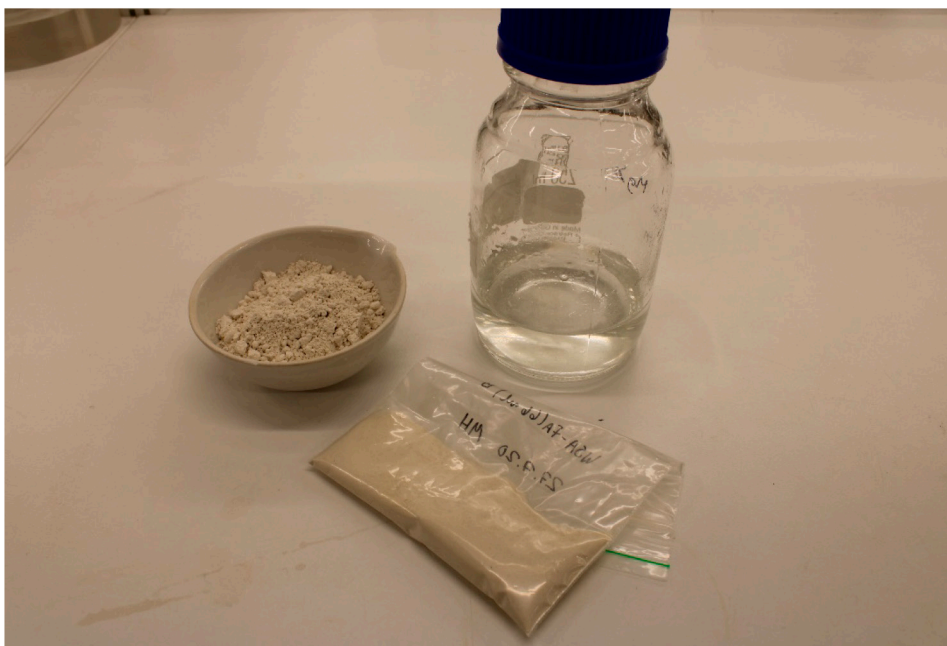

Figure 14   Clockwise from top left: untreated dolomite, $MgSO_4$ solution, and struvite precipitate.

Figure 15   The equipment used in the precipitation experiments. Precipitation reactor consists of a curved blade connected to a rotor, a 2-L decanter glass equipped with stators, and a pH meter.

This research is described in more detail in the following publications:

Pesonen, J., Sauvola, E., Hu, T., Tuomikoski, S. Use of side stream-based MgSO4 as a chemical precipitant in the simultaneous removal of nitrogen and phosphorus from wastewaters. Desalination and water treatment, 194 (2020), 389-395. DOI: 10.5004/dwt.2020.26037.

Pesonen, J., Myllymäki, P., Tuomikoski, S., Vervecken, G., Hu, T., Prokkola, H., Tynjälä, P., Lassi, U. Use of calcined dolomite as chemical precipitant in the simultaneous removal of ammonium and phosphate from synthetic wastewater and from agricultural sludge, ChemEngineering, 3(2) (2019), 40. DOI: 10.3390/chemengineering3020040.

3.2.3 Utilization of struvite as fertilizer

Struvite is a potential fertilizer that is included in the revised fertilizer legislation of the European Union [1]. Struvite has low water solubility and is regarded as a slow-release fertilizer that could reduce the eutrophication of waterways caused by excess use of water-soluble fertilizers [2], [3]. In this project, struvite formed in chemical precipitation was granulated with fly ash. In the granulation process, 40 g of fly ash was mixed with 10 g of struvite in an Eirich EL-1 laboratory mixer and 20 g of water was slowly added to the mixture. The mixer was stopped after an average granule size of around 5 mm

was achieved. Concentrations of nutrients and harmful elements in the granules were analyzed via nitric acid extraction. They are presented in Table V, along with the limit values of Finnish fertilizer degree [4]. Harmful element concentrations were below the Finnish limit values for both field and forest fertilizers and concentrations of nutrients were above the minimum limit values of Ca, P, and K. Liming capacity of the granules was 23.7% Ca, whereas the limit value for field fertilizers is ≥ 10% Ca. Therefore, these granules could be suitable for fertilizer use. The addition of struvite caused both P and Mg concentrations to double compared to using solely fly ash. A sequential leaching test was also performed for the struvite after electrochemical precipitation and showed that leaching of harmful elements was extremely low.

Table V Concentrations of nutrients and harmful elements of both fly ash (FA) and granules (GR) and limit values of Finnish fertilizer degree [4]. All concentrations are in mg/kg.

	Ca	K	P	Mg	As	Cd	Cr	Cu	Ni	Pb	Zn
FA	103000	7950	9920	19000	25	1.9	69	87	51	31	284
GR	89900	6075	21945	35724	21	1.1	70	76	65	35	240
Field / Forest	- / ≥ 60000	/ K + P ≥ 20000			25 / 40	1.5 / 25	300	600 / 700	100 / 150	100 / 150	1500 / 4500

References

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4 Small-scale demonstration and pilot case studies on geopolymer processes

Nutrient recovery from urban and industrial wastestreams is an emerging trend [1]. An increasing number of proposed technologies have been demonstrated recently not at laboratory scale but rather as small-scale pilot experiments or pre-industrial demonstrations. Moreover, although a wide variety of layouts for phosphorous recovery are presented in the literature [1], only fragmented or small-scale demonstrations have been reported for nitrogen [2]. Widely, only the removal (**not recovery**) of ammonium nitrogen by deaerating, aerobic treatment, or the ANAMMOX process is currently applied at municipal and industrial sites.

4.1 Small-scale demonstration of ammonium removal process

A laboratory-scale demonstration setup used for ammonium recovery from wastewaters is shown in Figure 16. The setup consisted of an adsorption/desorption unit, a storage tank for regeneration solution, an air-stripping tower, and a scrubbing unit.
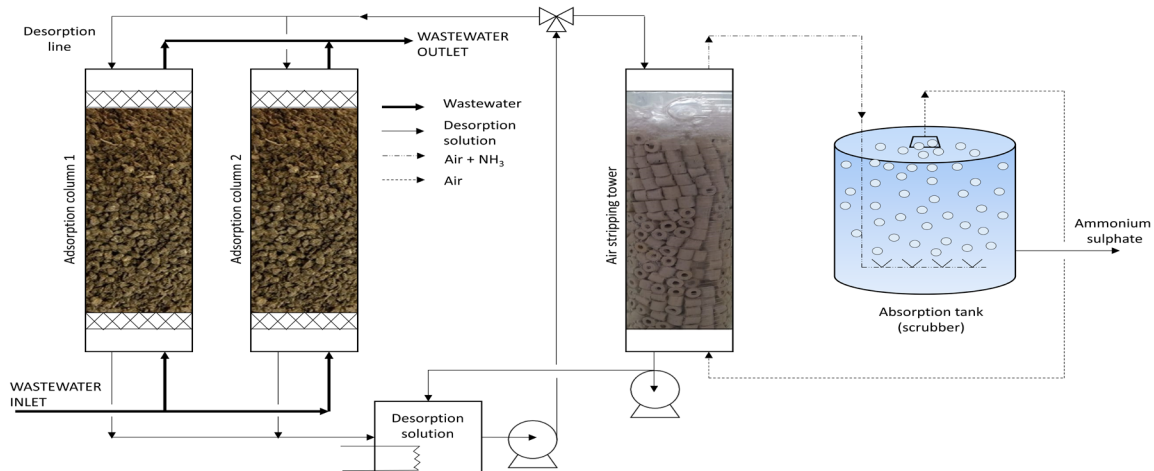

Figure 16   Stripping and scrubbing unit, schematic diagram.

The air-stripping block consisted of a vertical acrylate stripping column (diameter 11 cm, height 35 cm) jacketed by a temperature-isolating material to minimize possible heat loss. The tower was filled with Raschig rings (6 mm, packing factor 1600) and empty bed volume was 0.5 L. An air compressor provided air to the system via gas flow meter at a range of 1 to 6 L/min. A gas distributor was installed to ensure sufficient interfacial contact. In addition, a demister was installed at the top of the stripping column to prevent foam from entering the controlling valve or the absorption tank. Air was

supplied through packing material openings at the bottom of the tower as the ammonia-laden regeneration solution was pumped to the top of the packed tower from a storage tank via peristaltic pump. The purified solution was pumped out from the bottom of the tower via peristaltic pump back to the storage tank. The solution in the storage tank was preheated to the desired temperature using a hot plate (Fig. 17). Thermosensors were installed to control temperature in the liquid and gas phases. The sensors were connected to a temperature-controlling unit to track temperature changes and pre-set designated temperatures.
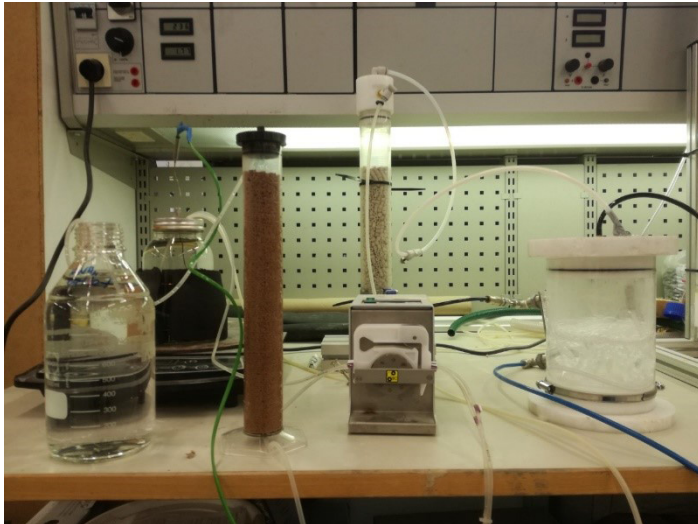

Figure 17   Stripping and scrubbing columns packed with Raschig rings.

The experiments were conducted under a variety of operational conditions, including changes in pH, composition of liquid phase, liquid flow rate, airflow rate, and temperatures. The air-stripping tower was loaded with a sample preheated to the designated temperatures (25, 30, 35, 40, and 45 °C). Prior to sample loading, the sample was adjusted to different pH values (10.5, 11, and 12) using solid NaOH. Three prescribed air flow rates were set at 1, 4, and 6 L/min. The stripped ammonia was absorbed by 500 mL of sulfuric acid (10%).

To remove up to 91% of ammonium from the regeneration solution, a working temperature of 40 °C was used, while air flow rates were maintained at the maximum available level. Treated solutions with lower pH required a longer residence time in the stripping tower to reach 90% of ammonium stripping from the regenerant. The regenerant was used five times for ammonium desorption from the adsorption unit. While the regeneration ability of the regenerant was not substantially decreased, the adsorption capacity of the adsorbent declined gradually. This could be attributed to competing ions in the regenerant.

The laboratory-scale demonstration using the transmembrane chemical absorption (TMCA) technique was carried out following air-stripping experiments to compare the feasibility of both approaches.

TMCA by a membrane contactor is a unique separation process that is transitioning from research and pilot phases to field installations. A recently published study [4] presents ammonium recovery from waters with high ammonium content (> 400 mg/L). For the first time, laboratory-scale tests demonstrated a recovery scheme of ammonium nitrogen from WWTP effluents (< 40 mg/L).

Consumption of chemicals is the largest expense in a TMCA process [5], since the dissolved ammonium ions must be converted to free ammonia gas by pH adjustment of the feed phase to remove ammonia from a wastewater stream. However, ammoniacal nitrogen, which is preconcentrated by adsorption, could be recovered from WWTP

effluents without pH adjustment of treated streams. Moreover, ammonium recovered in a form of liquid fertilizer could generate revenues to help cover the cost of processing.

The ammonia recovery system consisted of an adsorption/desorption unit, a storage tank for regeneration solution, and a 3M Liqui-Cel® membrane contactor (Fig. 18).

Figure 18   Liqui-Cel membrane unit, heater of inlet water, and a pumping station.

MKGP and FS MKGP adsorbents were used for removal of ammonium nitrogen from municipal wastewater after the biological treatment stage. Liquid phase obtained during adsorbent regeneration was purified in Liqui-Cel® membrane contactor to recover ammonium nitrogen as ammonium sulfate or phosphate. Purified regeneration solution was used repeatedly for further adsorbent regeneration. Five regeneration-purification cycles were conducted to estimate system sustainability and chemical consumption demand.

Operational conditions of the TMCA process, such as shellside and lumenside feed streams, temperature, and pH, were initially adjusted to gain maximal capacity of the setup. One 2.5×8 inch Liqui-Cel® contactor membrane was used to determine the optimal operational conditions that would guarantee high performance at the fastest recovery rate. The following operational conditions were found to be acceptable and economically viable: 100 L/h shellside and 60L/h lumenside feed streams, 40 ^{0}C as a minimum working temperature, and pH ≥ 10. Technical sulfuric or phosphoric acids, up to 5%, were used as a lumenside receiving phase. The concentration of ammonium-content salt in the resulting received phase after five cycles were 17% and 22% for phosphate and sulfate salt, respectively.

4.2 Pilot case study of the supported geopolymers

Supported geopolymer compositions for nutrient removal developed during the project were tested in a small-scale piloting experiment. For the first time, BFS-GP and MKGP were applied for phosphate and ammonium removal from drinking and natural waters in a passive barrier filtration unit. To decrease the production cost of adsorptive media, light expanded clay aggregate, which possesses several unique properties (porosity, non-toxicity, lightness of weight, buoyancy), was used as an inert supportive material (Fig. 19), while blast furnace slag and metakaolin were the primer materials for geopolymerization.
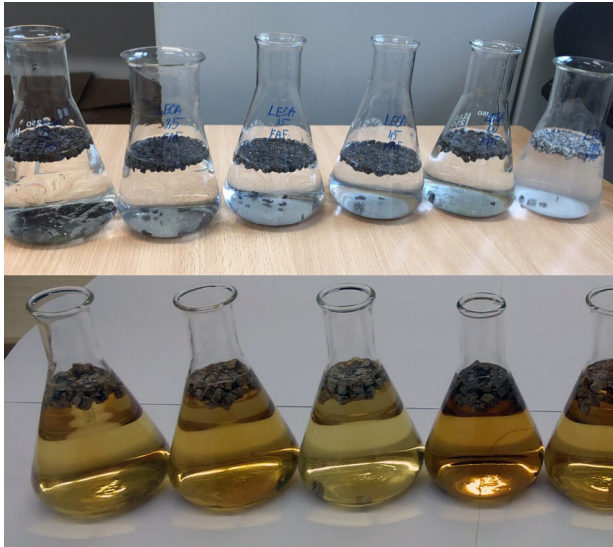

Figure 19   FAF-GP supported on inert materials.

Since LECA-MKGP and LECA-BFS geopolymers exhibited the most applicable service times in lab-scale demonstrations, they were chosen for further field trials on a problematic run-off point in the city of Kajaani. In 2020, during the course of a monitoring campaign in this city (Karelia CBC, PeatStop project), increased nutrient release into a city lake was observed (Fig. 20a). The concentration of phosphate was as high as 0.1 mg P/L, whereas the highest ammonium concentration found was 1.2 mg N/L.

Environmentally friendly and economically favorable GP-composites complying with the requirements of the circular economy concept were used as filling materials for a passive barrier filtration system (PBS) installed in a run-off outlet (Fig. 20b) near Kajaani Halli (Kajaani).

Figure 20a and b   Contaminated run-off water outlet.

The PBS was filled with two different types of LECA-GP to remove ammonium and phosphate from runoff water contaminated with nutrients (Fig. 21). The PBS was operated over 10 weeks, from June 2021 to September 2021. The temperature of run-off water ranged from 4.4 to 25.3 °C. The peak of total phosphorous concentration was 0.23 mg/L, while the peak of total nitrogen was 2.5 mg/L.

The supported geopolymers used were LECA-BFS and LECA-MK; 40L of each were placed in separate sections of the PBS (Fig. 22). Inlet and outlet water quality were monitored daily. Cumulative parameters of water quality after the PBS was installed, such as conductivity, TDS, and pH, were in accordance with water quality requirements, did not exceed a pH of 7.6, and had a conductivity of 0.3 mS. Reduction of total P, total N, and COD up to 12–21% was also observed. Removal rate of ammonium depended on its initial inlet concentration. However, after only 10 weeks of the PBS operation, outlet waters contained less than 0.02 mg/L ammonium, resulting in a reduction in ammonia load of more than 90% during the trial period. For phosphate, more than 60% of the inlet amount was removed from more than 100 m^3 (Table VI).

Figure 21   Semi-industrial granulation of MKGP supported on LECA.

Table VI   An example of inlet and outlet water quality during the PBS piloting, August 2021.

Parameter	before PBS	after PBS
Phosphate-ion, mg/L	0.042	0.01
P total, mg/L as PO4	0.11	0.03
NH_4-N, mg/L	0.18	0.01
N total, mg/L	1.5	1.2
COD, mg/L	17	11
pH	7.51	7.54
Cond, µS	210	259
TDS, mg/L	100	123

Figure 22   The field experiment of a passive barrier filtration unit.

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5 Conclusions

The WaterPro project aimed to develop water purification materials from industrial sidestreams and wastestreams. Available material streams from Finnish industries were identified and their potential as water purification material was studied. Both adsorption and precipitation methods were used to recover nutrients and metals from water.

Materials modified for adsorption experiments included metakaolin, blast furnace slag, ladle slag, Linz-Donawitz converter slag, fly ash, jarosite, analcime, brucite, hydromagnesite, and sawdust. It was noted that fiber sludge metakaolin-based geopolymers had better removal rates of ammonium than commercial zeolite samples or geopolymers made from commercial metakaolin. Removal rate exceeded 80% for wastewater effluents both before and after biological treatment. Removal rates of 96–97% for phosphorous were achieved. Supported metakaolin geopolymers, which can be regenerated using the same regeneration solutions for four times without stripping ammonium between cycles, were chosen for bigger scale experiments. Tests showed that total phosphorous amount in water decreased from 0.11 mg/L to 0.03 mg/L, while ammonium decreased from 0.18 mg/L to 0.01 mg/L. The next step is to study metakaolin geopolymers in on-site pilot-scale experiments using pilot-scale water treatment equipment developed during this project.

Chemical precipitation with precipitation chemicals modified from dolomite, fly ash, and calcium-rich sidestream to remove phosphate was researched. Removal rates of 80–90% were achieved. Adsorption experiments showed better phosphate recovery, with removal rates of up to 97%. Electrochemical precipitation showed the best results for removal of metals. For example, removal rates of over 99% were achieved for iron, copper, and nickel. The sludge formed from precipitation can be utilized in fertilizers, adsorbents, catalysts, and dyes. However, the composition and properties of sludge vary widely among different cases.

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