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Supported Geopolymer Adsorbents for Nutrient Removal from Urban Run-off Waters: Pilot Case Study

Tatiana Samarina[1], Outi Laatikainen[1]
[1]Kajaani University of Applied Sciences
Ketunpolku 1, Kajaani, FI-87101, Finland
tatiana.samarina@kamk.fi
outi.laatikainen@kamk.fi

Abstract
The new adsorbents consist of two layers and constitute a "core-shell" structure were developed and piloted in lab- and field scale. As a core layer, abundant and low-cost LECA was used, while the cover "shell" layer of geopolymers coating inert granules served as functional layer adsorbing pollutants. Two-layer structure allowed obtaining highly porous but light adsorbent granules, which may float in the near surface water layer. The approach substantially decreased a price of treatment technology due to less expenditure on functional materials on the one hand, and possible recycling potential on the other. Composite materials bind contaminants, preventing them from entering to the food chains or carrying them with hydrological flows, and repair of the natural circulation loops of elements. Since the adsorption materials were based on inorganic polymers constituting of a non-toxic aluminosilicate base, further potential applications of the material saturated with nutrients as promising slow-release fertilizers for forestry and agriculture were tested. Piloting of proposed materials in lab- and demo-scale on real matrices was carried out. The cost of adsorbents for water treatment was calculated, and cost-effective water treatment solutions based on supported adsorbents proposed.

***Keywords*:** nutrient removal, run-off water, adsorption, supported geopolymer, passive barrier filtration

1. Introduction

Phosphorus (P) and nitrogen (N) in their fixed forms are essential nutrients in modern agronomy [1]. In 2014, EU placed phosphate rock on the list of critical raw materials. It gave an impulse to create technologies for P recovery from secondary sources and made them attractive options in terms of economic importance and market supply potential [2]–[4]. Nitrogen fixation is attributed for 1% of global energy demand [5] and the production sites are great contributor to the GHG emission worldwide.

An excess of nutrients ends up in inland water bodies due to antrothogenic activities in urban areas and non-sustainable practices in rural ones causing environmental burden. In 2017, approximately 155 tonnes of P and 11090 tonnes of N were discharged into inland waters from municipal wastewater treatment plants in Finland [6]. Nutrient discharge from diffuse sources such as leaching from overfertilized fields, lawns, urban runoffs, peat bogs and ditches could not be estimated reliably. However non-point source pollution has long been considered an important factor affecting the level of eutrophication recently [7]. Ending up in water bodies, nutrients entails eutrophication problems, which, in turn, cause a number of issues from declining recreational potential of water bodies to reduction of biological diversity [8]. To close the nutrient loop, new and innovative ways for more efficient nutrient catching are therefore urgently necessary.

In this work, we present the piloting of low-cost composite adsorbents for nutrient removal from urban run-off waters. Light expanded clay aggregate (LECA) was chosen as a substrate material enabling to bring lightweight and floating properties to new composites, while inorganic polymers (geopolymers, GPs) served as functional responsive materials. In order to find cost-effective solution for non-point source pollution, various industrial by-products were used as precursors for manufacturing of adsorption layers on the adsorbents[9]. Despite the fact that LECA have been investigated previously as adsorptive material for nutrient removal [10], the efficiency and adsorption capacity of the raw material were low. Thus, the modification of the LECA surface with functional materials will enhance the adsorption of nutrients on LECA [11].

2. Materials and methods

2.1. Materials

Phosphoric acid (85%) and sodium hydroxide were purchased from VWR Chemicals. Sodium silicate – ZEOPOL 25 (42-46%, molar ratio $SiO_2:Na_2O$ is 2.4-2.6) was purchased from JV Huber. The kaolinite clay as metakaoline (MK) and blast furnace slag (BFS) was obtained from local providers (Finsement and Aquaminerals) in form of fine powder and used as received. Light expanded clay aggregate (LECA) was purchased from local store and sieved to fractions 1-2, 2-4, and 4-8 mm prior use.

2.2. Geopolymer composite preparation

Supported geopolymers were prepared by mixing of 500 g LECA with alkaline activator in Eirich laboratory mixer (type EL1), and a solid material (BFS or MK) was added at the last stage. Alkaline activator contained 6M or 8M sodium hydroxide for BFS and MK, *resp*., and sodium silicate in a weight ratio of 1.2. The mixtures were allowed to consolidate at ambient temperature for three days, and the granules with supported geopolymers were sieved and washed with deionized water until pH 7.8. Fractions with particle size of 2–4 mm were used for lab and field adsorption experiments.

3. Results and discussion

To decrease a production cost of adsorptive media by geopolymerization, LECA was used as an inert supportive material possessing a number of unique properties (porosity, non-toxicity, light in weight, buoyancy). To find the optimal composition of GPs, a number of parameters such as ratio of liquid and solid part, time of consolidation, steering speed of mixer, and concentration of activator were varied and reported elsewhere [12]. Stability of the prepared compositions was estimated visually and by mass of unattached solid matter (Fig. 1). The granules with maximum amount of attached solid material was chosen for further testing. The maximum content of waste materials used for composite preparation was 20 wt.%. Higher amount of a solid material caused a crumbling of adsorptive layers of GP-composites, and data on nutrient removal were no longer reliable.

Figure 1: LECA-BFS-based (left, *an excluded composition*) and LECA-BFS-based (right, *an optimised composition*) adsorbents with BFS functional layer attached after 24h of agitation._

To estimate the adsorption ability of chosen GP-composites prior real applications, laboratory pretesting and characterization by physical methods were carried out. To this end, natural and run-off waters were spiked with nutrients, and removal rates for each adsorbent was calculated after batch-top adsorption tests. The LECA composites with BFS showed high affinity to phosphate ions, while LECA-MKGP was effective towards ammonium removal. Adsorption capacities at preliminary experiments 8.7 mg P/g for LECA-BFS and 3.7 mg N/g for LECA-MKGP towards ammonium ions (Fig. 2) for run-off matrix. Thus, LECA-BFS and LECA-MKGP were chosen for piloting in the real conditions to treat water from a run-off output near a city lake of Kajaani.

Figure 2: LECA-BFS (left) and LECA-MKGP (right) collected after piloting.

For this purpose, a passive barrier filtration system was constructed and installed. The filter were filled with 40L of LECA-BFS and LECA-MKGP each to remove ammonium and phosphate from runoff water simultaneously (Fig. 3). Environmentally friendly and economically favourable GP-composites, complying with the requirements of circular economy concept, were used as filling materials for a passive barrier filtration system (PBS) installed in run-off outlet near Kajaani Halli (Kajaani). The layout had 5 sections filled with coarse gravel (10-12 cm) for pre-filtration, gravel (2-6 cm), LECA-MKGP, and LECA-BFS. The last slot was reserved for a flow measurements and sampling.

Figure 3: Contaminated run-off water outlet (left) and installation of a passive barrier filtration system (right).

Supported geopolymers, LECA-BFS and LECA-MK, 40L of each were placed in separate sections of the PBS. An inlet and outlet water quality were monitored daily. Cumulative parameters of water quality after the PBS such as conductivity, TDS, and pH were with accordance to water quality requirements and not exceed pH 7.6 with conductivity 0.3 mS. Reduction of total P, total N and COD up to 12-21 % was also observed (Table 1).

Table 1: 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	0.01
NH_4-N, mg/L	0.18	0.03
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

The PBS were operated within 10 weeks and about 100 m^3 of water were treated. An inlet and outlet water quality was monitored daily to prove the safety of the materials loaded for the environment and estimate the efficiency of the treatment. During the piloting period, outlet waters contained less than 0.01 mg/L of ammonium and a reduction of total P up to 60% was also observed.

At the final stage of the work, adsorbents saturated with nutrients in the PBS were used for germination and growth tests. To validate of crop response on soil amendment materials, LECA-based supported geopolymers with adsorbed ammonium and phosphate were mixed with an artificial soil substrate (ISO 11268-1:2012). Barley germination and growth test were conducted under controlled environment for 5 days (Fig. 4). Fresh and dry seedling weights, and length of roots were used to estimate the amendment potential of applied materials. In all tests, the germination rate was >95% (Fig. 4).
The LECA-BFS significantly promoted barley shoots growth and had positive influence on root system of seedlings (Fig. 5). To compare results, blank growth tests were made with artificial soil. The root system length increased by 2.58±0.71 cm when LECA-BFS saturated with phosphates was added to the soil mixture, whilst fresh mass of shoots increased by 1.8±0.5% (n=3, P=0,95). When LECA-MKGP saturated with ammonium was used, substantial reduction in rooting and dry mass of shoots were observed. The reason could be in a wrong concentration of soil amendment material, since ammonium is a highly reactive form of nitrogen. Instead, nitrate form of a soil improver could be used or lower dosage of LECA-MKGP should be applied. The root system length was reduced by 6.3±1.1cm (Fig. 5), though an increase in fresh mass of shoots by 6.1±0.9% was observed compare to blank growth test results (n=3, P=0,95).

Production costs of supported adsorbents were compared to the cost of geopolymers obtained as bulk materials. The final volumes of geopolymers and supported geopolymers produced in a semi-industrial high-stirring granulator would be the same, though mass of products would varying substantially due to the difference in a mass of the support. For LECA-MKGP the approximate price per ton could be 150 EUR (including electricity, chemicals, and water supply, but excluding the labor expenses), while for LECA-BFS the price per ton starts from 110 EUR. For bulk MKGP and BFS geopolymers, 310 EUR/t and 150 EUR/t would be the prices for the optimized compositions.

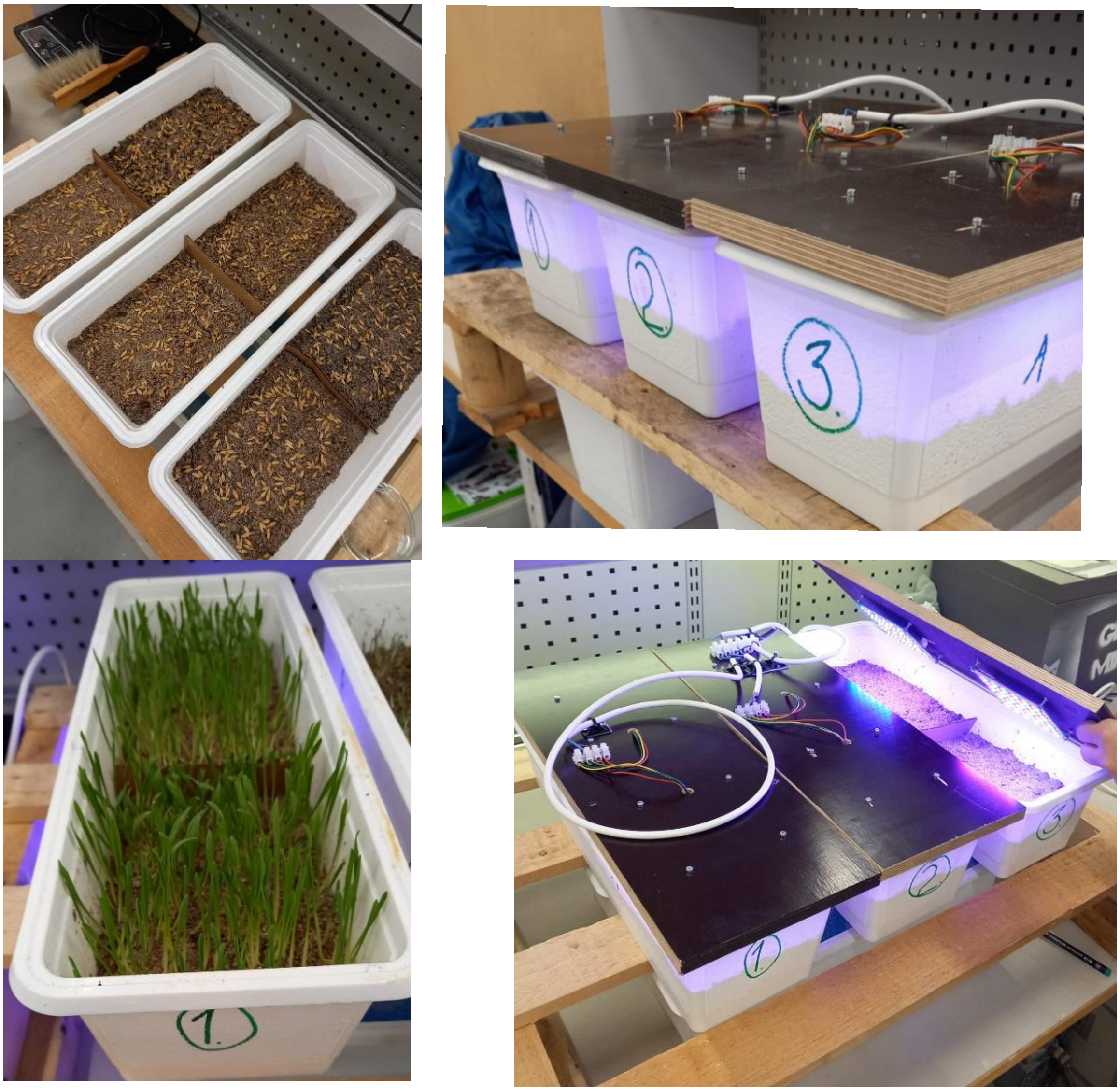

Figure 4: Growth modules with controlled conditions for germination and growth tests.
The germination test layout.

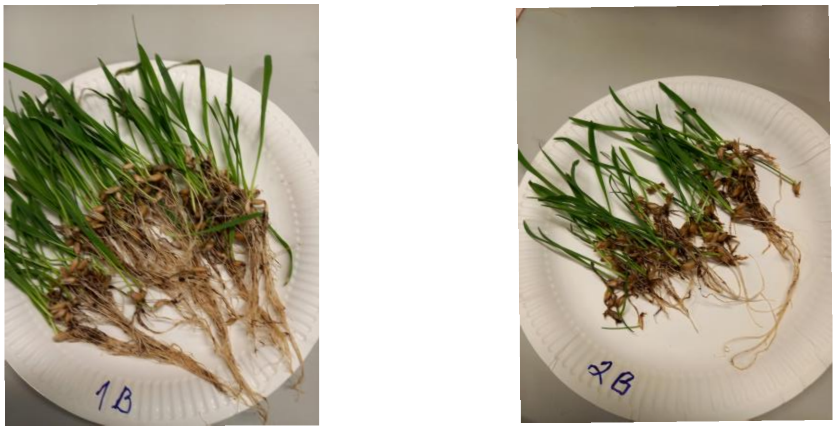

Figure 5: Barley shoots after 5 days of growing: artificial soil with LECA-BFS (1B) and artificial soil with LECA-MKGP (2B).

4. Conclusion

An innovative and simple way to produce new supported geopolymer adsorbents were demonstrated. It was found that LECA-BFS and LECA-MKGP are the best options for nutrient removal among all developed materials in terms of time of adsorption and adsorption capacity. Piloting of the proposed supported adsorbents in real conditions demonstrated their potential for a success treatment of non-point water pollution. The adsorbents enriched with nutrients could be used as a soil amendment agents since non-toxic support was used. A preliminary estimate of the cost of production showed a possible reduction in prices by at least 2,1 and 1,3 times for LECA-MKGP and LECA-BFS, respectively.

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