Sustainable use of crushed autoclaved aerated concrete (CAAC) as a filter medium in wastewater purification

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Abstract
Scrap material from the production of autoclaved aerated concrete (AAC) should be considered a valuable by-product and not a waste, as should residues from the demolition of houses built with AAC. This paper presents an innovative use of AAC that can contribute to environmental improvement. We tested crushed AAC (CAAC, 2-4 mm) for its phosphorus (P) removal efficiency by filtering a solution containing phosphate phosphorus (PO$_4$-P) or pure wastewater in batch, bench-scale and field pilot-scale experiments. Slow phosphate removal kinetics of CAAC were demonstrated, but the removal efficiency was very high (93-99%). Mineralogical analyses (by ICP-OES) of the solid CAAC after contact with flowing wastewater yielded concentrations of 39.6 g P kg$^{-1}$. Application of X-ray powder diffraction (XRPD) for mineral phase identification confirmed that the dominant mineral in AAC was tobermorite (Ca$_5$Si$_6$O$_{16}$(OH)$_2$·4H$_2$O). Dissolution of this crystalline structure was followed by formation of calcium phosphates and the porous, tobermorite-rich material produced proved excellent in removal of P and organic matter from domestic wastewater. Only crushing and sieving to achieve a suitable particle size distribution is needed prior to application in different technical solutions.

Keywords: By-product; Calcium phosphate; Phosphorus removal; Reactive material; Tobermorite

1 Introduction
In our work to identify natural materials and by-products for use as filter materials in on-site wastewater treatment, we found that scrap material from the production of autoclaved aerated concrete (AAC) is suitable for this purpose. AAC was invented in Sweden in 1923 and is now an attractive building material worldwide. It is used for plain masonry or insulating purposes and for reinforced components such as lintels and roof/floor and wall panels (Hellers & Schmidt, 2011). AAC is a porous material with very low density (275-400 kg m$^{-3}$), also known as gas concrete. AAC is manufactured from silica sand, cement, lime and water. It is aerated with the help of aluminium powder and thereafter autoclaved under pressure (180-200 °C, at about 1 MPa for around 10 h), which converts the minerals chemically into a strong crystal structure of tobermorite (Ca$_5$Si$_6$O$_{16}$(OH)$_2$·4H$_2$O). Tobermorite occurs in nature but is very rare. It belongs to a group of minerals known as calcium silicate hydrates, or CSH for short.

In this paper, we report on application of crushed AAC (CAAC) as a filter medium in reactive bed filter technology (RBF). RBF is designed according to the purpose of treatment, e.g. for stormwater, domestic wastewater or landfill leachate (Renman, 2008). The construction may be a filter well or a constructed wetland where the most important component is the reactive medium or sorbent. Many sorbents have been studied for their metal and phosphorus (P) removal capacities (Johansson Westholm, 2006; Cucarella & Renman, 2009; Vohla et al., 2011) but few have been applied in large-scale installations. Two examples of commercial success are the filter products Polonite® (Bioptech AB, Sweden) and EAF-slag (PhosphoReduc, USA). Reactive materials can be classified into two groups. The first type promotes chemical reactions that destroy the contaminant or transform it into a more benign species. The second type transfers the contaminant mass from the aqueous phase to the
solid phase (e.g. ion exchange, precipitation). Our research indicates that AAC, with its main component tobermorite, can be characterised as a reactive material of both groups.

Few data have been published on the sorption properties of tobermorite under dynamic conditions, i.e. in a stream of water. Komarneni et al. (1988) and Siauciunas et al. (2004) studied the ion exchange capacity of tobermorite and its metal removal. Oğuz et al. (2003) were among the first researchers to study removal of P from wastewater using AAC waste. A group of German scientists has applied tobermorite-rich waste compounds from the construction industry for seeded crystallisation of calcium phosphate (Berg et al., 2006; Ehbrecht et al., 2011).

Bed filters using reactive materials are an emerging technology for on-site wastewater treatment. In this paper we demonstrate the potential of CAAC as a filter material and promote this sustainable use of scrap material from AAC production. The RBF technology has several advantages, the most important of which are (Renman, 2008):

- Purification is achieved by treatment in materials of natural origin or by-products from industry
- Used solid filter materials or sludge from filtration and sedimentation of domestic wastewater are replaced regularly and returned to agriculture as P fertilisers and soil amendments
- Minor or no use of electricity, since pumps and other energy-consuming devices are not needed at all or only to a minor extent in the system
- A robust system in terms of function, control and management.

The purpose of this study was to characterise and evaluate the performance of CAAC for its ability to remove P from domestic wastewater. This is the first part of a long-term experiment that will form the basis for bringing this filter material into commercial use. Further papers will be presented on ongoing research on this unique material. There is a great motivation to develop sustainable solutions for P removal and recovery, since P is a limited resource and triggers the eutrophication of water bodies.

2 Materials and methods

The AAC used in the experiment was obtained from the company Aeroc AB. The material was crushed and sieved to a particle size of 2-4 mm. The elemental composition is given in Table 1 and the appearance of the CAAC is shown in Figure 1.

The material was characterised using a FlowSorb 2300 instrument for determination of specific surface area (Brunauer-Emmett-Teller, BET, method).

Batch experiments were performed to determine the maximum P sorption capacity on P solutions of different concentrations, prepared by dissolving K2HPO4 (s) in distilled water. A fixed amount of the material with mass M (g) was placed in an Erlenmeyer flask containing a volume V (L) of the prepared solution at one of a range of increasing concentrations. The amount of P sorbed to the material (S) was expressed in unit mass P (g) per unit mass of the material (kg) and calculated as:

\[
S = \frac{[(C_o - C_{eq}) \times V)]}{M} \tag{1}
\]

The batch experiment data were fitted to the Freundlich and Langmuir adsorption isotherms for AAC (see Cucarella & Renman, 2009, for more information on batch experiments).

The long-term performance was studied in the laboratory (at 20 °C) using a plastic box of length, 40.5 cm, width 21.4 cm and height 10.2 cm, representing a small-scale system. The box was filled with 6 L CAAC, which corresponded to 2912 g of material. Wastewater was collected every second week from a three-chamber septic tank serving one household and thereafter transported to the laboratory. The liquid (average P concentration 7.4 mg L\(^{-1}\)) was continuously pumped to the box with a flow rate of
Table 1. Chemical composition of the AAC used:
Oxides and major elements

<table>
<thead>
<tr>
<th>Constituent</th>
<th>% weight</th>
<th>g kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>51.4</td>
<td>-</td>
</tr>
<tr>
<td>CaO</td>
<td>26.3</td>
<td>-</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.95</td>
<td>-</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.1</td>
<td>-</td>
</tr>
<tr>
<td>Si</td>
<td>-</td>
<td>232</td>
</tr>
<tr>
<td>Ca</td>
<td>-</td>
<td>194</td>
</tr>
<tr>
<td>Al</td>
<td>-</td>
<td>10.0</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Figure 1. Crushed AAC prepared as a filter material (2-4 mm) for wastewater treatment.

approximately 120 mL h⁻¹. Sub-surface flow and saturated conditions were applied throughout the experiment. Influent and effluent samples were collected weekly. Samples from the bed itself were also collected from pipes inserted at two points; one in the influent area and one in the middle of the filter bed. The experiment lasted for 19 months including pumping breaks when management was not possible but the filter bed stayed under saturated conditions with wastewater.

Samples were filtered through a 0.45 μm filter before analysis of phosphate phosphorus (PO₄-P) using Flow Injection Analysis (FIA, Aquatec-Tecator). pH was measured on all unfiltered samples. Mineralogical analyses were performed by means of inductively coupled plasma optical emission spectrometry (ICP-OES) and X-ray powder diffraction (XRPD).

The removal capacity of the material (Rₘ, %), i.e. the P retention achieved for the volume of wastewater treated and hydraulic retention time was calculated as:

\[
R_m = \left(1 - \frac{C_e}{C_i}\right) \times 100
\]

where \( C_e \) is the effluent concentration and \( C_i \) is the influent concentration.

3 Results and discussion

3.1 Characteristics of the filter material

The CAAC (2-4 mm) used here was a very porous media. An initial porosity of 65% and hydraulic conductivity of 2500 m day⁻¹ made this filter material suitable for filtration. Moreover, the initial specific surface area (SSA) was 30.4 m² g⁻¹. Sampling of material in the inlet area of the box experiment after 1400 L of wastewater had been treated revealed that SSA has increased to 45.8 m² g⁻¹, probably due to accumulation of organic carbon. Despite visible enrichment of organic matter, at least in the first one-third of the box, no tendency for clogging and hydraulic failure was observed. Structural disintegration of the solid matrix could have been expected because of its chemical composition, but this was not observed. We measured BOD₇ on a few samples and found a removal of 80% for this small experimental filter bed. The decolourising ability of the material was apparent, since the effluent water was as clear as tap water. The influent wastewater had a pH ranging from 7.6 to 8.9, while in the filter bed effluent it had slightly increased, to 8.5-9.3.
3.2 Phosphorus removal capacity and kinetics – batch experiment

The results of the batch experiment are shown in Table 2. The equilibrium data fitted the Langmuir isotherm equation ($R^2 = 0.94$) better than the Freundlich equation. The highest sorption capacity was derived from the modelled data, which was not unexpected. Many studies have pointed out the limitations of using Langmuir isotherms to describe P sorption by filter materials (see discussion in Cucarella & Renman, 2009). Our kinetics study clearly showed that the CAAC investigated here needs a contact time with the P solution (5 mg L$^{-1}$) of 24 hours to approach almost 100% removal. This fact must be kept in mind during application of the filter medium in wastewater treatment. It is known that organic matter disturbs the sorption process, an effect that can be partly counteracted by longer contact time. CAAC is a hard structure, built by the presence of tobermorite. However this CSH triggers kinetically inhibited formation of calcium phosphate compounds. Torrent (1997) summarised several suggested theories explaining the slow steps of adsorption, which included initial formation of mononuclear complexes and rearrangement to form binuclear complexes, replacement of silicate in the sorbent, competing anions on the surface, and surface precipitation processes.

Table 2. Phosphorus sorption capacity of the 2-4 mm CAAC studied. Calculated values from triplicate samples, mean values ± SD.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>P sorption capacity (g kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>On-site wastewater* (P=10 mg L$^{-1}$)</td>
<td>28 ±4</td>
</tr>
<tr>
<td>Solution (P=10 mg L$^{-1}$)</td>
<td>57 ±2</td>
</tr>
</tbody>
</table>

The best fit of equilibrium data in the Langmuir isotherm expression predicted mono-layer coverage of P onto the CAAC surface. It was found that the pseudo-second order rate constants decreased with increasing initial concentrations (data not shown). The fitted and the experimental values were very close to each other. In the view of these results, it can be said that the pseudo-second order kinetic model provided a good correlation for the adsorption of P onto CAAC, in contrast to the pseudo-first order model.

3.3 Phosphorus removal capacity – box experiment

The results of the long-term box experiment are shown in Figure 2. Average P removal was 92.4% (as PO$_4$-P) and average effluent concentration was 0.57 mg L$^{-1}$. Mass balance calculations showed that 11.2 g of PO$_4$-P were bound to the entire volume of CAAC medium. Human excretion of P is about 700 g per year, of which more than 80% dissolves in the wastewater. A rough calculation on the basis of the flow data from our experiment shows that approximately 591 kg or 1.2 m$^3$ of CAAC would be enough to treat wastewater from one household (5 pe) during one year. The mass balance value of 3.86 g P kg$^{-1}$ removed by the material indicates that a much larger amount of CAAC (898 kg) is needed for meeting the purification goal of 90% P removal, a Swedish target that is generally not fulfilled for small-scale and on-site wastewater treatment systems in sensitive areas.

The incoming wastewater showed great variation in P concentrations (Figure 2). This wastewater was from a septic tank serving a single-family house. It is frequently observed that the P concentration varies considerably in such sewers, mainly because of temporary dilution by groundwater intrusion into cracked pipes. The variations in P load and in wastewater flow over time cause stress on all systems with filter media. This was not the case for our experimental box system, where flow was constant, evenly distributed over the day and kept below room temperature. For this reason we developed a pilot-scale treatment system at a private house near Stockholm. Monitoring of this system verified our laboratory results but the above-mentioned stress factors had a significant effect on the treatment results.
The actual content of P in the CAAC filter medium was investigated at the end of the experiment. The values found in samples from the inlet, middle and outlet area of the box were 39.6, 7.3 and 4.6 g P kg\(^{-1}\) dry matter, respectively. This demonstrates the capacity of CAAC for P recovery from wastewater and indicates that the filter bed was far from exhausted by a treated volume of 1436 L. Berg et al. (2006) studied the CSH-triggered P-binding mechanism and demonstrated crystallisation of calcium phosphate compounds. Moreover, they showed the reuse options for the products generated, which have been further developed by Ehbrecht et al. (2011) for municipal wastewater treatment. Recycling to agriculture would be feasible for this material in the same way as shown for other materials used in on-site wastewater treatment (e.g. Cucarella et al., 2008).

Tobermorite has a crucial role in the P-binding process. Figure 3 shows the XRPD spectrum of a sample collected from the outlet area of the box experiment. Quartz and tobermorite were identified as the main crystalline components but calcite was also present. The XRPD spectrum for the inlet area where the highest P content was recorded did not show presence of tobermorite. This indicates dissolution of the crystalline structure and formation of calcium phosphates. A sample from the filter bed was given to researchers using X-ray absorption near edge structure (XANES) spectroscopy for identification of chemical species. They found that CAAC contained 63% amorphous calcium phosphate (ACP) and 37% octacalcium phosphate (OCP) (Eveborn et al., 2009). This is a promising result in terms of the recycling potential of CAAC, as ACP is highly soluble and the P it contains is available for plant growth. Moreover the high P content, approaching 4% (w/w) after wastewater filtration, allows this sorbent to be classified as a fertiliser. The natural P content of phosphate rock (apatite) is about 14%.

![Figure 2. Changes in PO\(_4\)-P concentration in untreated wastewater (C in) and wastewater treated in the filter bed (C out). C1 and C2 are sampling points in the inlet and outlet area of the bed, respectively.](image-url)
4 Conclusions

- The CAAC filter medium is a new lightweight aggregate (LWA) that can be used in several wastewater treatment applications.
- Scrap material from AAC production can be used for manufacturing a novel filter product, for use in small-scale wastewater treatment in particular.
- The P reaction kinetics proved to be slow for the test material, implying that bed filter treatment systems should be constructed with long hydraulic retention time (24 hrs) for the wastewater.
- The formation of calcium phosphates is suggested to be connected to the dissolution of CSH compounds (tobermorite).
- Exhausted CAAC after wastewater filtration has a high content of total P (4% w/w) and is a possible material for recycling to agriculture.

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References


