PARTICIPATION OF POTASSIUM AND MAGNESIUM IN BIOLOGICAL PHOSPHOROUS REMOVAL

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ABSTRACT
The role of potassium and magnesium in the biological phosphorous removal was elucidated. Potassium and magnesium are the active counterions of bacteria polyphosphates. The metal ions are released or uptake in parallel to phosphates respectively under anaerobic and aerobic conditions. The important statement made in result of the carried out experiments was that K/P and Mg/P release ratios being time depended. Under anaerobic conditions the aforementioned ratios are distinctively decreasing.

Keywords
Activated sludge, magnesium, phosphorous removal, potassium

INTRODUCTION
Metal cations like calcium, potassium and magnesium does participate in biological phosphorous removal. There is however, no unanimous opinion about the character of the process. Potassium and magnesium were found to be taken up in Enhanced Biological Phosphorous Removal (EBPR) processes. It was demonstrated by several authors, that magnesium and potassium are present in intracellular polyphosphates granules, Roske et al. (1989), Schonborn et al. (2001). Determining the phosphorous uptake and release by Aicientobacter strain 210A, Van Groenstijn et al. (1988) stated that magnesium and potassium are the most important counterion of polyphosphate. It is not clear however, if the polyphosphates are formed as a result of chemical or biological processes.

The given here results are aiming at explaining the processes involved in potassium and magnesium uptake. The effects of anaerobic condition on phosphorous and potassium and magnesium release as well the effects of artificial acidification of the activated sludge were presented.

METHODOLOGY
Samples of activated sludge taken from the denitrification stage, of a full technical scale EBPR process treatment plant, were left in the laboratory for several days without aeration. Most often the process was carried out for 8 days. The samples were left at room temperature (18 to 20 °C) in dark, softly mixed manually twice a day. Immediately after the samples were brought to the laboratory, and later after one, four and eight days basic determinations were performed. Above all, determinations of phosphates, total phosphorous, potassium and magnesium in the liquor were
done. Determinations of phosphates and total phosphorous were done according to Standard Methods (1995). Potassium and magnesium were measured by atomic absorption spectrometry.

In parallel the same samples of activated sludge, on the first day, are treated with hydrochloric acid (1 molar) to different value of pH. Similar determinations as in the case of anaerobic tests were performed.

RESULTS
The release of phosphates under anaerobic conditions takes place in the so called dephosphatation stage of the EBPR process. If performed in the main sewage treatment stream anaerobic conditions in dephosphatation stage are maintained for several hours. If a side stream scheme of treatment is applied (e.g. a selector, digester) activated sludge is retained under anaerobic conditions even for few days.

The release of phosphates is time dependent, and the release rate decreases with time. The observed in our experiments release of phosphates was typical (Fig. 1). The phosphates concentration of about 6 to 8 mg PO₄/l increased up to range of 170 to 230 mg PO₄/l after 8 days.

![Figure 1. Phosphates resolution under anaerobic conditions.](image)
In parallel to phosphates release, a surprisingly large release of potassium was observed. During the first four days the potassium concentration increased from about 7 mg K/l to the level of 26 to 39 mg K/l (Fig. 2).

The release of potassium was however, no longer observed in the following days. Even a decrease of potassium was measured. In contrary the phosphates release continued also in the period from day 4 to day 8 (compare Fig 1 and 2).

![Graph](image)

**Figure 2.** Release of potassium under anaerobic conditions.

The possible explanation is that potassium polyphosphates are more readily resolubilised in comparison to other polyphosphates. The decrease of potassium concentration is not clear. Most probable chemical reactions with e.g. ammonia and phosphates take place.

Release of potassium is accompanied by changes of the redox potential. With the decrease of the redox potential the concentration of potassium increases. From the fourth day onwards there was a slight decrease in the potassium concentration and a slight increase of the redox potential (Fig. 3).

Under anaerobic conditions together with changes of the redox potential there was a pH decrease characteristic for the acidogenic phase of digestion. Decrease of pH was however, not distinct and in our experiments the ∆pH was below 0.5.
Addition of hydrochloric acid in increasing steps results in hydrolysis of the organic matter and consequently to resolution of potassium. Only at pH as low as 2.0 the concentration of potassium could be compared to that obtained as a result of biological processes (Fig. 4).

**Figure 3.** Changes of potassium and redox potential under anaerobic conditions.

**Figure 4.** The effects of acidification on potassium resolubilisation.
To illustrate the effects of chemical and biological reactions, the changes of potassium released by addition of acid and under anaerobic conditions in correlation to pH were presented in Fig. 5.

![Figure 5. Comparison of chemical and biological potassium resolubilisation.](image)

Under anaerobic conditions also release of magnesium was observed. It is characteristic that the changes of magnesium concentration during the 8 days of anaerobic conditions were similar to those of potassium (Fig. 6).

![Figure 6. Changes of magnesium concentration under anaerobic conditions.](image)
Also the correlation between magnesium and redox potential was very similar (Fig. 7).

**Figure 7.** Changes of magnesium and redox potential under anaerobic conditions.

Acidification of the activated sludge has little effect on magnesium resolubilisation. Only below a pH of 3.5 a distinct hydrolysis of polyphosphates could be observed (Fig. 8). The release of magnesium under anaerobic conditions with a pH decrease in the order of 0.5 and the required large decrease of pH by addition of HCl can be interpreted as a prove that magnesium is not forming inorganic salts, but is bound biologically in organic matter.

**Figure 8.** Effects of activated sludge acidification.
DISCUSSION

According to Arvin and Kristensen (1985) potassium and magnesium are released in anaerobic conditions at rates $K/P = 0.29$ and $Mg/P = 0.25$. Imai et al. (1988) had found a $Mg/P$ rate equal approximately 0.285. The results of our experiments suggest a variation of release rate with time – compare Fig. 1, 2 and 6.

During the 8 days the activated sludge was left under anaerobic conditions, the rate of $K/P$ and $Mg/p$ varied with time. Below in table 1, the range of determined rates after 1, 4 and 8 days are given.

**Table 1.** Release rates of potassium and magnesium under anaerobic conditions.

<table>
<thead>
<tr>
<th>Time of anaerobic conditions [days]</th>
<th>$K/P$ Rate</th>
<th>$Mg/P$ Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>range</td>
<td>average</td>
</tr>
<tr>
<td>1</td>
<td>0.27 – 0.4</td>
<td><strong>0.33</strong></td>
</tr>
<tr>
<td>4</td>
<td>0.17 – 0.23</td>
<td><strong>0.20</strong></td>
</tr>
<tr>
<td>8</td>
<td>0.15 – 0.16</td>
<td><strong>0.15</strong></td>
</tr>
</tbody>
</table>

Although the $K/P$ and $Mg/P$ rates obtained for the first day of anaerobic digestion are close to that given by Arvin, Holm and Kristensen (1985) they do not have any real value. First of all, they should be multiplied approximately by a factor of 2, splitting equally the amount of released phosphorous between potassium and magnesium. Secondly the rates of released phosphorous to released potassium and magnesium are decreasing with time (Fig. 9). These observations evidently exclude any speculation about the content of the discussed cations in extracellular polyphosphates in terms of $K/P$ or $Mg/P$ rate.

Based on full scale experiments at a EBPR treatment plant (Suschka a. Popławski (2001), a net uptake of potassium and magnesium was determined. In addition the behaviour of these cations under anaerobic sludge digestion in comparison to acidification (pH decrease) means that both potassium and magnesium are very active in the process of biological phosphorous removal.

![Figure 9. Changes of the K/P and Mg/P rate in the anaerobic process.](image-url)
The presence of magnesium at an influent concentration of less than 8mg/l was found by Imai et al. (1988) to be the limiting factor for effective EBPR. Stable results of phosphorus biological removal could not be achieved at lower concentrations of Mg.

CONCLUSION
Potassium and magnesium are very active in the process of biological phosphorous removal. The release of potassium and magnesium, under anaerobic conditions, was found to be time depended. There is a decrease in the release rate of K/P and Mg/P. That observation can be interpreted as the presence of other polyphosphates counterions with a lower resolution rate. It also evidence again the importance of potassium and magnesium in the EBPR process.

REFERENCES.
Suschka J., Popławski S.: Zmiany wapna i magnezu w procesach oczyszczania ścieków, Chemia i Inżynieria Ekologiczna (in press).