Relationship between the electric conductivity and phosphorus concentration variations in an enhanced biological nutrient removal process

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Abstract Phosphorus release and uptake in a sequencing batch reactor were monitored by the simple on-line measurements of electric conductivity (EC) and oxidation-reduction potential (ORP), and the result was verified by the measurement of phosphate concentration changes. The influence of nitrate ion presence on the phosphorus removal was evaluated by a jar test operated in the cyclic anaerobic (anoxic)–aerobic condition. The relationships of EC, ORP and metal species with phosphorus concentrations were investigated. Under strict anaerobic conditions, EC showed positive correlation with phosphorus concentrations, but it became negligible under anoxic conditions with nitrate present. Strong inverse correlation was found between ORP values and phosphorus concentration. The increase and decrease of magnesium and potassium ions took place in accordance with phosphorus release and uptake, and the relationship between the metal species and phosphorus changes was clearer in the anaerobic condition than anoxic condition.

Keywords Electric conductivity; metal species; ORP; phosphorus; sequencing batch reactor

Introduction

Increasing interest for the on-line control of biological nutrient removal (BNR) process has resulted in many researches for the use of simple parameters, such as electric conductivity (EC), oxidation-reduction potential (ORP) and pH, in the monitoring and the prediction of nitrogen and phosphorus concentration changes. Moral et al. (2005) observed a close relationship of EC to TKN, AN and K levels using pig slurries, while Akin and Ugurlu (2005) reported that denitrification and P removal could be easily predicted by pH and ORP values in a sequencing batch reactor. Maurer and Gujer (1995) used the EC value as an efficient tool in the monitoring denitrifying-P release process as it clearly showed the completion of denitrification and the beginning of P release under anoxic condition. These parameters are easily measured and can provide important information to adjust the duration of aerobic–anaerobic cycles, therefore resulting in the optimisation of BNR processes.

Electric conductivity is a measure of the mobility of various dissolved ions in aqueous solution. Where the interactions between the ions are small, the conductivity can be expressed as follows:

\[
\text{Conductivity} = \sum_{i} A_{i}^{+} z_{i}^{+} c_{i}^{+} + \sum_{i} A_{i}^{-} z_{i}^{-} c_{i}^{-} \quad (\text{S/m})
\]  

(1)

where \( A_{i} \) is the molar conductivity, \( z_{i} \) is the charge of the ion \( i \), and \( c_{i} \) is the concentration of the ion \( i \). During the phosphorus release and uptake in an enhanced BNR
process, the concentration changes of various ionic compounds take place. The ions involved in the BNR process may include bicarbonate, ammonia, nitrate, nitrite, acetate, phosphate and other metal ion species, and the forms of many ions alter in different pH conditions as induced from various biological reactions. Therefore, it is assumed that conductivity variation only cannot explain the phosphorus concentration changes in BNR systems. Although there are previous researches reporting strong correlations between the EC values and phosphorus changes, this needs to be verified. If the limited ionic conditions are allowed, the combination of EC and ORP monitoring may give valuable information for the phosphorus removal processes.

It is known that biological phosphorus release and uptake go with the concentration changes of specific metal species. In an aqueous system, phosphorus release and uptake take place as the negatively charged ortho-phosphate form; the co-transportation of metal species is accompanied to satisfy electro-neutrality of the system. Maurer and Gujer (1995) and Pattarkine and Randall (1999) found a strong relationship between the phosphate concentration and potassium and magnesium ions. This study uses four different metal species including sodium, magnesium, potassium and calcium, and measures the concentration changes along with the phosphorus removal. As the presence of nitrate in the anaerobic condition interferes with the P release, using various influent nitrate conditions, the amount of phosphorus release and uptake can be controlled in different ranges. At the same time, monitoring the metal species changes will give a clear relationship to the phosphorus changes. Increasing phosphorus and metal ion concentrations may enhance the influence on EC values. It can be expected that monitoring the EC values under the various nitrate conditions give a insight for describing both the nitrate and phosphorus changes during the anaerobic–aerobic cycles.

This study aims to evaluate EC and ORP values as simple monitoring techniques for biological phosphorus removal systems, investigate P removal under different nitrate loading conditions and identify the co-relationships between phosphorus concentration changes and various metal species.

Materials and methods

Sequencing batch reactor

An 8 L sequencing batch reactor (SBR) was operated in the cyclic anaerobic–aerobic condition for biological P removal. The reactor was equipped with a mechanical stirrer, an air blower and the sensors for EC, ORP, pH and temperature. An activated sludge collected from a local municipal wastewater treatment plant was used as a seeding culture, and a COD-modified municipal wastewater was introduced for the SBR operation. The organic matter in the influent was provided as acetate in 500 mgCOD/L.

Jar test

After the SBR reached a stable condition, the culture was separated into four jars (2.0 L) in a jar tester and operated under different nitrate conditions. Each jar was filled with 0.6 L of bacterial culture directly from the reactor and 1.0 L of synthesised wastewater. The experimental condition was divided into two phases; phase I was conducted under anaerobic–aerobic condition, and phase II was conducted with gradient nitrate ion present (10, 20 and 30 mg NO3^-N/L), therefore operated under anoxic–aerobic condition. As well as the monitoring of EC, ORP, pH and temperature, time course changes of organic matters (as COD), and ionic concentrations (NH4^+, NO3^-, NO2^- and PO4^3-) were measured after each anaerobic–aerobic cycle. The concentration changes of metal species (Na^+, Mg^2+, K^+ and Ca^2+) during the P release and uptake were also monitored. The jar tests were repeated five times until the analysed data showed consistent result. All the
analyses were performed in accordance with Standard Methods (APHA, 1999). Table 1 summarises the experimental condition of the jar test.

Results and discussions
Figure 1 illustrates the concentration changes of phosphate and nitrate, conductivity and ORP values, and the metal species during the anaerobic–aerobic jar tests. In the front row, phosphorus release and uptake and the nitrate changes are shown for each phase. While the amounts of phosphorus released and taken during the phase I were 23 and 27 mg/L, respectively, the phosphorus released during the phase II were 17, 13, 12 mg/L for the 10, 20 and 30 mg/L nitrate-N conditions, and the phosphorus uptake during the phase II were 20, 18 and 14 mg/L for the 10, 20 and 30 mg/L nitrate-N conditions. It clearly showed that the phosphorus release was lowered in anoxic conditions by the nitrate ion present, so was the subsequent uptake; however the amount of net phosphorus ion removed from the system was not much different. Where high nitrate concentration is introduced, the inhibiting effect may become significant. High nitrate should be removed first for the purpose of active phosphorus release and the subsequent uptake. The nitrate profile in the right front row graph indicated that the system allowed active denitrification and nitrification, at the same time as the P release and uptake.

With the increase and decrease of phosphorus ion concentrations, it was expected that correlation would be found between the electric conductivity and the concentration changes of phosphorus in the aqueous solution. The time-course EC and ORP changes during the phosphorus release-uptake are shown in the second row of Figure 1. Under the anaerobic conditions, a slight increase in the EC was observed in phase I, but a slight decrease occurred in a phase II, where significant denitrification took place. In the aerobic conditions, the conductivity values in both phases showed a decrease in various ranges, but it was not significant as expected from the phosphorus results. With other high levels of ions present, as in most wastewater treatment plants’ cases, it seems that monitoring only the EC values for phosphorus removal cannot provide viable information. In the systems where denitrification takes place in advance to the phosphorus release, EC values should give a better insight for the P reactions. This was not the case in this study. Unlike the EC values, ORP curves for both phases indicated clear inverse relationships to phosphorus release and uptake. ORP decrease in the anaerobic (anoxic) conditions ranged between 214 and 294 mV, and the increase in the aerobic conditions ranged between 290 and 383 mV.

In the last row of Figure 1, changes of metal species during the phosphorus release and uptake are illustrated. Among the four metal species analysed, potassium and magnesium ions showed better relationships with phosphorus changes. Where the highest phosphorus release took place in the anaerobic condition in phase I, highest magnesium ion release was also observed.

Table 1 Experimental condition

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<thead>
<tr>
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<th>Phase I</th>
<th>Phase II</th>
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<tr>
<td>NO₃⁻N (mg/L)</td>
<td>0</td>
<td>10, 20, 30</td>
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<tr>
<td>Reaction time</td>
<td>Anaerobic (anoxic): 2 h, Aerobic: 3 h</td>
<td></td>
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<tr>
<td>Influent composition (mg/L, modified to municipal wastewater)</td>
<td>NH₄⁺-N</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>PO₄³⁻</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>COD (as acetate)</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>MLSS</td>
<td>≈ 2200</td>
</tr>
<tr>
<td>F/M (kgBOD/kgMLSS-d)</td>
<td>≈ 0.1</td>
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Figure 2 describes the correlations of ORP and EC values with phosphorus concentration in anaerobic (anoxic) phosphorus release stage. The correlation types between ORP and phosphorus were similar and consistently negative in both phases, and the values of slope ($\Delta^{2}ORP \ mV/\Delta^{2}P \ mg/L$) were $-294, -256, -204$ and $-214$ for the influent nitrate-N conditions of 0, 10, 20 and 30 mg/L, respectively. The slopes of EC to P however, showed decreasing values with increasing influent nitrate concentration, and even converted from positive to negative. The values of EC to P slope were 2.2, 0.0, 2.1 and 6.3 ($\mu S-L/mg-cm$) for the influent nitrate-N conditions of 0, 10, 20 and 30 mg/L, respectively. As the EC values respond to the various ion species in aqueous solutions such as $\text{HCO}_3^-$, $\text{HPO}_4^{2-}$, $\text{H}_2\text{PO}_4^-$, $\text{PO}_4^{3-}$, $\text{NO}_3^-$, $\text{NO}_2^-$, $\text{NH}_4^+$, $\text{CH}_3\text{COO}^-$, $\text{K}^+$, $\text{Mg}^{2+}$, $\text{Ca}^{2+}$ and so on, the interpretation of EC values should take account of more complex biological processes in the reactor as well as the pH variations. Therefore, it may be concluded that EC monitoring not only provides valuable information for biological phosphorus removal, but can be worthwhile if it is measured together with the ORP values.

The relationships between the metal species and phosphorus concentrations are illustrated in Figure 3. As expected from the result in Figure 1, a strong relationship was found between the magnesium and phosphorus concentrations and also with the potassium ions. However, almost no difference in the calcium ion change was observed within the large phosphorus concentration ranges, and no relationship was shown between sodium and phosphorus concentrations. The ratios of metal species that are co-transported with phosphorus are listed in Table 2, showing that 0.18 g magnesium ions and 0.47 g potassium ions are transported for every single gram of phosphorus.
Figure 2 Correlations of ORP and conductivity with phosphorus concentrations under anaerobic (a) and anoxic (b-with nitrate present) conditions

Figure 3 Relationships between the concentrations of phosphorus and metal species: (a) magnesium, (b) potassium, (c) calcium, (d) sodium
Conclusions

In an enhanced biological phosphorus removal process, the relationships of EC, ORP and phosphorus concentrations were investigated. As phosphorus release took place under anaerobic (anoxic) conditions, a decrease in ORP values was observed, and the correlation was strong and similar within the four different nitrate conditions. Although EC values relate to phosphorus concentration changes, it appeared that complex ionic species in the wastewaters interfered with the interpretation of EC values to the phosphorus changes. Where high nitrate concentration variation occurs, it becomes more difficult to use EC for phosphorus monitoring. Therefore, it may be concluded that for the purpose of phosphorus removal, single ORP monitoring provides better information compared to EC monitoring.

The presence of nitrate in the biological phosphorus removal system appeared to affect the amounts of phosphorus release and uptake. Higher phosphorus release was observed when the system was operated in complete anaerobic conditions (without nitrate). Although the highest P uptake was also observed in the nitrate-free system, the difference of net phosphorus removal for all four systems with different nitrate conditions appeared insignificant in this study. It is obvious, however, that the presence of nitrate in the biological P removal system interferes with the anaerobic P release and the subsequent P uptake.

Under the anaerobic conditions, electric conductivity showed a strict positive relation with phosphorus concentrations, but the correlation became insignificant with nitrate present (anoxic condition). Simple ORP measurement showed a good inverse relationship to the phosphorus concentration changes in all conditions.

Phosphorus release and uptake took place with metal species changes and it showed good positive relationships between phosphorus and the ions of potassium and magnesium. For a gram of phosphorus changes, 0.18 g magnesium and 0.47 g potassium ions were co-transported.

References


Table 2 Ratios of metal ions co-transported with phosphorus (in mg)

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<thead>
<tr>
<th></th>
<th>This study</th>
<th>Aguado et al. (2006)</th>
<th>Maurer and Gujer (1995)</th>
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<tr>
<td>Mg(^{2+})/P</td>
<td>0.18</td>
<td>0.28</td>
<td>0.25</td>
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<tr>
<td>K(^{+})/P</td>
<td>0.46</td>
<td>0.35</td>
<td>0.37</td>
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