Simultaneous precipitation of phosphorus in a kraft pulp mill wastewater treatment plant

Sakari Toivakainen, Timo Laukkanen and Olli Dahl

ABSTRACT

Simultaneous precipitation (SP) using iron sulfates in the secondary treatment of elemental chlorine-free (ECF) kraft pulp mill wastewater was studied. In short-term pilot plant studies phosphorus reduction was improved from 58% up to 81% by adding 10 mgFe/L ferrous sulfate in the activated sludge (AS) process. The phosphorus reduction in full-scale experiment was about 80% when less than 10 mgFe/L was fed in with the influent of the AS plant. The reduction of phosphorus decreased with the dose of iron during the three month experiment. No notable change in either chemical oxygen demand (COD) or adsorbable organic halogen (AOX) reduction nor in the properties of sludge settling were observed during this SP experiment. Furthermore, no problems in sludge treatment due to increased iron concentrations in the waste sludge were reported. SP offers a simple way to decrease phosphorus discharges from AS plants instead of reliance on more expensive tertiary treatments.

Key words | activated sludge, iron salts, kraft pulp mill, phosphate, phosphorus, secondary treatment, simultaneous precipitation, wastewater

INTRODUCTION

Eutrophication is one of the major problems in water pollution control especially in Northern Europe, where effluent discharges flow into lakes and finally to the sensitive Baltic Sea. In order to control eutrophication, regulations are being tightened (HELCOM 2007) concerning phosphorus discharges. These tightening discharge regulations have created a need to intensify and improve existing wastewater treatment systems.

The activated sludge process (AS) is a typical secondary treatment for wastewater treatment in the kraft pulp mills (Thompson et al. 2001; Pokhrel & Viraraghavan 2004). The AS is based on microbial activity that includes uptake of phosphorus as a nutrient. Nevertheless, the AS processes in the pulp mills typically have a long sludge age and low net production of biomass, which leads to a low removal of the phosphorus within the biomass. If the pulp mill is integrated with a paper mill, the combined wastewater has a lower phosphorus concentration as paper mill effluents include only a small amount of phosphorus in relation to organic material. In comparison, mere pulp mill effluent often contains an excess of phosphorus for the biological AS process. Hence for pulp mill wastewater, the traditional AS cannot easily achieve the new regulatory goals of phosphorus reduction of over 50%. So pressure is increased to chemically precipitate phosphorus instead.

Aluminum precipitation is an efficient tertiary treatment method for decreasing phosphorus discharges, but it is expensive and produces secondary waste, which is difficult to treat further and reuse. Instead of a tertiary phase, several municipal wastewater treatment plants in Northern Europe have already successfully utilized ferrous chemicals in simultaneous precipitation (SP) for several decades. A wastewater treatment plant using SP can achieve as much as 95% reduction in phosphorus discharges (Statistics Finland 2010). However, the use of SP is not widespread in the forest products industry; even though SP has obvious advantages compared with aluminum-based tertiary treatment.

Ferrous chemicals are cheap and easy to handle, so they are commonly used for SP. However, pulp mill wastewaters contain different complexing agents, for example, tannins and lignin, which bind themselves to ferrous iron. These wood originated compounds are thought to slow down the oxidation of ferrous to ferric iron, which is needed for...
precipitation (Thes & Singer 1974) and therefore an increased ferrous-phosphorus ratio might be needed. On the other hand the amount of phosphorus in forest industry wastewaters is clearly lower than in municipal wastewaters and thus would possibly need less chemical precipitation. Furthermore, pulp and paper industry wastewater is relatively warm and the organic load is usually quite stable which might facilitate the purification process.

SP had already been considered for forest industry wastewater treatment at the end of 1980s, with both full and pilot-scale trials having taken place. The full-scale trials at a kraft pulp mill’s AS plant (Hyytiä et al. 1988) showed that phosphorus reduction could be improve from 30 to 67% using 90–100 g/m³ of ferrous sulfate. Recent studies on SP indicated a similar kind of results (Toivakainen et al. 2011) in short-term trials, both in the laboratory and on a pilot scale. The phosphorus reduction at an elemental chlorine-free (ECF) kraft pulp mill’s AS improved from 60 to 80% with 50 g/m³ of ferrous sulfate. In addition, the ferrous sulfate slightly improved the chemical oxygen demand (COD) reduction.

The Fe-salts affect not only the purification result but also the sludge characteristics and composition. The iron precipitate enhances the sludge settleability (Agridiotis et al. 2007) and sludge dewatering. Hence SP might improve the sludge treatment and thus decrease the need for additional dewatering chemicals.

SP and its suitability for kraft pulp mill wastewater treatment are not yet widely studied; published results are still scarce. This article represents practical knowledge and results from short-term pilot-scale trials as well as a full-scale experiment. The objective was to study the effects of the added ferrous and ferric chemicals on the AS process, especially on the treatment results and the sludge characteristics. The chemical feeding point was shifted in the pilot-scale trials when the effects of chemical feeding could be compared, whereas the full-scale experiment was performed with two different chemical dosage levels. Both ferrous and ferric sulfates were used for precipitation in this study.

MATERIALS AND METHODS

Kraft pulp mill

The full-scale experiment was performed in a Scandinavian ECF kraft pulp mill, which uses mainly pine. The production capacity is somewhat less than 400,000 ADt/a, and the mill was run close to its full capacity during the experimental period. The mill has its own AS plant for the secondary treatment of wastewater.

Pilot-scale studies

The pilot-scale studies took 18 d and were performed before the full-scale experiment. The pilot plant consisted of four parallel AS process units (4 × 10 L), which operated on a batch principle and simulated a plug flow process. One unit and the wastewater feed arrangements are represented in Figure 1. Each of the units were run in half day cycles (wastewater feed, aeration, clarification, effluent discharge), when the duration of the aeration and the clarification phase for the sludge were close to actual values compared with the AS process in the full-scale experiment. Also, sludge recycling ratio (compared with influent flow), sludge load and sludge age, as well as temperature were practically comparable with the parameters in the full-scale AS process except for the oxygen profile in the aeration stage. In the pilot-scale trials the dissolved oxygen concentration was kept above 2.0 mg/L during the whole aeration time. In contrast the concentration of dissolved oxygen at the beginning of the full-scale aeration basin was very low and increased after the first few hours of aeration. Table 1 shows both the pilot and the mill full-scale plant operation parameters during the experiments.

The influent for the pilot-scale process was pumped as a continuous flow (~0.2 L/min) from the pulp mill wastewater treatment process: the wastewater stream to the full-scale equalization basin. This wastewater was piped to the two pilot plant feeding tanks, which simulated the equalization basin in the pilot-scale plant. The first tank contained bottom sediment from the actual equalization basin of the mill. The sediment ash contained 60% calcium and the phosphorus concentration was about 0.9%. The full-scale wastewater was neutralized and the pH was 7.0 at the end of the equalization basin. While the hydraulic retention time (HRT) of the wastewater in the pilot-scale equalization basin was around 10 h, the pH rose from 5.7 to 7.2…7.5. Experience in the mill indicates that the phosphorus dissolves into the wastewater from the bottom sediment of the basin.

The pilot plant units were altered in terms of the Fe-salt and its feeding point. The first unit operated with ferric sulfate, which was added to the return sludge. The second and third unit was operated with ferrous sulfate. Precipitation chemical was added to the influent for the second unit, and during the aeration (2 h before its end) for the third unit. The Fe-salt concentration was 10 mgFe/L in each unit.
precipitation chemical addition. The reference unit was needed both for indicating the precipitating effects and again for evaluating the success of the pilot-scale simulation, when that was compared with the full-scale AS process.

Both influent and effluent were sampled for laboratory analyses. In addition, sludge settling was also observed and some sludge samples were examined with a microscope. The mixed liquor suspended solid (MLSS) concentration

### Table 1: Operation parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pilot-scale</th>
<th>Mill-scale reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRT in equalization</td>
<td>8–10 h</td>
<td>~12 h</td>
</tr>
<tr>
<td>Aeration phase</td>
<td>10 h</td>
<td>14.5 h</td>
</tr>
<tr>
<td>Settling phase</td>
<td>1.5 h</td>
<td></td>
</tr>
<tr>
<td>Aeration tank volume</td>
<td>10 L</td>
<td>55,000 m³</td>
</tr>
<tr>
<td>Wastewater inflow</td>
<td>10 L/d</td>
<td>~43,000 m³/d</td>
</tr>
<tr>
<td>Sludge recycling ratio</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>Sludge age</td>
<td>~34 d</td>
<td>~39 d</td>
</tr>
<tr>
<td>MLSS</td>
<td>4.3 g/L</td>
<td>5.9 g/L</td>
</tr>
<tr>
<td>Sludge load</td>
<td>0.045 kgBOD₇/kgMLSSd</td>
<td>0.033 kgBOD₇/kgMLSSd</td>
</tr>
<tr>
<td>Temperature</td>
<td>35 °C</td>
<td>37 °C</td>
</tr>
<tr>
<td>Dissolved oxygen at the beginning of aeration</td>
<td>3.0 mg/L</td>
<td>0.4 mg/L</td>
</tr>
<tr>
<td>pH, AS influent</td>
<td>7.2 … 7.5</td>
<td>7.0</td>
</tr>
<tr>
<td>pH, AS effluent</td>
<td>7.8 … 8.2</td>
<td>7.6 … 7.9</td>
</tr>
</tbody>
</table>

Figure 1 | Pilot-scale activated sludge process set-up.
of the sludge was determined before and after the trials. Furthermore, oxygen concentration and pH were also measured onsite from different units at different times.

**Full-scale experiment**

The wastewater treatment process of the pulp mill is shown in Figure 2. The Fe-salt feeding point is shown in the figure, as well as the sampling points for the full-scale experiment. The actual hydraulic residence time for the wastewater is about 24 h, which is taken into consideration when estimating the efficiency of the process.

At the beginning of the experiment, ferrous sulfate was fed in via a water solution to the influent flow before the aeration stage. At first the average dosage was 9.0 mgFe/L. The experiment continued with this dosage for 46 d, after which the ferrous feed was halved. This lower dose was used for the next 35 d. After this period there was a 5 d break from chemical addition. The precipitation chemical was switched to the ferric sulfate at the end of the experimental period, which was fed to the wastewater for 25 d, at a concentration of 8.8 mgFe/L.

The full-scale experiment gave results for phosphorus removal efficiency, comparing the AS process with the SP. The data measured the previous year were used for the comparable reference values. The pulp production rate was slightly lower in the previous year (1,000 ADt/d) compared with the rate during the experiment (1,100 ADt/d), so the COD load was correspondingly somewhat lower as well. Nevertheless, the average phosphorus load to the AS plant was 59 kgP/d in both years.

The influent and the effluent samples were collected as 1 d composite samples during the full-scale experiment. COD and total phosphorus concentrations were measured after the sample was retrieved. Biosludge samples were collected three times a week from the aeration basin. MLSS and sludge volume index (SVI) were determined immediately after each sample was collected. Portions of the effluent and biosludge samples were also frozen for later measurements. The concentrations of iron in the effluent and in the biosludge were measured within 2 weeks from thawed samples. The concentration of total phosphorus in the biosludge was also determined afterwards from the thawed samples.

**Analyses**

The concentrations of total phosphorus in the influent, effluent and biosludge were determined with a FIAstar™ 5000 Analyzer according to standard ISO 15681–1 from unfiltered samples. The concentration of iron in the effluent and biosludge was determined according to standard SFS 3028. Biosludge samples were dispersed with an IKA Ultra Turrax T 25 with maximum power for 1 min before analysis. COD concentrations were determined from filtrated (5 μm) influent and effluent samples by oxidation with dichromate according to standard method SFS 5504. The suspended solids concentration of the influent and effluent and also MLSS were determined according to standard method SFS-EN 872.

**RESULTS AND DISCUSSION**

**Pilot-scale studies**

The effects of the Fe-salt addition to the pilot-scale AS process are presented in Table 2. The concentrations and reductions obtained are average values from the three last cycles in the pilot plant trials. The reference values in the full-scale experiment are the average during the experimental period of measurements. When
comparing the full-scale reference values with the reference unit in the pilot-scale trials, the treatment results both for phosphorus and COD are fairly similar. Slight differences in the phosphorus reduction could be due to the higher phosphorus load in the full-scale experiment: more phosphorus dissolves in the full-scale equalization basin.

Table 2 also shows that when ferrous sulfate was added to the influent before aeration, the phosphorus concentration in the effluent decreased to half from its reference value and the phosphorus reduction improved from 58 to 81%. The ferrous sulfate addition at the end of the aeration period enhanced the phosphorus reduction as well, however not as efficiently as the feed at the beginning of aeration. Two hours seems not to be enough for the ferrous iron to oxidize and precipitate, because the Fe-residual in the effluent was remarkably higher. Also the ferric sulfate fed in the return sludge was not as efficient in the phosphorus precipitation as the ferrous sulfate at the beginning of the aeration, and the major part of the added ferric iron was discharged with the effluent.

The Fe-salt addition had little effect on the COD levels in the treated wastewater. Only when adding ferrous sulfate to the influent, did the COD levels improve during the trials. This COD reduction might be explained, at least partly, with the very clear effluent having a low level of suspended solids. In this case the suspended solids concentration was below 2 mg/L. In comparison, the effluent SS concentration was 8…10 mg/L in the other three units.

The use of ferrous sulfate decreased effluent SS concentration but simultaneously slowed down sludge settling when added at the beginning of the aeration. Instead, ferric sulfate added in the return sludge speeded up the sludge settling, nevertheless the effluent was not as clear – containing non-settled sludge particles.

### Table 2 | Total phosphorus, COD-, SS- and Fe-concentrations of the treated wastewater in the pilot-scale studies

<table>
<thead>
<tr>
<th></th>
<th>Total phosphorus, $P_{\text{tot}}$ (mg/L)</th>
<th>Reduction %</th>
<th>COD (mg/L)</th>
<th>Reduction %</th>
<th>SS (mg/L)</th>
<th>Fe Residual (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference, full-scale</td>
<td>0.59</td>
<td>61</td>
<td>441</td>
<td>52</td>
<td>n.a.a</td>
<td>n.a.a</td>
</tr>
<tr>
<td>Reference, pilot-scale</td>
<td>0.42</td>
<td>58</td>
<td>443</td>
<td>52</td>
<td>8.0</td>
<td>0.7</td>
</tr>
<tr>
<td>FeSO₄ feed in the influent</td>
<td>0.19</td>
<td>81</td>
<td>427</td>
<td>53</td>
<td>&lt;2</td>
<td>1.9</td>
</tr>
<tr>
<td>FeSO₄ feed during the aeration</td>
<td>0.33</td>
<td>68</td>
<td>435</td>
<td>53</td>
<td>7.9</td>
<td>3.4</td>
</tr>
<tr>
<td>Fe₂(SO₄)₃ feed in the return sludge</td>
<td>0.28</td>
<td>73</td>
<td>444</td>
<td>52</td>
<td>9.9</td>
<td>3.9</td>
</tr>
</tbody>
</table>

*aNot analyzed.

### Full-scale experiment

Figure 3 represents the effects of the Fe-salts on the phosphorus concentrations in the AS plant. The data were collected from the wastewater treatment plant both during the iron precipitation period (105 d) and 165 d prior to the experiment. Figure 3 also includes the reference values, i.e. the phosphorus levels in the purified wastewater from the previous year. The comparison with the previous year is needed, because the phosphorus levels rise noticeably during summertime, when also the experimental period was scheduled. When examining the reference values, the COD:P ratio was higher during the SP experiment.

The Fe-salt addition seemed to stabilize effluent phosphorus concentration at a low level, which was independent of the phosphorus load to the AS process. The higher Fe-dosage enhanced phosphorus reduction; however the ferrous and ferric sulfates did not differ explicitly. The phosphorus reduction was around 80% with 9.0 mgFe/L in a wastewater, and 68% with the halved dosage (4.4 mgFe/L). Phosphorus reduction was typically about 30…50% without the SP in that mill in summer.

The COD reductions were not markedly affected with Fe-salt addition. The COD reduction was slightly better than the same time the previous year. In addition, SP did not affect adsorbable organic halogen (AOX) reduction, which remained at average values.

As expected, the Fe-addition increased the Fe-concentration in the biosludge. The Fe-concentration was 2.5% at the beginning of the experiment and rose to 5% at the most. If the experiment had been continued longer, the Fe-concentration in the sludge would probably have increased further before a stable state was achieved between Fe-dosage, Fe-discharge within effluent and Fe-concentration in the sludge. The calculated theoretical Fe-concentration of the sludge in equilibrium was about 10%. According to
reports from the mill, the Fe-accumulation did not cause any problems in aeration, clarification nor in sludge treatment during or after the experiment. During the experiment, SVI was mainly below 90 mL/g and did not rise above 120 mL/g in any state. These values are typical for the AS plant in question.

The cost of the precipitation chemical was about 0.5 US cent/m³ in the full-scale SP experiment when ferrous sulfate (10 mgFe/L) was used. A typical price for ferrous sulfate is around 100 USD/ton. SP does not require any other (secondary) chemicals. For comparison, when aluminum-based chemical (250 USD/ton) is used for the tertiary treatment within a pulp mill wastewater treatment plant, the estimated precipitation chemical cost with average dosages is about 7.0 US cent/m³. In addition, other chemical costs (sulfuric acid, sodium hydroxide and polymer) will increase significantly the total chemical costs of this tertiary treatment.

CONCLUSIONS

The phosphorus discharges in an ECF kraft pulp mill can be reduced by adding iron salts to the AS process. The SP method seems to be a strong competitor for the more expensive tertiary treatments available, which produce undesired sludge.

SP is technically fairly simple, and intensifies the phosphorus reduction almost immediately on beginning the Fe-salt feed. The AS process with SP seems also to be quite resistant to fluctuations in phosphorus load. Furthermore, enhanced phosphorus reduction by SP gives opportunities to use phosphorus containing alkaline side streams from pulp processes for wastewater neutralization without increasing phosphorus discharges.

ACKNOWLEDGEMENT

The authors would like to thank the staff of the kraft pulp mill for help and fruitful co-operation and Heini Jokinen and Gary Watkins for language revisions. We are also very grateful to Ms Myrtel Kåll and Ms Maarit Niemi for help with the analysis.

REFERENCES


Hyytiä, H., Jokinen, S., Kukkonen, K. & Väänänen, P. 1988 Chemical waste water treatment in the pulp and paper

First received 16 April 2012; accepted in revised form 23 July 2012.