PRACTICAL EXPERIENCE WITH BIOLOGICAL REMOVAL OF PHOSPHORUS FROM PULP AND PAPER MILL EFFLUENTS

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ABSTRACT

The nutrient situation and nutrient removal policy in Finland are discussed and the principles of biological phosphorus removal are outlined.

The approach of Metsä-Serla Oy to the nutrient problem is described: Metsä-Serla has been studying biological phosphorus removal since 1987. At the beginning of 1989 plant-scale experiments were started at the Kirkniemi paper mill. The results have been promising, the highest removal rates obtained being over 90%.

Experimenting with biological phosphorus removal will be started at all Metsä-Serla's activated sludge plants (five in all) in the near future.

KEYWORDS

Pulp and paper mill effluents, nutrients, activated sludge, biological phosphorus removal.

INTRODUCTION

Effluent discharges in Finland have decreased steadily during the past two decades. The two traditionally biggest polluters, the pulp and paper industry and the municipalities, have been able to reduce their discharges by 70 - 90% since 1970. In the treatment of municipal effluent, a 90/90 reduction of BOD and phosphorus has been standard practice for a long time. In the treatment of pulp and paper mill effluents, the main emphasis has been on the removal of suspended solids and organic matter, with less attention given to the nutrients of these nutrient-deficient waters.

At present, Finland's total phosphorus discharge is estimated at 3000 - 6000 t/a (Heinonen, 1989,1990). The municipalities and forest industry discharge roughly 500 t/a and 800 t/a, respectively, while the rest emanates mainly from agriculture and cattle farming. The contribution from other industries,
e.g. fish farming, is still small (10 - 15 %) but rising. The wide variation in the estimates is due to difficulties in the estimation of agricultural discharges (Rekolainen and Kauppi, 1990).

The distribution and total amount are of the same order of magnitude as those in Sweden (Baltic Marine Environment Protection Commission, 1987), but they differ markedly from those in Central European countries. For instance in West Germany, over 50 % of the total discharge of 83000 t/a P comes with the domestic sewage (Anon., 1988).

With discharges of phosphorus in municipal effluents decreasing, the relative - and absolute - discharges from agriculture and from the pulp and paper industry have increased, and at present the main emphasis as regards nutrients is on limiting and reducing the discharge of phosphorus from these sources. By the year 1995 phosphorus discharges will have to be reduced by 50 % in all countries surrounding the Baltic Sea (Convention on the Protection of the Marine Environment of the Baltic Sea Area, 1988).

In Finland, the pulp and paper industry has become the main point-source discharger of phosphorus; of the ten biggest P dischargers nine are pulp (and paper) mills (National Board of Waters and the Environment in Finland, 1988). The considerable pressure being put on the industry is therefore understandable.

THE PULP AND PAPER INDUSTRY AND NUTRIENTS

The nutrient content of pulp and paper making effluents is very low, normally 1 - 3 mg/l P and 5 - 10 mg/l N. The nutrients are derived practically exclusively from wood, very little comes from other sources. The amount of phosphorus in Finnish pulpwood (pine, spruce, birch) varies between 0.005 and 0.015 % in the wood itself and between 0.03 and 0.07 % in the bark. The corresponding figures for nitrogen are 0.1 - 0.6 % and 0.3 - 1.3 % (Finnish Pulp and Paper Research Institute, 1977).

Practically all the P and N of the wood material dissolves in the pulping and bleaching processes and eventually ends up in the effluents, solid waste or flue gases. Expressed in grams per ton of product, the amounts dissolved equal 100 - 300 g/t of phosphorus and 1500 - 2000 g/t of nitrogen (Meloni, 1977). Some of the phosphorus ends up in the lime cycle, while some goes directly into the effluent. The P in the lime cycle is precipitated in the form of calcium phosphates. Because of the accumulation of P, the recaustizing lime may contain up to 1 - 2 per cent of phosphorus (Meloni, 1977, Ulmgren et al., 1988). Nitrogen behaves in the same way as phosphorus, except that the N that dissolves in the cooking liquor does not accumulate, but is burned and leaves the plant in the flue gases.

The discharges of P and N from Finnish pulp mills are typically 100 - 150 g/t P and 400 - 600 g/t N (Central Association of Finnish Forest Industries, 1989). The discharges, especially those of phosphorus, have risen considerably during the past ten years. There are numerous reasons.

- The production of pulp has somewhat increased. Practically all the pulp is bleached at present.

- Biological treatment has in some cases increased the nutrient discharges because the treatment plants have not always operated without problems.
A major portion of the lime and lime mud previously lost with the flue gases of the lime kiln is nowadays recovered and utilized in neutralizing the effluent. The phosphorus of the lime/lime mud mixture is released in the neutralizing process.

The P discharge of a paper mill is considerably less than that of a pulp mill. Depending on the type of product, the discharge varies between 5 and 50 grammes per ton, 20 g/t being a good average. The N discharges vary widely depending on the product and additives used; discharges of the order of 100 - 200 g/t are typical, but 1000 g/t is not uncommon.

The total P discharge from the pulp and paper industry in Finland is at present ca. 800 t/a. Pulp is responsible for 600 t/a and paper for 200 t/a.

The prospects for removing P from pulp and paper mill effluents by means of external treatment methods are limited. Practically the only conventional treatment method giving some degree of success is chemical precipitation. In paper mill effluents reasonably good results have been obtained with reasonable chemical dosages.

With pulp mill effluent the case is different. If bleaching effluent is present, the chemical dosages required are very high: 500 - 1000 mg/l can be regarded as the minimum no matter which coagulant is applied. Chemical coagulation of pulp mill effluents has been studied for well over 20 years with little practical success. One of the latest studies was published a few years ago (Jokinen, 1987).

The high consumption of coagulating chemical, for instance aluminium sulphate, is due to the fact that there are several competing reactions consuming the metal ion. The dominating reaction is that between lignin molecules and the metal ion (Smith and Christman, 1969, Luner et al., 1970); in addition, metal is consumed by complexing agents and by the precipitation reactions of sulphide and phosphorus. Only after all these reactions have taken place, is the formation of aluminium hydroxide possible, following which the reaction products can be coagulated and flocculated out of the solution.

**BIOLOGICAL PHOSPHORUS REMOVAL**

Removal of nutrients from waste waters by biological means, without the utilization of chemicals, has been among the principal goals of waste water research for many years. The results have been encouraging. The basic mechanisms of biological P removal are understood to such an extent that application of the method at full-scale plants is possible. This is true in spite of the fact that "the fundamental principles of the process of biological P removal from waste water are still unknown and that its working mechanism is mainly based on empirical experience" (Groenestijn, 1988). At present a few hundred treatment plants utilizing biological P removal are in operation all over the world and new ones are being constructed all the time. An excellent overview of the state of the art of biological P removal has been prepared by the German ATV-Arbeitsgruppe "Biologische Phosphorentfernung" (ATV, 1989).

Practically all the plants constructed so far are treating municipal sewage. The method seems to be best suited to large treatment plants, where the conditions are stable. One of the best-known examples is the Ruhleben plant in West Berlin, which treats 240000 m³/d of waste water (Peter and Sarfert, 1989). As is typical of biological P removal in cold climates, the process started slowly, improved gradually, and is at present giving constant
phosphorus concentrations of less than 0.5 mg/l P in the treated effluent. The lowest concentrations obtained are 0.1 - 0.3 mg/l. The results are so good that they cannot be obtained by chemical methods alone.

**The process and the mechanism**

At present there are numerous processes and process modifications able to remove more than 90 % of the phosphorus from the effluent. All the processes are modifications of the conventional activated sludge method. A common feature to them all is that the waste water and/or biological sludge is subjected to anaerobic conditions at some stage of treatment, preferably before being led off for aeration. This creates favourable conditions for the growth of bacteria able to absorb excessive amounts of P. Of the several different bacteria able to bind P, the so-called polyP bacteria, the best known is *Acinetobacter spp.* At plants where biological P removal is practised, *Acinetobacter* can represent up to 2/3 of the bacterial population (Lötter, 1985).

For additional information, see for instance (Groenestijn, 1989).

**Prerequisites and advantages of biological phosphorus removal**

For biological P removal to function properly, certain conditions have to be met.

- The anaerobic zone has to be truly anaerobic and long enough for the polyP bacteria to react. A redox potential of under -150 mV is recommended. The retention time is normally over one hour, but even less is enough in some cases (Daigger et al., 1987).

- Nitrate must not be present in the anaerobic stage. If nitrate is present, i.e. the zone is anoxic, the polyP bacteria cannot compete with nitrate reducers. Phosphorus removal is impaired or does not occur.

- A suitable carbon source in sufficient quantities has to be present. The preferred feed is acetic acid, but other low-molecular-weight substances can also be utilized. As a favourable condition for good P removal to take place, a P:BOD ratio of 0.03 - 0.05 has been given (ATV, 1989).

The advantages offered by biological phosphorus removal can be summarised as follows.

- The modification is cheap and easy to carry out and the results are good. In some cases the only modification needed is closing of the air supply to the aerators at the beginning of the aeration basin. This was done in Ruhleben.

- The energy consumption of a plant practising biological phosphorus removal is smaller than in a conventional plant. If the plant is equipped with nitrogen removal, reductions of 15 - 30 % are possible in domestic sewage (Randall, 1988).

- Because no chemicals are used, the process does not increase the sludge production of the activated sludge plant as does chemical precipitation of phosphorus. On the contrary, fewer sludge bulking problems have been reported (Peter and Sarfert, 1989).

- All in all, considerable savings can be expected. The best results have been obtained in plug-flow reactors, where the anaerobic stage
is before the aeration, and all the return sludge is led to this so-called anaerobic selector. The plug flow can be improved by dividing the aeration basin into separate compartments.

The main drawbacks are the slow start-up of the process and inconsistency of the treatment results; a constant removal rate cannot always be guaranteed.

Pulp and paper effluents and biological phosphorus removal
Pulp and paper effluents seem to be ideally suited for biological phosphorus removal. The waters are warm, suitable food is available in great quantities and the concentration of P is low, i.e. the COD:P ratio is favourable. Furthermore, at least in paper mill effluents, considerable quantities of *Acinetobacter* are present (Väätänen and Niemelä, 1982).

Because the waters are deficient in nutrients, phosphorus and nitrogen have to be added. Paper mill effluent demands the dosing of both P and N, whereas in the pulp mill effluent, only additional N is required; the amount of P dissolved from the wood in cooking and bleaching is enough to keep the activated sludge plant going. In both waters, a BOD:N:P ratio of 100:3-4:0.5-1 is typical. The dosing of P and N means an extra burden for the treatment plant: not only the original nutrients of the effluent, but even these additional nutrients have to be removed.

In Finland, the release and recycling of phosphorus from pulp and paper effluents was studied ten years ago. The principles of biological phosphorus removal were applied. As a result of this work the so-called Sibi process was developed (Isaaho et al., 1981). The process has been tested on the full industrial scale.

THE METSÄ-SERLA EXPERIENCE
Metsä-Serla Oy and its subsidiary Oy Metsä-Botnia Ab have pulp and paper production at eight locations in Finland. The overall annual production is one million tonnes of pulp and an equal amount of paper and board. Five of the mills treat their effluents in an activated sludge plant. The total phosphorus discharge is about 300 kg/d, i.e. of the same order of magnitude as the discharge from the city of Helsinki. Prior to 1989 none of the plants was equipped with phosphorus removal.

A smoothly operating activated sludge plant at a pulp or paper mill achieves a considerable P removal during normal operation. This has also been the case at the Metsä-Serla mills: the plant of the Äänekoski pulp and paper mills removes about half of the P entering the plant, while that of the Savon Sellu fluting mill gives a 75% reduction, producing an effluent with a P content of 0.5-1 mg/l. Similar results have been obtained at other Finnish mills.

Biological phosphorus removal has been practised at the Kirkniemi paper mill since the beginning of 1989. The mill produces 1000 t/d SC and LWC papers and all the process effluent (ca. 10000 m³/d) is treated in an activated sludge plant. The plant was constructed in 1984. In 1988 the original plant, with a capacity of 6 t/d BOD7, was enlarged for the treatment of 20 t/d BOD7. The enlargement cost FIM 15 and it was carried out by building a new aeration basin of 8000 m³ in addition of the previous one of 2000 m³. A new secondary clarifier was also constructed.
The layout of the plant is shown in Figure 1. The plant is equipped with 15 surface aerators with a total installed effect of 1305 kW. The old aeration basin is 3.6 m deep and completely mixed. The new one has three 7 m deep basins built for plug flow. One of the aims of this configuration is biological phosphorus removal.

The enlarged plant went into operation at the end of January 1989 and started to give results within a few weeks. The BOD, COD and suspended solids reached new levels after a month. Since the second week of operation, only 2/3 of the new aeration volume, with a reduced aerator capacity, has been in use (Fig. 1). The third line is utilized as an anaerobic step.

The discharges of nutrients also started to fall fairly rapidly, and in April the P discharge was down to 0.2 - 0.3 mg/l and that of N to 2 - 5 mg/l. This level was maintained till the end of May. Subsequently the P in the treated effluent jumped to 1.5 mg/l and stayed well over 2 mg/l throughout the summer. In September the P out suddenly dropped to 1.2 mg/l and after a few weeks was back to the 0.2 - 0.3 mg/l level where it has stayed ever since, with the exception of weeks 52/89 and 3/90. During week 52/89 the mill was closed down for 3 days during Christmas. Immediately after the standstill there occurred two major spills, one of oil, the other of coating slip. These events seem to give the elevated P discharges a "natural" explanation.

The behaviour of P during the summer is more problematic: P went high at exactly the time the mill started peroxide bleaching of mechanical pulp. Peroxide bleaching had never been practised at the mill before, and it is clear that the bacterial populations of the white water system and the treatment plant experienced a shock. This shock may or may not be the reason for the elevated summer discharge.

Table 1 and Fig. 2 present treatment results and phosphorus history throughout the year 1989. Typical operating conditions have been as follows: MLSS 6-9 g/l; sludge load 0.1-0.3 kg BOD7/kg MLSS; excess sludge 5-10 t/d; sludge age 5-10 d. Half of the effluent is treated in the old aeration before leading to the new one, another half is pumped directly into the new aerator.
FIG. 2. PHOSPHORUS REMOVAL SUMMARY
TABLE 1 Typical Treatment Results 1989

<table>
<thead>
<tr>
<th>Parameter, effluent out</th>
<th>January</th>
<th>April-May</th>
<th>Summer</th>
<th>November—&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS 100 - 200 200 - 300</td>
<td>40 - 80</td>
<td>40 - 80</td>
<td>10 - 30</td>
<td></td>
</tr>
<tr>
<td>BOD7 600 - 800</td>
<td>200 - 300 10 - 15</td>
<td>10 - 40</td>
<td>5 - 25</td>
<td></td>
</tr>
<tr>
<td>COD 1000 - 1500</td>
<td>500 - 700 200</td>
<td>200 - 400</td>
<td>150 - 300</td>
<td></td>
</tr>
<tr>
<td>P 0.8 - 1.2</td>
<td>1 - 1.5 0.2 - 0.5</td>
<td>2 - 3</td>
<td>0.2 - 0.5</td>
<td></td>
</tr>
<tr>
<td>PO₄-P &lt;0.1 - 0.4 &lt;0.01</td>
<td>&lt;0.2</td>
<td>1.3 - 2.6</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td>N 3 - 6</td>
<td>10 - 15 2 - 5</td>
<td>8 - 12</td>
<td>4 - 6</td>
<td></td>
</tr>
</tbody>
</table>

*) Summer values: N=10-12, P=2-3, PO₄-P=1-2 mg/l.

It is interesting to see that good P removal is always accompanied by very low levels of PO₄-P. When 0.2 - 0.3 mg/l P is obtained, the PO₄-P is without exception less than 0.1 mg/l. The N removal also is good, 60 - 70 %. As the removal of total P deteriorates, the reductions of PO₄ and N also decrease. The removal of P does not follow the behaviour of organic matter: BOD removal was good throughout the four-month summer period of 1989.

At first sight the good N removal looks like a mystery. Similar results have been observed at other plants equipped with surface aerators. The phenomenon is attributed to oxygen gradients between the water surface and the bottom. The anoxic conditions near the bottom make denitrification possible (Huyss-teen et al., 1990).

Is the P removal "real"?

In order to clarify whether the conditions in the plant are favourable for the generation of polyP bacteria, effluent from various parts of the aeration basins was analyzed for P and N at the Finnish Pulp and Paper Research Institute. In addition, the redox potentials of the samples were measured immediately after sampling. Both aeration basins were measured in the vicinity of all aerators, both surface and bottom.

According to the redox results, the conditions throughout the aeration basins are aerobic, and the standing aerators seem to have no effect on the redox potentials. The potentials are 100 - 200 mV everywhere. One anaerobic spot was found, however: in the C line of the new part of the plant (no waste water flow, one aerator in use, see Fig. 1) under the C 3 aerator on the bottom at a depth of 7 m there is an anaerobic layer of sludge with a distinct smell of hydrogen sulphide and a redox potential of -300 mV. The anaerobic spot also showed an elevated content of dissolved P (total P: 7.3 mg/l, PO₄-P: 7.0 mg/l), while the P contents elsewhere in aeration were less than 0.2 mg/l. The nitrate contents were practically zero throughout the aeration. It seems that this spot could be a site of enrichment for polyP bacteria. No bacterial analyses have been performed so far.

DISCUSSION

It is obvious that the good P removal at the plant is biological in nature. It also seems probable that a polyP mechanism is involved. What is open to discussion is where the bacteria are actually enriched: in the treatment plant or the white water system of the mill? The occurrence of Acinetobacter in large quantities in the white water system of the Kirkniemi mill (Väätänen and Niemelä, 1982) could explain the rapid start-up of the P removal process.
The main reason for the summer disturbance would be the killing of the *Acinetobacter* population of the white water system by the new peroxide bleaching process, and the reason for the long duration would be the slow build-up of the population again. The treatment plant itself is also gradually building up a polyP population, but the process is slow. So far, this is only speculation, and has to be confirmed by further research. Another factor that seems to be involved is temperature: similar elevated concentrations of dissolved phosphorus with impaired P removal have been experienced at the mill practically every year since the beginning of biological treatment.

**THE FUTURE**

The positive results obtained at Kirkniemi clearly indicate that biological removal of phosphorus is a promising new tool for reducing the phosphorus content of pulp and paper mill effluents. According to the experience gained so far, the sensitivity of the method to disturbances is still great, greater than that of BOD removal. Consequently, consistent removals of phosphorus to low levels cannot yet be guaranteed.

Biological phosphorus removal will be applied at other Metsä-Serla mills. Because all the mills and the treatment plants are different, the P removal process has to be tailored individually for each mill.

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