COMBINED CHEMICAL AND BIOLOGICAL REMOVAL OF PHOSPHATE IN ACTIVATED SLUDGE PLANTS

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ABSTRACT

Biological phosphate removal has been achieved in nutrient removal plants in Johannesburg by generating the required substrate for the process. Substrate generation has taken place by primary fermentation and subsequent elutriation. This technique, coupled with control of nitrate return to the anaerobic zone, has allowed phosphorus to be removed almost exclusively by biological means in plants designed for nutrient removal. However, operational problems with primary sedimentation tanks being used for fermentation, for which they were not designed, necessitated the occasional use of chemicals in the Northern Works plant. Contrary to current literature, the addition of ferric sulphate to this plant resulted in inhibition of polyphosphate storage; the cornerstone of the biological process.

Laboratory batch studies revealed that iron-treated activated sludge showed a lower propensity for ferric phosphate precipitation than an untreated sludge. These laboratory studies were borne out by practical experience on two extended aeration plants, not designed for nutrient removal. The performance of these plants with different chemicals is discussed and possible reasons are advanced for some of the plant observations.

KEYWORDS

Activated sludge; phosphate removal; biological nutrient removal; chemical precipitation.

INTRODUCTION

It is expected that the future demand for water in the Republic of South Africa will exceed the economically exploitable sources within two to three decades. Eutrophication in storage dams adds considerably to the cost of potable water treatment (Viljoen, 1984; Taylor et al., 1984). Phosphate is the limiting nutrient in most South African impoundments (Toerien et al., 1975), and in 1980 legislation was introduced to restrict the amount of phosphate entering river systems via sewage effluents. The promulgated limit of 1 mg P/l for certain catchments was however only enforced from 1985.

Johannesburg finds itself in the unenviable position of being situated in the middle of two drainage systems; namely, Southwards to the Vaal River and Northwards to the Hartebeespoort Dam. Both catchments are subject to the 1 mg P/l standard. Approximately 500 M€ sewage are treated daily at the five works in Johannesburg. Of this amount 400 M€ are treated by the activated sludge process.

During the last fifteen years researchers in Johannesburg have been striving to remove phosphate from sewage effluent in the most cost-effective manner. This has resulted in the optimisation of the biological process wherever possible. Osborn et al. (1986) showed that the additional cost of phosphate removal by chemical precipitation would be 4,94 US c/k€ in comparison to 3,86 US c/k€ for the biological option.

In spite of the disadvantage of high cost, the use of chemical precipitation cannot be avoided in older extended aeration plants not designed for nutrient removal.
Removal of phosphate from wastewater by chemical precipitation is a well known phenomenon and is widely used as a tertiary treatment to reduce effluent phosphate levels (Jenkins et al., 1971; Yeoman et al., 1988). The use of chemicals to supplement biological phosphate removal in activated sludge plants has also been successfully applied (Rabinowitz and Marais, 1980; Yeoman et al., 1988). These researchers observed no detrimental effect on the biological process by the addition of chemicals to the activated sludge system. Similar observations were also made by researchers studying specific aspects of phosphate precipitation in an activated sludge plant (Unz and Davis, 1975).

Likewise Mininni et al., (1985) observed no detrimental effect on the biological system. The absence of observable effects on the biological process reported by these researchers could well have been the result of a lack of satisfactory parameters to quantify any effects on the biological process.

When adding chemicals to the activated sludge process to supplement biological phosphate removal a number of factors have to be taken into account, not the least important being the selection of the chemical. Iron and aluminium salts are readily available in South Africa and can be used for this purpose. Optimisation of chemical phosphate removal in activated sludge plants centres around the best point of addition, the pacing of chemical to phosphate load and pH adjustment (Wiechers, 1987). Rabinowitz and Marais (1980) reported that the point of addition was in fact not critical.

Optimisation of the chemical process has a number of advantages: improved COD and suspended solids removal in addition to the phosphate removal giving rise to a higher quality effluent and control of sludge bulking and scum formation (Wiechers, 1986).

In this paper experience gained on two extended aeration activated sludge plants and two nutrient removal plants will be discussed in conjunction with some laboratory batch studies.

LABORATORY EXPERIMENTS

A number of preliminary laboratory tests were carried out simultaneously with the plant studies in order to clarify some aspects which could not easily be studied in large plants without disturbing their operation.

The phosphate precipitation efficiencies of ferric chloride, ferric sulphate and ferrous sulphate were compared in laboratory batch tests. Phosphate removing activated sludge mixed liquor was spiked with phosphate to a concentration of 50 mg P/l. Iron salts were added at a concentration of 100 mg Fe/l, and the mixed liquor aerated for 2 hours. Samples were taken every 30 minutes for phosphate determination.

Phosphate levels were reduced to below 1 mg P/l within 30 minutes in the presence of ferric and ferrous salts. Although the reaction rate with ferrous sulphate was slower than with ferric salts, this had no effect on the final phosphate concentration.

The slower rate was probably as a result of oxidation of the ferrous ion to the ferric form prior to reaction with phosphate. This will be discussed later in greater detail. One of the most important aspects in combined chemical and biological phosphorus removal is the estimation of the chemical dose required to precipitate only the phosphate not removed biologically. The optimum utilisation of the biological process is essential in order to achieve the most cost-effective removal. In order to monitor the efficiency of the biological process in the presence of chemical addition, either a specific biological parameter is required or an indirect method via quantification of the chemical precipitation. Some batch tests were carried out to try and address these aspects.

In attempting to assess the effect of chemical addition on the biological processes prevailing in a nutrient removal activated sludge plant certain studies were undertaken in the laboratory. The effect of iron salt addition on nitrogen metabolism was evaluated in batch studies. Ferric chloride, ferric sulphate and ferrous sulphate respectively were added to denitrifying mixed liquor in the mass ratio; Fe : P of 2:1. The rate of denitrification was determined by measuring the decrease in nitrate levels with time. The addition of iron salts had no significant effect on the rate of denitrification (See Figure 1).

A similar experiment was carried out to study nitrification in the presence of iron salts. Ferric chloride was added to nitrifying mixed liquor and the nitrification rate determined by measuring the ammonia levels at specified time intervals. In contrast to the denitrification process nitrification rates were in fact diminished by addition of iron salts (See Figure 2).
Dehydrogenase activity has been used by a number of researchers as an indicator of activated sludge biomass activity (Richards et al., 1984; Awong et al., 1985) and although no significant correlation between plant behaviour and this parameter was observed for large Johannesburg nutrient removal plants (Lötter, 1989), it was decided to use the parameter in laboratory scale experiments to evaluate the effect of iron salt addition on the activated sludge biomass activity.

Iron addition had no effect on the enzyme activity, therefore indicating that no general inhibitory effect is exerted on the biomass.

The "phosphate release test" was first described by Healey and Kerdachi (1987) and was used by these researchers to assess the amount of chemically bound phosphate in the sludge. The technique was subsequently applied to Johannesburg plants by Lötter (1989) in an attempt to establish a baseline value for this parameter in biological phosphate removal plants.

During these studies the test was applied to batch tests incorporating phosphate precipitation. Ferric chloride, ferric sulphate and ferrous sulphate were added to phosphate removing mixed liquor containing 15 mg P/l in the mass ratio Fe : P of 2:1. The mixed liquor was aerated for two hours and samples taken every 30 minutes for the phosphate release test, which was carried out as described by Lötter (1989). The results are shown in Figure 3. Contrary to expectation the control (no iron added) sludge appeared to contain less biological phosphate i.e. phosphate released by acetate addition, than the chemically treated sludge. These findings contrasted significantly with those of Healey and Kerdachi (1987) and the test was then used to compare one of the chemically treated Northern Works modules with an untreated module. Again no significant difference between the phosphate release test results were observed. This test is not considered useful for future plant monitoring and its use has been discontinued.

Anecdotal data (Personal Communication, 1988) have indicated that continuous dosing of iron salts to an activated sludge plant diminishes the plant's capacity to remove phosphate, necessitating higher and higher iron doses.
In an attempt to investigate this phenomenon, laboratory studies were undertaken where phosphate precipitation in a previously iron-treated sludge was compared to precipitation in a non-iron-treated sludge. Phosphate-removing activated sludge mixed liquor was spiked with phosphate to a concentration of 50 mg P/€. The sample was then divided in two and ferric chloride added to one at a concentration of 100 mg Fe/€. The mixed liquor was aerated for two hours and samples taken at thirty-minute intervals for iron and phosphate analysis. Both treated and untreated mixed liquors were respiked with phosphate and ferric chloride added to both. Samples were again taken at thirty-minute intervals during two hours' aeration. The experiment was repeated with ferric and ferrous sulphate. The results are shown in Figures 4, 5 and 6.

![Graph 1](https://iwaponline.com/wst/article-pdf/23/4-6/611/112672611.pdf)

**Figure 5:** The effect of ferric sulphate treatment on subsequent phosphate removal.

![Graph 2](https://iwaponline.com/wst/article-pdf/23/4-6/611/112672611.pdf)

**Figure 6:** The effect of ferrous sulphate treatment on subsequent phosphate removal.

Identical patterns were obtained for the three iron salts, except for the slower rate observed with ferrous sulphate. Comparison of figures a and b reveal that phosphate removal occurred almost exclusively by chemical precipitation under these experimental conditions. Phosphate removal by this mechanism was significantly inhibited by prior treatment with an iron salt. Compare figures c and d. In all cases the iron was fully utilized by the end of the aeration period. These results appear to confirm observations by plant operators that continuous iron salt addition results in reduced chemical precipitation efficiency which in turn leads to higher chemical doses. The reduction in phosphate removal was entirely due to a chemical phenomenon as biological removal played a negligible role under these experimental conditions. Another interesting aspect of these results is the similarity of precipitation efficiency achieved by ferric and ferrous salts. The 2:1 Fe:P mass ratio is equivalent to a molar ratio of 2:1:1 for ferric salts, which approximates the stoichiometric ratio (1:8:1) required for ferric phosphate precipitation. Ferrous phosphate precipitation on the other hand implies a stoichiometric ratio of 2.7:1, which is not provided by the dosing rate used in the experiment. The results therefore support the oxidation of ferrous ion to the ferric form prior to reaction with the phosphate.

ALEXANDRA WORKS

Alexandra Works is an extended aeration plant designed to nitrify completely. It consists of two aeration basins separated by a baffle; the first being 60% of the total volume. Aeration is achieved by surface aerators and the liquid retention time is 27 hours with a minimum sludge age of 13 days.

Although this plant was not designed for nutrient removal, it was possible to remove approximately 50% of the phosphate biologically by creating anaerobic zones at different sections of the plant (Nicholls, 1977). This resulted in effluent phosphate levels averaging 3 mg P/€. This was considered satisfactory until August 1985 when the 1 mg P/€ effluent standard was implemented.

Ferric chloride solution was added to the return sludge line from August 1985 to January 1986. pH adjustment was not necessary due to the denitrification taking place in the plant. The average iron dose during this period was well in excess of the mass ratio of Fe:P; 2:1 considered adequate for phosphorus precipitation. The apparent poor performance of chemical addition during this period appeared to be due to inconsistent dosage and loss of biological removal efficiency. The use of this chemical was discontinued at the end of January 1986 in order not to increase the chloride load on the Hartebeespoort dam which is used for the irrigation of the chloride-sensitive tobacco crop.
The dosing procedure was improved and, from January 1986 to October 1987, ferric sulphate solution was used. During this period an average of 525 kg iron was added to the plant daily, resulting in an effective Fe/P removal of 1.8. Iron dosing had to be maintained at the stoichiometric level in order to achieve effluent phosphate levels of less than 1 mg P/l, which indicates negligible biological removal occurring. The plant performance is shown in Figure 7.

![Effluent phosphate as P](image1)

**Figure 7**: Plant performance with ferric sulphate: Alexandra.

Although compliance with the effluent phosphate standard was achieved 70% of the time, unexplained deviations from the standard were observed. In an attempt to achieve more consistent compliance, this chemical was replaced with aluminium sulphate at the end of October. The performance of this chemical, which was used until June 1988, is shown in Figure 8. An average of 240 kg aluminium was added to the plant daily. This was close to the stoichiometric amount required to precipitate phosphate. After an initial period of poor removal, satisfactory precipitation was obtained and compliance with the effluent phosphate standard was achieved 90% of the time. However, after three months of stable operation, addition of this solution failed to reduce the phosphate level to 1 mg P/l. Increased dosage of aluminium failed to restore the phosphate precipitation. Again, based on dosing rates required to achieve the standard, biological removal appeared to be absent.

A higher dose rate of ferric sulphate i.e. average 630 kg iron/d was then used in an attempt to achieve levels of 1 mg P/l. The quality of the material available was variable and attempts to obtain consistent satisfactory removal were not successful, although the influent total phosphorus remained steady at around 16 mg P/l (See Figure 9).

![Effluent phosphate as P](image2)

**Figure 9**: Plant performance with ferric sulphate: Alexandra.

![Effluent phosphate as P](image3)

**Figure 10**: Plant performance with ferrous sulphate addition: Alexandra.
At this time a waste product of the iron and steel industry, ferrous sulphate solution, became available in sufficient quantities to treat this plant. At an average dosage rate of 455 kg iron/d phosphate removal was achieved to 1 mg P/l within days of using the chemical. Apart from a few unexplained hiccups (see Figure 10) consistent removal has been achieved with this chemical, which is currently still in use. Compliance with the effluent phosphate standard is currently achieved in excess of 95% of the time. The successful phosphate precipitation achieved with lower iron dose rates than used with ferric salts further supports the laboratory findings reported above that the ferrous ion is oxidized to the ferric form before reaction with phosphate. The poor denitrification rate achieved in this plant indicates that biological removal plays a secondary role. Approximately 190 - 230 kg phosphorus are being precipitated by iron, indicating iron dosing rates only a fraction in excess of the stoichiometric requirement for ferric phosphate formation.

OLIFANTSVLEI WORKS

The Olifantsvlei activated sludge plant was designed to treat 80 M€ of unsettled sewage in four parallel modules of 20 M€ each. The aeration tanks are divided into four compartments separated by baffles providing semi-plug-flow operation. The plant was designed to nitrify completely as is the case with Alexandra Works and has a liquid retention time of 27 hours. By switching off aerators in the first and third compartments, biological phosphate removal was achieved (Venter et al., 1987) with similar results to those obtained at the Alexandra Works. Effluent phosphate levels were reduced although not to consistently below 1 mg P/l. The creation of anaerobic conditions by switching of aerators is only possible when the carbon load is sufficiently low as not to require the full aeration capacity. The implementation of the 1 mg P/l standard and increased carbon load necessitated the use of chemicals at this plant; from August 1985 to the present ferric chloride solution has been used.

Ferric chloride solution was dosed in the feed at an average rate of 994 kg iron/d which resulted in a mass ratio of 1.7:1, Fe:P. Phosphate removal was satisfactory until the first half of 1988 when chemical dosing failed to reduce the effluent phosphate level to within 1 mg P/l (See Figure 11). Increasing the dose even to well above the stoichiometric level failed to reduce the phosphate levels to within the standard. Cessation of chemical dosing for a few days, then recommencing the previous dosing rate had the desired effect, and except for the odd occasion the phosphate level was achieved during the rest of 1988 and the beginning of 1989. In March and April 1989 problems were again experienced with compliance. A number of possible reasons were advanced for the apparent failure of the chemical to achieve the standard. Before the failure the load had increased and the dose had been raised accordingly to maintain approximately an Fe:P of 1.8:1. This dosage was subsequently increased to an Fe:P of 3:1 without success. Cessation of chemical dosing for a short period before recommencing treatment again had a beneficial effect on the chemical phosphate removal.
The Northern Works activated sludge plant was designed to treat 150 M\text{m}^3 of settled sewage in three identical modules of 50 M\text{m}^3 each. One of the three modules was subsequently modified to incorporate endogenous denitrification ahead of the anaerobic zone (Nicholls et al., 1987) (See Figure 12). Return sludge

![Diagram of Northern Works activated sludge plant](image)

**Figure 12**: Schematic layout of Northern Works activated sludge plant.

Fermentation and subsequent elutriation of primary sludge in the primary sedimentation tanks has allowed fairly consistent biological phosphate removal to be achieved at this plant (Osborn et al., 1986). Although fairly satisfactory phosphate removal (at least 75\% removal) was achieved, consistent 100\% compliance with the effluent phosphate standard remained elusive (See Figures 13 and 14). The difficulty in achieving consistent compliance with the standard arose from operational problems with the primary sedimentation tanks, which were not designed for fermentation and elutriation and heavy rainfall diluting the COD. Complete desludging is virtually impossible with the original design, and methanogenic bacteria proliferate due to the prolonged retention times. This reduces volatile acids for elutriation. Recycling of supernatant for elutriation is difficult within the constraints of these sedimentation tanks.

![Graphs showing plant performance](image)

**Figure 13**: Plant performance: Module 1

**Figure 14**: Plant performance: Module 3

Relaxations of the standard which had previously allowed experimentation with this plant had now lapsed and compliance with the standard was mandatory; chemical addition had to be practised.

Due to the unavailability of sufficient quantities of ferrous sulphate which was being used successfully at the nearby Alexandra Works, ferric sulphate solution was added to two modules of the plant in order to achieve phosphate levels of 1 mg P/l in the combined effluent from the three modules.

The comparison in performance between the two identical modules 1 and 3 is depicted in figures 15 and 17. With the exception of ferric sulphate addition to Module 1, both modules were operated in the same way. The graphs clearly show the consistent satisfactory phosphate removal in module 1, in addition the historical variability in effluent COD and suspended
solid levels was reduced. Effluent nitrate levels were however higher in this module. The ferric sulphate solution was added to the return sludge line in both modules 1 and 2. However, in module 2 the sludge is returned to an anoxic zone as opposed to an anaerobic zone in module 1. Figure 16 depicts the comparatively poorer phosphate removal performance in the former.

The dosing rate and mass of phosphorus removed during this period are shown in Figures 18 and 19. The iron dosage on this plant was controlled by reacting to on-line effluent phosphate data. As soon as the effluent phosphate dropped below 0.5 mg P/l dosing ceased and, as it rose above this level, dosing recommenced. It is clear from comparison of figures 18 and 19 that it was possible to maintain the dosing rate of module 1 within narrower units than module 2.

Considering the fine control exercised on the chemical dosing, it is assumed that all the iron added was utilized in phosphorus removal. Using this assumption the balance of the total phosphorus removal was assumed to have occurred via the the biological process. Comparing modules 1 and 2 in figures 18 and 19 show that the biological removal in module 2 was more severely affected by chemical addition than module 1.

The former module also consumed much less iron than its counterpart over the three-month period.

A further benefit obtained from chemical addition was the improvement in sludge settling properties as evidenced by the lower SVI values in the two chemically treated modules.
One of the main questions concerning combined chemical and biological phosphate removal had still not been satisfactorily answered; namely how does chemical addition affect the biological process? Chemical addition to the Northern Works plant provided the opportunity of investigating this question.

To this end phosphorus fractions in sludge before, after and during chemical addition were characterized by the CSIR as described by Osborn et al., (1989). The results are given in Table 1.

Table 1: Phosphorus fractions in Northern Works sludge.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phosphorus as P % (m/m)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Soluble and precipitated ortho-phosphate</td>
</tr>
<tr>
<td>Module 1 16/3/88 (No iron)</td>
<td>24</td>
</tr>
<tr>
<td>Module 1 17/1/89 (No iron)</td>
<td>22</td>
</tr>
<tr>
<td>Module 1 21/11/88 (No iron)</td>
<td>35</td>
</tr>
<tr>
<td>Module 1 7/3/89 (Iron)</td>
<td>57</td>
</tr>
<tr>
<td>Module 1 12/4/89 (No iron)</td>
<td>36</td>
</tr>
</tbody>
</table>

Microbiological evaluation of the sludge confirmed the reduction in polyphosphate observed in the chemical analysis.

Due to improved elutriation of primary fermented sludge coupled with improved denitrification, satisfactory phosphate removal was achieved without chemical addition, and at the end of March 1989, chemical dosing was discontinued (see figures 20, 21 and 22).

DISCUSSION AND CONCLUSIONS

Effect of chemical addition on the biological process

Laboratory batch tests confirmed the findings of previous researchers in that tests designed to detect alterations in biological activity produced negative results, with the exception of nitrification studies. The results of phosphorus fractionation studies on Northern Works demonstrated clearly that polyphosphate storage is inhibited by the addition of iron salts. The exact mechanism involved here requires further study. Although the results obtained during this study cannot be considered unequivocal, they provide enough evidence to suggest that further study into the mechanism of combined chemical and biological phosphate removal is imperative if these two processes are to be optimized.
The biochemical model of Wentzel et al., (1986) hypothesizes a hydroxyl phosphate transport system which could be affected by the addition of iron salts. Any effect on the membrane transport of phosphate would certainly affect biological removal. The build-up of ferric phosphate on the biomass could also have an effect on the biological process.

Chemical precipitation processes

The superior performance of Northern Works module 1 compared to module 2 indicates a clear difference between points of addition. The addition to an area of high phosphate concentration clearly had a beneficial effect on the precipitation process. The effect of this on the biological process has still to be determined. The oxidation of the ferrous ion to the ferric form before precipitation is supported by the results obtained in this study. However, the superior performance of this chemical relative to ferric salts has still to be explained. The inhibition of ferric phosphate precipitation by prior iron treatment shown in laboratory studies is borne out by the performance of the Alexandra and Olifantsvlei plants and to a certain extent by Northern Works module 2.

The beneficial effect of reducing dosing for a short time supports the idea that ferric phosphate precipitate build-up in the sludge inhibits the precipitation process. The mechanisms involved require further study, particularly in view of the fact that stringent legislation does not allow operators sufficient latitude to discharge non-complying effluent while the sludge recovers its precipitation propensity.

These studies have confirmed that combined chemical and biological phosphate removal is feasible in large activated sludge nutrient removal plants but also demonstrate the necessity of optimizing the biological process so as to minimize the use of chemicals not only from the point of view of cost but also precipitation efficiency. In view of the apparent progressive inhibitory effect of continuous iron dosage to an activated sludge plant on the biological as well as the chemical process, it is considered essential to investigate the addition of iron salts prior to primary fermentation. Laboratory batch studies to investigate this are being initiated in the near future.

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