Chemical wastewater treatment – a cost effective method to upgrade overloaded WWTPs

A. Szabó*, and I. Licskó**

*Hungarian Academy of Sciences, Water Resources Research Team, Műegyetem rkp 3. H-1111, Budapest, Hungary (E-mail: anita@vkkt.bme.hu)
**Budapest University of Technology and Economics, Department of Sanitary and Environmental Engineering, Műegyetem rkp 3. H-1111, Budapest, Hungary (E-mail: licsko@vkkt.bme.hu)

Abstract
Lab scale experiments were conducted to examine pollutant removal efficiencies of chemical pre-treatment. 60-85% of the COD and TOC, and 50-65% of the BOD₅ content of raw sewage could be removed by coagulation-flocculation and sedimentation. The minimum effective Al³⁺ and Fe³⁺ doses required for organic removal were in the range of 10-30 and 20-60 mg/L, respectively. The dose of chemicals necessary for optimal organic removal was sufficient to reduce TP below 1.0 mg/L and PO₄-P to less then 0.3 mg/L. Iron containing coagulants could play a major role in odour reduction, as H₂S content of the wastewater decreased significantly due to the addition of Fe(III)-salts. Introduction of chemical pre-treatment provides appropriate treated sewage quality and hydraulic load improvement of WWTPs at low cost. 250 000 USD/yr may be saved as operational cost when introducing chemical pre-treatment at a 13 000 m³/d capacity AS plant.

Keywords
Coagulation; cost saving; phosphorus; pre-precipitation; upgrading; wastewater

INTRODUCTION
Introducing the tax for the load of the environment (Hungarian Act LXXXIX of 2003) and adopting EU legislations (91/271/EEC) are expected to accelerate the development of the wastewater treatment sector in Hungary. Several new wastewater treatment plants are to be built and pollutant removal efficiencies are required to be improved at most of the ones (typically high loaded AS plants) constructed before 1990. Cost-efficient upgrading methods are needed to minimise the discharge of organic matter (COD) and total phosphorus (together with inorganic nitrogen) to surface waters. Since new regulations have been introduced, the removal of phosphorus is financially encouraged also on those areas where recipients are not sensitive to eutrophication. Because of several changes in the water sector (Buzás et al., 2003) wastewater flows have decreased and pollutant concentrations have increased in the past 15 years in Hungary. Due to the former improper design habits many of our treatment plants receive organic load higher then designed (Licskó et al., 1999; BME, 2004). At the same time, odour nuisance became more serious, as the residence time of sewage in collection system increased and anaerobic conditions have occurred more frequently (Szabó and László, 2002).

One of the possible upgrading methods is the combination of chemical wastewater treatment with biological treatment. Therefore, pollutant removal efficiencies of chemical pre-treatment in different wastewaters were investigated in lab scale experiments. The main objectives were: (1) examining and comparing the pollutant (mainly organic matter and phosphorus) removal efficiencies of different coagulants; (2) selecting the optimal coagulant and the required dose of the chemicals at each WWTP; (3) investigating the correlation between suspended solid (TSS) and total phosphorus (TP) removal; (4) examining the capability of chemicals to remove dissolved organics and different fractions of particulate organic matter; (5) examining the efficiency of iron(III)-containing chemicals in transforming volatile sulphur compounds into poorly water-soluble matters, and thus investigating the role of ferric salts in odour control; (6) estimating the cost of plant upgrading by chemical pre-treatment.
MATERIALS AND METHODS

Coagulation-flocculation Jar tests were carried out in 1-litre glass cylinders with a KEMIRA flocculator device (KEMIRA, 1990). Coagulation, flocculation and sedimentation were performed with the following parameters: 1 min rapid mix (350 rpm); 10 min slow mixing (20 rpm); 20 min settling. Different iron(III) and aluminium salts [Prefloc (iron(III)-sulphate), Bopac (poly-aluminium-chloride), FeCl₃·6H₂O and Al₂(SO₄)₃·18H₂O] were used as coagulants/precipitants. The parameters analysed before and after the coagulation-flocculation and phase separation were as follows: pH; chemical oxygen demand (COD); biochemical oxygen demand (BOD₅), total organic carbon (TOC), total phosphorus (TP), ortho-phosphate (PO₄-P) and total suspended solids (TSS). PO₄-P, dissolved organic carbon (DOC) and dissolved COD/BOD₅ values were measured in the filtrate of 0.45 um pore size membrane filter. Raw wastewater was taken from nine different municipal WWTPs in Hungary where possible plant upgrading by chemical pre-treatment was assessed. Experiments were carried out at original pH and alkalinity.

RESULTS AND DISCUSSION

Chemical pre-treatment can significantly reduce organic matter and phosphorus content of raw wastewater. Maximum removal rates of organics typically vary between 60-85% as COD and TOC and 50-65% as BOD₅ depending on the composition of raw sewage, type and dosage of coagulants (Figure 1.). Residual COD, TOC and BOD₅ concentrations are 130-250 mg/L; 40-70 mg/L and 80-130 mg/L, respectively.

![Figure 1. Removal of organic matter by feeding different coagulants](image)

Organic removal is determined mostly by the particulate matters, as primarily that is the fraction that can be removed by coagulation-flocculation and phase-separation with a high efficiency (Figure 2.). Practically all the organic matter >8 um can be coagulated and settled when applying high enough metal dose. In certain cases, significant part (15-40%) of the dissolved (<0.45 um) organic matter can also be removed; however in other wastewaters the removal of DOC (or dissolved COD) is negligible. At the nine investigated WWTPs due to the different raw wastewater composition significantly different coagulant dosages were required for appropriate organic removal. Comparing coagulants on molar base, aluminium and ferric salts removed COD, TOC and BOD₅ with similar efficiency. It is explained by the fact that approximately the same amount of active metal-hydroxide is formed from the same amount of added coagulant (metal-ion, expressed in mmol/L). The minimum effective Al³⁺ and Fe³⁺ doses required for organic removal were in the
range of 10-30 and 20-60 mg/L, respectively. Pre-polymerised Al salts provided similar organic matter removal efficiency than the simple trivalent metal salts.

The dosage of simple (trivalent) metal salts necessary for optimal organic removal was sufficient to reduce TP below 1.0 mg/L and dissolved phosphorus (PO₄-P) to less than 0.3 mg/L (Figure 3.). At high doses there is practically no residual PO₄-P present; however chemically treated wastewater contains small amount colloidal matters including a portion of the P containing precipitate. Consequently the residual phosphorus content depends on the removal efficiency of suspended solids (Figure 4.). Decreasing TP concentration below 0.5-1.0 mg/L often requires extra suspended solids removal (e.g. sand filtration).
While the different trivalent Al and Fe salts show similar efficiencies (on molar base) in phosphate precipitation, pre-polymerised salts are less efficient in removing PO₄-P (Figure 5.). Phosphate is primarily removed by chemical precipitate formation. As the extent of precipitate formation decreases with increasing OH/Me ratio; higher the basicity (polymerisation degree), lower the phosphate removal efficiency will be (Ratnaweera et al., 1992; Gilberg et al., 1996).

Results of lab experiments show that iron(III)-containing coagulants might be effective in odour reduction at WWTPs (Figure 6.). However, the very low coagulant dose, which can be sufficient to
decrease H₂S and different mercaptans, is not enough to precipitate PO₄-P completely (Figure 7.). Very often the efficient coagulation-flocculation of suspended matters and thus the removal of organic matters require even higher doses. With increasing coagulant doses we can reach that iron-sulphide and particulate organics, which appear in the form of colloid dispersion, can be converted into easily settleable flocs.

According to cost estimations, introduction of chemical pre-treatment provides appropriate quality and quantity (volume) improvement of WWTPs at low cost. The cost saving appears in the reduced oxygen utilization - initiated by organic load reduction - in the downstream treatment processes. Another important cost factor in Hungary is the tax for the load of environment that WWTPs are obliged to pay since 2004 when discharging - among others - COD and TP (Hungarian Act LXXXIX of 2003). Costs were evaluated based on a case study carried out at an activated sludge treatment plant having a wastewater flow of 13 000 m³/d. Not considering the costs of sludge treatment it is estimated that 250 000 USD may be saved annually as operational cost when introducing chemical pre-treatment (Table 1.).

### Table 1. Estimated annual operational costs of biological and combined chemical-biological treatment

<table>
<thead>
<tr>
<th></th>
<th>Activated sludge treatment with nitrification (13 000 m³/d)</th>
<th>Only biological treatment</th>
<th>Chemical pre-treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total oxygen consumption</td>
<td>1 370</td>
<td>1 000 kg O₂/h</td>
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<tr>
<td>Energy requirement for aeration</td>
<td>685</td>
<td>500 kWh</td>
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<tr>
<td>COD concentration in treated wastewater</td>
<td>65</td>
<td>45 mg/L</td>
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<tr>
<td>TP concentration in treated wastewater</td>
<td>11</td>
<td>1.5 mg/L</td>
<td></td>
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<tr>
<td>Energy cost</td>
<td>600 000</td>
<td>440 000 USD/year</td>
<td></td>
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<tr>
<td>Water pollution tax (after COD and TP)</td>
<td>370 000</td>
<td>110 000 USD/year</td>
<td></td>
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<tr>
<td>Coagulant cost</td>
<td>170 000</td>
<td>170 000 USD/year</td>
<td></td>
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<tr>
<td>Annual operational cost</td>
<td>970 000</td>
<td>720 000 USD/year</td>
<td>250 000 USD/year</td>
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<td>Annual savings</td>
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### CONCLUSION
Increased attention has been driven to more efficient pollutant removal at WWTPs by a new Hungarian law that stimulates WWTPs to minimise their COD and TP discharge to recipients by introducing a tax for the load of environment. Lab experiments conducted at 9 different WWTPs proved that coagulation-flocculation processes (that have been being applied in surface water treatment since decades) are able to transform suspended solids of wastewaters to settleable form. Non-settleable suspended solids of raw wastewater contribute to 30-45 % of the COD load of the biological treatment stage. This organic matter fraction can effectively be removed by chemical pre-treatment (coagulation-flocculation and settling) already in the primary sedimentation tank and thus only 25-35 % of the organic load present in raw wastewater reaches the aeration tank.

Based on the case studies it can be concluded that different coagulants show similar pollutant (COD, BOD₅, TSS, TP, PO₄-P) removal efficiencies; however pre-polymerised metal salts have smaller capability in phosphate precipitation. Removal of TP depends on the suspended solids removal rate, therefore very low residual TP can only be reached by applying phase-separation methods more efficient than settling. Iron(III)-containing coagulants can play a role in odour control at WWTPs as they are able to precipitate dissolved sulphides, thus prevent the formation of malodorous hydrogen-sulphide.
Normally, the price of the coagulant and the method of sludge treatment and utilization will be decisive when selecting the optimal coagulant. However, optimum doses might vary a lot depending on the objectives. Significantly different doses are needed for the sufficient removal of the different pollutant substances requires, reflecting a conflict that requires optimisation.

Chemical pre-treatment can provide a cost-effective method to upgrade high-loaded WWTPs. It was estimated that 250 000 USD may be saved annually as operational cost when introducing chemical pre-treatment at a 13 000 m³/d capacity activated sludge plant.

ACKNOWLEDGEMENT
Part of the research presented in this article was carried out in the frame of “Development of Advanced Wastewater Treatment Systems to Meet EU Requirement” national R&D programme.

REFERENCES