# Dissolved air flotation of bioreactor effluent using low dosages of polymer and iron

*Esa Melin, Herman Helness and Hallvard* Ødegaard

## **INTRODUCTION**

Many cities still discharge large amounts of inadequately treated wastewater to marine waters. In many of these cities, the effluent standard that is to be met is secondary treatment. Secondary treatment is, however, not implemented because of excessive costs, lack of available land, and costly sludge disposal. These cities need a treatment method that is compact, reaches secondary treatment effluent standard, and has a minimal sludge production. A competitive solution would be a treatment plant consisting of fine screening/sieving for primary treatment, a highly loaded biofilm reactor, and a highly loaded separation reactor (Ødegaard *et al.* 2000).

The major part of the organic loading from municipal wastewater is in particulate matter (Levine *et al.* 1985; Ødegaard 1998; 1999). Therefore, with a good separation process, the major part of the organic loading can be removed. However, concentration of soluble organic matter is often too high for treatment plants to meet secondary standards with particle removal only. In the high-rate treatment concept, the intention is to operate the bioreactor at such high loading rates that it removes soluble matter but hydrolysis of particulate organic matter

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does not take place. The removal of particulate organic matter is left for separation reactor after the bioreactor.

Compact biological treatment systems require biofilm reactors. Biofilters clog easily at high loads of particulate matter, which results in too frequent filter washing. For high-rate treatment concepts, a moving bed biofilm reactor (MBBR) has been shown to be a good alternative since the process can accept high particulate and soluble organic loading rates (Ødegaard *et al.* 2000).

One alternative for a high-rate separation process is flotation. The flotation system can be used with higher loading rates than sedimentation and has been shown to be effective in secondary wastewater treatment (Ødegaard 2000; Filho and Brandao 2000). With flotation, sludge settleability is not an issue. This can be a problem in a MBBR at high soluble COD loading rates (Ødegaard *et al.* 2000). Flotation has become more attractive after recent developments of a very highly loaded flotation process (so called turbulent flotation) where the surface loading can be as high as 25-40 m/h (Kiuru 2000).

Optimal separation processes require addition of a coagulant. Inorganic metal salts are often used. However, with high metal dosages, the sludge production becomes high because of chemical precipitation. With use of cationic polymer the sludge production can be reduced but the dosages required can be relatively high (Fettig *et al.* 1990). When an inorganic metal salt is combined with low dosages of polymer, the metal dosage and sludge production can be significantly reduced without compromising treatment efficiency (Ødegaard 1998).

This paper reports the results from preliminary screening test of different cationic polyacrylamide (PAM) and poly-diallyl-N,N-dimethylammonium chloride (polyDADMAC) polymers. The purpose was to investigate what kind of polymer is best for flotation of the MBBR effluent and to find optimal dosage for coagulation with combination of metal salt and polymer.

### **EXPERIMENTAL SET-UP**

#### **Flotation experiments**

The principle of the treatment process is presented in Figure 1. A laboratoryscale MBBR was used to treat domestic wastewater, which was pumped into a buffer tank from a nearby residential area. The MBBR loading was very high with a detention time of only 15 min. An Aztec flotation jar tester (Severn Trent Services, Capital Controls Ltd, England) was used for flotation tests. One-litre samples collected from the MBBR outlet were used in each jar.

The iron and polymer were dosed with syringes under rapid mixing (400 rpm) which was continued for 0.5-1 min. The water was then flocculated for 20

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min while mixing with 80 rpm. In the flotation step, 150 ml of dispersion water (15% recycle rate) was used, saturated with air under 5 bar pressure. Distilled water was used as dispersion water. The dilution effect of dispersion water is taken into account when calculating in the results. The samples from clarified water were taken 10 min after dispersion water was applied.

Iron was dosed as JKL (FeCl<sub>2</sub>SO<sub>4</sub>), which is a product of Kemira Chemicals. PAMs were manufactured by Kemira and polyDADMACs were from Cytec.



Figure 1. Schematic of the treatment process.

#### Experimental design and data analysis

Designed experiments were used to evaluate the effect of polymer properties and polymer and iron dosages on the treatment results. Figure 2 shows the design regions for molecular weight and charge density. Two different designs were used for PAMs. In addition, three different low molecular weight, high charge density polyDADMACs were tested.

The low iron dosages varied from 0 to 0.2 mmol Fe/l and polymer dosages from 0.5 to 3 mg/l. Some polyDADMAC tests were done with polymer dosages up to 3.4 mg/l and 0.3 mmol Fe/l. Since a real wastewater was used in the experiments, the wastewater quality could not be used as a design variable.

The results were evaluated using Partial Least Squares Regression (PLSR), a multivariate analysis method based on analysis of the variation in the data (Martens and Næs 1989). In the PLSR, a new set of x-variables called PLS components (PC) are computed in such a way that the first PC lies in the direction of the largest variation of the data. The second PC lies in the direction of second largest variation and so on. The logic is that the largest variation in the data is likely to be caused by important or real effects while small variations in

the data can be caused by less important effects or noise. One advantage of PLSR is that one avoids focusing on large variations in the x-data that have little importance for the variation in the response variables. Another advantage is that the PCs are orthogonal, i.e. linearly independent. Using PCs in regression can therefore overcome problems caused by collinear x-variables. However, one must be aware of the danger of over-fitting and meaningless results and put heavy emphasis on validation of the models.



Figure 2. Design regions for charge density and molecular weight ( $\blacksquare$  PAMs,  $\triangle$  polyDADMACs).

The multivariate regression model has so far been developed for suspended solids (SS) removal. The conclusions from the model are presented and the average results from experiments are used to illustrate the observed effects.

#### Wastewater

The effluent from the MBBR was used in the flotation tests. The water quality is presented in Table 1 for the tests with PAMs and polyDADMACs. The temperature of the water was 9-11°C.

Table 1. Raw water quality during the experminents.

	PAMs			PolyDADMACs		
	Average	Min	Max	Average	Min	Max
SS (mg/l)	143	98	187	111	53	163
COD (mg/l)	249	161	316	207	115	306
SCOD (mg/l)	67	51	92	61	39	125
pH	7.71	7.54	7.92	7.70	7.43	7.89

## **RESULTS AND DISCUSSION**

### Effect of polymer and iron dosage

The multivariate regression model shows that the treatment results are primarily governed by the polymer and iron dosages. The effect of polymer dosage was linear for both types of polymer. The response for iron dosage showed curvature, i.e. the effect of iron on the treatment results becomes smaller with increasing iron dosage. Figure 3 shows the average SS removals in all the tests with different polymers. Without metal coagulant, only moderate removal of SS is achieved. At PAM dosages of 1.75 and 3 mg/l, increasing iron dosage from 0.1 to 0.2 mmol Fe/l did not increase removal efficiency as much as demonstrated between no iron and 0.1 mmol Fe/l, explaining the curved response in the model. The curved response is difficult to see in the polyDADMAC results, probably due to variation in the wastewater quality as discussed below.



Figure 3. Effect of iron and PAM (a) or polyDADMAC (b) dosages on suspended solids removal (♦ 0 mmol Fe/l, □ 0.1 mmol Fe/l, ▲ 0.2 mmol Fe/l, ◊ 0.3 mmol Fe/l). Lines show model predictions.

The lines in Figure 3 show the model predictions for SS removal. The model fits the experimental results well and shows that the variations in the removal efficiency are a result of varying raw water quality rather than experimental error. Generally, the removal efficiency is similar between PAMs and polyDADMACs but polyDADMACs give slightly higher SS removal with 0.2 mmol Fe/l. With 3 mg/l of polymer and 0.2 mmol Fe/l the SS removal efficiency varied with PAMs from 72 to 89% resulting in 16-46 mgSS/l

(average 29 mgSS/l) in the treated water. With polyDADMACs, the removal efficiency varied from 79 to 91% with residual SS of 6-21 mg/l (average 14 mg/l). However, because of the variation in the wastewater quality (Table 1), it cannot be concluded that polyDADMACs in general give better results than PAMs.



Figure 4. Effect of iron and PAM (a) or polyDADMAC (b) dosages on COD removal (♦ 0 mmol Fe/l, □ 0.1 mmol Fe/l, ▲ 0.2 mmol Fe/l, ◊ 0.3 mmol Fe/l).



Figure 5. Effect of iron and PAM (a) or polyDADMAC (b) dosages on SCOD removal (♦ 0 mmol Fe/l, □ 0.1 mmol Fe/l, ▲ 0.2 mmol Fe/l, ◊ 0.3 mmol Fe/l).

Figure 4 shows the removal of chemical oxygen demand (COD) in the flotation tests. The removal patterns are the same as with SS although overall removal efficiencies are lower. Figure 5 shows the removal of soluble COD (SCOD). Only minor removal is observed in tests without metal coagulant and iron improves SCOD removal. Soluble COD is normally defined as the COD

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measured after filtering sample through GF/C filter, which has a nominal pore size of about 1  $\mu$ m. This fraction still includes some colloidal material and the truly soluble fraction is below 0.1  $\mu$ m. Therefore, the removal of SCOD can actually be coagulation of the colloidal fraction.

## Effect of raw water quality

The multivariate analysis indicates that the raw water SCOD and pH influenced SS concentration in clarified water with PAMs. In the case of polyDADMACs, the raw water COD and SS affected the treatment efficiency while pH and SCOD did not have a significant effect. Figure 6 shows the effect of raw water SCOD on SS removal for all the tests. With PAMs, removal efficiency decreases when SCOD is over 65-70 mg/l while the polyDADMAC results are unaffected by raw water SCOD. However, the results need to be verified by further tests because the PAM results with high SCOD concentration are from experiments without iron dosage while the polyDADMAC results with high SCOD concentration are from experiments with 0.2 mmol Fe/l.



Fig. 6. Effect of raw water SCOD on SS removal in flotation test using PAMs (a) and polyDADMACs (b) (♦ 0 mmol Fe/l, □ 0.1 mmol Fe/l, ▲ 0.2 mmol Fe/l). Lines show model predictions.

Figure 7 shows the results for both polymers. While they seem to confirm the model, the raw water pH varied only in a very narrow range (from 7.4 to 7.9) and therefore the results are not very conclusive. However, the results indicate that PAMs are more sensitive to raw water quality like SCOD and pH than polyDADMACs.





Fig. 7. Effect of raw water pH on SS removal in flotation test using PAMs (a) and polyDADMACs (b) (♦ 0 mmol Fe/l, □ 0.1 mmol Fe/l, ▲ 0.2 mmol Fe/l). Lines show model predictions.

## Effect of polymer properties

The model indicates that with PAMs there is an effect of the molecular weight that depends on the iron dose. The model predicts that when iron is not used or the dosage is low, it is a benefit to have a high molecular weight polymer. When the iron dosage is increased, slightly better results are predicted with a low molecular weight polymer. Figure 8a shows the average results from all the tests done with different polymers. It should be noted that the wastewater quality and average polymer dosages are not the same for the different data points. The average trends in the data for the different iron dosages support the results from the model. Without iron, the removal efficiency is lowest with low molecular weight PAMs. If the polymer is going to be used alone without metal coagulant, low molecular weight PAMs do not seem to be the best alternative as also observed by Pilipenko and Ødegaard (2002). In Figure 8b, the model prediction of the different data points is included. The good agreement between the model and the experimental results shows that the scatter in the results can largely be explained by the variation in the wastewater quality and polymer dosage.

The model for PAM indicates that a high charge density is a benefit. Figure 9a shows the removal efficiency versus charge density of the polymer with all the tested polymers. In these figures, also polyDADMAC is included for comparison (charge density 6.2 meq/g). The average trend in the PAM-data with iron doses of 0.1 and 0.2 mmol Fe/l supports the model, while the average trend for the PAM-data with no iron shows the opposite. However, this is due to two data points with high removal at charge densities of 0.3 and 1.8 meq/g. In

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Figure 9b, the model prediction of the different data points is included. The good agreement between the model and the experimental results indicate that the scatter in the results can largely be explained by the variation in the wastewater quality and polymer dosage. The results for both molecular weight and charge density demonstrate that although these polymer properties probably have an effect on the removal efficiency, they are small compared to the effect of dosage and wastewater quality.



Figure 8. The effect of molecular weight on SS removal efficiency with different iron dosages for all the tested PAMs (a) and the same results together with the model predictions (b) (♦ 0 mmol Fe/l, □ 0.1 mmol Fe/l, ▲ 0.2 mmol Fe/l).



Fig. 9. Effect of charge density of the polymer on the SS removal with all the tested polymers (a) and the same results together with the model predictions (b) ( $\blacklozenge$  0 mmol Fe/l,  $\Box$  0.1 mmol Fe/l,  $\blacktriangle$  0.2 mmol Fe/l).

There were no significant differences between the tested polyDADMACs. Also, the best PAMs performed equally with polyDADMACs. When a PAM is used together with iron, the best choice seems to be a medium molecular weight, high charge density polymer.

## COD fractions in the flotated water

In some tests, COD was analysed from water samples that were filtered through filters having different pore size. Figure 10 shows the COD fractions in raw water and flotated water. In the experiment, polyDADMAC was used at variable dosages (0.6-3.4 mg/l) and the iron dosage was 0.2 mmol Fe/l. The results show that particles above 11  $\mu$ m are effectively removed by flotation, which is consistent with general understanding that flotation is effective in removing particles down to 10  $\mu$ m in size (Kiuru 1990). The truly soluble COD fraction (<0.1  $\mu$ m) is the largest fraction in the clarified water and is not removed very well. Since the aim is removal of particulate organic matter, this size fraction is of no interest. The preceding biological process should be operated so that the truly soluble fraction is removed to desired levels. The results show that the observed SCOD removal is mostly the removal of colloidal material (size fraction 0.1-1  $\mu$ m). The 1-11  $\mu$ m size fraction is, however, critical for successful particle removal and further process optimisation should concentrate on good flocculation of this particle size range.



Figure 10. Particulate COD fractions in raw water and flotated water with different polyDADMAC dosages and 0.2 mmol Fe/l iron.

## CONCLUSIONS

- 1. The results show that good SS removal can be obtained by flotation when low dosages of iron and polymer were combined.
- 2. The dosages of iron and polymer together with raw water properties like SCOD are more important than molecular weight or charge density of the polymers.
- 3. There were no significant differences between polyDADMACs and the best PAMs. The results indicate that with metal coagulant, the best PAM is medium weight, high charge density polymer. Without metal, high molecular weight PAMs give the best result.
- 4. Multivariate analysis is a good tool when analysing results with variable water quality. Although the regression model developed for SS removal were able to predict the results well, it needs additional tests to fill the gaps in the data set and an independent verification test.

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## CONTACT

Hallvard Ødegaard, Department of Hydraulic and Environmental Engineering, Norwegian University of Science and Technology, N-7491 Trondheim, Norway. E-mail: <u>Hallvard.Odegaard@bygg.ntnu.no</u>