# DAF with cationic microbubbles

## -Treatment of oily waters-

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## Background

Many types of oily wastewaters are produced by various industries. The oil and grease concentration of these wastewaters varies significantly, from 14 even to 200 000 mg $L^{-1}$ [1] possessing a huge challenge to their treatment.

Dissolved air flotation (DAF) has been a widely used treatment method for oily wastewaters, because it has proved to be reliable and simple treatment method. The microbubbles are produced by dissolving air under pressure and releasing air supersaturated water to the vessel at normal air pressure. These unmodified microbubbles are known to be negatively charged [2]. The electrostatic repulsive force between the oil droplets (negatively charged) and microbubbles could be avoided by modifying the charge of microbubbles to cationic. The treatment of oily waters with modified bubbles, as far as we know, has not been previously published. Henderson et al. [3-5] studied the effect of different chemicals on air bubble charge, and treatment of algae containing water with these modified bubbles. They referred to the process where a positively charged chemical was added into the saturator for bubble modification as *PosiDAF*.

## Objectives

1. To study the efficiency of DAF for the treatment of 2 m-% oil-in-water (O/W) emulsions by adding a selected chemical directly into the saturator or by first performing coagulation-flocculation followed by DAF. For comparison PosiDAF with the most potential chemical was also performed on real oily wastewater samples.
   - The performance of DAF was evaluated by measuring chemical oxygen demand (COD), total surface charge (TSC) and with flow cytometry (FCM).
2. The usability of FCM was studied for the determination of hydrophobic particles in O/W emulsions and real oily wastewaters.
3. Study the interaction between microbubbles and *PolyDADMAC* polymer.

## Experimental

### 1. Samples

- 2 m-% synthetic O/W emulsions
- Real oily wastewaters from a commercial ultrafiltration (UF)-based treatment train (Fig. 1).

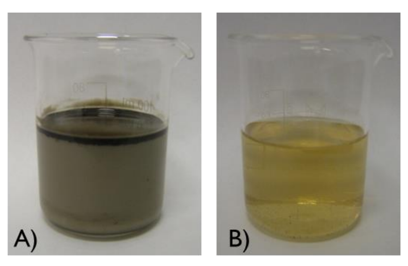


*Fig. 1. Real oily wastewater A) before and B) after UF treatment.*

### 2. Studied chemicals

- Cationic surfactant *CTAB* (cetyltrimethylammonium bromide, $C_{19}H_{42}BrN$) by Acros Organics.
- Polymer *PolyDADMAC* (polydiallyldimethyl-ammonium chloride, the concentration of 40%) by Kemira Oyj.
- Polymer *Epi-DMA* (epichlorohydrin-dimethylamine copolymer, the concentration of 50%) by Kemira Oyj.

### 3. Analyses

- COD, Hach Lange photometric cuvette test
- TSC, Mütek PCD 03 pH
- FCM (samples stained with Nile red), Partec CyFlow ML.

### 4. DAF set-up

The apparatus for DAF studies is presented in Fig. 2. DI-water was first added to the saturator until 10% of the packings was under water. The chemicals were studied by adding them directly to the saturator before pressurizing (5 bar) the vessel or first performing conventional coagulation-flocculation. The DI-water with/without chemical was circulated with a Tapflo diaphragm pump for four hours. DAF flotation studies were then performed. The samples were taken from the bottom of the flotation column 10 minutes after the feed of dispersion water was stopped.

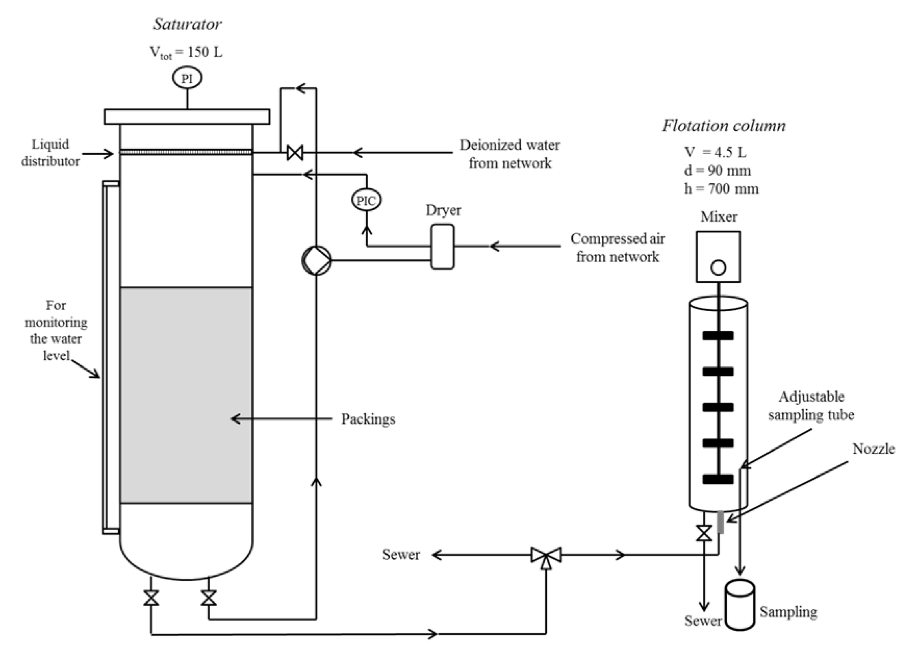


*Fig. 2. DAF set-up*

### 5. DAF studies

I. DAF studies without chemical for treatment of O/W emulsion.

II. *PosiDAF* studies for treatment of
   - O/W emulsions with *CTAB*, *PolyDADMAC* and *Epi-DMA*.
   - Real oily wastewaters with *PolyDADMAC*.

III. Coagulation-flocculation studies for O/W emulsions with *CTAB*, *PolyDADMAC* and *Epi-DMA* were performed by adding the chemical with different stock solution volumes into the column. Flash mixing at 400 rpm (60 s) and slow mixing at 40 rpm (15 min) were performed. Dispersion water was fed to the column after slow mixing. The samples were taken from the bottom of the column 10 minutes after the feed of dispersion water was stopped.

IV. The interaction between microbubbles and polymer was studied by performing *PosiDAF* with *PolyDADMAC* for pure DI-water and the conventional coagulation-flocculation for *PolyDADMAC*-water solution. After stopping the dispersion water feed, samples were taken as a function of time from different heights from the column.

## Results and Conclusions

- The COD reductions of O/W emulsions using *PosiDAF* with *PolyDADMAC* were higher than for conventional coagulation-flocculation followed by DAF (see Fig. 3).

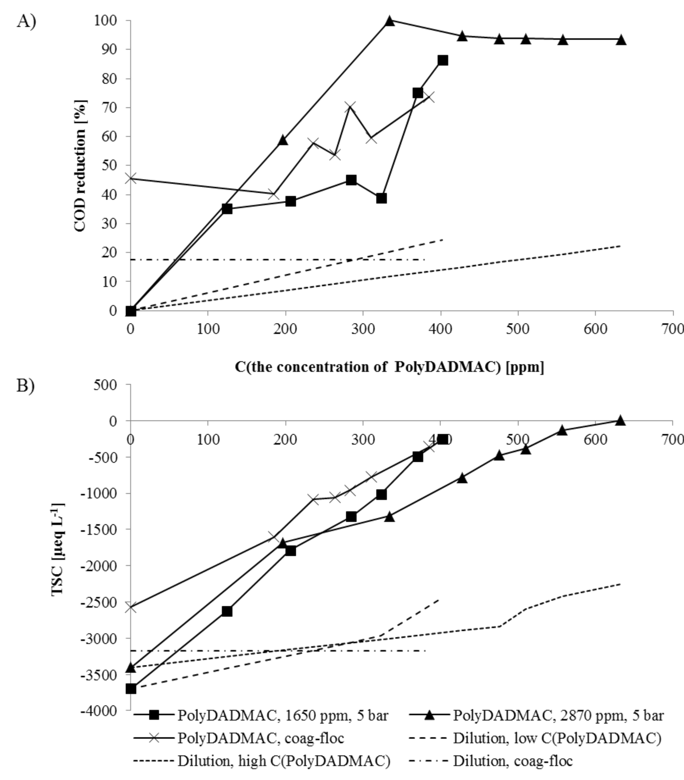


*Fig. 3. A) COD reductions and B) development of TSC values for DAF studies with PolyDADMAC for O/W emulsions.*

- *PosiDAF* with *PolyDADMAC* proved to be more efficient than with *Epi-DMA* for the treatment of O/W emulsions, probably due to its slightly higher MW.
- The performance of *PosiDAF* with *PolyDADMAC* in the treatment of real oily wastewater was very high; a COD reduction of 70% with an optimal dosage of 200 ppm *PolyDADMAC*.
- The performance of PosiDAF using the CTAB surfactant was poor, although better than for coagulation-flocculation with CTAB.
- The spreading of *PolyDADMAC* in function of time after feeding of dispersion water was stopped differed between *PosiDAF* and the conventional coagulation-flocculation.
  - ➢ An indication of cationic bubbles formed in PosiDAF with *PolyDADMAC*!
- FCM proved to be a potential analysis method for waters containing oils.
- *PosiDAF* proved to be effective treatment method for oily waters containing highly stable O/W emulsions.
- The article Karhu et al. [6] concerning all the results is in press.

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