EFFECT OF PRE-FLOTATION BY OILY WASTE WATER COMBINED TREATMENT

KISS ZS. L.1 – KESZTHELYI-SZABÓ G.1 – HODÚR C.1 – LÁSZLÓ ZS.1

1Szegedi Tudományegyetem, Mérnöki Kar, 6725 Szeged, Moszkvai krt. 9.

Summary
Large amount of oily wastewater is generated in process industries. The waste waters containing oil in low concentrations generally can not be purified by conventional treatments. The aim of our work was to investigate the effect of pre-flotation before ozonation combined with microfiltration (MF). The results showed that 2 minute long pre-flotation effectively reduced the oil content of the waste water, enhancing the efficiency of combined process. About 20% increased the COD elimination efficiency with pre-flotation and pre-ozonation combined with MF (90,00%) as alone the MF (70,45%). It was found that pre-ozonation changed the chemical nature of the emulsified particles, but depend on the time of the ozonation and therefore affected the filtration parameters, such as the retention increasing, and membrane surface hidrophobicity changed.

Introduction
The continuous expansion of hydrocarbon processing industry and the extensive utilization of oil-related products in most industrial branches (automobile industries, aircraft plants, chemical industries, machine shops, etc.), have increased the threat of oil pollution to the aquatic environment.[1-2] The oily wastewater emulsions change in the concentration range of 50–1000 mg/L.[3] The separation of oil from a dilute low concentration emulsions of oil and water is a problem that occurs in a number of aqueous discharges.[4] Conventional methods of oily wastewater treatment include gravity separation, air flotation, coagulation, demulsification and biochemical treatment, alone are not efficient enough to treat stable oil-in-water emulsions that contain oil droplets smaller than 20 \( \mu \text{m} \). But it can be combined with membrane separation to increase the separation efficiency. Flotation is an operation used to separate solids or liquids particles from a liquid phase. Flotation techniques, in which finely suspended particles are separated by adhering to the surface of rising bubbles, have proved efficient, practical and reliable separation methods for the removal of oils, as well as other contaminants, such as dissolved ions, fats, biomolecules and, or suspended solids from water. Flotation is mainly used, when the application of sedimentation is not feasible, due to the presence of extremely fine particles or globules, which do not possess a significant settling rate, because the phases do not appreciably differ in density from the parent liquid. The flotation process involves a number of physical phenomena simultaneously occurring while several variables have been found to influence the process. It has also been theoretically predicted that the collection efficiency of emulsions will be increased, by increasing the droplet size and decreasing the bubble size. [5-8] Nowadays, membrane separation techniques are continuously receiving increasing attention for the treatment of water containing high levels of organic matter, owing to their remarkable advantages such as superior water quality, the removal of a wide range of contaminants, easier control of the operation parameters and space saving capabilities. However, the decline
of membrane permeate flux during operation, due to fouling, is a significant limiting factor in the development and applicability of these membrane separation processes.[9, 10]

MF of oil-in-water emulsions has been investigated experimentally in recent decades. This membrane process has shown to be effective and represents a possible separation solution.[11–15] Membrane materials are also important for oil-in-water emulsion separation, and it has been recognised that hydrophilic materials are less sensitive to adsorption compared to hydrophobic ones; therefore, hydrophilic membrane materials may be considered as a key solution in reducing membrane fouling.[16] Pre-oxidation results in improved flocculation efficiency and particle removal during filtration.[17] In ozone-UF systems, the ozone treatment, like a pre-treatment, always causes a remarkable decrease in the cake resistance \((R_c)\) and an increase in the fouling resistance \((R_F)\).[18] Based on measurements of the particle-size distribution and the zeta potential, a reduction in \(R_c\) through ozonation was attributed to the increasing particle size, which was caused by "ozone-induced particle destabilisation".[18]

This article addresses the MF of oil-in-water emulsions when using pre-flotation and different pre-ozonation times before the filtration experiment. MF studies were targeted to study the effect of pre-flotation, pre-ozonation on the oily water emulsion and the filtration parameters (i.e., flux, filtration resistances and oil rejection).

**Materials and Methods**

**Materials**

A model oil-in-water emulsion, with an oil concentration of 0.01 wt.%, was prepared from petroleum (produced by Nógrádi Erdőkémia Kft. Hungary) by using ultrasonication for 20 min.

**Experimental Design**

The oil-in-water emulsion was treated with oxygen and ozone for a given time and the treated solution was then promptly used as the feed in the MF experiments. The volume of floated water was 0.5 L and the oxygen gas flow rate was 1 L min\(^{-1}\). The flotation experiment carried out in a batch reactor, it was used oxygen, the treatment time was 2 or 10 minute. After the flotation, it was separated with gravity.

Ozone was produced from oxygen (Linde, 3.5) by using a flow-type ozone generator (BMT 802X, Germany). The ozone-containing gas was bubbled continuously through a batch reactor (same as in the flotation experiment) during the treatment. The volume of treated water was 0.5 L and the gas flow rate was 1 L min\(^{-1}\). The ozone concentration in the gas was measured before and after the reactor by using a UV spectrophotometer (WPA Biowave 2+) at a wavelength of 254 nm. The amount of absorbed ozone was 1.15, 4.45, 18.96, 51.75 and 94.06 mg L\(^{-1}\) at treatment times of 2, 4, 8, 12 and 16 min, respectively. The membrane filtration experiments were carried out in a batch-stirred cell (Millipore, XFUF04701) with a capacity of 50 cm\(^3\). Flat-sheet polyethersulfone (PES) membranes with a pore size of 0.2 \(\mu\)m and a membrane effective area of 0.001734 m\(^2\) were used (PL series, Millipore). Before each MF experiment, the membrane was immersed in distilled water overnight. The initial feed volume was 50 cm\(^3\) and experiments were carried out at 10 kPa until 10 cm\(^3\) of the total sample had been filtered at a stirring speed of 50 rpm. Determination of the chemical oxygen demand (COD) was based on the standard method, which involves potassium dichromate oxidation. For the analyses, standard test tubes (Lovibond) were used. The digestions were carried out in a COD digester (Lovibond, ET 108) and the COD values were measured with a COD photometer (Lovibond PC-CheckIt). The particle-size distribution (within the range 0.1–1000
µm) was measured using a Mastersizer 2000 (Malvern Instruments); the injection temperature was 20 °C. Viscosity measurements were carried out with a Vibro viscometer (AND SV-10 A&D Company, Japan) in a temperature-controlled water bath (Cole Palmer, USA) at constant temperature of 20.0 ±0.1 °C. The density of each solution was measured at 20 °C with a Density 30PX digital density meter (Mettler Toledo, Japan). Membrane hydrophobicity was quantified by measuring the contact angle that was formed between the membrane surface (before and after filtration of solutions) and water. Contact angles were measured using the sessile drop method (Dataphysics Contact Angle System OCA15Pro, Germany).

**Resistance-in-Series Model**

The membrane resistance \( R_M \) was calculated as:[22]

\[
R_M = \frac{\Delta p}{J_w \eta_w} \text{ (m}^{-1}\text{)}
\]  

(1)

where \( \Delta p \) is the pressure difference between the two sides of the membrane (Pa), \( J_w \) is the water flux of the clean membrane and \( \eta_w \) is the viscosity of the water (Pas).

The \( R_F \) was determined by measuring the water flux through the membrane after the MF and rinsing it with deionised water to remove any particles of the residue layer from the surface, and then by subtracting the resistance of the clean membrane:

\[
R_F = \frac{\Delta p}{J_{wR} \eta_w} - R_M
\]  

(2)

where \( J_{wR} \) is the water flux after the concentration test. The resistance of the polarisation layer \( (R_P) \) can be calculated as:

\[
R_P = \frac{\Delta p}{J_c \eta_{ww}} - R_F - R_M
\]  

(3)

\( R_T \), the total resistance \((\text{m}^{-1})\), can be evaluated from the steady-state flux by using the resistance-in-series model:

\[
R_T = R_M + R_F + R_P
\]  

(4)

The selectivity of a membrane for a given solute can be expressed by the average retention \((R)\):[23]

\[
R = \left(1 - \frac{c}{c_0}\right) \cdot 100\%
\]  

(5)

where \( c \) is the average concentration of the solute in the permeate phase and \( c_0 \) is the concentration of the solute in the feed.

**Results and Discussion**

**Effect of pre-flotation**

In the first series of experiments, the effect of pre-flotation on COD elimination efficiency was investigated. Figure 1a demonstrates that the chemical oxygen demand (COD) elimination efficiency was reduced with flotation. Combination of two methods (pre-flotation and microfiltration) resulted higher purification. The results showed that 2 minute flotation gave higher COD reduction as 10 minute flotation, but stabilised flux value was slightly higher as 2 minute flotation (Figure 2b). This phenomenon can be explained by the effect of long time flotation, because long time flotation may be reduced the bigger droplet size oil rate on the top of the flotated solution, they can may be solved to the emulsion, as the Figure 1a presented, and therefore showed lower elimination efficiency at the combined membrane separation processes.
Effect of pre-ozonation on MF

In the next series of experiments after 2 minute flotation with O₂ was treated with O₃ (2-16 min). Pre-ozonated oil emulsions were filtered through 0.2 μm PES membranes. Figure 2a depicts stabilised fluxes with function of ozone treatment time (the 0 minute means 2 minute pre-flotation after microfiltration). It was found that pre-ozonation slightly decreased the flux, but increasing ozonation time increased the stabilised flux. The COD retention changed with flux; lower ozone doses decreased the COD retention, whereas further ozonation increased the COD retention. This can be explained by ozone-induced decomposition of hydrocarbon molecules. The smaller reaction products were able to pass through the membrane, resulting in a lower COD in the retention phase (Figure 2b). However, in oil emulsions in cross-flow MF above the membrane surface, the droplets may become deformed, break up and penetrate into the pores,[13] as the size of the drop is bigger than the size of the pore.[14] Further ozone treatment may be cause micelle formation of molecules and reduced the COD value after the longer ozone treatment, and reduced the concentration polarization caused retention, therefore, achieving a higher COD elimination. The highest COD elimination value was achieved after ozone treatment for 12 min.

Calculation of the filtration resistances also showed that the ozone treatment affected the polarisation layer resistances. Shorter ozonation times resulted in higher $R_p$ values (Figure 3), according to the lower flux. Further ozonation decreased the polarisation layer resistances. The COD elimination value (Figure 2b) and filtration resistances indicate that the optimum time for pre-ozonation before membrane separation is 12 min. The resistance value showed
that without pre-flotation and pre-ozonation achieved very similar resistances, as pre-flotated and 12 min ozonated wastewater, but the COD elimination was the best at pre-flotated and 12 min ozonated wastewater. The background of the decreased polarization layer resistance increased by ozonation time phenomena was the oil molecules polarity changing, therefore it can be diffused back into the bulk-feed solution.

As the ozone treatment changes the chemical nature of the particles in the emulsion (e.g., the polarity of ozonated molecules), the interaction between the solution and the membrane surface can also change. The contact angle measurements showed that after filtering the oily water, the membrane surface became less wettable than the clean membrane surface may be due to the oil content of the solution. But the filtration of ozone-treated solutions decreased the wettability of the membrane with increasing ozonation times (Figure 6). This phenomenon explains the increasing flux with increasing ozonation time; the increased hydrophilic character of the membrane helps to pass water through the membrane.

**Figure 3. Filtration resistances.**

**Figure 6. Changes of contact angle as a function of ozonation time.**

**Conclusions**

Untreated, pre-flotated and flotation-, ozone-treated petroleum (0.01 wt.%) oil-in-water emulsions were filtered with a 0.2 μm PES MF membrane. The results showed that 2 minute flotation helps to reduced the COD at the microfiltration permeate. It was found that pre-ozonation changed the chemical nature of the emulsified particles, causing a change in the interactions that occurred between the solution and the membrane surface, which thus affected the filtration parameters. A short ozone-treatment time caused degradation of long-chain hydrocarbon molecules, which were formed when smaller molecules and deposited on the membrane, resulting in a slightly decreased permeate flux and decreased COD retention.
Further ozone treatment led to a considerable amount of large amphiphilic molecules to be produced; micelle formation could occur, resulting in a less deformable particles. These particles diffused back into the bulk-feed solution, causing an increased COD retention.

Acknowledgements
The authors are grateful for the financial support provided by the OTKA project (project number OTKA K105021). The research is supported by the European Union and co-funded by the European Social Fund. Project title: “Green Energy Cooperation in Higher Education (GENCHE)” Project number: TÁMOP-4.1.1.C-12/1/KONV-2012-0012.

References