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DETERMINATION OF THE MODIFIED FOULING INDEX (MFI) AND COMPRESSIBILITY OF THE CAKE-LAYER ON A MEMBRANE DURING ULTRAFILTRATION FOR OILY WASTEWATER TREATMENT

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Oily wastewater is one of the major pollutants that occur in many industrial fields and it is very harmful to the environment, especially aquatic life. All conventional methods for the treatment of oily wastewater, such as dissolved air flotation (DAF), coalescence and adsorption have their advantages, but none is effective enough. Therefore, membrane technology appears to be a promising method which offers many possibilities regarding membrane materials, process configuration and operational parameters (high pressures, temperature, crossflow etc.). However, the main problem in membrane filtration is fouling. In this study the Membrane Filtration Index (MFI) was extended to improve the precision of MFI for oily wastewater. A tubular module with a PES membrane was used in a crossflow ultrafiltration mode. In order to examine the correlation between the measured cake resistance and rejection of different feed components (COD, TSS, Fe, etc.), laboratory analyses were performed. It was found that formed cakes were compressible and the values of cake resistances were almost the same for different parameters even if rejection values increased.

INTRODUCTION

Oil and grease are common pollutants in a wide range of industries. Stable oil in water emulsions are generated in diverse industrial technologies; steel, aluminium, food, textile, leather, petrochemical and metal finishing are some that report high levels of oil and grease in their effluents. In the past, waste emulsions were often discharged to either sewers or public waterways without prior treatment, causing environmental pollution and loss of oil. In recent years, considerable attention has been focused on the discharge of oily wastewaters, since these and oil in water emulsions are one of the main pollutants discharged to water environment. Pollution of water by oily hydrocarbons is especially harmful to aquatic life. Consequently, removing oil from wastewater is an important aspect of pollution control in many fields of industry[1].

The wastes include oil-water emulsions as well as free oils. During die-casting procedures, oil in water emulsions are used as lubricants and coolants in steel rolling operations. After being used, the fluids become less effective because of thermal degradation and contamination by substances during suspension and therefore, must be replaced periodically, generating a waste stream called 'spent cutting oil'. Spent cutting oil emulsions are one of the largest volumes of wastewater in the metal working industries.

Depending on specific applications, an oil in water emulsion can consist of up to 95% water, the rest being a complex aqueous mixture which comprises different kinds of oils (mineral, animal, vegetable and synthetic), alcohol, sequestrants, surfactants, emulsifiers, corrosion inhibitors, antifoaming and extreme pressure agents. The treatment and recovery of spent oils from oily wastewaters is of environmental and commercial importance.

OILY WASTEWATER TREATMENT

The removal of oily wastewater can be accomplished by means of several well known and widely accepted techniques. Conventional approaches to treat oily wastewaters include gravity separations, API unit and skimming, dissolved air flotation, de-emulsion coagulation and flocculation[2]. However, these methods are not effective for removing smaller oil droplets and emulsions[3]. Membrane technology has become a mature separation technology over the last 30 years and is becoming a promising technology. Membrane processes, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) are being increasingly applied in the treatment of oily wastewater, especially in applications where the value of the recovered material is high or in applications where the savings from the reduced waste volumes are high[4].

In order to separate oil from water by ultrafiltration, the emulsion containing cutting oil droplets with diameters of less than 5 μm is circulated through an ultrafilter equipped with a water permeable porous membrane, whose pores have a diameter of approximately 0.01 μm. Treatment processes employing ultrafiltration exhibit undoubted advantages. They consume very little energy, the treatment plants are small in size and, after treatment, the water is free from cutting oil. In addition, no on-going human maintenance is needed, as in the case of the physicochemical processes and, consequently, they can be easily automated which is a considerable advantage in the present context.

FILTRATION PERFORMANCE

The parameters that influence the filtration performance are the feed composition, membrane properties and filtration conditions[5]. Three main classes of phenomena concerning solvent and solute transport during membrane filtration are concentration polarization, internal mass transport and fouling[6]. They can be affected by changing the following parameters: hydrodynamics, mass transfer and thermodynamic equilibrium.

The primary limitation of the conventional crossflow UF system in the treatment of concentrated oily wastewater is the low flux observed at high oil concentrations because of membrane fouling, which can be reversible or irreversible. The fouling of membranes typically occurs because of the inorganic and organic particles present in the wastewaters which adhere to the surface and pores of the membrane as well as deposition of particles at the membrane surface due to concentration polarization. This results in a deterioration in performance (reduction of permeate flux) with a consequent increase of energy and membrane replacement costs[7].

MODIFIED FOULING INDEX (MFI) AND CAKE COMPRESSIBILITY

The accumulation of solids (fouling) takes place over three distinct stages:

1. Blocking filtration - blocking of pore spaces by solids whose size is at least that of the size of the pore spaces in the membrane
2. Cake filtration without compression- formation of a continuous deposit of particles that form a cake layer
3. Cake filtration with compression - as cake thickness and hydraulic gradients increase.

Solids (particles) that are retained by the membrane during filtration, add additional resistance to the membrane. The reduction in flux can be described by the resistance in series model[8]. Initially only the membrane provides a resistance to water flux and membrane permeability is a function of membrane properties such as thickness, pore size and porosity. Particles adsorbed inside pores or blocking pore entry restrict the flow and reduce the flux. Particles may build up on the membrane forming a filter cake. The standardized filtration tests called Membrane Filtration Index (or Modified Fouling Index, MFI) is based on cake filtration and can be used to model flux decline or pressure increase in order to maintain constant capacity in membrane systems. In general, smaller particles in the cake result in higher MFI values[9].

In this study, the MFI, a standard test for the rate at which particles clog a membrane filter, was extended to improve the precision of MFI for oily wastewater. The MFI was determined graphically as the slope of the linear portion of the curve obtained by plotting (t/V) against V, having units of s/L^2, considering the cumulative volume of filtrate (V) and filtration time (t). Assuming that pore blocking and adsorption is negligible compared to cake formation, MFI is given as

$$MFI = \frac{\mu \alpha C_b (1-\gamma)}{2 \Delta P A^2} \qquad (1)$$

where μ is the filtrate viscosity (Pa s), α the average specific resistance (m/kg), C_b the feed concentration (kg/m^3), γ the fraction of material that is removed from the membrane again (-), ΔP the pressure drop across the cake (Pa) and A the membrane area (m^2). The equation is based on Darcy's Law and it should also be noted that the MFI is also valid for compressible cakes as when the pressure drop over the cake is dominant, a linear relationship between t/V vs. V is apparent and the MFI value can then be determined.

For non-compressible cakes, α is a constant. When the cake is not compressible, high ΔP results in high flux. However, for wastewater, the specific resistance often increases linearly with increasing pressure drop so the flux is constant (and does not increase when pressure is increased). Hence, for non-compressible cakes MFI decreases with increasing pressure, whereas MFI is independent of pressure for highly compressible cakes

MATERIALS AND METHODS

A tubular module was used with a polyethersulphone (PES) membrane (area = 0.82 m^2) for evaluation of UF performance in a crossflow mode. The feed solution was oily wastewater from the metal industry which was filtered and the filtrate volume monitored. Operation of the pilot plant was for three months at more or less constant conditions. The feed and permeate samples were analysed for pH, conductivity, turbidity, COD, Fe, Al, TSS, and lipophilic compounds, according to standards (ISO and EPA), in order to examine rejection and membrane selectivity.

RESULTS AND DISCUSSION

Figures 1-3 present the results obtained from three months of operation. The points are experimental values, the curve represents the modelled calculations and the line shows the linear slope for obtaining the initial MFI values.

In the first month of operation, almost 7000 L of oily wastewater was filtered (Figure 1). From the linear second region, the MFI was determined to be 5.34x10^{-5}, which indicates that the fouling rate was quite low. The model fits the experimental values well. It should be noted that the model represented for MFI does not include the phenomenon of pore blocking, which may impact the resistance. Pore blocking occurs during the initial part of membrane filtration because the cake protects the membrane and collects fine particles. The intercept between the simulated curve and abscissa (V = 0) is a function of the initial resistance, which is the sum of membrane resistance and pore blocking resistance. The pore blocking resistance is unknown and initial values for the resistance were therefore excluded, since they influenced the calculations for the model.

In the second month of membrane operation, the model still fitted (R^2 = 0.96) the experimental values well. The volume of filtered oily wastewater was lower than before. The MFI was calculated to be 1.28x10^{-4} as determined from the slope of the line. The third region of the plot (after 3000 L) showed an increased slope compared to the value of MFI, which indicated a high level of cake clogging and/or cake compression.

In the third month of operation, about 4000 L of oily wastewater was filtered. From the linear part of the plot (1500-3000 L) the MFI was determined to be 1.71x10^{-4}. In this case some discrepancy between the modelled curve and experimental points was found, which showed a slightly slower fouling rate than predicted and also some inaccuracy and unevenness of operation. From the third region of the plot (above 3000 L) it can be seen that particles caused cake clogging and/or cake compression.

Cake Resistance and Feed Rejection

Membrane fouling is expected to affect solute rejection because the membrane fouling could originate from adsorption of organic species and adhesion of particles at the membrane or cake surfaces[10].

There are two types of hydraulic resistances that are generally encountered in UF, one is membrane resistance (R_m), the other is fouling resistance which can be cake resistance (R_c) as described by the MFI and/or pore blocking (R_p). Both the membrane and the thin cake layer offer resistances to solvent transport[11]. In our case the correlation between cake resistance and feed rejection was studied. The cake layer deposited over the membrane surfaces played an important role in solute rejection, i.e. the predominant solute removals were attributed to sieving and/or adsorption onto the cakes. Also, some parts of solutes were adsorbed into the membrane pores and surfaces[10].

Figure 4 shows the dependence of cake resistance on the rejection of specific parameters. From the data presented in Figure 4 a clear tendency cannot be seen. For iron (Fe) the rejection seems to be high if the resistance is high. In general, the highest rejection is obtained at the highest cake resistances. The resistance influence regarding COD rejection is between 0.02 and 0.04 for most of the time, even if rejection

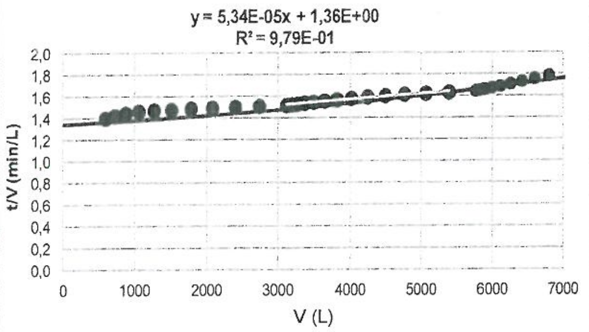

Figure 1: Operating within the first month: t/V vs. V.

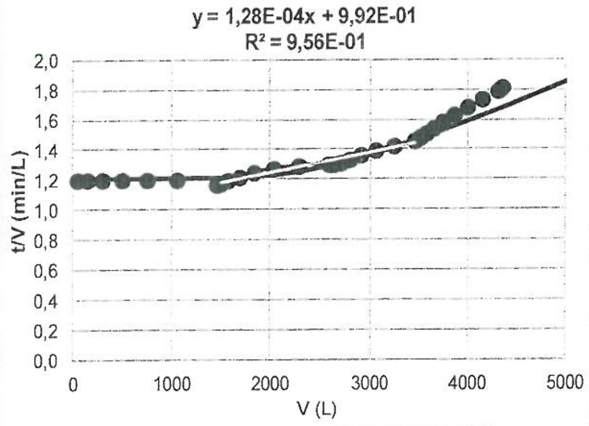

Figure 2: Operating within the second month: t/V vs. V.

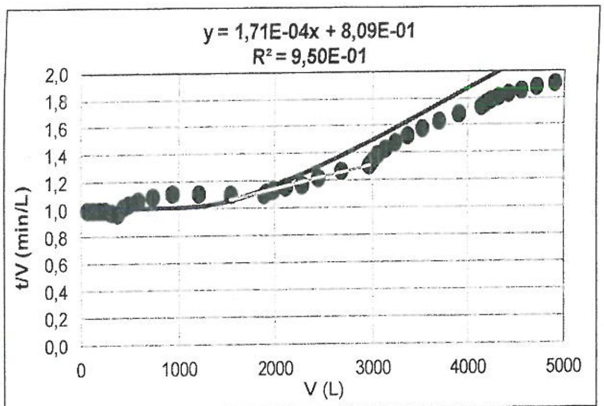

Figure 3: Operating within the third month: t/V vs. V.

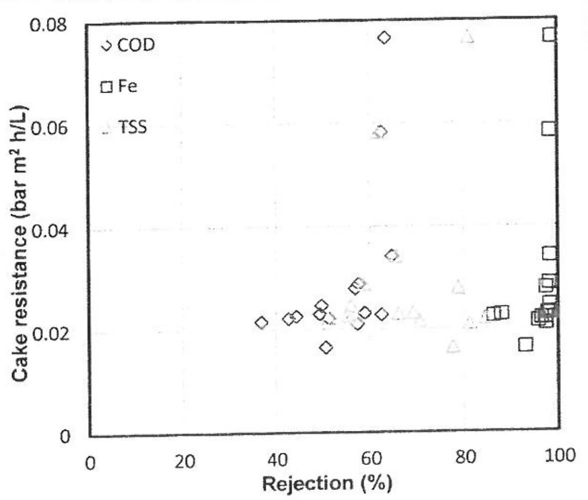

Figure 4: Cake resistance vs. rejection of COD, Fe ions and TSS.

increases. Within the same month, the rejection often increases with filtration time which may be due to fouling. For TSS the same explanation as for COD can be stated.

Moreover, the type of organic material (small molecules or large particles) is important for the rejection of COD. Similarly, for Fe rejection it is crucial if Fe is adsorbed onto particles which subsequently form larger molecules, which can be easily rejected by the membrane.

CONCLUSIONS

The loss of membrane performance due to fouling is one of the main impediments to the economic development of membrane processes for use in water and wastewater treatment[12]. In oily wastewater treatment fouling is inevitable and present to a significant degree due to the presence of COD, oils, TSS, Fe etc. UF is a suitable method for this wastewater, which can be confirmed by high rejection of COD, TSS and Fe. However, between operation months the membrane needed effective chemical cleaning due to a high level of fouling.

As presented in Figures 1-3, all values of MFI were very close and in all three cases compressible cake formation took place. It is important to expose increasing values of MFI through the months, which showed the growth of the fouling layer and compression/clogging of the fouling layer. The good fitting between experimental and modelled values was the confirmation of the model's suitability and good performance.

The correlation between cake resistance and rejection offered interesting findings where no clear tendency was observed, but the values of cake resistance are mostly in the same range for all parameters even if their rejection increased. In further investigations of oily wastewater treatment it would be better if the fouling rate were lower, which may be obtained by the use of ceramic or modified membranes.

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