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HIGHLY EFFICIENT PURIFICATION OF FINELY DISPERSED OIL CONTAMINATED WATERS BY COAGULATION/FLOCCULATION METHOD AND EFFECTS ON MEMBRANE FILTRATION

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ABSTRACT. In the present study the purification of finely dispersed oil contaminated water (100 ppm crude oil; $d_{oil\ droplets}$<2 μm) was investigated by using coagulation/flocculation process, membrane separation and combined methods. As coagulant, polyaluminum chloride (*Bopac*) iron(III) chloride and aluminum(III) chloride, while as flocculant anionic polyelectrolyte were applied. For the membrane separation, hydrophilic polyethersulfone (PES) microfilter (d=0.2 μm) was used, while for the determination of the purification efficiencies turbidity, chemical oxygen demand and extractable oil content were measured. The utilization of *Bopac* polyaluminum chloride coagulant (by setting Al^{3+} content to 20 ppm) resulted in high purification efficiency (96.7%). The extra addition of 1 ppm anionic polyelectrolyte lead to the increase in efficiency up to 98.8%. Due to the effective destabilization of oil in water emulsion the flux highly increased during the microfiltration of the emulsion, since both irreversible and reversible membrane resistances were greatly reduced.

Keywords: *oil contaminated waters, coagulation, flocculation, Bopac, membrane filtration*

INTRODUCTION

Large amount of oil contaminated waters are produced by many industrial processes, including food processing, petrochemical industries, metal industry and oily contaminants can appear in ground waters as well [1-6].

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For the elimination of oily pollutants of waters, the most common processes are gravity separation, centrifugation [7], skimming [8], flotation [9], thermal process [10], adsorption [6] and chemical destabilization [2, 5, 7, 10-12]. These traditional methods are sufficiently effective in case of free (or floating) oil ($d_{\text{oil droplets}}$>150 µm) and in case of coarse dispersions. However, oil in water emulsions (which is characterized in the literature by droplets smaller than 20 µm) and “dissolved oils” (when droplets are smaller than 5 µm) require to develop more effective destabilization methods and/or more effective water treatment processes [3, 13-17].

Membrane separation (micro- [15, 17-25] and ultrafiltration [13, 18, 23, 26-29]) can also be efficient for the treatment of these kind of water pollutants, however membrane fouling [10, 30] is a general problem (not only in case of oily contaminants), which inhibit the economic utilization in many cases. Microfilters have relatively higher fluxes compared to ultrafiltration, but the latter results in higher purification efficiency. To reduce fouling, highly hydrophilic membranes [25, 31, 32] can be used (in case oil in water emulsions), or membrane separation can be combined with other methods such as gas injection [33], ozonation [34, 35] or destabilization [5, 36]. In the recent study of M. Matos et al. [5] destabilization/centrifugation/ultrafiltration hybrid process was applied with high efficiency (97.4%) to purify oil in water emulsion, using calcium chloride coagulant and ZrO_2 ceramic ultrafilter (300 kDa) membrane. Their results are very promising, however the utilization of microfilter membranes (in order to achieve relatively higher fluxes) can be more preferable if the destabilization method is effective enough to allow its utilization with similarly high purification efficiency.

In the present study finely dispersed oil ($d_{\text{oil droplets}}$<2 µm) contaminated water was purified with destabilization, and the effect of pretreatment on membrane microfiltration was investigated.

For the destabilization of the emulsion polyaluminum chloride was used as coagulant. Polyaluminum chlorides are extensively used in water and waste water treatments, which have several beneficial properties in comparison with conventional aluminum chloride such as higher removal efficiency, lower pH sensitivity and lower residual Al^{3+} content [11, 12]. Polyaluminum chlorides contain $Al_2(OH)_2^{4+}$, $Al_8(OH)_{20}^{4+}$, $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ and other species [11, 37]. $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ (generally referred as Al_{13}) has been reported as the most effective species of polyaluminum chlorides, which has a pre-hydrolyzed structure with high positive charge (Al_{13}^{7+}) making it less sensitive to pH changes [11, 38-40]. Al_{13} can be described by the Keggin structure: The central tetrahedral AlO_4 unit is surrounded by octahedral AlO_6 units. This structure allows the molecule to hydrate and dehydrate without significant structural changes. These Al_{13} units can connect at the peaks and edges of octahedrals creating long chains which contain hydroxyl functional groups and cause high adsorption efficiency resulting in high elimination performance of colloid pollutants.

Since polyethersulfone is one of the most extensively used material to produce nano-, ultra-, and microfilter membranes [4, 23, 24, 41], because of its chemical- and thermal stability, easy processing and environmental endurance [4, 42], therefore in the present study polyethersulfone microfilter was used to eliminate the oily contaminants with and without the destabilization pretreatment. Permeate fluxes, resistances, fouling models and purification efficiencies were investigated in both cases.

RESULTS AND DISCUSSION

Destabilization of finely dispersed oil in water emulsion

In the first step *Bopac* was added into the emulsion in 6 different amounts which resulted in 2, 5, 10, 15, 20 and 40 ppm Al^{3+} content in the total volume. After 30 min sedimentation, the turbidity of the supernatants was measured and the purification efficiencies (**Figure 1**) were calculated from the initial turbidities (155±5).

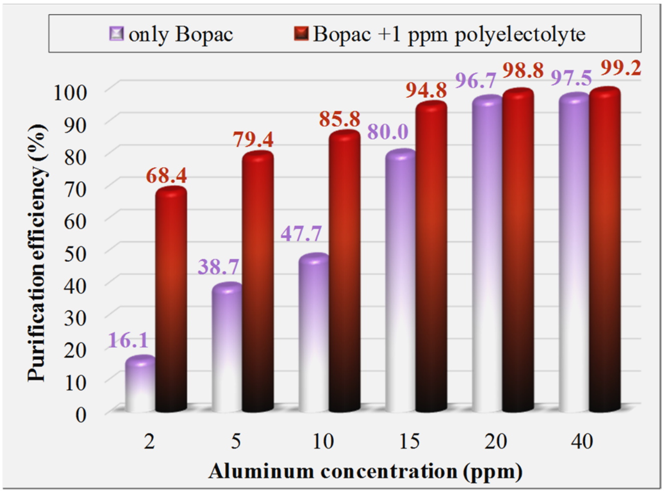

Figure 1. Purification efficiencies (calculated from turbidity values) in case of different *Bopac* coagulant dose (resulted 2, 5, 10, 15, 20 and 40 ppm aluminum content) with and without the addition of 1 ppm anionic polyelectrolyte flocculant.

As it can be seen in **Figure 1** higher coagulant dose resulted in increased purification efficiencies. It should be noted that in case of lower aluminum doses (2, 5 and 10 ppm Al^{3+} content) the created flakes were floating in the treated emulsions because of the very similar density of the flakes to water due to the low density of original oil droplets (~0.73 g/mL). At higher aluminum doses (15, 20, 40 ppm), the flakes were easily sedimented. 20 ppm aluminum concentration resulted in 96.7% purification efficiency, while double dose increased this value up to 97.5%, but this high concentration is not recommended because of the double amount of sediment.

Experiments were also carried out by the further addition of 1 ppm anionic polyelectrolyte to the emulsion as flocculant. In this series similar tendency was observed, however purification efficiencies were higher in all cases compared to the results in the absence of anionic polyelectrolyte (see **Figure 1**). By the utilization of flocculant the produced flakes were much bigger than in the absence of the polyelectrolyte, therefore the flakes sedimented much faster in case of 15, 20 and 40 ppm aluminum doses. At lower aluminum content (2,5 and 10 ppm) the flakes were floating in this case as well. 20 ppm aluminum concentration with the simultaneous utilization of 1 ppm anionic polyelectrolyte resulted in 98.8 % purification efficiency. However, doubled dose of aluminum (40 ppm) resulted in a marginally higher purification efficiency (99.2%) again, but the sediment volume was much higher in this case as well. Based on the achievable purification efficiencies and the sedimentation tendencies (see **Figure 2**), 20 ppm aluminum concentration and the extra addition of 1 ppm anionic polyelectrolyte can be beneficial.

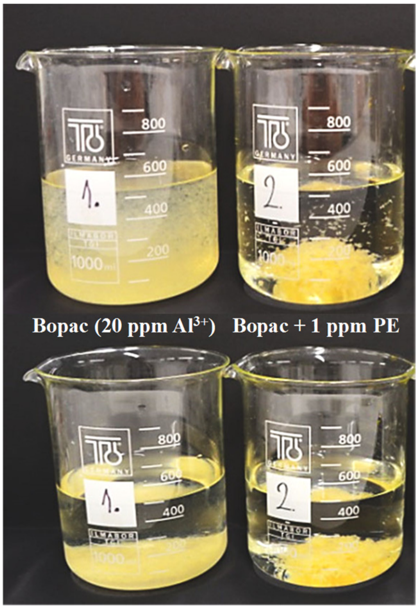

Figure 2. Sedimantation of the destabilized oil in water emulsion by *Bopac* coagulant (20 ppm aluminum content) and by the further addition of 1 ppm anionic polyelectrolyte. Top row: after 30 sec sedimentation; bottom row: after 30 min sedimentation.

Purification efficiencies were determined by measuring COD and extractable oil content as well (over the turbidity) when 20 ppm aluminum was applied with or without the utilization of 1ppm anionic polyelectrolyte. Results are shown in **Figure 3.**

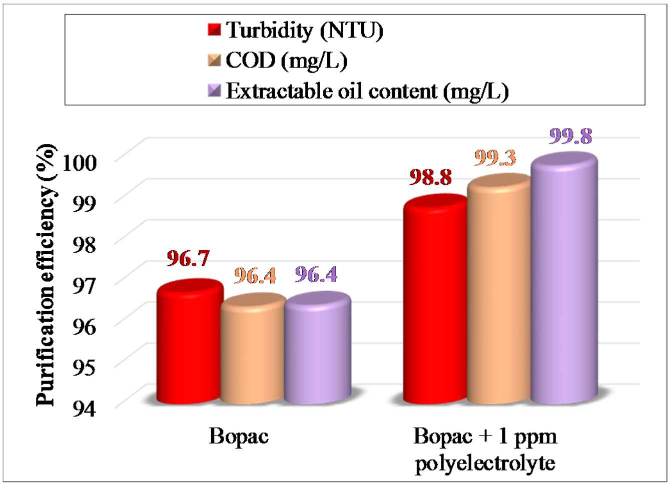

Figure 3. Purification efficiencies - calculated from turbidity, COD value and extractable oil content - in case of 20 ppm aluminum content with and without the addition of 1 ppm anionic polyelectrolyte flocculant.

Without the utilization of polyelectrolyte, the COD and extractable oil content eliminations are slightly smaller (96.4%) than colloid elimination (96.7% - determined by turbidity measurements) because of the small amount of water-soluble organic compounds. When the polyelectrolyte was also used, the determined COD and extractable oil content eliminations were higher (99.3 and 99.8%), which presumably due to the more effective adsorption of water-soluble organic compounds onto the flakes formed by the polyelectrolyte. These results also confirmed the beneficial utilization of 1 ppm anionic polyelectrolyte flocculant.

Additionally, conventional iron(III) chloride and aluminum(III) chloride were also applied as reference coagulants in calculated amounts, to set the Fe^{3+} or Al^{3+} concentration similarly to 20 ppm. Based on turbidity measurements iron(III) chloride resulted in a very low purification efficiency (33%) while aluminum(III) chloride was more efficient (72%), although to a substantially lower degree compared to the efficiency of polyaluminum chloride (96.7%) The outstanding purification efficiency of *Bopac* polyaluminum chloride can be explained by its pre-hydrolyzed form, the high basicity, and by the Keggin structure, which can results in higher adsorption ability compared to conventional aluminum coagulants.

Membrane microfiltration of finely dispersed oil in water emulsion

Finely dispersed oil in water emulsion was filtered by a polyethersulfone membrane microfilter (d_{pore}=0.2 μm), with and without the destabilization of the emulsion. In case of destabilization pretreatment, *Bopac* (20 ppm aluminum content) and anionic polyelectrolyte (1 ppm) were also used. The measured flux declines are presented in **Figure 4.** It can be seen, that in case of not pretreated oil in water emulsion the flux was rapidly and immensely declining, while in case of pretreated (destabilized) emulsion much higher flux was measured. Therefore, the total filtration time (until the VRR=5 filtration ratio) was only 406 s in case of the destabilized emulsion, while 5493 s in case of not-pretreated emulsion.

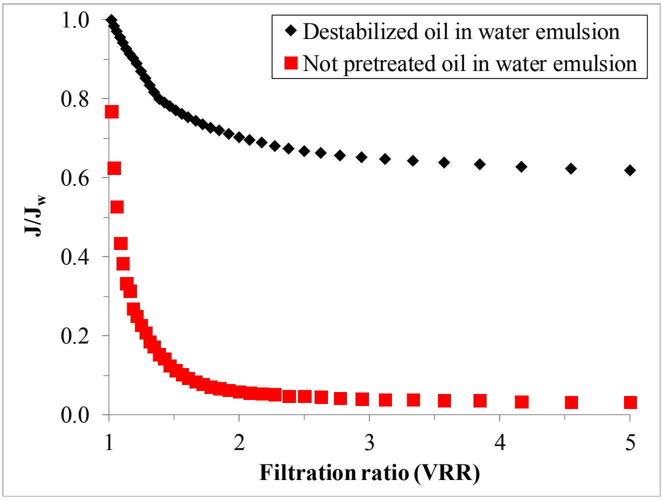

Figure 4. Measured fluxes during membrane microfiltration (PES – d_{pore}=0.2 μm) of oil in water emulsion with and without destabilization pretreatment (destabilization was carried out with *Bopac* – resulting 20 ppm aluminum content – and 1 ppm anionic polyelectrolyte).

Based on the calculations which are described in the “Experimental” section, in the “Resistance-in-series model” chapter, the different resistances were determined in both cases of filtrations. Results are presented in **Figure 5**, which demonstrates that the total resistance was ~96% lower in case of destabilized oil in water emulsion compared to the flux of not pretreated emulsion. Both irreversible- and reversible membrane resistances were also significantly reduced by the used destabilization pretreatment.

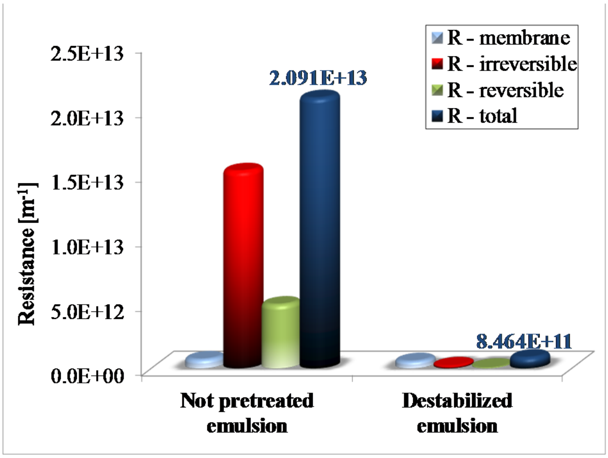

Figure 5. Different resistances in case of not pretreated and destabilized emulsion during the microfiltration.

Purification efficiency was 98% in case of not pretreated emulsion and 99% in case of destabilized emulsion (based on measured COD values), which means that the investigated oil in water emulsion can be effectively purified by membrane microfiltration without any pretreatment, but filtration resistances can be significantly reduced with the described destabilization method.

Additionally, widely used fouling models such as complete pore blocking-, gradual pore blocking-, intermediate filtration- and cake filtration models [38] were fitted onto the measured flux curves and it was found that both with or without the destabilization pretreatment the filtrations can be described mostly by the cake filtration model.

Comparing our results with the recent results of M. Matos et al. [5] (they applied destabilization/ultrafiltration (300 kDa) hybrid process with a 97.4% purification efficiency using calcium chloride coagulant and ZrO_2 ceramic ultrafilter) it can be concluded, that using polyaluminum chloride and anionic polyelectrolyte similarly very high purification efficiency can be achieved. Destabilized emulsion can be filtered with high flux and with high elimination efficiency by a microfilter, therefore the utilization of ultrafiltration is not necessary.

CONCLUSIONS

Bopac polyaluminum chloride successfully destabilized finely dispersed oil in water emulsions ($d_{\text{oil droplets}}$<2 µm) with high efficiency, without any additional flocculant, due to the high basicity, the pre-hydrolyzed form and the Keggin structure. The efficient doses are not lower than 15 ppm aluminum concentration (in case of 100 ppm oil content) since below this concentration the flakes were floating because of their low density. 20 ppm aluminum concentration resulted in 96.7% purification efficiency, while with the further addition of 1 ppm anionic polyelectrolyte the efficiency increased up to 98.8%, and the sedimentation ability was also significantly increased by the added flocculant.

The investigated finely dispersed oil in water emulsion can be effectively purified by membrane microfiltration without any pretreatment, but both irreversible- and reversible filtration resistances can be significantly reduced with the described destabilization method.

EXPERIMENTAL SECTION

Preparation of finely dispersed oil in water emulsion

Finely dispersed oil in water emulsion (c_{oil}=100 ppm; $d_{\text{oil droplets}}$=100-2000 nm) was prepared in two steps using crude oil (from *Algyő, Hungary*; supported by *MOL Zrt.*). Firstly 1 wt.% emulsion was prepared by intensive stirring (35000 rpm), then 5 mL of this emulsion was inoculated into 495 mL of model ground water directly below the transducer of an ultrasonic homogenizer (*Hielscher UP200S).* The duration of homogenization was 10 minutes, maximal amplitude and cycle was applied and the emulsion was thermostated to 25°C.

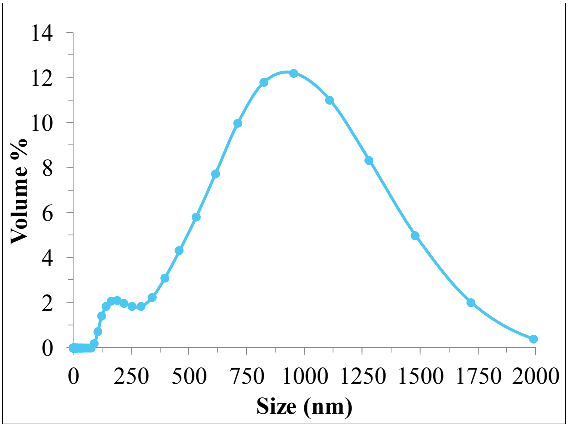

Figure 6. Size distribution of the investigated finely dispersed oil in water emulsion.

The investigated water was a model of real groundwater located in south Hungary, which contained the following salts: 2.26 g/L $NaHCO_3$; 53.4 mg/L NH_4Cl; 19.1 mg/L $CaCl_2$; 20.9 mg/L KCl; 93.5 mg/L NaCl; 4.5 mg/L $FeCl_3$ and 35.1 mg/L $MgSO_4$ (*Sigma Aldrich*; analytical grade). The size distribution of the oil droplets in the produced emulsion was described by dynamic light scattering using a *Malvern ZetaSizer4* type equipment (**Figure 6**).

Destabilization experiments

Coagulation/flocculation experiments were carried out in a four-backer Jar Test flocculator (*VELP Scientifica*) at room temperature. Coagulants and flocculant were added during intensive stirring (200 rpm); after 30 s homogenization 2 min slow stirring (20 rpm) was applied, then the formed flakes were left to settle for 30 min. As highly efficient coagulant a polyaluminum chloride (named as *"Bopac"*, produced by *Unichem Kft*.- Hungary) was used, while as reference coagulants iron(III) chloride, and aluminum(III) chloride (named as "*Unifloc-C*" and "*Unipac*" respectively; produced by *Unichem Kft*.- Hungary) were used. *Bopac* is an ACH type pre-hydrolyzed polyaluminum chloride which allowed in drinking water production with high basicity (82.0±2%) and with an $n_{Al}:n_{Cl}=2.0\pm0.2$ ratio. Enhanced flocculation was carried out by further addition of an anionic polyelectrolyte flocculant (named as "*Unifloc LT 27*"; produced by *Unichem Kft*.- Hungary).

Membrane filtration

Membrane filtration experiments were carried out in a batch-stirred membrane reactor (*Millipore XFUF07601;* produced *by New Logic Research Inc.*) equipped with a hydrophilic polyethersulfone (PES) microfilter membrane ($d_{pore}=0.2$ μm; filtration area was 0.00332 m^2). The applied transmembrane pressure was 0.1 MPa (provided by nitrogen gas). The volume of the treated emulsion was 250 mL and filtration was carried out until 200 mL of permeate was produced (VRR=5).

Determination of purification efficiency

Purification efficiencies were determined by measuring turbidity (*Hach 2100N*) and in some cases chemical oxygen demand (COD) and extractable oil content (TOG/TPH). COD values were measured by the standard potassium dichromate oxidation method using standard test tubes (*Hanna Instruments*) and applying digestions for 120 min at 150°C in a *Lovibond ET 108* type COD digester. The COD values were measured with a *Lovibond COD Vario* type COD photometer. Extractable oil content was measured by a *Wilks InfraCal TOG/TPH* type analyzer, using hexane as extracting solvent.

The purification efficiency (R) was determined as:

$$R = \left(1 - \frac{a}{a_0}\right) \cdot 100\% \qquad (1)$$

where a_0 is the turbidity, COD, or TOG/TPH values of the feed while a indicates the values of the permeate.

Resistance-in-series model

The membrane resistance (R_M) was calculated as [43]:

$$R_M = \frac{\Delta p}{J_w \eta_w} \quad [m^{-1}] \qquad (2)$$

where Δp is the transmembrane pressure (Pa), J_W is the water flux of the clean membrane and η_W is the viscosity of the water (Pas).

The irreversible resistance (R_{Irrev}) was determined by re-measuring the water flux on the used membrane after the filtration, followed by a purification step (intensive rinsing with distilled water):

$$R_{Irrev} = \frac{\Delta p}{J_{WA} \eta_W} - R_M \quad [m^{-1}] \qquad (3)$$

where J_{WA} is the water flux after the cleaning procedure.

The reversible resistance (R_{Rev}), caused by not adhered contaminants and concentration polarisation layer can be calculated as:

$$R_{Rev} = \frac{\Delta p}{J_c \eta_{WW}} - R_{Irrev} - R_M \quad [m^{-1}] \qquad (4)$$

where J_c is the flux at the end of the filtration and η_{ww} is the viscosity of wastewater. The total resistance (R_T) can be evaluated from the steady-state flux by using the resistance-in-series model:

$$R_T = R_M + R_{Irrev} + R_{Rev} \quad [m^{-1}] \qquad (5)$$

Fouling mechanisms were described with widely used filtration laws (complete pore blocking, gradual pore blocking, intermediate filtration and cake filtration) [44] to characterize membrane fouling.

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