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Synthesis of Separation Process for Waste Treatment of Oil-in-Water Emulsions

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A novel synthesis approach is proposed for designing integrated processes for oily wastewater treatment. A mixed-integer linear programming (MILP) model was developed based on the superstructure of alternative separation processes. These processes are grouped into three main sets, i.e. the pre-treatment, intermediate treatment, and final treatment, from which the optimal combination of technologies is selected in order to achieve the legally required effluent quality. The parametric analysis was performed by varying the input chemical oxygen demand (COD) values of oil-in-water emulsion between 1000 and 110 000 mg/L, yielding a variety of combinations of purification techniques. The optimal designs obtained indicate that oil-in-water emulsions can be treated successfully and profitably by integrated processes composed of the established separation techniques.

1. Introduction

Oil-in-water (O/W) emulsions, consisting of water, mineral or synthetic oils and different additives, are used in metal industry for mechanical surface processing to cool, lubricate and prevent corrosion. During these processes emulsions are degraded and have to be periodically replaced. Due to recent modifications of the emulsion composition (increasing fraction of synthetic oils), the development of new efficient separation technologies is required, which would fulfil legislation norms for discharging industrial wastewater, e.g. COD, mineral oils, the total organic carbon (TOC), lipophilic substances, BTX, AOX, etc.

Recent approaches are based on the experimental testing of various techniques in the laboratory or pilot scales, while the efficiency of treatment is evaluated in the terms of typical parameters' reduction, e.g. COD, conductivity, turbidity. Belsadock et al. (2007) combined coagulation and dissolved air flotation for treating mineral oil emulsion. The efficiencies of the chemical and the electrochemical coagulation were studied by Canizares et al. (2008) who observed high COD removals by both technologies. Gutierrez et al. (2008) reported the specific energy consumptions, and final COD and turbidity values obtained by centrifugation, ultrafiltration, and evaporation of O/W emulsions. A process diagram for treating the emulsions from a copper-rolling process was proposed by Gutierrez et al. (2011), involving four treatment steps: destabilization, centrifugation, ultrafiltration, end evaporation.

Although a great progress has been made in experimental studies of O/W emulsion treatment, the technical design and the overall economic performance of treatment processes were rarely taken into account. The aim of this research is thus to develop an approach to designing efficient and

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economically viable treatment technologies by applying mathematical programming approach combined with the laboratory experiments.

2. Description of the proposed synthesis approach

The proposed approach relies on the mathematical programming method, and comprises three main steps: 1) developing the superstructure of various separation techniques, e.g. chemical and/or biological treatment, multi-stage vacuum evaporation, ultrafiltration, electrocoagulation, adsorption etc., 2) modelling the superstructure as a mixed-integer linear programming model (MILP), and 3) solving the model with the available optimization algorithm. In parallel with the above steps, the laboratory experiments could be carried out for providing missing data when required, and gradually improving accuracy of developed mathematical model.
The superstructure for the synthesis of wastewater separation process (Figure 1) includes three main groups of treatment alternatives: pre-treatment, intermediate treatment and final treatment. The first group consists of chemical pre-treatment (CP), mechanical pre-treatment (MP), chemical mechanical pre-treatment (CMP), and skimming (ST). The second set consists of the electrocoagulation (EC), vacuum distillation (VD), ultrafiltration (UF1), and reverse osmosis (RO) following by the option of the sequential ultrafiltration (UF2) or bypass flow. The third set includes two optional alternatives, i.e. the biological treatment (BT), and the active charcoal adsorption (ACA). Single choice splitters (S) and mixers (M) allow the selection of various treatment alternatives depending on the input characteristics of oily wastewater and the required quality of aqueous effluent.

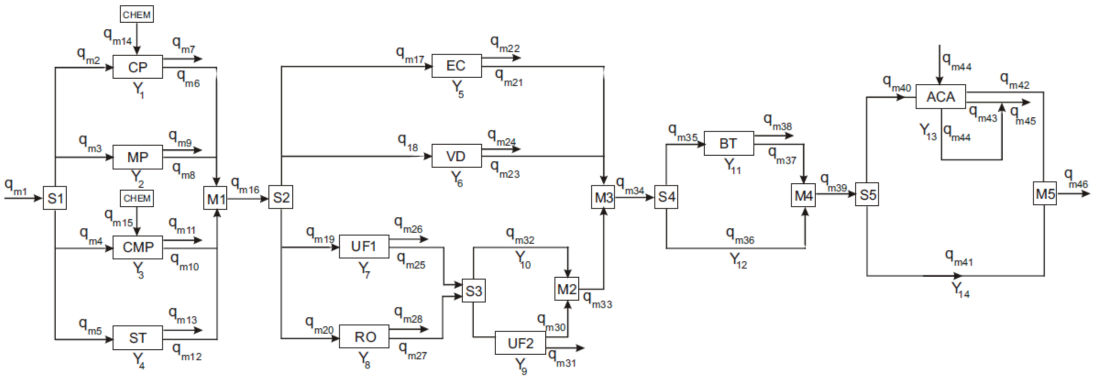

Figure 1: The superstructure of the wastewater separation process.

3. Mathematical model

The mathematical model of the above superstructure involves the models of the separation units, single-choice splitters and mixers, and the objective function, i.e. the maximum profit. The models of separation units are of three different types which are illustrated by the following units: a) mechanical pre-treatment model, b) chemical pre-treatment model, and c) active charcoal adsorption model. The model type a) was used also for units ST, EC, VD, UF1, UF2, RO, and BT treatment, while the model type b) was applied also to the CMP. Splitters and mixers models are presented by the units S1 and M1.

a) Mechanical pre-treatment (MP) mass balances:

$$q_{\mathrm{m},3} = q_{\mathrm{m},8} + q_{\mathrm{m},9} \quad (1)$$

$$q_{\mathrm{m},9} = r_{\mathrm{mp,s}} \cdot q_{\mathrm{m},3} \quad (2)$$

where the variable $q_{m,i}$ (t/h) is the mass flow of stream i, and $r_{mp,s}$ is the fraction of sludge generated.

Upper bound for total flow of inlet stream:

$$q_{m,3} = q_{m,3}^{up} \cdot y_2 \tag{3}$$

where y_j is the binary variable of process j, and $q_{m,i}^{up}$ (t/h) is the upper bound of stream i.

Aqueous outlet COD concentration of mechanical pre-treatment:

$$c_{COD,8} = f_{mp,r} \cdot c_{COD,3} \tag{4}$$

where the variable $c_{COD,i}$ (mg/L) is the COD value of stream i, and $f_{mp,r}$ is the fraction of residual COD in aqueous outlet.

Upper bound of COD concentration for inlet stream:

$$c_{COD,3} = c_{COD,3}^{up} \cdot y_2 \tag{5}$$

where $c_{COD,i}^{up}$ (mg/L) is the upper bound of COD in stream i.

Mechanical pre-treatment consumption of electricity:

$$E_{mp} = e_{mp} \cdot q_{m,3} \tag{6}$$

where the variable E_{mp} (kWh/h) is the electricity consumption, and e_{mp} (kWh/t) the specific electricity consumption.

b) Chemical pre-treatment (CP) mass balances:

$$q_{m,2} + q_{m,14} = q_{m,6} + q_{m,7} \tag{7}$$

$$q_{m,14} = f_{cp,c} \cdot q_{m,2} \tag{8}$$

$$q_{m,7} = r_{cp,s} \cdot \left(q_{m,2} + q_{m,14} \right) \tag{9}$$

where $f_{cp,c}$ (t/t) is the specific consumption of chemicals, and $r_{cp,s}$ the fraction of sludge generated.

Upper bound for stream 2 total mass flow:

$$q_{m,2} = q_{m,2}^{up} \cdot y_1 \tag{10}$$

Aqueous outlet COD concentration of chemical pre-treatment:

$$c_{COD,6} = f_{cp,r} \cdot c_{COD,2} \tag{11}$$

Upper bound of COD concentration for inlet stream:

$$c_{COD,2} = c_{COD,2}^{up} \cdot y_1 \tag{12}$$

Chemical pre-treatment consumption of electricity:

$$E_{cp} = e_{cp} \cdot \left(q_{m,2} + q_{m,14} \right) \tag{13}$$

c) Active charcoal adsorption (ACA) mass balances:

$$q_{\mathrm{m},40} = q_{\mathrm{m},42} + q_{\mathrm{m},43} \tag{14}$$

$$q_{\mathrm{m},43} = r_{\mathrm{aca,s}} \cdot q_{\mathrm{m},40} \tag{15}$$

Aqueous outlet COD concentration of active charcoal adsorption:

$$c_{\mathrm{COD},42} = f_{\mathrm{aca,r}} \cdot c_{\mathrm{COD},40} \tag{16}$$

Active charcoal consumption:

$$q_{\mathrm{m},44} = f_{\mathrm{aca,c}} \cdot q_{\mathrm{m},40} \tag{17}$$

where $f_{\mathrm{aca,c}}$ is the specific consumption of active charcoal (t/t).

Used active charcoal and sludge outlet:

$$q_{\mathrm{m},45} = q_{\mathrm{m},44} + q_{\mathrm{m},43} \tag{18}$$

d) Splitter 1 (S1) logical constraint and mass balances:

$$y_1 + y_2 + y_3 + y_4 = 1 \tag{19}$$

$$q_{\mathrm{m},2} + q_{\mathrm{m},3} + q_{\mathrm{m},4} + q_{\mathrm{m},5} = q_{\mathrm{m},1} \tag{20}$$

$$c_{\mathrm{COD},2} + c_{\mathrm{COD},3} + c_{\mathrm{COD},4} + c_{\mathrm{COD},5} = c_{\mathrm{COD},1} \tag{21}$$

e) Mixer 1 (M1) mass balances:

$$q_{\mathrm{m},6} + q_{\mathrm{m},8} + q_{\mathrm{m},10} + q_{\mathrm{m},12} = q_{\mathrm{m},16} \tag{22}$$

$$c_{\mathrm{COD},6} + c_{\mathrm{COD},8} + c_{\mathrm{COD},10} + c_{\mathrm{COD},12} = c_{\mathrm{COD},16} \tag{23}$$

f) Profit objective function:

$$\begin{aligned} \max P = {} & q_{\mathrm{m},1} \cdot c_1 \cdot f_{\mathrm{t}} - \left(q_{\mathrm{m},14} \cdot c_{14} + q_{\mathrm{m},15} \cdot c_{15} + q_{\mathrm{m},44} \cdot c_{44} \right) \cdot f_{\mathrm{t}} - E_{\mathrm{elec}} \cdot c_{\mathrm{elec}} \cdot f_{\mathrm{t}} - \\ & - c_{\mathrm{elec,fix}} - c_{other} - \left(D_{\mathrm{CP}} \cdot y_1 + D_{\mathrm{MP}} \cdot y_2 + D_{\mathrm{CMP}} \cdot y_3 + D_{\mathrm{ST}} \cdot y_4 + D_{\mathrm{EC}} \cdot y_5 + D_{\mathrm{VD}} \cdot y_6 \right) - \\ & - \left(D_{\mathrm{UF1}} \cdot y_7 + D_{\mathrm{RO}} \cdot y_8 + D_{\mathrm{UF2}} \cdot y_9 + D_{\mathrm{BT}} \cdot y_{11} + D_{\mathrm{ACA}} \cdot Yy_{13} \right) \end{aligned} \tag{24}$$

where P is the annual profit before taxes (k€/y), c_1 the income price of O/W emulsion (k€/t), f_{t} the annual operating time (h/y), c_{14} and c_{15} the purchase prices of chemicals (k€/t), c_{44} the price of active charcoal (k€/t), E_{elec} the total electricity consumption (kWh/h), c_{elec} the price of electricity (k€/kWh), $c_{\mathrm{elec,fix}}$ the fix price of electricity (k€/y), c_{other} the operating costs (k€/y), and D's the annualized investment of separation technologies (k€/y).

The above MILP synthesis model was applied to an existing industrial plant with fixed input capacity of O/W emulsion in the amount of 3060 t/y. The maximum allowed COD value of the aqueous effluent, i.e. stream no. 46, was set to 120 mg/L. As the input characteristics of O/E emulsions vary significantly, a parametric study was performed by varying the input COD value of the stream no. 1 in order to select the optimal separation technologies in the integrated treatment plant, and to study the economic performances of optimal designs.

4. Results and discussion

In the existing O/W treatment plant, the composition and characteristics of collected emulsions vary significantly. For example, the input COD values were measured as high as 300,000 mg/L, and besides, some emulsions were already pre-treated with specific chemicals. Therefore, the input COD value of stream 1 in the superstructure (Figure 1) was changed from 1,000 mg/L upwards, until the feasible solutions were obtained.

The highest COD value, for which the feasible solution was obtained, was 109,000 mg/L. Above this value it was not possible to reduce the effluent COD below 120 mg/L with the separation technologies available in the superstructure. The emulsions with COD above 109,000 mg/L would require a dilution with industrial water as a pre-treatment procedure in order to reduce the input COD value below the level suitable for treatment.

Optimal technologies selected in the range of COD between 1,000 and 109,000 mg/L are shown in Table 1. It could be seen, that integrated processes involve technologies from all three treatment groups, including the optional final-treatment, which could be attributed to strict criterion of final COD value in aqueous effluent. Chemical or chemical-mechanical processes were selected as pre-treatment technologies in the entire range of COD values. Regarding the intermediate-treatment methods, one-stage membrane processes were selected at low COD values (up to 36,000 mg/L), and two-stage membrane systems at the medium COD values (up to 55,000 mg/L). A vacuum distillation was selected above 5,000 mg/L because of higher efficiency in COD reduction. Among the final-treatment processes, the active charcoal adsorption alone was selected only at low COD values (up to 9,000 mg/L), while the combination of biological treatment and charcoal was necessary above this value in order to achieve the required effluent quality.

Table 1: Combination of processes for different input COD values

COD	Pre-treatment				Intermediate-treatment					Final-treatment	
(mgO_2/L)	CP	MP	CMP	ST	EC	VD	UF1	RO	UF2	BT	ACA
1,000	■						■				■
5,000	■						■				■
10,000			■				■				■
15,000	■						■			■	■
20,000	■						■			■	■
25,000			■				■			■	■
30,000			■					■		■	■
35,000			■					■		■	■
40,000			■				■		■	■	■
45,000			■					■	■	■	■
50,000			■					■	■	■	■
55,000			■					■	■	■	■
60,000	■					■				■	■
65,000	■					■				■	■
70,000	■					■				■	■
75,000	■					■				■	■
80,000	■					■				■	■
85,000	■					■				■	■
90,000			■			■				■	■
95,000			■			■				■	■
100,000			■			■				■	■
105,000			■			■				■	■
109,000			■			■				■	■

Results of the optimization show a decreasing value of annual profit (Figure 2) as a function of increasing input COD values of O/W emulsion. The complexity of the chosen separation techniques increases with increasing input COD, resulting in higher investment and operating costs, especially electricity consumption (Figure 3). In particular, a significant increase in electricity cost was observed at COD values above 56 000 mg/L, where vacuum distillation was included into the integrated process. This technology has the highest investment and operating costs from among the separation techniques discussed, however it was selected due to its high efficiency dealing with high polluted O/W emulsions.

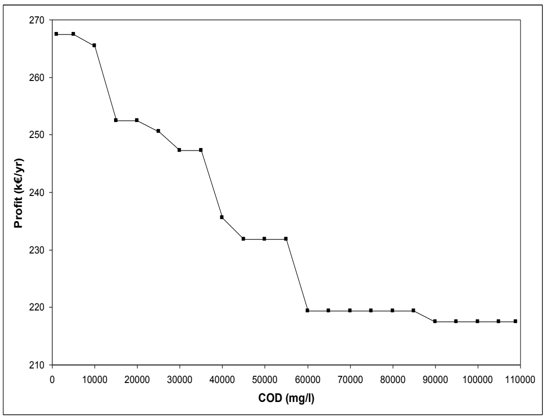

Figure 2: Profit depending on input COD value

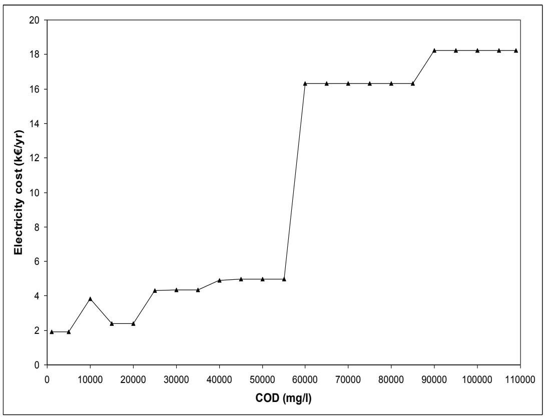

Figure 3: Electricity cost depending on input COD value.

5. Conclusions

MILP synthesis model was developed for selecting optimal separation technologies for treating oil-in-water emulsions at the maximum profit. The main goal was to reduce the COD value of aqueous effluent below 120 mg/L, which is the legal limit value for discharging effluents into surface waters.

A parametric study within the range of COD values between 1,000 and 109,000 mg/L showed that optimal integrated process would contain some chemical/mechanical pre-treatment method, and final treatment with biological technique and active charcoal. The selection of intermediate treatment, however, depends on the typical COD values of the input O/W emulsions. If these values do not exceed 56,000 mg/L, some combination of membrane processes would be sufficient, while vacuum evaporation would be preferable option at the higher COD values.

The MILP approach showed that oil-in-water emulsions can be treated successfully by suitable combinations of known existing separation techniques, yielding the highest profit and lowest impact on the aquatic life.

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