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Treatment of oil-in-water emulsions by a destabilization/ultrafiltration hybrid process: Statistical analysis of operating parameters

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ABSTRACT

A hybrid process has been studied for an oil-in-water (O/W) emulsion treatment. This process consisted of two stages: emulsion destabilization by coagulation/centrifugation with calcium chloride, and subsequent ultrafiltration (UF) using a 300 kDa tubular multichannel ZrO_2 ceramic membrane. The O/W emulsion was formulated from a commercial oil concentrate (1 wt % in distilled water) used in metalworking processes. The hybrid process was optimized in terms of ultrafiltration permeate flux and permeate quality parameters, such as chemical oxygen demand (COD), pH, conductivity and turbidity. Experiments' planning was designed using Taguchi method to determine the influence of four parameters (transmembrane pressure, feed flow rate to the UF module, destabilization temperature, and coagulant salt molar concentration) on a response factor, with three levels for each of them. The contribution of each factor was determined using a statistical analysis of variance (ANOVA). Transmembrane pressure and temperature were the most significant factors affecting permeate flux, while permeate quality, expressed as COD, was mainly influenced by UF feed flow rate and temperature. This behavior was slightly different when ultrafiltration was performed with 300 kDa flat ZrO_2 ceramic membranes.

1. Introduction

Metalworking fluids (MWFs) used in machining and rolling operations perform a number of functions, such as lubrication and cooling of workpiece, reduction of tool wear, improvement of surface finishing, and increase of tool life. Typically, they are oil-in-water (O/W) emulsions that become less effective after use, due to thermal degradation and contamination by substances in suspension or dissolved. Once they lose their functionality they have to be replaced, generating large volumes of oily effluents. These waste emulsions should be treated before their discharge in order to comply with environmental policy, due to their high organic content [1].

For each kind of effluent a specific oil/water separation process is used, depending on physical nature of the oil, total oil content, and chemical nature of other components. The most common treatment methods are chemical destabilization (coagulation/flocculation), electrocoagulation [2], centrifugation [3,4], membrane processes [5–10], and vacuum evaporation [11,12]. However, the combination of two or more of these separation techniques is required in many cases to obtain higher separation efficiencies. Methods such as membrane hybrid processes [13–16], membrane biological reactors [17], and destabilization/evaporation integrated processes [18] have shown successful results for the treatment of MWFs. Moreover, hybrid processes also allow obtaining high quality final effluents that could be suitable for several applications, such as process water or O/W emulsion reformulation. It has been reported that ultrafiltration permeates can be used for MWF reformulation, obtaining O/W emulsions with similar interfacial properties than the original one, taking into account their surfactant content [19].

The study and optimization of this kind of hybrid processes generally imply a high number of long-term experiments and a suitable experimental design should be very useful. Therefore, a statistical analysis (*i.e.* ANOVA) is required to find the most influencing factors and the optimum operating conditions. The number of experiments can be reduced by using the Taguchi experimental design, which facilitates the study of a system by a set of independent variables (factors) over a specific region of interest (levels) influencing a process response factor. Taguchi method is applied to factorial fractional design using orthogonal arrays (OA) and it is recommended for long or cumbersome experiments. It has been applied to microfiltration [20,21], ultrafiltration [22–26], nanofiltration [27,28], and reverse osmosis [29,30].

In this work a hybrid process, based in coagulation/centrifugation and ultrafiltration (UF) with tubular ceramic membranes, was studied for the treatment of an O/W emulsion prepared with a

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Nomenclature

ANOVA	analysis of variance
CCC	critical coagulation concentration (mol/L)
COD	chemical oxygen demand (mg/L)
J	permeate flux (L/m^{2}h)
M	coagulant salt concentration (mol/L)
MSD	mean standard deviation
n	number of observations
NTU	nephelometric turbidity units
Q	feed flow rate to ultrafiltration stage (L/h)
S/N	signal-to-noise ratio
T	destabilization temperature (ºC)
TMP	transmembrane pressure (bar)
Y	response factor value

commercial MWF. A coagulant salt, $CaCl_2$, was used as destabilization agent in the coagulation/centrifugation stage as reported in previous works [31–33]. The aqueous phase from centrifugation was fed into an UF stage using tubular ceramic membranes. The main objective was to estimate the optimum operating conditions for this hybrid process. Taguchi experimental design was applied and experimental results were analyzed using a statistical analysis of variance (ANOVA). Furthermore, the contribution of different factors was evaluated and compared with a similar hybrid process performed with flat ceramic UF membranes [32].

2. Materials and methods

2.1. Emulsion formulation

An oil-in-water (O/W) emulsion was formulated from Besol 5, a commercial oil concentrate (Brugarolas Co., Spain). The precise formulation of the oil concentrate is proprietary, but it contains a mixture of mineral oils and several additives, such as emulsifiers, stabilizers, biocides, and corrosion inhibitors. This emulsion was selected because of its long-term stability and its common use in Spanish workshops for a wide range of applications, such as cutting, drilling, or grinding processes [31]. This oil was dispersed (1 wt %) in distilled water using a rotor-stator homogenizer Miccra D-9 (ART, Germany), at 16000 rpm for 5 min. 8 L of O/W emulsion were prepared in two batches of 4 L. Formulated O/W emulsion had a pH value of 9.4, with a chemical oxygen demand (COD) of 25745 mg/L, a conductivity of 42.5 mS/cm, and a turbidity higher than 2000 NTU. Furthermore, its mean oil droplet size was 0.26 μm, with a surface tension of 31.2 mN/m, and a zeta potential of –71 mV.

2.2. Destabilization/centrifugation

Anhydrous $CaCl_2$ (reagent grade, Panreac Química S.A., Spain) was used as coagulant salt for emulsion destabilization, with concentrations according to the trial conditions planned in the experimental design. Furthermore the emulsion was heated for 30 min in a thermostatic bath for destabilization enhancement.

The destabilized emulsion was then centrifuged (Kubota 6300, Japan) for 15 min at 4500 rpm. Supernatant was removed and the remaining aqueous phase was further separated in a funnel and sent to the ultrafiltration stage. These operating conditions were selected taking into account previous studies where the same salt was used as demulsifying agent in hybrid membrane processes [31–33].

The zeta or electrokinetic potential is often a useful parameter for studying the emulsion stability since it reflects the electrostatic interactions of moving oil droplets [33]. Zeta potential of the initial emulsion was –71 mV, which indicated high stability due to electrostatic repulsions between oil droplets. Most O/W emulsions, like the one used in this study, are stabilized by surfactants that generate an electrostatic charge on the surface of the oil droplets. A double layer of counter-ions in solution builds up around the droplet and surface charges repel each other, making the emulsion stable. Calcium ions, resulting from $CaCl_2$ addition, compressed the electrical double layer and reduced repulsions among oil droplets, making them to coalesce and thus increasing mean droplet size and decreasing zeta potential [34].

Fig. 1a gives zeta potential and surface tension values as a function of coagulant concentration. Zeta potential measurements were made in a Zetasizer Nano ZS apparatus (Malvern Instruments Ltd., UK), whereas surface tension was determined following the Du Noüy's platinum ring method using a Sigma 700 tensiometer (KSV Instruments Ltd., Finland). It is observed in Fig. 1a that coagulant addition produced a large reduction of absolute zeta potential values until a plateau around neutrality was reached. Similar results have been reported in the literature [35]. A remarkable decrease in surface tension value was also observed as coagulant concentration increased, likely due to the free oil film formed at the emulsion surface after coalescence took place.

Changes in droplet size distribution, determined by laser-light scattering using a Mastersizer S long bench equipment (Malvern Instruments Ltd., UK), are depicted in Fig. 1b. It can be observed that the lack of electrostatic repulsions enhanced oil droplets coalescence, increasing the mean droplet size as $CaCl_2$ was added. However, only slight changes in oil droplet size were noticed for coagulant salt concentrations higher than 0.05 M, which is the critical coagulation concentration (CCC) for this emulsion [3,31].

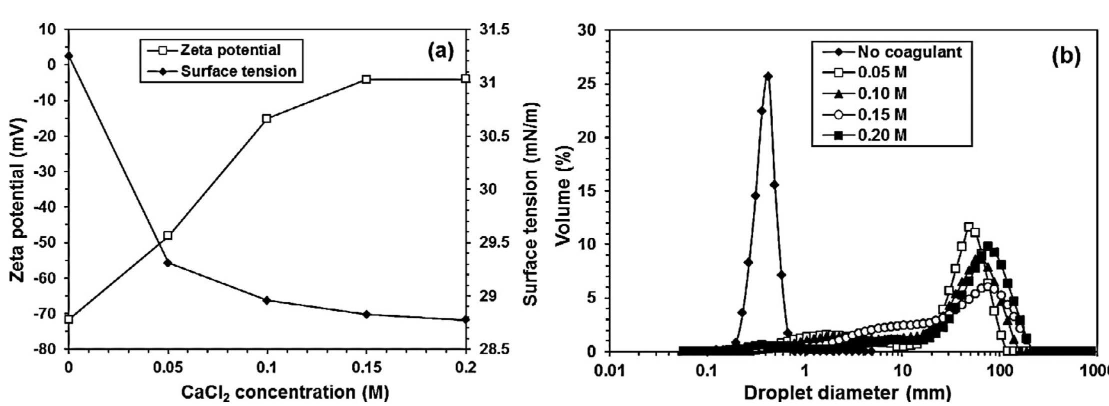

Fig. 1. Effect of $CaCl_2$ addition on (a) zeta potential and surface tension, and (b) droplet size distribution of initial O/W emulsion.