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# Influence of Coagulant Salt Addition on the Treatment of Oil-in-Water Emulsions by Centrifugation, Ultrafiltration, and Vacuum Evaporation

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**Abstract:** Droplet size is a key factor in the treatment of oil-in-water (O/W) emulsions, because of its influence on emulsion properties. The addition of a coagulant salt generally causes emulsion destabilization, increasing the droplet size, and enhancing coalescence between oil droplets, which helps its further treatment. The influence of $CaCl_2$ addition on droplet size distribution of a commercial O/W emulsion used in machining processes was studied in order to facilitate oil removal and to improve its further treatment by centrifugation, ultrafiltration (UF) and vacuum evaporation. The critical coagulation concentration (CCC) was observed at a $CaCl_2$ concentration of 0.05 M. The quality of the final aqueous effluent, expressed as its chemical oxygen demand (COD) value, was compared for all treatments. The highest COD values were obtained for centrifugation, while the COD of the UF permeate was approximately constant for all UF trials. The best effluent quality was obtained by vacuum evaporation. A combination of these techniques should be appropriate for most industrial treatments of O/W emulsions, depending on the subsequent use of the resulting aqueous effluent.

**Keywords:** O/W emulsions, droplet size distribution, coagulant salt, centrifugation, ultrafiltration, vacuum evaporation

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## INTRODUCTION

Oil-in-water (O/W) emulsions are present in several processes, mainly related to food, cosmetic, pharmaceutical, and metalworking industries. In some of them, such as food or cosmetic industries, they are commercial products but in other sectors, such as metalworking processes, where they are used for lubrication and cooling, they have to be discarded when they lose their functional properties. Hence, they must be treated to separate the oil before their disposal.

Nowadays, several treatments are being investigated in order to establish the best operating conditions for the highest oil removal efficiency and to obtain an aqueous effluent that can be safely discharged or reused into the process as cooling water or even as water to reformulate emulsions, such as deep bed filtration (1), centrifugation (2), ultrafiltration (3), distillation (4), vacuum evaporation (5), biological treatment (6), and hybrid processes (7).

The droplet size distribution plays an important role on O/W emulsion stability, since an increase of droplet size promotes the coalescence of oil droplets, causing emulsion destabilization. Droplet coalescence decreases the centrifugation time and power for oil separation (2). Furthermore, in membrane processes, such as ultrafiltration, oil droplets may permeate the membrane depending on its size. However, membrane fouling by oil droplets is a limiting factor, since they build a cake layer over the membrane surface, reducing the permeate flux (8, 9).

The influence of droplet size distribution on evaporation has not been yet studied in detail. According to Barrow and Pope (10) the larger the droplets, the slower the evaporation process of O/W emulsions. However, the addition of salts, surfactants, and additives decreases the evaporation rate and increases the boiling point (11–14).

In the present work, the effect of a coagulant salt addition on the droplet size distribution of a commercial O/W emulsion, used in machining processes, was studied in order to remove the oil and to improve its further treatment by centrifugation, ultrafiltration and vacuum evaporation. The main objective is to obtain an aqueous effluent of high quality (i.e., low COD and turbidity values) that could be discharged into the sewage system or reused into the process.

## MATERIALS AND METHODS

Oil-in-water emulsions were prepared from a commercial concentrate Besol 5 (Brugarolas Co., Spain), used in machining processes. Although its composition is proprietary, it consists of a mixture of mineral oils and several additives, such as emulsifiers, stabilizers, biocides or corrosion inhibitors. This oil concentrate was added to deionized water (Millipore Elix 5 deionizer) at a concentration of 1% w/v. The characteristics of the emulsion are summarized in Table 1.

*Table 1.* Characteristics of the emulsion studied

| Turbidity (NTU) | pH | COD (mg/L) | Conductivity (μS/cm) |
|---|---|---|---|
| 2500 | 9.8 | 20500 | 570 |

Coagulant salt, anhydrous calcium chloride ($CaCl_2$, reagent grade), supplied by Panreac Quimica S.A. (Barcelona, Spain), was added to the emulsion in a concentration range from 0.001–0.5 M.

Emulsion stability was studied using a Turbiscan LAb Expert (Formulaction Co., L'Union-Toulouse, France). This equipment permits to measure the transmission (180° from the incident light) and backscattering (135° from the incident light) of monochromatic light as a function of the emulsion height in a glass cell at different times. Droplet size distributions were measured by a laser light scattering technique, using a Mastersizer S long bench equipment (Malvern Instruments Ltd., Malvern, UK). Zeta potentials of oil droplets were determined using a Zetasizer 2000 (Malvern Instruments Ltd., Malvern, UK).

Centrifugation experiments were performed in a batch centrifuge WIFUG Labor 50 with a nominal speed of 3000 rpm.

Ultrafiltration (UF) experiments were carried out in total recycle mode using a tubular ceramic membrane Carbosep M308 (cut-off = 50 kg/mol), with an active layer of $ZrO_2/TiO_2$ supported on carbon and a total area of 0.05 $m^2$. The following operating conditions were used for all UF tests: $25 \pm 0.5$°C, crossflow velocity of 3.4 m/s, and a transmembrane pressure (TMP) range of 0.05–0.4 MPa.

Evaporation experiments were conducted in a Büchi R205 evaporator, consisting of a rotating flask immersed in a heating bath, where the O/W emulsion sample was control-heated to the desired temperature. The vapor was condensed in a water-refrigerated column and collected in a flask. The process was carried out at low pressure using a vacuum pump and a pressure control device. The vapor temperature was continuously monitored. In order to ensure good mixing, the rotation speed of the feed flask was set at 60 rpm.

The qualities of the feed and aqueous effluents obtained were evaluated in terms of analyses for chemical oxygen demand (COD), carried out by the reactor digestion method (15) using a Hach DR2010 UV spectrophotometer. Turbidity and conductivity values were measured using a Hach ratio XR turbidimeter and a Crison micro CM 2202 conductivity meter, respectively.

## RESULTS AND DISCUSSION

The influence of coagulant salt addition on droplet size distribution of the emulsion is shown in Fig. 1. It is observed an increase of oil droplet size

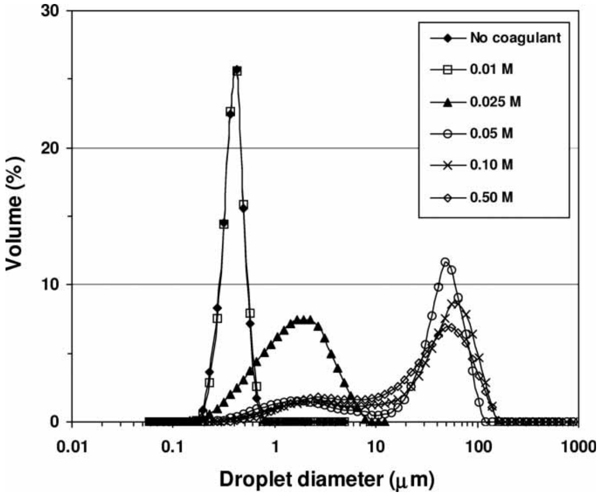

***Figure 1.*** Effect of $CaCl_2$ concentration on droplet size distribution of O/W emulsion, after fifteen minutes of slight stirring.

with salt concentration up to 0.05 M, corresponding to the critical coagulation concentration (CCC).

Figure 2 shows the emulsion stability as a function of time, determined by the light scattering technique using the Turbiscan apparatus. Emulsion stability was observed when no salt was added (Fig. 2A), with no increase in droplet size and just a slight creaming at the top of the sample (40–42 mm). For a salt concentration of 0.025 M (Fig. 2B), the backscattering decrease with time indicates that clarification occurs because of the increase of the droplet size. Furthermore, an increase of the backscattering at the top of the sample indicated that creaming also occurred. The addition of 0.05 M $CaCl_2$, corresponding to the CCC (Fig. 2C), results in a faster increase of droplet size, since the backscattering decrease is faster than in the previous case. However, after eight hours, the droplet size seems to be the same than for the 0.025 M addition. Creaming was also observed to a larger extent than in the case of 0.025 M. The addition of a high amount of salt (Fig. 2D) showed the same effects that in the previous cases (creaming, increase of oil droplet size and clarification around nearly all the sample) but in less time.

Figure 3 shows the pH change when the coagulant salt was added. A pH decrease was observed when $CaCl_2$ was added at low concentrations, whereas the pH remained constant at higher salt concentrations. It was also observed that when salt was added the absolute value of the zeta potential decreased substantially, which confirms the destabilization of the emulsion by decrease of the oil droplet charge.

Previous studies have indicated that coagulant salt decreases the pH of the emulsion as a result of the formation of different species of salt cation ($Ca^{2+}$)

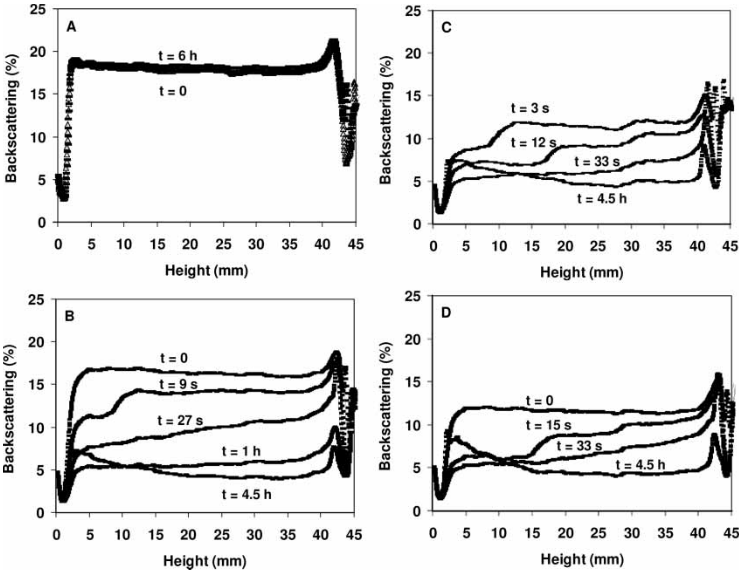

*Figure 2.* Effect of $CaCl_2$ addition on O/W emulsion stability along time: (A) No salt; (B) 0.025 M $CaCl_2$; (C) 0.05 M $CaCl_2$; (D) 0.10 M $CaCl_2$.

with the hydroxyl ions, causing $Ca(OH)_2$ precipitation, as it was reported elsewhere (16, 17).

Several studies confirm that the pH plays an important role on the zeta potential: as pH decreases, the zeta potential also decreases (18) because of the adsorption of $OH^-$ ions on the electrical double layer and an increase of

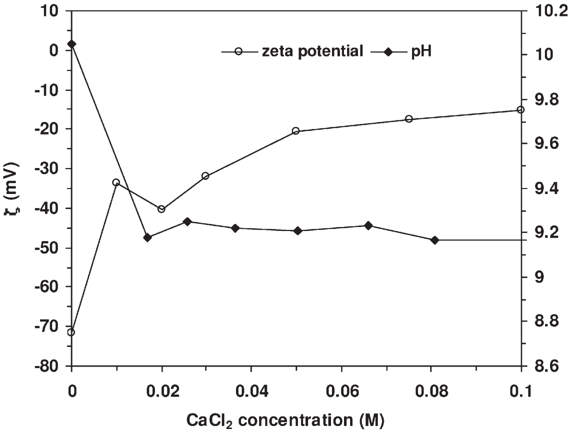

*Figure 3.* Effect of $CaCl_2$ concentration on pH and zeta potential values of the O/W emulsion.

the repulsive forces between oil droplets (19), while the $H^+$ ions have less affinity for the oil droplets (20).

The centrifugation of the emulsion at 3000 rpm for 15 minutes was carried out at different coagulant salt concentrations. A clear clarification was observed when 0.025–0.05 M $CaCl_2$ was added, that did not improve significantly at higher salt concentrations. Turbidities determined after centrifugation tests (Fig. 4) confirmed a high clarification at salt concentrations of 0.025–0.05 M, which increased up to 0.5 M, where the turbidity was nearly zero.

The same experiments were carried out with ultrafiltration (UF) and evaporation, to study the influence of oil droplet size. In Fig. 5, the evaporation rate (E), defined as the volume of condensate collected per unit time, and the permeate flux (J) of the emulsion are plotted as a function of salt concentration. Two relevant effects were observed at increasing salt concentrations:

i. an increase of the oil droplet size, and
ii. a reduction of the zeta potential absolute value.

An improvement of UF treatment was observed when oil droplet size increased, since there was less deposition of oil droplets on the membrane surface, and membrane fouling was reduced, improving permeate flux (8). Furthermore, the reduction of the zeta potential absolute value without increasing the oil droplet size causes a decrease in the repulsive forces between oil droplets and the membrane surface, which favors the deposition of the oil droplets, increasing membrane fouling and decreasing the permeate flux. This effect was observed for salt concentrations up to

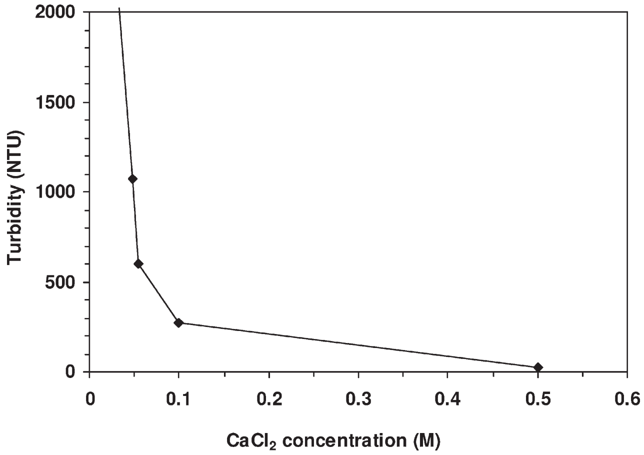

***Figure 4.*** Effect of $CaCl_2$ addition on turbidity after emulsion centrifugation at 3000 rpm for 15 minutes.

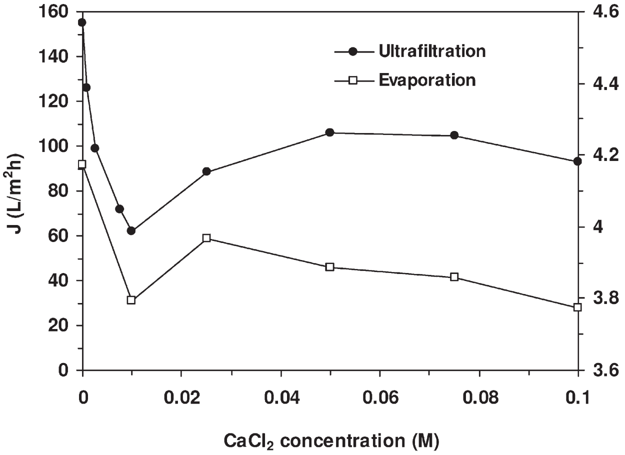

*Figure 5.* Permeate flux and evaporation rate of O/W emulsions at different coagulant salt concentrations.

0.01 M; at higher concentrations a permeate flux increase was observed up to 0.05 M $CaCl_2$, since the oil droplet size increases (9).

Despite the wide use of evaporation in industrial processes, few works have been carried out on O/W emulsions treatment, but previous studies have indicated its high efficiency at the optimum operating conditions (4, 5). The presence of salts reduced the emulsion evaporation rate and increased the boiling point (11). However, the evaporation rate of oil droplets in an O/W emulsion decreases when the droplet size increases (10, 21).

A similar behavior as for UF was observed for vacuum evaporation. A decrease of the evaporation rate was observed, since the addition of $CaCl_2$ lowered the absolute value of the zeta potential, making the emulsion less stable and increasing the free oil layer at the surface, that water has to cross to reach the vapor phase (5). Nevertheless, an increase of the droplet size for $CaCl_2$ concentrations in the range 0.01–0.025 M raised the evaporation rate, likely because of the presence of water layers between oil droplets. Above the concentration of 0.025 M, a decrease of the evaporation rate took place again: in this case, the reduction of zeta potential absolute value seems to be more relevant than the droplet size.

The quality of the aqueous phase, expressed as COD, obtained by centrifugation, ultrafiltration and vacuum evaporation is shown in Fig. 6. The highest COD values were obtained for centrifugation, where a clear decrease was obtained for coagulant salt concentrations above 0.025 M, and a clear clarification was also observed.

The permeate COD was approximately constant for all UF experiments: $CaCl_2$ concentration has an important role on permeate flux, but it is not so important regarding the quality of the permeate. No significant differences

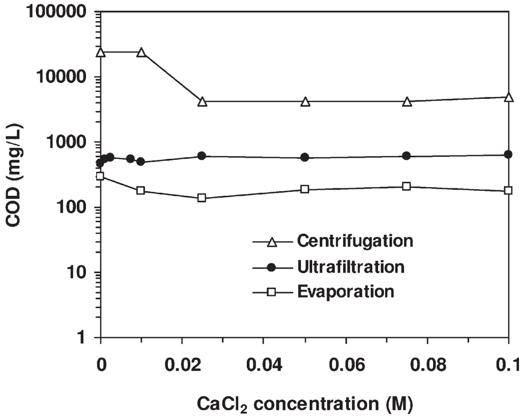

***Figure 6.*** Effect of $CaCl_2$ concentration on COD values of aqueous effluents obtained after centrifugation (3000 rpm for 15 minutes), ultrafiltration (transmembrane pressure: 0.36 MPa) and vacuum evaporation (40 kPa).

were found for vacuum evaporation; a lower value was observed at 0.025 M, corresponding to the highest evaporation rate: an increase of the droplet size increases the water evaporation rate, being more difficult to drag oil droplets while water goes up to the vapor phase.

A more detailed analysis of the aqueous phase obtained by vacuum evaporation was carried out regarding its quality and the volume reduction of the original emulsion at the end of each experiment; results are shown in Fig. 7.

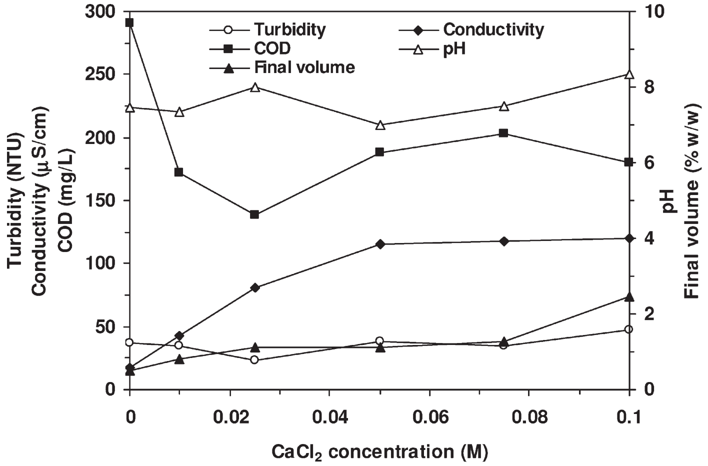

***Figure 7.*** Effect of $CaCl_2$ concentration on turbidity, conductivity, COD and pH of the aqueous effluent obtained, and on final volume of the concentrate, expressed as a percentage of the initial volume, after vacuum evaporation at 40 kPa.

A decrease in turbidity was also found at a $CaCl_2$ concentration of 0.025 M, the same value that resulted for the lowest COD. The pH remained approximately constant for all tests, with a slight increase at the concentration where the highest permeate quality and evaporation rate were obtained. It was concluded that the decrease in emulsion pH, before its treatment, does not to have a significant effect on the aqueous phase obtained by vacuum evaporation. As it might be expected, the conductivity and final volume of the concentrate (expressed as the w/w percentage of the initial O/W emulsion volume) both increased with the concentration of salt added. Moreover, COD and turbidities were lower than those obtained after centrifugation.

Emulsion treatment costs are not only a function of the technique employed, but also of the equipment used. The type of centrifuge, the UF module and membrane material and the type of evaporator (falling or rising film evaporator, thermal or mechanical vapor recompression, etc.) have a great influence on the treatment cost. Operation costs (expressed as energy consumption) for the industrial treatment of 1 $m^3$ of waste O/W emulsion were estimated, in order to compare the three aforementioned techniques (Table 2), with the purpose of obtaining an aqueous effluent of high quality (low COD and turbidity values). A Gea Westfalia Separator disc-stack centrifuge was considered for industrial centrifugation treatment, with a feed flow rate of 300 L/h, in order to have the residence time needed to obtain a good quality of the final aqueous effluent. For UF treatment, the permeate flux obtained with the Carbosep M308 membrane, when droplet coalescence took place, was considered. For the evaporation treatment, an industrial single-effect vacuum evaporator Vacudest-160, developed by Sidasa S.A., was selected for the calculations, and scale-up was carried out from experimental data. Estimation of energy consumption for UF and evaporation were based on the permeate flux and evaporation rate obtained using 0.25 M of $CaCl_2$.

Centrifugation seems to be the less expensive treatment, regarding energy consumption, but it yields an effluent of poor quality, compared with those obtained after treatment by ultrafiltration and evaporation at a laboratory scale (Table 2). It must be pointed out that the quality of these effluents can be improved when industrial equipment is used, specially for centrifugation

***Table 2.*** Estimated energy consumption for the treatment of 1 $m^3$ of waste O/W emulsion, and COD and turbidity values of the obtained aqueous effluent after each treatment

| | Centrifugation | Ultrafiltration | Evaporation |
|---|---|---|---|
| Energy consumption ($kWh/m^3$) | 5 | 18 | 70 |
| COD (mg/L) | 4200 | 598 | 138 |
| Turbidity (NTU) | 200 | $<1$ | 23 |

and evaporation, since for ultrafiltration a simple scale-up would be feasible. However, the best option should be a hybrid process, since a primary centrifugation stage would decrease the cost of secondary treatments such as ultrafiltration or evaporation.

## CONCLUSIONS

The addition of coagulant salt increased the oil droplet size of the O/W emulsions studied: the absolute value of the zeta potential decreased substantially, while the turbidity decreased due to the coalescence of the oil droplets, which form a top oil layer, leaving a clear aqueous phase at the bottom of the glass container. The critical coagulation concentration (CCC) was observed at a $CaCl_2$ concentration of 0.05 M. Furthermore, this addition also decreased the emulsions pH because of $Ca(OH)_2$ precipitation.

Centrifugation tests of the O/W emulsions showed that the turbidity of the resulting aqueous phase decreased as the concentration of coagulant salt increased, improving oil separation.

Ultrafiltration (UF) and evaporation tests of the O/W emulsion showed that both the permeate flux (J) and evaporation rate (E) decreased up to a coagulant salt concentration of 0.01 M, corresponding to the lower concentration where the increase of the oil droplets takes place. This behavior results from a decrease of the repulsive forces between oil droplets, with no increase of the droplet size.

The quality of the aqueous effluent, expressed as its chemical oxygen demand (COD), did not change for the UF tests in the whole range of coagulant salt concentration studied. In vacuum evaporation tests, a decrease of the COD, conductivity and turbidity was observed till a coagulant salt concentration of 0.025 M was reached. Above that concentration, an increase of these parameters was observed, likely because of the lower zeta potential absolute value, which results in a top oil layer that water must have to cross to reach the vapor phase, entraining oil droplets.

A combination of these techniques should be a suitable solution for most industrial treatments of O/W emulsions, depending on the subsequent use of the obtained aqueous effluent. A combination of centrifugation with ultrafiltration/evaporation would provide an aqueous effluent with reliable parameters, which might be reused or discharged, at lower operation costs than for a single ultrafiltration or evaporation treatment.

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