Comparison of separation processes for the treatment of emulsified oils from water

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Abstract

In this study, vacuum filtration, coagulation-flocculation, electrocoagulation and centrifugation were applied to separate emulsified oils from water. Two different types of cutting oils (BOR and EAL) were used in the preparation of oil emulsions. BOR has smaller oil droplets than EAL when they are mixed by water. It was not possible to separate BOR from water by microfiltration but 81.7% removal efficiency was obtained for EAL. Alum and ferric chloride were used as coagulants and optimum coagulant dosages, mixing time and pH were determined by performing jar tests. When alum was used as the coagulant, the removal efficiencies for BOR and EAL were 90% and 98%, respectively. In the case of ferric chloride, 98% oil removal was obtained for both emulsions. However, the optimum ferric chloride dosages were much higher than alum. The optimum alum and ferric chloride dosages for BOR emulsion were 0.83 g/L and 6 mg/L, respectively. In the case of EAL emulsion, the corresponding amounts were 4 mg/L and 8 mg/L. The flocculation time was determined around 45 minutes. In order to obtain 98% BOR removal, the emulsion was centrifuged at an angular velocity of 3000 rpm after the coagulation-flocculation process. On the other hand, when BOR and EAL were separated by electrocoagulation, 95% removal rates can be obtained for both oils applying 40 V difference to the aluminum electrodes for 35 minutes. According to the removal efficiencies obtained from the experiments and the preliminary cost analysis it can be concluded that the best method for separating emulsified oils from waters is the electrocoagulation.
Keywords: emulsified oils, oily wastewater, coagulation, electrocoagulation, filtration, centrifugation.

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1 Introduction

Emulsified oils or cutting fluids are usually composed of a mineral oil (40–80%), a surfactant, and some additives such as biocides, anti-degrading and anti-corrosive chemicals [1]. They are widely used in mechanical operations of cutting and machining metals and they combine the properties of cooling and lubrication. The use of cutting oils helps to increase the life of cutting tools, improve production efficiency, and provide more economical cutting speed. However, the physical and chemical properties of cutting oil deteriorate with time because of long usage [2]. Since they are classified as hazardous wastes their separation from wastewater becomes necessary.

The treatment of emulsified oils from wastewaters has been addressed by different techniques, but the most commonly used are membrane processes [3] and chemical destabilization [4], i.e., coagulation. Since cutting oils contain biocides to prevent their degradation sometimes biological processes can also be used for the treatment. In addition, when the effluent is highly polluted with soluble compounds and they cannot be removed by other techniques, distillation [5] can be an attractive alternative, despite of its high operation-cost.

Recently, there has been considerable interest in identifying new technologies that are capable of meeting more stringent treatment standards. For this purpose, electrocoagulation has a more prominent role in the treatment of waste cutting fluids, because it provides some significant advantages such as quite compact and easy operation and automation, no chemical additives, a shorter retention time, high sedimentation velocities, more easily dewatered and reduced amount of sludge due to the lower water content. It also can prevent the production of unwanted side-products [6].

Emulsions are unstable systems and tend to break down with time in order to minimize the interfacial area between the aqueous and the oil phase. Stability of emulsions is often related to zeta potential, i.e., the difference in potential between the surface of the tightly bound layer of ions on the oil droplet surface and the electro-neutral region of the solution [7]. The electrical charge on the droplet interface influences its interactions with other charged molecules, as well as its stability to aggregation. It might be expected that altering the surface density of hydroxyls on the droplets, by altering the pH, should affect the stability of the oil droplets and so change the average particle size of the droplets [8].

The purpose of this work was to compare vacuum filtration, coagulation-flocculation, electrocoagulation and centrifugation processes for the separation of emulsified oils from water. Oil in water emulsions were prepared using two cutting oils. The oil removal efficiencies for each separation process were evaluated by performing experiments depending on turbidity measurements.

2 Materials and methods

2.1 Preparation of oil emulsions

Oil emulsions were produced from two commonly used cutting fluids in industry, namely, Bor oil (BOR) and Tapmatic Aquacut for all metals except aluminum (EAL). Both cutting fluid is mainly composed of alkanes. The oil emulsions were prepared by mixing BOR or EAL to tap water at a volume percentage of 2; then the mixture was stirred mechanically for 30 minutes. The pH of emulsion was around 8 after mixing EAL or FAM with water. The emulsion pH was adjusted either by using hydrochloric acid or sodium hydroxide. In addition, the oil removal efficiencies were evaluated depending on turbidity measurements (Aqualytic AL450T).

2.2 Experimental procedures for separation methods

Cellulose nitrate filter papers (8μm) were used as the filter medium in vacuum filtration tests and 300 mL of emulsion was filtered. Coagulation and flocculation experiments were performed by using a jar apparatus. Alum ($Al_2(SO_4)_3$) and ferric chloride ($FeCl_3$) were used as coagulants. First, a stock solution (50 g/L or 100 g/L) was prepared for the coagulants. Then 4, 5, 6, 7, 8 and 9 mL from this stock solution were added to 300 mL oil emulsions to find the optimum dosage. After the evaluation of optimum dosages for the coagulants, the effects of mixing time and pH on oil removal efficiency was investigated. The centrifugation experiments were performed by using the oil emulsions that contains the evaluated optimum alum amount. The samples (50 mL) were centrifuged at 1000, 3000 and 4000 rpm for 15 minutes.

Electrocoagulation experiments were performed by using an electrokinetic unit, which has a volume of 1.75 L. Two aluminum plates were used as anode and cathode electrodes and they were 13 cm in length, 2 cm in width and 0.3 cm in thickness. The distance between electrodes was 1 cm. The applied voltages to the electrodes were kept constant at 40 V during the experiments and the volumetric flow rate of water was 20 mL/min.

2.3 Zeta potential measurements

Malvern Zetasizer-4, which calculates zeta potential depending on electrophoretic mobility, was used for the measurements. During the measurement, a sample of emulsion was placed into the measurement cell and an electrical field was applied to the electrodes. This causes any charged colloid in the emulsion to move towards the oppositely charged electrode at a velocity that depends on the magnitude of their charge. The colloid movement was recorded to a computer by taking the signals from the Unitron FSB-4X stereoscopic microscope. It features 20X wide field eyepieces in combination with a 4.0X paired objective. Overall magnification is 80X. This microscope is very adequate for colloids as small as 1.5 microns in size. Electrophoretic mobility of an oil droplet was obtained by tracking one oil droplet by pressing the mouse and holding it down while the droplets moves across the grid. Then the zeta potential is calculated by using Smouclowski equation.

3 Results and discussion

The volume percentages of oils (BOR and EAL) in water were 2%. The color of water was milky when it was mixed by BOR. In the case of EAL, the water was transparent. The physical properties of BOR and EAL emulsions were close to water. The density and viscosity of BOR were 1.035 g/cm^3 and 2.40 mPa.s., respectively. The corresponding values for EAL were 1.047 g/cm^3 and 1.37 mPa.s. Therefore, it was easy to prepare stable oil emulsions in water by using these cutting fluids. The stabilities of BOR and EAL emulsions were also investigated visually by monitoring the creaming behaviours of the emulsions for a month. The emulsions were placed into 50 mL graduated cylinders and if there was any phase separation it was recorded. After a month, almost no phase separation was observed for both emulsions and their separation was not possible by gravity.

Stability of emulsions is often related to zeta potential [9]. Therefore, variations in the zeta potentials of BOR and EAL droplets depending on pH (2, 4, 6, 8 and 10) were also investigated. For both emulsions, a strong dependency of zeta potential to pH was observed. It drops from 10 mV to -50 mV for BOR and EAL droplets when pH changes from 2 to 10. The isoelectric point for both emulsions was observed around pH 3. These results show that these emulsions are stable in alkaline conditions and can be easily destabilized by the adjustment of pH.

BOR and EAL emulsions were filtered through the cellulose nitrate filter paper using a vacuum filtration apparatus. The pore opening of filter medium was 8µm. It was not possible to separate BOR with this filter medium since the oil droplet diameters were much smaller. However, 81.7% removal was obtained for EAL. Therefore, the most important parameter to separate oil from water by filtration is the size of droplets.

The surface charges of oil droplets can be reduced by adding coagulants. The addition of coagulants results in coalescence of oil droplets. Alum and ferric chloride were tested as coagulants in the coagulation – flocculation experiments. The optimum coagulant dosages, mixing time and pH were determined for BOR and EAL oil emulsions by using a jar apparatus. Figure 1 shows the variations in the turbidity of emulsions with respect to alum dosages. It can be seen that the optimum alum dosages were 0.83 g/L and 4 g/L for BOR and EAL, respectively. The highest BOR removal was 90%. On the other hand, 98% of EAL was removed at the optimum alum dosage.

The optimum ferric chloride dosages for both emulsions were shown in Figure 2. It can be observed that the optimum ferric chloride dosages were 6 g/L and 8 g/L for BOR and EAL emulsions. For both emulsions, 98% oil removal was obtained at the optimum dosage.

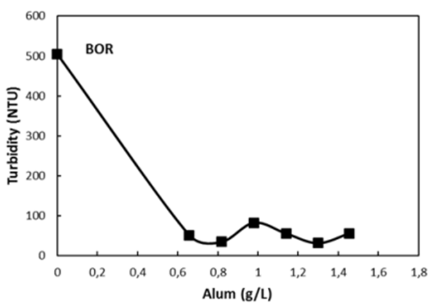

Figure 1: Optimum alum dosages for BOR and EAL oil emulsions.

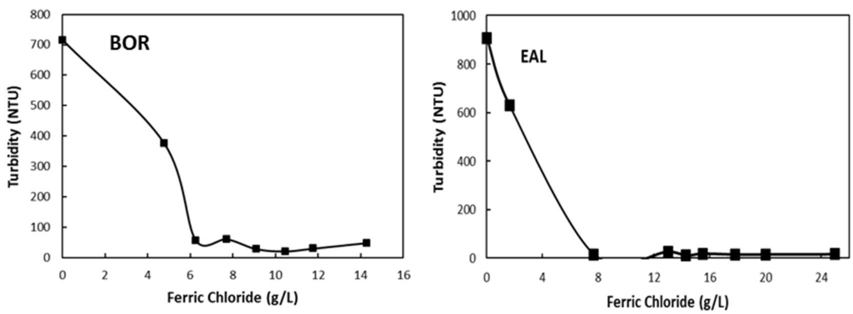

Figure 2: Optimum ferric chloride dosages for BOR and EAL oil emulsions.

After the evaluation of the optimum coagulant dosages, effects of mixing time and pH on oil removal efficiency were determined. Even though the turbidity dropped from 900 NTU to 100 NTU in 20 minutes, 45 minutes of mixing was necessary to reach 98% removal for EAL. The effects of pH on oil removal rates (turbidity) for alum and ferric chloride additions were shown in Figure 3 and Figure 4, respectively. BOR removal efficiency is a strong function of pH. In order to separate BOR from water by using alum, the suggested pH is around 8. In the case of the EAL removal, pH is suggested to be in between 4 to 6. When ferric chloride was added to the emulsions, the turbidity showed fluctuations, i.e., increases or decreases with an increase in pH. According to the results presented in Figure 4, when ferric chloride is used as the coagulant it is better to separate BOR or EAL from water by coagulation and flocculation operating at pH 8 or higher.

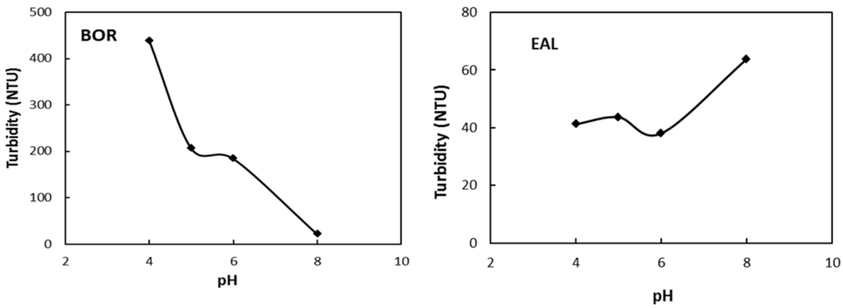

Figure 3: The variations in turbidity with respect to pH ($Al_2(SO_4)_3$).

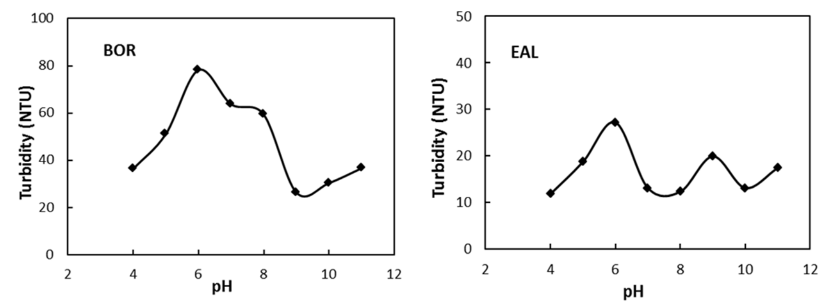

Figure 4: The variations in turbidity with respect to pH ($FeCl_3$).

Since the density of emulsions were very close to water it was not possible to separate BOR or EAL by only centrifugation. In order to increase BOR removal efficiency from 90% to 98%, the flocculated BOR emulsions with alum were centrifuged at different angular velocities. The results showed that 3000 rpm or higher values resulted in 98% removals.

During the electrocoagulation experiments, 40 V difference was applied to the aluminium electrodes. The initial pHs of waters in the experiments were 6 and 8 for BOR and EAL, respectively. The average currents passing through the cell was 0.9 A. For both oil emulsions, 95% oil removals were obtained in 35 minutes of operation.

When the removal rates obtained from each studied separation processes were analysed it can be seen that only the coagulation and electrocoagulation processes are comparable. The highest removal rates for BOR and EAL emulsions in coagulation were 98% whereas it was 95% in electrocoagulation. The price of ferric chloride becomes the basic parameter in the evaluation of operating cost for the coagulation process. On the other hand, the operating cost for the electrocoagulation process is equal to the multiplication of the current passing through the cell and the applied voltage to the electrodes in addition to the electrode prices. Since high amounts of ferric chloride is needed to reach 98% removals and the current passing through the cell during the electrocoagulation experiments were low, it can be concluded that the electrocoagulation process is the most effective process for the separation of emulsified oils.

4 Conclusions

The experimental results for the separations of BOR and EAL from water can be summarized as follows:

- The use of alum is recommended in the coagulation-flocculation process instead of ferric chloride since the optimum alum dosages are much lower.
- When alum is used as the coagulant the operating pH for the removal of BOR is suggested to be around 8. In the case of EAL, lower pH values than 7 is more effective to obtain better removal efficiencies.
- The highest removal efficiencies for BOR and EAL obtained from the coagulation-flocculation process using alum were 90% and 98%, respectively. The BOR removal efficiency can be increased to 98% by applying centrifugation to the flocculated BOR emulsions at an angular velocity of 3000 rpm.
- In the case of ferric chloride, 98% oil removals were obtained for both emulsions.
- When the removal rates and operating costs are taken into consideration the electrocoagulation process can be decided to be the most efficient method for the separation of emulsified oils from water.

Acknowledgement

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References

[1] Bensadok, K., Belkacem, M. & Nezzal, G., Treatment of cutting oil/water emulsion by coupling coagulation and dissolved air flotation. *Desalination* **206**, pp. 440–448, 2007.

[2] Bunturngpratoomrat, A., Pornsunthorntawee, O., Nitivattananon, S., Chavadej, J. & Chavadej, S., Cutting oil removal by continuous froth flotation with packing media under low interfacial tension conditions, *Separation and Purification Technology,* **107**, pp. 118–128, 2013.

[3] Cheryan, M. & Rajagopalan, N., Membrane treatment of oily streams. Wastewater treatment and waste reduction, *Journal of Membrane Science*, **151**, pp. 15–38, 1998.

[4] Pinotti, A. & Zaritzky, N., Effect of aluminum sulfate and cationic polyelectrolytes on the destabilization of emulsified wastes, *Waste Management*, **21**, pp. 535–542, 2001.

[5] Canizares, P., Garcia-Gomez, J., Martinez, F. & Rodrigo, M.A., Evaluation of a simple batch distillation process for treating wastes from metalworking industries, *Journal of Chemical Technology and Biotechnology*, **179**, pp. 533–539, 2004.
[6] Kobya, M., Ciftci, C., Bayramoglu, M. & Sensoy, M.T. Study on the treatment of waste metal cutting fluids using electrocoagulation, *Separation and Purification Technology*, **60**, pp. 285–291, 2008.
[7] G. Rios, G., Pazos, C. & Rios, J.C., Destabilization of cutting oil emulsions using inorganic salts as coagulants, *Colloids and Surfaces A*, **138**, pp. 383–389, 1998.
[8] Francis, M.J., Pashley, R.M., Further studies into oil droplet size manipulation, *Colloids and Surfaces A*, **334**, pp. 100–106, 2009.
[9] J. Drzymala, J., Sadowski, Z., Holysz, L. & Chibowski, Ice/water interface: zeta potential, point of zero charge, and hydrophobicity, *Journal of Colloid and Interface Science,* **220**, pp. 229–234, 1999.