Separation of oil-in-water emulsions by microbubble treatment and the effect of adding coagulant or cationic surfactant on removal efficiency

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ABSTRACT

This study examined the efficiencies of microbubble (MB) treatment, MB treatment with polyaluminium chloride (PAC) as a coagulant, and MB treatment with cetyltrimethylammonium chloride (CTAC) as a cationic surfactant in the separation of emulsified oil (EO) by modified column flotation. Batch mode experiments were conducted by synthesizing emulsified palm oil (d<20 μm), and the chemical oxygen demand (COD) of the influent and effluent was measured to evaluate the treatment performance. MB treatment with PAC and MB treatment with CTAC were found to be more efficient in EO removal than the MB treatment alone. At an EO concentration of ∼1,000 mg L⁻¹ (pH 7) and under identical treatment conditions (MB generation time: 2.5 min, flotation time: 30 min), MB treatment with PAC (50 mg L⁻¹) and that with CTAC (0.5 mg L⁻¹) showed equally high EO removal efficiencies of 92 and 89%, respectively. This result is of significant relevance to studies focusing on the development of economical and high-efficiency flotation systems. Furthermore, the effect of pH was investigated by varying the sample pH from 3 to 8, which showed that the EO separation efficiency of MB alone increased drastically from slightly alkaline to acidic condition.

Key words | cetyltrimethylammonium chloride, emulsified oil, flotation, microbubbles, polyaluminium chloride

INTRODUCTION

Separation of oil-in-water emulsion from wastewater effluents is important for improving the water quality, oil recovery, and water re-use, for protecting downstream facilities, and for ensuring compliance with environmental policies. Common pollutants found in the effluents of many industries are oil and grease, and their concentration in wastewater varies from a few mg L⁻¹ to as high as 5–10% by volume (Frank 1988; Lawrence et al. 2006). For instance, the concentration of oil and grease in palm oil mill effluent (POME) normally varies from 130 to 18,000 mg L⁻¹, and approximately 2,000 mg L⁻¹ is present in the form of emulsified oil (EO) (Ahmad et al. 2006; Lam & Lee 2011).

EO is a colloidal suspension of a liquid with droplet sizes of less than 20 μm, and thus, they can pass through the primary separator (Lawrence et al. 2006). In addition, EO remains stable over time as a result of a combination of some physical and chemical mechanisms (Frank 1988). Therefore, the removal of very fine oil droplets (2–50 μm) is difficult and very limited (Da Rosa & Rubio 2005; Lawrence et al. 2006). In practice, the emulsion can be separated by methods such as adsorption, coagulation, electro-coagulation, membrane filtration, biological treatment, flotation, and electro-coflotation (Lawrence et al. 2006; Bande et al. 2008). Among these methods, the combination of coagulation and flotation for the separation of EO has attracted attention from many researchers. Some reviews of the de-emulsification of oil-in-water emulsion by flotation methods are listed in Table 1.

In a flotation tank, the number of microbubbles (MBs) that can attach to a floc (~100 μm) is limited. Therefore, to produce large floc particles, coagulants are added and the detention time is adjusted such that MBs can attach to the floc particles (Edzwald 2010). MBs in water and EO carry...
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Reference:
2. Al-Shamrani et al. (2002)
3. Abid Baig et al. (2005)
5. Da Rosa & Rubio (2005)
6. Li et al. (2007)
8. Painmanakul et al. (2010)
negative charges, thus hindering the attachment without coagulation (Edzwald 2010). Therefore, besides coagulants, cationic surfactants are added to make the MBs positively charged (Henderson et al. 2008; Edzwald 2010). Although cationic-surfactant-treated absorption materials such as organoclay, wheat straw, and barley straw have been used to separate EO (Ibrahim et al. 2009), the performance of the combination of cationic surfactants and MBs in the separation has not been studied widely.

The main objective of this research was to evaluate and compare the effectiveness of EO separation by the flotation process under three process conditions: MB treatment only, MB treatment with polyaluminium chloride (PAC) as a coagulant (MB–PAC), and MB treatment with cetyltrimethylammonium chloride (CTAC) as a cationic surfactant (MB–CTAC). The experiments were conducted in batch mode to observe the effect of MBs, flotation time, PAC dosage, CTAC dosage, and pH on the flotation method.

MATERIALS AND METHODS

EO sample

EO with a concentration of ~1,000 mg L\(^{-1}\) was prepared from warm tap water (~40 °C) and palm oil product (Z67, Japan). The samples were mixed using a food mixer (volume 1.8 L). Batches of 1.0 L of sample were prepared. Samples of 20 mL were taken from 20 s to 30 min, and the EO particle size was determined using Olympus light microscope and Thoma hemocytometer (1/10 mm depth, 1/400 mm\(^2\)).

Experimental setup

A conventional jar test system with six beakers was used to investigate the optimum dose of PAC to coagulate the EO sample (~1,000 mg L\(^{-1}\)). A volume of 0.5 L of the sample was added to each beaker. The coagulant (PAC) was added with different dosages and the samples were rapidly mixed at 110 rpm for 2 min and then slowly mixed at 30 rpm for 10 min. After 10 min sedimentation time, 10 mL of the solutions was centrifuged at 1,250 rpm for 5 min and analyzed for the concentration of EO. The remaining samples were used to predict the volume of floated produce after 4 h sedimentation time by using 500 mL cylinders.

The laboratory setup for the flotation column used in this study (Figure 1) is modified from the Microcel flotation column (Rubio et al. 2002). The main components of the unit were a flotation tank, a stirrer, a thermometer, a pump, and an MB generator with an MB diffuser (egg-shaped BT-50 nozzle). The reactor was a columnar plastic tank with a working volume of 2.5 L (10.7 cm in diameter and 28 cm in height). The MB generator with the BT-50 nozzle has a high flow rate (~180 mL S\(^{-1}\)) and can produce MBs with sizes ranging from a few micrometers to several hundreds of micrometers. For each batch mode operation, 9 L samples were prepared, of which 6 L was used to restart the system twice. The pH of the samples was adjusted using 5.0 N H\(_2\)SO\(_4\) and 1.0 N NaOH and measured by a pH meter (D-13 Horiba). After adding the coagulant (PAC, 10 g L\(^{-1}\), type 30% Al\(_2\)(SO\(_4\))\(_3\)) or cationic surfactant (CTAC, 1 or 10 g L\(^{-1}\), CH\(_3\)(CH\(_2\))\(_{15}\)CH\(_2\)-N(CH\(_3\))\(_3\)Cl), the samples were mixed using a stirrer (Elela, type 2-2200) and then the MB generator was turned on. Treated water was taken from the bottom of the reactor.

Several methods can be used to analyze oil-in-water emulsions, such as \(n\)-hexane extraction, chemical oxygen demand (COD) analysis, spectrophotometric analysis, zeta-potential determination, and turbidity measurements. However, the most effective and simplest method is COD measurement (Painmanakul et al. 2010). In this research, the concentration of EO was measured by analyzing COD following the standard procedure (5220D, APHA 1998).
RESULTS AND DISCUSSION

Preparation of EO

The results showed that most of the free oil was transferred to EO ($d < 20 \mu m$) after 4 min of mixing (Figure 2(a)). In addition, UV spectrophotometry results obtained at an EO concentration of $1,012 \text{ mg L}^{-1}$ (mixing time: 4 min) showed two peaks at wavelengths of 278 and 284 nm. The absorbance values of the samples were determined at these wavelengths. A significant increase in the absorbance value at these two wavelengths was observed from 20 s to 4 min, after which no change was observed in the absorbance values (Figure 2(b)). Therefore, a mixing time of 4 min was chosen to prepare the EO in this research.

Effect of PAC dosage

The effect of PAC dosage on the separation of EO concentration of $1,007 \text{ mg L}^{-1}$ (COD: $\sim 3,138 \text{ mg L}^{-1}$) was investigated by batch coagulation tests. An increase in PAC concentration from 10 to 50 mg L$^{-1}$ resulted in a significantly higher percentage of EO removal. It was noticed that at a coagulant concentration of 50 mg L$^{-1}$ a 97% removal of EO was reached, creating about 40 ml L$^{-1}$ of floated product. In fact, the conventional coagulation method showed a high efficiency of EO removal at low PAC concentrations. These results can be explained by the high charge density of both PAC and EO in water (Ahmad et al. 2006). PAC is not only able to neutralize the negative charge of EO droplets, but also forms aluminium hydroxide flocs which plays an important role for a better coagulation (Takahide 1999). Still, the complex operation steps of the coagulation process, including flash mixing, slow mixing, and a long sedimentation time are a main weakness of this method. A PAC dosage of 50 mg L$^{-1}$ was selected to study other factors which influenced the flotation method.

Effect of MBs

In the batch mode of the flotation method, the effect of MBs was investigated at EO concentrations of 105 mg L$^{-1}$ (COD: $\sim 303 \text{ mg L}^{-1}$), 508 mg L$^{-1}$ (COD: $\sim 1,482 \text{ mg L}^{-1}$), and 1,007 mg L$^{-1}$ (COD: $\sim 3,138 \text{ mg L}^{-1}$), while the MB generator was operated from 2.5 to 60 min at pH 7.0 (Figure 3(a)). During this period, a steady rise in temperature was recorded from 38 to 74°C with an average increase of 0.6°C per minute. For all three concentrations of influents a slight decrease in EO concentration with time was observed. After 60 min of MB generation at EO influent concentrations of 105, 508 and 1,007 mg L$^{-1}$, the percentage of EO removal was 48, 41, and 29%, respectively. This low EO removal efficiency indicates that the interaction between the MBs and EO was weak. In addition, the operation of the MB generator for a long time and the increase in the temperature caused the MBs to rise fast to the surface.

Effect of flotation time

Flotation time plays an important role on the efficiency of flotation methods. In practice, a detention time from 1.5 to 2.5 min is usually selected to replicate flow conditions in the contact zone of the dissolved air flotation (DAF) process (Edzwald 2010). To investigate the effect of flotation time on EO removal, in this study an operation time of 2.5 min for the MB generator was selected. After 30 min flotation
time, both using PAC (50 mg L\(^{-1}\)) and CTAC (0.5 mg L\(^{-1}\)) a high efficiency of EO removal of 92 and 89% was achieved respectively (Figure 3(b)). Application of CTAC was revealed to be more effective than PAC in terms of flotation time as well as dosage. While a dosage of 0.5 mg L\(^{-1}\) of CTAC displayed a high EO removal efficiency within a short flotation time (2.5–5 min) and in addition created only a small amount of floated produce, PAC (50 mg L\(^{-1}\)) required over 10 min flotation time and produced more floated sludge.

It should be noted that the number of MBs that can attached to a floc (∼100 μm) is very limited (Edzwald 2010). For this reason, at the same flotation column volume, a change in the surface area (diameter) or height of the reactor could improve the efficiency of the treatment method. In addition, the mixing rate is an important factor that influences MB attachment to EO and/or flocs. Thus, besides affecting the separation of EO and/or floc particles, MBs generated by the diffuser produce the right chemical mixing condition. In the case of PAC (50 mg L\(^{-1}\)), the mixing procedure (rapid mixing at 300 rpm for 2 min, slow mixing at 30 rpm for 10 min) mostly transferred the EO to flocs. Therefore, the MBs mainly supported the separation between the two phases, i.e., water and solid (floc particles). In contrast, in the case of CTAC (0.5 mg L\(^{-1}\)), the MBs played the main role of mixing CTAC with the EO. The high efficiency of EO removal of the MB treatment with CTAC as compared with the MB treatment with PAC provides an important result for the development of a high efficiency and economic flotation system, especially because it does not require a complex mixing procedure.

Effect of CTAC dosage

The effect of CTAC dosage on the removal of EO was investigated by changing the CTAC dosage from 0.001 to 10 mg L\(^{-1}\). Here, an EO concentration of 1,005±1 mg L\(^{-1}\) (corresponding to a COD of 3,116±30 mg L\(^{-1}\)) was used, MB time was 2.5 min, pH was 7.0 and the flotation time ranged from 2.5 to 27.5 min (Figure 4). The use of CTAC was shown to be as effective as the use of PAC in the separation of EO with the highest percentage of EO removal recorded being 87±2.0 and 81±1.5% at a CTAC concentration of 0.5 and 1 mg L\(^{-1}\), respectively. At higher CTAC concentrations a sharp decrease of EO removal efficiency was observed and only 7±0.9% of EO was separated at a concentration of 10 mg L\(^{-1}\) CTAC.

Remarkably, by using a low concentration of CTAC as the cationic surfactant a large amount of EO can be removed. This
research indicated that this concentration is about 100 times smaller than the used PAC dosage (50 mg L\(^{-1}\)). Furthermore, a concentration of 0.5 mg L\(^{-1}\) CTAC is also lower than the concentrations used for other inorganic and/or organic emulsion breakers reported in previous studies (Table 1). For example, it required a concentration of Fe\(^{3+}\): 100 mg L\(^{-1}\) and sodium olate: 50 mg L\(^{-1}\) to separate 95\% of the EO with initial concentration of 500 mg L\(^{-1}\) (Zouboulis & Avranas 2000). As well, in order to remove an influent EO concentration of 100 mg L\(^{-1}\) to less than 10 mg L\(^{-1}\), a combination between two coagulation reagents (cationic polyacrylamide: 15 mg L\(^{-1}\) and PAC: 30 mg L\(^{-1}\)) was done (Li et al. 2007), etc. This can be explained by the fact that CTAC has a low molecular weight (MW = 500) and carries a residual positive charge. Therefore, CTAC is not only able to reduce the negative charges present on the surface of the oil droplets, but also adsors on the oil droplets to create macro-flocs (Moosai & Dawe 2003). On the other hand, CTAC could make the MB positively charged, leading to a higher chance of MB attaching to the EO and/or flocs, thereby increasing the oil-gas-floc size (Henderson et al. 2008).

The use of an excess concentration of CTAC was shown previously to decrease the flotation efficiency. Such a trend was also documented by Li et al. for their investigation on the effect of the feed concentration of the anionic surfactant sodium dodecyl sulfonate (Li et al. 2007). This situation is because the effectiveness of the surfactant strongly depends on the critical concentration that is required to form aggregates. Above this concentration micelles will be formed (Moosai & Dawe 2003). For that reason, in case of field operations it is suggested to monitor wastewater characteristics as well as surfactant dosages frequently.

**Effect of pH**

The pH value of a sample significantly enhances the efficiency of the EO breaking process through its impact on the surface charge of MB, oil droplets, and the resulting flocs (Zouboulis & Avranas 2000; Ahmad et al. 2006; Li et al. 2007). In this study, the effect of pH was studied by varying the pH from 3 to 8. The optimum concentrations of PAC (50 mg L\(^{-1}\)) and CTAC (0.5 mg L\(^{-1}\)) were used and MB time was 2.5 min (Figure 5). The three treatment methods were named MB, MB–PAC (50 mg L\(^{-1}\)) and MB–CTAC (0.5 mg L\(^{-1}\)). After adjustment of the pH and adding PAC or CTAC, the samples from MB–PAC (50 mg L\(^{-1}\)) treatment were rapidly mixed at 300 rpm for 2 min and slow mixed at 30 rpm for 10 min. For the two other methods, the samples were simply mixed rapidly at 300 rpm for 2 min. During the flotation stage, five samples for each method were taken at 2.5, 7.5, 12.5, 17.5, and 27.5 min.

Without PAC or CTAC, considering only the effect of pH, the separation of EO by MB was found to increase dramatically from 10±1.1\% at a slightly alkaline pH of 8, to 70±1.7\% under acidic conditions (pH 3). Traditionally, sulfuric acid has been applied as the first step in the emulsion breaking of oily wastewater in treatment plants. The strong acidic conditions may cause the protonation of the carboxylate ion in EO droplets to the carboxylic acid, allowing the oil droplets to agglomerate (Frank 1988). As a result, MBs have a higher chance to attach to the agglomerates’ surface. At pH 4, an EO removal efficiency of 69±2.0\% was reached. This result shows that it may be worthwhile to investigate the effect of MBs on the separation of acidic oily wastewater sources such as POME (pH 3.4–5.2) (Lam & Lee 2011). It should be noted, however, that after the emulsion breaking process the effluent acidic water needs to be neutralized.

Among the inorganic coagulants, PAC is well known to be a good candidate for the separation of EO within a wide pH range (5–7.5) (Takahide 1999; Ahmad et al. 2006). For the MB–PAC (50 mg L\(^{-1}\)) this research showed steady EO removal efficiencies of 86±2.8, 88±3.2, 87±5.9, 85±6.9, and 81±13.4\% when going from pH 3 to pH 7. The significant difference in standard deviations between the treatment methods can be explained by the effect of flotation time. Again, when comparing MB or MB–CTAC (0.5 mg L\(^{-1}\)) with MB–PAC (50 mg L\(^{-1}\)), MB–PAC (50 mg L\(^{-1}\)) generated the highest amount of floated product. With this high amount of floated product it could take more time for all the floc-bubble-aggregates and/or floc-aggregates to reach the surface. Consequently, 2.5–5 min flotation time was needed for
MB and MB–CTAC (0.5 mg L⁻¹) to reach the highest percentage of EO removal. In contrast, more than 10 min flotation time was needed for MB–PAC (50 mg L⁻¹).

MB–CTAC (0.5 mg L⁻¹) showed a high EO removal efficiency of 80±2.0, 81±2.6 and 86±1.6% when going from pH 5–7. Using a DAF column, Li et al. (2007) also indicated that the pH value should be adjusted from 5–9 when separating oil from wastewater (with initial EO concentration: 100 mg L⁻¹, PAC: 20.0 mg L⁻¹, sodium dodecyl sulfate: 5.0 mg L⁻¹, EO removal efficiency: approximately 77%). However, the reduced pH (pH 3–4) of the samples could have led to ionization of the EO droplets and, therefore, the addition of CTAC might have resulted in a reduction in EO separation efficiency (Ibrahim et al. 2009). According to the present results, a pH around neutrality gave the same EO separation efficiency for MB–PAC (50 mg L⁻¹) and MB–CTAC (0.5 mg L⁻¹).

CONCLUSIONS

This study evaluated the efficiency of MB treatment alone, MB treatment with PAC as the coagulant, and MB treatment with CTAC as the cationic surfactant in the separation of EO by modified column flotation under a high MB flow rate. The separation of oil-in-water emulsions is successfully achieved by the combination of MB–PAC or MB–CTAC. The use of MB treatment alone showed less impact on the EO removal efficiency than MB treatment with PAC or MB treatment with CTAC. However, MB treatment alone exhibited a significant EO removal efficiency in acidic water. A high concentration of emulsified palm oil (~1,000 mg L⁻¹) was successfully separated with an efficiency of approximately 90% by MB treatment with PAC (MB generation time: 2.5 min, PAC: 50 mg L⁻¹, pH: 3–7) and with an efficiency of more than 82% by MB treatment with CTAC (MB generation time: 2.5 min, CTAC: 0.5 mg L⁻¹, pH: 5–7). In conclusion, the data indicate a good EO removal efficiency at a low concentration of CTAC (0.5 mg L⁻¹), which was 100 times less than that of PAC dosage (50 mg L⁻¹). This result is interesting to consider the development of high efficiency and economical flotation systems.

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REFERENCES


Painmanakul, P., Sastaravet, P., Lersjintanakarn, S. & Khaodhiara, S. 2010 Effect of bubble hydrodynamic and


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