

ISSN 1682-296X (Print)

ISSN 1682-2978 (Online)



Bio Technology



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308 Lasani Town, Sargodha Road, Faisalabad - Pakistan

Treatment of Oily Waste Water Emulsions from Metallurgical Industries Using Microwave Irradiation

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Abstract: Emulsion waste water is one of the important industrial wastewaters, which results from the various manufacturing industries including the metal manufacturing and its processing. Wastewater treatment technologies utilizing flocculation and electrolysis have been used but these technologies have not been very helpful in resolving the problems in view of process consistency and economic merit. Aiming to mitigate the environmental hazard that these waste emulsions represent, a study was carried to investigate the microwave methods to destabilise water/oil emulsions without the addition of any destabilizing chemical agent. The experimental work consisted on breaking the simplest of the emulsions in terms of content, in order to obtain preliminary data that can help to extend the method to manage actual waste material. The samples consisted in water/oil emulsions waste (spent cutting oil), which was obtained from local metal industries. The sample emulsions underwent a domestic microwave radiating process at several exposure times. Certain factors, such as aromatic components and sodium hydroxide content and total heat exposure time proved to be the factors that more strongly affect the results. Within the category of paraffinic oils, light oils allow for quicker water separation than heavy oils. Also oils with higher aromatic content have higher viscosity, which makes the separation of water more difficult. It was observed in this study that emulsions added with acid up to a final concentration of 0.48 M, the separation efficiency and demulsification rate increased with increasing acid concentration. Hence microwave irradiation is an economical and rapid method for oil separation from oily waste water. Although this study was carried out on a lab scale basis, the process can scale up to a large industrial scale system. By using the microwave radiation, an aqueous phase recovery that ranged from 65 to 90% was obtained, which is a significant outcome that reveals the study of this technique needs to be taken further

Key words: Microwave irradiation, waste water/oil emulsion, water separation, demulsification

INTRODUCTION

Oily water emulsions are one of the main pollutants emitted into water by industries and domestic sewage. Emulsions are a suspension of droplets, greater than 0.1 μ in diameter, consisting of two completely immiscible liquids, one of which is dispersed throughout the other. Emulsions are frequently quite persistent in the environment and resist decomposing into their original constituents of oil and water. Emulsions are formed when one liquid is dispersed in a continuous liquid phase of a different composition. Two types of simple emulsions have been identified depending on which kind of liquid forms the continuous phase: (i) oil-in-water (O/W) for oil droplets dispersed in water; (ii) water-in-oil (W/O) for water droplets dispersed in oil (Schramm, 1992).

Industrial growth has accelerated the emission of various oily wastes from the sources such as

petrochemical and metallurgical industries, transportation and domestic sewage. These oily wastes are one of the major pollutants of the aquatic environment. Steel-mill industry, paper industry, textile industry, pharmaceutical industry, chemical industry and oil-production industry also produces oil emulsions as their waste. The engine wash, car wash station, aircraft wash or petrol station waste also contains oil emulsions. If left untreated, they often cause high wastewater treatment loads. This oil/wastewater substance can severely hamper recovery capabilities of skimmers; reduce pumping volumes; and increase handling, oily waste disposal, segregation and storage problems. In addition, non-mechanical response techniques, such as the use of dispersants and in situ burning, are rendered less effective or ineffective by formation of high-viscosity emulsions. If they reach onsite process equipment they can cause fouling and/or unit upsets. Thus, they are often the cause of increased

maintenance, corrosion and energy consumption. Despite the fact that the problem of oily sewage treatment exists for decades, it could be hardly said that it is solved. It is evidenced by the use even now of horizontal oil removers, facilities simple in design but extremely complicated in operation. The emphasis on reagent flotation did not bring the expected result. Sorption methods are competitive only when oil product concentration values are relatively small (Reed *et al.*, 1997; Fang *et al.*, 1989).

Microwave radiation can be used as an alternative method for emulsion breaking. This idea was first suggested by Klaila (1983) and Wolf (1986) in their patent documents. Other important studies and theoretical developments showed that microwave methods are able to destabilize water/oil emulsions by two means. First by increasing temperature, which reduces the continuous phase viscosity and breaks the outer film of the drops, thus allowing for coalescence; and second by rearranging the electrical charge distribution of the water molecules while rotating them and moving ions around the drops. These two actions combined result in the breaking of the emulsion without adding any chemical agent (Fang *et al.*, 1988; Fang and Lai, 1995).

In this study, oily waste water from a local metal industry will be treated to break the emulsion by means of coalescence using microwave radiation (Haque, 1999; Xia and Pickles, 1997). Oil-in-water emulsions are used as lubricants and coolants in steel cold rolling operations in metal industries. After being used the fluids become less effective because of thermal degradation and contamination by substances in the suspension and therefore must be replaced periodically, generating a waste stream called spent cutting-oil. Spent cutting-oil emulsions are one of the largest volumes of oily wastewater in metal working industries. They must be treated before its disposal. In this study several variables will be qualitatively studied in their effect over the emulsion breaking process: effect of exposure time of microwave radiation, effect of presence of NaOH, effect of lubricant viscosity and presence of acid. Temperature profiles will be checked for linearity and uniformity in order to establish that viscous water-oil emulsions are heated faster and quicker by microwave radiation than by conventional convective heating. Water separation percentages will offer a way to qualitatively estimate effectiveness of breaking process and total time needed for a maximum water recovery.

MATERIALS AND METHODS

Equipment: The main piece of equipment employed for this work was a domestic microwave oven. It has a

Table 1: Properties of Lubricant emulsions used in the experiments

Properties	Lubricant emulsion A	Lubricant emulsion B
Density at the rate of 20°C (g cm ⁻³)	0.8888	0.856
Cinematic Viscosity (cSt) at the rate of 40°C	539.30	21.06
At the rate of 100°C	33.44	4.14
Molecular weight	760	375.0
Aromatic content (% p)	48.2	17.5

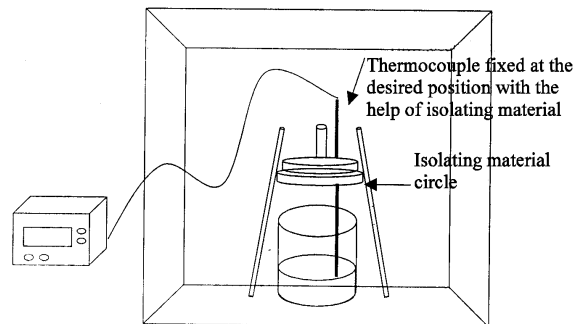


Fig. 1: The experimental set up for the temperature profile

volumetric capacity of 0.0235 m³, with an effective power of about 930 W. The experiments were carried out using full heating potency. For measuring temperature profiles along the sample, an array of nine thermocouples type J located and distributed as sketched in Fig. 1 and 2 were used. Readings were made by means of a temperature indicator with precision of $\pm 0.1^\circ\text{C}$. A pipette was used for aqueous phase extraction.

Sample: Sample for the present study was obtained from a local metal industry in Shah Alam Selangor. The sample was an oily wastewater emulsion (spent oil), which was used as a lubricant and coolant in steel cold rolling operations. Thermal degradation and contamination makes the fluid less effective, which requires periodic replacement and hence generating large volumes of oily wastewater emulsions. Two different waste lubricant emulsion samples were obtained. They were called lubricant emulsion A and B. Lubricant emulsion A had higher viscosity, molecular weight and aromatic content. The main properties of the two sample lubricants are shown in Table 1.

For samples in which NaOH was added, 1 mL of 1 M NaOH was used, for each 200 mL of emulsion. Effect of acid on demulsification was also studied. Only waste lubricant emulsion A was subjected to acid effect, where 4, 8, 12, 16 and 20 mL of 6 M HCl acid was used for a series of five sample of waste lubricant emulsion A respectively, giving a final concentration of 0.12, 0.24, 0.36, 0.48 and 0.6 M acid.

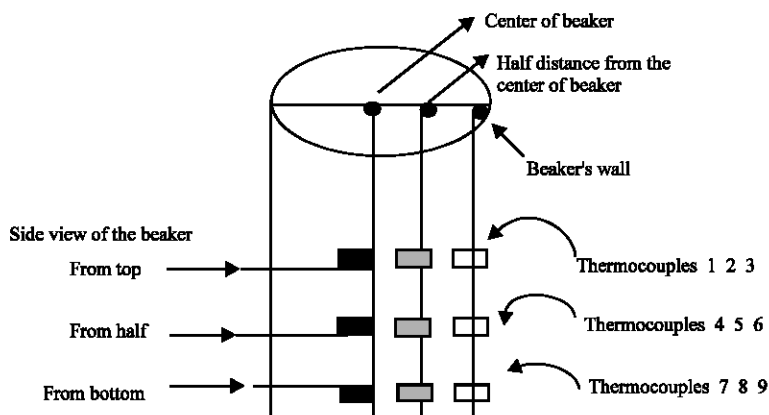


Fig. 2: Overview of the thermocouple arrangement to determine temperature in the beaker

Preliminary study on effect of microwave irradiation power and exposure time:

To verify the effect of microwave output power and irradiation time on the demulsification process, samples of 300 mL of waste lubricant emulsion A were subjected to microwave irradiation using power output of 230, 460, 700 and 930 W. For each of these output power a set of five exposure time were chosen, i.e., 30, 60, 120 240 and 300 sec. Based on the result obtained, all subsequent experiments were carried out at the optimum microwave output power.

Temperature profiles: A sample of approximately 200 mL of lubricant emulsion A was heated in the microwave oven for periods of 60, 120 and 240 sec. Once the exposure time was completed the sample was quickly attached to the set-up as shown in Fig. 1. Temperatures were obtained by recording readings of the three zones of the sample: top, half and bottom. Three reading per zone was recorded, one in the center of the beaker, half distance from the center of the beaker and near the beaker’s wall. Figure 2 shows the thermocouple arrangements.

Calculation of water recovery: Water recovery is the amount of aqueous phase that coalesces and separates from the emulsion after the radiation treatment. For determining the initial amount of water, the Karl-Fisher titration method was used (U.S. EPA NEIC Method-9000, 1991). Initial amount of water in the samples was denoted as V_i . After heating the sample by the predetermined exposure time t , (30, 60, 80, 120, 240 sec), the coalesced water volume V_s , was extracted by periods of 2, 5, 10, 25 and 60 min. These periods are accounted as sedimentation time, t_s . For each t_s a water separation percentage was calculated as below:

$$\text{Water separation (\%)} = V_s/V_i \times 100 \quad (1)$$

For each exposure time t , percentage of water separation (% water separation) was plotted against sedimentation time, t_s .

The separation efficiency (S) was defined as follows:

$$\text{Separation efficiency, } S = \frac{\text{Volume of separated water phase (mL)}}{\text{Original volume of water phase in sample (mL)}} \times 100\%$$

RESULTS AND DISCUSSION

Effect of NaOH presence and viscosity: Microwave power output and irradiation time have effects on the demulsification process. There was no aqueous phase separation observed with a 230 and 460 W power output even after 300 sec irradiation. Some separation could be seen with a power output of 700 W after 300 sec. However, with power output of around 930 W, a significant phase separation could be seen after 30 sec of irradiation. Demulsification rate increased with the irradiation time. However, irradiation time greater than 300 sec suffered from boiling over. Therefore, 930 W power output and irradiation time ranging from 30 to 240 sec were used for all subsequent experimental runs.

For both types of lubricant emulsion (A and B), it was observed that water separation percentage increases with increasing exposure time. This observation was for both the samples with and without NaOH (Fig. 3a, b and 4a, b). The maximum exposure time, which gives the highest water separation percentage, is between 240-300 sec. Beyond this time the emulsion solution would over boil. By comparing Fig. 3 (a) with 3 (b) and 4 (a) with 4 (b), it can be seen that without the presence of NaOH in the

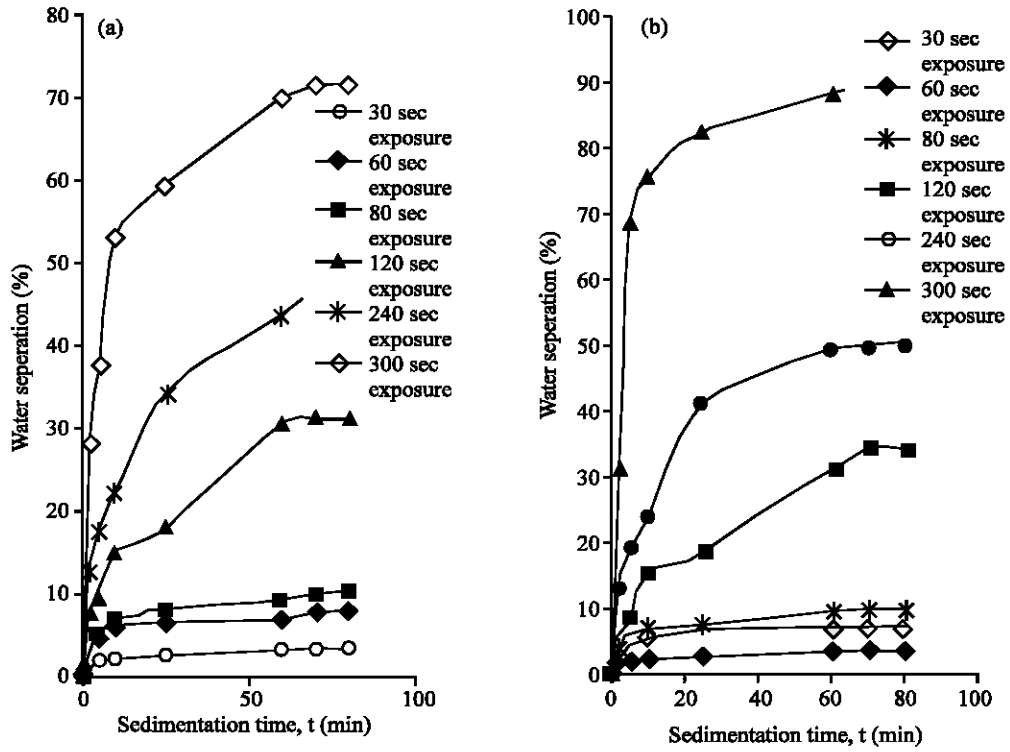


Fig. 3: Water separation % calculated at various sedimentation time interval for several exposure times, for lubricant emulsion-B (a) added with NaOH and (b) with no NaOH added to the emulsion

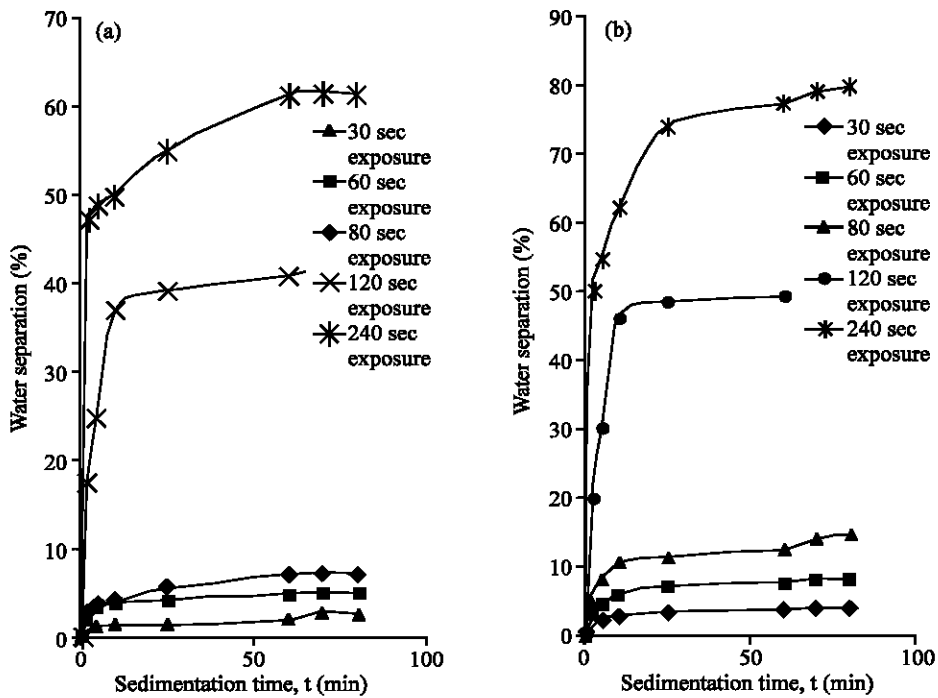


Fig. 4: Water separation % calculated at various sedimentation time interval for several exposure times, for lubricant emulsion-A (a) added with NaOH and (b) with no NaOH added to the emulsion

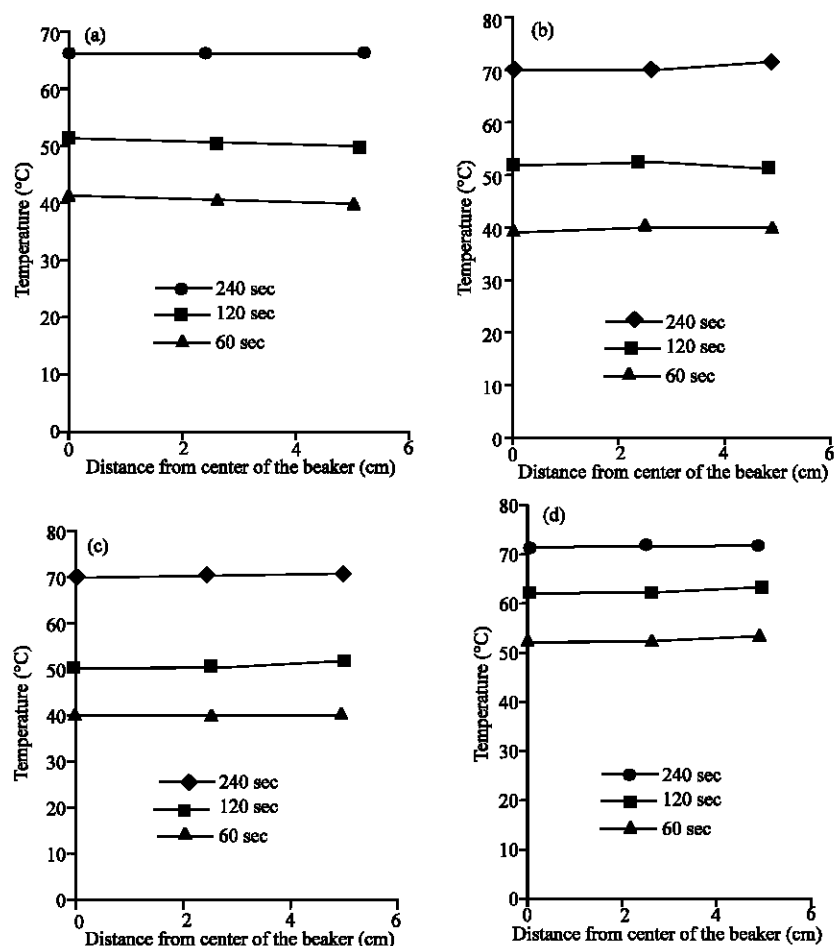


Fig. 5: Temperature profiles for several exposure times of lubricant emulsion A (a) on top of the beaker and no NaOH added; (b) on the half of the beaker and no NaOH added; (c) on the bottom of the beaker and no NaOH added; (d) on the half of the beaker and with NaOH added

emulsion, the water separation percentage is greater. The maximum water recovery for emulsions with NaOH added was around 70% (Fig. 3a), while emulsions without NaOH, had maximum water separation of slightly more than 90% (Fig. 3b) at the optimal exposure time.

Presence of NaOH in the emulsion has a stabilizing effect on the emulsion and hence reduction in total water separation percentage. This effect may be due to the NaOH neutralizing the free acids present in the emulsion. This increases the tensoactive action of the oil in the emulsion, thus stabilizing it and making it more difficult to be separated from the water phase (Young-Chae *et al.*, 1998; Thostenson and Chou, 1999).

The water separation process was also affected by the composition of the lubricant oil. Lubricant emulsion A which is composed of heavier oil with higher aromatic content and viscosity gave a maximum water separation of about 75% (Fig. 4a-c, without NaOH), while lubricant

emulsion B, which is composed of lighter oil with lower aromatic content and viscosity, had a maximum water separation of about 90% (Fig. 4b, without NaOH).

In general, results for lubricant emulsions B showed higher water recovery values in comparison with those from lubricant emulsion A. Within the category of paraffinic oils, light oils allow for quicker water separation than heavy oils. Also oils with higher aromatic content (like lubricant emulsion A, as shown in Table 1) have higher viscosity, which makes the separation of water difficult (Takahashi *et al.*, 1996; Thostenson and Chou, 1999).

Temperature profiles: Results obtained for temperature profiles after heating a sample with microwaves (930 W power output) during several different exposure times at different positions in the beaker are shown in Fig. 5 a-d. As we use the thermocouple to measure the degree of

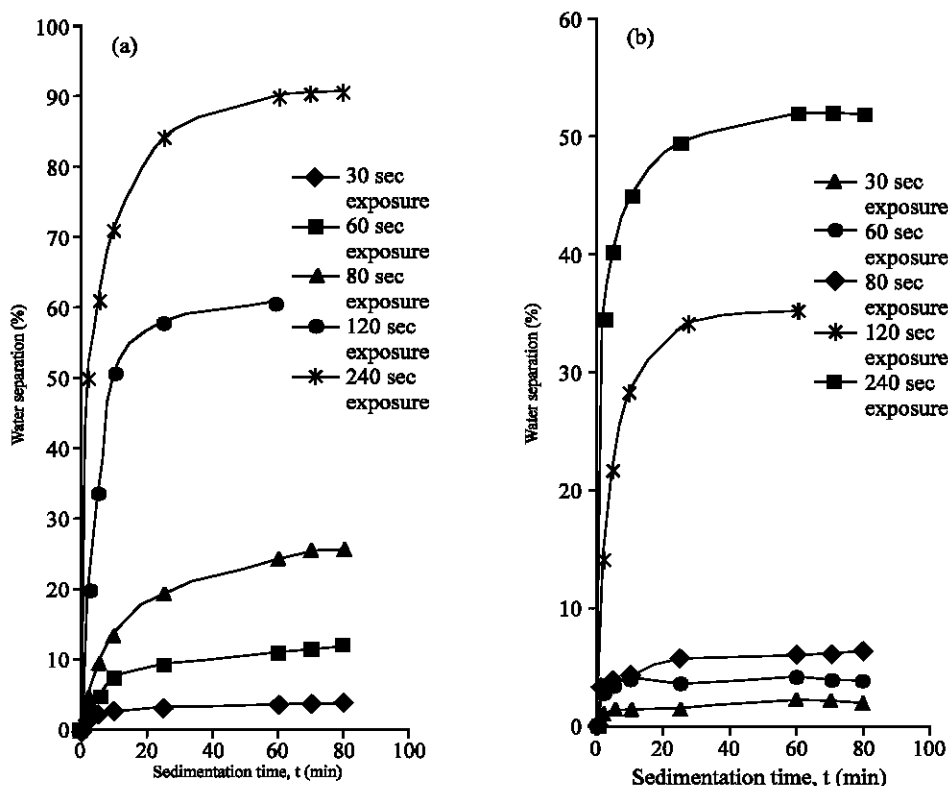


Fig. 6: Water separation % calculated at various sedimentation time interval for several exposure times, for lubricant emulsion-A, (a) with HCl acid (0.36 M final concentration) added to the emulsion and (b) with HCl acid (0.60 M final concentration) added to the emulsion

heat in the beaker after being heat by the microwave, it was observed that the temperature obtained either at the center of the beaker; half distance from the center of the beaker or at the bottom of the beaker is even throughout the beaker. Maximum temperature registered was around 72°C after 240 sec exposure in the microwave oven. This proved that the microwave heating is even throughout the process and no difference in the temperature of the emulsion at various positions in the beaker. By comparing Fig. 5b and 5d it can be observed that NaOH presence seems to increase temperature profile values.

The linear temperature profiles obtained verify a uniform and horizontal heating within the microwave oven (Fig. 5a-d). This confirms that viscous water-in-oil emulsions are heated more quickly and uniformly by microwaves than by conventional convective heating, thus providing a faster water-oil separation (Fang and Lai, 1991). In the presence of NaOH, probably the decrease in viscosity due to oil dispersion between NaOH produces more heating since the microwaves are more effectively absorbed (Fang and Lai, 1991; Barringer *et al.*, 1995). This effect relates to the increase in ionic diffusion (ions move the fluid while tending to align with the electric field). It

should be noted that although the heating is more effective in solutions with NaOH, the overall water separation is lower because as stated earlier NaOH increases the tensoactive action of the oil in the emulsion, which stabilizes the emulsion and making the separation of oil and water phase more difficult (Chih-Chieh and Yeong-Ching, 2002).

The effect of acids: Figure 6a and b shows respectively the effect of 0.36 M and 0.60 M HCl (final concentration) on the demulsification process of lubricant-emulsion A respectively. It was observed that internal aqueous solution with different amount of acids does affect the demulsification process. Separation efficiency and demulsification rate increased with the acid concentration. Ionic migration is thought to be responsible for this effect (Strauss and Trainor, 1995; Chih-Chieh and Yeong-Ching, 2002). Due to the effects of both dipole rotation and ionic conduction, acidified emulsions will have higher dissipation factor and thus higher microwave heating effect. A solution with high dissipation factor gives good microwave absorption capability and thus shows high microwave heating effect. This was clearly observed in

the experiments with emulsions added with acid up to a final concentration of 0.48 M. In this range of acid concentration the separation efficiency and demulsification rate increased with increasing acid concentration. However at acid concentrations greater than 0.5 M the dependence was different. The separation efficiency and demulsification rate decreased with acid concentrations higher than 0.5 M. The limitation of dipole rotation of water molecules due to salting effect, especially in the concentrated range, is thought to be responsible for this reverse effect (Chin-Chieh and Yeong-Ching, 2002; Larhed and Hallberg, 2001; Jassie *et al.*, 1997).

CONCLUSIONS

Microwave heating proved to be an effective method for breaking water-in-oil emulsions. It generates a uniform temperature profile in horizontal direction, thus providing a faster water- oil separation. Presence of NaOH in the emulsion acted as a stabilizing factor which resulted in lower water separation. Within the category of paraffinic oils, light oils allow for quicker water separation than heavy oils. Also oils with higher aromatic content have higher viscosity, which makes the separation of water more difficult. It was observed in this study that emulsions added with acid up to a final concentration of 0.48 M, the separation efficiency and demulsification rate increased with increasing acid concentration. However at acid concentrations greater than 0.5 M the dependence was different. The separation efficiency and demulsification rate decreased with acid concentrations higher than 0.5 M. From this study it can be said that microwave irradiation (plus addition of 0.48 M acid) is an economical and rapid method for oil separation from oily waste water. Although this study was carried out on a lab scale basis, the process can scale up to a large industrial scale system.

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