Korean J. of Chem. Eng., **6**(2) (1989) *81-87*

DEMULSIFICATION OF O/W EMULSION AND SUBSEQUENT WATER TREATMENT USING POWDER ADSORBENT

Sung-Sik LEE, Mitsuhiro NAKAMURA*, and Yasushi TAKEUCHI*

Department of Chemical Engineering, Dong-A University, Pusan 840, Korea
*Department of Industrial Chemistry, Meiji University, Kawasaki 214, Japan

(Received 15 January 1988 • accepted 30 August 1988)

Abstract—Demulsification of stable oil-in-water emulsion was studied using powder adsorbent. Among various adsorbents tested, activated carbon was found to be the most efficient regardless of the type of surfactants used. The more dose of activated carbon for the demulsification was required, the higher concentration of the surfactant as well as the larger amount of oil and the bigger size of the lipophilic and hydrophilic groups.

Empirical equations were obtained to correlate the dose of activated carbon to the residual concentration of oil as a function of the initial concentration of surfactant.

INTRODUCTION

Recently, the amount of emulsion-formed wastewater has been greatly increased from the machine and tool works and other sources, such as cleaning of oil tanks, separation of butter from milk, and removal of rubber from latex and household wastewater, etc.[1]. Such an emulsion stabilized by surfactant is thermodynamically stable and remains completely stable until the stability is changed by introducing a remover of the surfactant. As a consequence, the emulsion causes the pollution problem of lake and river.

To solve the problem, the process of emulsion-breaking and separation of emulsion from the effluent water are necessary. Techniques[2] of demulsification are classified as follows: (1) physical methods, such as gravity separation, fibrous and granular bed filtration, centrifugal coalescence, ultrafiltration, air flotation, freezing and electrically induced coalescence. (2) chemical methods, such as adjustment of pH and addition of large amount of cation or polymer as flocculants.

While the physical methods are generally energy-consuming, the chemical methods require the suitable flocculants depending on the emulsifier and its concentration for specific cases.

According to the works of Y. Takeuch et al.[3,4], the adsorption method is found to be very useful for the demulsification of oil-in-water (O/W) emulsion. The objective of this paper is to investigate more detail in the feasibility of demulsification using powder adsorbents.

To break the emulsion in the water, the powder was used to adsorb the surfactant at the interface of oil and water. In the cases, the optimum dose of powder adsorbent for demulsification of a stable O/W emulsion and the effect of initial concentration of the surfactant, the concentration and the type of oils, and HLB values of non-ionic surfactants on the separation of oils were studied.

EXPERIMENTAL

1. Materials

The oils used to prepare O/W emulsion were n-dodecane and salad oil. Their properties are shown in Table 1. Benzalkonium chloride, dodecylbenzene sulfonate (supplied by Tokyo Kasei), polyoxyethylene nonyl phenyl ethers (n = 15; Emulgen PI 20 T,; n = 17; Emulgen 911,: n = 20; Emulgen 913) and Tween 80 (Sorbitan monooleate with HLB = 20) (supplied Kao Co., Ltd.) were used as a cationic surfactant, an anionic surfactant and nonionic surfactants, respectively. Activated carbon (from Toyo Calgon Co., Filtrasorb 400), kaoline (Hisagi Co.) and bentonite (Natural and non-

Table 1. Properties of oils used (Temp. 298°K)

Oil	Density(kg/m^3)	Viscosity (cP)
N-Dodecane	751.3	1.26
Salad Oil	915.8	97.5

Table 2. Physical properties of adsorbents

The name of Adsorbent	Particle Size(m)	Surface Area(m^2/kg)	Total Pore Volume(m^3/kg)	Total Pore Area(m^2/kg)	Zeta Potential (mV)
Activated Carbon	8.77×10^{-5}	1.56×10^{6}	2.97×10^{-5}	2.64×10^{4}	-36.6
Bentonite	5.00×10^{-5}	8.09×10^{4}	6.14×10^{-6}	6.91×10^{3}	-15.5
Kaolinite	5.00×10^{-5}	5.23×10^{3}	4.36×10^{-7}	4.77×10^{2}	-27.7

treated), were used as powder adsorbent.

Their physical properties were measured by using surface area analyzer (Accusorb 2100-01) and Zeta potentiometer (Mitamura Scientific Co., cell thickness 1 mm). The results are summarized in Table 2.

2. Experimental procedures

Each sample was prepared by batchwise agitation method. A surfactant was first dissolved in deionized water and while being agitated continuously, a certain amount of oil was added slowly and further agitation was made for 15 hours at 298 K in a constant temperature bath. The emulsion was formed in a stirring glass vessel of 130 mm in diameter and 170 mm long with four baffles. A turbine-type impeller with six blades was installed and rotated at a controlled speed (usually 300 rpm). For the demulsification, a known amount of powder adsorbent of 150/200 mesh was washed many times by deionized water, then dried in advance and added to the stable emulsion solution, which has been found to last 144 hours [3].

The solution was continuously agitated for an hour and settled for 3 hours in the same emulsification equipment. Then a small amount of liquid was taken out at a given interval of time and the concentrations of surfactant and the oil were measured after separating adsorbents by glass filteration. The concentration of surfactant was measured with spectrophotometer (Shimazu Model UV-240).

The concentration of total organic carbon (T.O.C.) after removing the adsorbents was measured with a total organic carbon analyzer (Shimazu, TOC-10 B), and the concentration of oil was determined by careful calibration which was made from the difference between concentrations of TOC and surfactants. Microphotographs of the emulsion were taken with a microscope. The size of visible droplets and the size distribution were determined from the magnified photograph.

RESULTS AND DISCUSSION

1. Demulsification capacities of various adsorbents

Demulsification capacities of powder adsorbents from the adsorption of surfactants, were measured through the demulsification experiment.

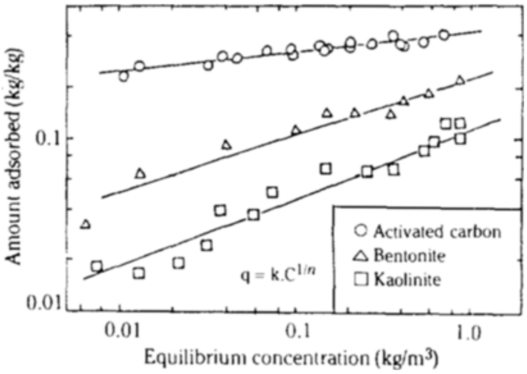


Fig. 1. Isotherms for Tween 80-various adsorbent powders at 298 K.

Figure 1 shows a typical set of adsorption isotherms of non-ionic surfactant, Tween 80, for various adsorbent at 298°K. All lines indicate in the figure that adsorption isotherm is Freundlich-type. Constants, k and n of Freundlich adsorption isotherm were estimated from the data shown in Figure 1 and the results are summarized in Table 3. For the adsorbed amount per unit surface area, kaolinite has the highest value, and bentonite and activated carbon have lower value in order. However, the adsorbed amount per unit weight amount was increased at higher values of the total pore volume and surface area, and it can be seen from the increasing order of kaolinite, bentonite and activated carbon.

Activated carbon showed the highest adsorption

Table 3. Freundlich constants for various systems

Adsorbent	Surfactant	k(-)	n(-)
Activated carbon	Tween 80	0.425	8.064
	D B S	0.387	14.000
	Benzalkonium chloride	0.387	14.000
Bentonite	Tween 80	0.227	2.958
	D B S	0.017	3.675
	Benzalkonium chloride	0.328	7.669
Kaolinite	Tween 80	0.112	2.494

capacity, and its capacity was not affected by any kind of surfactant, i.e., cationic, anionic and non-ionic surfactants, while other two adsorbents are affected by the behavior of ionic surfactants, while other two adsorbents are affected by the behavior of ionic surfactants. It is suggested that the activated carbon is the best adsorbent among those studied.

2. Demulsification of stable O/W emulsion by activated carbon powder

Figure 2 shows typical concentration variations with time during the adsorption by the addition of activated carbon. Results clearly indicate that the concentrations of oil, surfactant and TOC decreased with time. The extent of removal increased remarkably with increasing dose of activated carbon and reached over 90% of equilibrium in about an hour after the activated carbon was added. The residual concentration of the oil after 4 hour contact increased in proportion to residual concentration of surfactants as shown in Figure 3. Therefore, it is evident that the extent of demulsification by activated carbon depends mainly upon the adsorbed amount of surfactant. In Figures 4 and 5 the dose of activated carbon is plotted against the residual concentration of oil emulsified with Emulgen 911. The residual concentration of oil decreased linearly with the dose of activated carbon.

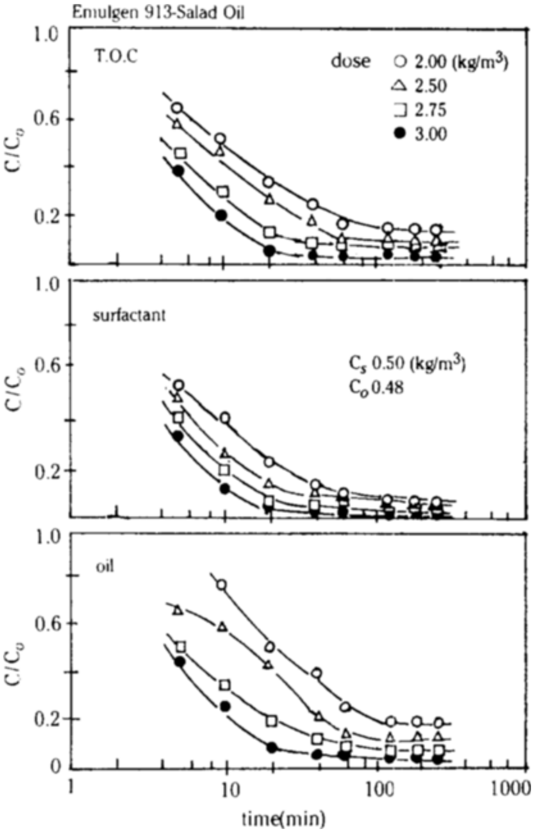


Fig. 2. Typical concentration decay curves for T.O.C, surfactant and oil by activated carbon adsorption.

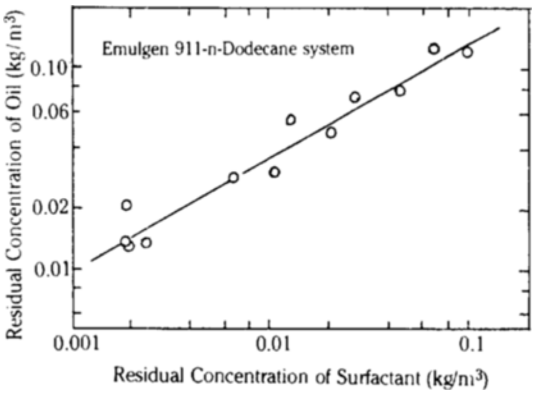


Fig. 3. Relationship between residual concentrations of oil and surfactant.

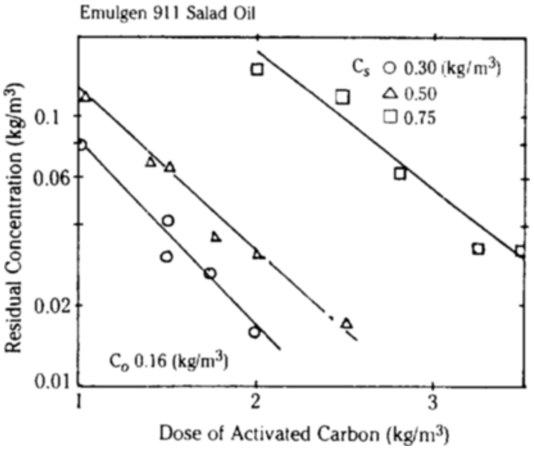


Fig. 4. Relationship between residual concentration of oil and dose of activated carbon for Emulgen 911 and salad oil system.

From these results, the following empirical equation was obtained to correlate the dose of adsorbents and residual concentration of the oil in water.

$$A = a + b \cdot C_s + f \cdot \log E \qquad (1)$$

where A is the dose of activated carbon, a, b, and f are the parameters which vary with the kind of surfactant and oil, C_s is the initial concentration of surfactant and E is the oil concentration. The parameters obtained for each investigated system are tabulated in Table 4 and some examples of comparison between values observed and those calculated are exhibited in Figure 6.

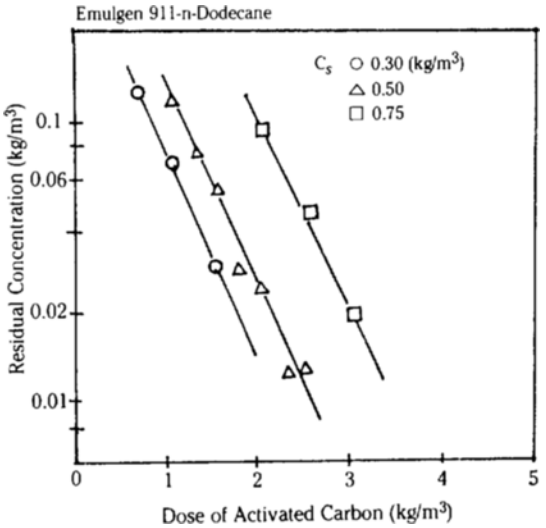


Fig. 5. Relationship between residual concentration of oil and dose of activated carbon for Emulgen 911 and n-Dodecane system.

3. The effects of the size of hydrophile and lipophile groups of non-ionic surfactant on the demulsification

In order to investigate the effect of the HLB (hydrophile lipophile balance) of non-ionic surfactant on the demulsification with activated carbon, the experiments were carried out with polyoxyethylene nonyl phenyl ether of different number of ethylene oxide unit as listed in Table 5.

The extent of demulsification by activated carbon decreased with the increase of HLB of surfactant as shown in Figure 7. In Figure 8, adsorption isotherms for non-ionic surfactants with three HLB on the activated carbon are shown. With the increase of HLB number, the extent of adsorption of surfactant from their aqueous solution decreased. From these results,

Table 4. The values of constants in Equation (1) for various systems

Surfactant	oils	a	b	f
Emulgen	n-Dodecane	1.64	2.94	-0.90
PI 20 T	Salad oil	0.85	1.31	-1.56
Emulgen	n-Dodecane	-1.42	2.40	-1.41
911	Salad oil	-2.09	3.69	-1.70
Emulgen	n-Dodecane	-1.91	3.37	-1.31
913	Salad oil	-1.67	3.95	-1.31
DBS	n-Dodecane	9.28	4.56	-4.88
	Salad oil	-4.40	0.75	-4.64
Benzalkonium	n-Dodecane	2.59	2.73	-1.07
Chloride	Salad oil	-5.15	4.93	-3.60

Table 5. Properties of non-ionic surfactant used

Surfactant	Number of ethylene oxide unit	HLB number by Davies method[1]
Emulgen PI 20T	15	13.2
Emulgen 911	17	13.7
Emulgen 913	20	14.5

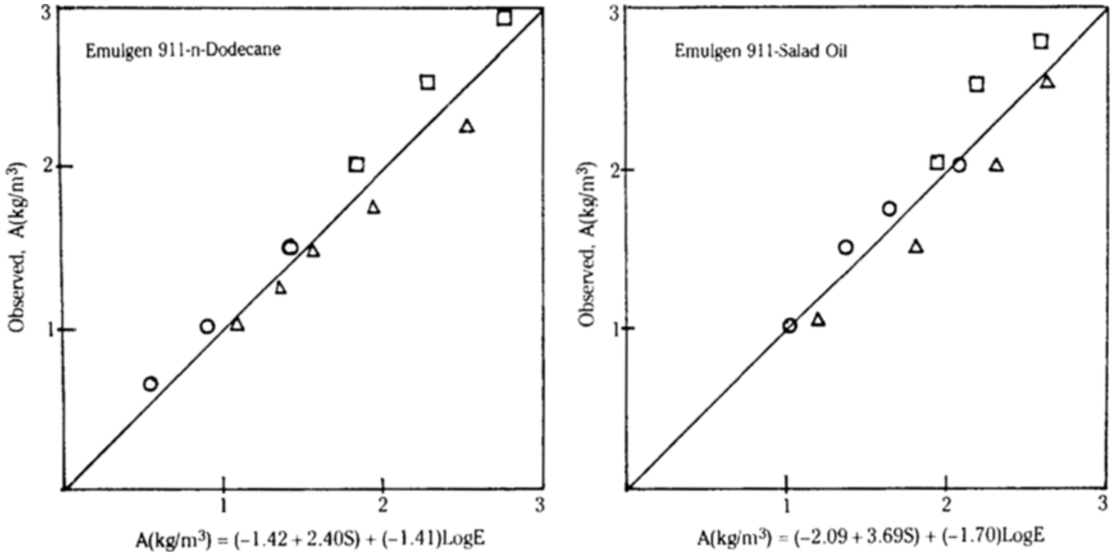


Fig. 6. Comparison of $A_{exp.}$ and $A_{emp.eq.}$ for dose of activated carbon.

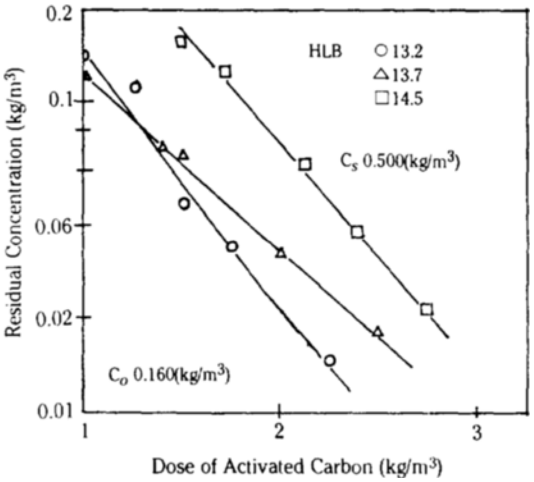


Fig. 7. Effect of HLB of surfactant on demulsification.

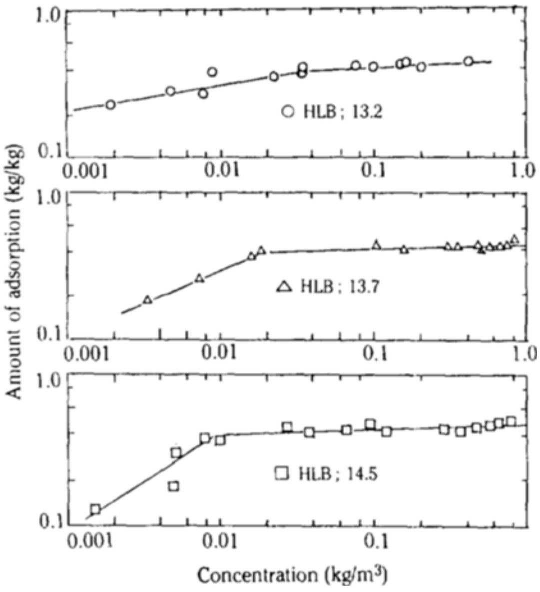


Fig. 8. The relationship between the amount adsorbed on activated carbon and equilibrium concentration of polyoxyethylene-nonyl-phenyl-ether.

it is clear that the HLB number (group number) is proportional to the number of the barriers to adsorption and demulsification.

4. Effect of oil concentration and the difference between two oils

Figure 9 shows how the final (residual) concentration of oil in water emulsified with non-ionic surfactant changes with the dose of activated carbon.

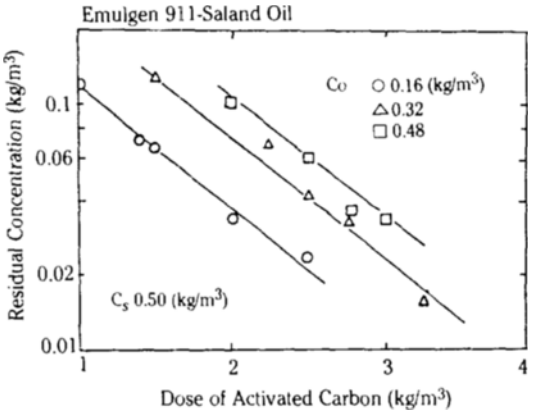
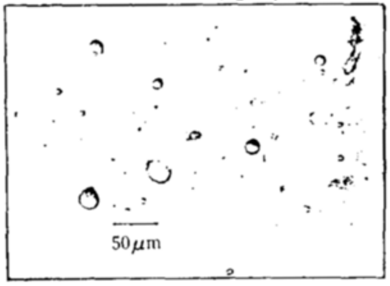
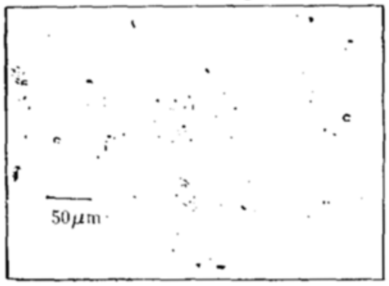


Fig. 9. Effect of oil concentration on demulsification by activated carbon.

Salad Oil 0.48 (kg/m^3)



Salad Oil 0.32 (kg/m^3)



Salad Oil 0.16 (kg/m^3)

Fig. 10. Typical microphotographs of salad oil droplets emulsified with Emulgen 911.
(Emulgen 911:0.5 (kg/m^3)).

Apparently, the dose of activated carbon required to achieve a certain residual concentration increased with increasing oil concentration even though the concentration of the surfactant was the same. The following empirical relationship was obtained to show a dose of activated carbon A needed to remove stable O/W emulsion for given initial and residual concentrations of oil, Co and E.

$$A = 2.89\,Co + (-2.05\log E) - 1.41 \qquad (2)$$

This relation may be explained by the fact that the number of oil droplets becomes larger with the volume fraction of oil, i.e., concentration, and the chance of hydrodynamic collision between powder adsorbents and oil droplets becomes less with increasing the number of droplets. Figure 10 shows the typical microphotograph of various concentrated emulsion. It can be seen that the sizes of droplets as well as their distribution vary significantly with the oil concentration. Figure 11 shows that salad oil is more stable than n-dodecane due to its higher viscosity on demulsification. However, no significant difference between these two oils was found in demulsification.

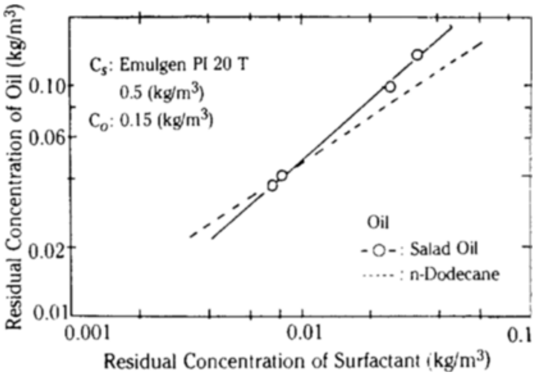


Fig. 11. Relationship between residual concentrations of oil and surfactant.

5. Droplet sizes and their distribution.

Figure 12 shows the progress of demulsification adding activated carbon powder. The droplet sizes and their distribution varied greatly with time during the demulsification after the activated carbon had been added. It is clear that the surfactant molecules which exist at the surface of droplets are adsorbed to the adsorbent, breaking the surface film of droplets, and then leading to the coalescence to form large new droplets.

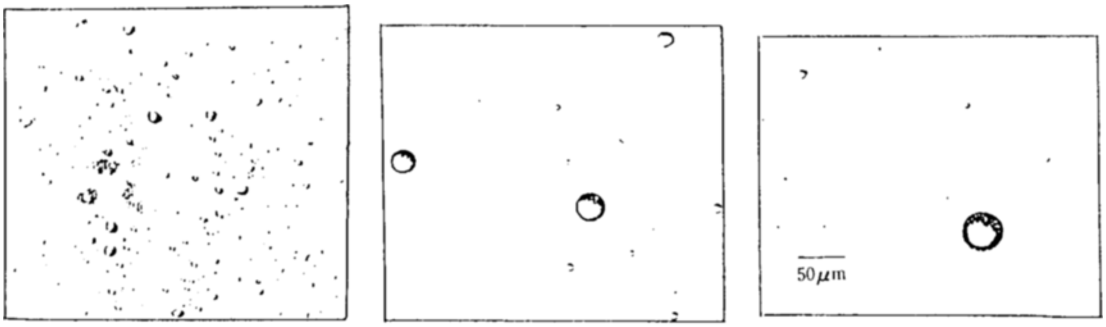
CONCLUSIONS

Demulsification of stable oil-in-water emulsion was studied using powder adsorbents and the analysis of the data revealed the following conclusions.

The activated carbon shows the highest efficiency as a demulsifier which adsorbs the surfactant from droplets interface and breaks down the emulsion regardless of emulsifier used. The dose of activated carbon for the demulsification increases with increase of the concentrations of surfactant and oil. The emulsion formed by non-ionic surfactant is more stable with the increase of the size of the lipophilic and hydrophilic groups and it requires more adsorbents for demulsification. Empirical equations are presented to calculate the dose of activated carbon and residual concentration.

ACKNOWLEDGEMENT

Part of this study was performed under the financial support of Korea Science and Engineering Foundation to S.S. Lee as a visiting scholarship. The authors



0 min after 20 min after 240 min

Fig. 12. Typical microphotographs of salad oil droplets emulsified with Emulgen 911 and contacted with activated carbon for certain times.

(Emulgen 911: 0.5 (kg/m^3), salad oil: 0.32 (kg/m^3), dose of activated carbon: 2.5 (kg/m^3)

would like to express their thanks to Mr. S. Suzuki and Mr. K. Suzuki for their assistance in experimental work.

NOMENCLATURE

A	:	Dose of activated carbon [kg/m^3]
a	:	Constant in Equation [kg/m^3]
b	:	Constant in Equation [-]
f	:	Constant in Equation [kg/m^3]
C_0	:	Initial concentration of oil [kg/m^3]
C_s	:	Initial concentration of surfactant [kg/m^3]
E	:	Concentration of oil [kg/m^3]

REFERENCES

1. Menon, V.M. and Wason, D.T.: "Encyclopedia of Emulsion Technology", Vol. 2 (P. Baker, ed) Dekker, New York, Chap. 1 (1985).
2. Lissant, K.J.: "Demulsification", M. Dekker, ed Dekke, New York, Chap. 4 (1983).
3. Takeuchi, Y., Yamazak., H., and Nakamula, M.: Preprint for 51st Annual Meeting of SCEJ, H-301, 329 (1986).
4. Takeuchi, Y.: Proceedings of The 3rd Symposium on the R-30 group of Special Research on Environmental Science, 31-32 (1986).