CHAPTER IV

RESULTS AND DISCUSSION

4.1 Simulated Wastewater

The simulated wastewater was prepared by dilution of anionic wax emulsion with water to obtain 5 different samples containing solid content, 0.3, 0.9, 3.0, 4.9, and 7.1 wt %. The samples were used to study on the effects of an electrolyte, temperature, and stirring rate on demulsification and phase separation. The optimum conditions were selected to apply for actual wastewater from tank flushing process in manufacturing of wax emulsion.

4.1.1 Effect of Electrolytes

4.1.1.1 Addition of Sodium chloride

The effect of NaCl on demulsification and phase separation are shown in Figures 4.1 to 4.4, for concentration of NaCl 1.0 to 10.0 wt %, and constant temperature at 25, 30, 40, and 50°C. The emulsified oil and wax particles aggregated to a large size and moved up to the surface with densely packed. As the result, clear water in the lower phase was developed. The volume of clear water decreased as the solid content in the simulated wastewater increased and NaCl concentration required to obtain maximum emulsified oil and solid content removal was increased as the solid content in the wastewater increased, i.e. 3.0 wt % NaCl for solid content lower than 1.0 %, 5.0 wt. % NaCl for 1.0-4.9 % solid content and 7.0 wt % NaCl for higher than 4.9 % solid content. The simulated wastewaters used in this study are anionic wax emulsion which is oil-in- water (O/W) emulsion. When NaCl is added into emulsified oil solution, Na^+ ions stabilize hydrophilic head group of surfactant, reduce electrostatic repulsion of ionic head group and simultaneously increase hydrophobicity to the surfactant structure, which prefers for solubilizing in oil to water. As the consequence, the phase separation of water occurs **[18]**. Increasing of NaCl concentration to 2.0 wt % for a low solid content caused the wax particles to aggregate to a larger size and eventually phase separation can occur.

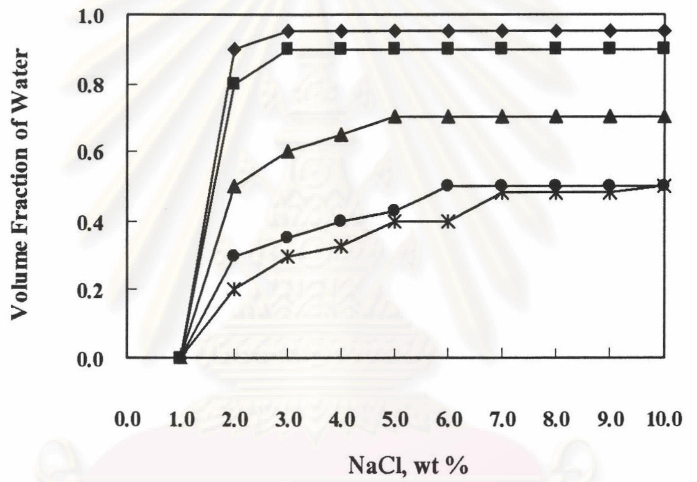

Figure 4.1 Volume fraction of water separated from the simulated wastewaters with different solid content when various amount of NaCl was added at 25°C; solid content 0.3% (◆), 0.9% (■), 3.0% (▲), 4.9% (●), and 7.1% (∗).

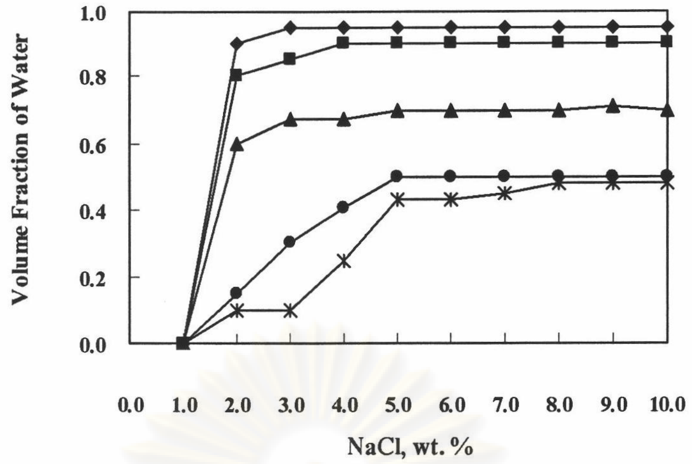

Figure 4.2 Volume fraction of water separated from the simulated wastewaters with different solid content when various amount of NaCl was added at 30°C; solid content 0.3% (◆), 0.9% (■), 3.0% (▲), 4.9% (●), and 7.1% (∗).

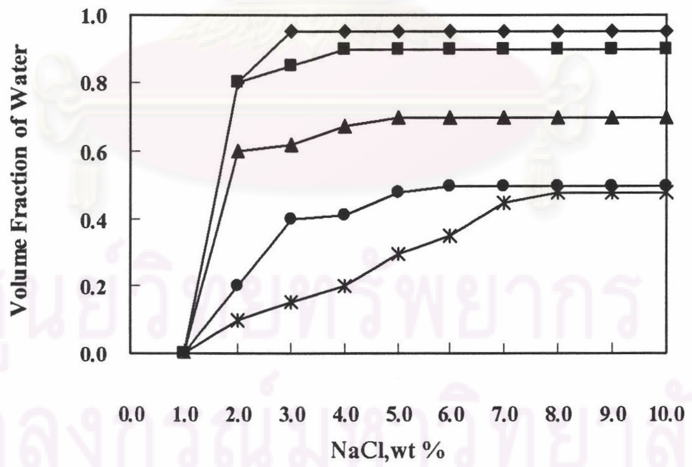

Figure 4.3 Volume fraction of water separated from the simulated wastewaters with different solid content when various amount of NaCl was added at 40°C; solid content 0.3% (◆), 0.9% (■), 3.0% (▲), 4.9% (●), and 7.1% (∗).

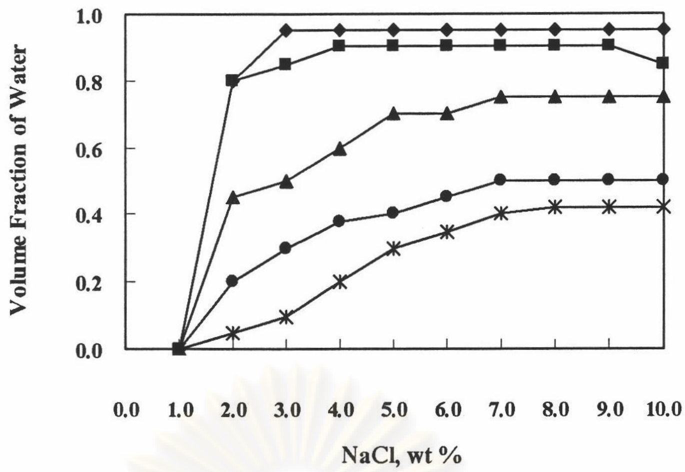

Figure 4.4 Volume fraction of water separated from the simulated wastewaters with different solid content when various amount of NaCl was added at 50°C; solid content 0.3% (◆), 0.9% (■), 3.0% (▲), 4.9% (●), and 7.1% (✳).

4.1.1.2 Addition of Aluminium ammonium sulfate

The effect of aluminium ammonium sulfate or alum on demulsification and phase separation are shown in Figures 4.5 to 4.8. The results showed that the wet cake solid content in the upper phase and clear water in the lower phase were well separated. The volume of clear water separated decreased as the solid content in the simulated wastewaters increased. Higher solid content required higher amount of alum to obtain maximum removal of oil and wax particle, i.e. 2.0 wt %, 4.0 wt %, and 5.0 wt % alum for the simulated wastewater containing low (<1.0 %), medium, and high (> 3.0 %) solid content, respectively. The amount of alum required for separation was less than that of NaCl. This can be explained that the binding between Al^{3+} ions and polar head of surfactants is in a better degree increase **[16]**. Furthermore, the simulated wastewater is anionic emulsion type unstable at pH below 7.0 **[5]** when alum added.

The binding of counterion increases with the increase in polarizability and valence, and decrease with increase in its hydrated radius of cation. Hydrated radius of Al^{3+} ions is less than Na^{+} ions, consequently amount of alum were used less than NaCl of the same conditions. When comparing a suitable amount of salt used for demulsification and phase separation, it is found that higher amount of NaCl is required at the same condition. The suitable amount of salts related a containment solid content of the simulated wastewater.

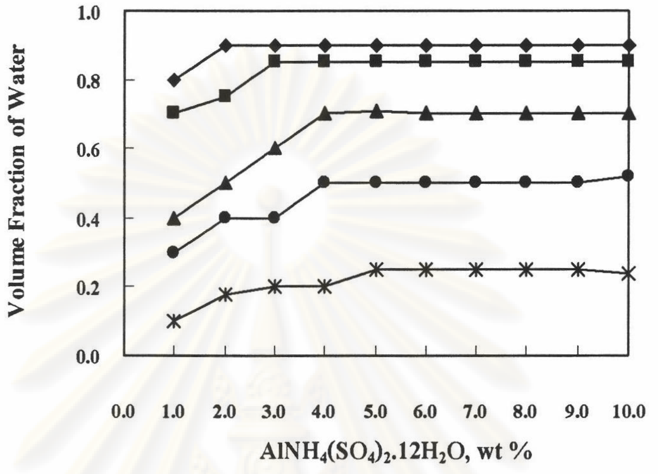

Figure 4.5 Volume fraction of water separated from the simulated wastewaters with different solid content when various amount of alum was added at 25°C; solid content 0.3% (◆), 0.9% (■), 3.0% (▲), 4.9% (●), and 7.1% (∗).

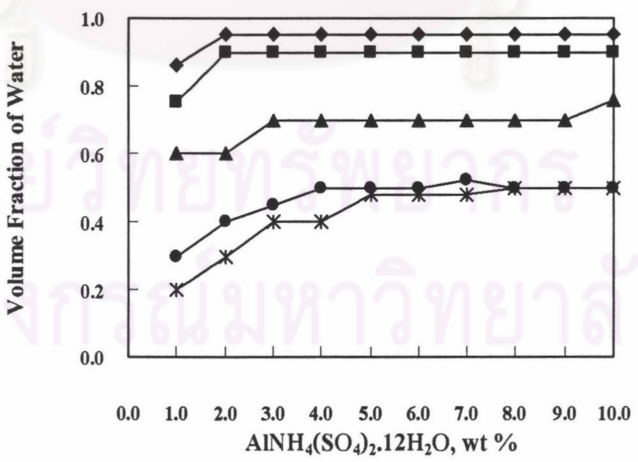

Figure 4.6 Volume fraction of water separated from the simulated wastewaters with different solid content when various amount of alum was added at 30°C; solid content 0.3% (◆), 0.9% (■), 3.0% (▲), 4.9% (●), and 7.1% (∗).

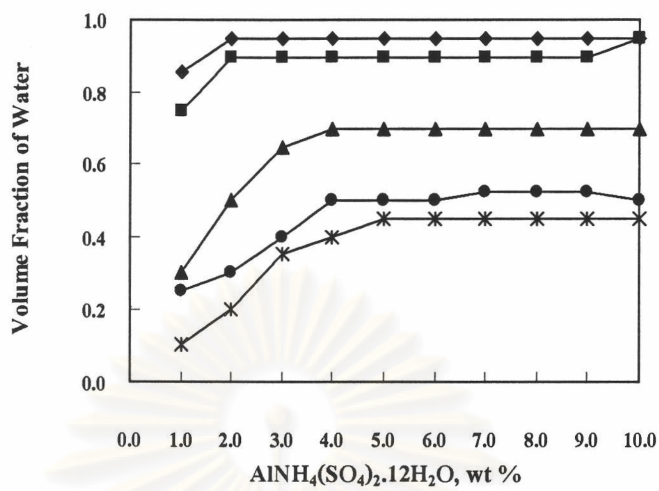

Figure 4.7 Volume fraction of water separated from the simulated wastewaters with different solid content when various amount of alum was added at 40°C; solid content 0.3% (◆), 0.9% (■), 3.0% (▲), 4.9% (●), and 7.1% (✳).

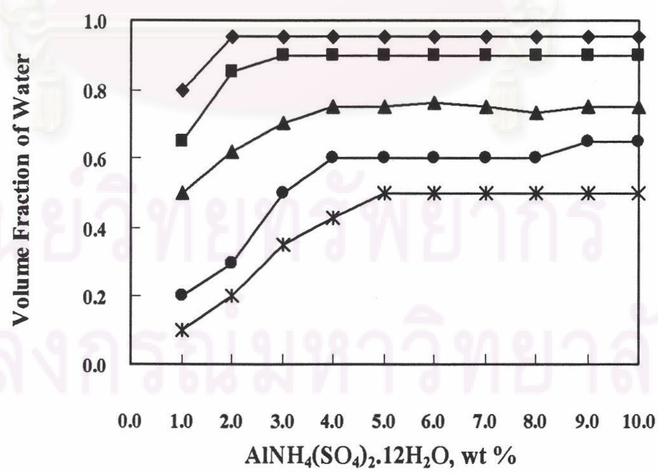

Figure 4.8 Volume fraction of water separated from the simulated wastewaters with different solid content when various amount of alum was added at 50°C; solid content 0.3% (◆), 0.9% (■), 3.0% (▲), 4.9% (●), and 7.1% (✳).

4.1.2 Effect of Temperature

4.1.2.1 Addition of Sodium chloride

The effect of temperature on phase separation of the simulated wastewater for 3.0 wt %, and 4.9 wt % solid content are shown in Figure 4.9 to 4.10. The result revealed that temperature had slight effect on the volume fraction of the water. The volume fraction of water significantly depend on solid content of wax particles as described in 4.1.1.1 and 4.1.1.2. The increase in temperature increases solubility of the surfactant and NaCl in the solution. Consequently more Na cations binding with polar head of surfactants can occur and the rate of phase separation increased.

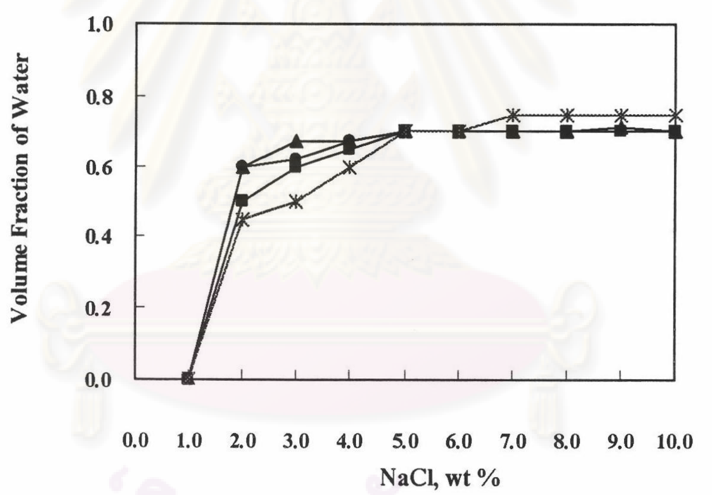

Figure 4.9 Volume fraction of water separated from the simulated wastewaters when suitable amount of NaCl was added for 3.0 % solid content; temperature at 25°C (◆), 30°C (■), 40°C (▲), and 50°C (●).

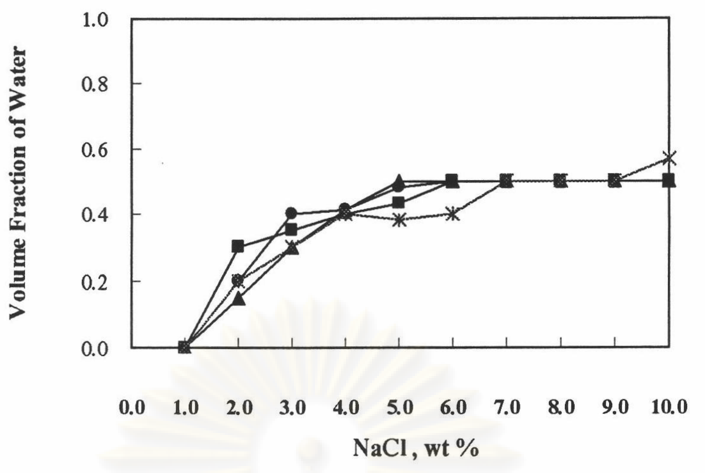

Figure 4.10 Volume fraction of water separated from the simulated wastewaters when suitable amount of NaCl was added for 4.9 % solid content; temperature at 25°C (◆), 30°C (■), 40°C (▲), and 50°C (●).

4.1.2.2 Addition of Aluminium ammonium sulfate

The effect of temperature on the phase separation of the simulated wastewater containing alum in the simulated wastewater for 3.0 % and 4.9 % solid content are shown in Figures 4.11 to 4.12. At low temperature (25°C), volume fraction of clear water was low, and increased when the temperature was increased (30, 40 and 50°C). The temperature has influenced solubility of the surfactants and salts **[19]**. The solubility of salt increased when temperature was increased. It was found that volume fraction of clear water was increased with temperature as well. When the temperature increases, more Al cations are available for binding with head of surfactants. Trivalent Al^{3+} ions is more capable to bind with surfactant than monovalent Na^{+} ions. Thus less amount of alum was used than sodium chloride. The maximum solubility of alum is 150 g/l at 20°C, increase temperature increase the solubility of alum in aqueous solution.

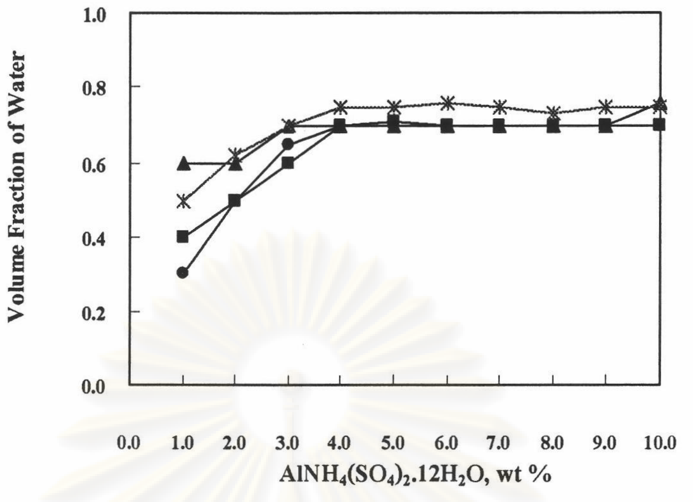

Figure 4.11 Volume fraction of water separated from the simulated wastewaters when suitable amount of alum was added for 3.0 % solid content; temperature at 25°C (◆), 30°C (■), 40°C (▲), and 50°C (●).

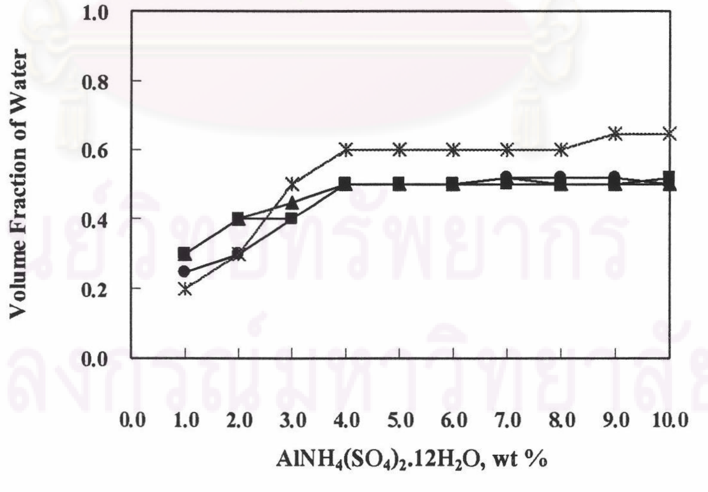

Figure 4.12 Volume fraction of water separated from the simulated wastewaters when suitable amount of alum was added for 4.9 % solid content; temperature at 25°C (◆), 30°C (■), 40°C (▲), and 50°C (●).

4.1.3 Effect of Stirring Rate

The speed of stirring while mixing the salt into the simulated wastewater was set at 300, 600, 900, and 1,200 rpm, the time of mixing was 20 minutes, and settling time was 60 minutes, volume of clear water was then measured.

4.1.3.1 Addition of Sodium chloride

The effect of stirring rate was investigated using the simulated wastewater containing 4.9 % solid content and 7.0 wt % NaCl at 25°C. The stirring rate was varied but the stirring time and settling time were kept at 20 minutes and 60 minutes, respectively. The results in Figure 4.13 showed that the volume fraction of clear water increased with the increase stirring rate. The same trends were obtained for all temperatures. The higher volume fraction was achieved at higher stirring rate because the stirring accelerated the suspending particles to move up and accumulated at the surface with densely packing.

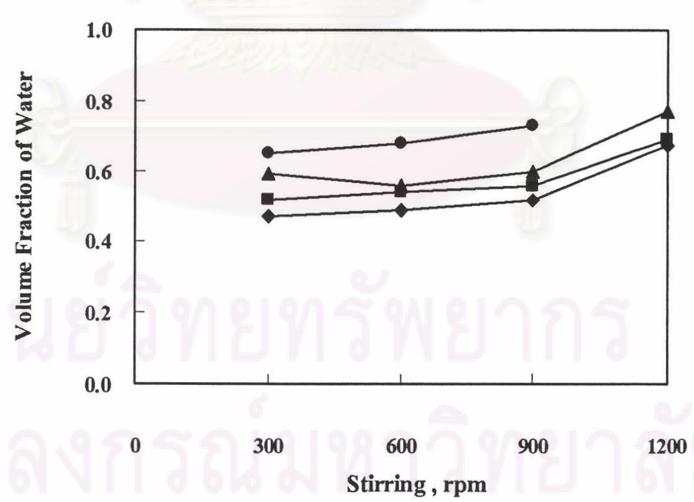

Figure 4.13 Effect of stirring rate on phase volume separation for the simulated wastewater containing 4.9 % solid content, 7.0 wt % NaCl was added, 20 minutes of stirring time, and 60 minutes of settling time. Temperature was set at 25°C (◆), 30°C (■), 40°C (▲), and 50°C (●).

Furthermore, higher temperature gave higher volume of clear water. High stirring rate at 1,200 rpm and very high temperature was difficult to operate because the suspending particles accumulated and became a lump. Therefore, the optimized stirring is the range 600-900 rpm for mixing efficiency of NaCl and simulated wastewater.

4.1.3.2 Addition of Aluminium ammonium sulfate

The effect of stirring rate was studied with the simulated wastewater containing 4.9 % solid content, and 4.0 wt % alum at controlled temperature 25°C. The stirring rate was varied while kept the stirring time at 20 minutes, and settling time at 60 minutes. The results in Figure 4.14 showed that the volume fraction of water increase with the increase stirring rate. The same results were obtained at the other temperatures and higher volume fractions were achieved at higher stirring rate and higher temperature.

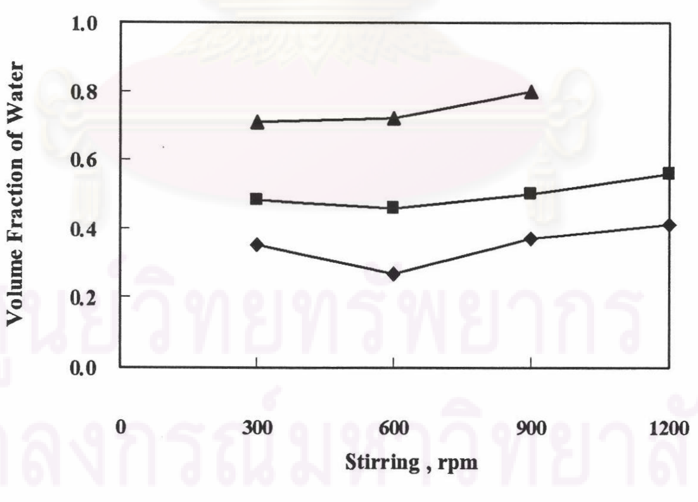

Figure 4.14 Effect of stirring rate on phase volume separation for the simulated wastewater containing 4.9 % solid content, 4.0 wt % alum was added, 20 minutes of stirring time, and 60 minutes of settling time. Temperature was set at 25°C (◆), 30°C (■), 40°C (▲), and 50°C (●).

High stirring rate above 900 rpm at high temperature (40°C) was difficult to operate due to similar problem stated in section 4.1.3.1. The temperature above 50°C that is closed to the melting point (62°C) of the wax particles will cause the solid wax particles to become liquid phase, change physical behavior of surfactant and alter the separation condition.

The optimized condition i.e., suitable amount of salts, and stirring rate for the simulated wastewater containing different solid content are concluded in Table 4.1. The criterion for optimum condition was that the maximum clear water was obtained with low amount of salt, stirring rate and temperature. A simulated wastewater containing 3.0 % and 4.9 % solid content has selected for study effected of temperature and stirring rate, because of an actual emulsified wastewater from wax emulsion process containing approximately 3-5 % solid content. After completed phase separation, the semisolid wax layer has been removed and clear water was characterized as the effluent standard.

In batch mode the simulated wastewater was performed in 2,000 ml beaker for each of a sample contained different composition i.e., 0.3, 0.9, 3.0, 4.9, and 7.1 % solid content. A mixture of salt and simulated wastewater kept in water bath with controlled temperature was at 30°C, mixing procedure operated the stirring rate at 600 rpm for 20 minutes, then kept undisturbed condition for settling and completed phase separation for 60 minutes.

Table 4.1 The optimized conditions for phase separation of the simulated wastewater.

Solid content wt %	**NaCl wt %**	**Alum wt %**	**Stirring rate rpm**
0.3	3.0	2.0	600-900
0.9	4.0	2.0	600-900
3.0	5.0	3.0	600-900
4.9	7.0	4.0	600-900
7.1	8.0	5.0	600-900

4.1.4 Water Quality of the Simulated Wastewater

The phase separation of clear water and solid wet cake were obtained. The clear water phase was analyzed for water quality, i.e. pH, total dissolved solids (TDS), suspended solids (SS), oil and grease (O/G), chemical oxygen demand (COD), salinity, and turbidity.

4.1.4.1 Treatment with Addition of Sodium chloride

The quality of water obtained after phase separation of the simulated wastewater are concluded and shown in Table 4.2 and compared with the limitation of effluent standard.

The *pH* of the simulated wastewater before salt adding was measured. The pH of clear water after semisolid wax particle was in a range 7.8-8.7. Different pH was due to dilution of wax emulsion of wax emulsion with different amount of water to desire different solid content of the simulated wastewaters. Addition of NaCl electrolyte has no effect on the change of pH for treatment.

Table 4.2 Water quality after removal of emulsified oil and solid content using NaCl.

Solid content wt %	**pH**	**TDS mg/l**	**SS mg/l**	**O/G mg/l**	**COD mg/l**	**Salinity ppt**	**Turbidity NTU**
0.3	7.8	31,500	2.8	1.3	174	29.8	10.5
0.9	7.9	39,920	2.8	0.3	280	40.6	4.6
3.0	8.4	50,200	<0.4	<0.3	650	51.5	1.3
4.9	8.4	71,740	<0.4	<0.3	2,200	72.0	1.2
7.1	8.7	84,940	<0.4	<0.3	2,600	82.0	1.1
Effluent standard*	5.5-9.0	<3,000	<50	<5.0	<120		

* Limitation of effluent standard **[20]**

Total dissolved solid (TDS) in a clear water phase after wax particles were removed, the results are shown in Table 4.2. The results showed that the TDS were increased from 31,500 mg/l to 84,940 mg/l, TDS are related to the amount of salts added in which TDS increase, as NaCl is increase due to higher amount of solid content present in the simulated wastewater. The results exceeded the effluent standard.

Suspended solid (SS) were analyzed by filtered a sample through a weighed standard glass-fiber and residue retained on the filter is dried to a constant weigh at 103-105 °C. The results are shown in Table 4.2. The suspended solid was much less than the limit reported for the effluent standard (50 mg/l) for all simulated wastewater samples

Oil and grease (O/G) were analyzed by partition-gravimetric method and the results are shown in Table 4.2. The O/G in the water phase was much less than the effluent standard (<5 mg/l) for all simulated samples similar a suspended solid parameter. It was shown that the wax particles were effectively removed from the clear water phase when suitable amount of NaCl was added.

Chemical oxygen demand (COD), the results are shown in Table 4.2. The chemical oxygen demand or COD represents the oxygen equivalent of organic matter content of the sample that is susceptible to oxidation by strong chemical oxidant. The COD values increased from 174 mg/l to 2,600 mg/l with the increase of added NaCl from 3.0 to 8.0 wt %, thus COD is depend on the amount of NaCl added. The high level of COD was not directly represented oxidized organic matter when Cl^- ions was present in the water. Potassium dichromate ($K_2Cr_2O_7$) as oxidizing agent can react with Cl^-, so the Cl^- ions interfere COD determination. Furthermore, the results of O/G were very low which indicated that the high COD results could not be due to organic matter.

Salinity is one factor for evaluating water quality for a containment of salt or an electrolyte in water. The results of salinity are shown in Table 4.2. The results showed that salinity (29.8 to 82.0 ppt) was increased with increasing NaCl used (3.0 to 8.0 wt%). However, salinity is not limited in the effluent standard.

Turbidity is caused by suspended matter, such as clay, silt, finely divided organic and inorganic matter, and soluble color organic compound **[17]**. The results are shown in Table 4.2, at a low NaCl (3.0 wt %) added into the low solid content of simulated wastewater, the turbidity of water phase was 10.5 NTU. Higher NaCl was required as the solid content in the sample increased, however turbidity value were decreased (4.6 to 1.1 NTU) for 0.9 to 7.1 % solid content.

4.1.4.2 Treatment with Addition of Aluminium ammonium sulfate

The suitable amount of aluminium ammonium sulfate or alum was used to demusify an emulsion. The results of water quality are shown in Table 4.3 and compared with the limitation of effluent standard.

The *pH* of the clear water after wax particle has been removed is shown in Table 4.3. The results showed that pH decreased from the preliminary simulated wastewater (7.0 to 8.8) and further decreased as increase alum, because alum is acidic inorganic salt (10 % in aqueous solution, pH is 2.6). Decreasing pH is due to dissociated of alum in aqueous solution. Increasing amount of alum increased proton (H^+) in the solution and acidity of clear water is obtained. The pH of the clear water exceeded the standard effluent (5.5 to 9.0) when more than 2.0 wt % alum was used. Treatment of wastewater with alum required neutralization of the clear water after removal of emulsified oil and solid content.

Table 4.3 Water quality after removal of emulsified oil and solid content using aluminium ammonium sulfate.

Solids content wt. %	pH	TDS mg/l	SS mg/l	O/G mg/l	COD mg/l	Salinity ppt	Turbidity NTU
0.3	5.8	12,660	<0.4	<0.3	130	12.5	0.5
0.9	5.5	12,800	<0.4	<0.3	230	13.0	0.2
3.0	4.7	20,140	<0.4	<0.3	610	20.0	10.4
4.9	4.0	27,040	<0.4	<0.3	1,200	25.0	10.3
7.1	3.7	34,540	<0.4	<0.3	1,800	31.0	10.2
Effluent standard*	5.5-9.0	<3,000	<50	<5.0	<120		

* Limitation of effluent standard **[20]**

Total dissolved solid (TDS), the results of TDS of clear water after wax particle removal are shown in Table 4.3. The results showed that the TDS exceeded the effluent standard and were increased from 12,660 mg/l to 34,540 mg/l, when were related to amount of alum used (2.0 to 5.0 wt %).

Suspended solid (SS), the results are shown in Table 4.3. The results were much less than 50 mg/l for all simulated wastewater samples. The results showed that highly effective removal of wax particle from emulsified wastewater was obtained.

Oil and grease (O/G). The results are shown in Table 4.3. The wax particles were effectively removed from the wastewater when suitable amount of alum was added. The lower amount of alum than NaCl added in the same simulated wastewater sample was achieved. All of results were much less than the effluent standard (5 mg/l).

Chemical oxygen demand (COD). The results are shown in Table 4.3. The COD values increased from 130 mg/l to 1,800 mg/l with increasing alum from 2.0 wt % to 5.0 wt %, thus COD is related to alum used. When compared alum conditions for all results were lower than NaCl, the amounts of alum used were lower than NaCl.

Salinity. The results are shown in Table 4.3. The results showed that salinity (12.5 ppt to 31.0 ppt) were increased with increasing alum used.

Turbidity. The results of turbidity of the clear water phase are shown in Table 4.3. The results were much less than 10 NTU for all of samples. The results were indicated that fine particles were completely removed from water phase when the optimized alum used.

Investigated of Na^+ and Al^{3+} ions remaining in the aqueous and solid wax portion were analyzed by inductive couple plasma (ICP). The results are shown in Table 4.4 for NaCl addition. The results showed that most NaCl added were present in the aqueous phase and very small amount in the solid wax portion.

Table 4.4 Sodium content (Na) in water phase and solid wax portion of the simulated wastewater.

Solid content wt %	**NaCl wt %**	**Na in water phase ppm**	**Na in solid wax phase ppm**
0.3	3.0	12,167	255
0.9	4.0	16,675	313
3.0	5.0	19,649	388
4.9	7.0	32,484	439
7.1	8.0	35,412	587

Table 4.5 shows that most aluminium (Al) are present in aqueous phase and very small amount in solid wax portion after alum was added into the simulated emulsified wastewater.

Table 4.5 Aluminium content (Al) in water phase and solid wax portion of the simulated wastewater.

Solid content wt %	**Alum wt %**	**Al in water phase ppm**	**Al in solid wax phase ppm**
0.3	2.0	1,210	20
0.9	2.0	1,329	32
3.0	3.0	1,917	117
4.9	4.0	2,629	202
7.1	5.0	3,268	300

For both metal content i.e., sodium and aluminium are most present in water phase, which confirmed that total dissolved solid in the clear water is increase, when increase amount of salt was added.

4.2 Emulsified Wastewater

An actual emulsified wastewater from tank flushing process of wax emulsion manufacturing was analyzed for solid composition by moisture balance method. The result reported 2.5 % solid content. The optimized conditions were selected according to solid content i.e., 5.0 wt % NaCl or 3.0 wt % alum, stirring rate at 600 rpm, stirring time 20 minutes, settling time 60 minutes and controlled temperature at 30°C for further study. The demulsification and phase separation of clear water and solid wet cake were obtained. The clear water phase were analyzed for water quality, i.e., pH, total dissolved solids (TDS), solids suspended (SS), oil and grease (O/G), chemical oxygen demand (COD), salinity, and turbidity.

4.2.1 Water Quality of Emulsified Wastewater

The results of water quality are shown in Table 4.6.

Table 4.6 Water quality of actual emulsified wastewater after the wax particles removed with NaCl and aluminium ammonium sulfate addition, and effluent standards.

Type of salt addition	pH	TDS mg/l	SS mg/l	O/G mg/l	COD mg/l	Salinity ppt	Turbidity NTU
NaCl	9.0	49,899	6.0	5.1	1,390	50	2.0
Alum	3.6	19,053	9.0	2.5	1,129	7	0.0
Effluent standard*	5.5-9.0	<3,000	<50	<5.0	<120		

* Limitation of effluent standard **[20]**

The result in Table 4.6 shows that pH was 9.0 with NaCl addition, which was slightly decreased from the initial actual wastewater (9.1), and still not exceeded the effluent standard. Whereas treating with alum salt, the result showed that pH was acidic (3.6), which was much less than the effluent standard limit.

Total dissolved solid (TDS). The results are shown in Table 4.6. The results showed that the TDS was 49,899 mg/l with NaCl addition, and 19,053 mg/l with alum addition. The results obtained were similar to the simulated wastewater.

Suspended solid (SS). The results of suspended solids are shown in Table 4.6. Suspended solid was 6.0 mg/l for NaCl addition, and 9.0 mg/l for alum addition. Both salts gave obtained a good SS removal within the effluent standard limit (< 50 mg/l).

Oil and grease (O/G). The results are shown in Table 4.6. The O/G in the clear water phase was 5.1 mg/l with NaCl addition and 2.5 mg/l with alum addition. The result indicated that the efficiency of alum higher than NaCl for separation of emulsified wastewater.

Chemical oxygen demand (COD). The results of actual wastewater are shown in Table 4.4. The COD is 49,844 mg/l with NaCl addition and 19,053 mg/l with alum addition. The results showed that the COD values were exceeded the effluent standard for both salts addition.

Salinity. The results are shown in Table 4.6. The results showed that salinity is 50 ppt for NaCl addition and 7 ppt for alum addition.

Turbidity. The results are shown in Table 4.6. For both salts addition, turbidity value was much less than 10 NTU.

From above results of water quality for the simulated and actual emulsified wastewater can be concluded that:

Oil and grease, suspended solid and turbidity representing high efficiency of wax particle removal were achieved for suitable amount of NaCl or alum added and processed at optimized conditions.

The pH values are acidic when alum was added. It indicated that neutralization process is required for treat aqueous phase before it can be discharged. For NaCl addition pH is predicable unchanged.

Total dissolved solid, salinity, and chemical oxygen demand were related to amount of salts added, the value increase with increase salt concentration. The results were exceeding the limitation of effluent standard.