DEMULSIFICATION OF CUTTING FLUID BEFORE DISPOSAL TO THE ENVIRONMENT

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ABSTRACT

In this research the treatment of 7201 cutting fluid was carried out to decrease its environmental impact on water resources after being used and being less effective due to the action of contaminants.

The breaking of emulsion was carried out using two methods: The first method was by using acid and/or heat. 1 molar sulfuric acid was used to decrease pH to 1.5 whth heating the emulsion to 90 ºC. It was found that the acid is the dominating factor in emulsion breaking and the maximum efficiency achieved was 85% after one day using (10335 ppm) sulfuric acid. The second method was by using two different types of coagulants calcium chloride (CaCl2) and ferric chloride (FeCl3) at different emulsified oil concentrations (2, 4, 6, 8, 10% by volume.), and the residual oil concentration in water layer was measured for each experiment.

It was found that using ferric chloride (FeCl3) gave the best emulsion breaking and least residual oil concentration in water layer for all emulsified oil concentrations.

الخلاصـة

تم في هذا البحث معالجة سائل القطع نوع 7201 المنتج في مصفى الدورة في بغداد لتقليل تاثيره السيء على البيئة المائية بعد تلفه نتيجة الاستعمال وتكاثر الاحياء المجهرية فيه وقد تمت المعالجة بطريقتين تتمثل الاولى بكسراستحلاب سائل القطع بواسطة حامض الكبريتيك (بتركيز 1 مولاري) مع التسخين لغاية 90 درجة مئوية وقد وجد بان التاثير الاكبر كان للحامض وليس للحرارة ولم تتعدى كفائة الفصل بهذه الطريقة % 85 بعد مرور يوم كامل باستعمال حامض كبريتيك بكمية (10335) جزء بالمليون. الطريقة الثانية كانت باستعمال كلوريد الكالسيوم وكلوريد الحديديك وباستعمال عدة تراكيز للزيت المستحلب (2, 4, 6, 8, 10% حجما). وقد وجد بان استعمال كلوريد الحديديك يعطي افضل نتائج في كسر الاستحلاب باستعمال كمية اقل منه وان تركيز الزيت في الطبقة المائية يكون اقل ايضا .

KEY WORD

Demulsification, cutting fluid, environment,

INTRODUCTION

Metal working fluids are engineering materials that are employed in metal working processes. In manufacturing activities metal working fluids used for material removal processes are known as cutting and grinding fluids **.**

Cutting fluid pumps over the cutting site of machines such as lathes, milling machines, shapers and saws for cooling the tool, work piece and chips
or for lubricating

A variety of cutting fluids are available to satisfy the requirements of machining processes. The four basic types of cutting fluids are as follows:

Straight oils, synthetic fluids, semi-synthetic fluids and emulsifiable cutting fluid which are the largest type of cutting fluids.

After being used the fluids become less effective because of their thermal degradation and contamination by substances in suspension therefore they must be replaced periodically, generating a waste stream called spent cutting oil (José, 2002**)**. It is desirable then to separate the oil phase from the water phase, in order to minimize the disposal costs and to minimize the negative impact of fluid disposal on the environment **(**Ian, 2005).

Spent metal cutting fluids may be considered hazardous wastes due to the products formulation or by absorbing contaminants through metal working operations (Joseph, 1999).

The environmental impact of metal working wastes can be acute. Heavy metals, acids, surfactants and oils are all highly toxic to aquatic life. Serious stream degradation results from the direct discharge of insufficiently treated metal wastes.

Oils in drinking water sources cause objectionable taste and odours, turbidity and film, and make filtration treatment difficult. Bioassay data indicate that oil is toxic to fish. In greater quantities, it limits oxygen transfer, hindering biological activity **(**Abid, 2004**).**

In general, no single treatment process or commercial device will remove all forms of oil (free, emulsified or dissolved) in oil-water mixtures.

The most commonly used method to break the emulsion is chemical treatment (chemical addition). (Dennis, 1982).

Process wastewater from metal working operations contains free or suspended oil and emulsified oil. These oils originate mainly from parts washer overflow and machining coolant dumping, and the concentration typically ranges from 1,000 - 10,000 ppm as emulsified oil and perhaps 30,000 ppm as free suspended and floating oil (Gealer, 1980**).**

The breaking of emulsions is necessary in many industrial operations, million of dollars are being spent each year in preventing or breaking an emulsion

Emulsion breaking can be very complex, because no two emulsions are alike. Even emulsions from a single source can vary over time. The result is that emulsion breakers, or demulsifiers, must be selected, and even formulated on a case-by-case basis **(**champ, 2008).

There are different actions of chemicals in breaking of emulsion which include:

a - Balance or reverse interfacial surface tension, (addition of other type of surfactant).

b- Precipitate emulsifying agents, traditionally sulfuric acid has been used in oily waste treatment plants as the first step in emulsion breaking.

c- Neutralize stabilizing electrical charges. The accumulated electric charges on the emulsified droplet are neutralized by introducing a charge opposite to that of the droplet

Chemical emulsion breakers provide this opposite charge and cause flocculation to form larger particles for subsequent removal.

The dielectric characteristics of water and oil cause emulsified oil droplets to carry negative charges. Therefore, to destabilize an oil-in-water emulsion, a cationic (positive charge) emulsion breaker should be used **(**Kemmer, 1988).

A common method of determining relative emulsion stability of water-in-oil or oil-in-water is a simple bottle test method (batch separation test). This batch method is an attractive method for the study of separation behavior of emulsions due to its simple and inexpensive experiments.

This method is recommended by Fuchs Lubricating Company, Nalco Water Company and Others (FUCHS, 2005 , Shweta, 2005, Christine, 2001, Taylor, 1994). This test measures the time required for an oil-water mixture to separate by gravity as well as quantity of residual oil remain in the water layer after separation and finding the best required time to complete the demulsification process (separation time) and the effect of emulsified oil concentration.

Experimental work and procedure.

Preparation of 7201 oil emulsion (10% by vol.):

The emulsion was prepared by adding 150 ml of cutting oil (7201) to 600 ml of deionized water (as recommended by oil manufacturer) followed by mixing for 5 minutes using mechanical stirrer at 1500 rpm. 750 ml of deionized water was added gradually while mixing for 10 min at 1500 rpm to form 1.5 liter of emulsion (Kutweel. 2007)

The mixture was diluted by mixing with deionized water to produce other concentrations of cutting fluid (8%, 6%, 4% and 2%) by volume respectively.

Breaking the emulsion of 7201 cutting fluid using sulfuric acid:

This was done by adding 1 molar sulfuric acid to 100 ml of emulsion until pH equal to 1.5 while heating it until reaches 90Cº and kept at this temperature for 15 minutes. The mixture was placed into graduated cylinder to measure the volume of the separated oil layer. The evaluation is based on the volume of the separated layer (Figure 1).

Fig. 1 Emulsion breaking evaluation was based on the volume of the separated layers.

Breaking the emulsion of 7201 cutting fluid using coagulants:

This procedure was carried out as following:

a- solution of 10% by wt. of ferric chloride ($FeCl_3$) was made (each 10 gm was dissolved in 90 ml of deionized water). For ($CaCl_2$) solution of 20% by wt. was made (each 20 gm was dissolved in 80 ml of deionized water).

b- specific quantity of coagulant solution was added to 100 ml 2% by vol. emulsion at 25 ºC and mixed for one minutes using magnetic stirrer. The mixture was poured into graduated cylinder which was placed in a water bath at 25 ºC. The volume of separated oil layer was measured at intervals for 30 minutes.

c- The evaluation of the emulsion breaking was based on the volume of the separated oil layer (if the volume of separated oil layer was less than the initial emulsified oil concentration (2% by vol.) then the quantity of coagulant was increased and the procedure was repeated until the volume of the separated oil layer equal to the initial emulsified oil concentration**.**

d- When the separated oil layer volume was equal to the initial emulsified oil concentration a sample (10-15 ml) was taken from the water layer for the determination of pH and the residual oil concentration in water layer using U.V spectrophotometer.

e- The procedure was repeated for emulsified oil concentration of 4%, 6%, 8%, 10% vol. respectively.

f- The procedure (steps by step) was repeated for both types of coagulants.

g- The evaluation of the emulsion breaking was based on both of the volume of separated layer as well as the residual oil concentration in water layer.

Analytical method

Determination of Oil Concentration

Ultraviolet spectrophotometer (UV) was used for measuring oil concentrations directly at 204 nm . Calibration curve was carried out using different concentrations of emulsion of (25, 50, 75, 100, 125, 150) ppm. Absorbance of these samples was measured. (Figure 2). The calibration curve for these concentrations against absorbance was plotted as shown in Figure (3**).**

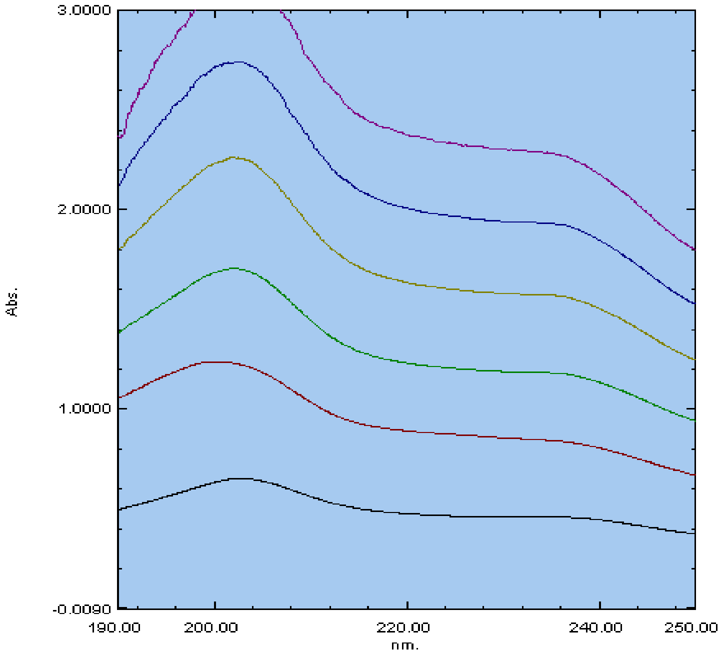

Fig. 2 Reading of U.V using different concentrations of emulsified oil.

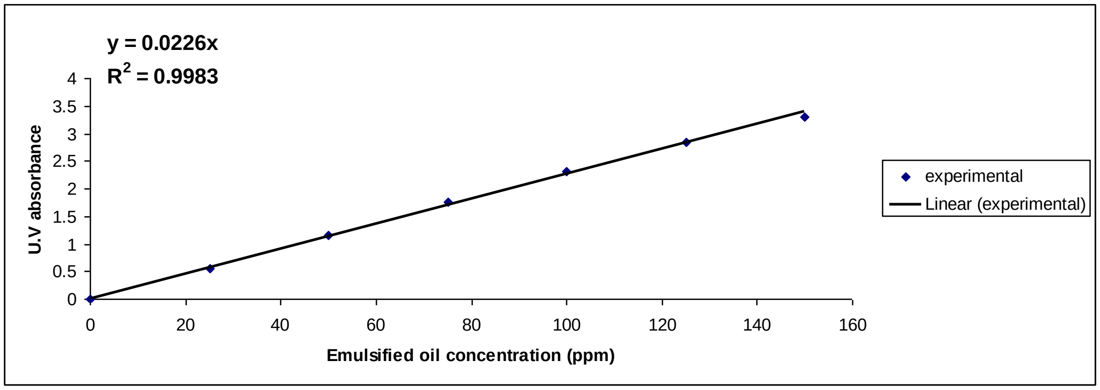

Fig. 3 Calibration curve for different concentrations of emulsified oil against absorbance of U.V.

RESULTS AND DISCUSSION

Effect of using sulfuric acid and/or heat to break 7201 cutting fluid emulsion:

The first experiment was done using heat only, the temperature was raised gradually to 100 ºC (it takes 30 minutes) the volume of the separated oil layer was 1.2 ml (equal to 12% of oil).

The second experiment was carried out using 1 molar sulfuric acid to decrease the pH of 10% by vol. emulsion to 1.47. The volume of the separated oil layer was 6.3 ml (equal to 63% of oil), at temperature 33 ºC.

The third experiment was done using 1 molar sulfuric acid to decrease the pH of the emulsion to 3 and the temperature was raised gradually to 100 ºC. The volume of the separated oil was 2.5 ml (equal to 25% of oil). The heating was stopped and the volume was observed with time for 40 minutes. The final volume was 3 ml (equal to 30% of oil) (Figure. 4). After 5 days at room temperature the volume of the separated oil layer was 4 ml (equal to 40% of oil).

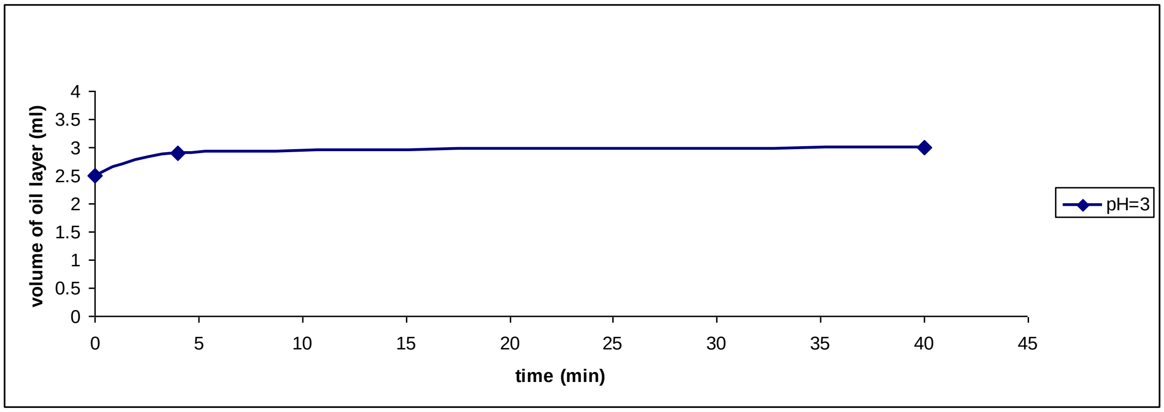

Fig. 4 Effect of sulfuric acid and heating (100 ºC) to break emulsion.

The fourth experiment was carried out using 1 molar sulfuric acid to decrease the pH of 10% by volume emulsion to 1.5 and the temperature was raised gradually to 90 ºC and kept at this temperature for 15 minutes. The volume of the separated oil layer was 7.2 ml (equal to 72% of oil). After 1 day at room temperature the volume of the separated oil layer was 8.5 ml.

Examining experiment one and two it can be seen that the emulsion breaking efficiency for heating is only 12% while the emulsion breaking efficiency for sulfuric acid is 63%.

These efficiencies are low compares with using heating and acid together as in experiment four.

The third experiment showed that using heat and acid at pH=3 together lead to increases the emulsion breaking from 12% -25%.

These results indicated progress in the efficiencies compared with first experiment.

The fourth experiment indicated that by decreasing pH from 3 to 1.5 leads to increase in the emulsion breaking efficiency from 25% to 72 % even so decreasing the temperature from 100Cº to 90 ºC. This behavior showed that the acid is the dominating factor in emulsion breaking.

All the experiments which were carried out as mentioned above showed low efficiencies (72% after 15 minutes), knowing that best experiment consumed 9 ml of 1 molar sulfuric acid for 100 ml of 10% by vol. emulsion (equal to 10335 ppm of acid) which is a high quantity compared to the quantity of coagulants .

The other disadvantage of using acid is that the water layer is highly acidic and needs a treatment to raise pH before discharging to water streams by using suitable alkaline materials like sodium hydroxide (NaOH) solution. As well as the risk of using, handling and storing of highly corrosive and hazardous materials (sulfuric acid and sodium hydroxide).

From above it was clear that using acid and heat were not the best choice to treat the 7201 cutting fluid emulsion where the efficiency of emulsion breaking didn't exceed 85% after 5 days.

Therefore the experiments were shifted to the following experiments to achieve higher efficiencies.

Effects of coagulation to break 7201 cutting fluid emulsion:

The decision was made to carry out the research by studying the factors effecting emulsion breaking by coagulation process with different types of coagulants calcium chloride ($CaCl_2$) and ferric chloride ($FeCl_3$). Knowing that for using these coagulants, any experiment which did not give an oil layer volume equal to the initial oil volume in emulsion or did not reach the steady state within 30 minutes was rejected.

The coagulation process depends strongly on the charge of particles (droplets); the maximum rate of flotation can be achieved when the zeta potential of the particles is zero.

The addition of chemicals overcomes the repulsive effects of the electrical double layers to allow the finally sized oil droplets to form larger droplets through coalescence.

Using calcium chloride as coagulant:

Different oil in water emulsion concentrations (2%, 4%, 6%, 8%, 10% by volume) were studied by using 20% wt solution of $CaCl_2$ as coagulant because it is highly soluble salt.

The experimental results were plotted in Figures (5 - 9) as oil layer volume (visual observation) with time. These figures showed that the oil layer volume increased with time.

Examining figures (5 - 7) it can be seen that adding 1 ml of 20% by wt $CaCl_2$ will break emulsion for oil concentration 2%,4%,6% respectively while adding 1.1 ml and 1.3 ml will break emulsion of oil concentration 8% , 10% respectively (Figures 8 and 9). Therefore it is clear that the use of $CaCl_2$ had low efficiency at low oil concentration.

The experimental results showed also that the residual oil concentrations in water layer are proportional to the initial oil concentration (Figure 10).

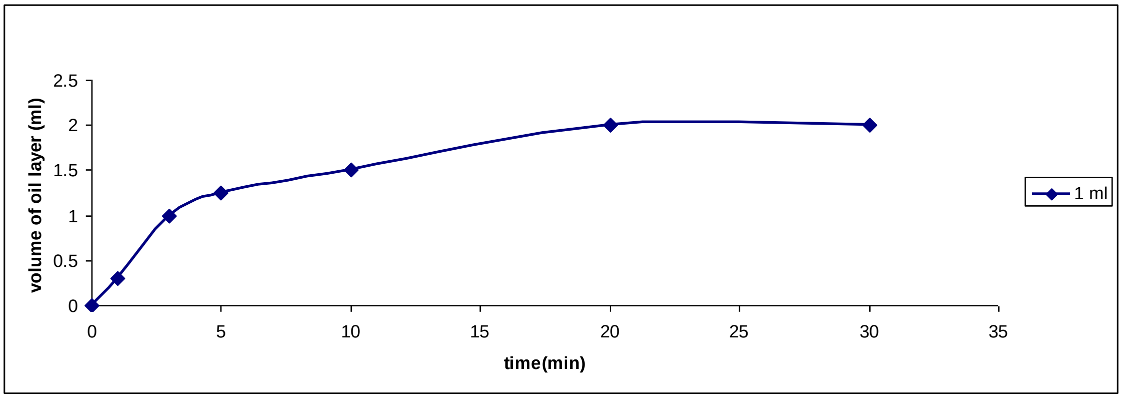

Fig. 5 Effect of using 20% by wt. CaCl2 to break 2% by vol. emulsion at 25 ºC.

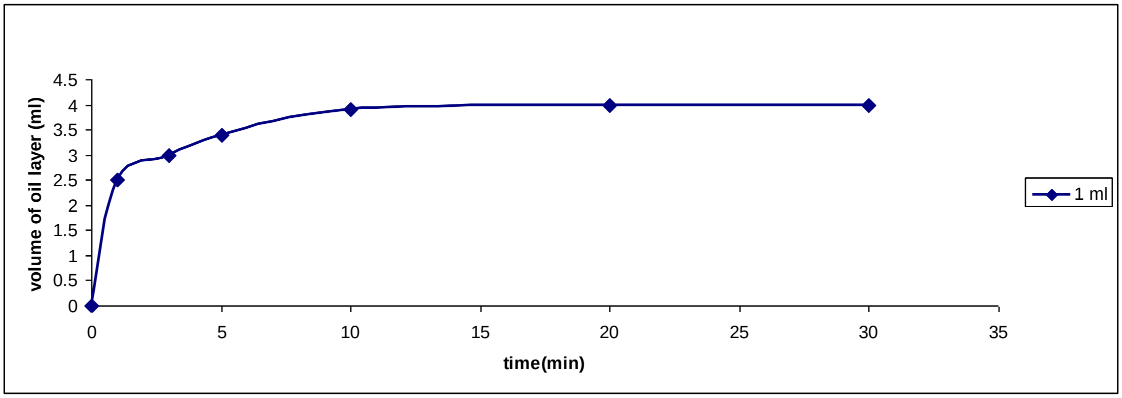

Fig. 6 Effect of using 20% by wt. CaCl2 to break 4% by vol. emulsion at 25 ºC.

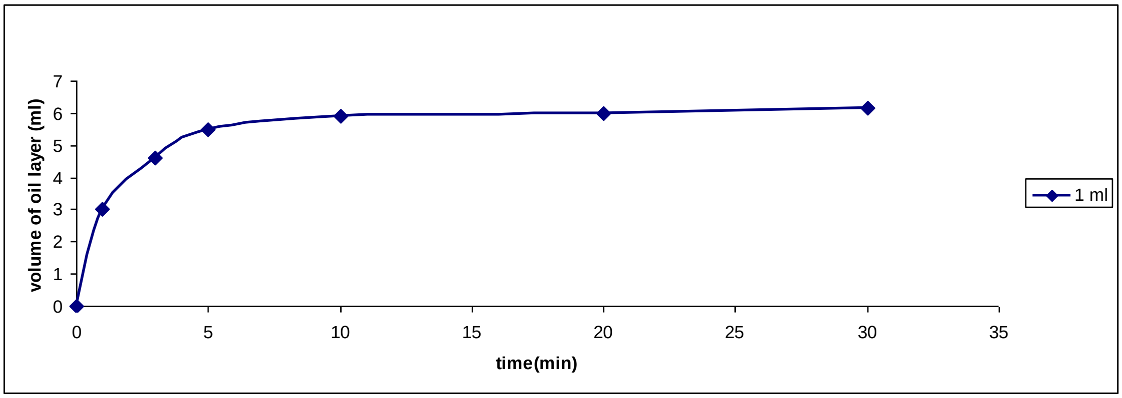

Fig. 7 Effect of using 20% by wt. CaCl2 to break 6% by vol. emulsion at 25 ºC.

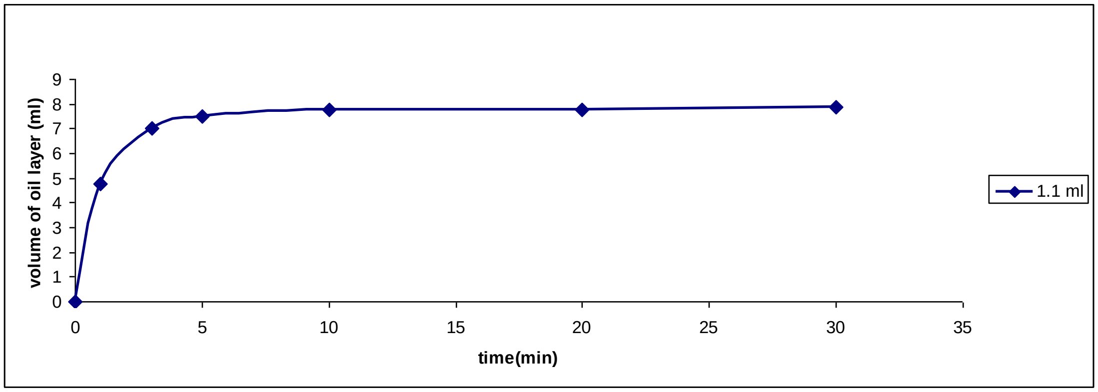

Fig. 8 **Effect of using 20% by wt. CaCl2 to break 8% by vol. emulsion at 25 ºC.**

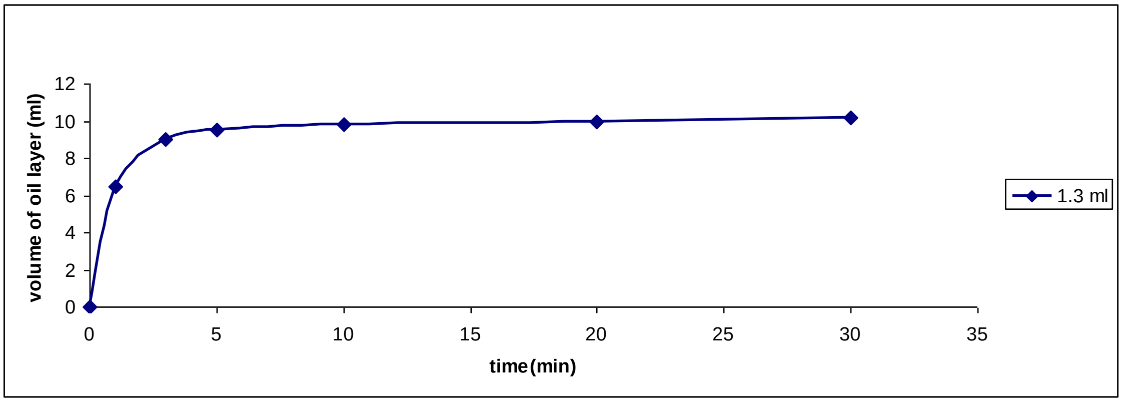

Fig. 9 Effect of using 20% by wt. CaCl2 to break 10% by vol. emulsion at 25 ºC.

Effects of oil in water emulsion concentration on CaCl2 quantity as coagulant.

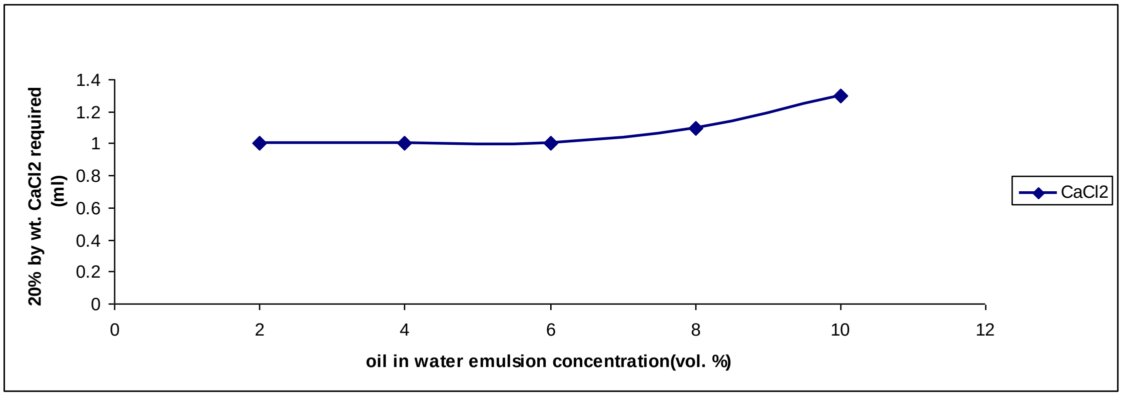

Fig. 10 Effect of using 20% by wt. CaCl2 to break emulsion with various concentrations at 25 ºC.

Effects of CaCl2 on oil concentration in water layer after coagulation (The quantity of residual oil):

The quantity of residual oil in water layer after coagulation using 20% by wt. CaCl**2** to break emulsion is proportional to the initial emulsified oil (Figure 11).

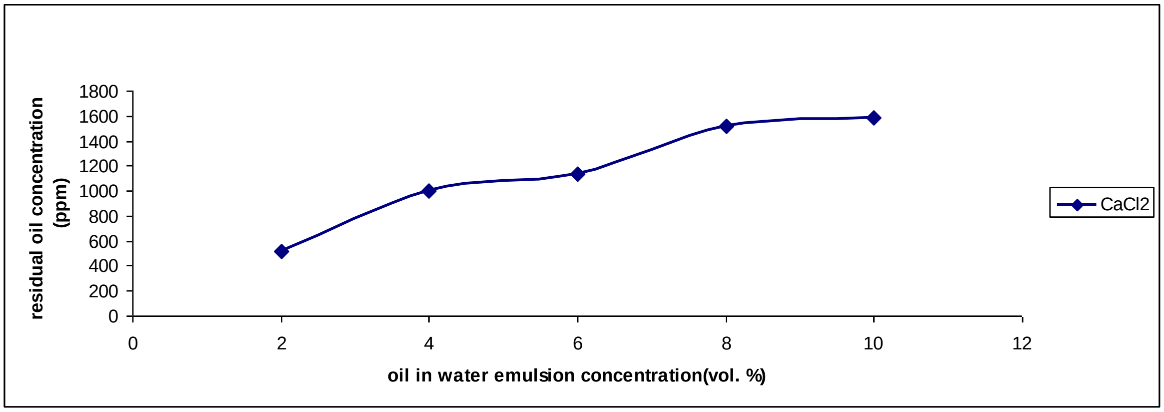

Fig. 11 Effect of using 20% wt. CaCl2 to break emulsion with various concentrations on residual oil at 25 ºC.

USING FECL3 AS COAGULANT:

Different oil in water emulsion concentrations (2%, 4%, 6%, 8%, 10% by volume) were studied by using 10% by wt. solution of FeCl**3** as coagulant.

The experimental results were plotted in Figures (12 – 18) as oil layer volume (visual observation) with time. These figures showed that the oil layer volume increased with time.

Examining Figures(12 -16) it can be seen that adding (0.5, 0.6, 0.9, 1.1 and 1.2 ml) of 10% by wt. FeCl**3** will break emulsion for oil concentration 2%, 4%, 6%, 8% and 10% respectively (Figure 17). The experimental results showed also that the residual oil concentrations in water layer are proportional to the initial oil concentration (Figure 18).

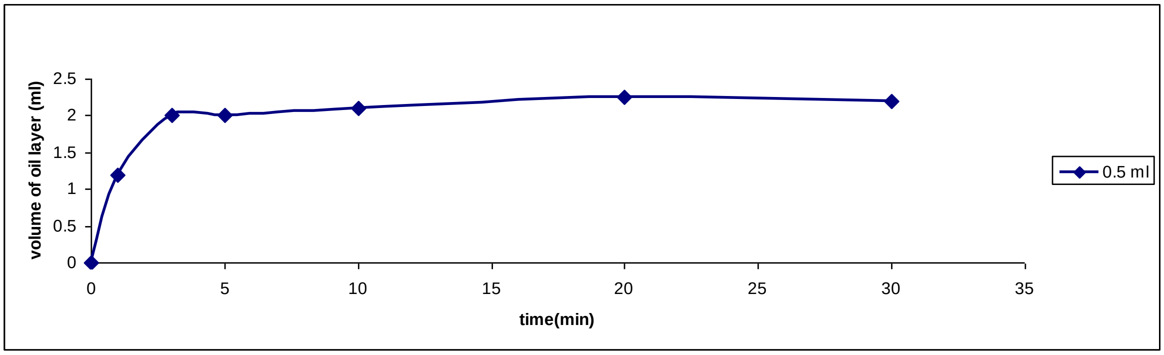

Fig. 12 Effect of using 10% by wt. FeCl3 to break 2% by vol. emulsion at 25 ºC.

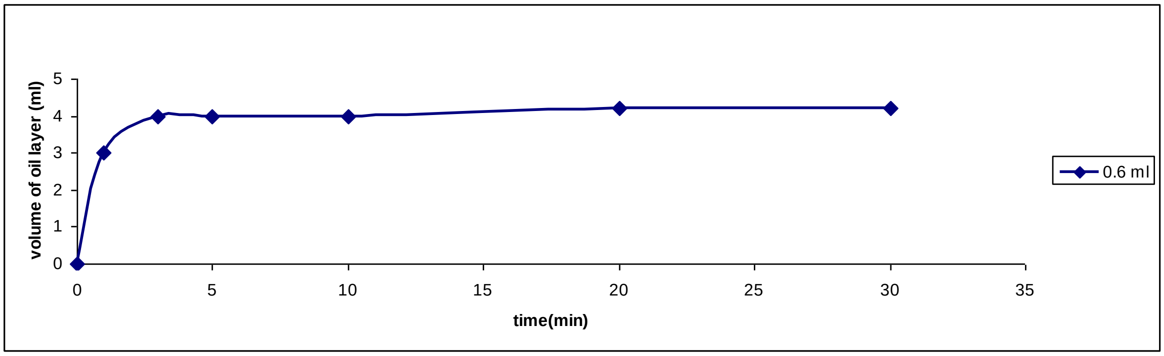

Fig. 13 Effect of using 10% by wt. FeCl3 to break 4% by vol. emulsion at 25 ºC.

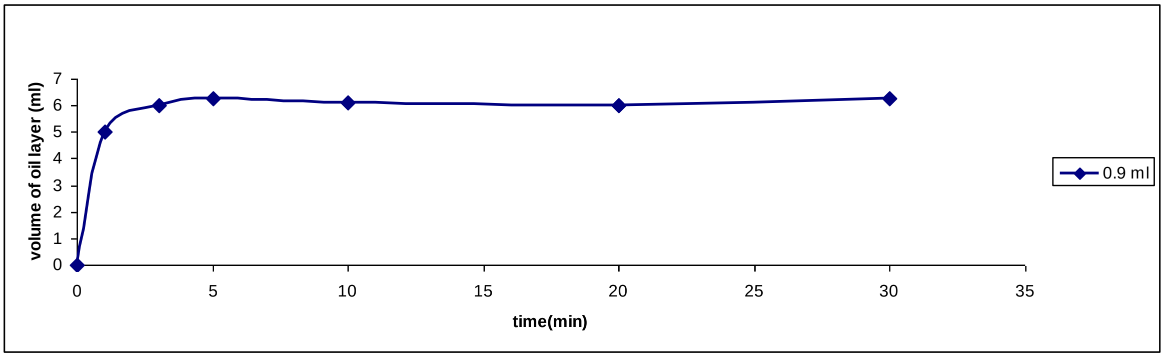

Fig. 14 Effect of using 10% by wt. FeCl3 to break 6% by vol. emulsion at 25 ºC.

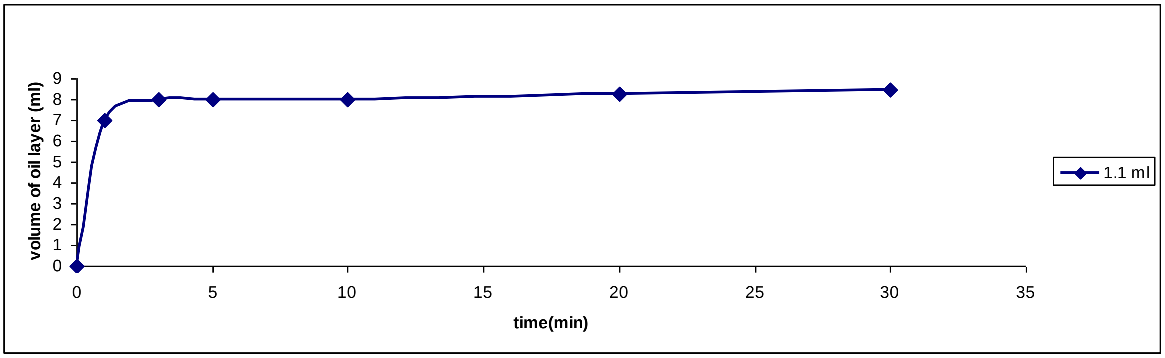

Fig. 15 Effect of using 10% by wt. FeCl3 to break 8% by vol. emulsion at 25 ºC.

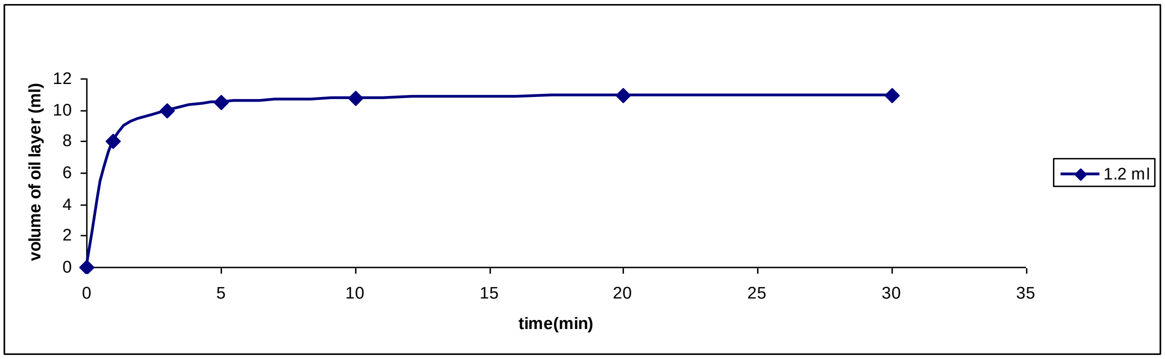

Fig. 16 Effect of using 10% by wt. FeCl3 to break 10% by vol. emulsion at 25 ºC.

Effects of oil in water emulsion concentration on FeCl3 quantity required as coagulant.

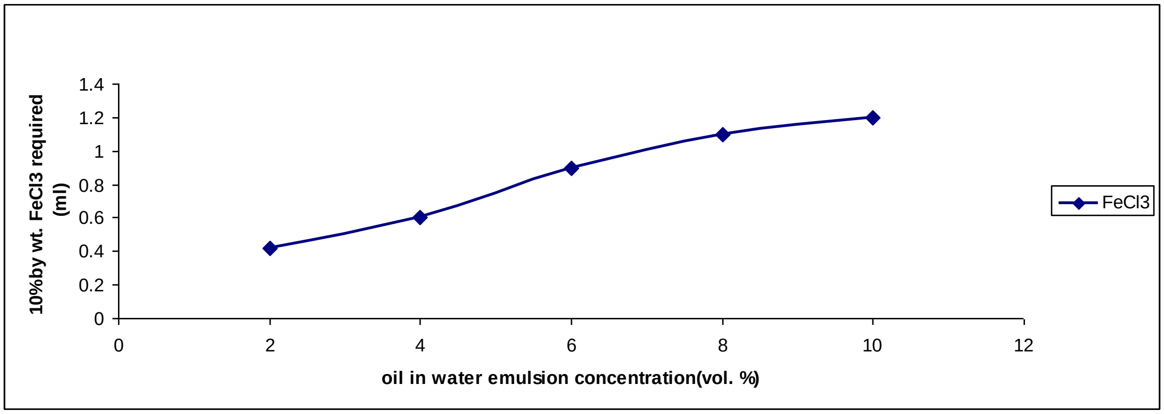

Fig. 17 Effect of using 10% by wt. FeCl3 to break emulsion with various concentrations at 25 ºC.

Effects of FeCl3 on oil concentration in water layer after coagulation (the quantity of residual oil):

The quantity of residual oil in water layer after coagulation using 10% by wt. FeCl**3** to break emulsion is proportional to the initial emulsified oil (Figure 18).

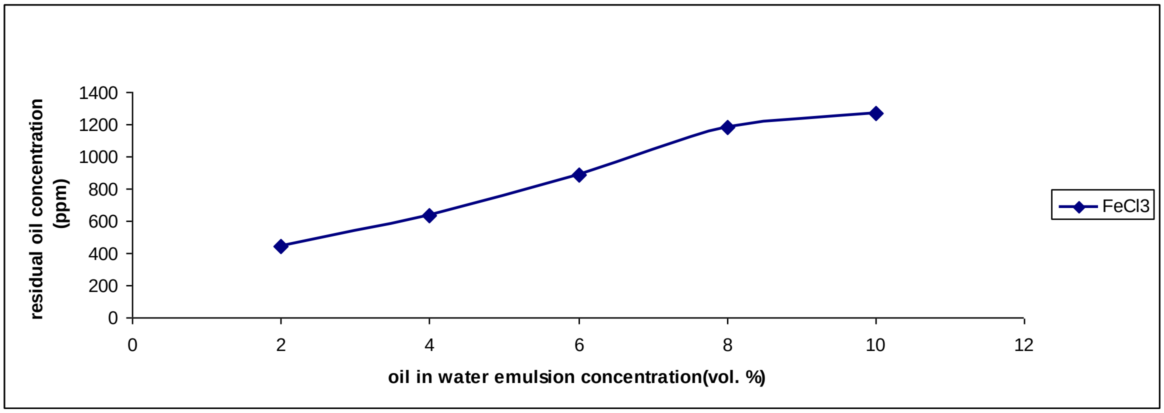

Fig. 18 Effect of using 10% by wt. FeCl3 to break emulsion at various concentrations on residual oil at 25 °C.

CONCLUSIONS:

- For 7201 cutting fluid emulsion sulfuric acid and heating up to 90C° will break about 85% of the emulsion. But this method consumes time for heating, breaking and for cooling the liquid layer before further treatment. It consumes high quantity of acid and alkaline materials in addition to the risk of handling, using and storing of these materials. So this method is not the best choice to treat the oily wastewater generated from spent 7201 cutting fluid.
- 2-The use of coagulant will save heating power, time, and chemical materials
- 3-The required time to finish the coagulation, coalescence and the separation processes is only 20 minutes if high mixing speed or long mixing time (3 minutes) is used.
- 4- The use of $CaCl_2$ was less effective compared with $FeCl_3$ but it has a very good advantage because it dose not decrease pH, so it is less harmful to pipes and equipments, and water layer needs no neutralization step after separation.

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