

Characteristics and treatability of oil-bearing wastes from aluminum alloy machining operations

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Received 30 March 2007; received in revised form 11 June 2007; accepted 31 July 2007

Available online 6 August 2007

Abstract

Enomoto Industry Co., exclusively uses water-based cutting fluids in its aluminum alloy machining operations. Since the cost of disposal can be much greater than the cost of purchase, the treatability of spent cutting fluids is becoming a major criterion for cutting fluid selection. Samples were collected from the machining lines at Enomoto's facility to determine their characteristics and evaluate their treatability with centrifugation, chemical coagulation and electrochemical coagulation. As expected, oil and grease (O&G) and total suspended solids (TSS) are the main reasons that spent cutting fluids are prohibited from being discharged into local swage systems. The average O&G found in the spent cutting fluids is 87,354 mg/L with TSS of more than 70,000 mg/L. Both O&G and TSS are the major contributors to the high turbidity of these waste effluents. A centrifuge with a relative centrifugal force of $1318 \times g$, was able to reduce 60% of the turbidity. By adding the coagulant aluminum chloride, the oil–water emulsion was destabilized, and the turbidity was reduced from 3249 Formazin Attenuation Units (FAU) to around 314 FAU. With freshly generated aluminum ions in the spent cutting fluid, the electrochemical process destabilized the oil–water emulsion system. The coalesced oil droplets were adsorbed onto the highly dispersed aluminum coagulant. The oil-rich sludge that was generated in the operation was then floated to the surface, forming a blanket that was removed by skimming. The electrochemical treatment was able to reduce the turbidity to less than 14 FAU, which is the detection limit of the Hach DR/4000 UV–vis spectrophotometer.

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Keywords: Oil and grease; Total suspended solids; Turbidity; Chemical coagulation; Electrochemical coagulation

1. Introduction

Enomoto Industry Co., exclusively uses water-based cutting fluid in its aluminum alloy machining operation. After spraying onto the work pieces, the cutting fluid is collected together with aluminum chips, coarse particles, fine particles, sludge and others. The chips are settled on a conveyor at the bottom of a collecting pan, and are carried out of the cutting fluid mechanically, while coarse particles are removed by drum filter. However, fine particles remain suspended in the emulsion. Even when recycling options are used, the cutting fluids have a finite useful life. The disposal of cutting fluids involves the evaluation of corrosion, dermal irritation, reduced tool life, color and odor [1,2]. The disposability of the spent cutting fluids is becoming a major

criterion for cutting fluid selection, since the cost of disposal can be much greater than the cost of purchase.

Currently, the pretreatment of spent, water-based cutting fluids is to remove the water portion from the cutting fluids, so that the remaining concentrate can be disposed of at lower cost. Pretreatment is usually divided into three steps. The primary treatment utilized is to separate the floatable and non-emulsified oils and suspended solids from the cutting fluid through sedimentation, filtration, centrifugation, skimming and coalescing [3,4]. Secondary treatment includes evaporation, chemical treatment and ultrafiltration. Evaporation is easy to operate and can reduce the disposed mass by 90%. However, the intense energy input is significant enough to offset most of the disposal cost savings. In water-based cutting fluid, oil droplets are stabilized by surfactants, forming micelles in aqueous solutions. Chemical treatment of an oil-in-water emulsion is usually directed toward the destabilization of the dispersed oil droplets, or the destruction of emulsifying agents present in a first stage, followed by

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the removal of the separated oil [5,6]. Although other coagulants are under development, ferric and aluminum salts are still the most widely used agents for demulsification. The process usually consists of the rapid mixing of the coagulant chemicals with the emulsion, followed by flocculation and flotation, or settling.

Ultrafiltration is a pressure driven process that uses the sieving action of polymeric membranes to control the flow of molecules and particles larger than the membrane pores [7–9]. Water, dissolved salts and metals, along with very small organic molecules, pass through the membrane, while high-molecular weight compounds, such as hydrocarbons, fats and grease are trapped. Typical ultrafiltration membranes have a porosity of about 80%, and average pore sizes ranging between 0.1 and 1.0 μm . Such membranes, characterized by means of a nominal molecular weight cut off, are available in 1000, 10,000, 100,000 and 1,000,000 Da. Molecular weights between 500 and 300,000 Da are commonly found in these kinds of wastes.

Depending on local regulations, secondary treatment can be acceptable for sewer discharge, but in some districts, the spent cutting fluids may have to undergo a tertiary treatment. One such tertiary treatment is reverse osmosis, which is similar to ultrafiltration, except that it operates under much higher pressure due to the smaller pore size on the membranes. The membranes in reverse osmosis treatment, provide a barrier to the transfer of small molecules and dissolved organics, so are effective for removing water-soluble organics, chlorides and phosphates [10]. Another type of process uses activated carbon to adsorb dissolved organics. However, the most common method for treating water-soluble organics uses biological treatment [3,4,11].

In the early 1980s, researchers at the Ford Motor Co. in Dearborn, MI, tested a newly designed electrochemical reactor in a manufacturing plant that represented highly varied machining operations [12]. It was found that when direct current is applied to water through a pair of electrodes, water molecules are broken down into hydrogen and oxygen gases. However, when the anode is made of metals that have lower oxidation potentials than water (such as iron and aluminum), the anode is dissolved to produce metal ions. The metal ions react with hydroxyl ions, the by-products of hydrogen generation, to produce metal hydroxides. As the electrochemical reaction progresses, the ionic strength of the wastewater increases, and the pH rises. The net result of these reactions is that the emulsion is destabilized, and the dispersed oil droplets begin to coalesce. Ultimately, the destabilized oil droplets are adsorbed into the highly dispersed ferric or aluminum hydroxide particles. The oil-rich sludge floats to the top of the solution. This process was able to reduce the turbidity of the incoming oily wastewater from 2500 NTU (Nephelometer Turbidity Unit) to less than 5 NTU, with a power consumption of 6 kWh/1000 gal. Electrochemical methods for wastewater demulsification have since become an active area of research and development [13–17]. A thorough review on electrochemical technologies for industrial wastewater treatment has been done by Chen [18].

The United States federal government's role in wastewater pretreatment began with the passage of the Clean Water Act in 1972. The Act called for the Environmental Protection Agency (EPA) to develop national pretreatment standards to con-

trol industrial discharges into sewage systems. The standards in effect today consist of two sets of rules: categorical pretreatment standards and prohibited discharge standards. Approximately 1500 publicly owned treatment works (POTW) are participating in the National Pretreatment Program by developing their own local programs. In 1985, the EPA approved the City of New Bedford's industrial pretreatment program and authorized the city to implement this program. The primary responsibilities are (1) adapt federal discharge limitations, or develop local discharge limitations, (2) identify all industrial users (IU) and characterize their pollutant discharges, (3) notify IUs of applicable pretreatment standards, (4) receive and review self-monitoring reports, (5) investigate instances of non-compliance and (6) publish significant non-compliance (SNC). In many cases, federal pretreatment standards do not meet the water quality limitations placed upon the POTW discharge. This has resulted in local municipal authorities adapting much more stringent discharge limitations. Table 1 shows the more stringent regulations and discharge limitations developed and enforced by the City of New Bedford.

The objective of this research is to characterize spent cutting fluid from Enomoto's facility and to evaluate pretreatment methods, such as centrifugation, chemical coagulation and electrochemical coagulation, for the feasibility of on site disposal into local sewage systems.

2. Waste characterization

Cutting fluid samples were collected from sumps in the aluminum machining lines at Enomoto's facility. According to their appearances, the samples were designated as either yellow-white or green-gray. The colors were caused by different machining operations since both fluids were generated from the same starting solution. The samples were characterized using different methods and techniques. Six randomly selected samples were analyzed for their metal contents, total suspended solids (TSS)

Table 1
Local effluent limitations (mg/L) for the City of New Bedford in Massachusetts

Parameter	Limit
Arsenic	1.4
Cadmium	1.2
Chromium(VI)	4.8
Copper	2.3
Cyanide	1.9
Lead	0.6
Mercury	0.01
Nickel	2.0
PCBs	0–0.05
Silver	1.2
Zinc	4.2
Oil and grease	100
pH	5.5–9.5 S.U.
BOD and TSS surcharge system	<50 lbs/day, no charge 51–150 lbs/day, \$0.05/lb 151–250 lbs/day, \$0.07/lb >251 lbs/day, \$0.10/lb

BOD: biochemical oxygen demand; TSS: total suspended solids.

and filterable suspended solids. Eight samples were analyzed for oil and grease (O&G) content. Due to extremely high O&G content, green-gray samples were dropped from further investigation for disposal. Instead, a study was initiated to test the feasibility of regenerating the cutting fluid. Five samples were analyzed for turbidity. Six samples were collected to quantify aluminum particles. In addition, scanning electron microscopy was employed for detailed characterization of those particles.

2.1. Chemical analysis

Following the procedures from the Hach Water Analysis Handbook [19] that was adapted from the Standard Methods for the Examination of Water and Wastewater [20], a mild digestion was performed on the samples. Five milliliters of 90% nitric acid (HNO_3), and 5 cm^3 of 1N hydrochloric acid (HCl) were used for the green-gray samples. Nitric acid (0.2N) and 0.1N HCl were used for the yellow-white samples. After the acid was added, the beakers containing the acidified samples were boiled on a hot plate until the volume was reduced to about 20 cm^3 . The sample preparation procedure resulted dark orange and yellow solutions, with thin layers of oil floating on the top.

2.1.1. Aluminum

The aluminum content was determined by using Method 8012 of the Hach Water Analysis Handbook. The original samples were too concentrated, thus, all of the samples were diluted to a factor of 25. The Hamilton Gastight syringe was used to measure 1 cm^3 of the sample, to be diluted to 25 cm^3 of the cell volume. The diluted samples were analyzed using Hach DR/4000 UV–vis spectrophotometer. This was completed on six samples in order to perform a statistical analysis.

2.1.2. Chromium

Hexavalent chromium (Cr(VI)) was determined colorimetrically, as the complex of chromium and 1,5-diphenylcarbohydrazine with the UV–vis spectrophotometer at a wavelength of 540 nm. A sample of 10 cm^3 was used for the analysis. The blank was the sample that was not mixed with any reagent. No dilution factor was applied to the samples. Experimental details are described in Method 8023 of the Hach Water Analysis Handbook [19].

2.1.3. Copper

Copper in the sample reacts with a salt of bicinchoninic acid to form a purple colored complex in proportion to copper concentration. The intensity was taken at a wavelength of 560 nm with the UV–vis spectrophotometer. A sample of 10 cm^3 was used for the analysis. The blank was the sample that was not mixed with any reagent. No dilution factor was applied to the samples. The procedure is described in Hach Method 8506 as Bicinchoninate Method.

2.1.4. Nickel

Nickel content was determined by 1-(2-pyridylazo)-2-naphthol (PAN) Method (Hach Method 8150). Almost all the

metal ions react with the 1-(2-pyridylazo)-2-naphthol indicator. The sample is buffered and treated with pyrophosphate to remove ferric ions first. After the ions react with the indicator, EDTA is added to destroy all metal complexes except for nickel and cobalt. The method actually measures both nickel and cobalt on the same sample. A sample of 10 cm^3 was used for the analysis. The blank was deionized water. No dilution factor was applied to the samples.

2.1.5. Zinc

The zinc content was determined by Zincon Method as Method 8009 in the Hach Water Analysis Handbook. In this method, metal ions are complexed with cyanide. The addition of cyclohexanone causes a selective release of zinc. The zinc then reacts with 2-carboxy-2'-hydroxy-5'-sulfoformazyl benzene (zincon) indicator. The zinc concentration is proportional to the resulting blue color at 620 nm. A 10- cm^3 yellow-white sample was used for the analysis. The blank was the same sample that was not mixed with any reagent. No dilution factor was applied to the samples. For the green-gray sample, 5 cm^3 of the sample was diluted to 20 cm^3 .

2.1.6. Arsenic, cadmium and lead

Arsenic, cadmium and lead contents were determined by atomic absorption spectroscopy with a Perkin-Elmer AAnalyst 300 Atomic Absorption Spectrophotometer. Calibration curves were prepared by sequential dilution of 1000 $\mu\text{g}/\text{cm}^3$ standard solutions purchased from Perkin-Elmer. Five percent nitric acid was used as the blank. Experimental details are described in the Standard Methods for the Examination of Water and Wastewater [20].

2.2. Metal content

The metal contents in both yellow-white and green-gray samples are shown in Table 2. Each value represents an analysis of an average of six samples. The aluminum content in the yellow-white samples is relatively high. It indicates that some of the fine aluminum particles accumulated during the duty cycles were dissolved in the solution to produce aluminum ions. A possible explanation is that due to biological activities, a small portion of cutting oil was decomposed to produce organic acids, thus increasing the solubility of aluminum in the solution. Some researchers suggest that the high aluminum content might be due to the high temperature and pressure conditions in machining operations while others suggest that the acid digestion during sample preparation might have caused the dissolution of filterable suspended aluminum particles. The alarming finding is that the lead content in the green-gray samples is higher than the

Table 2
Metal content in the spent cutting fluids from Enomoto's facility (mg/L)

Sample	Al ³⁺	Zn ²⁺	Cu ²⁺	Ni ²⁺	Cr ⁶⁺	Cd ²⁺	As ²⁺	Pb ²⁺
Yellow-white	46.8	1.34	1.43	0.13	0.14	BDL	0.36	BDL
Green-gray	1.67	0.19	1.43	0.06	0.28	BDL	0.67	6.73

BDL: beyond detection limit.

Table 3
Total suspended solids in the spent cutting fluids from Enomoto's facility (mg/L)

Sample	Total suspended solids (mg/L)	
	Yellow-white	Green-gray
1	5355	76826
2	5170	79352
3	5301	71599
4	5377	75938
5	5069	73604
6	5383	76826
Average	5275.8	75690.8

local limit. Since no lead containing materials had been used in the process, the source of lead is still under investigation. However, to ensure compliance, samples were collected and sent to outside labs for confirmation.

2.3. TSS

The TSS was determined by heating 10 cm³ of the sample at 105 °C, in order to evaporate water. Residual solid on the disk was weighed to the nearest 0.4 mg by an analytical balance. Table 3 shows the TSS content of the samples analyzed. The average TSS of the six yellow-white samples was 5276 mg/L, while that of the green-gray samples was 75,691 mg/L. The relatively large value of the standard error is due to heterogeneity of the samples.

2.4. Filterable suspended solids

The same procedure for TSS analysis was used to determine the filterable suspended solid, using extra filtration. Twenty milliliters of each sample were collected and filtered through a Fisher-brand Q8 Quantitative filter paper to remove some of the oil and large metal particles. Table 4 shows the results from these measurements. The test shows how treatable the sample is. The average value of the filterable suspended solids for yellow-white samples was 3098 mg/L, while that of the green-gray samples was 60,383 mg/L. The results indicate that a significant amount of solid residue would be present in the sample, even if filtration

Table 4
Filterable suspended solids in mg/L

Sample	Filterable suspended solids (mg/L)	
	Yellow-white	Green-gray
1	3020	55700
2	3068	59400
3	3205	59600
4		59600
5		63600
6		64400
Average	3097.7	60383.0

were utilized. More treatment procedures would be required to treat the spent cutting fluid for onsite disposal.

2.5. O&G

The cutting fluid was prepared by mixing 10% by volume of the cutting oil (Isamu Paint Co.) with tap water. In the duty cycles, some of the cutting oil evaporates while tramp oil may accumulate in the solution. The Hach Method 10056 was used to determine the O&G in the spent cutting fluid samples. A sample of 350 cm³ was collected for the analysis. Twenty milliliters of methylene chloride was added to the sample to extract the organic content from the aqueous solution. The procedure was repeated three times to ensure the completion of the extraction. After separation from the aqueous layer, the organic portion was distilled to remove the solvent. The residue was cooled down to room temperature before weighing. The green-gray sample that had a thick layer of oil floating on the surface produced 87,354 mg/L of O&G. The yellow-white sample that had a light-yellow color and a thinner layer of oil on the top of the water layer produced 21,955 mg/L. One interesting observation was that paint had been extracted from the organic layer. The paint was a white-peach color that was synonymous with the color of the wastewater. When the solvent was boiled off, there was some O&G mixed in with the paint in the sample.

2.6. Aluminum particles

Aluminum particles were determined by filtration and gravimetric measurement. A long neck glass funnel and a 25-cm³ graduated cylinder were utilized to measure 20 cm³ of the spent cutting fluid. The samples were filtered through a suction filtration unit, and the metal pieces were left on the Fisher-brand Q8 Quantitative filter paper (Fisher Scientific). The filter paper was dried at 103 °C for 1 h. Once cooled down to room temperature, the samples were weighed to determine the amount of metal pieces on the paper. This test was only used for the yellow-white samples because the green-gray samples did not contain any scrap metal. Six samples were randomly taken from the same process for analysis. The results are presented in Table 5. The average value of the metal aluminum particles was 189.6 mg/L. In the duty cycles, tramp oil, dust and sludge along with aluminum particles may accumulate in the cutting

Table 5
Turbidity and aluminum particles of the spent cutting fluid samples from Enomoto's facility

Sample	Aluminum particle (mg/L)	Turbidity (FAU)
1	186.5	8990
2	100.5	9070
3	197.0	9125
4	156.5	9110
5	258.5	9070
6	238.5	
Average	189.6	9073

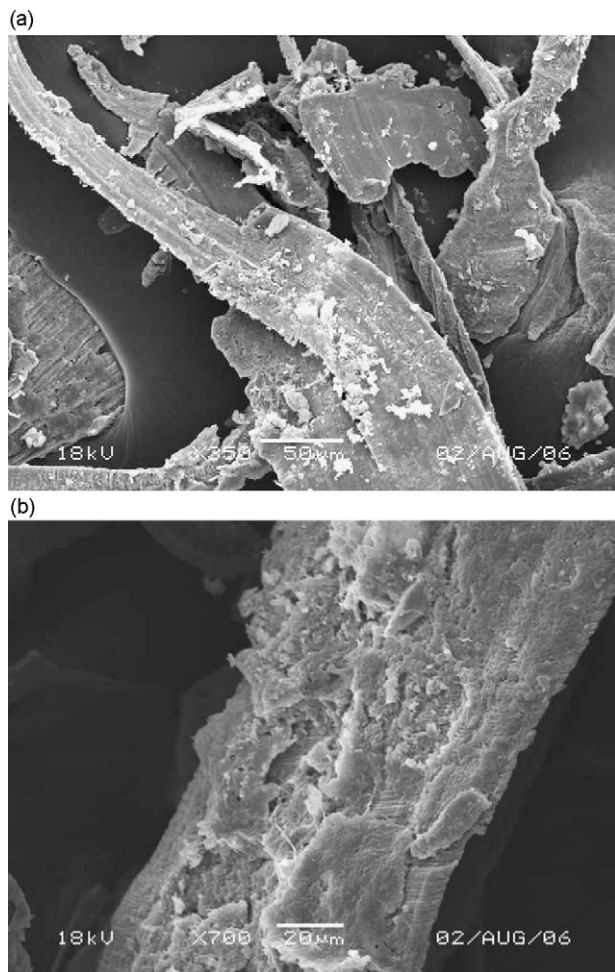


Fig. 1. (a) SEM image of aluminum particles from the yellow-white samples at 350 \times and (b) SEM image of aluminum particles from the yellow-white samples at 700 \times .

fluid. It is essential to identify the suspended particles in order to select a suitable separation method. A JSM 5610 scanning electron microscope (Jeol) was used to confirm the aluminum particles. Fig. 1a and b shows the shape, texture and size of the fine aluminum pieces from the yellow-white samples. From analyzing the zoom-in views of the aluminum metal pieces, there was some residue present. The pieces are assumed to be the oily residues because of the amount of O&G in the sample. The comparison with the pure aluminum powders from Sigma–Aldrich reinforced the notion that there were contaminants on the aluminum pieces.

2.7. Turbidity

The turbidity was measured with the Hach DR/4000 spectrophotometer. The Method 10047 was developed for testing turbidity in water, wastewater, estuary water, seawater and industrial process water. Results were given in Formazin Attenuation Units (FAU), and the estimated detection limit for the DR/4000 Spectrophotometer is 14 FAU. A 20-cm³ class A pipette was used to transfer the oily sample to a 250-mL erlenmeyer flask. Samples were diluted until turbidities were within 5000 FAU,

the detection range of this method. The result of the analysis is presented in Table 5. The average turbidity of the yellow-white sample was 9073 FAU.

3. Treatability study

After examining the spent cutting fluid samples, suspended solids and O&G were found the main reasons that spent cutting fluids were prohibited from being discharged into local sewage systems. A study was initiated to test the feasibility of sedimentation, centrifugation, coagulation and electrochemical methods for treatment of the spent cutting fluid. Since both suspended solid and O&G are closely related to the turbidity, the treatability test started with establishing the correlation between oil content and turbidity. Once established, turbidity was used as the index throughout the test to evaluate the effectiveness of each treatment method. The synthetic oil-bearing wastes were treated by gravity separation, centrifugation, chemical coagulation and electrochemical coagulation. The electrochemical method was effective and was selected for further study [17].

3.1. Emulsion stability

Synthetic oil–water emulsions were prepared by mixing motor oil with tap water, and by mixing cutting oil with tap water. To stabilize two motor oil emulsions, Equate hand soap (Vi-Jon Laboratories) and sunlight grease fighter (Phoenix Brands) were each added. A sample of cutting oil mixed with water, and the two motor oil emulsions were prepared to an absorbance level of between 2.0 and 2.5 absorbance units (AU) at 720 nm. Immediately after mixing, a portion of the sample was transferred to a cuvet in a Perkin-Elmer Lambda EZ 201 UV–vis Spectrometer, where the variations of absorbance were continuously monitored and recorded. Fig. 2 shows that in terms of stabilizing the oil–water emulsions, both detergents were ineffective. Within 15 min, the hand soap stabilized emulsion split into two layers. It took 40 min for the sunlight stabilized emulsion to reach the same level of separation. However, there was always a residual absorbance of 0.5 AU in the samples. The cutting fluid emulsion was very stable. Remaining stagnant for 1 h had almost no effect on its appearance. The spectrophotometer detected only a drop

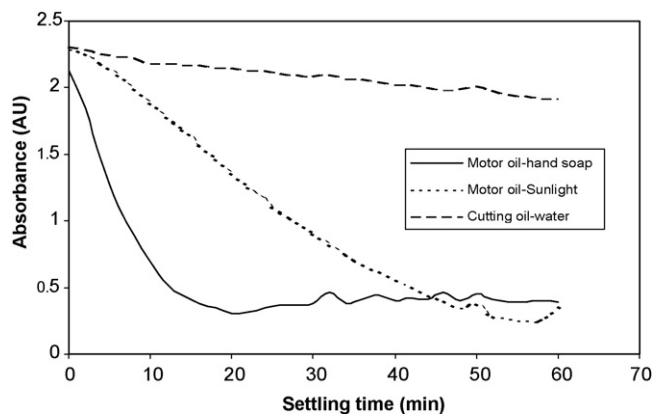


Fig. 2. Stability of oil-in-water emulsions.

of a few hundredths of an AU on absorbance. It is clear that a settling chamber will have little or no effect in the treatment of spent cutting fluids.

3.2. Oil content versus turbidity

In order to use turbidity as an index for treatment evaluation, a set of experiments was performed to establish the correlation between oil content in the emulsion and its turbidity. The calibration curves allow estimating oil content during treatment test without getting into tedious O&G analysis. Samples were taken for turbidity measurements, while oil drops were added to the detergent–water mixtures. Fig. 3 shows that both cutting fluid emulsions and sunlight stabilized emulsions have a reasonable correlation between oil content and turbidity measurements. The correlation coefficient for cutting fluid is 0.57 FAU/(mg/L), while that of the sunlight stabilized emulsion is 0.83 FAU/(mg/L). A significant linear relationship deviation was observed on the hand soap stabilized emulsion. This deviation is due to the instability of the oil–water system.

3.3. Centrifugation

Centrifugal decanters are widely used in industry for suspended particle separation. Without a suitable emulsifier, oil can be easily separated from an oil–water emulsion by centrifugation as well. A set of experiments was performed in order to evaluate the potential of using centrifuge to treat the oil-bearing wastes. A Cole Parmer 17250 Fixed Speed Centrifuge was used to provide a relative centrifugal force of $1318 \times g$ for the test. Detergent stabilized emulsion samples were prepared by mixing 3 g of motor oil and 2 g of sunlight in 500 cm³ of tap water, and 4 g of motor oil and 1 g of hand soap in 300 cm³ of tap water. For cutting fluid samples, 5 cm³ of cutting oil was added to 100 cm³ of tap water. After mixing for 1 min, all three samples had initial turbidities of around 1400 FAU. Fig. 4 shows the change of turbidity after the emulsions are subjected to centrifugation for 10, 20, 30, 60, 120 and 300 s. Both detergent stabilized emulsions were unstable under centrifugation. The turbidities dropped from 1400 to less than 80 FAU in 20 s of treatment. After the centrifugation, a

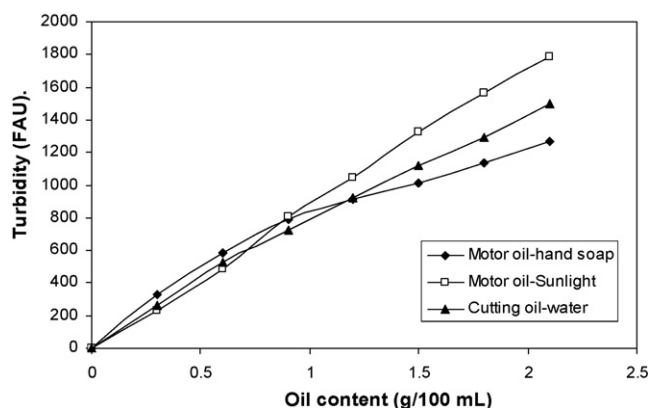


Fig. 3. Correlation between oil content vs. turbidity.

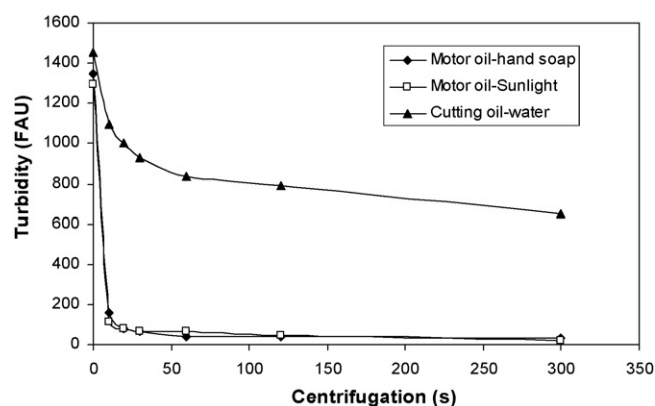


Fig. 4. Effect on turbidity after the emulsion is subjected to centrifugation.

layer of oil floated to the surface of the liquid, instead of settling on the bottom of the test tube. Low-oil content emulsions are stable even under a strong centrifugal force. For the cutting fluid samples, turbidity dropped about 40%, from 1451 to 838 FAU in the first 60 s, and stabilized at 650 FAU. A mechanism to break the emulsion is essential for centrifugation to be effective in treating spent cutting fluid.

3.4. Chemical coagulation

Emulsions can be broken down by acidification, the addition of aluminum or iron salts, or the use of emulsion-breaking polymers. Although other coagulants are under development, aluminum and ferric salts are still the most widely used agents. A set of experiments was conducted to confirm the effectiveness of aluminum ions for demulsification. Emulsion samples were prepared by mixing 2.1 cm³ of motor oil and 1 cm³ of sunlight with 100 cm³ of tap water, and 2.1 cm³ of cutting oil with 100 cm³ of tap water. These samples, along with a spent cutting fluid sample were tested in a modified jar test procedure. Small increments of aluminum chloride (AlCl₃) were added to 100 cm³ of each sample in a beaker on top of a magnetic stirrer. After each addition and rapid mixing, the mixture settled for 10 min and then turbidity was measured. The turbidity relationships are shown in Fig. 5. Although the spent cutting fluid had a higher initial turbidity, it responded to the treatment well.

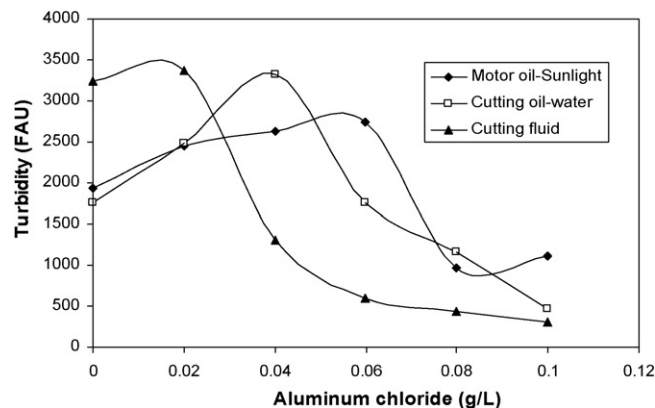


Fig. 5. Effect on turbidity after the emulsion is subjected to chemical treatment.

By adding 1 g/L of AlCl_3 in the solution, the turbidity dropped from 3249 to 314 FAU. Even with different initial pH, the final pH was around 4.5. The addition of high-valence Al^{3+} ions neutralizes the negative charge on the colloid, thus destabilizing the dispersed oil droplets. After entering the aqueous solution, the Al^{3+} ions undergo hydrolysis, forming $\text{Al}(\text{OH})_3$ precipitate and a variety of dissolved complex ions. The net result of the reactions is that the emulsion is destabilized, and the colloidal oil particles begin to coalesce. After treatment, all three samples had significant residual turbidity. It is believed that due to the low pH, some of the $\text{Al}(\text{OH})_3$ precipitate dissolves in the aqueous solution and forms gelatin-like complex, which causes the turbidity. A solubility diagram for aluminum in water indicates that at alkaline pH values ($\text{pH} > 8$), the principal soluble species present at equilibrium with gibbsite is the monomeric anion, $\text{Al}(\text{OH})_4^-$. At lower pH levels ($\text{pH} < 6$), the dominant soluble species at equilibrium with gibbsite are cationic monomers such as Al^{3+} . The lowest solubility limit is at pH 6.5, where the solubility of aluminum compound is less than 10^{-6} mol/L [21]. A pH adjustment to 6.5 is essential in bringing down the solubility of $\text{Al}(\text{OH})_3$ and thus the turbidity of the solution.

3.5. Electrochemical treatment

One way of producing metal ions in an aqueous solution is through anodic dissolution of sacrificial electrodes. A cutting fluid demulsification study of freshly generated aluminum coagulant was conducted in a bench-scale electrochemical system, as shown in Fig. 6. The system consists of a dc power supply, a power control and measurement unit, an electrochemical reactor, a reservoir, a feed pump, a flow control valve, a flow-measuring unit, and a circulation pump. The reactor is made of acrylic plastic, with an active volume of 88 cm^3 . The anode is made of aluminum sheet, and the cathode is made of graphite sheet. The electrodes are situated approximately 1 cm apart from each other and are submerged in the solution. The cathode and anode each has a surface of 88 cm^2 . The system was operated in a simple batch recirculation mode, with a circulation pump, to prevent sedimentation.

Emulsion samples were prepared by mixing 10 cm^3 of pure cutting oil with 500 cm^3 of tap water. Two grams of sodium

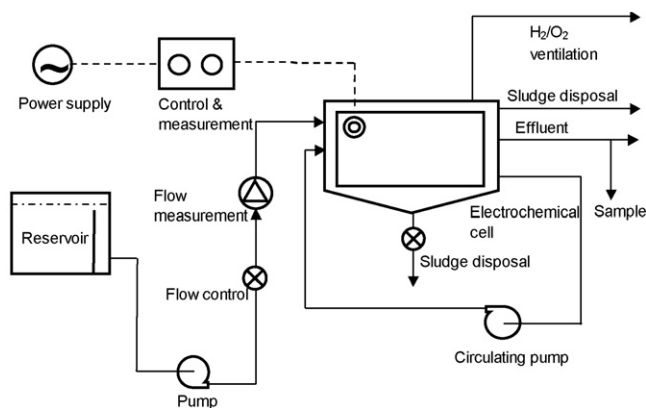


Fig. 6. Schematic of the electrochemical coagulation system.

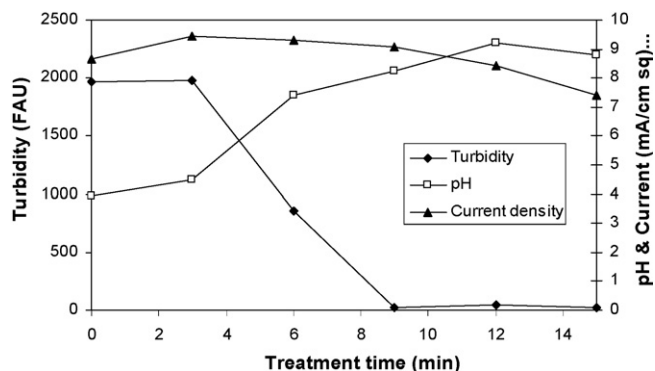
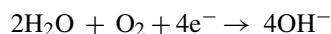
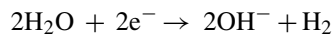


Fig. 7. Variations of key parameters during electrochemical treatment.

chloride (NaCl) were added to the mixture, to provide extra electrical conductivity. The solution was pumped into the reactor, where 5 V dc was applied across the 1 cm gap. Samples were taken from the reactor during the treatment timeline to determine the turbidity and pH. Fig. 7 shows the variations of the key parameters during the electrochemical treatment of the freshly prepared cutting fluid. Initially, the solution has a turbidity of 1970 FAU and a pH of 3.9. With 2 g/L of NaCl in the solution, the applied voltage resulted in a current of 0.76 A in the reactor. The pH increased with treatment time and stabilized at around 9 in 9 min. The current began to drop after 9 min of treatment. It is believed that the NaCl was consumed in the process and caused a lower electrical conductivity thus a lower current in the solution. Passivation may have played a role in the current drop in the reactor as well. During treatment, oxide formation on the anode and/or oil deposits on the electrodes may have increased the resistance and lowered the current between the electrode pair. The turbidity dropped to 25 FAU in 9 min of treatment and a significant amount of sludge was observed on top of the solution.

The principal reaction in most electrochemical processes is the reaction of the electrode material itself. At large cathodic potentials, local hydroxyl ions (OH^-) can be generated due to water and oxygen reduction.



With aluminum sheets as consumable electrodes, Al^{3+} ions are produced on the anodes.



As a result of the high pH, precipitates of $\text{Al}(\text{OH})_3$ are formed and remain in the solution. The most recent report cited by Metcalf and Eddy [22] from a number of researchers identifies the major aluminum hydrolysis products as AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_4^-$ and $\text{Al}(\text{OH})_3$. The precipitates gradually age by crystallization through a series of hydroxyl compounds. The hydroxide gel crystallizes to orthorhombic bohmite, to monoclinic bayerite and then to monoclinic hydrargillite. Once formed, the aluminum hydroxide destabilizes the oil–water system, adsorbs the coalesced oil, and is then floated to the top of

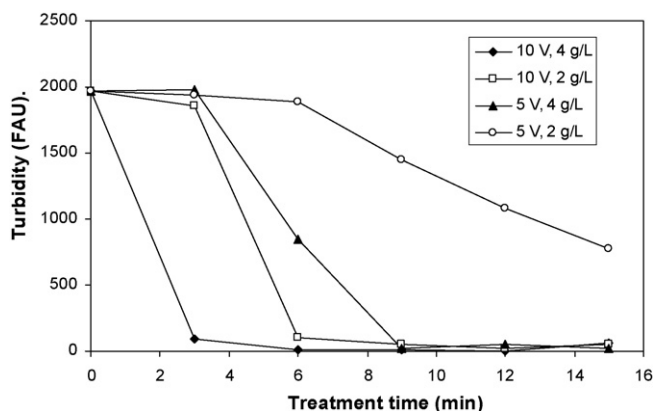


Fig. 8. Effect of applied voltage with NaCl concentration on turbidity.

the solution by the hydrogen bubbles, which are generated in water electrolysis.

Fig. 8 shows the effect of applied voltages with NaCl concentration on turbidity reduction. With 10 V dc and 4 g/L NaCl in the solution, the system started reducing turbidity the moment voltage was applied to the reactor. A current of 2.5 A was carried through the reactor. The turbidity was reduced from 1967 to 95 FAU in 3 min, and was further reduced to less than 14 FAU, the detection limit of the Hach spectrophotometer. With 5 V dc applied to the same solution, the system generated enough coagulant and started to reduce the turbidity in 3 min. Ultimately, the turbidity was reduced to 25 FAU. When the concentration of NaCl was reduced to 2 g/L, a voltage of 10 V dc could still draw enough current to generate coagulant for the treatment. Turbidity started to drop in 3 min and continued to drop until it reached 50 FAU in 6 min. With 5 V dc applied to a solution of 2 g/L NaCl, the system was unable to generate enough coagulant for turbidity reduction. The current across the reactor was only 0.4 A, which was less than the 20% used in the previous test (10 V dc and 4 g/L NaCl).

In view of the effectiveness of electrochemical treatment, spent cutting fluid was collected and tested in the system. Based on the previous study, 1 and 2 g/L of NaCl were added to the cutting fluid sample to increase their conductivity. The initial turbidity of the sample was 3261 FAU. The solution was pumped into the reactor for treatment. Fig. 9 shows the effect of applied

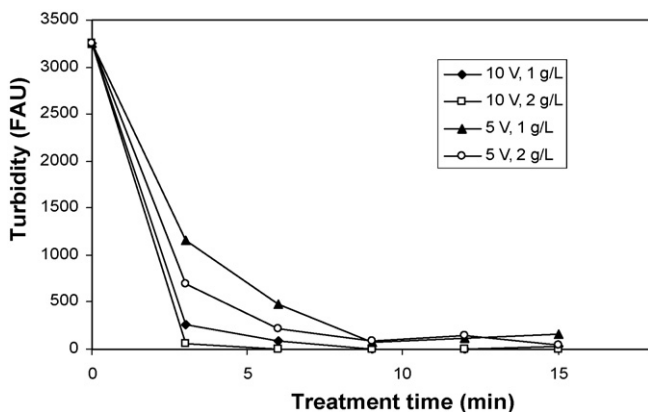


Fig. 9. Effect of applied voltage with NaCl concentration on turbidity reduction.

voltages with NaCl concentrations on turbidity reduction. With a 10 V dc applied to the two electrodes, the voltage drew a current of 1.5 A through the solution of 2 g/L NaCl. The turbidity was reduced to 60 FAU in 3 min, and continued to decrease to beyond the detection limit of the spectrophotometer. In all cases, the electrochemical treatment was more effective on spent cutting fluid than on freshly prepared cutting fluid. This is due to the intrinsic difference between the conductivity of the two samples. Additionally, the emulsion in the spent cutting fluid is not as stable as that in the freshly prepared ones. It is believed that some of the ingredients found in the solution that stabilize the emulsion, are lost through evaporation or decomposition in the duty cycles.

4. Conclusions

In general, metal contents remaining in spent cutting fluids from aluminum alloy machining operations are well within the discharge limits for most POTW's in the U.S. However, TSS and O&G are way beyond allowable discharge limits.

Some POTW's provide a method that allows their discharge, with a surcharge fee attached. TSS and O&G are the major contributors to turbidity in various industrial wastewaters. Due to the fact that most oil–water emulsions are stabilized by surfactants, in most situations, physical treatments are not effective.

Chemical coagulants are effective in breaking down emulsions by neutralizing the negative charge on micells, thus destabilize the oil–water system. Some coalesced oil will be adsorbed into the coagulant and separated from the water.

Another method of generating coagulant in an aqueous solution is with electrolysis. When aluminum sheets are used as sacrificial electrodes, an electrochemical reactor will generate aluminum ions by anodic dissolution. The aluminum ions react with the hydroxyl groups, which are generated on the cathode to produce aluminum hydroxide. The system effectively reduces the turbidity in the spent cutting fluid from 3261 to 60 FAU in 3 min of treatment, and the turbidity continued to decrease to beyond the detection limit of the spectrophotometer.

Acknowledgement

The authors are grateful to Ms. Juliana Smith, the research management coordinator of the Advanced Technology and Manufacturing Center at the University of Massachusetts-Dartmouth for editing this manuscript.

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