

**Removal of Machine industrial from wastewater using cylindrical flow reactor by electrochemical oxidation and optimization of treatment conditions**

C.Kalaivanan<sup>1</sup> M.Yosuva Suvaikin<sup>2\*</sup>,

Department of Chemistry, K.Ramakrishnann College Technology Tiruchirappalli-620019

Department of Chemistry, Assistant professor, H.H The Rajah's College, Pudukkottai.

**Abstract**

This work examines the use of electro oxidation for treatment of wash water obtained from industry. Cutting oil was mainly found in the wastewater. The effluent was treated using NaCl as supporting electrolyte using a cylindrical flow reactor in continuous (single pass) mode under various current densities (2-5 A/dm<sup>2</sup>) and different flow rate (10-40 L/h). By cyclic voltammetric (CV) analysis, the best condition for maximum redox reaction was found. Efficiency of COD reduction and power consumption were studied for each operating conditions. From the results maximum COD reduction of about 93.3 % was obtained at a flow rate of 10 L/h with applied current density of 4 A/dm<sup>2</sup>. FT-IR spectra studies showed that during electrooxidation, the intensities of characteristic functional groups such as C-H, O-H were reduced and also some new peaks comes to appear. Probable theory, reaction mechanism and modeling were proposed for the oxidation of machine industrial effluent. All the experimental results have indicated that electrooxidation treatment was very effective and was capable of elevating quality of the treated wastewater effluent to the reuse standard of the machine industry.

**Keywords:** cutting oil effluent; removal efficiency; NaCl; Electrochemical oxidation, Ti/RuO<sub>2</sub> anode.

**INTRODUCTION**

Metal working fluids (MWF) are commonly used in manufacturing and machining industries for cooling and lubricating. There are four major classes of MWF: (i) which contain lubricant base oils without water (straight oils), (ii) composed of an aqueous oil emulsion with oil in high concentration (soluble oils) or (iii) lower concentration (semi synthetic MWF) and (iv) formulated with no petroleum oils (synthetic fluid) The cutting

oils called also soluble oils are used in particular during mechanical operations of cutting and shaping metals. They combine the properties of cooling and lubrication. They are generally obtained by addition demulgation agents, cotensioactifs, and various bactericidal and anti-corrosive additives which emulsify mineral oil in water. These cutting fluids lose their effectiveness with the time of the months because of their thermal degradations and their pollution by the suspended matter and free oils of lubrication .It is so necessary to carry out their replacement periodically and to get rid of the worn effluents. The forward thrust constitutes a danger to the environment because these effluents very charged into surface-active and organic pollutants, present varying DOC. from 3 to 200 g/L . Moreover, because of their great capacity of penetration in the ground, they constitute a very serious threat for the groundwater. Oil and grease is a common pollutant in a wide range of industries. Stable oil-water emulsions are generated in diverse industrial technologies. Industries such as steel, aluminum, food, textile, leather, petrochemical and metal finishing are some that report high levels of oil and grease in their effluents. For instance, in metal working industry oil-water emulsion is often used as coolant and lubricant to decrease the destruction of tool and die. In the past time the used emulsion was often discharged to either sanitary sewers or public waterways without previous treatment, causing environmental pollution and loss of oil. Conventional methods for oily emulsion separation are classified to physical and chemical processes. Conventional approaches to treating oily wastewaters have included gravity and skimming, dissolved air flotation, demulsification, coagulation and flocculation. Gravity separation followed by skimming is effective in removing free oil from wastewater. Oil-water separators such as the API separator and its variations have found widespread acceptance as an effective, low cost, primary treatment step. These, however, are not effective in removing smaller oil droplets and emulsions. Oil that adheres to the surface of solid particles can be effectively removed by sedimentation in a primary clarifier.

Cutting oils are metalworking fluids used to dissipate heat and to provide lubrication between the face of the cutting tool and the metal being cut. Typical cutting oil normally contains oil, water, and additives (fatty acids, surfactants, biocides, etc.). After a long use, cutting oils accumulate physical and chemical contaminants, losing its lubricating and refrigerating properties and generating a toxic waste, which contains heavy metals, biocides, microorganisms and harmful decomposition products. Conventional

treatment methods as evaporation, membrane or chemical separation have major disadvantages since they generate a concentrated stream that is more harmful than the original waste. Generally, it is a waste too dilute to be incinerated, and due to its toxicity, it is difficult to treat biologically.

Cutting fluids are various fluids that are used in machining to cool and lubricate the cutting tool. There are various kinds of cutting fluids, which include oils, oil-water emulsions, pastes, gels, and mists. They may be made from petroleum distillates, animal fats, plant oils, or other raw ingredients. Depending on context and on which type of cutting fluid is being considered, it may be referred to as cutting fluid, cutting oil, cutting compound, coolant, or lubricant. They are generally obtained by addition demulcation agents, cotensioactifs, and various bactericidal and anti-corrosive additives which emulsify mineral oil in water.

Cutting fluids have been introduced into the cutting process with the purpose to improve the characteristics of the tribological processes which are always present on the contact surfaces between the tool and the workpiece. The use of cutting fluids increases the tool life, contributes to a more economical cutting speed and generally improves the efficiency of the production systems when taken as a whole.

## **2. THEORETICAL APPROACH**

In the electrochemical process, the pollutants are destroyed by either the direct or indirect oxidation process. In direct anodic oxidation process, the pollutants are first adsorbed on the anode surface and then destroyed by the anodic electron transfer reaction. In an indirect oxidation process, strong oxidants such as hypochlorite ion/chlorine, ozone and hydrogen peroxide are electrochemically generated. The pollutants are then destroyed in the bulk solution by oxidation reaction of the generated oxidant. All the oxidants are generated in situ and are utilized immediately. Among the oxidants, generation of hypochlorite ion is cheaper and most of the effluents have a certain amount of chloride. Though direct electrolysis of organic compounds at the anode surface is also possible, a major portion of oxidation is mediated by active chloro species

when conducting electrochemical oxidation in the presence of chloride using an undivided cell.

The mechanism of electrochemical oxidation of wastewater is a complex phenomenon involving coupling of electron transfer reaction with a dissociate chemisorptions step. Basically two different processes occur at the anode; on anode having high electro-catalytic activity, oxidation occurs at the electrode surface (direct electrolysis); on metal oxide electrode, oxidation occurs via surface mediator on the anodic surface, where they are generated continuously [indirect electrolysis]. In direct electrolysis, the rate of oxidation is depending on electrode activity, pollutants diffusion rate and current density. On the other hand, temperature, pH and diffusion rate of generated oxidants determine the rate of oxidation in indirect electrolysis. In indirect electro-oxidation, chloride salts of sodium or potassium are added to the wastewater for better conductivity and generation of hypochlorite ions/chlorine.

### **2.1. Anodic Reactions**

In electrochemical conversion the high molecular weight aromatic compounds and aliphatic chains are broken to intermediate products for further processing. In electrochemical combustion the organics are completely oxidized to CO<sub>2</sub> and H<sub>2</sub>O. A brief explanation of reaction mechanism taking place at metal oxide electrode is enumerated below:

The generation of chlorine from chloride ion in anodic oxidation is given in Eq. (1)  
(Main reaction):

Side reaction is given in Eq. (2):



### **2.2. Cathodic reaction**

Cathodic reaction is given in Eq. (3):



### 2.3. Reaction in bulk solution

The role of hypochlorite in electrochemical treatment of cutting oil effluent via chloride ion generation is given below:



The electro-oxidation of wastewater in the presence of a supporting electrolyte is influenced by various operating parameters. The progress of the destruction of the organic pollutant has been monitored by COD estimation. The potentials required for oxidation of organic pollutants are generally high and the production of oxygen from the electrolysis of water molecules may determine the reaction yield. The instantaneous current efficiency (ICE) may be defined as:

$$\text{ICE} = \left[ \frac{\Delta_{\text{COD}} F V}{8 I \Delta t} \right] \quad (35)$$

Where F is faraday constant;  $\Delta_{\text{COD}}$  is difference in COD between initial and final in mg/L; V is volume of reactor in litre; I is current passed in ampere;  $\Delta t$  is time interval in seconds.

The instantaneous current efficiency is a measure of efficiency of electro-oxidation. The ICE has been estimated for all the experimental runs in the present investigation and critically examined.

### 2.3. Electrolytic cylindrical flow reactor

Fig. 1 depicts a schematic diagram of flow reactor set-up. Experiments have been conducted in electrolytic flow reactor consist of a cathode made up of stainless-steel pipe of 110 cm height and 7 cm diameter and Ti/RuO<sub>2</sub> coated expanded mesh cylinder was used as a catalytic anode, measuring 100 cm long and 5 cm diameter which was held axially inside the cathode such that 1 cm as inter-electrode distance. Provisions are made for electrical connections so as to constitute an electrolytic cell. The capacity of the cell is

4.5 L. The cell had one inlet at the bottom cover and one outlet at the top cover. It is connected to 100 A and 50 V DC regulated power supply. Reservoir, pump, flow meter and electrolytic flow reactor are connected using silicone rubber tubes.

#### **2.4. Experimental procedure**

Samples to be treated were taken in the reservoir and fed into the reactor; NaCl salt was added as electrolyte medium to adjust a fixed strength ionic solution. By adjusting the rotameter, the flow rate was found. The required current was passed using regulated power supply and cell voltage was noted for each flow rate. The effluent was allowed to flow at single pass from bottom of the cell. After attaining steady-state, the outlet samples were collected and subjected to COD, FT-IR analysis. The various experimental conditions and parameters were studied at different current densities such as 2, 3, 4 and 5 A/dm<sup>2</sup>. For each current density the experiment was repeated for different flow rate of effluent to the reactor 10, 20, 30, 40 L/h.

### **DETERMINATION OF COD**

#### **DEFINITION**

Chemical oxygen demand is the oxygen required for chemical oxidation of organic matter with the help of strong chemical oxidant.

The test was based on treating the waste with a know amount of dichromate, digesting at an elevated temperature to oxidize the organic matter and titrating the unconsumed dichromate. The oxygen equivalent of dichromate destroyed is reported as the COD

#### **APPARATUS**

Reflux apparatus, consisting of a 500 ml flat-bottomed flask with ground glass joint and a condenser.

#### **Procedure**

Place 0.4 g of HgSO<sub>4</sub> in a reflux flask and add 1 ml of the sample or an aliquot of the sample. Mix well and add 2 ml of 0.25N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution. Drop some pumice stones

and slowly add 3 ml of H<sub>2</sub>SO<sub>4</sub>-Ag<sub>2</sub>SO<sub>4</sub> Reagent while continuously swirling the flask. If the color changes to green, add more K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and H<sub>2</sub>SO<sub>4</sub> - Ag<sub>2</sub>SO<sub>4</sub> reagent or alternatively discard the solution and take a fresh sample with lesser aliquot. Mix the contents of the flask thoroughly. Connect the flask to the condenser and slowly heat flask. Reflux for at least 2 hours at about 148°C. Cool and wash down the condenser with distilled water such that the washings fall in to the flask. Dilute to about 150 ml cool and titrate the unrelated K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> with the N/10 ferrous ammonium sulfates solution using Ferroin as indicator. The color change at the end point is from blue green to wine red.

Perform blank experiment with distilled water instead of sample.

### **Calculation**

COD (mg/l) =  $(V_1 - V_2) \times N \times 8 \times 100 / X$  Where,

V<sub>1</sub> = Volume of ferrous ammonium sulphate run down in the blank experiment

V<sub>2</sub> = Volume of ferrous ammonium sulphate run down in the test experiment

N = Normality of ferrous ammonium sulphate solution, and

X = Volume of test sample taken % destruction

The extent of destruction of COD was calculated as follows

$$\% \text{ COD removal} = (\text{COD}_{\text{initial}} - \text{COD}_{\text{final}}) / \text{COD}_{\text{initial}}$$

### **RESULTS AND DISCUSSION**

The effect of the parameter such as flow rate and current density on rate of COD removal was investigated in a pilot scale cylindrical flow electrolyzer in a single pass for cutting oil effluent in a NaCl electrolyte medium. The option for the above medium was based on CV scan as given in Fig.3 the following data such as specific power consumption mass flux and mass transfer coefficient were computed for various flow rate and current densities is given Table 2. the COD reduction and shown in Fig 2. The FTIR, NMR-spectra and HPLC obtained for the outlet samples are given in Fig.3, 4 and 5 and the above studies were carried out under ambient conditions.

### **2.5. Effect of current density and flow rate on COD removal**

An increase in flow rate has resulted in a decrease in the removal efficiency as it can be seen from Fig. 6. Experiments were conducted at four different current densities from 2 to 5 A/dm<sup>2</sup>. COD reduction efficiency increases with increase in current density and decreases with increase in flow rate. When the current density increases, the rate of generation of hypochlorite ion increased. The increase in hypochlorite ions approaches equilibrium with degradation of organics. Results showed (Table 3) that higher COD reduction occurred at higher charge input and electrolysis (residence time) time. A high detention time resulting from a low flow rate has caused an increase in the removal efficiency. The easily oxidizable organics present in the effluent contribute to the decrease in the COD at low flow rate.

In this study, the increase in flow rate from 10 to 40 L/h leads to gradual decrease in the COD removal at 40 L/h. The maximum possible COD reduction was 93.3 % at 10 L/h and 4 A/dm<sup>2</sup>. At high flow rates (40 L/h) and lower current density (2 A/dm<sup>2</sup>) the COD reduction was found to be low (85 %).

### **2.6. FT-IR spectral studies**

The FT-IR spectra for untreated and treated Machine industry effluent were recorded on Thermo Nicolet Nexus 670 FT-IR spectrophotometer with the region between 400 and 4000 cm<sup>-1</sup>. The samples were pressed with pure KBr crystals to prepare pellets and used for analysis. From the spectra (Fig. 3) it can be concluded that some structural changes might have occurred during the electrochemical oxidation process. The peaks covering the region 500-3500 cm<sup>-1</sup> (dashed lines) shows most of the peaks of raw effluent was gone in the spectrum of treated effluent. Peaks at 3438, 2923, 2853, 1674, 1376, 699 and 533 cm<sup>-1</sup> due to the characteristic absorption peaks of OH (alcohol, H bonded stretching), OH (Carboxylic acid stretching), C-H stretching, C-N, (CH<sub>2</sub>, CH<sub>3</sub> bending), (C-H bend) and C-Br halide stretching groups. The characteristic absorption peaks of alcoholic O-H group were found at 3438 and 1376 cm<sup>-1</sup>. The cyclic and acyclic ether linkage(C-O-C) absorbs at 1190 and 1118 cm<sup>-1</sup>. After treatment, the intensities of amine and O-H groups were reduced. This mainly due to the fact that the organics present in cutting oil wastewater are converted into other secondary products. The reduction of peak intensity at 2923, 1461,

1376,533  $\text{cm}^{-1}$  may be the breaking up of cyclic ether linkage (C-O-C) and form a tetrahydropyran and cyclohexane rings. Appearance of new peaks at 2102 and 735  $\text{cm}^{-1}$  and a low intense peak at 1445  $\text{cm}^{-1}$  proves the formation of cyclohexane and tetrahydropyran ring in effluent. From the results, all characteristic absorption peaks were reduced in the spectra. This indicates that the organics present in the effluent might be converted into some other products like formic acid, carboxylic acid and acetic acids. Further these acids might be converted to  $\text{CO}_2$  and water.

## 2.7 HPLC

HPLC samples were prepared from ethyl acetate-extracted dried solution. Fig. 4(a) shows the chromatogram of untreated effluent, the major peak was obtained at 3.2 min (retention time). After treatment the intensity of peak was reduced drastically which was clearly shown in the Fig. 4 (b). In the effluent samples two peaks were observed in the range of 3-4 and also extra two peaks in the range of 4-5. For the treated sample, the peaks in the range 4-5 were disappeared and also the second peak also disappeared. Only the peak number one was observed.

## 2.8. Effect of current density and flow rate on power consumption

Electrochemical treatment is undoubtedly an energy-intense process and its efficiency is usually assessed in terms of specific energy consumption (SEC). This is defined as the amount of energy consumed per unit mass of organic load (e.g. COD) removed. Energy consumption is directly affected by the current density applied to the system. To enumerate the effect of current density and flow rate on power consumption, the current was varied from 2 to 5  $\text{A}/\text{dm}^2$ . The SEC is expressed in kWh/kg of COD removal and is given as:

$$\text{Energy Consumption} = \left( \frac{IVt}{\text{vol}} \right) / \Delta_{\text{COD}} \quad (37)$$

Where  $\Delta_{\text{COD}}$  is difference in COD between initial and final in g/L; vol. is volume of reactor in liter; I is current passed in Ampere; t is retention time in hour; V is cell voltage in Volt.

It was found that SEC was the highest at lower flow rates at all current densities under study. A significant reduce in SEC was observed when flow rate increased in the electrochemical system. From Table 2, SEC was reduced

from 17.021 to 0.967 kWh/g of COD removed at 4 A/dm<sup>2</sup> in 0.44 hr duration. Increase in the current density increases the power consumption at flow rates. Furthermore, higher current density could bring high electric energy consumption and operating cost. This may bring a certain industrial application prospect.

It is also interesting to note that the mass flux of the system decreases linearly with the decrease in flow rate (Table 2). At 5 A/dm<sup>2</sup>, the mass flux was found to be 26.595 g COD/h dm<sup>2</sup> at flow rate of 10 L/h and mass flux of 1.511 g COD/h dm<sup>2</sup> at flow rate of 40 L/h. As mass flux depends on the time of operation, the effect of residence time plays an important role in the process. The current density is directly proportional to the mass flux. These results are shown in Table 2. At current density of 2 A/dm<sup>2</sup> and flow rate of 10 L/h, the mass flux was 0.4939 g COD/h dm<sup>2</sup>, but high current density (5 A/dm<sup>2</sup>) with same flow rate mass flux was increased to 0.5026 g COD/h dm<sup>2</sup>.

Mass transfer coefficient increases with increase in flow rate as well as increase in current density. The mass transfer coefficient 0.00024 cm/s was found to be high in the case of 40 L/h and 5 A/dm<sup>2</sup>. As time of operation reduces, mass transfer coefficient increases steadily. It has a direct relation to the current density and flow rate, indicated in the table. It increases with increase in flow rate at all current densities and it is due to rapid reaction that is followed by a slow reaction at high current density. Results clearly indicate that current density and flow rate strongly influences the rate of reaction.

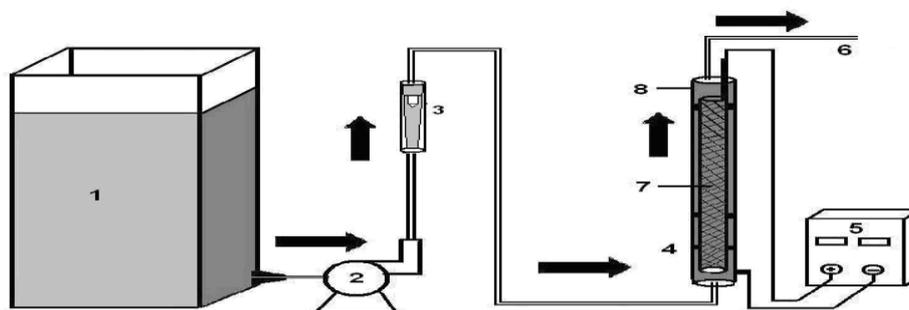
### **2.9. Percentage of COD reduction and ICE**

The Instantaneous current efficiency (ICE) was calculated for all the experiments in the present investigation. The variation of ICE along with percentage of COD reduction with current density is given in Fig. 6. It can be noticed from the figure that the percentage of COD reduction and ICE increase in current density initially and decreases beyond 4 A/dm<sup>2</sup>.

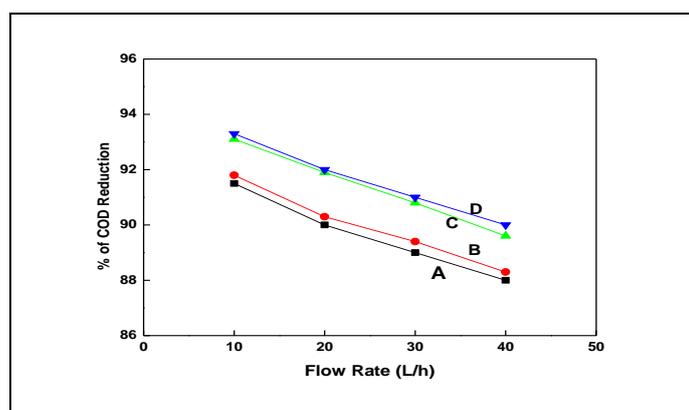
### **3.0. Effect of the electrolyte concentration**

NaCl can enhance the degradation efficiency and shorten reaction time, may be due to the reaction between the generated chlorine/hypochlorite and organic molecule. When the concentration of NaCl increases, solution conductivity was improved which leads to less power consumption. Increasing the concentration of NaCl up to 4 g/L

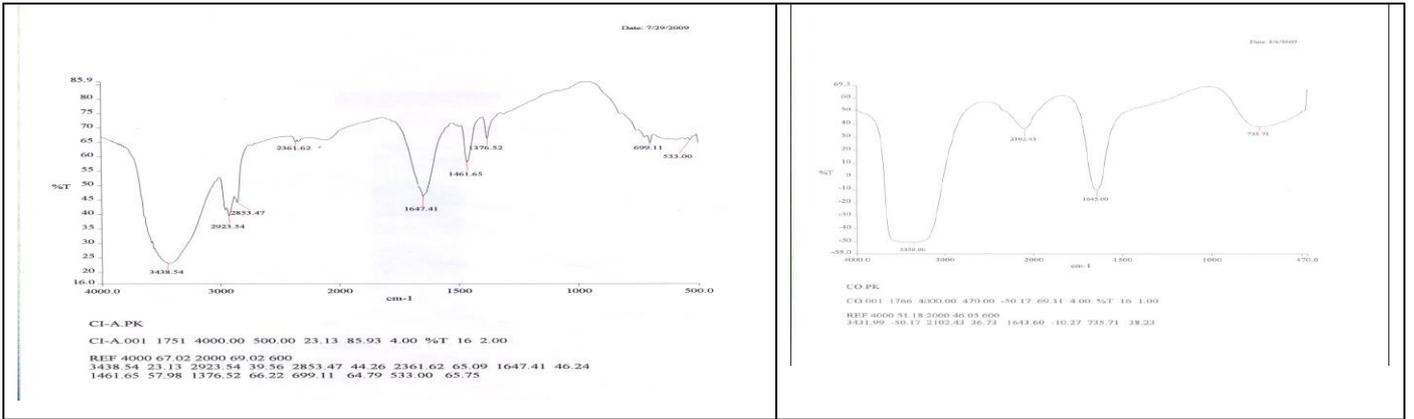
accelerated the removal rate, enabling complete mineralization of organics to extent of 93.3 % COD reduction efficiency in 0.44 hr (Fig.7). A further increase in NaCl concentration (up to 5 g/L) did not bring about any improvement in COD reduction efficiency, so the optimal NaCl concentration used in the successive experiments was 4g/L.



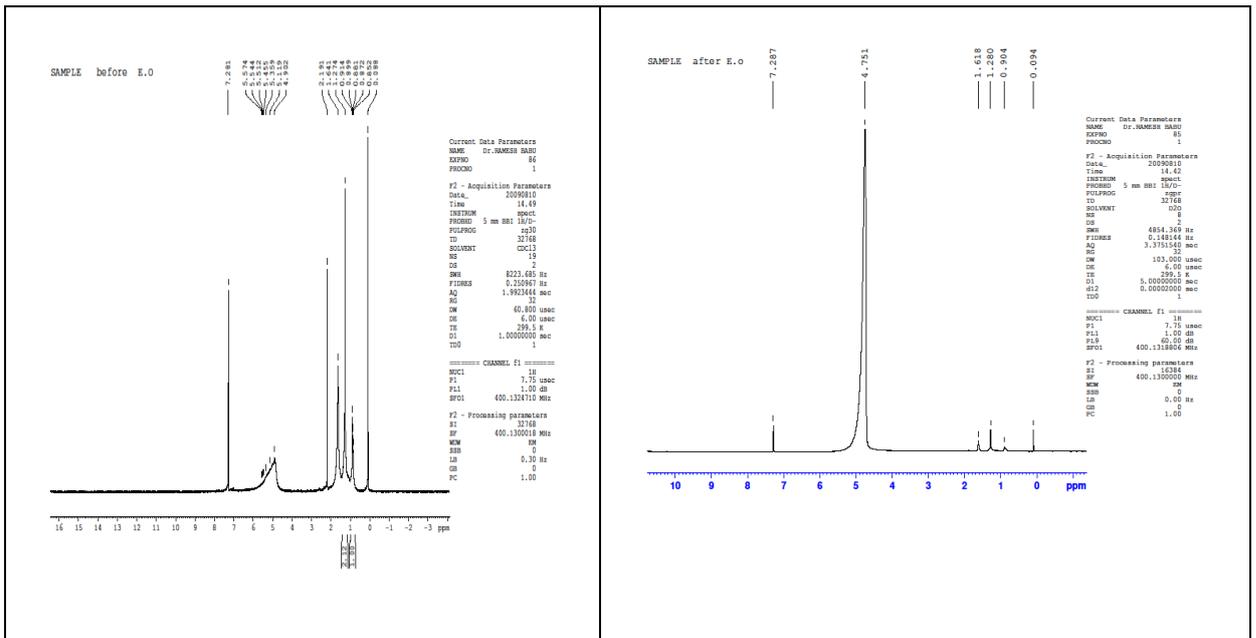
**Fig.1. Schematic diagram of flow reactor set-up: (1) reservoir; (2) pump; (3) rotameter; (4) electrolytic cell; (5) DC power supply; (6) treated effluent; (7) Ti/RuO<sub>2</sub> coated expanded mesh - anode; (8) stainless-steel – cathode.**



**Fig.2. Effect of COD reduction on flow rate at different current densities: (NaCl: 4g/L).**

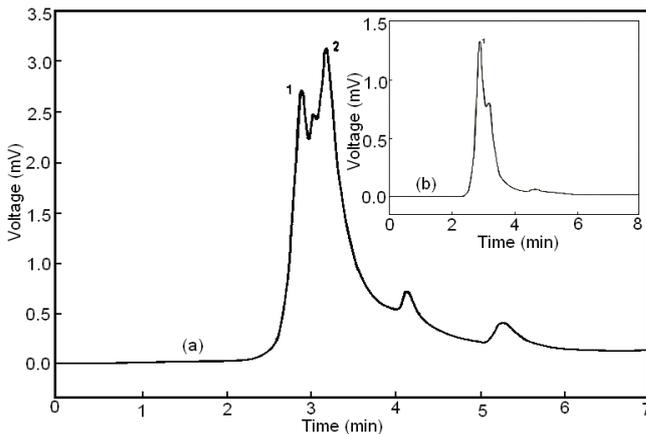


**Fig.3. FT-IR spectrum of cutting oil effluent (Current density 4 A/dm<sup>2</sup> at 10 L/h; NaCl: 4 g/L).a- Before treatment NaCl: 4 g/L). After treatment**

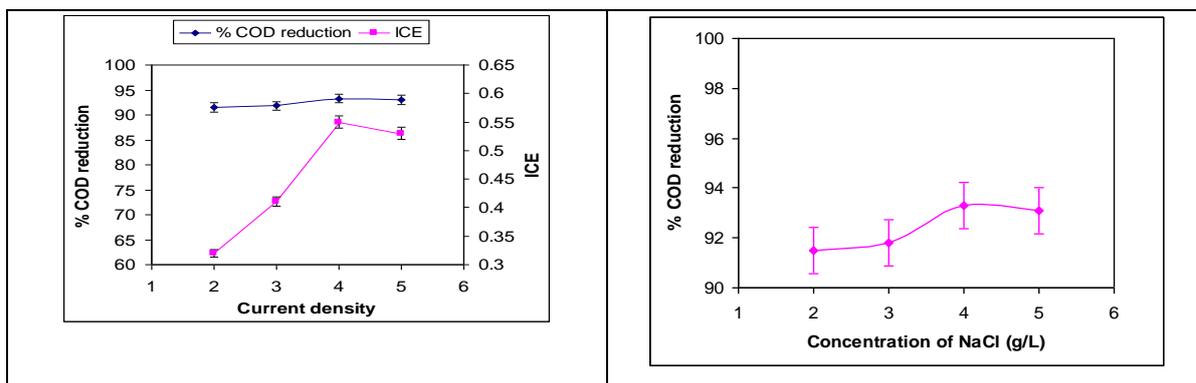


**Fig.4. NMR- spectrum of cutting oil effluent (Current density 4 A/dm<sup>2</sup> at 10 L/h; NaCl: 4 g/L).**

**1. BEFORE TREATMENT 2.AFTER TREATMENT.**



**Fig.5.HPLC data for cutting oil effluent**  
**A- BEFORE TREATMENT B- AFTER TREATMENT.**



**Fig.6. Variation of percentage COD reduction and instantaneous current efficiency (ICE) at different current density (Time: 0.44h).**

**Fig.7. Variation of percentage COD reduction with different concentration of NaCl (Current density: 4 A/dm<sup>2</sup>).**

## CONCLUSION

In the present study, the feasibility of an electrochemical oxidation process for cutting oil effluent treatment was investigated. Cutting oil effluent was treated using Ti/RuO<sub>2</sub> as anode and stainless steel as cathode. The experimental results of the lab-scale setup indicated that the cylindrical flow reactor was very effective and reliable for treating machining industry effluent. Under the most favorable treatment conditions, COD reduction was 93.3 % at 4 A/dm<sup>2</sup> in the flow rate of 10 L/h in 4 g/L NaCl. COD reduction performance was affected by flow rate. Both mass flux and mass transfer coefficient (2.137 g COD/h dm<sup>2</sup> and 0.00024 cm/s) are higher in the case of high flow rate (40 L/h) and current density (5 A/dm<sup>2</sup>). The results of this study are unique and could provide important information for practical applications. This method may be utilized for the treatment of other organic pollutants and help to meet the requirements for wastewater discharged to environment. For the industrial application, flow cell method can be recommended with two or more reactors in series. The process should be made according to the demand and effluent quality.

## REFERENCE

- [1] Bo Wang; Lin Gu; Hongzhu Ma. Electrochemical oxidation of pulp and paper making wastewater assisted by transition metal modified kaolin. *J. Hazard. Mater.* 2007, 143(1-2), 198-205.
- [2] Deng, Y.; Englehardt, J.D. Electrochemical oxidation for landfill leachate treatment, *Waste Management.* 2007, 27(3), 380-388.
- [3] Ghoreishi, S.M.; Haghighi, R. Chemical catalytic reaction and biological oxidation for treatment of non-biodegradable textile effluent. *Chem. Engg. J.* 2003, 95(1), 163-170.
- [4] Guohua Chen Electrochemical technologies in wastewater treatment *Separation and Purification Technology*, 2004, 38 11–41
- [5]. Hu X., Bekassy-Molnar E., Vatai Gy. Study of ultrafiltration behaviour of emulsified metalworking fluids based on environmental protection. *Desalination* 2002 149, 191-197.
- [6]. Hu X., Bekassy-Molnar E., Vatai Gy. Study of transmembrane pressure and gel resistance in ultrafiltration of oily emulsion. *Desalination.*2004 163, 355-360.
- [7] Howell J.K., Lucke W.E., Steigerwald J.C. AAMA Metalworking fluids symposium. Deaborn, Michigan, November 1995, 13-16.
- [8] Hui Zhang; Chengzhi Fei; Daobin Zhang; Feng Tang. Degradation of 4-nitrophenol in aqueous medium by electro-Fenton method. *J. Hazard. Mater.* 2007, 145(1-2), 227-232.
- [9] H. Bergmann a., A. Rittel a, T. Iourtchouk a, K. Schoeps a, K. Bouzek b Electrochemical treatment of cooling lubricants *Chemical Engineering and Processing*, 2003 42 105- 119
- [10] J.M. Burke, Waste treatment of metalworking fluids, a comparison of three common methods, *Lubrication Eng.* 1991, 47 (4) 238.

- [11] Jezabel S´anchez-Oneto, Juan R. Portela, Enrique Nebot, Enrique Mart´inez de la Ossa Hydrothermal oxidation: Application to the treatment of different cutting fluid wastes *Journal of Hazardous Materials*, 2007, 144 639–644
- [12] Juan R. Portela., J. L´opez, E. Nebot, E. Mart´inez de la Ossa Elimination of cutting oil wastes by promoted hydrothermal oxidation, *Journal of Hazardous Materials* 2001 B88 95–106
- [13] K.Benzadock,M.Belkacem,G.Nezzal, Treatment of cutting oil/water emulsion by coupling coagulation and dissolved air flotation . *Desalination* 2007, 206 440–448
- [14] L.S. Cleseeri, A.E.Greenberg, A.D.Eaton, *Standard Methods for Examinations of water and Waste water*, 20<sup>th</sup> ed, American Public Health Association, American Water Works Association and Water environment Federation, 1998
- [15] M. Sandin and I. Mattsbybaltzer, Control of microbial-growth in toilets-based metal-working fluids, *Int. Biodeterioration*, 1991, 27 61–74.
- [16] M. Sokovic and K. Mijanovic, Ecological aspects of cutting fluids and to their quantifiable influence on parameters of the cutting processes. *J. Mater. Process. Technol.*, 2001, 109 181–189.
- [17] M. Perez, R. Rodriguez-Cano, L.I. Romero, D. Sales Anaerobic thermophilic digestion of cutting oil wastewater: Effect of co-substrate *Biochemical Engineering Journal* 2006, 29 250–257
- [18] M. Perez, R. Rodriguez-Cano, L.I. Romero, D. Sales Performance of anaerobic thermophilic fluidized bed in the treatment of cutting-oil wastewater *Bioresource Technology* 2007, 98 3456–3463
- [19] Mohamed Tir, Nadji Moulai-Mostefa, Optimization of oil removal from oily wastewater by electrocoagulation using response surface method *Journal of Hazardous Materials* 2008, 158 107–115
- [20] Pablo Canizares, Fabiola Mart´inez, Justo Lobato, Manuel Andr´es Rodrigo Break-up of oil-in-water emulsions by electrochemical techniques *Journal of Hazardous Materials* 2007, 145 233–240

- [21] Peter janknecht,anand.lopes,and ade liom.mendes Removalof Industrial Cutting Oil from Oil Emulsions by Polymeric Ultra- and Microfiltration Membranes Environ. Sci. Technol. 2004, 38, 4878-4883