International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.5, No.3, pp 1320-1325, April-June 2013

IPACT-2013[14th – 15th March 2013]

National Conference on Industrial Pollution And Control Technology-2013

Electrochemical Treatment of Oily wastewaters (shipyards) for removal of organics and water Reclamation

Mahesh.S*, Chethan., Deepthi., Meghana.K, Lohit K.

Department of Environmental Engineering, SJCE, Mysore – 570 006; Karnataka,India.

***Corres. Author: mahina1963@rediffmail.com**

Abstract: In this paper, we present COD removal and water reclamation possibilities from electrochemical coagulation (ECC) of oily wastewaters with simultaneous removal of COD and color. Sacrificial electrode (Iron and Aluminum) dissolutions controlled by the cell voltage and current density were found as key factors for the formation of well settleable sludge ascribing water reclamation. ECC treated water slurry showed excellent settleability and filterability characteristics obtaining a clear supernatant. Optimal batch operating conditions using iron electrodes were: 6 iron plate electrodes in a 1.5L ECR with an applied cell voltage of 8.5V, run for 60 min electrolyze time (6E, 1.5L, 8.5V, 60min ET). Water reclamation of ~80%, with simultaneous color and COD removals of ~96% and 82% was achieved from the initial value of 1800 PCUs and 1200 mg/L respectively. Sacrificial electrodes developed dents on its surface during treatment at active zones. These active zones were seen swarmed with flocs after ECC, polarity reversal was resorted to remove the floc swarm on the sacrificial electrodes. The zero value of ΔpH lies at the pH_0 value of 6.45 for iron electrodes, which is considered as the pH_{pzc} of the dried sludge obtained from the batch ECC treatment of oily wastewater.
Key words: ECC, COD, color, water reclamation, oily wastewaters.

1.0 Introduction

Oily wastewaters from onshore and offshore industry and from engine rooms of ships (bilge waters) are one of the major pollutants of the aquatic environment[1]. Oil spills or discarded oil from various sources take months to oxidize and decompose. Most of these chemicals are lipophilic in nature and so enter the biosystem causing toxicity. One liter of oil spill – intentional or accidental can spread over 4000 square kilometers disconnecting air and water interactions and requires 3.3 kg of oxygen for complete degradation. More than 200 submarine oil seepages have occurred throughout the world. Black water contain most nitrogen, grey water contain most carbon in soluble form and therefore biodegrades faster than black water, but pink waters and bilge waters are not easily biodegradable and chemical treatment methods cause secondary pollution as well.

Light and medium fraction of oil evaporates, but the heavier fraction like – heavy oil, grease, wax (10 – 40% carbon) form together complicated chains rings, polycyclic and heterocyclic structures and fused ring systems. The structural complexities make these compounds resistant to natural decay and degradation.

Currently available treatment technologies for oily wastewaters originating from ships consists of a series of physical and chemical steps namely free oil removal, suspended solids removal dissolved air flotation, clarification and filtration. Some soluble organic components like surfactants go untreated in this treatment sequence resulting in increased COD and BOD in the effluent. Problems associated with biodegradation or bio-remediation is that the addition of nitrogen and phosphorus to oil spills can increase bioremediation rates significantly. Biological treatment of oily waste streams demand a larger HRT and less removal of organics. At present there is no single treatment technology that can meet the discharge requirements for oily wastewaters, henceforth the novel electrochemical coagulation Technology (ECCT) as a stand-alone treatment system to handle oily wastewaters is proposed in the present investigation.

2.0 Materials and Methods[2-6]

The wastewater for use in all the ECC experiments was collected from a ship maintaining unit. Raw wastewater samples were collected in polymer containers, characterized and used as is in the laboratory batch scale ECC experiments. Characterization for physico-chemical parameters were carried out as per Standard methods[2]. Fig 1 shows the schematic experimental set-up of the batch ECC. Iron and aluminum sheets cut to required shape were used as sacrificial electrodes to generate in-situ electro-coagulants in the bulk solution. Fibrous steel wool was also used as sacrificial anode for comparison.

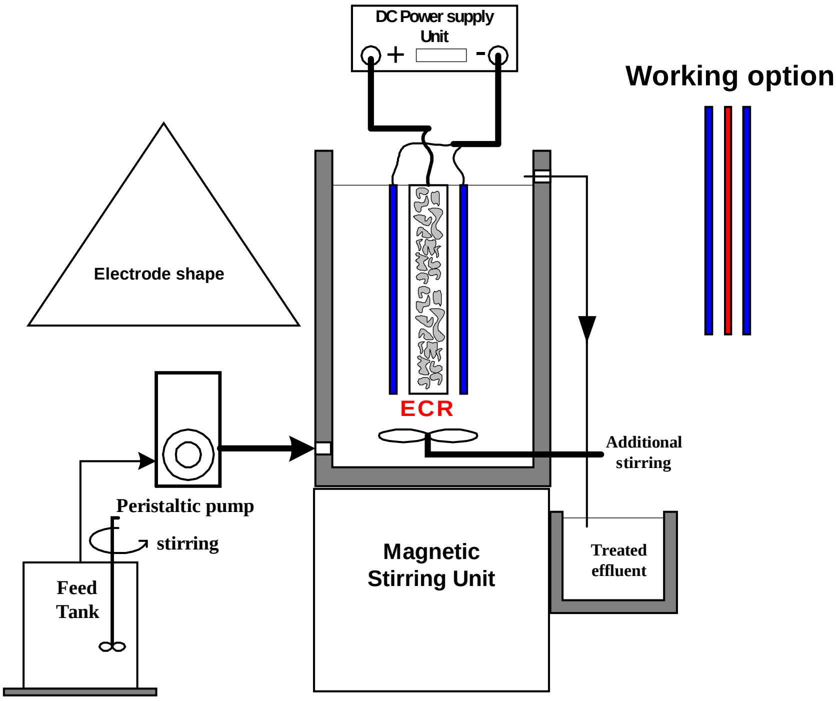

Fig. 1. Laboratory bench scale ECC experimental set-up

3.0 Results and Discussion

Untreated raw oily wastewater used in the ECC studies had the characteristics: pH_o 7.28-7.40; SS_o 390-420mg/L; COD 1350-1800mg/L; O & G_o 440-590 mg/L; Alkalinity as $CaCO_3$ 590-620mg/L; Total hardness 560-610mg/L; K_o 450-480 mg/L; Ca 280-300mg/L; and Chlorides 1250-1380mg/L.

Fig 2. shows % COD removal during ECC of oily wastewater for varying iron electrode sets (2, 4, 6 and 8 electrodes) at different receiving applied cell voltages. As can be seen in the plot, a 6 electrode combination with an applied cell voltage of 8.5V provides as much as ~83% COD removal (238mg/L) from its initial value of 1400mg/L. Electrolyze times of 60 min was found sufficient to remove COD levels to less than the desired discharge standards. Hence, all experiments that followed were carried out at 9V, 60 min ET, 6 Fe electrodes and an electrode spacing of 1cm.

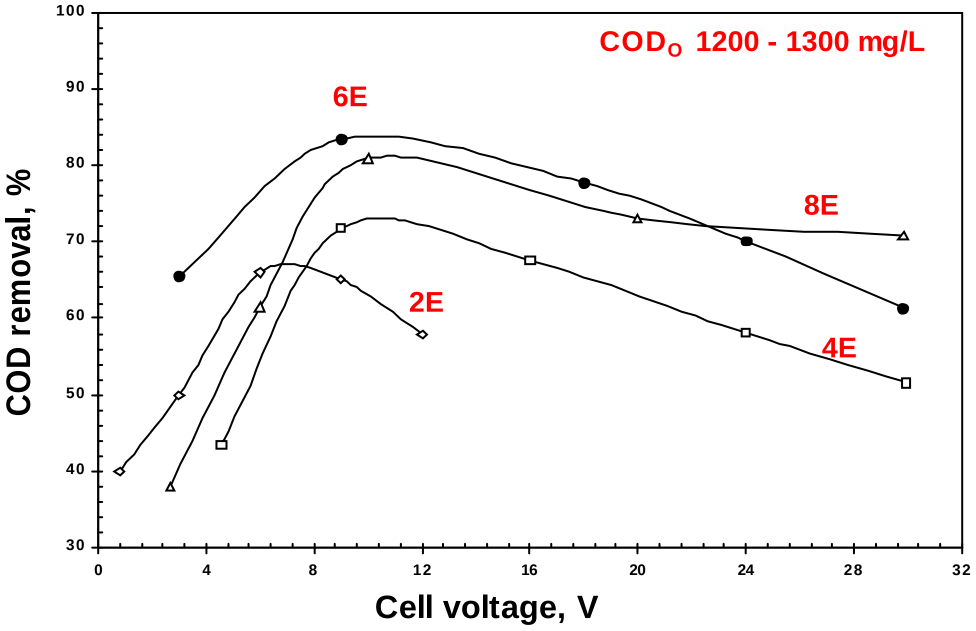

Fig 2. COD degradation curves as a function of different applied voltages

COD: 1600-1800 mg/L, pH_0= 7.28, T = 28^{o}C, number of electrodes = 2,4,6,8.

To enhance settling properties of ECC generated sludge, Percol and PAC was used as aid in quantities 25, 50, 100, 200, and 400mg/L added to the ECR in different experimental runs. COD removals with aid improved marginally, however, settling characteristics improved with SVI values well under control below the value of 100, with significant filtration speed achieved.

Fig 3. shows COD removal as a function of ET for different applied cell voltages while using iron as sacrificial electrodes. As can be seen from the plot, 8.5 – 9 V of applied cell voltage was found sufficient to bring down the COD value to near discharge standards of 250 mg/L with a small amount of soluble COD still remaining in the ECC treated effluent.

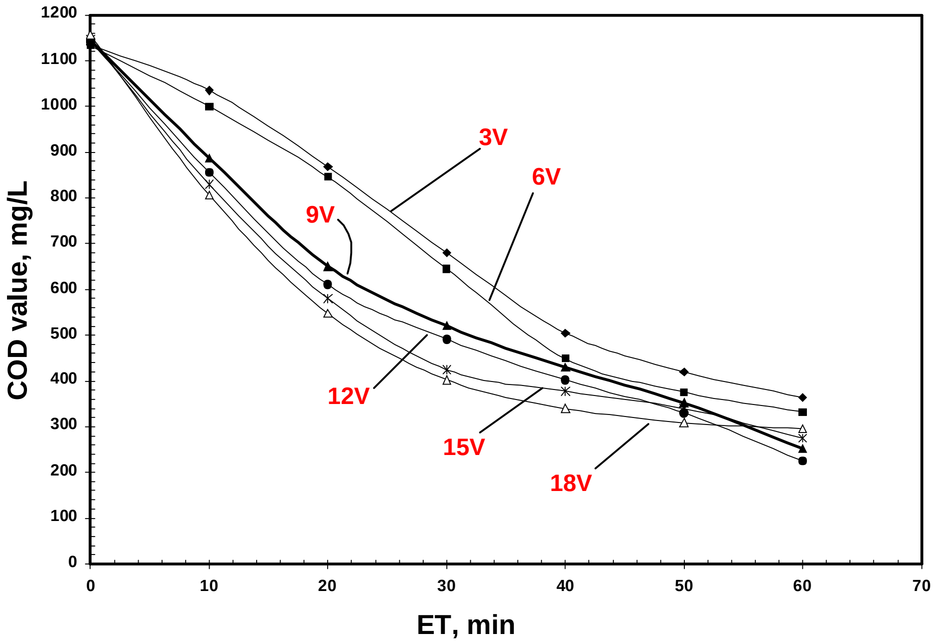

Fig 3. COD degradation curves as a function of electrolyze time for different applied cell voltages

pH change was observed and a slight increase in bulk solution temperature during ECC. pH was seen to change from 7.28 before ECC to 9.89 just after after ECC. Fig 4. shows electrode combinations in their bipolar arrangement in a batch ECR. The extreme electrodes are seen to erode quickly providing in-situ electro-coagulants sufficient enough to removal COD and color as also solids from wastewater. The sludge obtained was sturdy and had excellent settling and filterability characteristics, ascribed to the combination of Al^{3+} and Fe^{3+} metal ions. Pit densities on extreme electrodes were of the order of 10 – 12 per cm^2 at the end of each cycle when every time new electrodes were used.

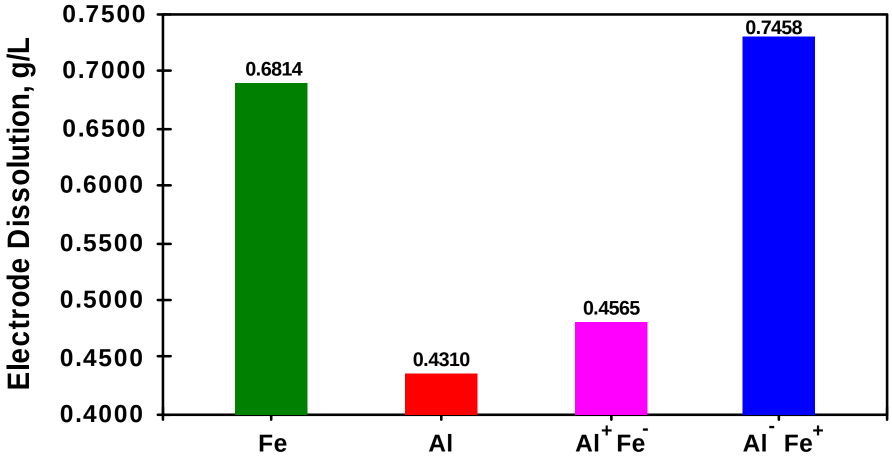

Fig 4. Electrode dissolution as a function of Cell voltage for isolated electrodes and electrode combinations

Fig 5. shows settling of ECC generated slurry in a 1L measuring column with sludge-slurry interface recorded as a function of settling time. Hazy interface (Type – I discrete settling) was seen up to 10 min settling time after which a clear interface was observed. At 30 min settling time, all the sludge-flocs were seen to reach the compression zone (Type –IV settling). Iron electrodes were seen to show good settling properties as compared to aluminum. Electrode consumptions of 0.68kg/m^3 and 0.43kg/m^3 was observed for iron and aluminum electrodes respectively. Fig 6 shows electrodes just as they appear after ECC. Active zones on the electrodes were seen flocked up by electro-flocs requiring PR.

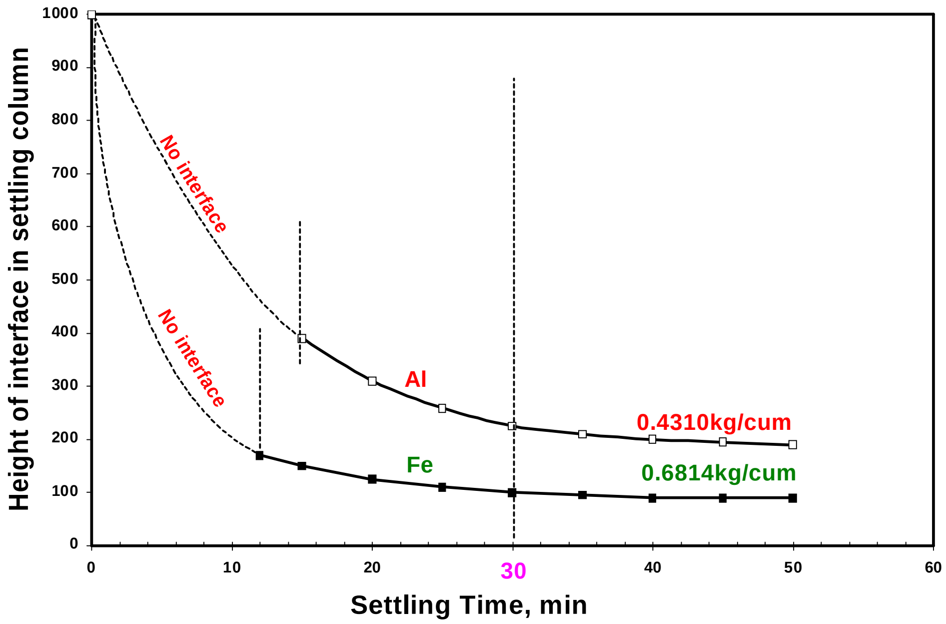

Fig 5. Settling curves for iron and aluminum electrodes as a function of settling time at optimal operating conditions

Compared to the conventional chemical coagulation using alum and ferric salts, ECC using metal electyrodes were foud to bring more satisfying results. Filtrability of ECC treated effluent had excellent clarity with least cake resistance value showing complete filtration and only 8% moisture in the cake. The filtered supernatant showed water reclamation of as much as ~80%, i.e. ~800mL of water was reclaimed of 1000mL of wastewater treated. The flocs settled was dried in the hot air oven to obtain iron rich sturdy floc-sludge having calorific value 56% that of coal. Fig 7. shows sludge obtained after ECC.

Fig 6. Electrodes just after ECC

Fig 7. Electrochemically obtained sludge

4.0 Conclusion

Based on the experimental results the following conclusions are drawn:

- 6 electrode configuration, at an operating cell voltage of 8.5 - 9V, and an electrolyze time of 60min, and a spacing of 1cm, maximum COD removal was found to be 83 - 85% from its initial value of ~1150mg/L.
- The sludge generated from iron electrodes showed comparatively good settleability and filterability characteristics. Use of aid improved settling characteristics, with marginal improvement in COD removal.
- Electrode consumptions of 0.68kg/m^3 and 0.43kg/m^3 was observed for iron and aluminum electrodes respectively.
- The filtered supernatant showed water reclamation of as much as ~80%, i.e. ~800mL of water was reclaimed of 1000mL of wastewater treated.

5.0 Acknowledgement

The authors thank DRDO-NRB, New Delhi, for providing funding for carrying out this research activity.

6.0 References

1. Karakulski, K.; Morawski, W.A.; Grzechulska, J. Purification of bilge water by hybrid ultrafiltration and photocatalytic processes. Sep. Purif. Technol. 1998, 14, 163-173.
2. APHA. Standard methods for the examination of water and wastewater, 21st ed., American Public Health Association, Washington DC, 2005.
3. MaCabe, W. L.; Smith, J. C.; Harriot, P. Unit Operations of Chemical Engineering, 6th ed.; McGraw-Hill, New York, 2001.
4. Mahesh, S.; Prasad, B.; Mall, I. D.; Mishra, I. M. Electrochemical degradation of pulp and paper mill wastewater. Part 1. COD and color removal. Ind. Eng. Chem. Res. 2006, 45(8), 2830-2839.
5. Mahesh, S.; Prasad, B.; Mall, I. D.; Mishra, I. M. Electrochemical Degradation of Pulp and Paper Mill Wastewater. Part 2. Characterization and Analysis of Sludge, Ind. Eng. Chem. Res. 2006, 45(16), 5766-5774.
6. Mahesh, S.; Prasad, B.; Mall, I. D.; Mishra, I. M. Electrochemical Degradation of Pulp and Paper Mill Wastewater. Eighth International Symposium on Advances in Electrochemical Sciences and Technology (ISAEST-8), National Institute of Oceanography (NIO) and held at Goa, India, Nov. 28-30, 2006.

*****