



A Review of treatment of oily waste water by electrocoagulation

Manoj Kumar¹, Taiyabsiddiqui², HaniPatel³, TusharParmar⁴, NikunjZala⁵

¹Department of Environment science and technology,

²Department of Environment science and technology,

³Department of Environment science and technology,

⁴Department of Environment science and technology,

⁵Department of Environment science and technology.

Abstract — Oil pollution in water usually comes in four states that are free oil, heavy oil, emulsified and dissolved oil, where the droplets are fully dispersed and not visible. Emulsified oil droplets are the most common in industrial oily wastewater and are extremely difficult to separate. The methodology for separating the oil is dependent on the oil droplet size. We are applying electrocoagulation process by using Aluminium, iron and combination of both electrodes for treatment of oily wastewater. The current density, initial pH, electrocoagulation time will play an important role in decreasing the turbidity and increase oil removal from emulsion. This process will separate the oil from the oily wastewater as well as it is effective in the reduction of chemical oxygen demand.

Keywords- electrocoagulation, oily wastewater, Aluminium electrode, iron electrode, current density.

I. INTRODUCTION

Electrocoagulation technology has been proposed for the treatment of raw waters and wastewater. With this technology, metal cations are produced on the electrodes via electrolysis and these cations form various hydroxides in the water depending on the water pH.

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In addition to this main reaction, several side reactions, such as hydrogen bubble formation and the reduction of metals on cathodes, also take place in the cell.

Electrocoagulation involves the in situ generation of coagulants by dissolving electrically either Aluminium or iron ions from Aluminium or iron electrodes, respectively.

The metal ions generation takes place at the anode, hydrogen gas is released from the cathode. The hydrogen gas would also help to float the flocculated particles out of the water. This process sometimes is called electro flocculation. It is schematically shown in Figure. The electrodes can be arranged in a mono-polar or bi-polar mode.

II. Optional methods

1. Dissolved air flotation
2. Induced air flotation
3. ultrafiltration removal of oil and grease
4. biological treatment

We can either select any one or combination of techniques given above depends upon the feasibility of reuse of treated waste water or recovered waste, as well as type of the industry.

2.1 Dissolved air flotation

Dissolved air flotation (DAF) devices utilize the gravity separation concept for the removal of oil and grease from wastewater but tend to be more effective than API Separators in removing the dispersed oil mixture because the buoyancy differential is enhanced by induced small air bubbles. Coagulant aids such as polyelectrolytes are commonly used to promote agglomeration of the oil-bearing matter into large flocs which are more easily removed. The DAF device is reported effective in producing an effluent with 1 to 20 mg/l of oil and grease.

The use of chemical coagulants, such as alum or iron salts, has been an integral part of the DAF process where emulsion breaking is necessary. These chemicals function by modifying the liquid/liquid and liquid/air surface properties. For instance, those coagulants serve to decrease the interfacial tension between the dispersed oil phase and the wastewater and increase the interfacial tension between the air bubbler and the oil phase. Consequently, these chemicals and physical phenomena tend to increase air bubble-oil droplet adhesion. Enhancing this adhesion may also involve acidification and demulsification. With a properly operating DAF unit, refineries can remove oil and grease globules greater than 40 microns. These coagulants react as follows:



the effects of coagulant chemicals on oil and grease removal. These figures indicate that the best result can be obtained at pH 8.5. In this particular case, the initial concentration of oil and grease was 200 mg/l. Almost 100 percent of the oil and grease was removed at the alum dosage of 100 mg/l while almost 100 percent of the oil and grease was removed at 50 mg/l of dosage of ferric sulfate. It is also noted that more than 85 percent of the oil and grease was removed with only 10 mg/l of ferric sulfate at pH 8.5. As seen, pH is a major control parameter for coagulation and higher dosage of coagulant is not necessarily effective in oil and grease removal.

2.2 Induced Air Flotation Oil-Water Separation

The WEMCO unit, or WEMCO Depulator, is an example of an Induced Air Flotation (IAF) device which is often used by crude oil producers and some petroleum refineries. The cross section of an IAF unit. The principle of the IAF is that an intimate mixture of air and mineral-laden liquid is forced through nozzles which provide the separating action necessary to create millions of bubbles. The bubbles are then disseminated throughout the flotation chamber. Oil and suspended solids attached to their bubbles are carried to the surface of the water where they form a froth. A skimmer paddle sweeps the oil and solids-laden froth into an overflow chamber. Some units use nitrogen gas or natural gas drawn with crude oil instead of induction of air in order to exclude oxygen from the WEMCO unit. Mittelhauser Corporation in Berkeley, California reported that IAF and DAF units following a properly designed API separator can achieve 95 and 98 percent oil and grease removal, respectively.

2.3 Ultrafiltration Removal of Oil and Grease

Carbon adsorption or membrane filtration using reverse osmosis treatment is very effective to remove dissolved and emulsified oils. The concept of ultrafiltration is based on the sieving action of a membrane retaining molecules larger than the membrane pores. Reverse osmosis uses a semipermeable membrane to filter dissolved matter using very high pressures; an extremely high quality feed is required for the efficient operation of reverse osmosis facilities. The effluent from these operations contains essentially no oil and grease. However due to the large capital and operating costs associated with these devices, they are utilized very infrequently. In the Districts' service area only one refinery has such a treatment facility (carbon adsorption) and this process is used only to treat lightly contaminated rainwater runoff when it cannot be accommodated by other treatment procedures.

2.4 Biological Treatment

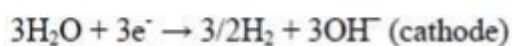
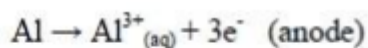
Biological treatment is generally effective in degrading dissolved oils and other types of stabilized emulsions which cannot be destabilized by chemical coagulants. However, a biological system is only effective on highly dilute oil-contaminated wastewaters because mineral-based oils are adsorbed by the microorganisms faster than they can be metabolized. Inactivated sludge systems, the adsorbed oil tends to damage sludge settling characteristics and cause system failure. It has been reported that biological organisms are efficient in oxidizing dispersed or emulsified oil, but large amounts of free oil (in excess of approximately 0.1 lb/lb MSLVSS) must be avoided. At present, the oil processing industries in the Districts' service have not found it necessary to install biological treatment systems to the discharge limit of 75 mg/l limit of oil and grease. Biologically treated effluent typically contains less than 10 mg/l of oil and grease.

2.5 Electrocoagulation Method

Water may be present as free water or emulsified water. Oil emulsions are mixtures of oil and water and can be defined as a mixture of two immiscible or partially miscible liquids, one of which is dispersed in the other in the form of droplets, and is stabilized by an emulsifying agent. There are many sources of oily wastewater in industries such as crude oil fractionation, thermal and catalytic cracking, and washing of tanks. Also, oil-water emulsions are widely used in metal industries in processes such as shaping, rolling and forging. Chemically stabilized oil-water emulsions present several environmental problems to water sources, including high BOD, odor, and turbidity. These problems affect the aquatic life and its severity depends on the source of waste. In petroleum industries emulsions can be difficult to treat and may cause several operational problems [1]. O/W emulsions typically contain from 100 to 1000 ppm of oil with drop diameter from 0.1 to 10 µm, while the allowable limit for oils and greases in wastewater discharged into open water streams is 10 ppm. Therefore, it becomes essential to remove oil from wastewater before it is discharged for final disposal [2-5]. Emulsion separation into oil and water can be done using several methods such as chemical, thermal, mechanical and electrical

methods. The most common one is the chemical method where chemicals are added to neutralize the stabilizing effect of emulsifying agents. It may also require the use of electric field, heat and coalescers to completely break the emulsion. The promising methods based on electrochemical principals are electrocoagulation, electroflotation, electrodecantation, and others [6-14]. Electrocoagulation is receiving a great attention for removing organic pollutants from wastewater due to its advantages compared to the others. Electrocoagulation considered to be versatile and safety, no auxiliary chemicals required and do not produce waste and can be easily combined with other technologies.

In case of aluminum as an electrode material, the electrocoagulation process occurs via series steps and can be simply presented as follows:



The generated Al ions combine with water and hydroxyl ions to form corresponding hydroxides and/or polyhydroxides. The formed hydroxides and polyhydroxides remain in the aqueous medium as gelatinous suspensions, which can neutralize the colloidal charges, resulting in destabilization of the emulsion. Hydrogen bubbles formed at the cathode improves oil separation efficiency via (i) the rising bubbles assist in mixing of the anodically dissolved Al^{3+} ions with the bulk of the solution (ii) the hydrogen bubbles can adhere to the flocculated species and induces its floatation.

Electrocoagulation does not use expensive chemicals but, uses cheap scrap iron and aluminum; this in addition to the simple design of the electrocoagulation cell which makes the capital and operating cost of electrocoagulation much less than that of chemical coagulation and the process has been proven to be more efficient compared to other methods. The efficiency of electrocoagulation process in removing pollutants from water is affected by various parameters. like BOD, benzene, ammonia etc

To assess the economic feasibility of electrocoagulation in comparison with other demulsification techniques such as chemical coagulation and ultrafiltration, electrical energy consumption and Al metal consumption were calculated for 99% demulsification. Electrical energy consumption (E.C) in k.W.h/m³ of the treated effluent was calculated from the formula:

$$EEC = \frac{E \times I}{1000 \times Q}$$

Where, E is the cell voltage, I is the cell current and Q is the volume of solution treated/hour.

Electrical energy consumption was calculated for 99% demulsification of initial oil concentration of 500 ppm, under different conditions. The cell voltage fluctuated between 5 and 16 volts, while the 99% demulsification time ranged from 30 to 45 minutes. The average electrical energy consumption ranged from 3 to 9 kW·h/m³ of treated emulsion. The amount of Al metal consumed in demulsification was calculated from Faraday's law

$$m = e \times I \times t = \frac{27}{3 \times 96500} \times I \times t$$

Where m is the amount of Al dissolved in grams; e is the electrochemical equivalent, I is the cell current; and t is the electrolysis time required to remove 99% of the oil. For the aforementioned case where the electrolysis time ranged from 30 to 45 min the amount of Al consumed ranged from 0.061 to 0.168 g/m³ of treated emulsion.

III. Factors affecting EC

There are various parameters which have an effect on the efficiency of the EC in removing the pollutants from water. The factors which are known to have an effect are:

- **Material of the electrodes** can be iron, aluminium and/or inert material (typically cathodes). Iron and aluminium ions and hydroxides have different chemistries and applications.

- **pH of the solution** has an effect on the speciation of metal hydroxides in the solution and also on the zeta potential of the colloidal particles. It also affects the dissolution of aluminium cathodes.
- **Current density** is proportional to the amount of electrochemical reactions taking place on the electrode surface.
- **Treatment time** or electric charge added per volume is proportional to the amount of coagulants produced in the EC system and other reactions taking place in the system.
- **Electrode potential** defines which reactions occur on the electrode surface.
- **Concentration of the pollutants** affects the removal efficiency because coagulation does not follow zeroth-order reaction kinetics but rather pseudo second or first-order kinetics.
- **Concentration of anions**, such as sulphate or fluoride, affects the composition of hydroxides because they can replace hydroxide ions in the precipitates.
- **Temperature** affects floc formation, reaction rates and conductivity. Depending on the pollutant, increasing temperature can have a negative or a positive effect on removal efficiency.
- **Other parameters**, such as hydrodynamic conditions and inter-electrode distance, may have effect on efficiency of the treatment and electricity consumption.

Advantages of electrocoagulation technique:

- The electro flocculation process, using an aluminum electrode, presented better results as compared with the physico-chemical process.
- Process avoids the use of chemicals.
- The equipment required for Electro coagulation process is simple, compact and easy to operate and handle the problems encountered during running.
- Simple and compact treatment facility results in relatively low cost and there is a possibility of complete automation.
- Electro coagulation process has the advantage of removing the smallest colloidal particles because the applied electric field sets them in faster motion thereby facilitating the agglomeration.
- It is a low sludge producing process, and the sludge formed during the process tends to be readily settable and easy to dewater, as it is mainly composed of metallic oxides/hydroxides.
- The flocks formed during the electro coagulation process tend to be much larger, more stable; therefore can be separated by filtration.
- Electro coagulation effluent can be reused with a lower water recovery cost, due to the low dissolved solids content as compared with other chemical treatment effluent.
- The gas bubbles produced during electrolysis can carry the pollutant on the top of the solution where it can be more easily concentrated, collected, and removed.
- The process has no moving parts and most of the process is controlled electrically, therefore requires less maintenance.
- The electrocoagulation technique can be conveniently used in rural areas where electricity is not available, as alternative power generated from solar panels can be used as power source.

CONCLUSIONS

A new electrocoagulation cell consists of a horizontal spiral aluminum anode and a horizontal disc aluminum cathode was used in oil/water emulsion breaking. The cell makes an efficient use of the hydrogen bubbles evolved at the cathode to improve the floatation ability of the cell and at the same time allows the use of the anode inner surface as a heat exchanger to control temperature and also provides a large electrode area per unit volume of the cell. The effect of various operational parameters on % removal of oil was investigated. The results showed that the % removal increases with the increase in current density, initial pH in the range (3-8) and electrolyte concentration. While the % removal decreases with the increase in oil concentration.

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