



ELECTROCOAGULATION TECHNIQUE IN PETROCHEMICAL WASTE WATER TREATMENT: A REVIEW

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Abstract: Petroleum/petrochemical industries unavoidably generate large volumes of oily wastewater. The environmentally acceptable disposal of oily wastewater is a current challenge to the petroleum industry. Nowadays, more attention has been focused on the treatment techniques of oily wastewater. Therefore, oily wastewater treatment has become an urgent problem, and it must be explored and resolved by every oilfield and petroleum company. There are several techniques employed for treating the same. Comparison is done with electrocoagulation technique which comes out to be the one of the better method for treatment of waste water from petrochemical industry.

Keywords: Electrocoagulation, waste water, petrochemical

I. INTRODUCTION

Industrial development in recent decades has been a major contributor to the degradation of water quality, both through negligence in treatment of wastewater before discharge into receiving bodies and accidental pollutant spills in aquatic environments. The chemical industry comprises the companies that produce industrial chemicals. Basic chemicals or commodity chemicals are a broad chemical category including pharmaceutical products, polymers, bulk petrochemicals and intermediates, other derivatives and basic industrials, inorganic/organic chemicals, and fertilizers. The chemical industry is of importance in terms of its impact on the environment.

Chemical industrial wastewaters mostly contain organic and inorganic matter in varying concentrations. There are many materials in the chemical industries which are toxic, mutagenic, carcinogenic or simply almost non-biodegradable which leads to a wide range of substances that cannot be easily degraded. For example, surfactant and petroleum hydrocarbons, among others chemical products that are being used in chemical industry reduce performance efficiency of many treatment unit operations [2]. Oil and its derivatives has created havoc in water bodies and also irregularity in maintenance of underwater pipelines are creating dilemma [1].

Petrochemical industries cause considerable water and air pollutions by discharging their effluents into various receiving bodies such as public sewers and rivers. Large amount of wastewater is produced from petrochemical manufacturing processes like desalting, hydro cracking, hydro skimming, and vapor condensate. Now a days a wide variety of pollutants including non-biodegradable organics are usually encountered in petrochemical wastewater. These organics are highly toxic and inhibitory to microbial activity. This kind of wastewater is characterized by high chemical and biological oxygen demand (COD and BOD), large amounts of suspended particulate matter, oil and grease, sulphides, ammonia. Treatment of petrochemical wastewater has become a subject of interest due to stringent effluent regulations (imposed by authorized body such as EPA) and increasing need for reuse of treated water [3].

Even though it appears to be in plentiful supply on the earth's surface, water is a rare and precious commodity, and only an infinitesimal part of the earth's water reserves (approximately 0.03%) constitutes the water resource which is available for human activities. The growth of the world's population and industry has given rise to a constantly growing demand for water in proportion to the supply available, which remains constant. Thus, it is necessary to minimize its consumption and it is also necessary to return it back to the environment with the minimum contamination load because of the limited capacity of self-purification, hence the importance of waste water treatment process [1, 2].

II. TREATMENT METHODS

2.1 Physico-chemical method

2.1.1 Oil-water Separation

Oil and grease is the most common pollutant available in a wide range of chemical industries. Oil refineries, petrochemical plant, chemical plant, textile and food processing industries report high levels of oil and grease in their effluents. The API oil – water separator is designed to separate the oil and suspended solids from their wastewater effluents. The name is derived from the fact that such separators are designed according to standards published by the American Petroleum Institute [2]. This separator is not effective for separation of oil droplets and emulsions. Oil that adheres to the surface of solid particles can be effectively removed by sedimentation in a primary clarifier. Dissolved air flotation (DAF) uses air to increase the buoyancy of smaller oil droplets and enhance separation. Emulsified oil in the DAF influent is removed by de-emulsification with chemicals, thermal energy or both. DAF units typically employ chemicals to promote coagulation and increase flock size to facilitate separation.

2.1.2 Coagulation-Flocculation

The chemistry of coagulation-flocculation is developed from electricity [6]. Electricity describes the behavior of charged particles given their attraction/repulsion tendencies. Suspended solids possess negative charge in water. Since their surface charge is the same, they tend to stabilize and repel one another when they come close to one another. The coagulation flocculation process aim to destabilize the charged particles of suspended solids. Proper application of the process take into account adequate understanding of certain interaction factors which include the source of the charge, composition of the charge, particle size, shape, and density of the suspended particles. Addition of coagulants with charges opposite those of the suspended particles is the first approach to destabilize the particles' charge. Coagulants are added to water and wastewater to neutralize the negative charge of suspended particles [7]. Upon neutralization, the suspended particles stick together to form slightly larger particles. Rapid mixing to effectively disperse the coagulant and encourage particle collision is applied for efficient coagulation. This process is followed by a flocculation process where gentle mixing increases the particle size from sub-micro floc to visible suspended solids.

2.1.3 Adsorption method

Adsorption is a natural process by which molecules of a dissolved compound collect on and adhere to the surface of an adsorbent solid. Granular activated carbon is a particularly good adsorbent medium due to its high surface area to volume ratio [2]. Many industries release heavy metals content to water bodies. Granular activated carbon can be employed to adsorb these pollutants on the surface of the granulated particle and it also helps to reduce the COD of the waste water. Zeolites are also used widely for adsorption of pollutants. Zeolites are an important class of aluminosilicates used as catalysts and adsorbents [8]. An important property of zeolites is the capacity to be easily regenerated while keeping their initial properties. Adsorption from an aqueous solution depends not only on the zeolite pore structure but also on the competition between the organic adsorbate and water for the adsorption site. Different kinds of zeolites such as ZSM-5, HFAU etc. can be employed for this purpose.

2.2 Biological treatment

2.2.1 Aerobic treatment

Aerobic degradation in the presence of oxygen is considered to be a relatively simple, inexpensive and environmentally sound way to degrade wastes. Factors that are critical in the optimal degradation of the selected substrate include the temperature, moisture, pH, nutrients and aeration rate that the bacterial culture is exposed to, with temperature and aeration being two of the most critical parameters that determine the degradation rates by the microorganism. Soluble organic sources of biochemical oxygen demand (BOD) can be removed by any viable microbial process, aerobic, anaerobic or anoxic. However, aerobic processes are typically used as the principal means of BOD reduction of domestic wastewater because the aerobic microbial reactions are fast, typically 10 times faster than anaerobic microbial reactions [2, 9]. Therefore, aerobic reactors can be built relatively small and open to the atmosphere, yielding the most economical means of BOD reduction.

2.2.2 Anaerobic treatment

Anaerobic reactor differs from the aerobic reactors primarily because the former must be closed in order to exclude oxygen from the system, since this could interfere with anaerobic metabolism [2, 9]. An anaerobic reactor must be providing with an appropriate vent or a collection system to remove the gases (mainly methane and carbon dioxide) produced during anaerobiosis. Anaerobic microbial processes are known to have several important advantages over aerobic microbial processes: lower production rate of sludge, operable at higher influent BOD and toxics levels, no cost associated with delivering oxygen to the reactor, production of a useful by-product, methane (biogas). However, anaerobic processes have higher capital and operating expenses than aerobic processes because the anaerobic systems must be closed and heated. Thus, anaerobic bioprocesses for treatment of hazardous wastewater streams are typically limited to treatment of low-flow-rate streams such as industrial effluent.

2.3 Membrane Treatment

In general, a membrane is a barrier that separates the two phases and controls the transmission of different chemical components in a certain approach [10]. Membrane separation technology is the use of a special porous material manufactured for the interception role in the physical removal of a certain way of the trapped particle size of contaminants. The membrane separation technology is characterized by: waste oil according to the particle size membrane MWCO (molecular weight cut off) reasonable certainty and the process in general has no phase change, a direct realization of oil–water separator, without pharmaceutical dosing, so less pollution, reprocessing costs low, the separation process has less energy consumption, separation of water has low oil content, but good effect.

Pressure driven processes such as ultra-filtration, micro-filtration, reverse-osmosis and nano-filtration can be employed to remove the COD and heavy metals from the industrial waste water. Membrane bio-reactors (MBR) are also used now a day. Membrane bioreactors use a combination of the activated sludge process with an additional membrane separation process [10].

The advantages offered by MBRs over traditional activated sludge systems include reduced footprints, a decrease in sludge production, improved effluent quality and efficient treatment of wastewaters with varying contamination peaks. Some disadvantages of this system include frequent membrane monitoring and maintenance requirements, relatively high running costs and there is a limitation as to the pressures, temperatures and pH to which the system can be exposed. These reactors have been used in the treatment of a vast range of different wastewaters from municipal or industrial such as pharmaceutical industry and petroleum industry.

2.4 Chemical oxidation

Oxidation, by definition, is a process by which electrons are transferred from one substance to another. This leads to a potential expressed in volts referred to a normalized hydrogen electrode [2]. From this, oxidation potentials of the different compounds are obtained. Chemical oxidation appears to be one of the solutions to be able to comply with the legislation with respect to discharge in a determined receptor medium. It can also be considered as an economically viable previous stage to a secondary treatment of biological oxidation for the destruction of non-biodegradable compounds, which inhibit the process. The chemical oxidation processes can be divided in two classes: Classical Chemical Treatments and Advanced Oxidation Processes (AOPs).

2.5 Electrocoagulation

Electro coagulation is the process of destabilizing suspended, emulsified, or dissolved contaminants in an aqueous medium by introducing an electric current into the medium. In its simplest form, an electro coagulation reactor may be made up of an electrolytic cell with one anode and one cathode [11]. The conductive metal plates are commonly known as 'sacrificial electrodes'. For example, aluminum anodes are used to produce aluminum cations which have the same effect as the addition of Al based coagulants in conventional treatment systems.

Electro coagulation has the advantage of removing the smallest colloidal particles compared with traditional flocculation–coagulation, such charged particles have a greater probability of being coagulated and destabilized because of the electric field that sets them in motion [12]. In addition, electro coagulation is capable of reducing waste production from wastewater treatment and also reduces the time necessary for treatment.

2.5.1 Principle and working

The electro coagulation process operates on the base of the principle that the cations produced electrolytically from iron and/or aluminum anodes which is responsible for the increasing of the coagulation of contaminants from an aqueous medium. Electrophoretic motion tends to concentrate negatively charged particles in the region of the anode and positively charged particles in the region of the cathode. The consumable metal anodes are used to continuously produce polyvalent metal cations in the region of the anode [13]. These cations neutralize the negative charge of the particles moved towards the anodes by production of polyvalent cations from the oxidation of the sacrificial anodes (Fe and Al) and the electrolysis gases like hydrogen evolved at the anode and oxygen evolved at the cathode [14,15]. This process involves three successive stages:

- Formation of coagulants by electrolytic oxidation of the sacrificial electrode
- Destabilization of the contaminants, particulate suspension and breaking of emulsions
- Aggregation of the destabilized phase to form flocs.

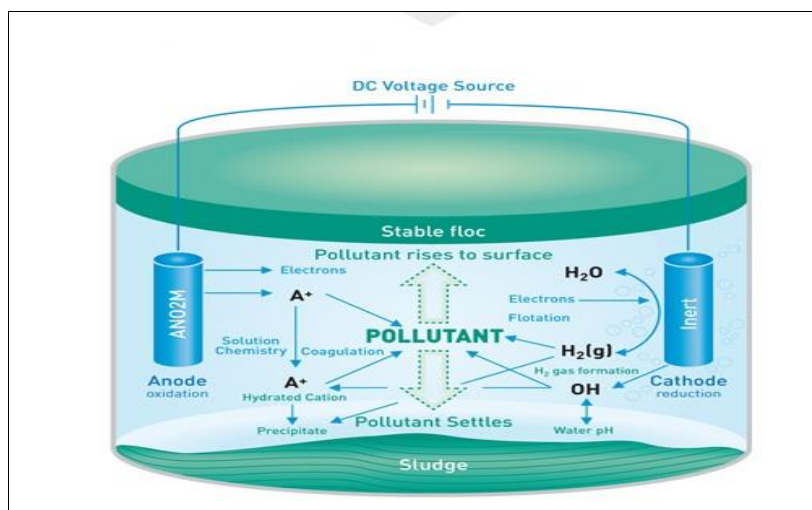
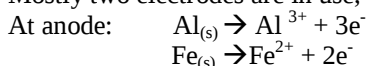


Fig. : 2.1 Electro coagulation process

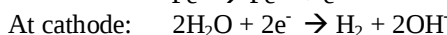
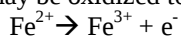
2.5.2 Mechanism

All electro coagulation reactors are electrochemical cells that consist of an electrode arrangement in contact with the polluted water, with coagulant production in situ being their distinguishing feature. To release the coagulant, an applied potential difference across the electrodes is required. The mechanism of the electro coagulation is based on electrolytic process which includes reactions on anode and cathode.

Mostly two electrodes are in use, they are Al and Fe [16]. The basic mechanisms of both electrodes are as shown



Ferrous iron may be oxidized to Fe^{3+} by atmospheric oxygen or anode oxidation [17, 18], and may be considered as



Electrochemically generated metal cations will react spontaneously, forming various monomeric species such as $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_4^-$ which finally transform into $\text{Al}(\text{OH})_3$ and ferric ions generated electrochemically may form monomeric ions, ferric hydroxo complexes with OH^- ions, and polymeric species [16, 17]. These species/ions are: FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{OH})_4^-$ which further react to form $\text{Fe}(\text{OH})_3$.

Aluminum and iron hydrolysis products then destabilize pollutants present in the solution, allowing agglomeration and further separation from the solution by settling or flotation. The formation of these complexes depends strongly on the pH of the solution. Above pH 9, $\text{Al}(\text{OH})_4^-$ and $\text{Fe}(\text{OH})_4^-$ are the dominant species.

In addition to dissolving of aluminum and iron production, other electrochemical reactions can also take place in the EC system [19]. They are

- hydrogen formation at the cathodes
- increase of pH due to the formation of hydroxyl ions or the consumption of hydronium ions/protons
- Reduction of metal ions on the cathodes.

2.5.3 Treatment parameters

There are various parameters which have an effect on the efficiency of the EC in removing the pollutants from water. **Material of the electrodes:** Optimal material selection depends on the pollutants to be removed and the chemical properties of the electrolyte. In general, aluminum seems to be superior compared to iron in most cases when only the efficiency of the treatment is considered. Inert electrodes, such as metal oxide coated titanium, are used as cathodes in some constructions **pH of solution** should be above 3 or else aluminum ion would not be released efficiently. **Current density** is directly proportional to the rate of electrochemical reactions taking place on the electrode surface and it also has an influence on the electrode potential, which defines the reactions taking place on the electrode surface [19]. It seems that on iron and aluminum anodes, dissolution reaction is the primary reaction, and the proportion of other reactions is insignificant at the typical current densities and electrode potentials when pH is neutral or acidic.

Removal of colour, COD and phenol decreased by 10–20% when **temperature** increased from 293 K to 333 K. It has been suggested that when temperature is too high, there is a shrinkage of large pores of the $\text{Al}(\text{OH})_3$ gel, which causes the formation of dense flocs that are more likely to deposit on the electrode surface [19]. Increasing temperature also enhances the solubility of aluminium. However, it seems that increasing temperature can have positive and negative effects on the removal efficiency. It is possible that the effect of temperature on removal efficiency depends on the removal mechanism of pollutants.

Table 2.1 shows the comparative studies of petrochemicals removal from waste water using various techniques out of which electrocoagulation seems to be promising

Table.2.1: Comparative study of various methods

METHODS	COD	TURBIDITY	PHENOL	HC/GREASE/OIL	REFERENCE
PHYSICO-CHEMICAL	>71.8	95.6	> 82	>96	2, 20
BIOLOGICAL	97			94	2,9
MEMBRANE	76	<0.2 NTU		97	9,10
CHEMICAL OXIDATION	70.1	71.58	94	>95	21
ELECTRO COAGULATION	88.7	96.5	99.5	> 99	

Electrocoagulation technique has many advantages but major disadvantage is an impermeable formation of oxides film form on the cathode, so efficiency of electro coagulation cell and high conductivity of the waste water suspension is required

III CASE STUDY

Powell Water Systems, Inc. was formed by Scott Wade Powell to develop and market a functional operating water treatment system utilizing electrocoagulation and supporting equipment. The fundamental design requirements of Powell Water Systems, Inc. include quality electrocoagulation equipment that is operator friendly, utilizing readily available components, coupled with energy efficiency [22]. The Powell Water Systems, Inc. technology efficiently removes a wide range of contaminants with a single system. Traditional water treatment would require a different type of equipment to remove bacteria, silt, pesticides, heavy metals, and oil from water. The broad-spectrum treatment effect allows one system to remove multiple contaminates at the single contaminant equipment cost, space, and time. Refinery waste water can be treated .They have shown the case of treating the hydrogen condensate.

Table: 3.1 Major pollutants from hydrocarbon condensate

POLLUTANTS	INFLUENT (mg/l)	EFFLUENT(mg/l)	PERCENTAGE REMOVAL
COD	10000	1250	87.5
TOTAL OIL AND GREASE	1610	47	97.1
PHENOL	520	145	72.1

McKay Creek Technologies Ltd. was formed to develop an electrocoagulation process to treat the oily wastewater generated by the Washington Marine Group fleet and shipyards. Both salt and fresh water are contaminated with oil and grease, diesel and a full range of marine fuel oils, as well as suspended solids and metals (primarily iron and zinc) from corrosion of the steel barges and bilges and mechanical parts. Petroleum hydrocarbons are present in wastewater both as “free oil” (petroleum hydrocarbons that separate from wastewater and float to the liquid surface) and as “emulsified oil” (petroleum hydrocarbons that remain in stable suspension and do not separate from the wastewater).

Table: 3.2 Removal of hydrocarbon pollutants

CONTAMINANTS	INFLUENT (µg/l)	EFFLUENT (µg/l)	PERMISSIBLE LIMIT (µg/l)
TOTAL PAHs	5250	Less than detect	1000
TOTAL BTX	2374	13.7	1000
MTBE	170	<0.05	0.05
HYDROCARBON OIL AND GREASE	2350000	<2000	15000

IV. CONCLUSION

Electrocoagulation is electrochemical technique with many applications. Oily waste in aqueous solution can be removed efficiently. For the removal of contaminants from industrial waste water especially petrochemical industries, there are various techniques available. It has been seen that the removal efficiency of the pollutants depends on the current density. With the increase in current, the floc formation increases but up to certain limit. If this limit is crossed then there will be decrease in efficiency. For removal of phenol extensive research has been carried out and maximum removal of phenol is by electrocoagulation process. After going through literatures we can conclude that electrocoagulation technique is good or we may say preferable because it gives better efficiency in removal of contaminants compared to conventional method and also it has simple design and can handle variations.

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