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Research Article

Removal Of Oil From Oily Wastewater By Electrochemical With Iron And Aluminium Plate Electrodes.

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Abstract :

This paper is intended to provide a review of the published literature on the topic of electrocoagulation . Water treatment processes for oil and COD are discussed, including electrocoagulation technology. Electrochemical technology is a simple and environmentally friendly technique that produces less sludge compared to other treatments. Coagulant produces from dissolution of the sacrificial anode and formation of metal hydroxides. Efficiency of the process depends on the distance between electrodes, electrodes submerged depth and number of electrodes.

Keyword: oil , COD , removal , oily wastewater , electrochemical.

1. Introduction

Although water is an essential element for life on planet Earth. However, only 1% or less is drinkable(Al-Saati N Het al.,2019 and Zubaidi S L et al., 2019). Due to population growth, one of the main challenges currently facing human civilization is the provision of sufficient quantities of potable water (Emamjomeh M M et al., 2020 and Zubaidi S L et al., 2020). Therefore, the ability of mankind to obtain sufficient sources of the required water should be considered as an essential global problem. Achieving sustainable solutions for water management is the possible solution for this challenge. The population of the world is over 7 billion and is estimated to reach 10 billion by 2040 (Coleman D 2004). Climate change also negatively affects fresh water resources in the middle of cities, which in turn affects the sustainable development of water availability and thus affects economic and social activities (Zubaidi S L et al., 2019). Additionally, several studies have shown that freshwater resources are commonly influenced by contamination (Hashim K S et al., 2019 and Hussein A H et al., 2019). Water scarcity situations are faced in different regions around the world, which means that the gap between water supply and demand is likely to grow in the future. In 2010, the European Environment Agency reported that municipal water consumption is driven by complex interactions between human and natural system factors on multiple spatial and time scales(Hashim K et al., 2020). There is an inevitable need to maximise wastewater treatment. In order to avoid potential global crises. Due to depleting available resources of clean and potable water, making use of unlimited available saltwater in the oceans, and reducing discharges from water treatment plants. Thousands of years ago, people attempted and succeeded in improving the water quality through processes of treatment such as the chemical alum addition, boiling, straining, and filtering through charcoal to separate suspended solids from water(Nguyen D D et al., 2017). To remove inorganic pollutants from water supplies, many common treatment techniques are nowadays used. For instance, coagulation and precipitation, this treatment system has some disadvantages, such as dealing with large amounts of chemicals and the formation of great quantities of sludge that may be harmful to the environment and difficult to get rid of (Duan, J et al 2003). While in adsorption, ion exchange, and membrane separations, there are some problems such as the additional costs connected with elimination of utilised regenerants materials and regeneration(Li Y

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et al., 2006 and Lin Let al., 2014). Nutrients (oil and COD) , which are present in different concentrations in water where the excess of concentration leads to contamination of water and wastewater. The electrocoagulation was more effective to eliminate TDS and presented higher removal of turbidity compared to chemical coagulation. Based on the analysis, the electrocoagulation is more efficient that the textile effluent treated can be reused or rejected without risk in the environment (Gzar, H. A et al., 2020). The produced water considers as the largest waste stream in the oilfields and refineries, which has a high concentration of hydrocarbons, heavy metals besides other pollutants (Gzar, H. A et al., 2021). he desorption study revealed that fluoride adsorption onto concrete particles was chemical in nature. The kinetic of adsorption was fitted well with second-order rate model, while the adsorption behavior obeyed Freundlich model(Gzar, H. A et al., 2020).

2. Electrochemical cell

The removal of oil and COD was carried out using an EC reactor. The electrochemical cell is rectangular in dimensions length 20cm x high 14cm x width 10cm and with 6mm thickness made in a Plexiglas material plastic served as the EC reactor. The electrodes iron and aluminium with dimensions (length 8cm x high 20cm x width 0.1cm), as cathodes and anodes As shown in figure (1).

Fig 1. A photograph of the EC cell 1. Power supply 2. EC cell. 3.The electrodes (Aluminium and Iron). 4. Pump

3. wastewater sample

The wastewater samples were collected from the wastewater treatment plant of Al-Doura Oil Refinery. This refinery is an integrated oil industrial complex that is one of the oldest major oil refineries in Iraq, located in the southeastern part of Baghdad city. The foundation stone was laid in 1953 and work began in 1955. Its production is 140,000 barrels per day It is located on an area of 2,500,000 square meters. The refinery produces automobile gasoline, liquefied gas, jet fuel, gas oil, diesel, crude oil, grease, wax, and asphalt. It also contains an advanced plant for the manufacture of plastic cans for filling the produced oils, which produces about 80 thousand cans per month. The samples were collected from locations after API separates units and were stored in plastic containers at room temp (25 °C). The characteristics of the collected samples are shown in Table (3.1).

Table 0.1: Characteristics of the oily wastewater collected from Al-Doura Refinery.

Parameter	**Unit**	**Value**	**Permissible Limits**
pH	-	7.3-7.8	6.0-8.5
Oil concentration	mg/L	50-100	5
COD concentration	mg/L	320-1150	125
TSS	mg/L	150-750	20

4 . Apparatuses and Materials

4.1 Apparatuses

In the experiments the following apparatuses were used

1. Batch electrolytic: a reactor with dimensions (length20cm x high 14cm x width 10cm and 0.6 cm thickness) made in a Plexiglas material.
2. Digital DC power supply: An experiment with a digital laboratory DC power supply, the current was in the range of 0-10 A and the voltage was between 0 and 30 V.
3. The electrodes iron and aluminum with dimensions (length 8cm x high 20cm x width 0.1cm and 0.1 cm thickness), as cathodes and anodes
4. A small 2-liter tanks.
5. Sensitive electrical balance: it is used to determine the weight of the used materials
6. Peristaltic pump.
7. UV- Spectrophotometer: This instrument is used to determine the initial and final concentrations of pollutants single beam UV spectrophotometer.
8. Digital pH meter: It is used for measuring the pH of the solution.
9. Glassware: volumetric flasks, pipette and other glassware are used in this study.

4.2 Materials

Chemicals used in the experiments:

1. HCl

a) to remove the oxide and passivation layers from the electrodes with (35%).

b) to make the PH acid.

2. NaOH to make the PH basicity.
3. NaCl to prepare sample to get maximum value of removal.
4. Hexamethyltetramine to remove the oxide and passivation layers from the electrodes with (2.8%).

5.Oil concentration measurement

The oil content is measured by the Gravimetric Analysis Method, in which the oil is extracted from the oily wastewater sample by an organic solvent according to the Environmental Protection Agency Method (EPA method 1664) for oil in water analysis (Telliard et al., 1999)

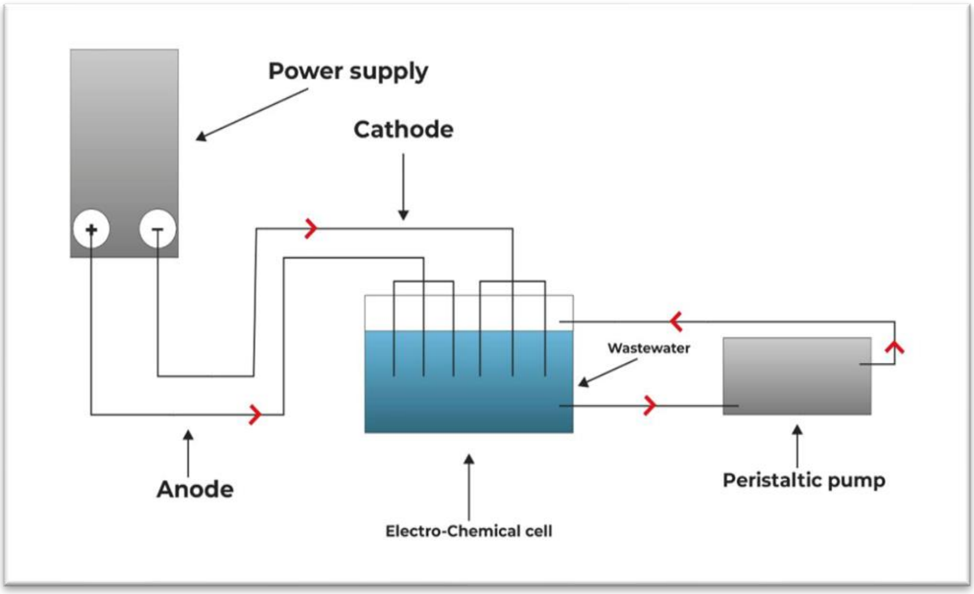

Fig 2. Schematic diagram of the EC cell

5.2 Test procedure

1- A 500 mL of sample is taken by conical flasks
2- 2 mL of HCl (1:1) is added to the sample of 500 mL
3- 15 mL of Hexane (C_6H_{14}) is added to the solution as an organic solvent, well shaken and stagnated for enough time.
4- The layer formed by hexane is abstracted then filtered by a filter paper (type Whatman No. 42) that contained Anhydrous sodium sulfate (Na2SO4) to get rid of the moisture.
5- The filtrate is collected by a known weight clean flask
6- Again adding 15 mL of Hexane and repeat steps 3, 4 and 5 (i.e. collecting 45 mL of Hexane in the flask). The amount of added Hexane depends on the amount of oil in the sample.
7- Then the sample evaporated in Hot Bath
8- The sample is placed in an Oven of 70 C for 15 minutes, cooled then weighted, figure (3.3) shows a photograph of the collected amount of oil of the samples at the end of testing procedure.

5.2 Calculation of oil concentration

Oil (mg/L) =$\frac{(A-B)x106}{\text{Voulme Sample(ml)}}$

A: The weight of the flask before drying (g).
B: The weight of the flask after drying (g)

Fig 3. A Photograph of the collected amount of oil of the samples at the end of testing procedure.

6. Chemical oxygen demand (COD)

Chemical oxygen demand (COD) is a measure of water and wastewater quality. The COD test is often used to monitor the efficiency of a water treatment plant. This test is based on the fact that a strong oxidizing agent, under acidic conditions, can oxidize almost any organic compound to carbon dioxide. COD is the amount of oxygen consumed to chemically oxidize organic water pollutants into inorganic end products. Unit of measurement (mg/L)

6.1 Test procedure

1. take 2 ml from refinery wastewater.
2. placed refinery wastewater the pipette concentration (0-150) mg/l.
3. mixed well the sample done placed in a thermal reactor for 2 hours at a temperature of 148^0C to oxidize the sample.
4. Then cooled sample and placed in a Spectrophotometric device

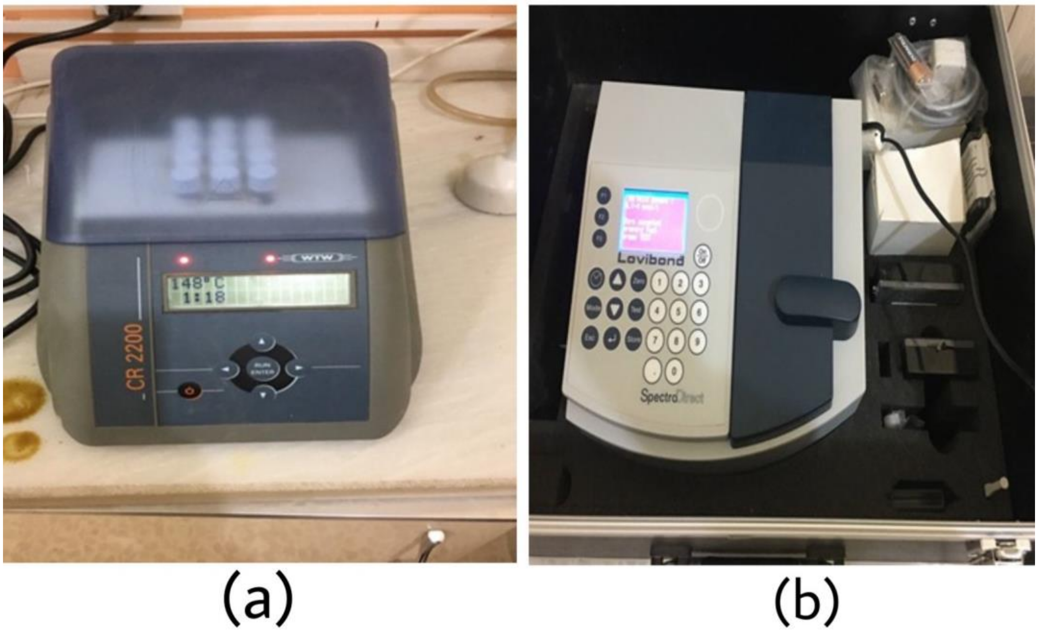

Fig 4 . (a) UV spectrophotometer device, and (b) thermal reactor device.

7. Evaluation of Removal efficiency

The result of the treated samples using the electrocoagulation are compared with their original values. The performance of EC process is determined from its efficiency in removing the pollutant level. Samples that treated by EC cell were analyzed by Shimadzumodel UV spectrophotometer. The removal efficiency of oil and COD in the refinery wastewater treated by electrochemical is calculated as follows by Eq.

$$R = \frac{C_{\circ} - C_{e}}{C_{\circ}} \times 100$$

Where:
R = removal efficiency
Co = initial concentration (mg/L)
C = stands for concentration at any time (mg/L).

8. Factors influencing the mechanism of electrochemical

8.1Effect of pH electrochemical

The pH of the water influences the dissolution of metal hydroxides and the current efficiency of the electrochemical process. The release of chlorine may also be impaired if there are chloride ions found. In general. A more effective removal of contaminants occurs near a pH 7. However, because of the difference in conductivity, the energy exhaustion is higher at the neutral pH. The pH influence is not important at high conductivity. The pH of the effluent reduces after treatment with electrocoagulation for the alkaline effect but rises for the acidic effect. In the reaction of a cathode, a rise in the pH in the acidic situation leads to the evolution of hydrogen [Vik E A et al.,1982]. The pH reduces due to the generation of Al(OH)3 at the anode, which leads to the release of H+ ions, in addition to the reaction of oxygen evolution

8.2 **Effect of time electrochemical** .

The electrolysis time determines the rate at which metal ions are produced from the electrodes. COD and oil removal efficiencies are directly dependent on metal concentration ions produced by the electrodes. This subject is justified by Faraday's law. According to Faraday's law (equation1), theoretically, the amount of coagulant is directly proportional to the current applied to the electrolytic cell and time.

$$\mathbf{C} = \frac{MIt}{n\,F\,V} \qquad (1)$$

where *M*, *I*, *t*, *n*, *F* and *V* stand for the molecular weight of the metal (g/mol), and the current (A), time (s), metal valency (3 for Al and 2 for Fe), Faraday's constant (96500 C/mol) and wastewater volume, respectively. At the beginning of the EC process, in the experiments the COD and oil removal efficiency is low since the rate at the initial times the production of metal ions from the electrodes is low; However, when the time of electrolysis increases, the concentration of metal ions and their hydroxide clusters increase; thus, COD and oil removal efficiencies increase (Ji et al., 2015) . electrolysis is required to generate adequate amount of Al^{+3} ions and aggregated flocs need the time to be formed. It is well known that the electrolysis time is proportional with coagulant concentration in the reaction medium which leads to higher pollutant removal (Redah et al., 2016).

8.3 Effect of voltage on electrochemical

The removal efficiencies of COD and oil increases with an increase in voltage. The applied voltage is an important parameter for the COD and oil removal since it determines the coagulant dosage rate, concentration of metal ions and their hydroxide flocks. When voltage increases, the concentration of metal ions and their hydroxide flock increase to absorb hydrocarbons. That subject is justifiable by Faraday's law. Thus, the COD and oil removal efficiencies are increased. In addition to decreasing bubble size, the bubble generation rate increases with the increasing of voltage, which is beneficial for pollutants removal agreed with (farhadi et al ., 2012). Since this has caused that the contact between hydroxide flock and pollutants increases, the flotation process is improved and pollutants are rapidly removed.

8.4 Effect of supporting electrolyte on electrochemical

In this section, different sodium chloride concentrations were used to evaluate the effect of the solution conductivity on EC. It should be noted that the solution conductivity affects the cell voltage, current efficiency and consumption of energy in electrolytic cell. The experiments were conducted at 0.5 g/L of NaCl which gave the best removal of pollutants. Very low removal is observed without adding NaCl to the solution, which is due to the fact that high electric conductivity is needed in order to use the EC is potential to remove the pollutants which oil refinery wastewater does not possess it. NaCI solution was selected as an electrolyte since it has several advantages, i.e., chloride ions could significantly reduce the adverse effects of other anions such as HCO and SO. The presence of the carbonate ion would lead to the precipitation of Ca^{2+} or Mg^{2+} ions that form an insulating layer on the surface of the electrodes. This insulating layer would sharply increase the ohmic resistance of the electrochemical cell and result in a significant reduction in the current efficiency and treatment conversion. Hence, it is suggested that among the present anions, there should be 20 % CI to ensure a normal operation of EC in water treatment (parsa et al., 2011). Conductivity causes an increase in current density; thus, more amount of coagulant can be introduced to the media. In addition, NaCl causes an increase in CI ions that chloride ions can remove the formed passivation layer on electrode surface. Thus, availability of metal hydroxide in the solution leads to an increase in the COD and oil removal efficiency.

8.5 Effect of electrode material on electrochemical

Aluminum and iron are cheap ,The results reveal that the aluminum electrode as anode and cathode has the highest effect on reduction of COD and oil from wastewater. Iron electrode as sacrificial anode appeared greenish at first resulting from Fe^{+2} ions and then turned into yellow resulting from Fe^{+3} ion in the effluent. During the electrolysis of iron electrode, Fe^{+2} is the common ion produced. It can be oxidized easily into Fe^{3+} using dissolved oxygen in water. Moreover, there is Fe^{+2} in yellow particles of $Fe\ (OH)_3$, and it is difficult to be settled. Furthermore, iron electrode becomes corroded at open circuit; therefore, the iron electrode is not preferred. Furthermore, effluent with aluminum electrodes was found very clear and stable. Conductivity of aluminum electrode is more than iron electrode, which results in greater formation of coagulant of aluminum into the media. Hydroxide of aluminum is more stable than hydroxide of iron and also absorption strength of hydroxide of aluminum is more than hydroxide of iron. Hence, results using aluminum electrode for anode and cathode chosen comparing to other electrode sets, agreed with (Safari et al., 2016, Fadali et al., 2015 and Amani et al., 2014).

8.6 Effect of initial concentration on electrochemical

In the experiments the Removal efficiency for higher concentration of oil and COD is lower compared to its lower concentrations when using the conditions, which are optimized for lower concentrations. Since the formation amounts of the coagulant are insufficient, the EC process needs more time and voltage to achieve the same removal efficiency as concentrations is lowered. This is consistent with the studies of (Canizares et al., 2007 and Safari et al., 2016). COD removal efficiency from breakup of oil-in-water emulsions. They observed that the COD and oil removal efficiency was decreased when COD and oil concentration is increased.

9. Conclusions

Because of the many pollutants discharged to the river, especially oil and COD . These pollutants, if their concentrations exceed the permissible limits, it will lead to many health and environmental problems. It is crucial to choose a treatment appropriate to the type and amount of the pollutant, the cost and efficiency resulting from it. Unlike traditional treatments such as coagulation and sedimentation, electrochemical is an alternative treatment process for water and wastewater that is characterised by simplicity in terms of tools and operation, its appropriate cost and efficiency, and the removal of different types of pollutants and does not require the addition of chemicals. It generates coagulants on-site from the dissolution of the anode and the formation of metal hydroxides thus reducing the production of sludge and materials harmful to the environment. Although electrocoagulation has many advantages, but its disadvantages require the periodic replacement of sacrificial anodes and cathode .

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