وزارة التعليم العالي والبحث العلمي

جامعة ديالى –كلية الهندسة

قسم الهندسة الكيمياوية

أداء عملية التخثر الكهربائي متبوعة بالامتزاز لتحسين معالجة مياه الصرف الصناعي

رسالة مقدمة الى

قسم الهندسة الكيمياوية/ كلية الهندسة / جامعة ديالى كجزء من متطلبات الدراسة لنيل درجة الماجستير في الهندسة الكيمياوية

من قبل

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Abstract

Industrial wastewater such as the discharge wastewater from petroleum refinery at the local Middle Oil Company/ the East Baghdad field.

Characterized by its complex high concentration of pollutants than the allowable limit by, such as chemical oxygen demand (COD) and oil content, therefore, the main purpose of this work is to study the efficacy of combine and hybrid treatment approach combining electrocoagulation (EC) and adsorption (AD) techniques to chemical oxygen demand (COD) removal and Oil content from industrial wastewater (oily water).

The properties of the real polluted wastewater involved chemical oxygen demand (COD) 9340 ppm, and Oil content 673.20 ppm.

The experimental work was carried out by four types of treatment processes: the electrocoagulation process (EC) and the adsorption process (AD), combine and hybrid between as.

In the electrocoagulation method, aluminum was used as the anode (110 mm long and 50 mm in diameter 3 millimeters thick) and 316 stainless steel as the cathode (89 millimeters in diameter, 110 millimeters in length, and 3 millimeters thick) at the electrodes are in the form of hollow tubular.

In the adsorption method using titanium dioxide (TiO_2) was used in form of a Nanomaterial powder tetragonal structure and anatase phase.

The study systematically examined key operational parameters influencing both EC and AD processes, including current density (ranging from 5 to 25 mA/cm^2), pH levels (ranging from 2 to 10), electrolysis time (ranging from 10 to 30 minutes), adsorbent dosage (ranging from 0.05 to 0.3 g), and residence time(ranging from 10 to 90 min)the parameters are optimized using (3-level, 3-factor) Box–Behnken design (BBD) is one of the best designs used in Response Surface Methodology (RSM), was adopted as an experimental design to satisfy and examine the process variables that affected on the COD removal and oil removal achieve maximum removal while minimizing energy consumption .

The sludge produced during electrocoagulation process was analyzed by scanning electron microscope (SEM), Energy Dispersive X-ray spectroscopy (EDX) and X-RAY Diffraction (XRD).

The adsorbent material (TiO_2) was tested to ensure its specifications by scanning electron microscope (SEM), X-RAY Diffraction (XRD), FTIR Spectra and BET Surface Area.

In the adsorption process apply three isotherm models (Langmuir, Freundlich and Temkin models) were applied. The equilibrium data were best represented by the Freundlich isotherm. The adsorption process can be well described by pseudo-second order adsorption kinetic model.

Experimental results demonstrated that the stand alone EC process achieved a COD removal efficiency of up to 81.05 % and oil removal 100% under best conditions (current density of 25 mA/cm^2, pH of 10, and electrolysis time of 20 minutes), with an energy consumption 1.086 KWh/m^3. Similarly, the adsorption process alone showed high removal efficiencies achieved a COD removal efficiency of up to 81.44 % and oil removal 100% under optimal conditions (Dose of 0.175 g, pH of 10, and time of 90 minutes).

However, the integrated EC-AD approach surpassed both methods individually, attaining COD removal efficiencies of up to 85.44% (residual COD 1360 ppm) and oil content achieved of 100%(residual oil 0 ppm),

Chapter One

Introduction

1.1 General Overview.

Rapid urbanization, industrialization, and population increase have made water quality and the amount of clean water available a major concern, particularly for third-world nations(Jalil et al., 2019). Wastewater from various industries, along with other anthropogenic and natural processes, continuously contaminates rivers, canals, estuaries, and other bodies of water. Wastewater can contribute to the depletion of clean water supplies in addition to causing irreparable harm to the ecosystem(Saravanan et al., 2021). Therefore, it is crucial to treat wastewaters before releasing them into the environment in order to reduce contamination and to take into account the possibility of reusing them (Naje et al., 2013).

Despite the fact that wastewater treatment technology is already a well-established science, more economical, chemical- and energy-efficient methods still need to be developed. Furthermore, research is being conducted to develop alternative wastewater treatment methods that are more effective than traditional methods like ion exchange, aerobic and anaerobic treatment, advanced oxidation processes, electrochemical techniques electrocoagulation, electro oxidation, and electro flotation), etc., as wastewater discharge standards become stricter(Aladily et al., 2025). The electrocoagulation (EC) procedure has been suggested as one of the aforementioned treatments for purifying water and eliminating various types of impurities (Abdulkadhim, 2018).

1.2 Wastewater Treatment Technologies

Wastewater impurities can be eliminated using physical, chemical, or biological techniques. Different wastewater treatment processes are combined into various systems, which are categorized as primary, secondary, and tertiary waste-water treatment, to accomplish varying levels of contaminant removal (Dhote, 2012) shown in **Fig(1.1).** In addition to removing and controlling pollutions, more thorough wastewater treatment involves eliminating some pollutants. In land-based applications, waste water is also treated using natural systems. As demonstrated by the basic flow of a wastewater treatment process and the techniques employed, sludge arising from wastewater treatment operations is treated using a variety of methods to lower its water and organic content and make it appropriate for final disposal and reuse.(Salgot et al., 2018)

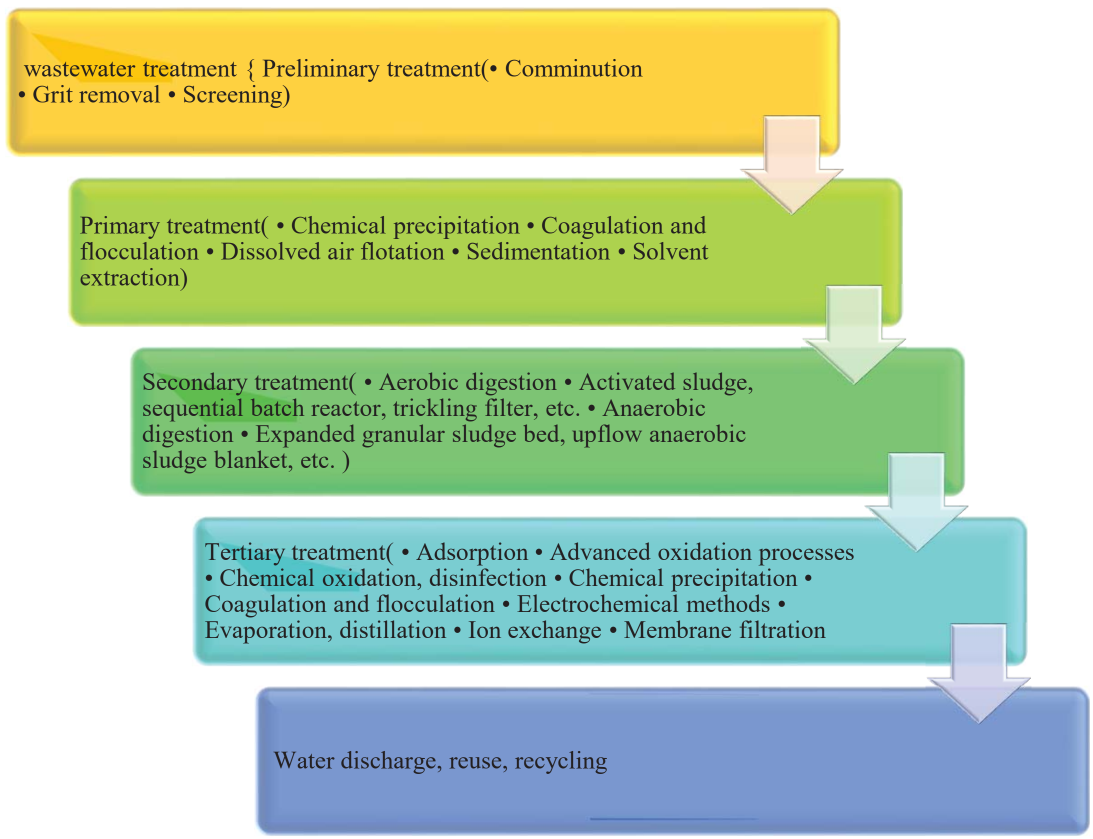

Fig. (1.1) The general flow of a wastewater treatment process and the techniques used (Kato et al., 2024)

1.3 Effect of Industrial Wastewater.

Industrial wastewater is indeed a significant environmental concern due to its potentially hazardous effects on ecosystems, public health, and the economy(Nahiun et al., 2021). The reference to the adverse effects of industrial wastewater that provided highlights the various ways in which it can impact both the environment and human activities. It is regarded as hazardous industrial wastewater due to the following reasons:

- **a)** Contaminants in generated water seep into subsurface water supplies, affecting drinking water, groundwater supplies, and aquatic resources.
- **b)** Endangering organisms' health due to the presence of poisonous substances
- **c)** Contamination of the atmosphere
- **d)** Impact on crop production
- **e)** The aggregation of dispersed pollutants may cause environmental harm and pose safety risks.
- **f)** Additionally, water-dependent economic activities suffer greatly when water quality and quantity fall short of the bare minimum, which may have an effect on a nation's yearly GDP (Ivanova, 2010).

1.4 Controlling and Treatment of Oil Industry Wastewater

The complete elimination of effluents from chemical and petroleum industries is not feasible; however, recent advancements in treatment technologies offer improved water management practices that help reduce raw water consumption and operational costs. In the oil refining sector, the wastewater generated typically contains high pollutant loads, including hydrocarbons, suspended solids, heavy metals, and other hazardous substances, which can lead to significant environmental degradation if not properly managed (Varjani, 2020).

The treatment of refinery wastewater generally involves three main approaches: source control, pretreatment, and end-of-pipe treatment, all of which are often implemented within the facility. Source control focuses on minimizing the overall pollutant load through optimized water use, internal recycling, and reuse strategies. Pretreatment techniques aim to reduce or eliminate contaminants at the source before they enter the main wastewater stream, often enabling the recovery of valuable materials. Finally, end-of-pipe treatment ensures that the remaining pollutants are treated to meet regulatory discharge standards and protect downstream water quality (Wang et al., 2005).

1.5 Electrocoagulation Technology (EC)

The metal ions produced in situ from the dissolution of the anode's electrode material, referred to as a 'sacrificial anode,' act as coagulants within the aqueous solution (Boinpally et al., 2023).

Vik et al originally proposed electrochemical treatment (EC) in London in 1889. At that time, a sewage treatment plant was constructed, and electrochemical treatment was used by combining household wastewater with salty (sea water) (Vik, 1984).Ship bilge water was treated using the electrocoagulation process, which was initially developed in 1906 by A. E. Dietrich. In 1909, J.T. Harries received a patent in the United States for electrolytic wastewater treatment with iron and aluminum sacrificial anodes. Numerous water and wastewater applications under various circumstances then ensued (Naje et al., 2013, Holt, 2002).

The benefits and uses of electrochemistry, flotation, and coagulation are combined in EC(Abbas, 2015).

The EC method entails applying electric current to destabilize the charge of ions present in wastewater, followed by electrode dissolution and the trapping of metal ions (for metal recovery) or contaminants (for wastewater treatment) in flocs(Jovanović et al., 2021).

The physiochemical characteristics of coagulants, include:

- the solubility of metal hydroxides, are significantly affected by pH conditions.
- Metal hydroxides' electrical conductivity and
- The coagulant complexes' colloidal particle sizes, Alkaline and neutral media are therefore favored for coagulation.

utilized industries like metal plating, textiles, oil and gas, food processing, and for treating landfill leachate to remove heavy metals, dyes, oils, and organic pollutants(Genethliou et al., 2023).

1.6 Adsorption Technology (AD).

Adsorption is a mass transfer process that transfers dissolved ions from a gas or liquid to an adsorbent, which is a solid surface. Adsorbents are substances that have been adsorbed onto them. There are two types of adsorptions: "physical" and "chemical" (chemisorption) (Alam et al., 2022).

AD process dates back to ancient times when materials like charcoal were used for water purification. Its scientific application began in the 18th century, with the development of activated carbon in the early 1900s significantly advancing its use in industries for removing contaminants from liquids and gases. Today, it is widely applied in environmental and industrial processes (Jalil et al., 2019).

Van der Waals forces are involved in physical adsorption, which is reversible with weak bonds. Strong bonds are formed between the adsorbent and the adsorbate through chemisorption, which is irreversible. It is an essential component of numerous large-scale processes, including liquid purification and separation (Kato et al., 2024).

a) Adsorbate molecule transport in the solution phase is known as bulk diffusion.

b) Film diffusion: the movement of the adsorbate molecules via a hydrodynamic boundary layer (film) from the bulk solution to the adsorbent surface.

c) Intra-particle diffusion: the movement of adsorbate molecules through the adsorbent pores from the exterior surface of the adsorbent.

d) Adsorption is the process in which the adsorbate attaches to the surface of the adsorbent through physical or chemical interactions.

(AD) methods are applied in water and wastewater treatment, air purification, and industrial processes to remove pollutants like heavy metals, dyes, organic compounds, and gases (Genethliou et al., 2023).

1.7 Case Study

This research is concerned with utilizing an electrocoagulation and adsorption techniques ((EC and AD)) using a batch reactor for the treatment of the petroleum refinery wastewater ((PRW)) from the ((MIDDLE OIL COMPANY)) that combines the wastewater resulting from all operations in the unit of the refinery which is taken from Fields east of Baghdad/Iraq.

1.8 Objective of research.

I. Select a case study of wastewater from Al MIDDLE OIL COMPANY and applied two methods of treatment ((EC & AD)) with a design of tubular electrocoagulation reactor to remove the pollutants.

II. Determine the extent to which the treatment process improves if electrocoagulation is followed by an adsorption process

III. Examine the impacts of the EC parameters; ((applied current density, pH and Time)) and the adsorption Parameter ((Dose of adsorbent, pH and residence time)) on many main objectives of the electrocoagulation process; by removal of COD and Oil content and energy consumption.

IV. Utilizing the response surface methodology (RSM) for optimizing the response's operational conditions that are influenced by various operating variables of the EC and AD processes.

V. Examine the differences between EC, AD, EC followed by AD, and hybrid EC and AD treatment methods to identify the most effective way to remove pollutants that yields the highest removal efficiency of COD and oil, which is then approved with a standard limit for reuse**.**