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Feasibility of electrocoagulation method in reducing the pollution load of petrochemical industry wastewater

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Abstract
The petrochemical industry is one of the main consumers of fresh water, through which a large amount of wastewater enters the water environment. The disposal of such sewage is a concern because it leads to odors and the spread of diseases in local rivers and fresh water sources. Wastewater from petrochemical industries contains significant amounts of COD, turbidity, FOG and BTEX, which can lead to environmental degradation if not properly treated before discharge. Due to the high concentration of organic substances and suspended solids in wastewater, it is necessary to pre-treat the wastewater of petrochemical industries before successive electrooxidation operations. Conventional treatment processes are not able to treat the pollutants and contaminants in the wastewater of petrochemical industries to a reasonable extent, and hence advanced treatment processes are necessary. For this study, a laboratory-scale electrocoagulation treatment process was used to investigate the successful reduction of pollutants including COD, turbidity, and color. In the process of electrocoagulation with aluminum anode, experiments were carried out in a continuous reactor. The effect of operating parameters such as applied current and initial pH of the solution was investigated. The pollutant removal efficiency through COD, turbidity and color was measured as 67.5, 98.7 and 88.5%, respectively. This removal rate was obtained in the experimental conditions of initial pH 5, applied current A 2.5 and electrolysis time 3 hours. Electrocoagulation mechanism was modeled using adsorption isotherms. Adsorption of pollutants in wastewater on the surface of flocs was modeled using Freundlich, Langmuir, Temkin and Dubinin-Radoshkevich isotherms. The Freundlich isotherm model satisfactorily matched the experimental observations for the electrocoagulation process.

Keywords: *Petrochemical wastewater, Electrocoagulation, Turbidity, COD.*

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I. INTRODUCTION

Global demand for petroleum products is increasing rapidly. As a result, our environment is exposed to increasingly dangerous effects (Abbar & Alkurdi, 2021). One of these effects is caused by the large amounts of wastewater produced during crude oil processing. Approximately, for every ton of crude oil produced, 0.6 to 1.4 times as much wastewater is produced, which has high levels of pollutants (Ghanim & Hamza, 2018). It is estimated that the petrochemical industry produces an average of 5.34 billion liters of wastewater per day globally (Alkurdi & Abbar, 2020).

Wastewaters from petrochemical industries are a significant source of pollution, showing high concentrations of organic and inorganic pollutants, with high amounts of chemical oxygen demand (COD), turbidity, benzene, toluene, ethylene, and xylene (BTEX) and fat. are known as oil and grease (FOG) (Kesob & Abbar, 2022). These pollutants have various adverse effects on the surrounding environment. Due to the presence of these pollutants, petrochemical industry effluents are classified as hazardous wastes by many environmental regulations around the world (Jiad & Abbar, 2023). Therefore, before discharging wastewater from petrochemical industries into the environment, the amount of these pollutants should be reduced to acceptable levels (Akkaya, 2022). Several different purification methods including membrane ultrafiltration (Ahmad et al., 2020), biological purification (Crini & Lichtfouse, 2019), coagulation, flocculation and flotation (Zhao et al., 2021), electrooxidation, electrocoagulation, electrofenton (Martínez- Huitle & Panizza, 2018) and surface absorption (Rashid et al., 2021) have been designed to meet the criteria of environmental regulations to achieve this goal. However, each of these methods may not be successful in managing all types of wastewaters and cannot deal with all types of pollutants. Combined approaches are often needed to treat petrochemical industry wastewater, which is a highly polluted effluent (Wang et al., 2017).

While the electro-oxidation process is very effective in completely removing turbidity from the wastewater of petrochemical industries, the treatment of highly polluted wastewater with COD values above 2000 mg/L cannot be effectively achieved using the electro-oxidation process alone (Akkaya, 2022). As a result, in order to ensure the complete and successful removal of pollutants, treatment methods usually based on the combination of mechanical or physicochemical processes, such as oil-water separation and coagulation, together with electro-oxidation operations must be carried out to ensure the complete and successful removal of pollutants. Kassob & Abbar, 2022). Therefore, the current research seeks to investigate the possibility of using the electrooxidation method to improve the wastewater treatment process of petrochemical industries. The secondary objectives of the research are to study the effect of initial pH and current density in the electrocoagulation process on the removal efficiency of turbidity, color and COD from petrochemical waste water.

II. MATERIALS AND METHODS

2.1 Research design

The aim of the electrocoagulation process was to effectively reduce organic pollutants from the wastewater of petrochemical industries before the electrooxidation process. A laboratory-scale electrocoagulation reactor was used to treat wastewater from petrochemical industries. The electrocoagulation system is shown in Figure 1. The electrocoagulation system consists of a 4 L rectangular Plexiglas reactor, a hot plate magnetic stirrer and a magnetic stirrer bar, and a direct current (DC) power supply. In this system, 6 rectangular aluminum plate electrodes with dimensions of 100*6*100 mm thickness and a surface area of 1344 cm2 were used as anode and cathode. Aluminum electrodes were connected in a unipolar configuration and immersed in the reactor. The distance between two adjacent electrode plates was maintained at 3 cm during the experiment. Aluminum plates were connected to the positive and negative terminals of the power supply, and the cell voltage was recorded to estimate energy consumption. DC current from the DC power supply was passed through the solution through 6 aluminum plates during the electrolysis run. A hot plate magnetic stirrer and a magnetic stirrer bar were used to maintain homogeneity in the electrocoagulation reactor. Stirring was done at a constant speed of 300 rpm (Faraj et al., 2024).

The initial pH of the wastewater was adjusted to the desired pH value by adding 1 M H_2SO_4 and NaOH in the range of 2 to 8. After acidification, the effluent was added to the electrocoagulation reactor. Effluent electrolysis was started by adjusting the electric current by applying the determined current density. Before starting the electrocoagulation process, the current was set between 1.5 and 2.5 amps. Al monopolar plate electrodes were used in electrocoagulation treatment configuration and the distance between each pair of electrodes was 3 cm. The electrodes were placed in 3 L wastewater and connected to the DC power supply terminal.

The solution volume was kept constant at 3 liters, electrolysis time at 3 hours, temperature at 25°C and stirring speed at 300 rpm. The studied parameters including pH and current density were changed in order to evaluate their effect on the removal efficiency. Each experiment was repeated twice to evaluate the reproducibility of the data. During electrocoagulation, samples were removed at different time intervals and filtered through 0.45 μm filters. Then the filtered sample was stored in the refrigerator at 4°C and used for chemical analysis.

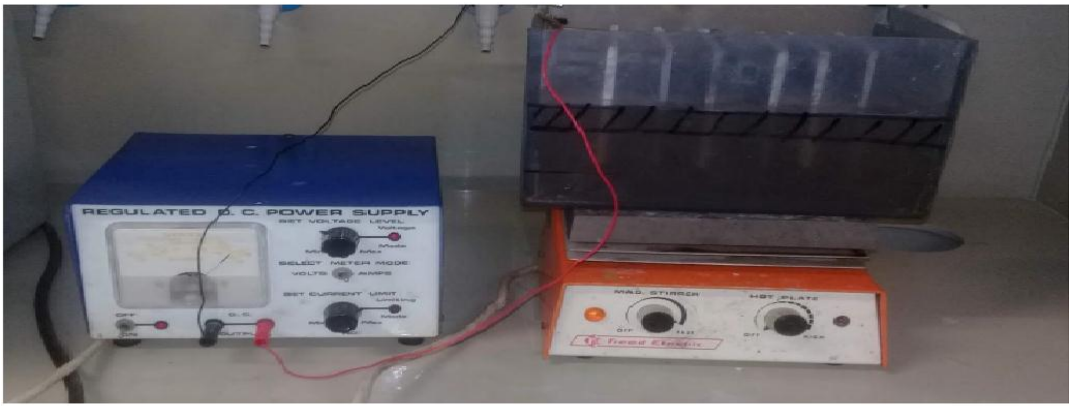


Figure 1: The electrocoagulation process used in the present study

2.2 Analyzes and chemicals

Conductivity, pH, and turbidity were measured using a conductivity meter, pH, and turbidity meter (Hanna), respectively. In this research, Shazand petrochemical complex wastewater was used as the test solution. Petrochemical industry effluent is characterized by high concentration of chemical oxygen demand (COD), oil and grease (FOG) and turbidity. COD was measured by reactor digestion method using Hanna apparatus. Briefly, the measurement of parameters by the Hanna apparatus involves adding a sample solution to a vial containing a reagent that is heated for a certain period of time and then cooled to room temperature. Then the concentration of the desired parameter is measured using the Hanna device. The range of COD vials was between 500-10000 mg/liter and the appropriate dilution factor was used to measure concentrations higher than this range.

High grade chemicals and reagents were used for this research. Sodium chloride (NaCl), sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) were purchased from Merck. All the solutions used in this study were prepared using water from an ultrapure purification system (MQ, Millipore) and 1 M H_2SO_4 or NaOH was used to adjust the pH.

III. RESULTS AND DISCUSSION

3.1 Characteristics of petrochemical industry wastewater

Petrochemical industry effluent used in this study was tested for specific characteristics. Average values are shown in Table 1. The values of COD, FOG and BTEX are much higher than the wastewater output standard.

Table 1: Characteristics of studied petrochemical industry wastewater

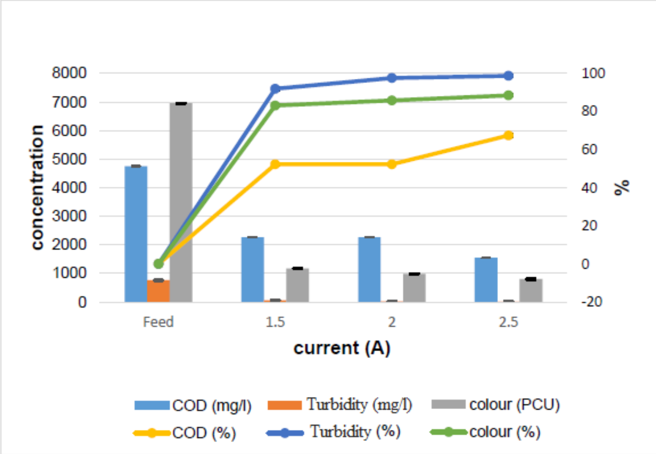
Parameters	Tested Values	Discharge standard
pH	6.52	6.5-8.5
Salinity (mg/l)	7480	-
Conductivity (μS/cm)	9670	700
Colour (PCU)	6952	75
Benzene (μg/l)	1186.8	-
Ethylbenzene (μg/l)	26.29	-
Mp-Xylene (μg/l)	122.4	-
o-Xylene (μg/l)	122.5	-
Toluene (μg/l)	141.6	-
Oil and grease (mg/l)	37	10
Turbidity (NTU)	763	50
COD (mg/l)	4753	200

3.2 Electrocoagulation of petrochemical industry wastewater

3.2.1 Flow effect

In a continuous electrocoagulation process, current is a critical parameter; Because it is the only parameter that can be directly controlled. Rashid et al. (2021) suggest that both coagulant dose and bubble generation rate can be directly determined by flow. Therefore, experiments were conducted to quantify the effect of operating flow when varying from 1.5 to 2.5 on COD, color, and turbidity. As shown in Figure 2, the highest current allowed the greatest removal. This observation is attributed to the fact that a high current produces a significant amount of oxidized aluminum, resulting in a larger amount of sediment to remove colloidal particles. In addition, Belibagli et al. (2024) reported that bubble density increases and decreases with increasing flow. As a result, it brings the best removal of pollutants and sludge flotation.

Therefore, an increase in current means an increase in the amount of coagulant (Al^{3+}) produced by the electrochemical dissolution of the aluminum anode. In fact, the amount of coagulant produced in a fixed time in the electrocoagulation cell is related to the amount of current using Faraday's law. In the present research, a current of about 2.5 and pH equal to 2 is sufficient for better electrolyte flocculation and as a result maximum removal efficiency (COD: 67.5%, turbidity: 98.7% and color: 88.5%) (Figure 2a).



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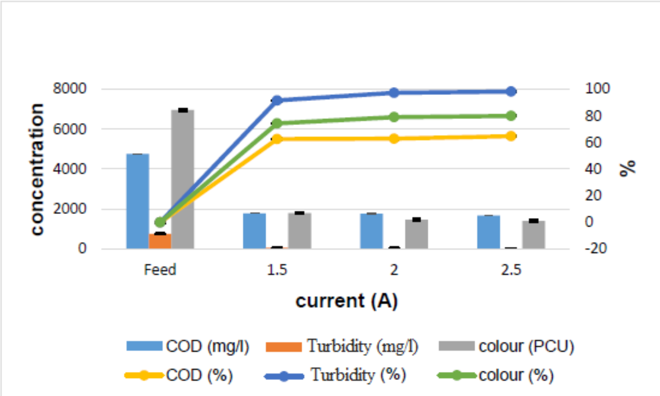

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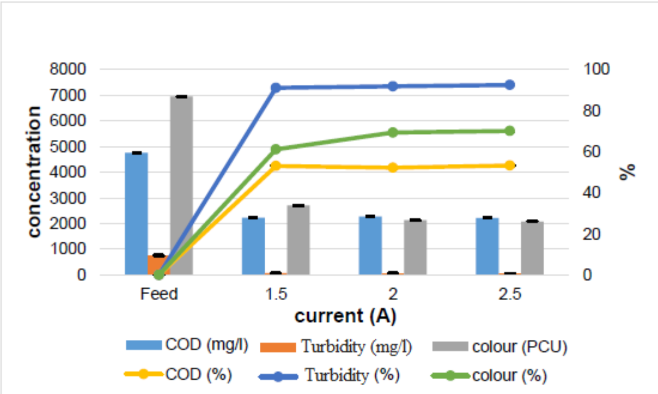

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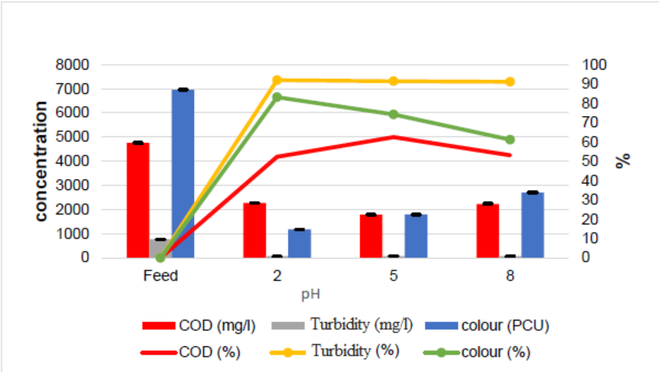
Figure 2: Effect of flow on removal of COD, turbidity and color; a) pH=2, b) pH=5, and c) pH=8

3.2.2 Effect of pH

Figure 3 show COD removal efficiency, turbidity and color as a function of pH. The highest rate of removal of COD, turbidity and color has been observed in acidic environment. In comparison, the removal efficiency decreased at pH 8. Therefore, it can be said that at a pH equal to 8, aluminum hydroxide flocs are less reactive and flocculation is less effective due to the formation of small flocs that cause the formation of sediment on the anode and lead to an increase in the ohmic resistance of PRW (Isik et al., 2020).



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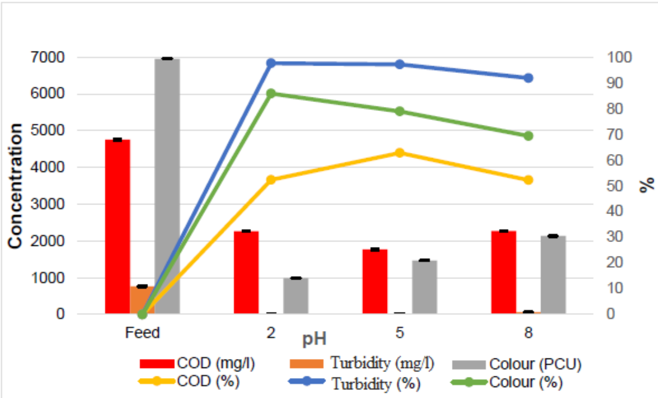

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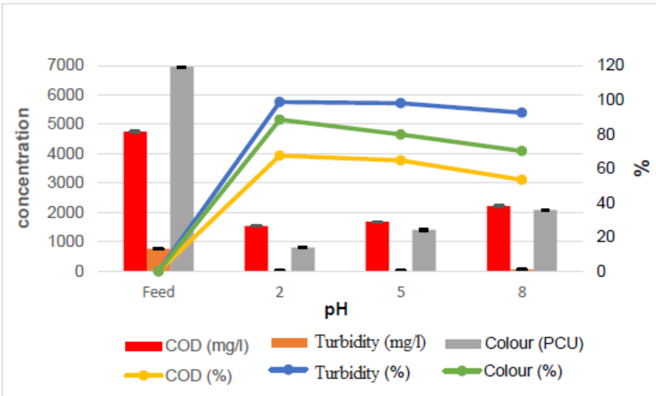

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Figure 3: Effect of pH on removal of COD, turbidity and color; a) flow=1.5 A, b) flow=2 A, and c) flow=2.5 A

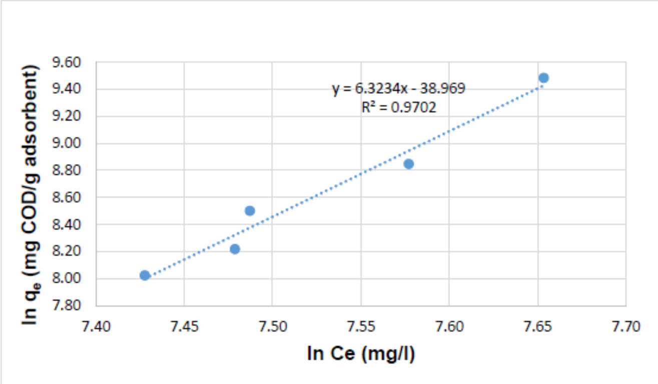
The initial pH of the petrochemical industry effluent is a critical parameter in determining the efficiency of the EC process. The effect of pH on COD, turbidity and color degradation varied from 2 to 8 (Figure 4). During the process, the pH of the treated emulsion is increased to the basic pH. The increase in pH is due to the release of CO2 from the wastewater due to H2 bubbles. Also, chemical dissolution of aluminum consumes hydrogen ions and increases the pH (Zazou et al., 2019).

3.3 Electrocoagulation modeling through adsorption isotherms

Since pollutant removal is similar to the surface adsorption process (except for the production of coagulants), the adsorption isotherm model can be useful for describing experimental isotherm data and identifying the adsorption mechanism. Therefore, isotherm models with two parameters have been considered to establish a relationship between COD values, turbidity and color adsorbed on aluminum hydroxides and its equilibrium concentration in the effluent of petrochemical industries (Qin et al., 2023). COD removal, turbidity and color were modeled by Freundlich, Langmuir, Temkin and Dubinin-Radoshkevich adsorption isotherm models at constant pH 5.

3.3.1 Freundlich adsorption isotherm

Freundlich adsorption isotherm linear model was used to test the adsorption data. KF and n values were determined through the width from the origin and the slopes of the Freundlich plots (Table 2). A value of n between 1 and 10 indicates beneficial absorption, while reduced values between 0 and 10 indicate favorable absorption (Alkurdi & Abbar, 2020). The values of KF and n also determine the slope and curvature of the isotherm. Also, the Freundlich equation provides an adequate description of the absorption data in a low concentration spectrum. The values of KF and n indicate easy removal of pollutants from wastewater and high capacity for adsorption (Talhajt et al., 2023). The value of n, which is related to the distribution of bonded ions on the adsorbent surface, was calculated to be less than 1 for COD absorption, turbidity and color, which indicates optimal absorption.



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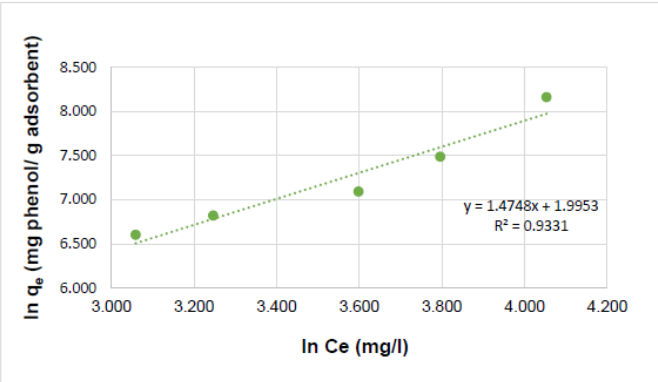

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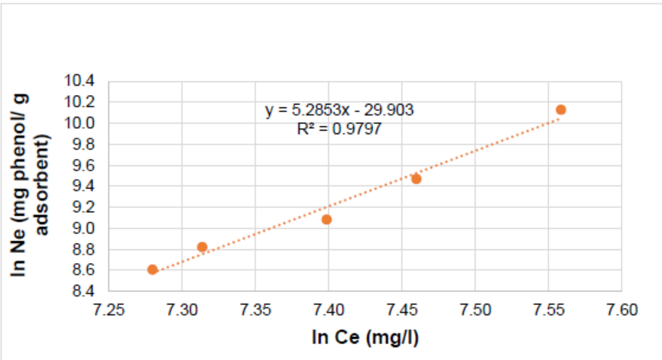

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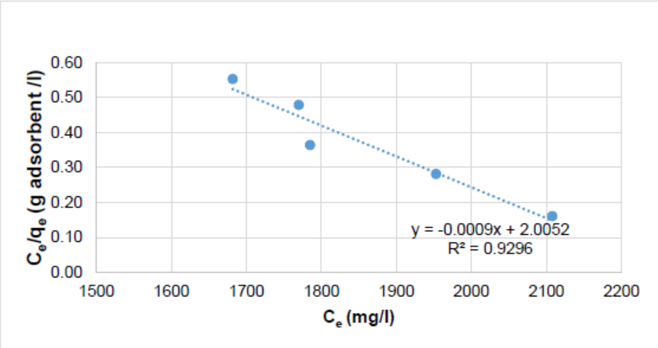
Figure 4: Freundlich diagram for removal of COD, turbidity and color

3.3.2 Langmuir adsorption isotherm

Plots of 1/qe for COD, turbidity, and color absorption as a function of 1/Ce are shown in Figure 5. The linear regression equations for the Langmuir isotherm for the adsorption process were obtained through Figs. Using these regression equations and linear graphs, the values of monolayer capacity (qmax) and Langmuir constant (KL) were calculated (Table 2). Graphs for COD and color were found to be linear with strong correlation coefficients (<0.9), which shows the applicability of the Langmuir model in these analyses. The correlation coefficient of turbidity was obtained as 0.7.16.



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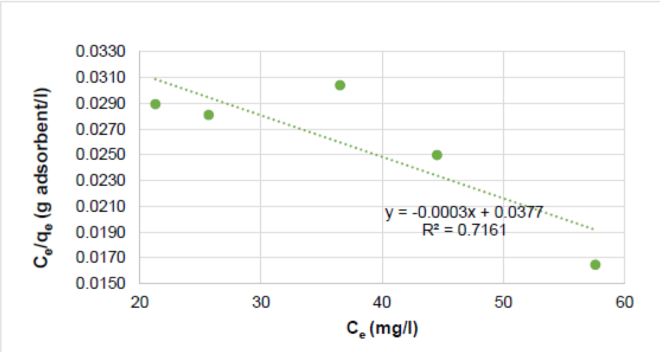

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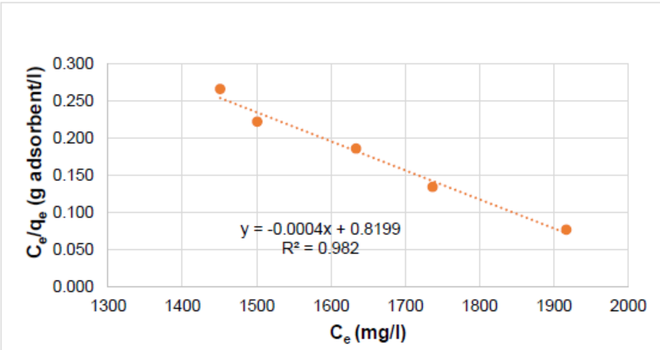

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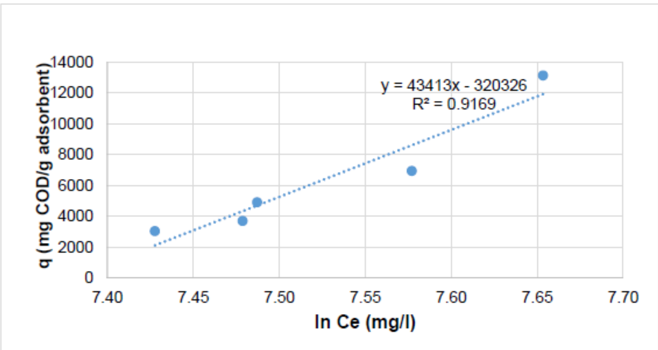
Figure 5: Langmuir diagram for removal of COD, turbidity and color

3.3.3 Temkin adsorption isotherm

KT and B constants are calculated by plotting q versus ln Ce. Figure 6 shows that the Temkin isotherm model simulations do not have acceptable correlations with experimental observations for turbidity and color.



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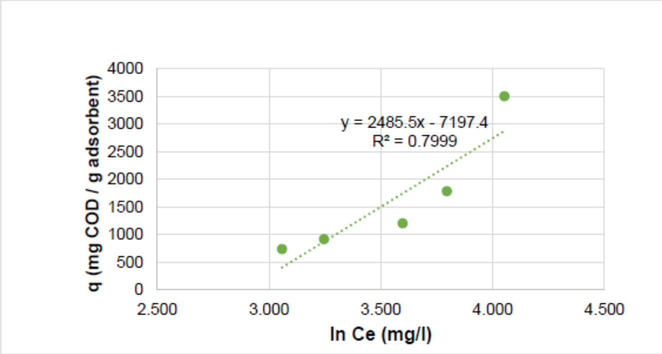

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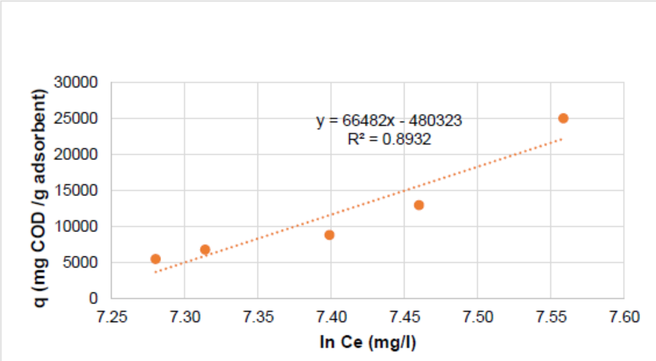

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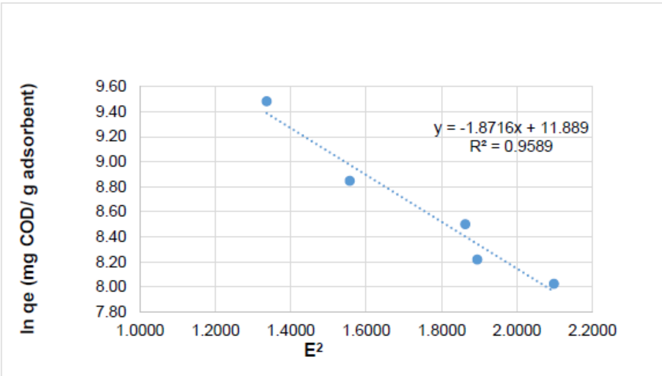
Figure 6: Temkin diagram for removal of COD, turbidity and color

3.3.4 Temkin adsorption isotherm

The regression equation and R2 values of Dubinin-Radoshkevich model for COD, turbidity and color are shown in Figure 7. From these figures, it was observed that this isotherm provides an excellent description of the adsorption process in the investigated concentration range. Table 2 shows the adsorption energy (Es) and the Dubinin-Radoshkevich isotherm constants. High values of Xm indicate high adsorption potential for COD, turbidity and color. Es values often reflect the physical absorption phase. The obtained positive ES indicates an endothermic adsorption process that favors adsorption at lower temperatures. These results are consistent with the study conducted by Marmanis et al. (2022) is consistent and the Dubinin-Radoshkevich isotherm provides a complete fit of the adsorption cycle.



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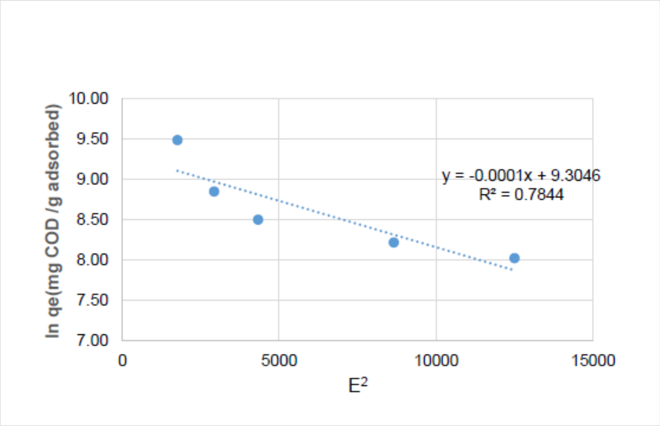

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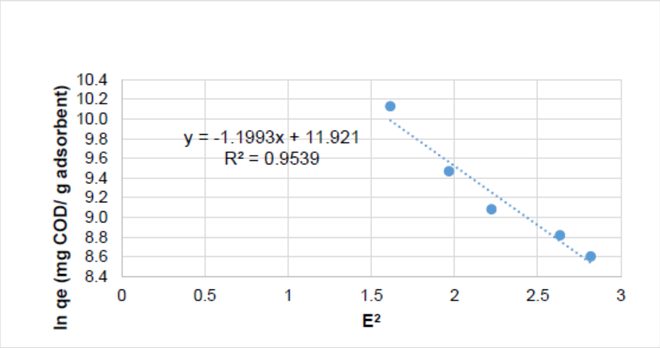

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Figure 7: Dubinin-Radoshkevich diagram for removal of COD, turbidity and color

3.3.5 Comparison of isotherms

By comparing all the studied adsorption isotherms, linear graphs were obtained that showed the application of these isotherms in the adsorption process. Table 2 shows a comparison of the regression coefficient (R2) for four isotherm models. The acceptability and suitability of the isotherm equation with equilibrium data is based on the values of correlation coefficients. R2 values for Dubinin-Radushkevich isotherm for turbidity, COD and color are 0.7844, 0.9589 and 0.9539 respectively. Moreover, Freundlich isotherm was the best fit for COD and turbidity while Langmuir was the best fit for color. The values obtained from Temkin isotherm for removal of COD, turbidity and color were 0.9169, 0.7999 and 0.8932, respectively. These values were lower than the results obtained from Freundlich, Langmuir and D-R isotherms, which indicates that the Temkin isotherm does not describe well the equilibrium data of adsorption of COD, turbidity and color on aluminum electrodes. Therefore, the compliance isotherm does not correspond well to the adsorption process. Therefore, the results show that the adsorption isotherm models fit the data in the following order: Freundlich > Dubinin-Radoshkevich > Langmuir > Temkin.

Table 2: Isotherm constants for absorption of COD, turbidity and color

Isotherm models	Parameters	COD	Turbidity	Colour
Freundlich	n	0.158	0.68	0.19
	K_F (g^{-1})	1.19E^{-17}	7.4	1.0E^{-13}
	R^2	0.9702	0.9331	0.9797
Langmuir	q_{max} (mg/g)	-1111	-3333	-2500
	K_L (mg^{-1})	-0.00045	-0.00797	-0.0004879
	R^2	0.9296	0.7161	0.982
Temkin	B	43413	2485.5	66482
	K_T (g^{-1})	6.24E^{-04}	0.0553	7.28E^{-04}
	R^2	0.9169	0.7999	0.8932
Dubinin-Radushkevich	β (mg^{-1})	-1.87	-0.0001	-1.20
	X_m (mg/g)	145655.6	10988	150391.9
	E_s (kJ/mol)	0.52	70.71	0.65
	R^2	0.9589	0.7844	0.9539

IV. CONCLUSION

In this study, petrochemical industry wastewater was treated using electrocoagulation process. The initial pH and the current applied affected the removal efficiency of COD, turbidity, color and FOG from the petrochemical industry effluent during the electrocoagulation process. Optimum value of COD, turbidity and color were observed, respectively, 67.5%, 98.7% and 88.5% under experimental conditions of initial pH 5, applied current 2.5 amps and electrolysis time 3 hours. Freundlich adsorption isotherm of pollutant removal satisfactorily matched the experimental observations. This resulted in a treated effluent that met national effluent standards. Therefore, electrocoagulation is a viable process for petrochemical industry wastewater treatment.

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