Original Research Article

Treatment of Effluent from the Olefin Unit of Marun Petrochemical Complex Using Advanced Photocatalytic Oxidation Method

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ABSTRACT

The urgent need for water in industries and the large volume of wastewater discharge has prioritized wastewater treatment and water recycling in the research and operational projects of various public and private companies. In this context, Marun Petrochemical Company has established a treatment plant to recover water from its wastewater, aiming to not only provide part of its water needs through treated effluent, but also to reduce disposal costs and wastewater-related issues. This study uses a batch slurry photoreactor for laboratory-scale experiments. The statistical results of this study show that reducing pH and increasing catalyst concentration lead to higher Chemical Oxygen Demand (COD) removal. In addition, it was revealed that increasing the amount of co-oxidant results in further COD reduction at higher pH levels is attributed to a strong antagonistic interaction between the pH and co-oxidant parameters.

Introduction

The most common biological wastewater treatment process is the activated sludge process, which includes aeration, sedimentation, and filtration stages [1,2]. By integrating sedimentation, aeration, and filtration units and replacing membranes within a reactor, water molecules pass through while large particles, such as biological flocs and pollutants, remain trapped behind the membrane [3,4]. This system is referred to as a Membrane Bioreactor (MBR), where biological reactions for treatment and pollutant separation occur within a single system [5,6]. This method ensures that the quality of the treated effluent will be such that organic colloidal materials, macromolecules, and bacteria will be effectively removed without requiring additional treatment methods [7,8]. In this study, the effluent from the Olefin Unit of Marun Petrochemical Complex, with a nominal capacity of 1.1 million tons of ethylene, one of the largest mega-olefins plants in Iran and globally, was examined.

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Table 1: Wastewater specifications of the Olefin unit

Unit	Value	Characteristic	
Cubic meters per hour	23.4	Normal	Flow rate
Cubic meters per hour	150	Maximum	
degrees centigrade	45	Temperature	
mg/L	800-1500	COD	
mg /L	200-1000	BOD5	
mg /L	10-30	Oil/HC	
mg /L	10	TSS	
mg /L	500-2000	TDS	
mg /L	<8	pH	
mg /L	1-5	Phenolic compounds	
mg /L	>10	H_2S	

Marun Petrochemical Company operates several units producing different types of effluent, and the characteristics of the Olefin effluent, as well as the types of pollutants present, vary accordingly. The detailed specifications are provided in Table 1. The novelty of this study is treatment of wastewater with techniques other than biological methods [9,10].

Materials and Methods

Figure 1 displays a schematic diagram of the experimental setup. The relevant photocatalyst in the photocatalytic degradation process with ultraviolet light was used as dispersed slurry in the solution. This photoreactor is equipped with a stirrer with three blades, an air rotameter, and a thermometer. For the lamps placement, eight UV-C lamps with a power of eight watts inside the photoreactor, tubes with a size of 452 cm made of quartz were placed vertically in the desired locations. The temperature range recorded in all stages of the relevant experiments was between 26 and 27 °C, which indicates the same temperature condition of the reaction. This photoreactor operates under atmospheric conditions and also to supply the oxygen needed for photocatalytic reactions, a circular air distributor (sparger) was used. The air consumed is produced by an air pump whose intensity is controlled by a rotameter. Concerning the advantages mentioned for the titanium oxide photocatalyst, in this study, the photocatalytic degradation process in ultraviolet light using a commercial titanium oxide photocatalyst (TiO_2-p25) was investigated. It is notable that this is just a translation of the text provided and may need to be edited or revised to fit the specific requirements and style of the Journal of Engineering in Industrial Research. In addition, it is important to ensure that all technical terms and units are correctly translated and used in accordance with the journal's guidelines.

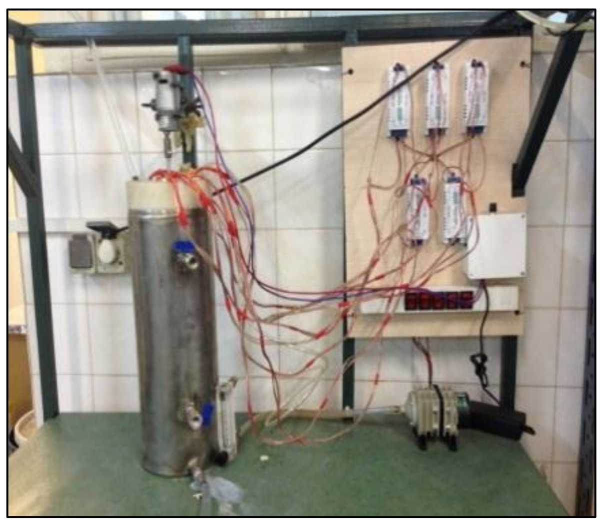

Figure 1: The applied photoreactor.

COD measurement

This experiment was conducted based on method 5220D from the Standard Methods for the Examination of Water and Wastewater. For COD measurement, Merck's pre-prepared tests were used. Specifically, 0.3 mL of solution A and 2.85 mL of solution B were added to an empty vial, followed by the addition of 3 mL of the sample. After thorough mixing, the vial was placed in a thermoreactor (WTW CR 2200) at

150 °C for 2 hours. After cooling, the absorbance of the solution was measured at a wavelength of 605 nm. The obtained absorbance was multiplied by a specific coefficient (295-) to calculate the COD concentration in mg/L. Finally, the COD removal efficiency was calculated using the equation, where COD_0 is the initial COD and COD represents the COD at the end of the reaction.

Photocatalyst analysis methods

In this study, commercial titanium dioxide (TiO_2-P25) photocatalyst from Degussa was used. To confirm the structure, purity, and integrity of the commercial photocatalyst, as well as to ensure the purity of the samples and determine the crystalline phase, X-ray diffraction (XRD) spectroscopy was performed using an Equinox model XRD device from INEL. Statistical Design of Photocatalytic Degradation Experiments Since the design must account for both the effects of individual variables and their interactions on the response, designs like Taguchi or factorial designs, which eliminate experiments that show interaction effects, were not suitable. Therefore, the method chosen to meet these requirements is the Response Surface Methodology (RSM). Concerning the better and more appropriate distribution of the Box-Behnken method compared to the Central Composite Design (CCD), the experiments were designed using this method. All operations and calculations related to the experimental design optimization were carried out using the Design Expert software.

Photocatalytic experiment

The desired amount of photocatalyst was dissolved in 200 mL of distilled water and added to the real wastewater solution, as presented in Table 2. The solution was then diluted to a final volume of 2 liters. The pH of the solution was adjusted using either 0.1 M sulfuric acid or sodium hydroxide, and the suspension was transferred to the photoreactor. The reactor contents were stirred in the dark for 30 minutes before the lamps were turned on to establish equilibrium between adsorption and desorption on the catalyst. During this time, a thermal jacket was used to control the temperature. After 30 minutes, a sample was taken from the reactor using a sampling valve located at the bottom. A COD test was performed on this sample, and it showed no significant difference from the initial COD, indicating that adsorption had little effect on COD reduction. Afterwards, all eight lamps were turned on simultaneously, and airflow was initiated. After 90 minutes, a sample was taken from the photoreactor, and the COD of the wastewater was measured for each sample.

Table 2: Characteristics of the effluent of this study

parameter	Unit	Value
COD	ppm	280
BOD	ppm	55
pH	-	7.1
Phenol	ppm	4
TDS	ppm	570

Experimental

In this section, the performance of the photocatalytic degradation process of wastewater from the Marun Petrochemical Company's olefin unit under ultraviolet light is statistically evaluated and compared using Design Expert software. The level of these parameters is listed in Table 3.

After designing the experiments according to Table 4, a total of 30 experiments were conducted, taking into account the values of various parameters. As shown in Table 1, it is evident that with a decrease in pH and an increase in catalyst concentration, the reduction in COD becomes more significant.

Table 3: Selection of the effective factors of this study

Parameter name	Parameter symbol
Photocatalyst concentration	A
Auxiliary oxidizer (H_2O_2)	B
pH primary	C
Aeration intensity	D

Table 4: Test matrix

Run	Amount of photocatalyst (g/l)	The amount of auxiliary oxidant (g/l)	pH	The amount of ventilation (l/min)	Removal percentage COD (model)	Removal percentage COD (Experimental)
1	0.1	0	7	6	57.66	56.45
2	1	0	7	6	61.62	61.73
3	0.1	10	7	6	25.00	24.87
4	1	10	7	6	63.74	63.00
5	0.55	5	5	2	22.11	22.16
6	0.55	5	9	2	63.11	62.13
7	0.55	5	5	10	53.01	55.56
8	0.55	5	9	10	73.05	74.12
9	0.1	5	7	2	23.60	23.45
10	1	5	7	2	65.18	67.17
11	0.1	5	7	10	59.10	58.98
12	1	5	7	10	70.52	71.87
13	0.55	0	5	6	62.28	62.67
14	0.55	10	5	6	15.00	16.31
15	0.55	0	9	6	53.44	53.12
16	0.55	10	9	6	72.38	71.14
17	0.1	5	5	6	17.31	17.78
18	1	5	5	6	67.55	67.12
19	0.1	5	9	6	71.57	70.00
20	1	5	9	6	74.33	74.12
21	0.55	0	7	2	44.56	45.56
22	0.55	10	7	2	24.14	24.12
23	0.55	0	7	10	64.98	64.54
24	0.55	10	7	10	44.56	45.12
25	0.55	5	7	6	66.78	67.32
26	0.10	5	5	6	67.07	68.23
27	0.55	5	9	10	64.81	64.11
28	0.55	0	9	2	64.94	65.12
29	0.10	10	7	6	67.92	68.34

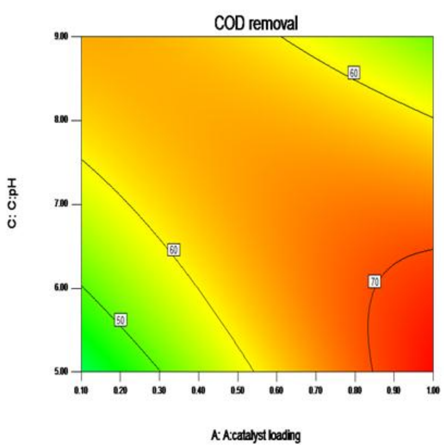

Figure 2: 2D diagram of the response of the model according to the amount of catalyst and pH.

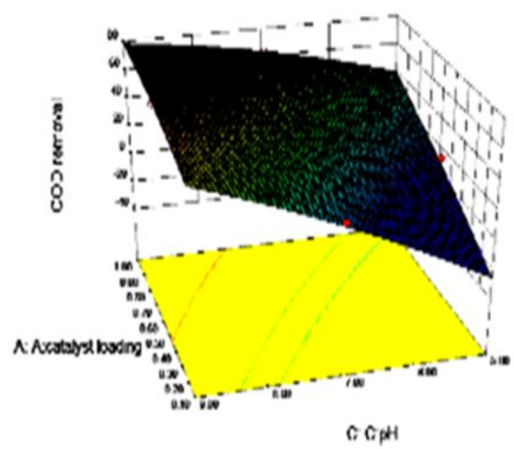

Figure 3: 3D diagram of model response according to catalyst amount and pH.

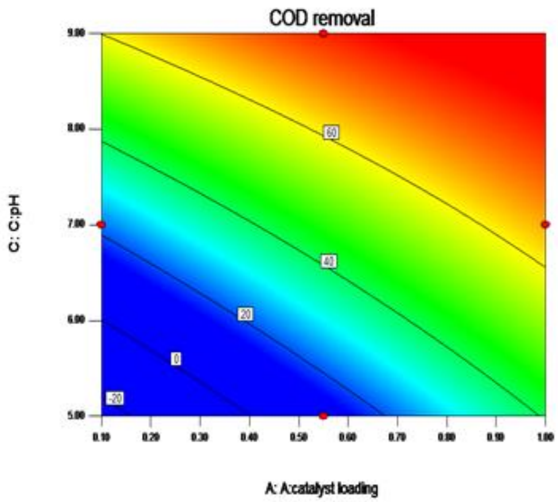

Figure 4: Comparison chart of pH parameters and auxiliary oxidant.

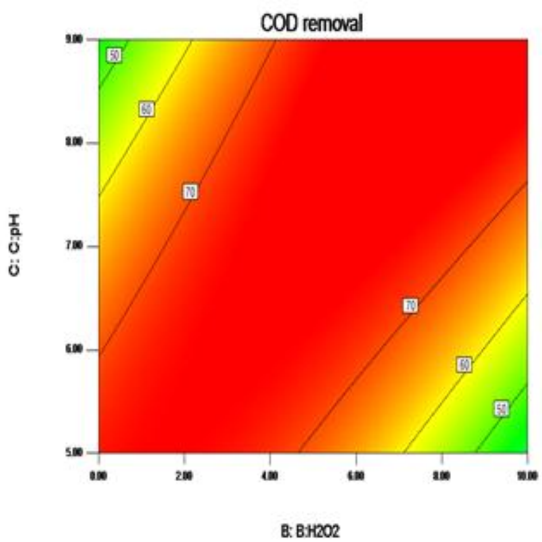

Figure 5: 2D diagram of the response of the model according to the amount of auxiliary oxidant and pH.

It is clearly observed from Table 2 that with an increase in the auxiliary oxidant concentration, a more significant reduction in COD is observed at higher pH levels. This can be attributed to the strong interaction effect between the pH and auxiliary oxidant parameters. Notably, this interaction effect is clearly evident in the previously presented ray diagram. To better understand the interaction between pH and oxidant parameters, attention should be given to the interaction charts in Table 3.

Table 3 illustrates the significant interaction effect between the two aforementioned parameters, particularly when the catalyst concentration is higher Figure 2-4. From Table (4), it is also clearly observed that an increase in each of the parameters individually leads to a decrease in efficiency. In contrast, when both parameters are set at their median values, the greatest reduction in COD is observed, which further supports the existence of an interaction effect between these two parameters.

Conclusion

The results of the titanium oxide photocatalyst analysis indicate that it has smaller particle sizes, an appropriate distribution of crystalline phases, and the ability to be excited under UV light. The statistical results of this study show that a decrease in pH and an increase in catalyst concentration lead to a greater reduction in COD. Furthermore, the results indicate that an increase in the auxiliary oxidant concentration results in a greater reduction in COD at higher pH levels, which is due to the strong interaction effect between the pH and auxiliary oxidant parameters Figure 4.

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