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Ultraviolet Photocatalytic Treatment of Petroleum Refinery Wastewater: A Case Study of Azzawiya Refinery, Libya

Abdulbasit M. Abeish
Petroleum Department-Engineering Faculty/ Gharyan University

* Corresponding Email: ***abdulbasitabeish@gmail.com***

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Abstract

Petroleum refinery wastewater contains complex mixtures of refractory organic and inorganic contaminants that are difficult to remove using conventional treatment technologies. This study investigated the feasibility of ultraviolet (UV)-assisted photocatalytic oxidation using zinc oxide (ZnO) as a photocatalyst for the treatment of wastewater collected from the Azzawiya Oil Refinery, Libya. Wastewater samples obtained after the API oil separator were characterized based on pH, chemical oxygen demand (COD), and turbidity. The photocatalytic performance was evaluated by examining the effects of ZnO dosage, solution pH, ferrous ion (Fe^{2+}) concentration, and ferric ion (Fe^{3+}) concentration on COD removal under UV irradiation. Experimental results demonstrated that photocatalytic efficiency was strongly influenced by the operating conditions. The optimum treatment performance was achieved using a ZnO dosage of 0.6 g L^{-1} at pH 5. The addition of iron ions further enhanced the degradation process by suppressing electron–hole recombination and promoting hydroxyl radical generation. The highest COD removal efficiency of 78.41% was obtained at a ferrous ion concentration of 10 mg L^{-1}, while ferric ions achieved a maximum COD removal of approximately 73% at an optimum concentration of 15 mg L^{-1}. The proposed degradation pathway indicated that aromatic hydrocarbons and phenolic compounds were progressively oxidized into intermediate products before complete mineralization into carbon dioxide and water. Overall, the findings demonstrate that UV/ZnO photocatalysis, particularly when enhanced with ferrous ions, represents an effective advanced oxidation process for improving the quality of petroleum refinery wastewater and offers considerable potential as a polishing treatment for refinery effluents.

Key Words: Petroleum refinery wastewater, photocatalysis, COD .

1. Introduction

The Azzawiya Refinery is the largest oil refinery in Libya and one of the country's most important petroleum-processing facilities. It is located in the coastal city of Azzawiya, approximately 50 km west of Tripoli, and is operated by the National Oil Corporation through the Azzawiya Oil Refining Company. The refinery was commissioned in the 1970s and was designed to process crude oil produced from Libya's major oil fields Figure 1.1. It has a refining capacity of approximately 120,000 barrels of crude oil per day, although actual

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production may vary depending on operational and economic conditions. The refinery produces a range of petroleum products including gasoline, diesel fuel, liquefied petroleum gas (LPG), jet fuel, fuel oil, and asphalt [1].


Figure 1 Azzawiya Oil Refinery

Like many petroleum refineries, the Azzawiya Refinery generates industrial wastewater containing hydrocarbons, phenolic compounds, suspended solids, sulfides, ammonia, and other organic contaminants. Therefore, wastewater treatment systems are employed to reduce pollutant concentrations before discharge, helping to minimize environmental impacts on nearby coastal and terrestrial ecosystems. Refinery operations generate substantial quantities of wastewater originating from crude oil processing units, tank farms, cooling systems, equipment cleaning, storm water runoff, and utility operations. This wastewater contains a variety of contaminants including free and emulsified oils, suspended solids, phenolic compounds, hydrocarbons, sulfides, ammonia, and other organic pollutants [2]. To comply with environmental regulations and minimize impacts on the Mediterranean coastal environment, the refinery employs a multi-stage wastewater treatment system Figure 2.

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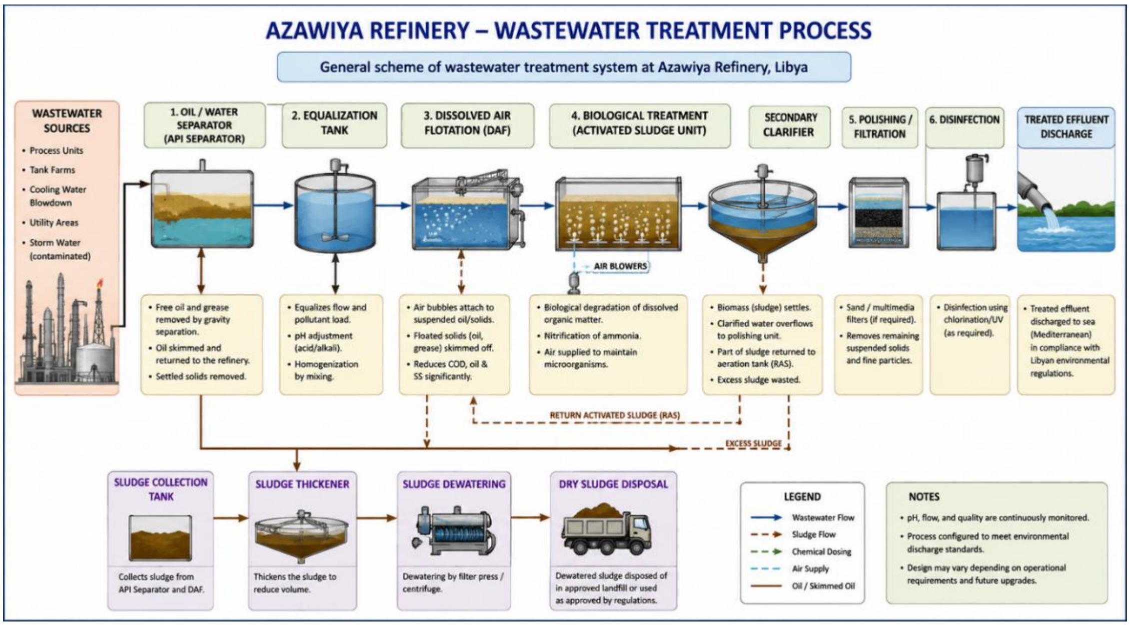

Figure 2 schematic diagram showing the wastewater treatment process at Azzawiya Refinery (oil separator → equalization tank → dissolved air flotation → biological treatment → polishing unit)

The first stage of treatment involves the removal of free oil and grease using an American Petroleum Institute (API) separator Figure 3. Wastewater enters large gravity-separation basins where the density difference between oil and water allows oil droplets to rise to the surface while heavier solids settle at the bottom. The recovered oil is collected and returned for reprocessing, while settled sludge is removed for further handling.

Figure 3 American Petroleum Institute (API) separator at Azzawiya Refinery

Following primary separation, wastewater is directed to an equalization tank. This unit serves to homogenize wastewater characteristics, equalize flow rates, and reduce fluctuations in pollutant concentrations. The pH may also be adjusted in this stage to provide suitable conditions for downstream treatment processes. The equalized wastewater is then treated in a Dissolved Air Flotation (DAF) unit. Fine air bubbles are introduced into the wastewater, attaching to suspended oil droplets and solid particles. These particles float to the surface where they are removed mechanically. The DAF process significantly reduces oil content, suspended solids, and part of the chemical oxygen demand (COD) [3]. After physical treatment, the wastewater undergoes biological treatment in activated sludge reactors. In this stage, aerobic microorganisms degrade dissolved organic contaminants by converting them into carbon dioxide, water, and microbial biomass [4]. Aeration systems continuously supply oxygen to maintain microbial activity and enhance the degradation of biodegradable pollutants. Before discharge, the treated wastewater may undergo disinfection using chlorination or ultraviolet (UV) irradiation. This step reduces pathogenic microorganisms and ensures compliance with environmental discharge standards. The treated effluent is continuously monitored for key parameters such as pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD), total suspended solids (TSS), oil and grease, and phenolic compounds [5,6]. Once regulatory requirements are met, the treated water is safely discharged or reused for selected industrial purposes. Sludge generated from the API separator and biological treatment process is collected and transferred to sludge thickening and dewatering units. Mechanical dewatering methods such as filter presses or centrifuges are commonly employed to reduce sludge volume before final disposal or further treatment. The raw effluent characterization and their suggested limitations standards that should be followed by petroleum refineries such as Chemical Oxygen Demand (COD) and Phenols are shown in Table 1 [7, 2, 8].

Table 1 Typical Characteristic of raw petroleum refinery effluent and their limitations

Parameter	Symbol	Raw effluent(mg/L)	Limit (mg/L)
Chemical oxygen demand	COD	850-1020	100-200
Biochemical oxygen demand	BOD_5	570-600	50-100
Total petroleum hydrocarbon	TPH	50-100	15-30
Phenols	Ph	98-120	0.1-5.0
pH	pH	8.0-9.3	7.0-8.0

Petroleum refinery wastewater typically contains elevated concentrations of organic and inorganic pollutants. Important quality indicators include chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), total petroleum hydrocarbons (TPH), phenols, and pH.

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Raw refinery effluents often exceed recommended discharge limits, making advanced treatment technologies necessary. Effluent in the Azzawiya refinery can be generated by the following ways:

- Crude oil which contains significant amounts of water coming from drilling processes. This water has to be extracted before the crude oil can be fed to the refining units.
- Washing the holds of the ships that deliver crude oil to the refinery.
- Refining processes that use massive amounts of water to produce the final products.
- The sealed surfaces that collect storm water during rainfall seasons which have potential to be contaminated.

Therefore, the present study aims to characterize the physicochemical properties of Azzawiya Refinery wastewater and assess the feasibility of UV photocatalytic degradation as an advanced treatment technology. Particular emphasis is placed on evaluating the effects of critical operating parameters, such as photocatalyst dosage, pH, and metal ions concentrations, on degradation performance. In addition, a reaction pathway is proposed is performed to provide a comprehensive understanding of the photocatalytic oxidation mechanism.

2. Material and Methods

2.1 Sample Collection

All samples were collected from Azzawiya refinery after API separator and kept at 5^0C, the regular experiments were carried out under different conditions. The collected samples from the refinery were physically and chemically checked in order to measure some key parameters.

2.2 Preliminary Characterization

Samples collected from the refinery were analyzed for pH, chemical oxygen demand (COD), and turbidity. The wastewater exhibited alkaline conditions (pH 8–9.5), which is slightly high due to the high concentration of organic compounds in the effluent, and elevated COD values near 880 mg/L. This factor can provide a significant indication for the degree of photocatalytic degradation of petroleum refinery effluent, therefore; the COD removal efficiency was used as an indicator to monitor all degradation profiles of the real effluent samples. The dark brown appearance of the effluent corresponded to noticeable turbidity caused by suspended and dissolved matter which gave the effluent high turbidity about 7.9 mg/L.

2.3 UV Photocatalytic Experiments

Photocatalytic degradation experiments were performed in a laboratory-scale batch reactor

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under ultraviolet (UV) irradiation. A 250 mL glass beaker was used as the reaction vessel, with zinc oxide (ZnO) serving as the photocatalyst and a UV lamp (212 nm) providing the irradiation source, as illustrated in Figure 4.

Figure 4 UV Box of the Treatment

The effects of key operational parameters, including photocatalyst dosage, solution pH, ferrous ion (Fe^{2+}) concentration, and ferric ion (Fe^{3+}) concentration, were systematically investigated to determine the optimum conditions for the photocatalytic treatment process.

3. Results and Discussion

3.1 Effect of Photocatalyst Loading

Increasing ZnO dose from 0.3 to 0.8 g/L at natural pH (9) significantly improved pollutant degradation due to the availability of more active adsorption sites and enhanced hydroxyl radical (•OH) generation [9, 10]. Figure 5. Beyond 0.6 g/L, degradation efficiency declined because excessive catalyst concentrations increased suspension turbidity and reduced light penetration [11]. Therefore, 0.6 g/L was identified as the optimum catalyst dosage.

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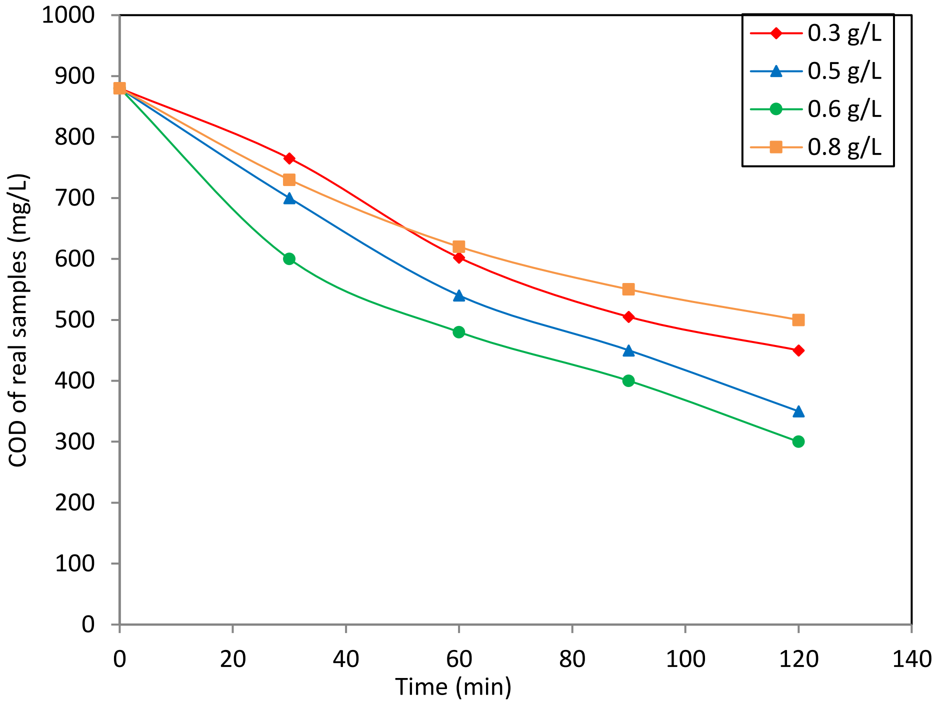

Figure 5 Influence of ZnO doses on UV oxidation of petroleum refinery effluent

3.2 Effect of pH

The solution pH strongly influenced photocatalytic performance. Based on the pH, the photocatalyst surface will be either charged positively (for pH < pzc) or negatively (for pH > pzc), or neutral (for pH ≈ pzc) [12, 11]. This pH mechanism significantly affects the adsorption and desorption of pollutants on the ZnO surface. To study the influence of pH on the photocatalytic degradation, set of experiments were carried out at various pH values, ranging from 3 to 9 using the optimum concentration ZnO (0.6 g/L) as shown in Figure 6. Some literature stated that ZnO surface has the net positive charge at low pH value, while the organic compounds such as chlorophenols are mainly negatively charged. Consequently, at low pH values the adsorption of pollutants on ZnO active sites can be significantly enhanced leading to increase in degradation rates. Maximum degradation occurred at pH 5, where favourable electrostatic interactions enhanced adsorption of contaminants onto the ZnO surface. Both highly acidic and alkaline conditions resulted in lower degradation efficiencies.

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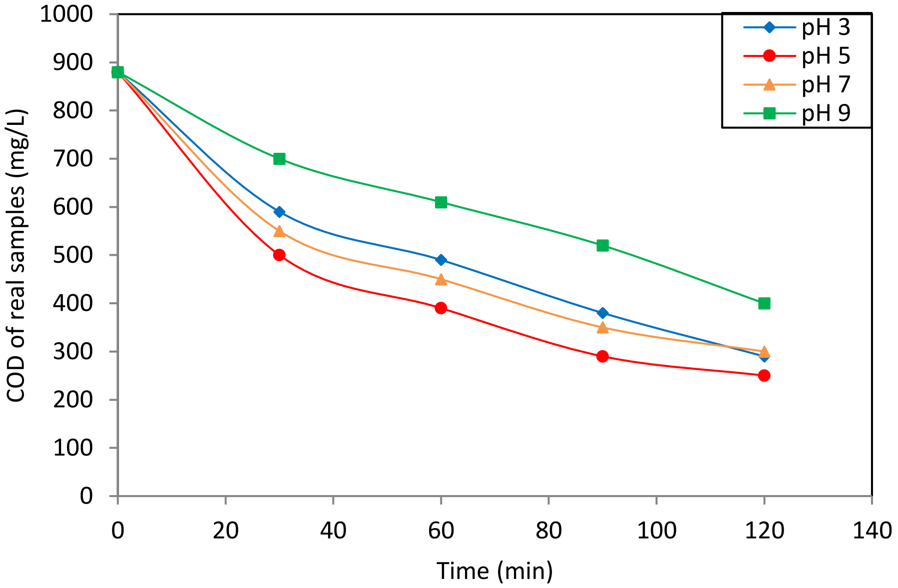

Figure 6 Influence of pH on the on UV oxidation of petroleum refinery effluent (0.6 mg/L ZnO)

3.3 Effect of Ferrous Ions

The addition of Fe^{2+} ions improved photocatalytic oxidation by reducing electron–hole recombination and promoting hydroxyl radical [12]. The highest COD removal (78.41%) was obtained at 10 mg/L Fe^{2+} Figure 7. Further increases in iron concentration negatively affected performance due to increased recombination effects.

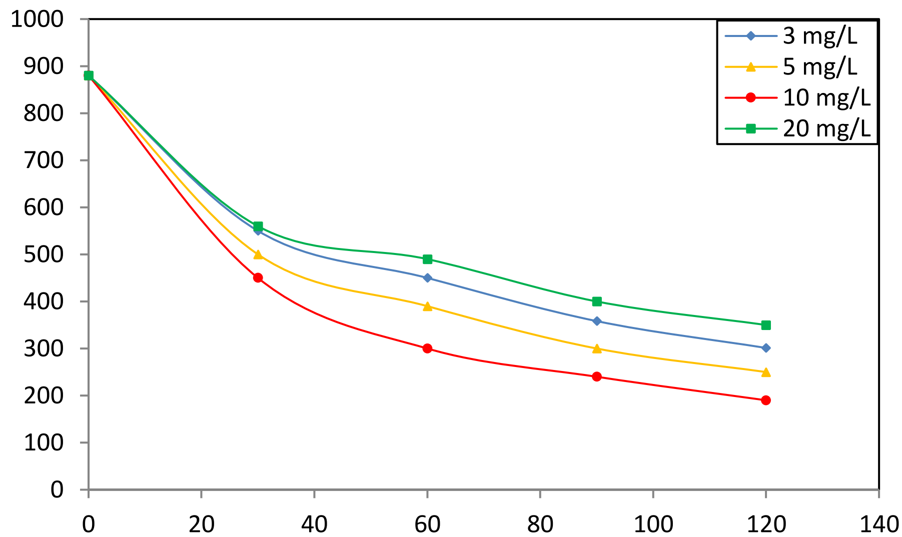

Figure 7 Influence of Fe^{2+} ions the on UV oxidation of petroleum refinery effluent (0.6 g/L ZnO, pH = 5)

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3.4 Effect of Ferric Ions

Ferric ions also enhanced degradation efficiency due to their ability to reduce the e-¬ /h+ recombination by trapping the electrons. The optimum Fe^{3+} concentration was found to be 15 mg/L Figure 8. Although ferric ions improved treatment performance (73% COD removal), ferrous ions produced slightly higher degradation rates under similar operating conditions. However, both of them can be considered as effective enhancers for solar photocatalytic degradation of petroleum refinery effluent.

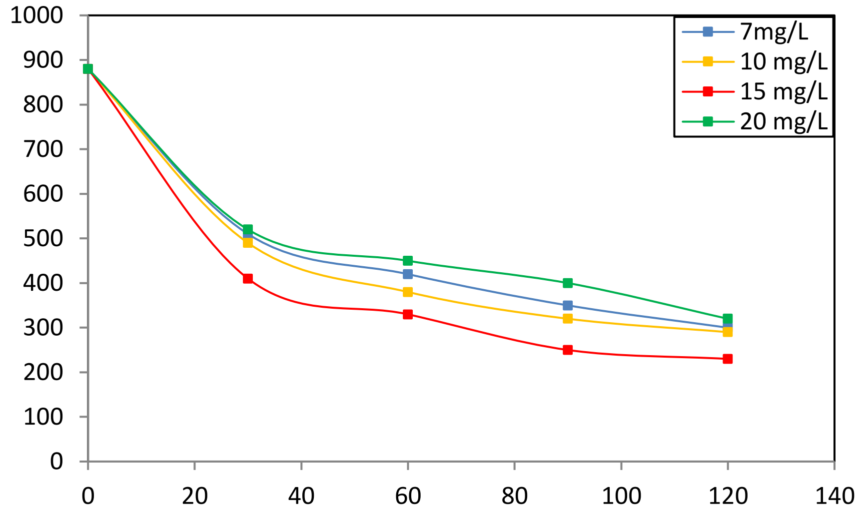

Figure 8 Influence of Fe^{3+} ions on UV oxidation of petroleum refinery effluent (0.6 g/L ZnO, pH=5)

3.5 Reaction Pathways

A raw petroleum refinery effluent consists of oil, grease, chlorides, ammonia, sulphides, phenols, chlorophenols and many other various organic compounds. In fact, COD degradation measurement gives only a general picture about the quality of treatment. Therefore, it is hard to know the reaction pathway of each pollutant present in the effluent and the final compounds produced. Photocatalytic oxidation proceeds primarily through attack by hydroxyl radicals. Aromatic hydrocarbons and chlorophenols are transformed into intermediate compounds such as phenol, catechol, hydroquinone, benzoquinone, and organic acids before eventual mineralization to carbon dioxide and water. For instance, benzene react with •OH radicals generating phenol and then converts to dihydroxybenzenes which has two hydroxyl groups substituted onto a benzene ring such as catechol, hydroquinone, and resorcinol [13]. Xylene which usually presents in petroleum refinery effluent can be oxidised to primary compounds such as methylbenzene and benzoquinone which convert to carboxylic acids such as oxalic and malonic acids [14].

4. Conclusion

This study demonstrated the effectiveness of UV/ZnO photocatalytic oxidation as an advanced treatment technology for petroleum refinery wastewater collected from the Azzawiya Oil Refinery, Libya. The wastewater exhibited high organic pollution, characterized by elevated COD and alkaline pH, indicating the need for further treatment beyond conventional refinery processes. The photocatalytic degradation efficiency was found to depend strongly on operating conditions, including catalyst dosage, solution pH, and the presence of transition metal ions. Among the investigated parameters, a ZnO dosage of 0.6 g L^{-1} provided the highest photocatalytic activity, while further increases in catalyst loading reduced treatment efficiency because of light scattering and reduced UV penetration. Acidic conditions significantly enhanced the oxidation process, with optimum degradation occurring at pH 5 owing to improved adsorption of pollutants onto the ZnO surface and increased hydroxyl radical formation. The addition of iron ions further improved photocatalytic performance by reducing electron–hole recombination. Ferrous ions exhibited superior catalytic activity compared with ferric ions, producing a maximum COD removal efficiency of 78.41% at 10 mg L^{-1}, whereas ferric ions achieved approximately 73% COD removal at an optimum concentration of 15 mg L^{-1}. Future research should investigate the mineralization efficiency using total organic carbon (TOC) analysis and identify degradation intermediates through chromatographic techniques.

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