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Photocatalytic treatment of petroleum refinery wastewater by ZnO nanoparticles immobilized on a concrete substrate

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Abstract

The petroleum industry's operations often involve substantial water usage, resulting in vast quantities of contaminated water, with a volume of the polluted water body estimated as about half the quantity of oil utilized in the refinement process. This wastewater contains various substances that are harmful to the health and environment, including hydrocarbons, heavy metals, and other toxic chemicals. This research aims to explore photocatalytic synthesis of zinc oxide nanoparticles to treat oil refinery wastewater. The effectiveness of this approach will be assessed by measuring the rate of Chemical Oxygen Demand (COD) reduction while identifying the best conditions to achieve the best performance and maximizing energy efficiency. Various operational conditions that drive the influence on the wastewater treatment process were investigated, including pH of 3, 5, 7, and 9, flow rate of 0.25, 0.5, 0.75, and 1.0 l/min, and the amount of the photocatalyst used per unit area (20, 40, 60, 80, 100 g/m^2). Under optimum conditions, the photocatalytic method was applied with the following parameters: a COD of 1278 mg/l, a pH level of 7, a catalyst density of 80 g/m^2, an effluent flow of 0.25 l/min, an irradiation power of 65 W, and an airflow of 100 cubic centimeters per minute. After 120 minutes, the COD reduction efficiency reached 76%, requiring energy consumption of 173.4 kW.hr/m^3.

Keywords: photocatalytic; immobilization; COD removal; ZnO nanoparticles; wastewater.

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1- Introduction

Water is indispensable for life, as every organism requires it as a necessity. Rapid industrial and economic expansion has driven a significant rise in population, and development has essentially led to the generation of an increasing amount of wastewater [1-2]. Industrial zones in particular consistently generate large quantities of wastewater at high rates and often dispose of it without proper management or treatment [3]. Petroleum refineries are among the vital industries that produce wastewater loaded with various amounts of organic and inorganic contaminants [4]. The organic and inorganic pollutants could include sulfides, phenol, BTEX, hydrocarbons, and heavy metals [5]. PRWW treatment generally involves two primary stages: the pretreatment phase, aims to reduce contaminants like oil, grease, and suspended solids, followed by the pollutant degradation stage to achieve acceptable discharge levels [6-8]. Techniques like filtration, adsorption, coagulation, membrane, advanced oxidation processes (AOPs), and chemical oxidation are commonly used [8-12]. Typically, the effectiveness of these treatments is measured by their ability to remove oils, grease, phenols, sulfates, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), and heavy metal concentrations [13-15]. Consequently, advanced oxidation processes like photocatalysis and Fenton oxidation are increasingly favored due to their effectiveness in eliminating stable petroleum pollutants [16-19]. Recent advances in treatment technologies can be attributed to significant progress in material science, which has enhanced the approach to addressing emerging contaminants [3].

Photocatalysis is currently recognized as one of the most sophisticated and eco-friendly methods due to its ability to break down the organic pollutants in different types of wastewaters [20]. A photo-catalyst is typically described as a substance, typically metal oxides such as titanium oxide (TiO_2), that can break down harmful substances when exposed to sunlight, including UV rays [21]. The process involves exciting electron pairs in the valence band using UV light. This excitement leads them to absorb energy higher than the band gap energy. Consequently, this process creates a vacancy in the valence band (h^+) and simultaneously produces an electron (e^-) in the conduction band, the hole (h^+) and electron (e^-) species will subsequently interact with water or oxygen molecules to form hydroxyl (OH^-) or peroxide radicals, which can break down or decompose organic

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compounds [21-22]. The photolytic activity inherent in photocatalysis is initially triggered when the semiconductor absorbs energy that is equal to or greater than the semiconductor's band gap, exemplified by materials like TiO_2 [23]. The method functions by creating holes in the catalysts, which then produce highly reactive hydroxyl radicals with significant redox potentials, including $•O_{2-}$, H_2O_2, and $•O_2$. These radicals play a crucial role in the mechanism of the photocatalytic reaction [24]. Utilizing photocatalysis has become advanced, practical, and efficient for treating wastewater to break down organic pollutants [24-25]

Zinc oxide (ZnO) is an inorganic, slightly water-soluble semiconductor material that exists in the form of a white powder. It is an essential and superior alternative to TiO_2 in photocatalytic applications due to its non-toxic nature, low cost, and high response efficiency. Previous studies have shown that the effectiveness of ZnO is higher than that of titanium dioxide [23]. However, there is a similarity in the photocatalytic properties of both materials due to the similarity of the electronic structure, e.g., the band gap (eV). In addition, ZnO has a broad ability to capture the spectrum of solar radiation compared to TiO_2, in addition to its lower cost, which makes it more widely used in photocatalytic applications compared to other semiconductors, especially TiO_2 [26-27].

Photocatalysts come in different forms depending on the type of application; for example, they can be in a powder form, thin films, or other shaping structures [28]. The nano-sized photocatalysts have faster reaction rates compared to their bulk counterparts, attributed to their smaller dimensions and larger surface area [29]. However, utilizing nanoparticles for treating wastewater and breaking down pollutants is challenging due to the quick recombination losses and insufficient use of the solar spectrum [30]. The equations below show the mechanics of the advanced oxidation process (photo/metal oxide (MO)):

Starting reaction:

$$MO + h\nu \rightarrow MO\ (h^+ + e^-) \quad (1)$$

Oxidative reactions

$$h^+ + H_2O \rightarrow H^+ + •OH \quad (2)$$

$$2\ h^+ + 2\ H_2O \rightarrow 2\ H^+ + H_2O_2 \quad (3)$$

$$H_2O_2 \rightarrow 2\ •OH \quad (4)$$

Reductive reactions

$$e^- + O_2 \rightarrow •O_2^- \quad (5)$$

$$O_2^- + H_2O + H^+ \rightarrow H_2O_2 + O_2 \quad (6)$$

$$H_2O_2 \rightarrow 2\ •OH \quad (7)$$

This study aims to apply a photocatalytic method by using a novel approach designed for a photoreactor to treat wastewater produced by oil refineries. The novelty is based on adopting an innovative approach that involves introducing pollutants into the reactor with a 3 mm thick flow layer, facilitating the passage of ultraviolet rays and easy access to the catalyst surface, increasing treatment efficiency, and reducing processing time compared to previous studies. For this purpose, biosynthetic nano-zinc oxide immobilized onto a concrete surface was utilized, alongside ultraviolet light as the radiation source.

2- Experimental work

2.1. Wastewater characterization

In this study, wastewater from the Al-Diwaniyah oil refinery in Iraq served as a sample for research and investigation. The sample contained a mixture of heavy and light hydrocarbons and was collected prior to biological treatment. Its characteristics are outlined in Table 1.

Table 1. Qualities of effluents from Al-Diwaniyah oil refiner

Parameter	pH	COD (mg/l)	Turbidity (NTU)	Conductivity (mS/cm)	Phenol (mg/l)	T.D.S. (mg/l)	SO_4^{-2} (mg/l)	Cl^- (mg/l)
value	7	1278	25.6	11.5	13.6	4575	122	2055

2.2. Photo system

The photocatalytic reactor was designed as a water conduit, depicted in Fig. 1. The photoreactor is constructed from Calvinize, a material known for its resistance to corrosion, and measures 90 cm × 11 cm × 10 cm. The entire reactor's surface was illuminated by a 65 W UVC lamp, measuring 90 cm in length, positioned 5 cm above the wastewater surface. The rate at which the wastewater enters the reactor was maintained at 0.25, 0.5, 0.75, and 1.0 l/min, and the layer of contaminated water in motion measured 3 mm in thickness, while the dimensions of the concrete layer measured 900 cm^2 in surface area and 3 cm in thickness. Previous studies have led to the selection of a specific concrete blend designed (ASTM C457-1992) to support the adherence of nano-zinc oxide particles on its surface [31]. Ultimately, every element that impacts the functioning of the photocatalytic reactor has been stabilized. Table 2 shows the hydraulic and volumetric characteristics of the reactor.

Fig. 2 shows the photolysis semi-batch (recycling) setup used for the wastewater treatment. This system comprises a photoreactor linked to a 1.25-liter reflux tank. It also includes a pulse pump (type HYBL5LNPVF001, Italy) and a recycling pump, each with a capacity to circulate 1.0 l/min, aimed at moving and recycling contaminants. These pumps are connected

to a tank that circulates the solution to maintain uniformity of the waste, ensure the release of hydrogen gases, and prevent foaming. Additionally, an air pump (model-ACO-208, 45W China) is attached to the circulation tank to saturate the solution with oxygen for the completion of the photocatalysis process. Also included are a liquid flow meter (type-ZYIA, 0.25–1.0 l/min), an air flow meter (0-500 ml/min), and various valves intended for different functions. An electronic pH meter was employed to ascertain the pH levels of the electrolyte (type - PH211, HNNA Instrument Inc., Romania).

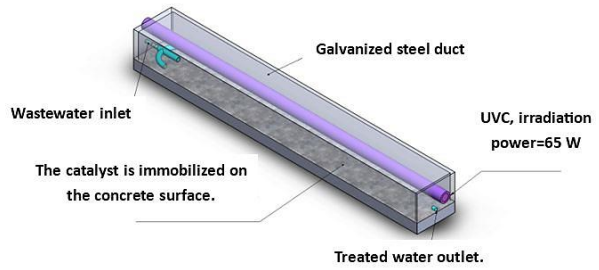

Fig. 1. Schematics of the photoreactor show the structure and the wastewater flow

Table 2. The hydraulic and volumetric properties of the reactor

Parameters	Value
Reactor's effective capacity (cm^3)	270
Effluent rate (l/min)	0.25-1.0
Thickness of the flow layer (mm)	3
reactor slope	0.1
Distance of the UV Lamp (cm)	5

Operational tasks involve connecting the photoreactor to a DC power supply (UNI-T, UTP3315TFL-II, China). To sustain the system's efficiency, the floor of the photoreactor is meticulously cleaned. All experiments were performed at an ambient temperature of 25 °C.

Following the assessment of acidity with 1M HCl or 1M NaOH, 1.25 liters of wastewater were transferred to the reservoir. At fixed intervals, samples were extracted for analysis. The samples were filtered using filter paper to eliminate any suspended particles and left to settle for 24 hours. To determine the Chemical Oxygen Demand (COD), measurements were taken every 15 minutes throughout the treatment using a thermos-reactor (Model: RD-125) and a spectrophotometer (Model: MD-200), both provided by Lovibond. Each run included three COD measurements, and the average was used for this study.

2.3. Experiments and analytical methods

In the method of photocatalysis, the use of energy is a crucial factor, as it depends on electrical power. Therefore, assessments were conducted to analyze energy consumption and to decrease the COD to determine the optimal conditions. The efficiency of COD elimination was calculated as follows [32]:

$$RE= (CODo - COD)/(CODo)*100 \quad (8)$$

Where the term RE is the efficiency of reduction, COD_o is the initial chemical oxygen demand, measured in milligrams per liter (mg/L), and COD is the chemical oxygen demand measured after the initial assessment, also in milligrams per liter (mg/L).

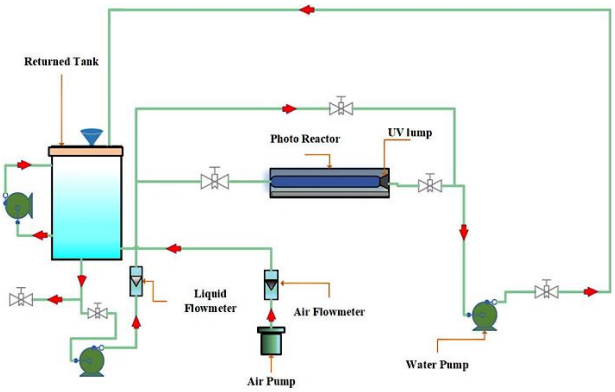

Fig. 2. Schematics showing the process flow diagram including the water tank, photoreactor, pumps, valves, and flow meters

The calculation of energy usage, measured in kilowatt-hours per cubic meter of eliminated COD, is calculated as follows [33].

$$EEC = \frac{P*t*1000}{V*\log(\frac{COD_0}{COD})} \quad (9)$$

In this context, it refers to the specific energy consumption. P is the electrical power, which is measured in kW, t is the time duration of the reaction, in hours (hr.), V is the the volume of wastewater in liters (L).

3- Result and discussion

Fig. 3 shows the effectiveness of COD reduction using photocatalytic techniques. The setup for the photocatalytic process included a catalyst at a concentration of 80 g/m^2 (29.63 g/l), airflow maintained at 100 ml/min, wastewater flow rate at 0.25 l/min, a 65W- UVC lamp, and a neutral pH of 7. Fig. 3 shows that photocatalytic treatment succeeded in lowering COD from an initial level of 1278 mg/L to a final value of 306 mg/L to obtain a reduction efficiency of 76% over a period of 120 minutes.

3.1. Effect of pH

The pH level is crucial to determining the effectiveness of the methods for removing contaminants from oil refinery wastewater, particularly its impact on the photocatalytic of oil-based pollutants. Four separate tests were performed, each at different pH levels (3, 5, 7, 9).

According to Fig. 4, the rates of pollutant reduction in these tests were 65%, 70%, 76%, and 72% for pHs 3, 5, 7, and 9, respectively. The most effective reduction occurred at a pH of 7, a finding that aligns closely with results obtained at a pH of 8 in the presence of nano-zinc oxide [34]. These observations suggest that zinc oxide is positively charged at around a pH of 7 but exhibits a negative or slightly positive charge on the catalyst's surface when the pH is below or above 7. For the contaminants in the oil refinery wastewater, pH plays an essential role in the effectiveness of the processes used to reduce pollutants from oil refinery wastewater, especially its direct effect on the photocatalytic process to treat such oil pollutants. Four experiments were conducted with a different pH for each of them (3, 5, 7, 9). As Fig. 4 shows, the reduction for these experiments reached 65%, 70%, 76%, and 72% at pH of 3, 5, 7, and 9, respectively. The highest efficiency was at a pH of 7, and this result is very close when using a pH of 8 in the presence of nano-zinc oxide [34]. This result gives a clear indication that zinc oxide has a positive charge at a pH of around 7. The pollutants present in oil refinery wastewater are ionized due to the presence of the hydroxyl ion and thus have a negative charge, while the surface of the catalyst carries a positive charge, so attraction occurs between the pollutants and the catalyst, which leads to the removal of the pollutants [35].

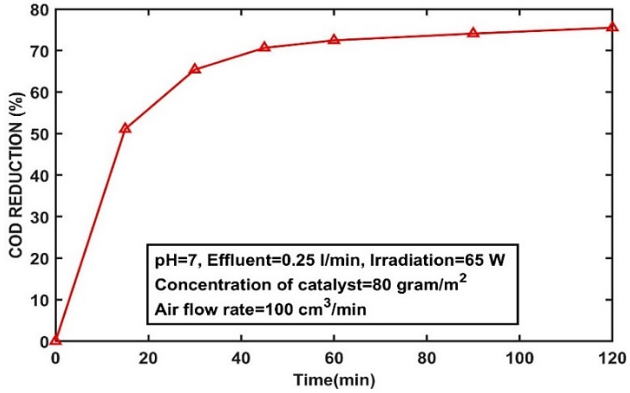

Fig. 3. COD reduction (%) vs. time for the photocatalytic processes at optimum conditions

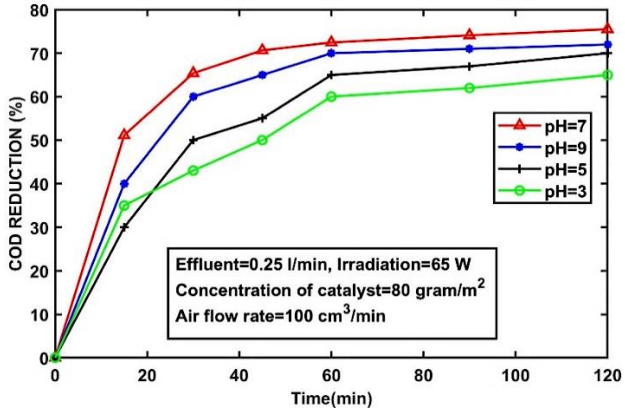

Fig. 4. COD reduction (%) vs. time at different pH

3.2. Effect of catalyst density

In the experimental setup to measure the effectiveness of nano-zinc oxide in a photoreactor, various concentrations were tested by applying the catalyst at five different surface densities: 20, 40, 60, 80, and 100 grams per square meter. The corresponding reduction efficiencies recorded were 61%, 65%, 71%, 76%, and 74%, as depicted in Fig. 5. Analysis of the data revealed that the optimum catalyst density for maximum reduction efficiency was 80 g/m². It was observed that removal efficiency improved with an increase in catalyst density up to 80 g/m² due to a higher number of catalyst particles [35]. However, further increasing the density beyond 80 g/m² resulted in reduced efficiency, attributed to particle overcrowding, which diminished the effective surface area available for the reaction [36].

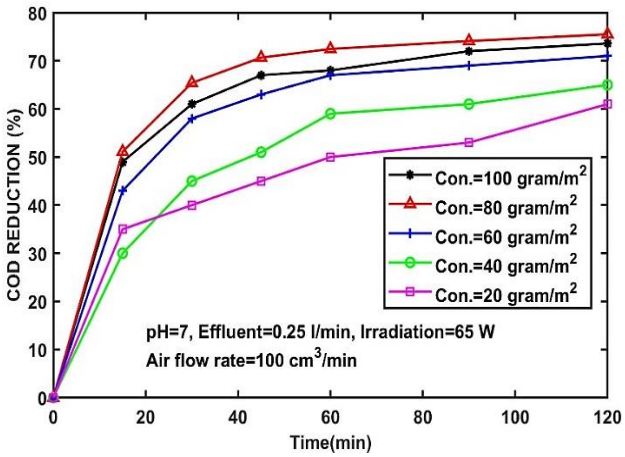

Fig. 5. COD reduction (%) vs. time at different concentrations of catalyst

3.3. Effect of flow rate

Research was conducted to explore how different flow rates affect the rate at which pollutants are reduced. Four separate experiments were set up, each utilizing a distinct flow rate within the parameters of 0.25, 0.50, 0.75, and 1.0 l/min. According to the data presented in Fig. 6, the optimum reduction of pollutants occurred at the lowest flow rate of 0.25 l/min. It was observed that an increase in flow rate resulted in a diminished reduction rate. This phenomenon can be attributed to the decreased residence time of the treatment within the reactor, which was recorded as 1.068, 0.534, 0.356, and 0.276 minutes, corresponding to the flow rates of 0.25, 0.50, 0.75, and 1.0 l/min, respectively. This study is unique as there are no prior studies that have specifically focused on the impact of flow rate on the efficiency of pollutant reduction.

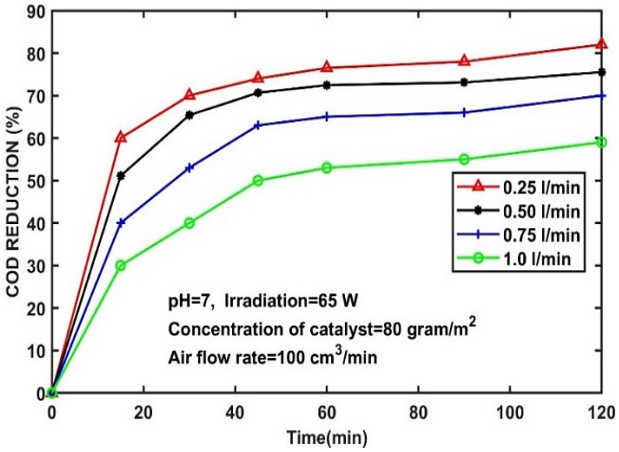

Fig. 6. COD reduction (%) vs. time at different flow rates

To assess the validity of our study, we compared our research findings with those of earlier studies, aiming to verify the accuracy and relevance of our results. This comparison allowed us to assess the reliability of the present study outcomes within the context of existing knowledge in the field.

Ghasemi and colleagues [37] investigated the treatment of PRWW using photocatalytic breakdown with a TiO_2/Fe-ZSM-5 photocatalyst. The Fe-ZSM-5 zeolite was created through a sol-gel process, resulting in a specific surface area of 304.6 m^2/g and 29.28% TiO_2 loading. The study achieved approximately 80% COD reduction under specific conditions: pH 4, photocatalyst concentration of 2.1 g/L, and UV exposure at 45°C for 240 minutes. Another study investigated the efficacy of the photocatalytic technique for treating oil refinery wastewater, employing TiO_2 as a catalyst [38]. They utilized a 400-watt UV-C lamp as the light source, with experimental conditions set at a pH of 3, catalyst concentration of 100 mg/L, and temperature of 45°C. The results showed that the Chemical Oxygen Demand (COD) reduction rate from the wastewater was about 76% after 120 minutes and 72% after 90 minutes of treatment [38]. A circular photoreactor was also used to process refinery wastewater under optimized conditions. These included a pH of 3, a temperature of 318 K, and a titanium dioxide concentration of 100 mg/L. The light source consisted of a UV lamp with 400 watts of power, emitting wavelengths between 200 and 500 nm. The treatment duration was set at 240 minutes. The outcome demonstrated an approximate 90% reduction in Chemical Oxygen Demand (COD) [39].

The results of our study showed agreement with previous studies, and there may be a slight difference due to the difference in the method of using the catalyst with the difference in the operating conditions used in this study (pH, catalyst density, light intensity, and flow rate).

3.4. Assessment of energy consumed

The photocatalytic method was used to treat a sample of wastewater generated from the Diwaniyah refinery. The treatment time was about 120 minutes; this specific time resulted in an energy consumption of about 173.74 kWh/m^3.

3.5. Photocatalysis kinetic analysis

The adsorption capacity data gathered from experiments was utilized to determine the correlation factor. This calculation aimed to assess how well the data aligned with two relationships: the pseudo first-order model, known as Lagergren's rate law (Eq. 10), and the pseudo second-order rate law (Eq. 11) [40-41].

$$\ln(q_e - q_t) = \ln(q_e) - K_1 t \quad (10)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^{\,2}} + \frac{t}{q_e} \quad (11)$$

q_t and q_e are the adsorption capacities (mg/g), representing the amount of COD adsorbed per unit mass of ZnO at time t and at equilibrium, respectively. The pseudo-first-order rate constant (min^{-1}) is symbolized by K_1, while K_2 signifies the pseudo-second-order rate constant (g/(mg.min).

The Fig. 7 presented in Fig. 7a and Fig. 7b indicate a correlation coefficient of 0.65 for the pseudo-first-order equation and 0.914 for the pseudo-second-order equation, respectively. These visual representations highlight the disparity in correlation between the two equations. Consequently, the pseudo-second order equation was selected to represent the reaction kinetics.

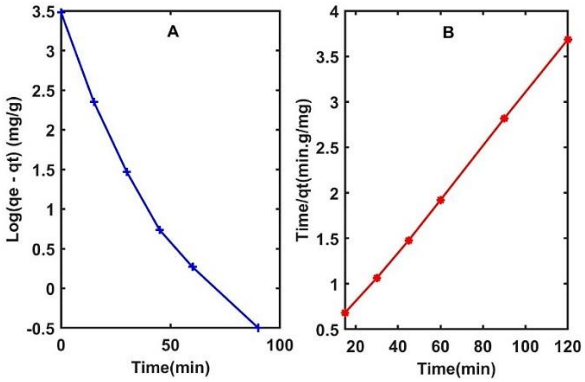

Fig. 7. Data of actual vs. time, (a) pseudo-first-order model, (b) pseudo-second-order model

To find the constants of the equation representing the system (pseudo second order), the experimental data were plotted as shown in Fig. 8. In addition, the theoretical data were plotted for the purpose of comparison with the experimental data (Fig. 8). The calculation of constants is presented in Table 3.

Table 3. Coefficients calculated from practical data

Conc. of ZnO (g/m^2)	Conc. of ZnO (g/L)	Intercept (min.g/mg)	q_e (mg/g)	K_2 (g/mg.min)
80	29.63	0.681	34.96	1.4E-3

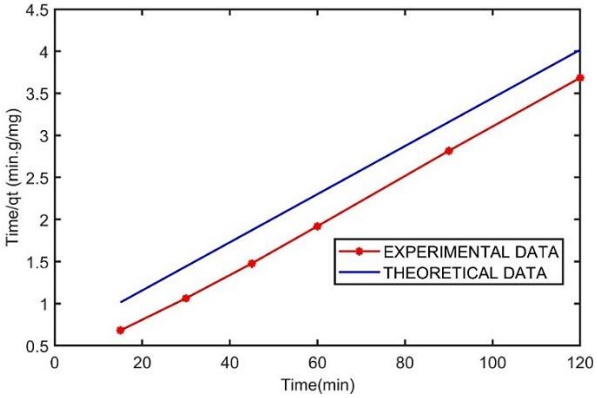

Fig. 8. Time/qt vs. time for experimental data and theoretical data

The pseudo-second order model was applied to adjust the kinetic data, yielding a constant k of 1.4E-3 g/mg.min from Fig. 8. This result suggests that the process can be classified as adsorption. The kinetic analysis for the previous studies indicates that the rate-limiting factor in the adsorption is the intraparticle diffusion process [42]. The accuracy of the kinetic model was assessed by comparing experimental data with the predictions of the proposed kinetic mathematical model, as illustrated in Fig. 8. This comparison strongly supports the selection of the second-order kinetic model, as its predictions closely align with the observed experimental results. Previous studies corroborate the present study findings, indicating that the reaction adheres to a pseudo second-order kinetic equation [43].

3.6. Comparison with previous works

Previous studies are listed in Table 4 that focused on the use of nano zinc oxide and others as a photocatalyst for wastewater treatment and immobilized on a concrete surface.

Table 4. Summary of previous works

Study Focus	Research Results	References
The removal of phenol from wastewater under various operating conditions, including pH, catalyst density (TiO_2), and irradiation source distance.	The results indicated that the best reduction rate was about 80% at pH 12, catalyst density about 75 g/m2, and the source distance had no noticeable effect with a treatment time of 4 hr.	[34]
Mahdia and colleagues conducted experiments on wastewater contaminated with diesel and crude oil using a photocatalytic method. They employed nano zinc oxide particles fixed on concrete surfaces as a catalyst. The researchers investigated various operational parameters, including pH levels (3, 5, 8.5, 11), catalyst concentration (20, 40, 60, 80, 100 g/m^2), and light intensity (16, 24, 32, 40 W).	The best reduction rate of about 67% was obtained at the following operating conditions: pH 5, catalyst density 80 g/m^2, radiation power 40 W with a treatment time of about 5 hours.	[37]
This research aims to investigate the efficacy of treating wastewater from oil refineries using a photocatalytic method. The process involves zinc oxide fixed on a concrete surface functioning as a catalyst. The study examines various operational parameters, including pH levels (3, 5, 7, 9), catalyst density (20, 40, 60, 80, 100 g/m^2), and flow rates (0.25, 0.5, 0.75, 1 l/min).	A reduction rate of about 76% was obtained at the following operating conditions: pH of 7, catalyst density of 80 g/m^2, flow rate of 0.25 L/min with a treatment time of 120 minutes.	Present work

3.7. Development and improvement

The present study enhanced and optimized the effectiveness of the photocatalytic method for addressing various pollutants, including cyclic compounds with poor light-transmitting properties that impede ultraviolet radiation from reaching the catalyst affixed to a concrete surface. This improvement was achieved by implementing a novel photoreactor design, utilized for the first time to process contaminants such as phenol. The innovative approach involved introducing pollutants into the reactor with a 3 mm thick flow layer, facilitating the passage of ultraviolet rays and easy access to the catalyst surface. This resulted in increased treatment efficiency and reduced processing time compared to previous techniques.

4- Conclusion

The results of this study show that employing concrete as an immobilization for the photocatalyst proves to be an efficient method for its application as flooring within the photoreactor. Under optimum conditions, which include a pH = 7 and a catalyst concentration of 80 g/m^2, a flow rate of 0.25 l/min, and irradiation power of 65 W, the photocatalyst method achieved a 76% removal rate through 120 minutes. The findings also revealed that when the catalyst exceeds 80 g/m^2, there is a decline in the efficiency of removal. Additionally, a slower wastewater flow rate enhances the effectiveness of the removal process. Finally, about 173. 72KWh/m^3 of energy was consumed for about 120 minutes.

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المعالجة الضوئية لمياه الصرف الصحي لمصافي البترول باستخدام جسيمات نانوية من أكسيد الزنك مثبتة على ركيزة خرسانية

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الخلاصة

غالبًا ما تنطوي عمليات صناعة النفط على استخدام كميات كبيرة من المياه، مما يؤدي إلى توليد مياه ملوثة. وحجم هذه المياه الملوثة كبير، حيث يصل إلى ما يقرب من نصف كمية النفط المستخدم في عملية التكرير. وتحتوي هذه المياه العادمة على مواد مختلفة ضارة بالبيئة، بما في ذلك المواد الهيدروكربونية والمعادن الثقيلة وغيرها من المواد الكيميائية السامة ويركز هذا البحث على استخدام طريقة التحفيز الضوئي باستخدام أكسيد الزنك النانوي المُصنَّع حيويًا لمعالجة مياه الصرف الصحي في مصافي النفط. سيتم تقييم فعالية هذا النهج من خلال قياس معدل تخفيض الطلب على الأكسجين الكيميائي (COD) مع تحديد أفضل الظروف لتحقيق أعلى أداء وتعظيم كفاءة الطاقة. في ظل الظروف المثالية، تم تطبيق طريقة التحفيز الضوئي باستخدام المعلمات التالية COD :بمقدار ١٢٧٨ مجم/لتر، ومستوى الرقم الهيدروجيني ٧، وكثافة المحفز ٨٠ غرامًا لكل متر مربع، وتدفق النفايات السائلة بمقدار ٠,٥ لتر في الدقيقة، وقدرة التشعيع بقوة ٦٥ واط، وتدفق هواء ١٠٠ سم مكعب في الدقيقة. وبعد مدة ١٢٠ دقيقة، وصلت كفاءة إزالة COD إلى ٧٦% ومعدل استهلاك الطاقة ٢٨,٤ كيلووات ساعةاكغم COD.

الكلمات الدالة: محفز، إزالة COD، محفز ضوئي، المياه الملوثة.