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A Comparative Study of Using Nano Tio_2 and Zno for COD Removal from Petroleum Refinery Wastewater by combining ElectroFenton Process and UV Photocatalysis

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Abstract

In this study, the efficiencies of two photo-catalysts in a hybrid process composed of electro-Fenton and photo-catalytic process used for treating petroleum refinery wastewater (PRW) were evaluated and compered. Effects of current density (5 and 10 mA/cm^2), photo-catalyst dosage (0.1 and 0.3 g/L), and Fe^{2+} concentration (0.1 and 0.2 mM) were considered. Results revealed that increasing current density has a positive effect on the removal of COD for both catalysts with higher removal obtained using ZnO catalyst. Increasing the dosage of catalyst has also a progressive effect on the removal of COD for both catalysts while increasing Fe^{2+} concentration has a positive effect on the removal of COD in case of using TiO_2 and a negative impact in case of using ZnO. The best removal efficiency (87.68%) corresponding to a final COD of 50 ppm can be obtained at a dosage of ZnO of 0.3g/ L, pH of 3, current density of 10 mA/cm^2 and Fe^{2+} concentration of 0.1 mM during 40 min in which an energy consumption of 20.88 $kWh/m^3$was required. In case of TiO_2 catalyst, removal of 83.99% can be obtained at TiO_2 dosage of 0.3g/ L, pH of 3, current density of 10 mA/cm^2 , and Fe^{2+} concentration of 0.2 mM during 40 min in which an energy consumption of 25.5$kWh/m^3$was required. This is an indication that ZnO has better photo-catalytic efficiency than TiO_2. However, both of catalysts have the ability to reduce the COD level below the limiting value (100 ppm) for discharging to environment.

Keywords: COD; Electro-Fenton; ZnO; Photo-catalysis; TiO_2.

1. Introduction

Petroleum refineries are substantial water consumers; the size and contaminant composition of refinery wastewater depends on the size of the refinery and the configuration of the process [1, 2]. Wastewater from oil refineries is classified as hazardous industrial waste because it contains toxic components such as hydrocarbons, phenols, and heavy metals [1, 2]. These toxic compounds harm and destroy plants, aquatic life, and water resources [1, 2]. Many processes can be used to treat wastewater in oil refineries, such as biological processes, membrane filtration, and coagulation/flocculation. Traditional treatment processes do not always meet legal standards for reuse or discharge into the environment [1, 2].

Recently, electrochemical processes have attained notable interest due to their advantages, including ambient operation conditions, scalability and easy performance. These processes are assumed to be capable of degrading various contaminants [3]. Electro-Fenton (EF) process is an electro-chemical treatment process in which Fe^{2+} is added externally and H_2O_2 is generated

at the cathode surface by the $2e^-$ reduction of O_2 (Eq. (1), then generating OH• and Fe^{3+} form the bulk reaction between Fe^{2+} with H_2O_2 (Eq. (2)) [4]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\bullet \quad (2)$$

Photo-catalysis has appeared as an encouraging process with its capacity to completely mineralize organic pollutants [5]. Photo-catalysis has several advantages such as the contaminants decomposing completely into CO_2 and H_2O, inexpensive, non-toxic, and recyclable used catalysts [5]. Zinc Oxide (ZnO) was widely utilized as a photo-catalyst due to its properties, which include a direct and wide band gap of 3.5eV, strong oxidation ability and It delivers more OH• than TiO_2 [5]. The degradation mechanism of photo-catalysts can be described as follows [6]:

$$TiO_2 + hv \text{ (energy from light)} \rightarrow e^- + h^+ \quad (3)$$

$$ZnO + hv \text{ (energy from light)} \rightarrow e^- + h^+ \quad (4)$$

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

$$h^+ + H_2O \rightarrow H^+ + OH\bullet \quad (6)$$

The complexity of the organic pollutants in industrial wastewater sometimes makes a sole treatment process inadequate; therefore, some types of industrial wastewater treatment processes must be combined with other treatment methods [7].

In the present work, a novel EF reactor equipped with a cathode made by macro porous graphite was investigated in a batch-recirculation mode of operation with a photo reactor to treat PRW by both EF and photo-catalysis processes which lowered the demerits of using single process. Furthermore, a comparison was made between using two photo-catalysts, TiO_2 and ZnO, for eliminating COD from PRW by merging EF with photo-catalytic processes. In addition, the effect of current density, dosage of catalyst, and Fe^{2+} concentration on the removal of COD was also investigated.

2. Materials and methods

2.1 Features of petroleum refinery discharges

The case study in this work was effluent water from Al-DORA refinery plant, Iraq. 40 L were pulled from the tank before the biological treating unit and kept at 4°C during the experimental program. To reduce suspended solids, present in the effluent, a filtration step was performed using Puchner filter with Whatman filter paper (grade 1, 11μm pore size). Table 1 demonstrates the features of the biologically treated effluent in comparison with the untreated wastewater as provided by the refinery administration.

Table 1. Characterization of wastewater discharged from Al-DORA refinery plant.

Property	In	Out	Unit
pH	.67	7.4	-
Temperature	24	21	ºC
TDS	5565	4897	Ppm
BOD	182	21	Ppm
COD	406	102	Ppm
Phenol	19	0.04	Ppm
Oil	.253	.117	mg/L
Turbidity	34	.730	NTU
PO_4^{3-}	0.12	0.8	Ppm
Cl^-	903	449	Ppm

2.2 Chemicals

Zinc oxide (ZnO) Nano-particles (purity 99.5%, APS 35-55 nm) was utilized as a catalyst for photo degradation and supplied from (NANOSHELL LLC, USA), Nano-particles of Titanium Dioxide (TiO_2) having particle size in the range of 10-30 nm (Anatase type, purity 99.5%,) was utilized as a photo-catalyst. It was obtained from (Sky Spring Nanomaterial Inc, Houston, USA). Sodium hydroxide (NaOH) (97.5 % Thomas Baker, India) was utilized to regulate pH value to base effect, Hydrochloric Acid (HCl) (37– 38 % , TEDIA COMPANY, INC) was used to adjust the pH value to an acid effect , Sodium chloride (NaCl) (99.5% , THOMAS BAKER, India) was used to increase the conductivity of solution.

2.3 The EF and Photo-catalytic system

The photo-catalysis-EF system includes two core parts: the EF reactor and the photo reactor; linked by a dosing pump in a batch recirculation design and a compressor with a liquid and air flow meters. A schematic diagram of the photo-catalysis-EF system is shown in Figure 1. The full description of the system design is previously mentioned [8].

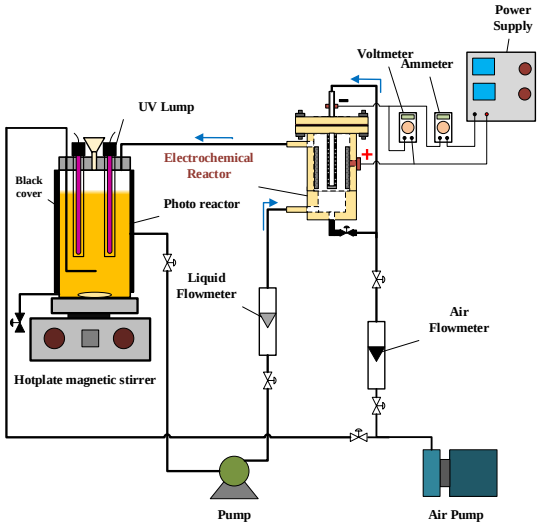

Fig. 1. Photocatalysis-EF system.

2.4 Procedure

A 0.75 L of wastewater was decanted within a 1L black painted beaker to confirm dark conditions. Then, Na_2SO_4 was added at a concentration of 0.05M, and the required amount of catalysts were also added. The beaker was put on a hot plate magnetic stirrer (Heidolph, MR Hei-standard, Germany) for thirty minutes to dissolve electrolyte elements and attain adsorption equilibrium between photo-catalysts and pollutants. Fe^{+2} was added and mixed for 5 minutes after altering the pH of the solution to 4, and then the pH was lowered to 3. Prior to starting the treatment, the UV lamps were turned on. Hereafter, the solution was decanted in the photo reactor, and the magnetic hot-plate stirrer was switched on at 300 rpm. Then, the pump was switched on to mix the solution between the EF and photo reactor at a 200 ml/min flow rate. The compressor was switched on for 15 minutes at a 3 L/min flow rate after the stabilization of circulation to provide the needed O_2 to start H_2O_2 generation and assure the homogeneousness of the solution within the photo-reactor. A DC power supply (UNI-T, UTP3315TFL-II, China) was switched on to deliver the required current for each run. After the finish of the run, the pH of the solution was revised to 8 to precipitate remaining iron sludge. Eventually, by dual filter papers, the solution filtered to confirm the elimination of the photo-catalysts and take a sample for analysis of COD.

2.5 Analytical Methods

In wastewater treatment, COD was used as an accurate method for determining constituents of wastewater (organic and inorganic compounds). This test can measure the level of these compounds according to the quantity of oxygen needed to oxidize them and convert them to CO_2 and H_2O. In the present work, COD was removed as a response to validating the hybrid process and its capability for incinerating organic pollutants in wastewater from petroleum refineries. The test is based on taking 2 ml of effluent and digesting it with an oxidizing agent ($K_2Cr_2O_7$) after putting it in a thermal reactor (RD125, Lovibond) for 120 min at 150 °C. After cooling the sample to ambient temperature, a spectrophotometer (MD200, Lovibond) was used to find the COD value. A digital pH meter (HANNA Instrument Inc. Romania) was used to measure the pH of the solution.

2.6 Performance evaluation

The performance of the combined process was identified by calculating the efficiency of COD removing based on (Eq. 7) [6]:

$$RE\% = \frac{COD_i - COD_f}{COD_i} \times 100 \quad (7)$$

In (Eq. 7), COD_i refers to the initial value of COD and COD_f refers to the final value of COD in (ppm) respectively, while RE% denotes the COD removal efficiency.

At the advanced oxidation processes such as EO and photo-catalyst process, electrical energy consumption is the main economic factor that indicates the successful of the process. In the present work, calculating the consumption of electrical energy in the process of photo-catalysis process according to the proposal of (IUPAC) was termed as EEC_1 (Eq. 8) [6]:

$$EEC_1 = \frac{P \times t \times 1000}{V \times \log\left(\frac{COD_o}{COD_f}\right)}$$

(8)

In (Eq. 8), P represents to the UV lump rated power in kW, V denotes solution volume in liter, and time of reaction denoted by (t) in hour and EEC_1 refers to the electrical energy of photo-catalytic process in kWh/m^3.

For the EF process, (Eq. 9) could be adopted for calculating the consumption of electrical energy [6]:

$$EEC_2 = \frac{U \times I \times t}{V}$$

(9)

In (Eq. 9), U refers to the voltage of cell in volt and I to the applied current in ampere while the consumed electrical energy in EF is referred as EEC_2 (kWh/m^3). Consequently, the energy consumed for the combined system would be the sum of EEC_2 with EEC_1 and termed as a total electrical energy (EEC_T).

3. Results and Discussion

3.1 Effect of Current density

Figure 2 shows the effect of current density on COD removal using two photo-catalysts (TiO_2 and ZnO) at constant dosage of 0.1g/L and Fe^{2+} concentration 0.1 mM.

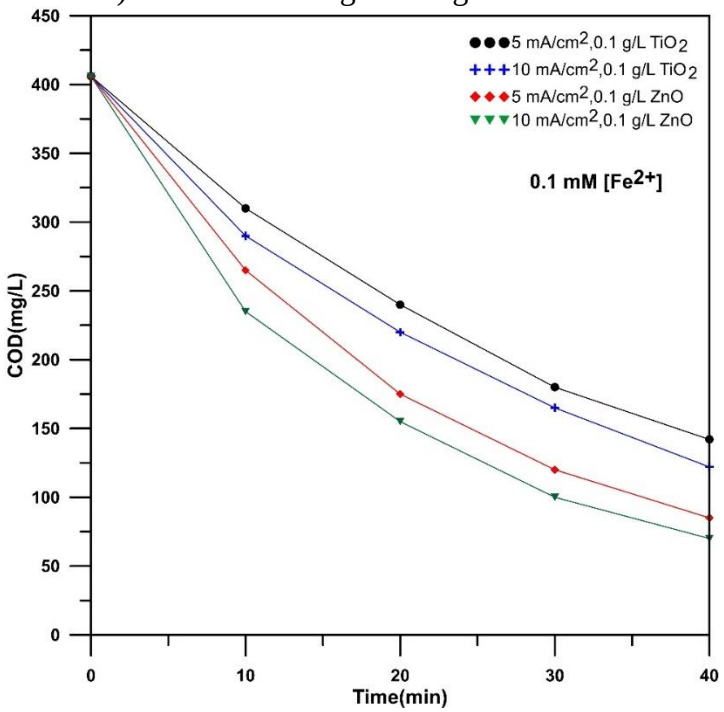

Fig. 2. Effect of current density on COD removal using TiO_2 and ZnO

It can be noticed that increased current density results in a decrease in the final value of COD, hence increasing COD removal efficiency when using both catalysts. However, using ZnO offers higher removal of COD in comparison with TiO_2. The enhancement in the removal rate of COD as the current density increases is due to the higher generation of H_2O_2 from (Eq. 1) which increases OH• generation from (Eq. 2).

3.2 Effect of photo-catalyst dosage

Figure 3 shows the effect of photo-catalyst dosage on COD removal at 10 mA/cm^2 constant current density and Fe^{2+} concentration 0.1 mM.

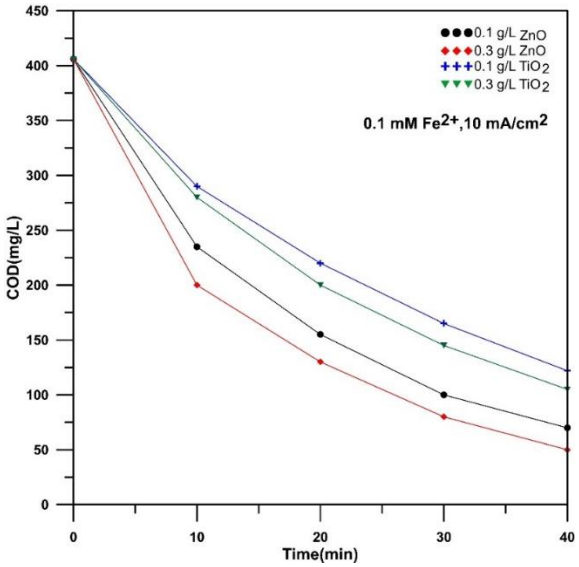

Fig. 3. Effect of photo-catalyst dosage on COD removal

Figure 3 shows that increasing the catalyst dosage decreases the final value of COD, hence increasing COD removal efficiency when using both catalysts. However, using ZnO offers higher removal of COD in comparison with TiO_2. This could be due to the generation of more active sites on the catalysts' surface at higher dosages, which increase OH• production [9]. Most previous studies indicated that increasing ZnO doses increase removal efficiency owing to the increase in (e^-/h^+), which improves the produced OH• [9].

3.3 Effect of Fe^{2+} concentration

Figure 4 shows the effect of Fe^{2+} concentration on COD removal at constant current density of 10 m A/cm^2 and 0.3 g/L dosage of catalyst.

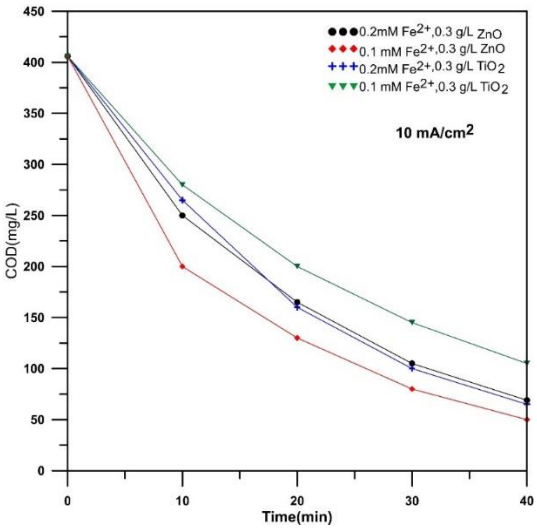

Fig. 4. Effect of Fe^{2+} concentration on COD removal using TiO_2 and ZnO

It was noted that the increasing Fe^{2+} concentration results in an increasing COD removal rate in the case of using TiO_2, while the opposite effect was observed regarding ZnO.

In the case of TiO_2, the behavior can be interpreted (Eq. 1) in which the quantities of OH• produced are related to the addition of Fe^{2+} [9]. In the case of ZnO, increasing the Fe^{2+} dose decreases the removal rate of COD; this could be due to the low surface area of ZnO compared with TiO_2, besides the appearance of brown color in the solution as the concentration of Fe^{2+} increases, which makes the solution turbid and delays the absorption of UV light by ZnO [10, 11]. In addition to the scavenger role of Fe^{2+} (Eq. 10). The OH• and Fe^{2+} can cooperate when there is an additional of Fe^{2+}. Thus, the OH• level in the process will decline, along with the efficiency of the process [10, 11].

$$Fe^{2+} + OH\bullet \rightarrow Fe^{3+} + OH^{-} \quad (14)$$

A comparison between TiO_2 and ZnO revealed that the higher removal efficiency (87.68%) can be obtained when using ZnO photo-catalyst with a dosage of 0.3g/ L and operating at 10 mA/cm^2 current density and Fe^{2+} concentration of 0.1 mM during 40 min. in this case the energy consumption was found to be 20.88 kWh/m^3. In the case of TiO_2 catalyst, a removal efficiency of 83.99% can be obtained at a dosage of TiO_2 of 0.3g/ L, pH of 3, current density of 10 mA/cm^2, and Fe^{2+} concentration of 0.2 mM operating for 40 min in which energy consumption of 25.5kWh/m^3 was required. Both catalysts can reduce the COD level below 100 ppm at a relatively lower energy cost.

4. Conclusions

A successful comparison between two photo-catalysts used for COD removal using a combined process (EF with photo-catalytic system) was successfully achieved. Results confirmed that current density significantly affects COD removal, followed by catalyst dosage and, finally, Fe^{2+} concentration. Fe^{2+} concentration has two effects on the COD; the first causes enhancement of COD removal in the case of using TiO_2, while the second causes the COD removal in the case of using ZnO. The higher removal efficiency of 87.68% can be obtained when using ZnO photo-catalyst at a ZnO dosage of 0.3g/ L, operating at 10 mA/cm^2 current density and a Fe^{2+} concentration of 0.1 mM during 40 min. While a slight decrease in the removal of COD using TiO_2 was observed. Both catalysts could successfully be applied to treat PRW by a lower cost.

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