Raw Industrial Wastewater Treatment Using Fenton, Photo Fenton and Photo Catalytic: A Comparison Study

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Abstract. This work implemented solar TiO2 photocatalysis, Fenton, and photo-Fenton separately for treating raw petroleum refinery wastewater (PRW) in terms of its COD and TOC removal. The effect of irradiation and reaction time along with initial pH on the degradation profiles was assessed and compared. The experimental work then revealed that maximum removal efficiency of COD and TOC by solar TiO2 photocatalysis was 48.2 and 53.3%, respectively while photo-Fenton reached 54.1 and 59.1%, respectively. Photo-assisted process was found significantly better than dark mechanism, especially for TiO2 catalysis. In addition, employing acidic condition in the range of 3 to 5 in both photocatalysis and photo-Fenton processes resulted in the obvious improvement of pollutant degradation. Eventually, the kinetic study indicated that the degradation of COD and TOC is suitable to pseudo-first-order pattern by reaching high R2 values.

1. Introduction

Petroleum refinery can be considered as one of industrial sectors that utilize large amount of water for its multiple manufacturing processes, and as a consequence, it produces large amount of wastewater containing various organic and non-organic compounds [1]. Discharging harmful wastewater into the environment without being treated will lead to detrimental impact on both human health and environmental sustainability. The presence of pollutants in the wastewater such as phenol, suspended solid, heavy metals, oil, dyes, and aromatic compounds results in a toxic and carcinogenic water stream [2, 3]. Therefore, the negative impacts of disposed petroleum refinery wastewater (PRW) has to be mitigated by implementing various wastewater treatment methods before it can be flowed to the final disposal places in open environment or recycled for energy sources, water process, or irrigation purpose [3-5].

There are various existing technologies for wastewater treatment such as membrane filtration, adsorption, flocculation/coagulation, and advanced oxidation processes (AOPs) [3, 6-8]. Among others, AOPs including photo-Fenton and photocatalytic degradation have been considered as part of the effective and efficient treatment modes to treat petroleum refinery and other industrial wastewaters due to its capability on organic compounds mineralization [9]. The use of natural solar light or artificial UV light could boost Fenton and catalytic agents to accelerate oxidation process for COD, dyes, and other targeted contaminants removal [10-12].

Several metal oxides including TiO2, ZnO, MgO3, ZnS, and CdS can be used as photocatalysts. Then among these semiconductors, TiO2 has been reported as a suitable photocatalyst agent used to degrade organic pollutants in aqueous solutions. It can offer several advantageous features such as safety aspect, resistance to photo corrosion, better catalytic efficiency, and being reliable for absorbing...
radiation at lower wavelengths \[13, 14\]. The general reactions of TiO\(_2\) photocatalytics can be written as follows \[15\]:

\[
\begin{align*}
\text{TiO}_2 + \text{hv} & \rightarrow \text{TiO}_2 (e_{\text{cb}}^- + h_{\text{vb}}^+) \quad (1) \\
\text{TiO}_2(h_{\text{vb}}^+) + \text{H}_2\text{O} & \rightarrow \text{TiO}_2 + \text{H}^+ + \text{OH}^- \quad (2) \\
\text{Organic compound} + \text{TiO}_2(h_{\text{vb}}^+) & \rightarrow \text{Oxidation products} \quad (3) \\
\text{Organic compound} + \text{TiO}_2(e_{\text{cb}}^-) & \rightarrow \text{Reduction products} \quad (4)
\end{align*}
\]

With \(h_{\text{vb}}^+\) and \(e_{\text{cb}}^-\) are the charge carrier of valance band hole and conduction band electron \((e_{\text{CB}}^-)\), respectively. Furthermore, the mechanism of generating the hydroxyl radicals in photo Fenton can be generalized as follow \[16-18\]:

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{HO}^- \quad (5) \\
\text{Fe} + \text{H}_2\text{O} + \text{hv} & \rightarrow \text{Fe}^{2+} + \text{HO}^- + \text{H}^+ \quad (6)
\end{align*}
\]

In the presence of organic matter, the hydroxyl radicals will react with it, giving the rise to further oxidize harmless products as follows:

\[
\text{HO} + \text{RH} \stackrel{\text{chain propagation}}{\rightarrow} \text{CO}_2 + \text{H}_2\text{O} \quad (7)
\]

Although some research has been devoted to pollutant degradation using oxidation processes, the treatment of raw PRW using photo-Fenton and photocatalysis considering their comparison under specific operating conditions still need to be further investigated. Therefore, the aims of this work were: (1) to compare the efficiency of photo-Fenton and photocatalytic treatment for COD and TOC reduction in raw PRW using a solar simulator as a light source based on irradiation and reaction time, (2) to specifically measure and compare photo-assisted reaction against dark process, and (3) to assess the effect of initial pH on the removal efficiency.

2. Materials and methods

2.1 Raw wastewater sample

The collected sample from petroleum refinery wastewater pond was physically and chemically characterized for measuring several initial parameters such as pH, TOC, COD and turbidity, and the results are displayed in Table 1. This raw sample was previously filtered through a sieve to remove solid particles greater than a millimeter in size. After analysis, the filtered sample was then placed in the laboratory fridge at a temperature of less than 4 °C to minimize deterioration.

2.2 Chemicals and analytical methods

Hydrogen peroxide (H\(_2\)O\(_2\), 30\%), Hydrochloric acid (HCl, 32\%), Ferrous sulphate hydrate (FeSO\(_4\). \(7\)H\(_2\)O, 99\%), and Titanium (IV) oxide (TiO\(_2\):P25, 99.7\% anatase) from Sigma-Aldrich were used in this work. The measurement of COD concentration was conducted using HACH DRB200 reactor, DR890 colorimeter and HACH COD reagent vials, HR 0-1500 mg/L from Rowe according to the procedure handbook provided (standard method 5220 D) \[19\]. TOC concentration was analysed using a Shimadzu TOC-V CPH analyser.

| Parameter | Raw PRE |
|-----------|---------|
| Turbidity (mg/L) | 7.4 |
| COD (mg/L) | 850 |
| pH | 9.2 |
| TOC (mg/L) | 120 |
| Color | Yellowish brown |

Table 1. Characterization of raw PRE used in this work
2.3 Batch experimental set up
All experiments were carried using a 250 mL Pyrex glass beaker as a reactor in batch mode equipped with a magnetic stirrer. Solar simulator having light intensity of 1000 mW/cm² was used as an irradiation light source. The sample from batch reactor were withdrawn at specific time using a gas tight syringe and filtrate using 0.45 µm PVDF membrane syringe before TOC and COD analysis. TOC and COD concentration were used as standard parameters of treatment efficiency.

3. Result and discussion

3.1 Effect of irradiation and reaction time
Figs. 1 and 2 show the effect of both irradiation and reaction time on the removal efficiency of COD and TOC from raw PRW under specific operating conditions. Based on Fig. 1, it is obviously clear that light irradiation plays a critical role in the effort of TiO₂ to mineralize organic compounds contained in raw wastewater into harmful substances. Photocatalytic process could perform much better than dark catalytic reaction by specifically reaching the removal efficiency of COD and TOC of 48.2 and 53.3%, respectively. It happened within 100 min of irradiation and reaction time. In contrast, under the same operating conditions, dark catalytic reaction could only reach 15.5 and 20.8% of COD and TOC removal efficiency, respectively. In addition, the fast increasing tendency of COD and TOC removal efficiency occurred in the first 60 min before it slowing down. Reversely, the absence of solar light in dark catalytic reaction resulted in less difference of COD and TOC profiles during the whole reaction time. This can be attributed to the function of solar irradiation as the energy source to break down both organic and inorganic substances in the wastewater [20]. It also relates to the photogenerated holes formed when TiO₂ nanoparticles get UV or visible light exposure leading to oxidation reaction with .OH or H₂O generating .OH radical. Those hydroxyl radicals are responsible for organic compound degradation including COD and TOC reduction [21].

![Figure 1. Effect of irradiation and reaction time on removal efficiency for dark and photo catalytic treatment (pH= 3, TiO₂ = 1 g/L).](image-url)
In accordance with Fenton and photo-Fenton (Fig. 2), COD and TOC removal efficiency showed closer gap among them. However, the existence of light irradiation in photo-Fenton process still defines its superiority to the dark Fenton by reaching COD and TOC removal efficiency of 54.1 and 59.1%, respectively. This achievement was better than dark reactions that only reached 35 and 54% of COD and TOC degradation, respectively. However, the absence of light irradiation still gives averagely satisfactory removal efficiency considering short time range and relatively low dosage of H$_2$O$_2$ and FeSO$_4$.7H$_2$O. The formation of strong hydroxyl radicals in the presence of ferrous salt and oxidation process of Fe$^{2+}$ to Fe$^{3+}$ may be accountable for this performance [8].

### 3.2 Effect of pH

The effect of pH on the performance of TiO$_2$ particles and Fenton along with or without the existence of solar light is depicted in Figs. 3 and 4. Looking at the figures, acidic condition seems to be a supportive environment for oxidation process to mineralize organic and inorganic contaminants. While Fig. 3 confirms that mineralization process through photocatalytic reaction mostly occurred better at pH 5, slightly followed by pH 3, by reaching optimum removal efficiency of more than 45 and 43% for COD and TOC, respectively. Fig. 4 informs pH 3 as a better operating condition for photo-Fenton process by successfully reaching more than 40 and 54% of COD and TOC removal efficiency, respectively. In contrast, at its initial pH 9, the removal efficiency of both COD and TOC was significantly lower. For photocatalytic reaction, the reason behind this phenomena could be related to the electrostatic interaction between active semiconductor sites and substrate molecules where the interaction may influence the encounter probability of produced hydroxyl radicals with pollutant particles [22]. In addition, literature reports that photo-Fenton process works well at acidic conditions. This study proved that pH 3 as a proper operating condition for both Fenton and photo Fenton while pH 5 as a better point for solar TiO$_2$ photocatalysis.

![Figure 2](image-url) **Figure 2.** Effect of irradiation and reaction time on removal efficiency for Fenton and photo Fenton (pH=3, H$_2$O$_2$= 1 g/L, FeSO$_4$.7H$_2$O= 1 g/L).

![Figure 3](image-url) **Figure 3.** Effect of pH on removal efficiency for dark and photo catalytic treatment (t = 60 min, TiO$_2$ = 1 g/L).
3.3 Degradation kinetics

A pseudo-first order formula has been well accepted for expressing the photocatalysis, Fenton and photo-Fenton demonstrated as follows [23, 24]:

$$-\frac{dC}{dt} = k_{obs}C$$

(8)

An integration process of Eq. (8) results in:

$$\ln \frac{C_0}{C} = k_{obs}t$$

(9)

where $K_{obs}$, $C_0$, and $C$ are constant reaction rate, initial concentration of targeted pollutant, and concentration of pollutant remained in the solution at time $t$. The values of $ln (C_0/C)$ versus irradiation time in both photocatalysis and photo-Fenton processes are displayed in Figs. 5 and 6. Least square regression was used to calculate $K_{obs}$ and $R^2$ for each COD and TOC shown in Table 2. Based on the table, it can be assumed that pseudo-first-order equation can be fully accepted to the photocatalysis, Fenton, and photo-Fenton processes due to high $R^2$ values.

Table 2. Degradation kinetic analysis for COD and TOC in PRW used in this work

| PRW parameter | Solar light/ TiO$_2$ | TiO$_2$ (dark) | Solar light/ Fenton | Fenton (dark) |
|---------------|----------------------|----------------|---------------------|--------------|
|               | $K_{obs}$ | $R^2$ | $K_{obs}$ | $R^2$ | $K_{obs}$ | $R^2$ | $K_{obs}$ | $R^2$ |
| COD           | 0.0077    | 0.9737 | 0.002    | 0.9228 | 0.0085  | 0.9872 | 0.0026  | 0.9798 |
| TOC           | 0.0091    | 0.9524 | 0.0026   | 0.9624 | 0.0109  | 0.9408 | 0.0091  | 0.9752 |
Conclusion
This study separately applied advanced oxidation processes for purifying raw PRW using solar TiO$_2$ photocatalysis, Fenton, and photo-Fenton. The experimental work leads to the assumption that, for catalytic reaction using TiO$_2$, the existence of light has more significant effect on the removal efficiency of COD and TOC in the solution than that of Fenton/photo-Fenton process. However, light irradiation has also beneficial influence on the increase in removal efficiency for photo-Fenton reaction. Additionally, acidic condition, range from pH 3 to 5, was found as favorable environment for better hydroxyl radical generation to mineralize organic and inorganic compounds in the raw industrial solution.

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