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Photocatalytic Removal of Pollutants from Petroleum Refinery Effluent

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Abstract

The effectiveness of solar photocatalytic degradation to remove organic pollutants from petroleum refinery effluent was investigated in terms of COD reduction. Several parameters such as TiO_2 loading, pH, ferrous ions (Fe^{2+}) and ferric ions (Fe^{3+}) were studied. Results of the effect of TiO_2 loading indicated that COD removal efficiency increased with increasing TiO_2 doses due to the higher total available surface area of the adsorbent. The highest COD removal was found at 0.7 mg/L TiO_2. The maximum degradation efficiency of COD (77 %) was found at pH 5. The addition of ferrous ions (Fe^{2+}) and ferric ions (Fe^{3+}) to the suspension solution significantly increased the degradation efficiency. The optimum values of Fe^{2+} and Fe^{3+} were 15 mg/L and 20 mg/L respectively. The solar photocatalytic degradation efficiency of usingFe^{2+} was slightly higher than that of Fe^{3+}. Comparing with the solar photocatalytic degradation of the synthetic samples (4-CP and 2,4-DCP), the degradation efficiency of the petroleum refinery effluent is less than that of synthetic samples. However, the maximum COD degradation efficiency (77%) achieved significantly shows the ability of the solar photocatalytic degradation process to effectively treat highly polluted water.

Keywords: Solar photocatalytic degradation, petroleum refinery effluent, COD

1. Introduction

Water pollution has become one of the main threats that face humanity today. Increasing everyday people activities lead to contamination of water sources including oceans, rivers, lakes and ground water. This contamination contributes to generating large amounts of polluted water that people cannot use in their daily life. Contaminated water is generated from many different sources involving petroleum refineries, dyes, drugs, paper, textile dye, detergents, surfactants, pesticides, herbicides, insecticides and pharmaceutical manufacturers [1]. These chemical contaminants can be organic pollutants such as alkanes, aliphatic, alcohols and aromatic compounds or inorganic like heavy metals, including lead, mercury, nickel, silver and cadmium. In addition, water can be contaminated by pathogens such as bacteria, viruses and fungi [2].

One of the main sources of chemical toxic pollutants in water is petroleum refineries and oil industries. Oil refineries usually need large amounts of water to perform several processes like a crude distillation unit and a catalytic cracking unit. The amount of water used for refinery processes is 0.4-1.6 times the amount of oil processed [3]. The use of water in these processes leads to polluted water by many highly toxic compounds such as aliphatic and aromatic petroleum hydrocarbons. Aromatic hydrocarbons such as chlorophenols and benzene are well known toxic compounds due to their high polycyclic aromatics content leading to more environmental problems [4]. The characterisation of petroleum refinery effluents depends on the process configuration and operating procedures. All

of the pollutants can exist in groundwater and surface waters which can cause environmental problems for both aquatic life and human health. Most of the petroleum refinery pollutants are extremely toxic and can lead to serious diseases in humans even at very low concentrations. For instance, the presence of chlorophenolic compounds, which are one of the main contaminants in refinery effluents, in drinking water can negatively affect the human central nervous system and might cause some carcinogenic diseases at higher doses [5].
To overcome these environmental problems, polluted water has to be treated and reused efficiently. In general, wastewater treatment can be dividedintofour categories: mechanical, biological, physical and chemical processes [6]. Usually, the first step of petroleum refinery wastewater treatment is filtration and elimination of the suspended solids, followed by biological treatment. Other physical treatments such as activated carbon and air stripping can be used to treat non-biodegradable compounds. However, these methods have some limitations and disadvantages. Advanced Oxidation Processes (AOPs) are one of the most effective and widely used methods for wastewater treatment. These methods offer several advantages including the complete mineralisation of the organic contaminants, using solar light as a viable alternative source of UV and cheaper than the granular-activated carbon and UV/O_3 processes [7]. The main power of this chemical treatment comes from producing hydroxyl radicals (•OH) which can effectively destroy all organic contaminants and mineralise them into CO_2 and H_2O. Among all AOPs, the photocatalytic degradation process has been stated as appropriate technique to destroy and mineralise refractory organic pollutants [8,9]. The efficiency of this method usually comes by using a suitable photocatalyst such as titanium dioxide (TiO_2) and UV or solar source. In addition, it has some features such as ambient operating conditions, complete destruction of pollutants and their intermediates, and relatively low operating cost [10]. Therefore, the aim of this study is to investigate the solar photocatalytic degradation of petroleum refinery effluent using some chemical enhancers such as Fe^{2+} and Fe^{3+}. In addition, a comparison of photocatalytic degradation between synthetic and real samples will be performed. Finally, a kinetic model of COD degradation using L-H equation is proposed.

2. Material and methods

2.1. Materials

In this study, the following chemicals were used as received without any further treatment: raw petroleum refinery effluent,4-Chlorophenol (4-CP, 99%), 2,4-Dichlorophenol (2,4-DCP 98%), Hydroquinone (HQ, 98%), 4-Chlorocatechol (4-cCat, 99%), Phenol (Ph, 99%), Hydrochloric acid (HCl, 32%), Ferrous sulphate hydrate ($FeSO_4$. $7H_2O$, 99%), chloride hexahydrate ($FeCl_3 \bullet 6H_2O$, 97%) and Titanium (IV) oxide (TiO_2-P25, 99.7% anatase). All of these chemicals were purchased from Sigma-Aldrich.

2.2. Effluent Degradation Experiments

All samples were collected from British Petroleum (BP) Refinery located in Kwinana, Western Australia (32.2295° S, 115.7649° E). The samples were taken from the outlet of the Dissolved Air Flotation (DAF) system and the inlet of the Biological Treatment Unit (BTU). Upon arrival, all samples were stored at 5 0C. the regular experiments were carried out under different conditions. To minimise and save the amount of raw refinery effluent consumed in the experiments, 250 mL Pyrex glass beaker as a reactor equipped with a magnetic stirrer was used. The samples were characterised before the experiments to obtain their chemical and physical properties. The characterisation of the petroleum refinery effluent samples is shown in Table 2.1. The colour of the samples was slightly dark brown due to the some traces of oil. The pH samples of effluent samples used in the experimental studies was 9.1. The COD and TOC concentrations of the samples were 840 and 120 mg/L respectively. Some key parameters that mainly affect the photocatalytic degradation of organic pollutants were investigated including TiO_2 doses, pH, ferrous ion (Fe^{2+}), and ferric ion (Fe^{3+}). The optimum values of these parameters for achieving the maximum degradation efficiency wereobtained. The solar-photocatalytic degradation of these samples was carried out using different concentrations of TiO2, Fe^{2+}, and Fe^{3+} as well as various pH.
The experiments were conducted using Solar Simulator (Sun 2000 210 × 210 mm, Abet Technologies Model 11044) to irradiate the reactor. The

Table 2.1: Chemical characteristics of Kwinana refinery effluent

Parameter	Value
Colour	Brown
pH	9.1
Turbidity (mg/L)	7.4
COD (mg/L)	840
TOC (mg/L)	120
TDS (mg/L)	1750

light intensity of the Solar Simulator was 1000 mW/cm2.COD was the indicator for measuring the degradation efficiency of the samples.

2.3. COD Degradation Analysis

A DR/2400 HACH spectrophotometer was used to measure COD which follows the standard procedure of sample digestion. The mg/L results are defined as the mg of O_2 consumed per litter of sample under conditions of this procedure. In this case, the sample is heated for two hours with a strong oxidising agent, potassium dichromate leading to reduce the dichromate ion (Cr_2O_{72}-) to green chromic ion (Cr^{3+}). Then, the amount of Cr^{3+} produced is determined. The COD reagent also contains silver and mercury ions. Silver is a catalyst, and mercury is used to complex the chloride interference.

3. Results and Discussion

3.1. Effect of TiO_2 Loading

To keep the efficiency of the added TiO_2, it is necessary to choose the optimum dose of TiO_2 according to the type and concentration of pollutants. The influence of addition of TiO_2 (0.3 -0.9 g/L) on the solar photocatalytic degradation of the refinery effluent samples at natural pH (9.1) is shown in Figure 1. All experiments were conducted in the dark for 30 min to make sure that the steady state of adsorption is reached and the degradation initiates at the equilibrium of adsorption. The addition of TiO_2 from 0.3 g/L to 0.7 g/L increases the degradation from 42% to 72% within 240 min solar irradiation. This result is logical due to increase in the active sites for adsorption of the pollutants on the photocatalyst surface as well as the enhanced generation of free hydroxyl radicals (•OH). However, when the TiO_2 concentration is higher than 0.7 g/L the degradation rate decreases due to the higher turbidity of the suspension which leads to absorb most of the incident photons by the slurry [11]. Thus, 0.7 g/L TiO_2concentration was selected as an optimum dose for further photocatalytic degradation experiments.

3.2. Effect of pH

It is well known that pH can affect the mechanism and routes of photocatalytic degradation. The TiO_2point of zero charge (pzc) is between pH 5.6 and 6.4 [12]. Thus, based on the pH, the photocatalyst surface will be either charged positively (for pH $^{<}$pzc) or negatively (for pH $^{>}$pzc), or neutral (for pH $\approx$ pzc) (See Figure 3.1).

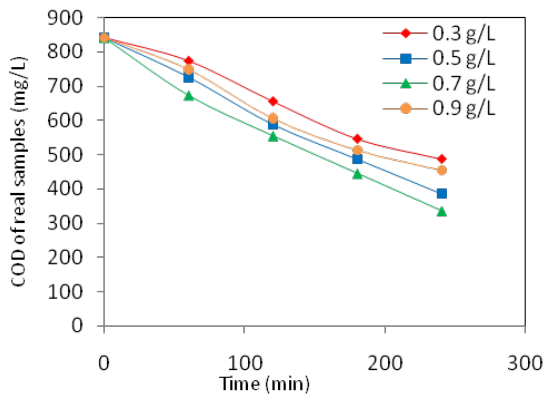

Figure 3.1: Influence of TiO_2 doses on solar photocatalytic degradation of petroleum refinery effluent

This pH mechanism significantly affects the adsorption and desorption of pollutants on the TiO_2 surface. As petroleum refinery effluent contains different organic contaminants such as hydrocarbons and chlorophenols which are discharged at various pH values, thus; it is essential to investigate the role of pH on the solar photocatalytic degradation of the refinery effluent. 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 value of TiO_2 (0.7 g/L) as shown in Figure 3.2. It can be observed that the maximum rate of degradation was achieved at pH 5. Some literature [13,14] stated that TiO_2 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 TiO_2 active sites can be significantly enhanced leading to increase in degradation rates. Therefore, all samples were adjusted to pH 5 prior to each experiment to ensure that the maximum degradation efficiency can be achieved.

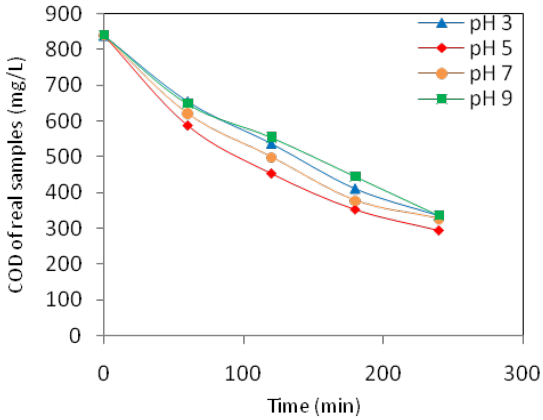

Figure 3.2: Influence of pH on the on solar photocatalytic degradation of petroleum refinery effluent

3.3. Effect of Ferrous Ions (Fe^{2+})

The use of metal ions like ferrous/ferric ions in the solar photocatalytic degradation can effectively increase the degradation rate of organic pollutants. Therefore, to enhance the efficiency of solar photocatalytic degradation of the petroleum refinery effluent, different ferrous ions (Fe^{2+}) concentrations were used as additives (see Figure 3.3). It can be noticed from Figure 3 that the maximum COD removal was at 15 mg/L Fe^{2+}. However, at high ferrous concentrations the degradation efficiency decreases. This result can be clarified by the fact that the recombination of the e^-/h^+ pairs increases at high metal ions doses leading to reduce •OH radicals [15].

3.4. Effect of Ferric Ions (Fe^{3+})

Another metal ion which is ferric ion (Fe^{3+}) was also used in the solar photocatalytic degradation of the petroleum refinery effluent. Influence of variousFe^{3+} doses (7 – 25 mg/L) on the photocatalytic degradation was investigated (see Figure 3.4). It can be observed that the COD degradation rate increases with the increase of Fe^{3+} concentration up to 20 mg/L and then decreases. As mentioned before that all metal ions can significantly enhance the degradation rate due to

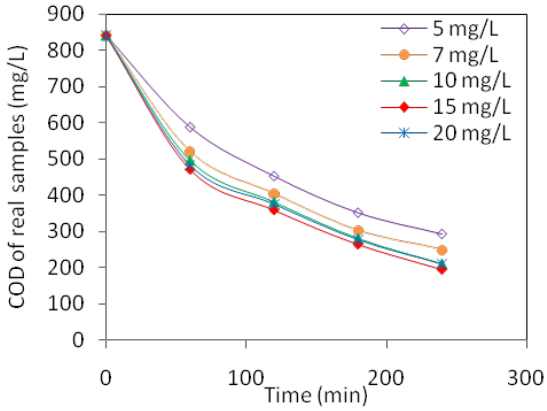

Figure 3.3: Influence of ferrous (Fe^{2+}) ions the on solar photocatalytic degradation of petroleum refinery effluent

their ability to reduce the e^-/h^+ recombination by trapping the electrons. To compare the effectiveness of ferric ions with ferrous ions, it is clear that the efficiency of ferrous is slightly higher than that of ferric. However, both of them can be considered as effective enhancers for solar photocatalytic degradation of petroleum refinery effluent.

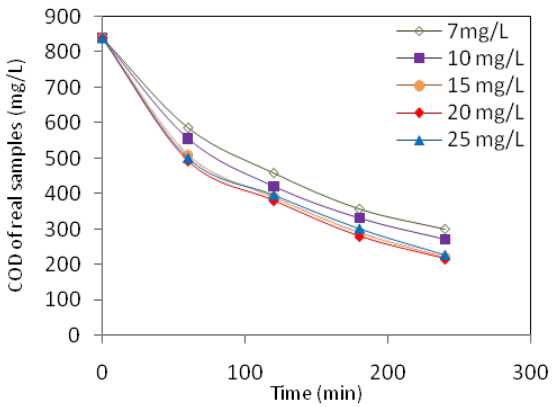

Figure 3.4: Influence of ferric (Fe^{3+}) ions on solar photocatalytic degradation of petroleum refinery effluent

3.5. Comparison Between Synthetic and Real Samples

As mentioned in our previous work [16,17] all samples used in the solar photocatalytic degradation were synthetically made which include 4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP). In order to investigate the potential of solar photocatalytic degradation for treating petroleum refinery effluent, a comparison between synthetic and real

samples involving the key parameters was performed in this work. This study can significantly give a good approach for using solar photocatalytic oxidation as an effective large-scale method. Figure 3.5 shows the optimum values of using TiO_2 as a photocatalyst to degrade three different samples: one organic pollutant, two organic pollutants, and the real sample. It is clear that there is no difference between one and two compound and the optimum concentration was 0.5 g/L TiO_2. This is due to the low concentrations of organic compounds used and no other pollutants present in the suspension.

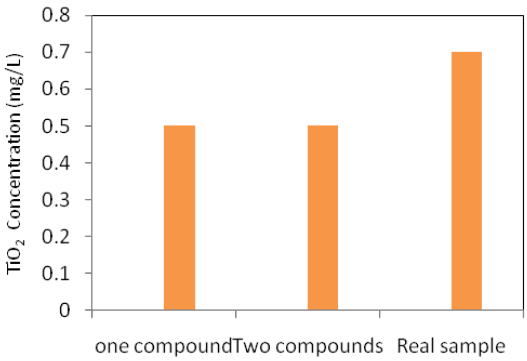

Figure 3.5: Optimum values of TiO_2 used in different cases

However, the maximum degradation of the petroleum refinery samples (Kwinana refinery) was achieved at 0.7 g/L. This indicates that the more polluted water needs more active sites requiring high photocatalyst doses. On the contrary, due to the higher turbidity of petroleum refinery samples with higher doses of TiO2 (above 0.7 g/L), the light inside the suspension solution can be scattered leading to lower the degradation efficiency.
The iron ions including ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions were used to enhance the solar photocatalytic degradation efficiency of synthetic chlorophenols mixtures as mentioned our previous work [18]. These chemical enhancers were also used in the solar photocatalytic degradation of the petroleum refinery effluent. Figure 3.6 illustrates the optimum values of Fe^{2+} and Fe^{3+} achieved in the solar photocatalytic degradation of two compounds (4-CP and 2,4-DCP) and the petroleum refinery effluent. The maximum COD degradation efficiencies of chlorophenols mixture using Fe2+ and Fe3+ were achieved at 7 and 10 mg/L respectively. However, the highest COD removals of the petroleum refinery effluent using Fe^{2+} and Fe^{3+} were 15 and 20 mg/L respectively. It is clear that the highly polluted water needs more iron ions loaded to achieve the best results.

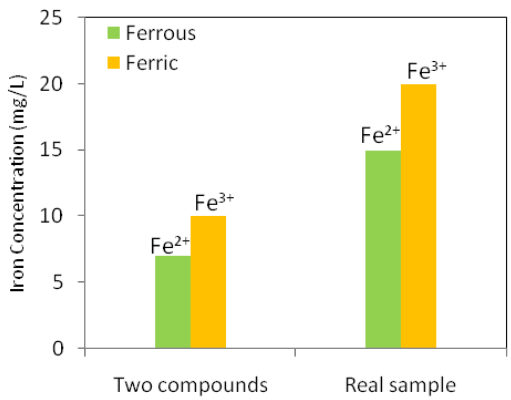

Figure 3.6: Optimum values of ferrous and ferric ions used in two cases

However; these chemicals can significantly increase the operation cost of the solar photocatalytic degradation process, therefore; it is essential to search for natural iron sources to make this method cost-effective.
Even though, the overall COD removal efficiency of the solar photocatalytic degradation decreases with the increase of water pollution but this method significantly shows a good potential to degrade most of organic pollutants. Figure 3.7 shows COD concentrations before and after the treatment of different cases at their optimum conditions. It can be noticed that the initial COD concentration increases with the increase of organic pollutants. The initial COD concentration (before treatment) of one, two compound and real sample were 70, 120, and 840 mg/L respectively. The final COD concentration (after treatment) of one, two, and real sample were 20, 50, and 195 mg/L respectively. It is very important to mention that the real samples contain various inorganic and organic pollutants which can highly reduce the degradation efficiency.
However, the COD removal efficiency of the petroleum refinery effluent (77 %) obtained in this study clearly shows that the solar photocatalytic degradation process can effectively degrade highly polluted water.

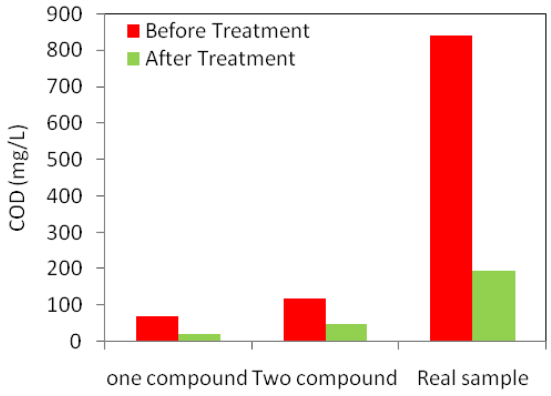

Figure 3.7: COD concentrations before and after the treatment of different cases at the optimum conditions

3.6. Kinetic Modelling

It is well accepted that the rates of formation and disappearance of all chemicals during the photocatalytic degradation time can be modelled using Langmuir Henshilwood L-H equation (Equation 3.1) which considers the adsorption of the chemicals on the catalyst surface and the kinetic reaction constants. The general form of this equation for the system is represented by [19].

$$r_i = \frac{dC_i}{dt} = \frac{k_i C_i}{1 + \sum_{j-1}^{n} K_j C_j} \tag{3.1}$$

The above equation can be used in terms of COD degradation as following:

$$r_{COD} = -\frac{dC_{COD}}{dt} = \frac{k_{COD} C_{COD}}{1 + k_{COD} C_{COD}} \tag{3.2}$$

or

$$\frac{dC_{COD}}{dt} = -\frac{k_{COD} C_{COD}}{1 + k_{COD} C_{COD}} \tag{3.3}$$

Where, C_{COD} is the COD at any time (mg/L), k_{COD} is the reaction rate constant of COD (min^{-1}), and K_{COD} is the adsorption constant of COD (min^{-1}).

After estimating the best parameters, the mathematical model can be applied to predict the behaviour of the photocatalytic degradation of COD in the petroleum refinery effluent. Equation 3.3 cannot be solved analytically, therefore, for estimating the reaction and adsorption rate constants; two built-in MATLAB subroutines were used: Least Square Curve Fit (lsqcurvefit) for the minimisation of the objective function and Ordinary Differential Equations Solver (ode45) for the numerical integration of the differential equations. Equation 3 has been applied to estimate k_{COD} and K_{COD} in both cases of using ferrous and ferric. Table 3.1 summarises the reaction rate constants and the adsorption constants of the COD degradation in case of ferrous and ferric use.

Table 3.1: Reaction and adsorption rate constants of COD degradation in case of ferrous and ferric use

Parameter (min^{-1})	Ferrous (Fe^{2+}) use	Ferric (Fe^{3+}) use
kCOD	0.04	0.03
KCOD	0.01	0.0065

It can be clearly noticed from Table 2 that the reaction rate constant of COD (k_{COD}) of ferrous is slightly higher than that of ferric. This indicates that the photocatalytic degradation activity of ferrous is better than that of ferric. Figure 3.8 shows the experimental and estimated concentration profiles for the solar photocatalytic degradation of petroleum refinery effluent at 0.7g/L TiO_2, 15 mg/L Fe^{2+}. It can be seen that the kinetic model predicts very well the experimental data of COD solar photocatalytic degradation.

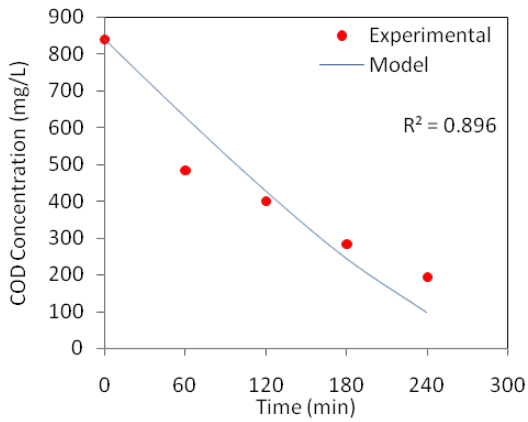

Figure 3.8: Experimental and estimated concentration profiles for photocatalytic degradation of petroleum refinery effluent (0.7g/L TiO_2, 15 mg/L Fe^{2+})

Figure 3.9 also represents the experimental and estimated concentration profiles for photocatalytic degradation of petroleum refinery effluent at 0.7 g/L TiO_2, 20 mg/L Fe^{3+}. It is clear that there is no much difference between using ferrous and

ferric and the kinetic model can effectively fit the experimental data.

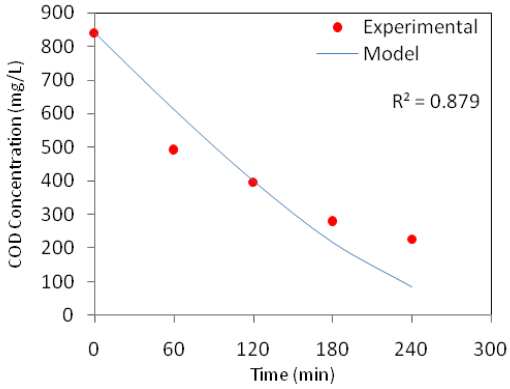

Figure 3.9: Experimental and estimated concentration profiles for photocatalytic degradation of petroleum refinery effluent (0.7g/L TiO_2, 20 mg/L Fe^{3+})

4. Conclusion

Results of the effect of TiO_2 loading indicated that COD removal efficiency increased with increasing TiO_2 doses due to the higher total available surface area of the adsorbent. The highest COD removal was found at 0.7 mg/L TiO_2. The photocatalytic degradation rate in the acidic medium was higher than that of the base medium. The maximum degradation efficiency of COD was found at pH 5. The addition of ferrous ions (Fe^{2+}) to the suspension solution significantly increased the degradation efficiency. The optimum value of ferrous ions (Fe^{2+}) was found at 15 mg/L. The COD reduction of petroleum refinery effluent was also enhanced when Fe^{3+} added to the suspension solution. The optimum value of Fe^{3+} concentration was found at 20 mg/L. However, the solar photocatalytic degradation efficiency of using ferrous ions (Fe^{2+}) was slightly higher than that of ferric ions (Fe^{3+}). The degradation efficiency of the petroleum refinery effluent is less than that of synthetic samples. This is attributed to the high COD concentration in the real samples which requires more chemicals and irradiation time. The kinetic model proposed gives a good fitting between experimental and theoretical data.

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