Enhanced photocatalytic degradation of pollutants in petroleum refinery wastewater under mild conditions

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Abstract

A circulating photocatalytic reactor was used for removing aliphatic and aromatic organic pollutants in refinery wastewater. The TiO_2 added wastewater samples, while saturating with air, were irradiated with an immersed mercury UV lamp (400 W, 200–550 nm).

Optimal catalyst concentration, fluid pH and temperature were obtained at amounts of near 100 mg L^{-1}, 3 and 318 K, respectively. A maximum reduction in chemical oxygen demand of more than 90% was achieved after about 4 h irradiation and hence, 73% after about only 90 min; significant pollutant removal was also achievable in the other conditions. The identification of the organic pollutants, provided by means of a GC/MS and a GC analysis systems, equipped with headspace injection technique, showed that the major compounds were different fractions of petroleum aliphatic hydrocarbons (up to C_{10}) and the well-known aromatic compounds such as benzene, toluene and ethylbenzene. The results showed a high efficiency degradation of all of these pollutants.

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Keywords: Photocatalysis; Petroleum refinery wastewater; TiO_2; Process optimization; AOP

1. Introduction

In petroleum and petrochemical industries, a high interest is dedicated to the improvement of wastewater management through optimization of water use and introduction of recycling technologies within production units. The traditional treatment of refinery wastewater is based on the physicochemical and mechanical methods and further biological treatment in the integrated activated sludge treatment unit. With respect to the fact that different concentrations of aliphatic and aromatic petroleum hydrocarbons are present in the wastewater, among which the aromatic fraction is not readily degraded by the conventional treatments and is more toxic, there is still a need for advanced techniques to remove this sort of pollutants as much as possible.

Several solutions are proposed in this regard; including use of coagulants [1,2], coagulation enhanced by centrifugation [3], ultra filtration [4,5] or sorption on organo-minerals [6]; with a level of advantage for each of them.

The photocatalysis is one of the techniques, which are so called "advanced oxidation processes (AOPs)". These processes can completely degrade the organic pollutants into harmless inorganic substances such as CO_2 and H_2O under moderate conditions. The AOPs are characterized by the production of OH$^\bullet$ radicals which are extraordinary reactive species (oxidation potential 2.8 V) and capable of mineralizing organic pollutants [7]. They are also characterized by a little selectivity of attack, which is a useful attribute for an oxidant used in wastewater treatment. They attack most of the organic molecules with different rates; therefore, providing a valuable technique when multi-contaminated wastewater, e.g. refinery wastewater is considered. The photocatalysis has been tested on many different compounds including environmentally relevant organic compounds and in many different processes [8–10].

In this regard and for enhancement in efficiency, the use of TiO_2 catalyst has gradually attracted more interest. It is due to the point that TiO_2 is the most acceptable and a very cheap catalytic material; also that having the capability of recovery from treated wastewater [11]. The more activity of the UV/TiO_2 process is due to the well known fact that when TiO_2 is illuminated with UV light, electrons are promoted from the valance band to the conduction band of the semi-conducting oxide to give

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electron–hole pairs. The valance band hole $h_{vb}{}^{+}$ potential is positive enough to generate hydroxyl radicals at the surface. Also, the conduction band electron ($e_{CB}{}^{-}$) is negative enough to reduce the oxygen molecules, present in the solution, which in-turn leads to generate another series of hydroxyl radicals [11–13].

This paper presents the studies on degradation of organic pollutants in the real refinery wastewater before reaching to the biological treatment, using the UV/TiO$_2$ process. The most appropriate advantage is using the inexpensive and recoverable catalyst.

This sort of processes, for degradation of organic compounds, may be considered for preliminary application in the refinery wastewater treatments after physicochemically treatments to avoid solids and colloids [14,15].

2. Experimental

2.1. Materials

The laboratory tests were performed using the pretreated refinery wastewater samples (after coagulation and flotation). The samples were collected from the point that the wastewater is just leaving the dissolved air flotation (DAF) and just at the inlet to the biological treatment unit in the Arak refinery plant. The chemical oxygen demand (COD), measured for this point, was within the range 170–180 mg L^{-1}. Other specifications were—pH: 6.5–7.5, turbidity: 50–95, Ntu and total dissolved solids: 420–650 mg L^{-1}.

Titanium dioxide, provided by Merck, was used. It is in anatase form (99%); BET surface area of 14.68 m^2 g^{-1} and the average particle diameter of 27.6 μm [16]. Sulfuric acid and sodium hydroxide solutions were used to adjust the pH of wastewater samples.

The standard reagents and solutions, required for measuring the COD in closed reflux-colorimetric method [17] and for the calibration of spectrophotometer (manual procedure of working with HACH, DR/2000 spectrophotometer, 2002) were prepared from Merck products.

2.2. Setup

Experiments were carried out in an annular vertical reactor, similar to that used in our previous work [13] with the capacity of about 850 mL and a conic shape in the lower part of its body. The UV lamp (22 cm body length and 16 cm arc length) was a mercury 400 W (200–550 nm) lamp, having the highest irradiation peak at 365 nm (measured with a TOPCON UV-R-1 spectroradiometer). The intensity of ultraviolet light around the lamp at this wavelength was about 520 mW/cm^2. The emitted lights are mainly within the range of UVA and UVB. The UV lamp was positioned inside a quartz tube and totally immersed in the reactor; therefore, the maximum light utilization was achieved. A pump was located below the reactor and provided an adjustable circulating stream, feeding from top of the reactor and discharging to the bottom, just below the lamp, for the well-mixing and fluidizing of catalyst particles along the quartz tube. It was not expected that a single pass of polluted water through a short reactor would give adequate degradation. Recently Bickley et al. [11] have used a batch circulating reactor system with horizontal lamps. If particles in the water surrounding a lamp are well-mixed, then each particle on average achieves equal exposure. For regulating the temperature, the reactor vessel was equipped with a water-flow jacket, using an external circulating flow of a thermostat bath. Since the photocatalysis is sustained by a ready supply of dissolved oxygen, air was supplied to the reaction system at a constant flow-rate using a micro-air compressor.

2.3. Procedure and analysis

To run experiments 850 mL of a sample, containing a known level of initial organic compounds (COD: 170–180 mg L^{-1}) and with the appropriate amount of added catalyst was transferred to the reactor. The solution was then exposed to continuous aerating and circulating. After adjustment of temperature and pH, the UV irradiation was begun. The reactor was then covered with a protective aluminum shield. Typical reaction runs lasted some times between 120 and 240 min.

Samples (2.5 mL) were taken at regular time intervals (30 min) and then centrifuged in order to the separation of TiO$_2$ particles. The appropriate COD was measured by the standard closed reflux and colorimetric method [17] using a COD reactor (HACH) and a spectrophotometer (HACH, DR/2000). Colorimetric reaction vessels were capped culture tubes.

In order to identify the present organic compounds in the samples and to compare the efficiency of degradation for different compounds, 10 mL samples of wastewater were taken before and after the degradation. The catalyst particles were separated and analyzed by means of the headspace technique. The samples were poured in 20 mL headspace equipment (HS 2000, Thermo Quest) to be analyzed through the chromatograms. The identification of the compounds in the wastewater was performed by means of the headspace sampler, coupled to a GC/MS system (Thermo Quest). On the other hand, the quantitative analysis was carried out by means of the headspace, coupled to a GC/FID (Thermo Quest) system, equipped with a 50 m/0.32 mm CP-Sil 5 CB column. The applied separation conditions were similar to those applied by Stepnowski et al. [15], working on petroleum wastewater.

3. Results and discussion

Data at different conditions were obtained and analyzed using the parameter R, as the COD removal fraction (or efficiency in R, %) as:

$$R = \frac{[COD]_0 - [COD]_t}{[COD]_0} \tag{1}$$

where $[COD]_0$ and $[COD]_t$ are the initial and at any irradiation time COD values.

In preliminary experiments to examine the influence of UV light and the adsorption of pollutants, experiments were carried out for the cases of under no light (darkness or black run) and with UV light (both with 200 mg L^{-1} of TiO$_2$, under the natural solution pH of 6.5 and temperature of 303 K). As Fig. 1 shows,
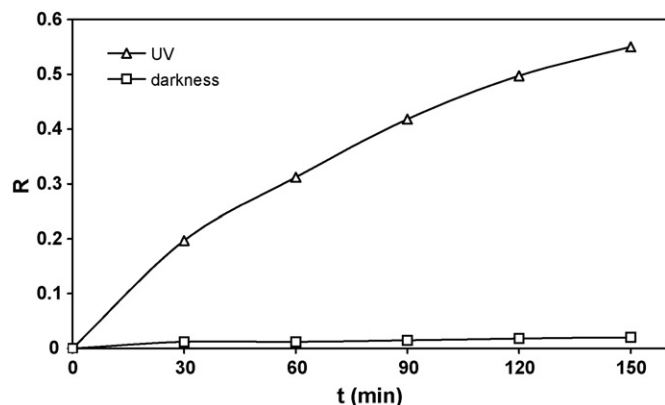
Fig. 1. The effect of UV light on degradation of wastewater; pH 6.5, $T = 303$ K and $[TiO_2] = 200$ mg L^{-1}.

very low reduction in COD was found in the absence of light. The increase of temperature to 318 K with the same pH and catalyst concentration did not cause significant change in COD values. This low change in COD can be attributed to either very low adsorption of organic compounds by TiO$_2$ particles, or to the volatility of a part of light hydrocarbons due to the air flow or heating the reactor.

3.1. Effect of catalyst concentration

A series of experiments was carried out to find the influence of TiO$_2$ concentration. The rates of reaction have been found in some cases to improve, as catalyst concentration increases and then falling slowly or becoming nearly independent of concentration. The results are in agreement with our previous works [13,18] and those reported in the literature [11,19,20] for different organic materials. Results illustrated in Fig. 2 show the variation of degradation at two typical times of 60 and 120 min. With catalyst concentrations up to about 100 mg L^{-1}, the degradation increases; while it decreases mildly above this concentration during the same irradiation times. Similar behavior was observed for other times of irradiation. Various reasons for this behavior have been offered without much conviction or quantification. A possible explanation is that increased turbidity
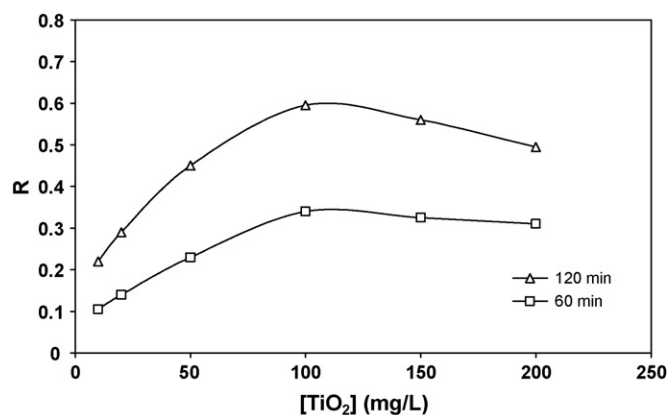

Fig. 2. Effect of catalyst concentration on degradation of wastewater at two typical irradiation times; pH 6.5 and $T = 303$ K.
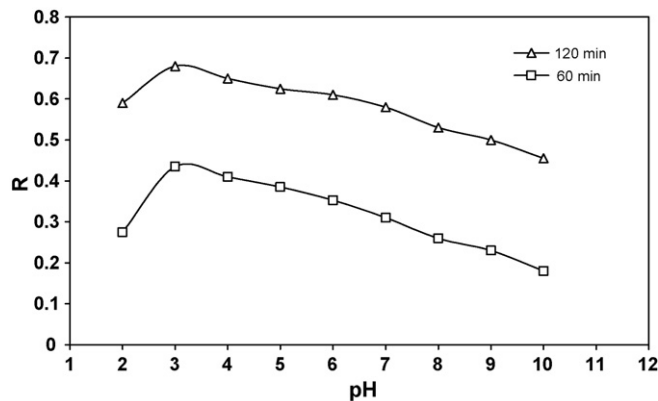

Fig. 3. Effect of pH on degradation of wastewater at two typical times; $[TiO_2] = 100$ mg L^{-1} and $T = 303$ K.

of the solution reduces the light transmission through the solution, while below this level of concentration; it is assumed that the catalyst surface and the absorption of light by TiO$_2$ particles are limiting. Another case may be that of a near total light extinction which is occurred by catalyst particles at an optimum concentration [11]. The optimum catalyst concentration, obtained in this work, is far less than the range of 3–10 g L^{-1}, required as the optimum TiO$_2$ catalyst concentrations, reported by Alhakimi et al. [21,22] for degradation of potassium hydrogen phthalate and 4-chlorophenol as model compounds of refinery wastewater content under sunlight. The efficient use of power and the optimization of catalyst concentration are key factors in achieving a satisfactory design.

3.2. Effect of pH

Results obtained from experiments with varying pH from 2 to 10 and at typical times of 60 and 120 min are illustrated in Fig. 3. The maximum removal of wastewater organic pollutants (about 70% in 120 min) is obtained at pH values around 3. This subject may be argued with the help of pH of zero point of charge (pH$_{zpc}$) and the adsorption of the pollutants on the catalyst. Since TiO$_2$ has an amphoteric character with a point of zero charge 6.25 [23,24], the electron–hole formation, to adsorb the anions, is to be favored under conditions in which pH < pH$_{zpc}$. However, under conditions of low pH (<3), the adsorption of present anions formed from dissociation of added sulfuric acid, reduces the chance of adsorption of organic materials into catalyst surface and therefore the rate of oxidation will be reduced [24]. Alhakimi et al. [21] showed that the degradation rate of potassium hydrogen phthalate is 3.5 times higher in acidic media (pH 3–5) compared to basic media (pH 7–11).

As is presented in Fig. 3, the degradation is still significant under favorable higher pH values. For example, COD reductions of 63% and 61% can be obtained with the pH values of 5 and 6, respectively; under temperature of 303 K and after 120 min irradiation.

3.3. Effect of temperature

Fig. 4 shows the removal of organic compounds in refinery wastewater for the experiments conducted at different tempera-
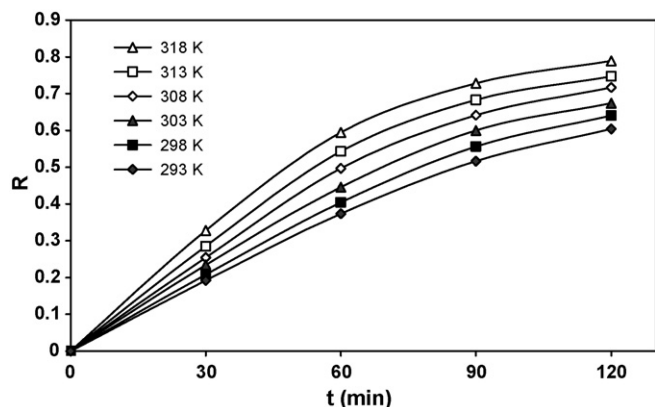
Fig. 4. Effect of temperature on degradation; pH 3 and $[TiO_2] = 100 \, mg \, L^{-1}$.

Fig. 6. Degradation of wastewater under optimum conditions.

tures. The positive influence of the temperature can be observed. Increase of temperature from 293 to 318 K has reduced the required time for the pollutants removal. For the removal of around 60%, for instance, the required time has been decreased from more than 120 min to about 60 min and similarly in most cases to about the half time, within the temperature range. The photocatalytic degradation is favored for most cases by increasing temperature. The reason is related to the TiO_2 electron transfers in valance bond to higher energy levels and hence facilitating the electron–hole production.

Temperatures higher than 318 K cause vaporization of water under ambient pressure and will change the concentration of organic wastewater pollutants; therefore, this temperature can be considered as a mild optimum temperature in the operating conditions. As it was mentioned in the beginning of Section 3, no significant change in COD values was happened due to the just heating the samples, up to 318 K.

Fig. 5 shows the comparison between three considered influencing parameters for a total irradiation time of 120 min. As it is obvious, the catalyst concentration has the most significant influence, within the ranges used in this study.
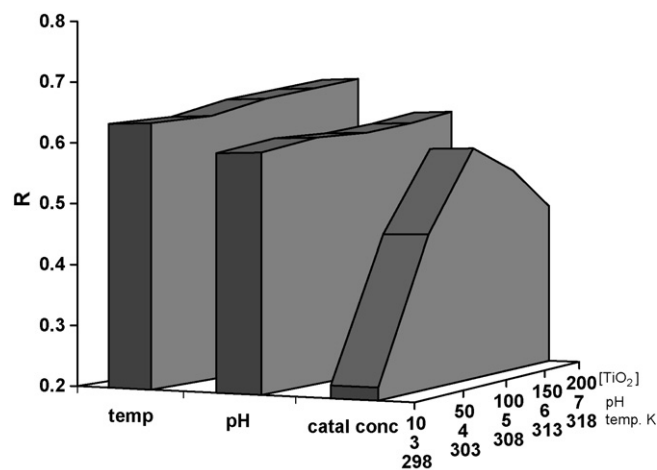
3.4. Applying the optimum conditions

As was investigated, the optimum catalyst concentration, pH and temperature of the solution, for the highest removal, are $100 \, mg \, L^{-1}$, 3 and 318 K respectively.

Degradation of refinery wastewater, under the optimum conditions, consequently provided more than 90% removal of organic pollutants in about 240 min (Fig. 6) and of course, high efficiencies were still available in lower irradiation times (73% in about 90 min and 80% in about 120 min). This shows that the process is promising for the refinery wastewater treatment. Stepnowsky et al. [15] have reported a total reduction of pollutants in refinery wastewater after about 24 h irradiation using UV/H_2O_2 process. It is interesting to note that the wastewater, used in this work, has to stay about 18 h in the biological treatment section to find a 77% reduction in the COD. Alhakimi et al. [21] applied the optimal conditions, obtained from potassium hydrogen phthalate (as a model compound) to the real wastewater samples from Ras Lanuf Oil Co. and a degradation of about 80% of organic pollutants has been achieved after about 5 h irradiation.

Fig. 5. Comparison between the influencing parameters within the range used, for the irradiation time of 120 min. The conditions of data: $T = 303 \, K$ and pH 6.5 for catalyst concentration variation; $T = 303 \, K$ and $[TiO_2] = 100 \, mg \, L^{-1}$ for pH variation; $[TiO_2] = 100 \, mg \, L^{-1}$ and pH 3 for temperature variation.
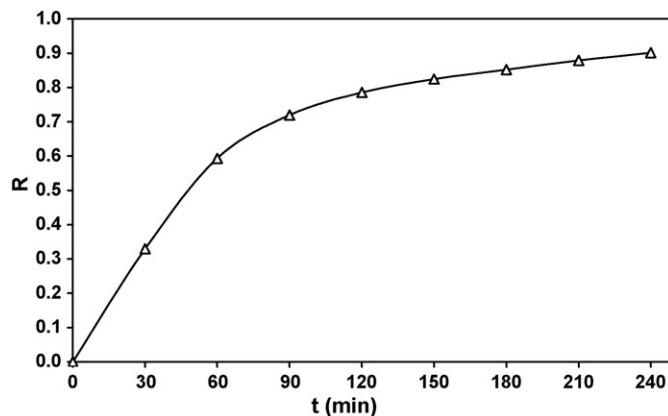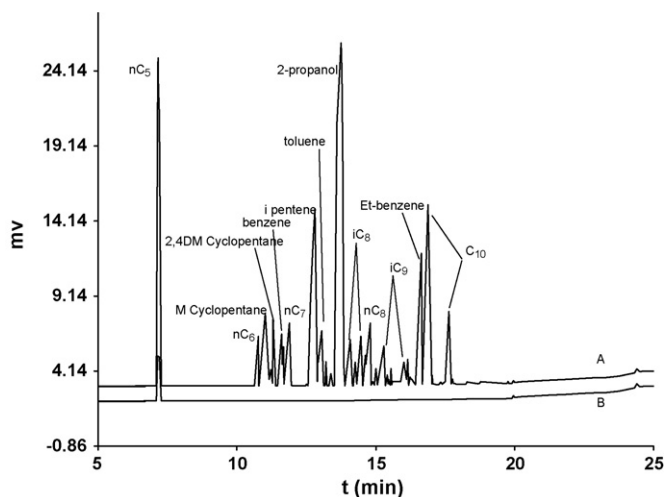

Fig. 7. Comparison of chromatograms before (A) and after (B) UV/TiO_2 degradation in 4 h irradiation under optimum conditions.

3.5. Identification analysis

Fig. 7 presents the chromatograms of the analyzing wastewater before and after the degradation under optimum conditions. The major peaks have been labeled by name according to the GC/MS identification. The majority of the identified peaks consisted of aliphatic hydrocarbons (n-branched and cycloalkanes, up to C_{10}). Also, the aromatic compounds (toluene, benzene, ethylbenzene) were present. The heavier fractions such as polyaromatic hydrocarbons were eliminated from the wastewater during the mechanical and physio-chemical pre-treatments of the wastewater in the refinery plant studied. 2-Propanol was added to the sample for better identifications. Comparison of two chromatograms (A and B) in Fig. 7 shows that except for pentane, having the highest concentration, all pollutants degrade at relatively high efficiencies.

4. Conclusions

As a simple photocatalytic degradation process, mainly featured by using a circulating and direct irradiation reactor, was used for the treatment of the refinery wastewater. An optimal and relatively very low catalyst concentration ($100\,mg\,L^{-1}$) was obtained for which a significant high degradation was provided. Under the mild optimum conditions, a degradation efficiency of more than 90% of the organic pollutants was achieved when applying near 4 h irradiation and significant removal can also be obtained in much shorter times, around 90 or 120 min. This has an industrially interest when this method is considered as an alternative or synergetic process for biological degradation, having a minimum of 18 h residence time required to provide only 77% COD removal.

The analysis of the contained materials showed that the efficiency of the applied degradation system is high for all the identified present organic pollutants.

Despite a number of limitations, this process is economically attractive and may be considered as an efficient unit in the refinery wastewater treatment. The further investigations should involve determining of deactivation rate or number of periods that catalyst can be used for this reaction and the catalyst separation feasibility, although in its low amount.

Acknowledgement

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