



Photocatalytic Pollutant Removal from Petroleum Refinery Wastewater with TiO₂ Nano-particles

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Abstract

A circulating photocatalytic reactor was used for removing the organic pollutants in refinery wastewater. The nano-TiO₂ added wastewater samples, while saturating with air, were irradiated with an immersed mercury UV lamp (400 W, 200–550 nm). Optimal catalyst concentration, fluid and temperature were obtained at amounts of near 100 mg L⁻¹, 3 and 45 °C, respectively. A maximum reduction in chemical oxygen demand of more than 78% was achieved after about 120 min irradiation and hence, 72% 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 and aromatic compounds. The results showed a high efficiency degradation of all of these pollutants.

Keywords: Nano-photocatalyst; Petroleum refinery wastewater; Process optimization; AOP

Introduction

The traditional treatment of refinery wastewater is based on the physicochemical and mechanical methods and further biological treatment in the integrated activated sludge treatment units. 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 coagulation enhanced by centrifugation [1], ultra filtration [2,3] or sorption on organo-minerals [4] 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 CO₂ and H₂O under moderate conditions. The AOPs are characterized by the production of OH[·] radicals which are extraordinary reactive species (oxidation potential 2.8 V) and capable of mineralizing organic pollutants [5]. They are also characterized by a little selectivity of attack which is a useful attribute as an oxidant for multi



compounds, e.g. refinery wastewaters. The photocatalysis has been tested on many individual compounds including environmentally relevant pollutants and in many different processes. In this regard and for enhancement in efficiency, the use of UV/TiO₂ process has attracted a high interest. It is due to the point that TiO₂ is the most acceptable and a suitable price catalytic material. This paper evaluates the performance of a reactor for degradation of organic pollutants in the real refinery wastewater when nanoTiO₂ is used in photocatalytic process.

Experimental

Materials: The laboratory experiments were performed using the pretreated refinery wastewater samples just at the inlet to the biological treatment unit in the Kermanshah refinery plant. The chemical oxygen demand (COD), measured for this point, was within the range 200 – 220 mg L⁻¹. Other specifications were pH: 6.5-7.5 and turbidity: 30-100 Ntu. It was attempted to collect the samples under regular refinery unit operations to maintain the chemical content and other specifications almost constant.

Titanium dioxide nano-particle, photocatalytic standard P25, provided by Plasmachem company (Germany) was used. It is in mixed rutile and anatase form (purity more than 99.5%) with average particle size of 21±5 nm and specific surface of 50±10 m² g⁻¹.

The standard reagents and solutions, required for measuring the COD in closed reflux-colorimetric method [6] and for the calibration of spectrophotometer (manual procedure of working with HACH, DR/2000 spectrophotometer, 2002) were prepared from Merck products.

Setup: Experiments were carried out in an annular vertical reactor, similar to that used in our previous work [7] with the capacity of about 850 mL and a conic shape in the lower part of its body. The UV lamp was a mercury 400 W (200-550 nm) lamp, having the highest irradiation peak at 365 nm (measured with a TOPCON UV-R-1 spectro-radiometer). 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 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 for the well-mixing along the quartz tube. 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.

To run experiments the wastewater sample with the appropriate amount of added catalyst was first sonicated in order to homogenize the solution with nano particles and then 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.

Samples (2.5 mL) were taken at regular time intervals (30 min) and the appropriate COD was measured by the standard closed reflux and colorimetric method [6] using a COD reactor (HACH) and a spectrophotometer (HACH, DR/2000), calibrated with potassium hydrogen phthalate. 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 and analyzed by means of the headspace technique coupled to a GC / MS system. Also, the quantitative analysis was carried out by means of the



headspace, coupled to a GC / FID system. The applied separation conditions were similar to those applied by Stepnowski et al. [8], working on petroleum wastewater.

Results and Discussion

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

$$X = \frac{[\text{COD}]_0 - [\text{COD}]_t}{[\text{COD}]_0} \quad (1)$$

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

Preliminary experiments with the aim of seeking if the adsorption of pollutants onto the surface of catalyst is happened were carried out under darkness with 100 mg L^{-1} of TiO_2 particles under natural pH of 6.8 and temperature of 20°C . A reduction of only about 5% was obtained after 150 min. This low change can be attributed to either very low adsorption of organic compounds by nano particles, or to the volatility of a part of hydrocarbons due to the air flow.

Effect of catalyst concentration: Results illustrated in Fig. 1 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 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 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 [9]. The efficient use of power and the optimization of catalyst concentration are key factors in achieving a satisfactory design in this regard.

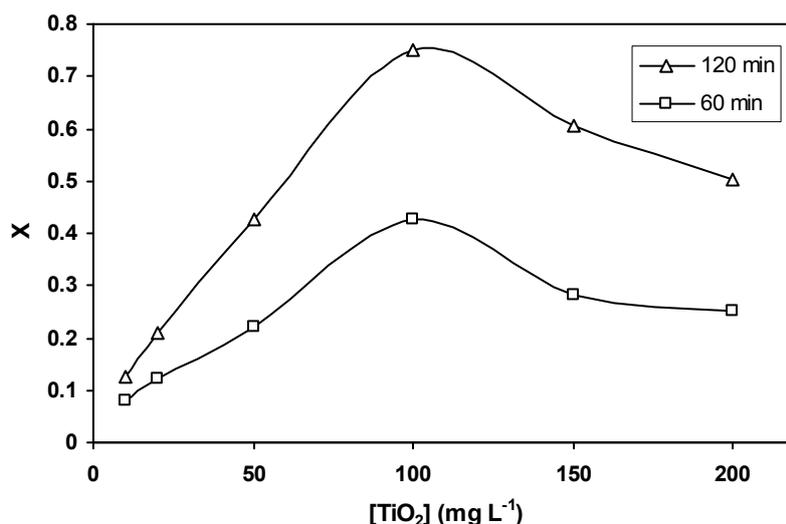


Figure 1. Effect of catalyst concentration on degradation of wastewater at two typical irradiation times; pH=6.5 and $T=20^\circ \text{C}$.



Effect of pH: Results were obtained with varying pH from 2 to 10 at different times. The maximum removal of wastewater organic pollutants was achieved at pH values around 3 (Fig. 2).

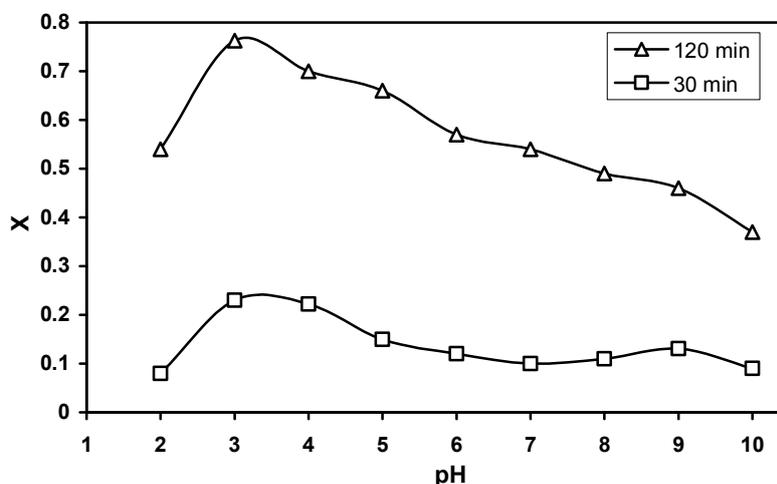


Figure 2. Effect of pH on degradation of wastewater at two typical irradiation times; $[\text{TiO}_2]=100 \text{ mg L}^{-1}$ and $T=20 \text{ }^\circ\text{C}$.

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 [10], the electron hole formation, to adsorb the anions, is to be favored under conditions in which $\text{pH} < \text{pH}_{\text{zpc}}$. 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 [10].

Effect of temperature: Figure 3 shows the removal of organic compounds in refinery wastewater for the experiments conducted at different temperatures. The positive influence of temperature can be observed.

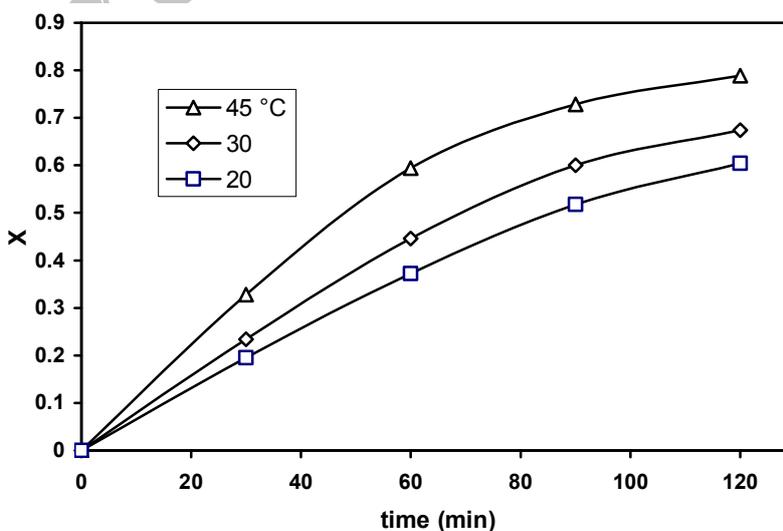


Figure 3. Effect of temperature on degradation; $\text{pH}=3$ and $[\text{TiO}_2]=100 \text{ mg L}^{-1}$.



Increase of temperature from 20 to 45 °C 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 100 min to about 60 min and similarly in most cases within the used temperature range. The photocatalytic degradation is favored for most cases by increasing temperature. The reason is related to the TiO₂ electron transfers in valance bond to higher energy levels and hence facilitating the electron hole production. Temperatures higher than 45 °C 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 was investigated, the optimum catalyst concentration, pH and temperature of the solution, for the highest removal, are 100 mg L⁻¹, 3 and 45 °C respectively.

Degradation of refinery wastewater, under the optimum conditions, consequently provided more than 78% removal of organic pollutants in about 120 min (Fig. 3) and of course, high efficiencies were still available in lower irradiation times (about 72% in 90 min for instance). 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 / H₂O₂ process.

Identification analysis: The obtained chromatograms of the analyzing wastewater before and after the degradation under optimum conditions and the peaks identified according to the GC / MS show that waste-water consisted of compounds including compounds such as methyl tetra butyl ether, phenol, tetramethyl phenol, naphthalene, tetradecane and 4-chloro 3-methyl phenol. The heavier fractions such as poly-aromatic 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. The obtained chromatograms after photocatalytic treatment show that all pollutants degrade at relatively high efficiencies.

Conclusions

The TiO₂ nano particles were used as photocatalyst for the removal of organic pollutants in refinery wastewater, using a simple and perfect receiving irradiation reactor. 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 78% of the organic pollutants was achieved when applying near 120 min irradiation and significant removal can also be obtained in much shorter times, around 90 or 60 min. This has an industrially interest when this method is considered as an alternative or synergetic process for biological degradation, having high residence times, required to provide significant 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. The further investigations should involve determining of deactivation rate or number of periods that catalyst can be used for this purpose and how easily the catalyst particles can be separated.

Acknowledgements

The authors wish to acknowledge the financial support by the Jahad Danesgahi research center and Kermanshah petroleum refinery company.



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آلودگی زدائی از پساب پالایشگاه نفت بروش فوتوکاتالیزوری با استفاده از نانو ذرات دی اکسید تیتان

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چکیده

۳/۵ cm

در این کار از یک راکتور فوتوکاتالیزوری مجهز به جریان چرخشی بمنظور زدودن مواد آلی آلاینده موجود در پساب پالایشگاه استفاده بعمل آمده است. ذرات TiO_2 به نمونه های پساب اضافه و در حالیکه با هوا اشباع می گردیدند با یک لامپ جیوه ای فرابنفش (۴۰۰ W, ۲۰۰-۵۵۰ nm) غوطه ور درون راکتور تحت تابش قرار می گرفتند. شرایط بهینه حاصل برای غلظت کاتالیزور، pH و دما بترتیب $3, 100 \text{ mg L}^{-1}$ و 45°C حاصل گردیدند. میزان کاهش در اکسیژن مورد نیاز شیمیائی برابر ۷۸٪، بعد از حدود ۱۲۰ دقیقه تابش و البته ۷۲٪ بعد از حدود فقط ۹۰ دقیقه حاصل گردید. میزان زدایش قابل توجهی در زمانهای کمتر نیز قابل حصول است. تعیین هویت آلاینده های آلی توسط دستگاه GC/MS و GC که مجهز به روش تزریق از فضای بالائی است انجام و معلوم شد که مقادیر مختلفی از ترکیبات خطی و حلقوی نفتی در پساب بوده که تجزیه فوتوکاتالیستی موجب تجزیه با راندمان بالای آنها می شود.

واژه های کلیدی: نانو فوتوکاتالیزور، پساب پالایشگاه نفت، بهینه سازی فرآیند، فرآیندهای اکسیداسیون پیشرفته

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