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Research Article

Organic Pollutants Removal from Petroleum Refinery Wastewater with Nanotitania Photocatalyst and UV Light Emission

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A real petroleum refinery wastewater, containing a range of aliphatic and aromatic organic compounds, was treated using nanotitania particles, as the photocatalyst in UV/TiO₂ process. Samples were collected from the inlet point of the biological treatment unit. A conic-shape, circulating, and upward mixing reactor, without dead zone, was employed. The light source was an immersed mercury UV lamp (400 W, 200–550 nm). Optimal suspended catalyst concentration, fluid pH, and temperature were obtained at amounts of near 100 mg·L⁻¹, 3 and 45°C, respectively. A maximum reduction in chemical oxygen demand (COD) of more than 78% was achieved after about 120 min and, hence, 72% after only 90 min. Significant pollutant degradation was also relevant under other conditions. The identification analysis of the organic pollutants, provided by means of a GC/MS, equipped with headspace injection technique, showed that different petroleum compounds were degraded with high efficiencies.

1. Introduction

The traditional treatment of refinery wastewater is based on the physicochemical and mechanical methods and further biological treatments in the integrated activated sludge treatment units. With respect to the fact that different concentrations of aliphatic and aromatic petroleum hydrocarbons are present in refinery wastewaters, 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 organominerals [4] with a level of advantage for each.

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 multicomponents, for example, refinery wastewaters. The photocatalysis has been tested on many individual compounds including environmentally relevant pollutants and in many different processes.

Considerable interest has been shown in application of UV/TiO₂ process as an AOP [6]. It is due to the point that TiO₂ has proven to be an excellent photocatalyst material by which many organic substrates have been shown to be oxidatively (in some cases reductively) degraded and undergone fast mineralization under UV light exposure [7]. Some efforts have also been focused on exploring methods to utilize the sunlight and shift the TiO₂ photocatalytic response to the visible region. For instance, the TiO₂ structure has been doped with various transition-metal ions including V, Mn, Cr, Au, Pt, Fe, and Co ions [8].

This paper evaluates the application of nanotitania and the performance of a photocatalytic reactor for the aim of organic pollutants removal from the real refinery wastewater before reaching to the biological treatment unit. It has

an industrially interest when this photocatalytic method is considered as an alternative or synergetic process for biological degradation with high residence time, and required to provide significant COD removal. The results are expected to fulfill the primary required data on application of nanophotocatalyst particles for the treatment of petroleum refinery wastewater.

2. Experimental Protocols

2.1. Materials. The experiments were performed with the pretreated refinery wastewater samples which were collected just at the inlet of the biological treatment unit in the Kermanshah (Iran) refinery plant. The chemical oxygen demand (COD), measured for samples at 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 nanoparticles photocatalytic standard P25, provided by Plasma-Chem company (Germany), was used. It contains both rutile and anatase forms (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, needed for measuring the COD in closed reflux-colorimetric method [9] 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 conducted in an annular vertical reactor, similar to that used in our previous works [10, 11] with the capacity of about 850 mL and a conic shape in the lower part of its body. The reactor performance has the advantage of uniform upward mixing with a circulating stream, provided by a pump. There is no dead zone in the space of the reactor. Conventional cylindrical reactors usually suffer a low circulating flow rate due to weak suction flow, required from top of the reactor and also presence of the dead zones. 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-R1 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 lamp was positioned inside a quartz tube and totally immersed in the reactor; therefore, the maximum light utilization was achieved. The pump was located below the reactor and provided an adjustable circulating stream for the well mixing along the quartz tube. Meanwhile, the reactor 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 nanoparticles 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 started.

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 (APHA, 1989) using a COD reactor (HACH) and a spectrophotometer (HACH, DR/2000), calibrated with potassium hydrogen phthalate. No sensible change in the trend of wastewater COD variation was relevant due to the lamp starting up and reaching steady-state irradiation. 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. The applied separation conditions were similar to those applied by Stepnowski et al. [12], working on petroleum wastewater.

3. Results and Discussion

Data at different conditions were obtained and analyzed using the parameter X , as the COD removal fraction (or efficiency in $X\%$, when multiplied by 100) as

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

where $[\text{COD}]_0$ and $[\text{COD}]_t$ stand the initial and after any irradiation time, COD values.

In a precedent study, for the aim of seeking if the adsorption of pollutants onto the surface of catalyst is happened; the wastewater sample with 100 mg·L⁻¹ of TiO₂ particles was maintained under natural pH of 6.8 and temperature of 20°C, under darkness. A reduction of only about 5% in COD was obtained after 150 min. This low change can be attributed to very low adsorption of organic compounds by nano titania particles. In the case of significant dark adsorption, the starting time for the experiments should be considered after adsorption completement [13].

3.1. Effect of Catalyst Concentration. Almost no pollutant elimination was achieved with UV light alone, while results illustrated in Figure 1 show the significant degradation in the presence of nanocatalyst particles. The variation of pollutants removal after two typical times of 60 and 120 min indicates that with catalyst concentrations up to about 100 mg·L⁻¹, the degradation increases; however, above this concentration, a decrease is appropriate after the same irradiation times. Similar behavior was observed after other examined times. Various reasons for this behavior have been offered without much conviction or quantification [6]. An explanation is that increased turbidity of the solution reduces the light transmission through the solution (shielding effect) which is relevant for TiO₂ concentrations more than about 100 mg·L⁻¹. Whereas, below this catalyst concentration, it is assumed that the catalyst surface and the absorption of light by TiO₂ particles are limiting. Another reason may be due to a near total light extinction which is occurred by catalyst particles at an optimum concentration [14]. The efficient use

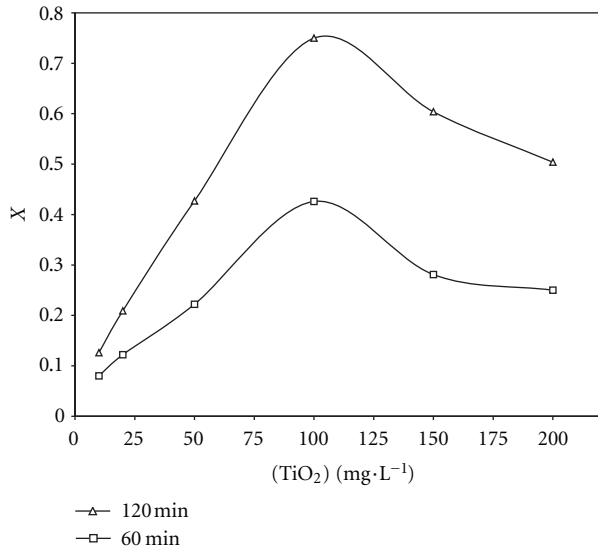


FIGURE 1: Effect of catalyst concentration on degradation of wastewater at two typical irradiation times: pH = 6.5 and $T = 20^{\circ}\text{C}$.

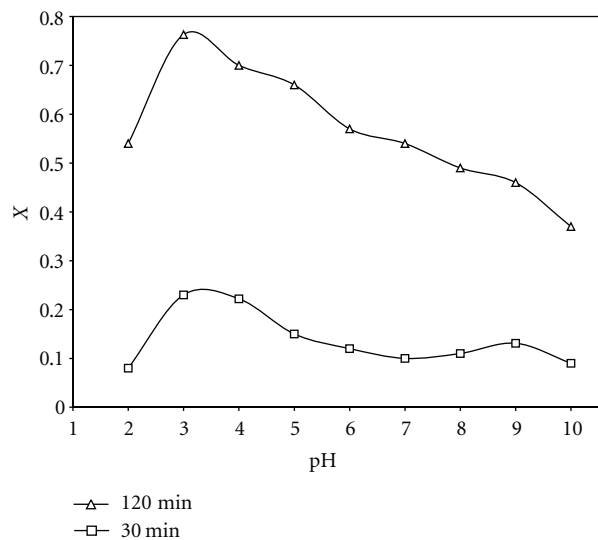


FIGURE 2: Effect of pH on degradation of wastewater at two typical irradiation times: $[\text{TiO}_2] = 100 \text{ mg}\cdot\text{L}^{-1}$ and $T = 20^{\circ}\text{C}$.

of power and the optimization of catalyst concentration are key factors in achieving a satisfactory design in this regard.

3.2. Effect of pH. pH has important influence on pollutant molecules, catalyst surface charge, and also on the mechanism and the rate of hydroxyl radical generation [15]. 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 (Figure 2). This finding can 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 zero point charge pH of 6.25 [15], the electron hole formation, to adsorb the anions, is to be favored under conditions in which $\text{pH} < \text{pH}_{\text{zpc}}$. It is while, under conditions of low pH (< 3),

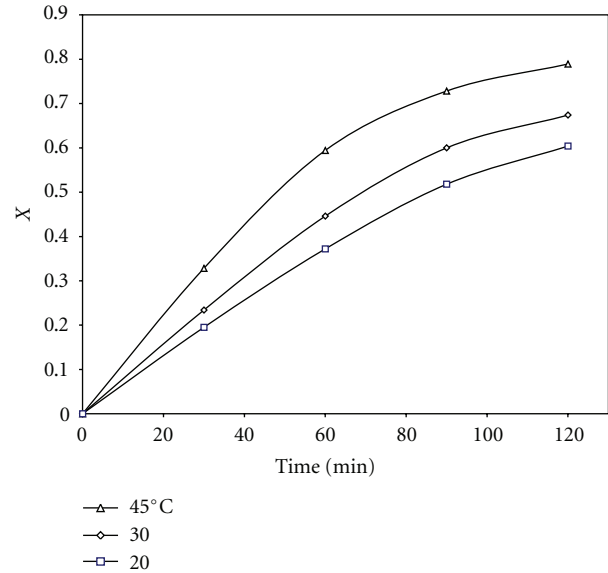


FIGURE 3: Effect of temperature on degradation, pH = 3 and $[\text{TiO}_2] = 100 \text{ mg}\cdot\text{L}^{-1}$.

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 [16].

3.3. Effect of Temperature. Figure 3 shows the removal of organic compounds in the refinery wastewater for experiments conducted at different temperatures. The positive influence of temperature can be observed. Increase of temperature from 20 to 45°C has reduced the required time for the pollutants removal. For the removal of about 60%, for instance, the required time has been decreased from more than 100 min to about 60 min. 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. The recombination of electron hole on the surface of photocatalysts will be also promoted by temperature enhancement; however, logically, this promotion will be less extensive when density of the electron holes is high due to high TiO_2 dosage and effective irradiation. Meanwhile, temperature reduces the oxygen solubility in water which is not desirable [11]. On the other hand, increasing temperature causes a global reaction improvement, according to the Arrhenius equation, but an entropy increase and a less adsorption tendency into the catalyst surface is also occurred for the organic molecules. Overall, a positive influence is provided with temperature rise, within the used range. 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.

According to the above-mentioned results in different sections, the optimum catalyst concentration, pH, and temperature of the solution, for the highest removal, are $100 \text{ mg}\cdot\text{L}^{-1}$, 3 and 45°C , respectively.

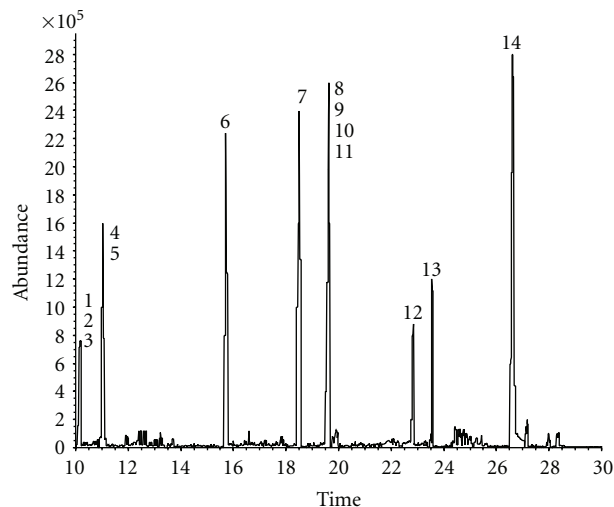


FIGURE 4: Chromatogram of refinery wastewater before treatment, 1: 2-methoxy-2-methylpropane, 2: cyclopropane, 3: benzaldehyde, 4: methyl-tetrabutyl ether 5: phenol, 6: 2,3,5,6-tetramethylphenol, 7: naphthalene 8: xylene, 9: 2,4-dimethylphenol (xylenol), 10: 2,5-dimethyl-3-ethylphenol, 11: octamethylcyclotetrasiloxane, 12: tetradecane, 13: 4-chloro-3-methylphenol, 14: 3-*tert*-butylphenol.

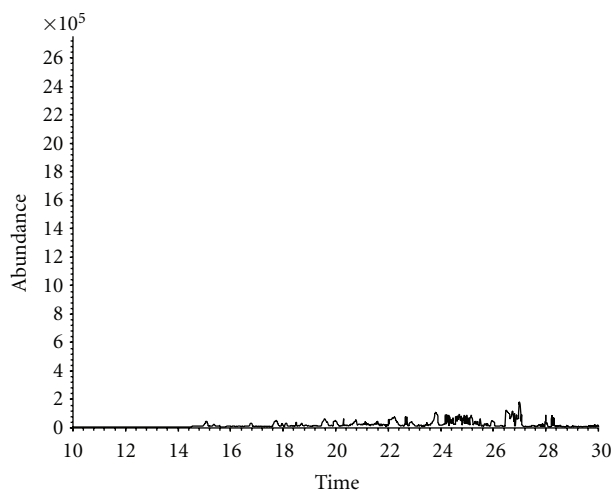


FIGURE 5: Chromatogram of refinery wastewater after treatment under optimum conditions after 120 min.

Degradation of refinery wastewater, under the optimum conditions, consequently provided more than 78% removal of organic pollutants in about 120 min (Figure 3), and, of course, high efficiencies are 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. [12] have reported a total reduction of pollutants in refinery wastewater after about 24 h irradiation using UV/H₂O₂ process.

3.4. Identification Analysis. The obtained chromatograms of the analysing wastewater samples before and after the degradation process, under optimum conditions, are presented in Figures 4 and 5, respectively. The major peaks have

been labeled and named according to the GC/MS identification. This analysis shows that wastewater consists of compounds, such as methyl-tetrabutyl ether, phenol, 2,3,5,6-tetramethylphenol, naphthalene, xylene, tetradecane, 4-chloro-3-methylphenol, and 3-*tert*-butylphenol. The heavier fractions such as poly-aromatic hydrocarbons were eliminated from the wastewater during the mechanical and physicochemical pretreatments of the wastewater in the refinery plant studied. 2-Propanol was added to the samples for identifications. The obtained chromatogram after photocatalytic treatment shows that all mentioned pollutants are degraded with high efficiencies, and their concentrations become nil.

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.

4. Conclusions

The TiO₂ nanoparticles were pronounced as an effective photocatalyst for the removal of organic pollutants in real refinery wastewater, using a simple and perfect irradiation receiving reactor. A very low catalyst concentration of 100 mg·L⁻¹ under pH of 3 and temperature of 45°C can be introduced as the optimum operating conditions. Under these conditions, a degradation efficiency of more than 78% of the organic pollutants, determined with COD criterion, was achieved when applying near 120 min irradiation, and significant removal can still be obtained in much shorter times, after about 90 or even 60 min. The analysis of the present compounds showed that the efficiency of the applied degradation system is high for different identified organic pollutants, especially for aromatic compounds.

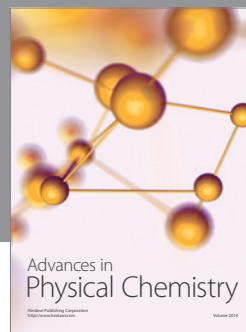
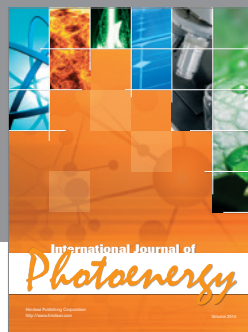
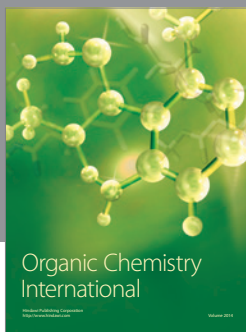
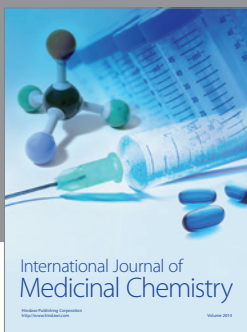
Acknowledgment

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