Photodegradation and removal of phenol and phenolic derivatives from petroleum refinery wastewater using nanoparticles of TiO₂

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Abstract
This study explores the potential application of TiO₂ photocatalysis as primary degradation system of phenol and phenolic derivatives from refinery wastewater. The removal of phenol was investigated in terms of various parameters namely: pH, temperature and catalyst concentration. Determination of phenol and phenolic derivatives compounds is carried out by gas chromatography using a flame ionization detector. In order to analyze the process, chemical oxygen demand fraction (R) was studied. The region of the exploration for the process was taken as the area enclosed by pH (2-10), temperature (293-318 k) and catalyst concentration (10-200 mg/l) boundaries. The optimum conditions for phenol and phenolic derivatives removal were found to be 3, 318 k and 100 mg/l, respectively, for pH, temperature and catalyst concentration. The results showed that, at optimum conditions, remarkable removal of 90% of phenol after 2 h can be achieved. The main feature of this work is the use of inexpensive and recoverable catalyst and may be considered for preliminary application in the refinery wastewater treatments after physicochemical treatments to avoid solids and colloids.
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Keywords: Refinery waste water; Photocatalytic degradation; Phenol and phenolic compound; Chemical oxygen demand fraction.

1. Introduction
Treatment of industrial wastewaters is a problem of major concern nowadays. More strict regulations are being imposed, which persevere on the need to develop and employ treatment technologies capable to deal with the hazardous pollutants present in many industrial waste streams [1]. Wastewater containing phenolic compounds presents a serious discharge problem due to their poor biodegradability, high toxicity and ecological aspects [2]. Phenols are widely distributed as environmental pollutants. They exist in different concentrations in wastewaters disposed from many industrial processes, including coking, synthetic rubber, plastics, paper, oil refineries, petrochemical, ceramic, steel, conversion processes and phenolic resin industries [3, 4]. Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential harm to human health [5, 6]. Wastewaters containing phenols and other toxic compounds need careful treatment before discharge into the receiving bodies of water.

Biological treatment, activated carbon adsorption, solvent extraction, chemical oxidation and electrochemical methods are the most widely used methods for removing phenol and phenolic compounds from wastewaters [7–12]. Such problems as high cost, low efficiency, and generation of toxic by-products are associated with the above methods [13].

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. Research efforts in photocatalysis have dramatically expanded since the discovery of the photocatalytic properties of TiO_2 and the demonstration of its effectiveness to generate hydroxyl radicals in the presence of UV light [8]. The more activity of the UV/TiO_2 process may be 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 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 [9, 10].

There are several methods that can be used to determine the content of monoaromatic hydrocarbons in a water sample. Techniques such as gas chromatography (GC) and liquid chromatography (LC) can provide quantitative and constituent- specific analysis of volatile hydrocarbons. Several reports have shown that preferred methods to determine monoaromatic compounds in water are GC/flame ionization detector (FID) [11-14], GC/photo ionization detector (PID) [15, 16], GC/mass spectrometry (MS) (USEPA standard method, 8260B) [17, 18].

This paper introduces the studies on the degradation of these component in the petroleum refinery waste water before reading to the biological treatment using nanoparticles of TiO_2 and UV light. The main feature of this work is the use of 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 physicochemical treatments to avoid solids and colloids [19-21].

2. Experimental

2.1 Chemicals

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 into the biological treatment unit in the Kermanshah refinery plant. The nanoparticles of TiO_2 mixed phase of anatase: rutile with highest activity with 21nm in size were purchased from plasmachem Co. Surface area by BET is 80 m^2g^{-1} [22]. The analysis of wastewater is illustrated in Table 1.

Table 1. Physical characteristic of wastewater before and after coagulation and flotation treatment

Parameter	Analyse before treatment	Analyse after treatment
pH	6.5-7.5	3
Phenol content (ppm)	220	34
COD(ppm)	200-220	18-20
Turbidiy(NTU)	30-100	18

2.2 Apparatus

Experiments were carried out in an annular vertical reactor with the capacity of about 850 ml and a conic shape in the lower part of its body. The UV lamp (22cm body length and 16cm arc length) was a mercury 400 W (200-550nm) lamp. 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 nanoparticles of catalyst along the quartz tube. It was not expected that a single pass of polluted water through a short reactor would give adequate degradation. Recently, Bickly et. al, [23] 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 achieve 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 reactor system at a constant flow-rate using a micro-air compressor. Figure 1 shows the experimental set up of the photoreactor for the treatment of phenol and phenolic derivatives in petroleum refinery wastewater.
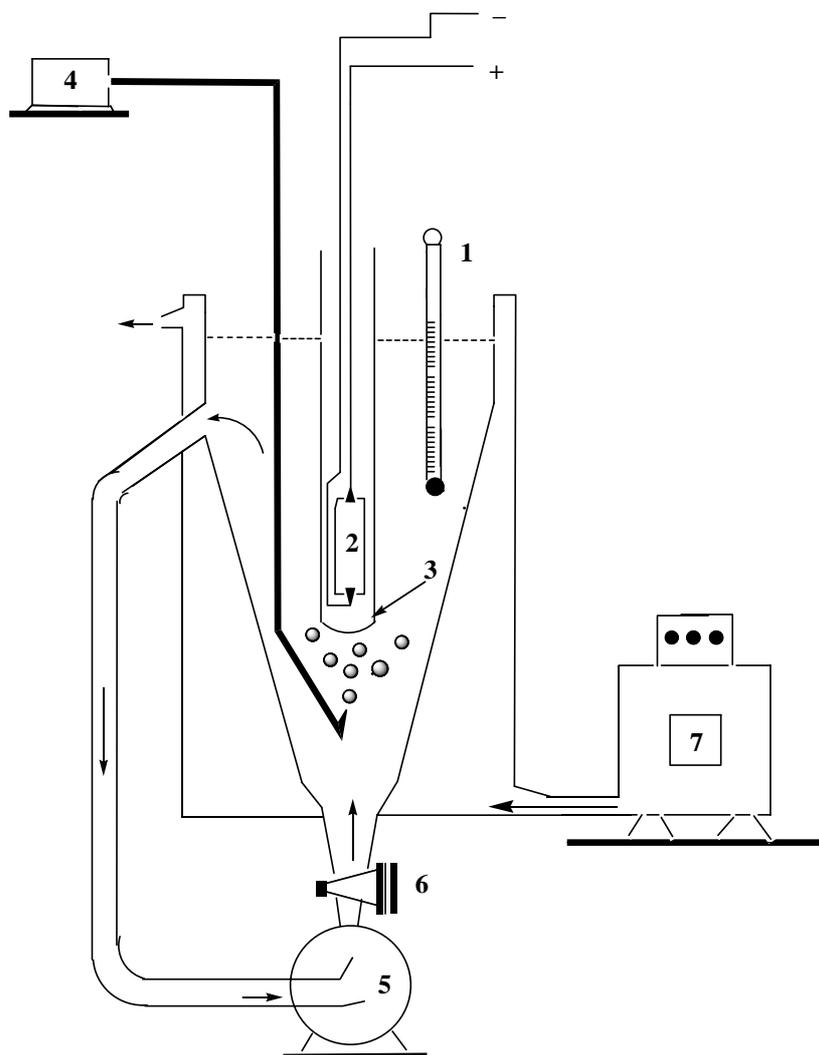
Figure 1. Experimental set up of photoreactor for the treatment of phenolic compounds

2.3 Procedure and analysis
To run experiments, 850 ml of a sample containing phenolic compounds with 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. Samples (2.5 ml) were taken at regular time. Quantitative analysis for phenolic compounds was performed by headspace/GC/FID and standard substance. Headspace conditions: DANI HSS 86.50 headspace sampler, equilibration time 20 min at 70° C. GC conditions: Chromatograph HP5890 series I I/FID, carrier gas N_2, Column primary pressure 3 psi, HP-5 capillary column (30 m×0.32mm×0.25μm), inlet temperature 250° C, detector temperature 300° C and GC oven temperature was held constant at 35° C. Measuring period were chosen according to the investigated substances. Qualitative analyses for the phenol and phenolic derivatives degradation were carried out by headspace/GC/FID and standard substance. Headspace conditions: same as for quantitative analyses. GC conditions: chromatograph HP5890 series I I/FID, carrier gas N_2, column primary pressure 15 psi, Al_2O_3/KCl capillary column (50 m×0.32 mm), inlet temperature 250° C, detector temperature 300° C, GC oven temperature was held 3 minutes at 110° C, then increased with 10° C/min to 200 ° C for 8 minutes [24].

3. Results and discussion

3.1 COD removal fraction

In different experiments, removal of phenolic compounds has been revealed with COD index. COD is the chemical oxygen demand index for organic compounds presence in the environment. At different conditions, the data were obtained and analyzed using the parameter R, as the COD removal fraction (or efficiency in R %) :

$$R = \frac{[COD]_0 - [COD]_t}{[COD]_0} \qquad (1)$$

where $[COD]_0$ and $[COD]_t$ are the initial and at any irradiation time COD values. In preliminary experiments, the influence of UV light and the adsorption of these compounds were studied. Experiments were carried out for the cases under no light (darkness or black run) and with UV light (both with 100 mg L^{-1} of TiO$_2$, and temperature of 303 K). Figure 2 shows, very low reduction of COD which was found in the absence of light. The increase of temperature to 318 K and catalyst concentration did not show significant change in COD values. This low change in COD can be attributed to either very low adsorption of phenolic compounds by TiO$_2$ particles, or to the volatility of a part of light hydrocarbons due to the air flow or heating the reactor.
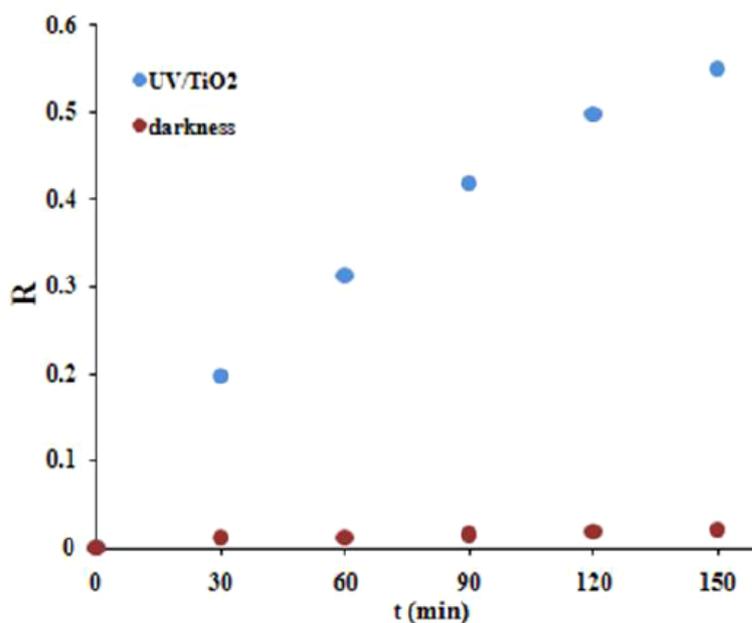
Figure 2. The effect of UV light on degradation of phenolic compounds; pH=6.5, T=303 K and [TiO$_2$]=100 mg L^{-1}

3.2 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. As it is illustrated in Figure 3, the degradation is increased by the variation of degradation at two typical times of 60 and 120 min with catalyst concentrations up to about 100 mg L^{-1}. Similar behavior was observed for other times of irradiation. For this behavior, various reasons have been offered without much conviction or quantification. The increase turbidity of the solution (value of NTU) reduces the light transmission through the solution, while it is assumed below this level of concentration. This observation is because of the catalyst surface and the absorption of light by limit TiO$_2$ particles. Another case may be due to a near total light extinction which is occurred by catalyst particles at an optimum concentration [25]. The efficient use of power and the optimization of catalyst concentration are key factors in achieving a satisfactory design.
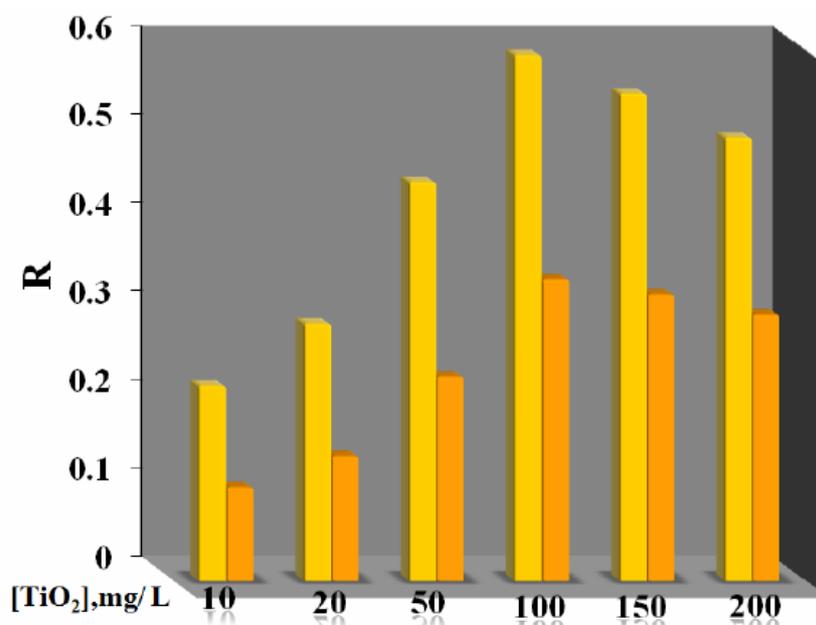
Figure 3. Effect of catalyst concentration on degradation of phenol and phenolic compounds at two typical irradiation times; pH=6.5 and T=303 K

3.3 Effect of pH

An important parameter in the photocatalysis is the pH reaction, since it determines the surface charge properties of the photocatalyst and therefore the adsorption behavior of the pollutant and also the size of aggregates it forms. To study the pH effect, the pH was varied from 2 to 10 and at typical times of 60 and 120 min which are illustrated in Figure 4. The maximum removal of phenolic compounds in petroleum refinery wastewater is obtained at pH=3. This may be argued with the help of pH of zero point of charge (pHzpc) and the adsorption of the pollutants on the catalyst. Since TiO_2 has an amphoteric character with a point of zero charge 6.25 [26], the electron hole formation to absorb 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.
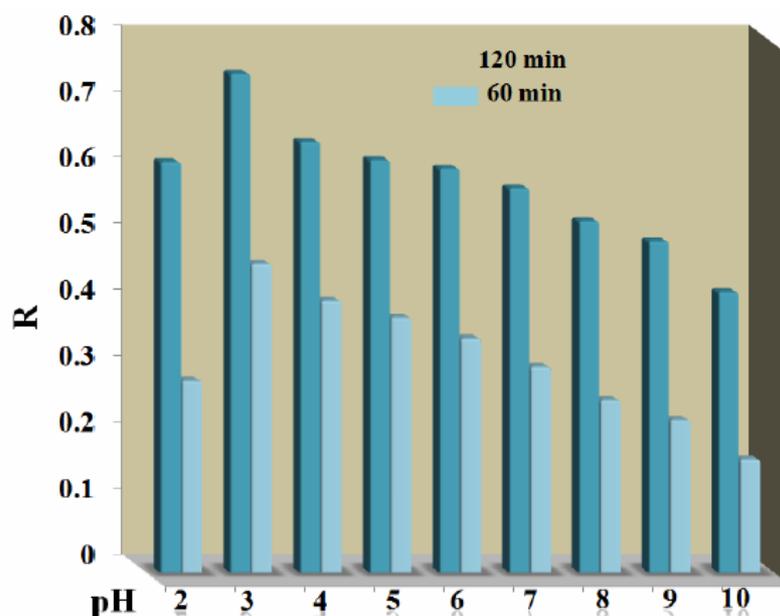
Figure 4. Effect of pH on degradiation of phenol and phenilic compounds at two typical times; [Tio2]=100 mg/l and T=303 K

3.4 Effect of temperature
Figure 5 shows the removal of phenolic compounds in refinery wastewater for the experiments conducted at different temperatures. The positive influence of the temperature can be observed. Increase of temperature from 293 to 318 k has reduced the required time for these component removals. The photocatalytic degradation is favored for most cases by increasing temperature. The reason is related to the TiO_2 electron transfers in valance band 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 phenolic compounds in wastewater, therefore, this temperature can be considered as a mild optimum temperature in the operating conditions.
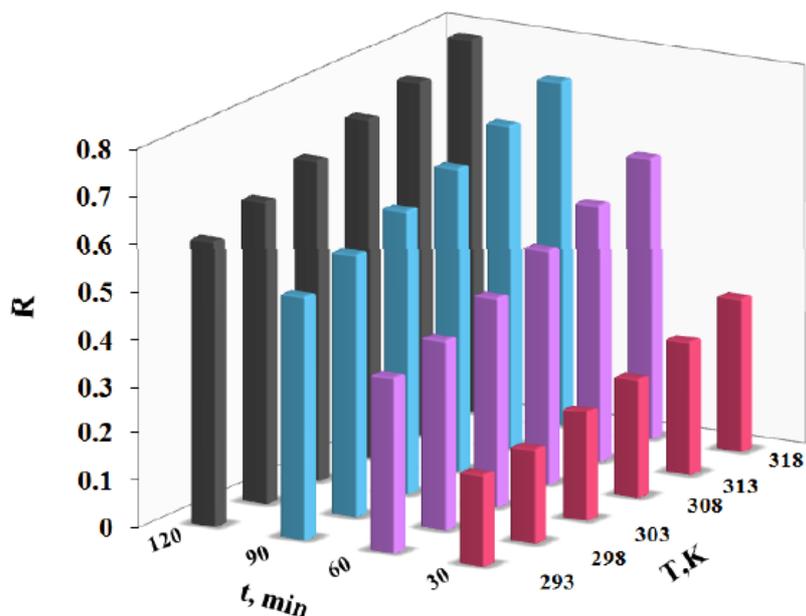
Figure 5. Effect of temperature on degradation; pH=3 and $[TiO_2]=100$ mg L^{-1}

3.5 Applying the optimum conditions
The optimum catalyst concentration, temperature and pH of the solution for the highest removal are 100 mgL^{-1}, 318 k and pH=3 respectively. Consequently, degradation of phenolic component in petroleum refinery wastewater provided was more than 90% removal of these component about 120 min. This shows that the process is promising for the removal of phenolic compounds in the refinery wastewater. Figure 6 compares the chromatograms of phenolic compounds before and after treatment by the photocatalyst.
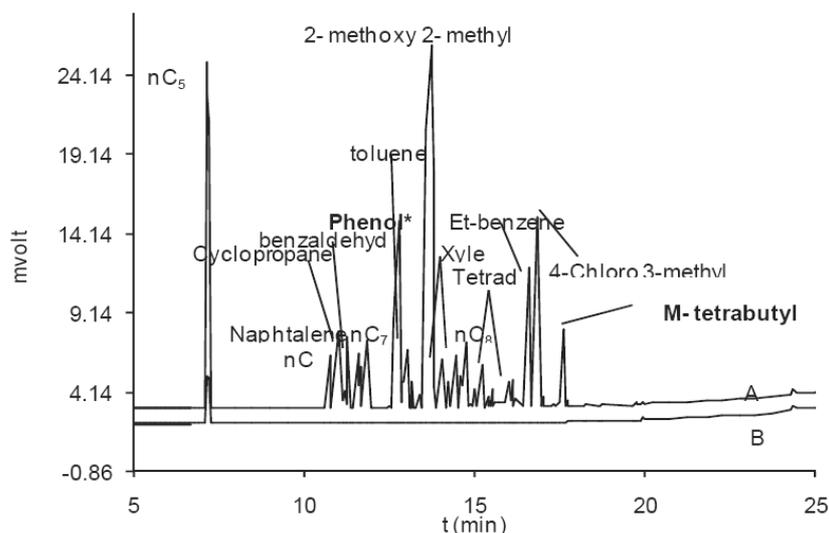
Figure 6. Comparison of chromatograms for degradation of phenol & M-tetrabutyl phenol compounds in petroleum refinery wastewater at 120 min irradiation under optimum conditions

4. Conclusion

The degradation of the phenol and phenolic compounds using a circulating and direct irradiation reactor seems to be a very efficient method for petroleum refinery wastewater as revealed by the present study. Experimental parameters such as pH, temperature and catalyst concentration were investigated for phenol removal. The optimum catalyst concentration, temperature and pH of the solution for the highest removal were 100 mgL^{-1}, 318 k and pH=3, respectively. The experimental results revealed that the phenol degradation efficiency is enhanced by applying near 240 min irradiation and significant removal can also be obtained in much shorter times around 90-120 min.

This study has an industrially interest when this method is considered as an alternative or synergetic process for biological degradation. Despite a number of limitations, this process is economically attractive and may be considered as an efficient unit in the refinery wastewater treatment.

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