

# Photocatalytic Degradation of Phenol using Fe-TiO<sub>2</sub> by Different Illumination Sources

Reyad Awwad Shawabkeh (Corresponding author)

Department of Chemical Engineering, King Fahd University of Petroleum & Minerals

Dhahran, 31261, Saudi Arabia

E-mail: rshawabk@kfupm.edu.sa

Omar A. Khashman

Department of Environmental Engineering, Al-Hussein Bin Talal University

Maan, Jordan

Gasan I. Bisharat

Department of Chemical Engineering, Mutah University

Karak, 61710, Jordan

## Abstract

A Fe-doped titanium dioxide (Fe-TiO<sub>2</sub>) was prepared using hydrothermal method and used for degradation of phenol from aqueous solution. The samples were characterized by X-ray diffraction (XRD) and showed a presence of both TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> peaks. The photocatalytic activity of Fe-TiO<sub>2</sub> catalyst was evaluated for oxidation of phenol in aqueous solution using different illumination sources. Visible light irradiation from sun, UV light sources with 190 and 390 nm, fluorescence and dark environment were used and found that the degradation of phenol was in the order of 7.8%, 12%, 7.5%, 6.8% and 5% obtained after 24 h, respectively. It was found that the increase in exposure time to UV, the increase in solution temperature and pH have increased the rate of phenol degradation in solution. This rate was best fitted using first order kinetic model with reaction constant of  $6.268 \times 10^{-3}$ .

**Keywords:** Titanium dioxide, Iron oxides, Adsorption, XRD, Phenol

## 1. Introduction

Phenolic compounds are considered one of the major hazardous materials that have a perilous impact on environment. These materials were listed by The Agency for Toxic Substances and Disease Registry-USA (ATSDR) as one of the year 2007 priority contaminants that have significant potential threat to human health. Exposure to these compounds can cause liver damage, hemolytic anemia, paralysis and severe injury to the internal organs in human body (ATSDR, 2007). The maximum allowable limit for phenol concentration in water as set by Environmental Protection Agency (EPA) is 4 mg/L (EPA, 2007). As the concentration of phenols in the downstream gets much higher than this value, it becomes an urgent need for preventing such pollutants from entering water resources. Different technological treatment method could be employed for minimizing the concentration of phenols in aqueous solutions. These methods include chlorination (Ge, Zhu, & Wang, 2008; Sharma, et al., 2009), solvent extraction (Egorov, Smirnova, & Pletnev, 2008; Juang, Huang, & Hsu, 2008), adsorption (Shawabkeh & Abu-Nameh, 2007) and membrane process (Lee, Huang, Lee, Pan, & Chang, 2008; Mortaheb, Amini, Sadeghian, Mokhtarani, & Daneshyar, 2008; Wu & Li, 2008). These processes are either costly or have the inherent drawbacks due to the tendency of the formation of secondary toxic materials (Busca, Berardinelli, Resini, & Arrighi, 2008; Patra & Munichandraiah, 2008). Alternatively, photocatalytic degradation method can be employed to organics to produce harmless and low-molecular-weight compounds, particularly CO<sub>2</sub> and H<sub>2</sub>O.

Photo-oxidation of phenols can be attained by contacting these mixtures with semiconductors, particularly TiO<sub>2</sub>, and exposure to a UV illumination source that has energy higher than the band gap of these semiconductors. When illumination occurs on the surface of the semiconductors, the conduction band electrons and valence band

holes were generated at the interface of the solid-solution leading to oxidizing the phenolic compound to less harmful ones. The efficiency of this process depends on the type of the semiconductor, the intensity and wave length of the light, the solution characteristics and the exposure time.

Titanium dioxide is one of the well know semiconductor that is used in photocatalytic reactions. It can generate highly reactive oxygen species such as  $O_2^-$ ,  $HO_2^*$  and  $HO^*$  leading to the oxidation of a wide variety of aliphatic and aromatic hydrocarbons (Granados O, Paez M, Martinez O, & Paez-Mozo, 2005). Unlikely,  $TiO_2$  is less active in the visible region and only anatase crystalline form of  $TiO_2$  could be photoactive. Therefore, several attempts were performed to enhance the photocatalytic activity of  $TiO_2$ . These include doping of transition metals into the surface of  $TiO_2$  (Nahar, Hasegawa, Kagaya, & Kuroda, 2007; Wang, Ye, Wu, & Hu, 2008), acid pre-treatment of the anatase surface (Colon, Sanchez-Espana, Hidalgo, & Navio, 2006), impregnation with different dyestuff and complexes (Escobar, et al., 2008; Kawamura, Okuto, Taruta, Takusagawa, & Kitajima, 1996; Moon, Yun, Chung, Kang, & Yi, 2003), modification with other semiconductors (Ma, Brown, Howe, Overbury, & Dai, 2008) or supporting on surface of activated carbon, aluminosilicates and zeolite (Gan, Liu, Zhang, & Chen, 2008; Jayasankar, Ananthakumar, Mukundan, Wunderlich, & Warriar, 2008; Mahalakshmi, Vishnu Priya, Arabindoo, Palanichamy, & Murugesan, 2008; Razavi, Rahimpour, & Kaboli, 2008; Yang, Liu, Yang, & Yu, 2008).

Iron oxides are widely used in water treatments as adsorbents and amphoteric ion exchangers because they readily undergo reduction or oxidation, depending upon the surrounding conditions (Nganai, Lomnicki, & Dellinger, 2009). The photocatalytic of iron doped  $TiO_2$  is used to extend the photocatalyst's response into the visible region and hence improve the oxidation of several organic compounds such as chloroform, toluene, benzene, alcohols and ethers (Gan, et al., 2008).

This work aims at doping iron oxides into  $TiO_2$  surface and utilizes the produced catalyst for degradation of phenol from aqueous solution.

## 2. Materials and methods

### 2.1 Materials

Titanium dioxide (Degussa P25; composed of 80% anatase and 20% rutile) was purchased from Degussa Chemicals (Hanau, Germany) and used without further treatment. Nitric acid, ferric nitrate and high purity phenol were supplied by Sigma-Aldrich Chemical Company. All solutions were prepared using deionized water from a Milli Q system (Millipore, France). All glassware were Pyrex washed with soap, rinsed with nitric acid the washed with deionized water.

### 2.2 Catalyst preparation and characterization

Two hundred grams of  $TiO_2$  were mixed with 100 ml of concentrated nitric acid and kept under vigorous stirring for 30 minutes. After mixing, the acid treated  $TiO_2$  is filtrated, washed with deionized water, dried at 105 °C and stored in a closed container. Five grams of the acid treated titania was added to 200 ml of 6.2 mM  $Fe(NO_3)_3 \cdot 9H_2O$  and mixed for 30 minutes. Then, the mixture was transferred into 1 L Teflon-lined autoclave and placed in an oven at 180 °C for 24 h. The sample is then calcinated in a muffle furnace at 500±25 °C for 7 hours. The produced material was washed with deionized water, dried at 105 °C and stored in a cool dry place for further usage.

Samples of the doped  $TiO_2$  were characterized using an X-Ray diffraction (XRD) using PAN analytical X-Ray, Philips analytical. The dried sample was tested at 40 kV and 40 mA; the spectra were analyzed using PC-ADP diffraction software. Caption microscope images were performed using MIC-D digital microscope (Olympus-Japan) where 0.1g sample was scanned at 10µm grids.

### 2.3 Photo-oxidation experiments

In order to test the effect of light source and catalyst activity on oxidation of phenol, ten samples of 116 mg/L phenol each were treated with 0.2 g either  $TiO_2$  or  $Fe-TiO_2$  in 100 ml and exposed to different light source environments such as UV 190-250 nm, UV 390 nm, sun light, fluorescence light (405 nm) and dark place. Blank samples were also treated in same manner for the purpose of comparison. After 24 h of shaking at isothermal

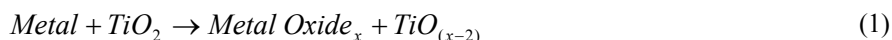
temperature ( $25 \pm 1$  °C), the samples were analyzed using Thermoelectron Heλiosα UV-Vis Spectrophotometer operated at a wavelength of 267 nm.

Isotherm study of phenol degradation was carried out in a set of 9 (100 ml) Erlenmeyer flasks. Samples of 0.1 g each of the Fe-TiO<sub>2</sub> was added to 50 ml phenol solutions (25-200 mg/L) and shaken isothermally ( $25 \pm 1$  °C) for 30 h under UV 190 nm. The solution was maintained at pH 10.55 by adding few drops of sodium hydroxide solution. Then at the end of the isotherm experiments the solution was settled down for 1 h, centrifuged at 4000 rpm and analyzed using the UV-Vis spectrophotometer. The difference between the initial and final concentration of phenol was measured. Similar procedures were carried out to obtain the effect of variation of temperature and solution pH.

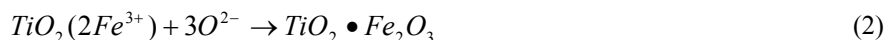
Kinetic experiments were conducted by mixing 1000 ml of 116 mg/L phenol solution with 2.0g Fe-TiO<sub>2</sub> in a baffled glass beaker (2000 ml) fitted with a triple-blade electrical stirrer. The mixture was illuminated with UV 190 nm for 30 minute. The pH was controlled at  $10.55 \pm 0.01$  and the temperature was maintained constant at ( $25 \pm 1$  °C. Aliquots were syringed out periodically during irradiation time using fritted glass filter, centrifuged at 4000 rpm for 5 minutes and then analyzed by using UV-Vis Spectrophotometer.

### 3. Results and discussion

The commercial titanium dioxide was treated with nitric acid followed by doping of iron oxide onto the surface. The formation of iron oxide on the surface of TiO<sub>2</sub> occurred because the process is thermodynamically favorable. Persuod and Madey (Bahnemann, Bockelmann, Goslich, Hilgendorff, & Weichgrebe, 1993) showed that if a metal is deposited on surface of TiO<sub>2</sub>, this metal should reduce the TiO<sub>2</sub> to Ti<sub>2</sub>O<sub>3</sub> or TiO, and itself become oxidized according:



In the presence of oxygen and calcinations at 500 °C, the adsorbed iron will produce iron oxide film doped on the surface of TiO<sub>2</sub> as (Bahnemann, et al., 1993; Grey & Ward, 1973; Sposite, 1989) :



XRD analysis of the produced sample (Figure 1) was examined using Cu-K radiation which shows two major peaks in the region 25-60 2θ. The peak at 29.49 2θ is due to the presence of TiO<sub>2</sub> while the one at 34.29 is due to the formation of Fe<sub>2</sub>O<sub>3</sub>.

Microscopic image for the doped samples is shown in Figure 2. It is shown a highly porous material with agglomerated TiO<sub>2</sub> placed on iron oxide surface occurred. An irregular and porous surface is observed where the dark area represents the iron oxides surrounded by the TiO<sub>2</sub>. The external diameter of the macrospores is ranging from 1-10 μm.

The doped TiO<sub>2</sub> was further tested for its oxidation potential against phenol and compared with that of TiO<sub>2</sub>. Figure 3 illustrates the effect of light sources on the degradation of phenol. It is cleared that the maximum removal of phenol is attained using UV 190 nm, followed by sun light, UV 390 and fluorescence lights. The experiments that conducted in the dark place were considered as blank samples and the percent reduction in phenol concentration attained by this sample could be explained by an adsorption process took place at the surface of Fe-TiO<sub>2</sub>. The highest degradation efficiency of phenol at 190 nm is attributed to the high energy associated with this wavelength. The difference between final concentrations of phenol obtained by the samples treated at different light sources and those of blank represent the percent of phenol reduction. Therefore, this light source was further used for studying the kinetics of phenol degradation.

This degradation mechanism of phenol over the surface of Fe-TiO<sub>2</sub> may explained by the oxidation of phenol using hydroxyl radical generated in solution. The phenol molecules are adsorbed by the surface of iron oxides coated on TiO<sub>2</sub> particles as a result of decreasing the surface tension of solution. When UV light illuminates at energy higher than the band gap of TiO<sub>2</sub> it generates conduction band electrons and valence band holes. The valence band hole can either be trapped at the surface of the TiO<sub>2</sub> or react with surface hydroxyl ions in water to form hydroxyl radical which oxidize phenol in both cases according (Lifongo, Bowden, & Brimblecombe, 2004):



On the other hand, the conduction band electrons either reduce  $H^+$  in solution to form  $H_{2(g)}$  or reacts with oxygen to form super-oxide radical,  $O_2^{\bullet-}$  according



Then the  $OH^{\bullet}$  radical react with phenol ( $C_6H_6O$ ) to produce carbon dioxide and water as (Gondal & Seddigi, 2006)



### 3.1 Effect of degradation parameters

The photocatalytic degradation of phenol was studied over a wide range of initial concentration from 25 to 200 mg/L (Figure 4). At low concentration (25-75 mg/L) a maximum degradation was achieved to reach a value of 18.5%, while a decrease in this capacity is occurred with further increasing in phenol concentration. This is due to the absorption of major illuminated light by phenol molecules which reduced the photocatalytic activity of the  $TiO_2$  (Das, Parida, & De, 2005). Therefore, less phenol molecules will be degraded per a unit dose of  $TiO_2$ .

On the other hand, fixed phenol solutions were irradiated at different pH values and found that the increase in solution pH will increase the percent degradation (Figure 5). The maximum removal value was 20.86% obtained at pH 10 while this value decreased to 4.2% at pH 2. The decrease in phenol degradation with decreasing pH may be attributed to the decrease in hydroxyl ions that are needed to react with valence band hole to form hydroxyl radicals as shown in Equation 7 (Colon, et al., 2006). In contrast, the adsorption of organics from aqueous solutions is increased with decreasing the pH as a result of neutralization of the surface of adsorbent with the excessive hydrogen ions in the solution which gives a controversially contradiction conclusion. However, this is not the case here because the hydrogen ions are consumed by reaction with conduction band electrons to liberate hydrogen gas.

Effect of temperature on the degradation of phenol is illustrated in Figure 6. As the solution temperature increases the percent degradation of phenol is increased. This increase could be explained by the enhancement of the reaction rate took place between the phenol molecules and the hydroxyl radicals (Daneshvar, Rabbani, Modirshahla, & Behnajady, 2004). Moreover, the enhancement of the degradation is probably due to the increasing collision frequency of phenol molecules (Evgenidou, Fytianos, & Poullos, 2005).

The rate of decrease of phenol concentration in solution is assumed to follow a first order reaction as

$$\frac{-dC_{ph}}{dt} = kC_{ph} \quad (10)$$

Where  $C_{ph}$  is the concentration of phenol in solution at a given time,  $t$ , and  $k$  is the reaction rate constant,

The integration to the above equation yield an exponential concentration profile with time according

$$C_{ph} = C_{o,ph} e^{-kt} \quad (11)$$

Where  $C_{o,ph}$  is the initial phenol concentration in solution. The experimental data in Figure 7 were fitted to the above equation and the value of the reaction constant,  $k$ , was found to be  $6.268 \times 10^{-3}$  with regression coefficient of 0.973 and  $\sum (error)^2 = 26.6$ .

## 4. Conclusion

It has been experimentally demonstrated that titanium dioxide doped with iron oxides could be used to photo-degrade phenol. This degradation is best attained at low solution acidity (pH ~ 10) and high temperature value using UV 254 nm irradiation source. The higher initial concentration of phenol will decrease the efficiency

of degradation process. The presence of iron oxides increased the adsorption of phenol and hence the rate of degradation. This catalyst can be employed commercially as a wastewater treatment filter, which has a low cost, non toxic, and has a good potential for selective removal of target solutes form solution.

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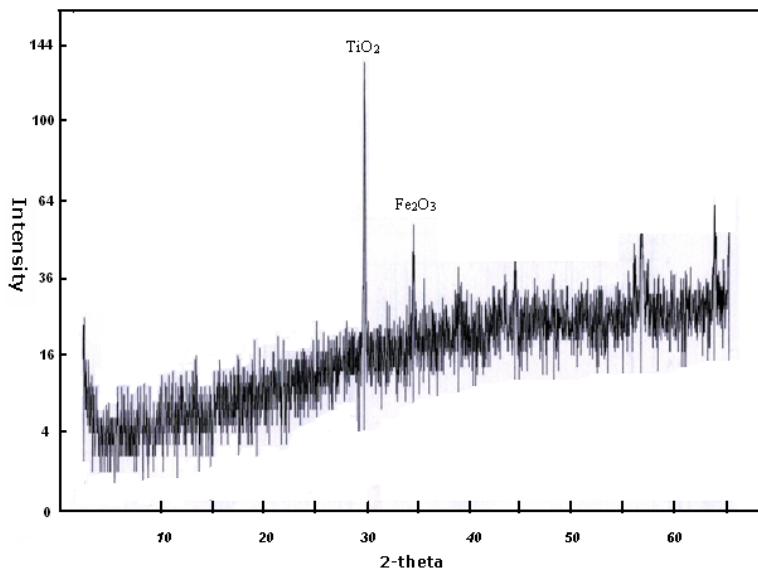


Figure 1. XRD pattern for the doped titanium dioxide



Figure 2. Microscopic image of the doped TiO<sub>2</sub>

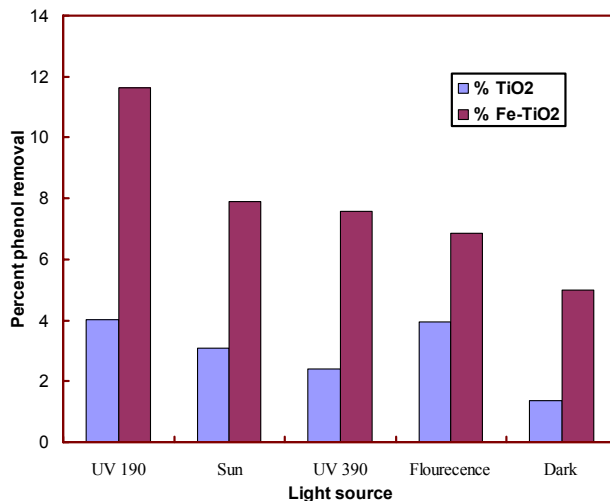


Figure 3. Effect of different light source on the degradation of phenol

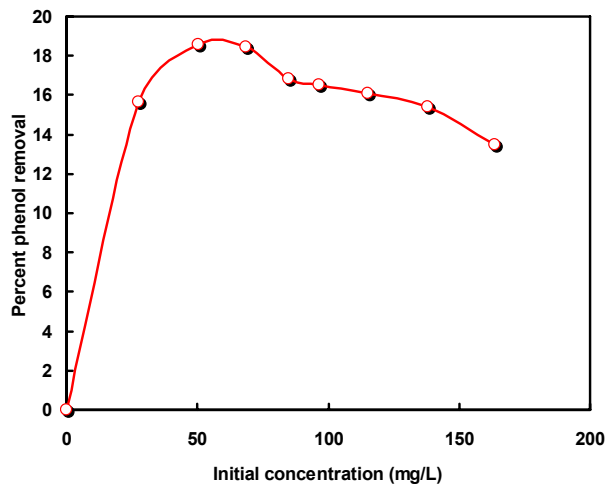


Figure 4. Effect of initial concentration on phenol degradation

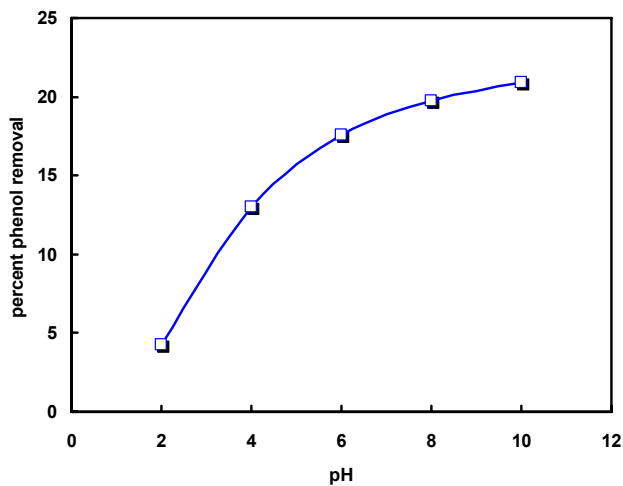


Figure 5. Effect pH on photo-degradation of phenol from aqueous solution



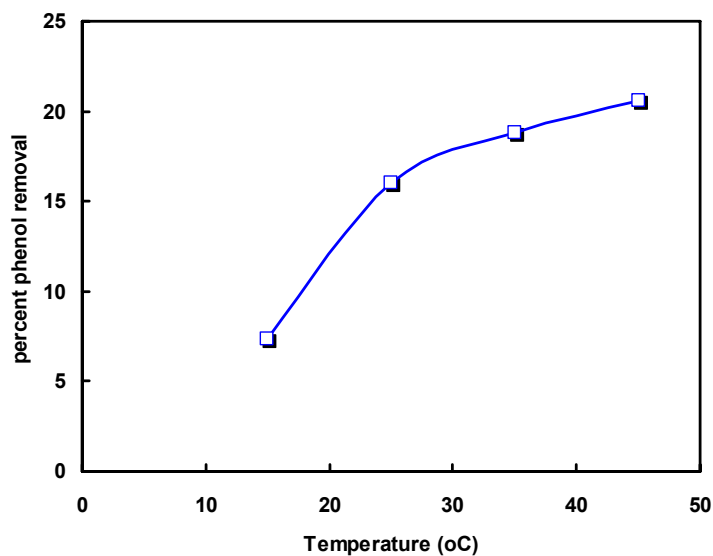


Figure 6. Effect of temperature on phenol photocatalytic degradation

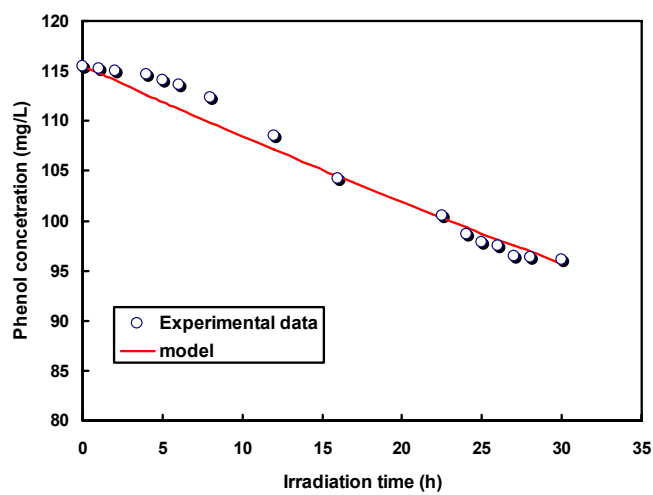


Figure 7. Rate of kinetic of phenol removal from aqueous solution