Photocatalytic degradation of phenolic effluents in petroleum refineries

Elias Daher, Clovis Francis and Wael Hamd*

Scientific Research Center in Engineering (CRSI), Faculty of Engineering, Petrochemical Department, Lebanese University, Campus Rafic Hariri, Al Hadat, Lebanon.

*wael.hamd@hotmail.fr

Abstract. Petroleum refinery effluents such as phenol are very toxic and impose a serious ecological issues. The employment of UV/ZnO NRs system for the degradation of phenol in aqueous solution has been investigated in the present study. The ZnO NRs were synthesized by hydrothermal growth method and characterized spectroscopically exploiting SEM and UV-VIS. It was noticed that the degradation of phenol depends on several operational parameters such as the initial concentration (5ppm, 10 ppm or 20 ppm), the irradiation time (between 0 and 10 hours), and the UV light energy (365 nm or 254 nm). The photocatalytic degradation rates of phenol was observed to follow the pseudo first order kinetics according to the Langmuir-Hinshelwood model. An efficient degradation of about 90 % was registered under 254 nm for an irradiation time of 10 hours.

Keywords. Petroleum refinery, Photocatalysis, Phenol, ZnO NRs

1. Introduction

Petroleum industries are taking a large part in the global economy as well as in the development of oil-producing countries. However, petroleum effluents with high concentration toxic molecules such as phenolic compounds (real oil refinery effluents can reach as high concentration of phenol as 200 mg/l [1]) are imposing a serious ecological problem threatening water supplies and human health, due to their poor biodegradability, high toxicity (individual concentration should be under 0.1 mg/l [2]), endocrine disrupting abilities and carcinogenic behavior [3-5]. Phenol precisely is an ubiquitous environmental pollutant, thus, it is being released mainly by refineries waste water [6] in addition to certain petrochemical industries as synthetic rubber, plastics, paper, ceramic, conversion processes and phenolic resin industries [7, 8]. This pollutant is finding its way into surface and groundwater as well when it is not treated properly [9].

Different treatment technologies are involved in phenol removal, such as biological treatment [10], mechanical approaches (as flocculation, precipitation, granular activated carbon (GAC), reverse osmosis (RO) [11]) and advanced oxidation processes (AOPs). Among these, AOPs are an innovative approach that produces high reactive hydroxyl radicals (OH•) contributing in the deterioration of the toxic molecules present in water [12,13]. Heterogeneous photocatalysis is one of the popular AOPs for providing complete degradation of these molecules into CO2, H2O and mineral acids [14, 15]. Furthermore, it is cost-effective, safe, non-selective and compatible to treat a large range of organic contaminants [16]. In addition no further separations are needed compared to homogenous photocatalysis.

An ideal photocatalytic material provides simultaneously, a high surface area with high light energy conversion efficiency. It should be non-toxic, biologically and chemically inert, stable for long periods of time and easily processable. However, there is no such material or system that fulfills all these requirements. Among various metal oxides, ZnO is considered a credible semiconductor for having distinctive advantages, such as: easy fabrication routes, practical modifications of the surface structure, higher electron mobility than traditional semiconductor TiO2 [17-20], and providing the option of being synthesized into nanorods by a simple and low cost hydrothermal method [21]. In this work we present a kinetic study of mineralization of phenol with different initial concentration in water (5 ppm, 10 ppm and 20 ppm) under UV light at 365 nm and 254 nm using ZnO nanorods (NRs) grown on a glass substrate. An approximately total removal of phenol (~90 %) without any addition of external oxidant molecules was observed.
2. Sources of Phenolic Compounds From Refineries.

In general, cracking processes (as FCC) are the primary source of phenolic waste water [6, 22-24] in refineries. Thus, catalytic cracking waste water processes produce the bigger fraction of phenolic compounds. The main fractionator overhead reflux drum produces impurities and phenols. Caustic treatment of cracked gasoline removes sulfur and phenolic compounds and it is considered as well another source of phenol. [6].

Moreover, Duo-Sol extraction by using phenol as a solvent, hydrocracking and thermal cracking processes (including visbreakers, delayed coking, and steam crackers [6]) are also an additional source of phenolic wastewaters. Finally a refinery distillation column still a basic source of phenolic compounds where this last can be produced in the sour water reflux-drum effluent and in the desalter whenever this component is used [25].

According to the API classification [6] the source of phenol in petroleum refineries are classified as shown in the following table. Class A refineries (no cracking) produce only 0.03 lbs of phenol per 1000 bbl refined. Whereas, classes B through E (with cracking), produce much higher levels of phenol (1.54-4.02 lbs/1000 bbl).

| Refinery class | Processes                           |
|---------------|------------------------------------|
| (A)           | Crude Distillation                 |
| (B)           | Cracking                           |
| (C)           | Cracking & petrochemicals          |
| (D)           | Cracking & lubes                   |
| (E)           | Cracking, lubes & petrochemicals   |

Table.1 Source of phenolic effluents from refineries according to API classification, Class A refineries (no cracking), classes B through E (with cracking) [6].

3. Materials and Methods for ZnO NRs Synthesis

3.1 Materials

Analytical grade zinc acetate dehydrate (Zn (CH₃COO)₂·2H₂O) from ACROS organics span, Zinc nitrate hexahydrate (Zn (NO₃)₂·6H₂O) from ACROS organics span, hexamethylenetetramine ((CH₂)₆N₄) from ACROS organics span, Phenol detached crystals from Fischer Scientific U.K. Standard microscope glass slides were used as substrates for the growth of ZnO NRs.

3.2 Synthesis of ZnO NRs coated glass substrate

ZnO nanorods were grown hydrothermally on microscope glass substrates under optimized conditions [21] as follows: The substrates were pre-cleaned successively by sonication in soap water, ethanol, acetone and deionized (DI) water for 15 minutes for each. A ZnO layer was seeded on the pre-heated cleaned substrates (at 350 °C) using spray pyrolysis of 10 mM zinc acetate [Zn (CH₃COO)₂·2H₂O] in DI water at a rate of 1 mL/min (from a distance of 20 cm). Then, the seeded substrates were placed in a chemical bath containing equimolar (10mM) concentration of zinc nitrate hexahydrate [Zn(NO₃)₂·6H₂O] and hexamethylenetetramine ((CH₂)₆N₄) in DI water. Thereafter, they were placed in a closed batches under 100 °C for 9 hours, where the precursor solution had been replenished every 3 hours. Therefore, the prepared samples were annealed at 350°C for 1 hour as an optimum heat treatment temperature.

3.3 Characterization Techniques

The synthesized ZnO NRs morphology was characterized by scanning electron microscopy (SEM; Model: AIS 2300C SERON technologies, Korea) operated at 20 kV.

A UV/Vis spectrometer (spectord 50 plus from analytic-jena, Germany) was used to measure the absorption of the as prepared ZnO NRs between 350 to 800 nm and the absorption of phenol solution during the photocatalytic degradation.

3.4 Photocatalytic Tests

The photocatalytic degradation of phenol was performed under a UV light (λ=254 nm and λ=365 nm) using the as prepared ZnO NRs described in the previous section. The photo-reactors were kept in the dark in order to avoid any reflected sunlight from the surrounding. Thus, the ZnO NRs substrates (3.5 cm × 2.5 cm), were immersed inside Pyrex Petri dishes filled with an aqueous solution of phenol (5, 10 and 20 ppm), with the photocatalyst surface facing the UV light source. After an equilibration in the dark for 2 h, a photocatalytic degradation of phenol was carried out under UV light for a maximum time15 hours.

3.5 Analytical method

Photocatalytic degradation of phenol was plotted by measuring the optical absorption spectrum of the
phenol solution from 190 to 800 nm at regular time intervals (from 0 to 15 hours). Thus, an aliquot of phenol solution was tested in a quartz cuvette in a UV/Vis spectrometer (specord 50 plus from analytic-jena, Germany). The concentration of phenol was evaluated based on the reduction in absorption intensity at $\lambda_{\text{max}} = 270$ nm and plotted as $C_t/C_0$ versus time, where $C_t$ represents the concentration of phenol at time ‘t’ and $C_0$ represents its initial concentration. The photocatalytic degradation efficiency was calculated as the following:

$$\text{Photodegradation efficiency} = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (1)$$

4. Results and Discussion

4.1 Characterization of ZnO NRs

The morphology of the as prepared ZnO nanorods was studied using scanning electron microscope (SEM) where the structure of these ZnO nanorods could be seen, as shown in Figure 1. The ZnO nanorods have an average length of about 6 μm as shown in, with an average diameter of about 300 nm.

Room temperature optical absorption of the ZnO NRs is shown in Figure 2. The nanorods exhibit strong absorption above 350 nm due to its wide band gap [16] and show an extension of the absorption edge into the visible region.

4.2 Photodegradation of phenol

A comparative photodegradation of phenol under a UV light ($\lambda = 365$ nm) for three different concentrations of 5, 10 and 20 ppm over ZnO NRs, are shown successively in Figure 3,4,5. Pure solutions of phenol were used as references. Hence, $A/A_0$ was plotted versus irradiation time where A presents the intensity of absorbance of phenol at $\lambda=270$ nm and $A_0$ represents its initial value.

It was observed that pure phenol exhibits a surprising increase in its absorbance as time goes on and reaches its maximum value at the end of the experiment after 10 hours (references curves). This is probably due to the slow transformation of phenol under UV light to its intermediates; such as p-benzoquinonone, catechol, and p-hydroquinone; that have a similar range of absorbance [26-28]. The reaction of phenol with a hydroxyl radical (OH•) (generated by direct photolysis of water) produces these new intermediates [29] by the introduction of an additional -OH group (auxochrome) to the original molecule of phenol leading to an increase in the intensity of absorption at $\lambda_{\text{max}}=70$ nm (this behavior is known as a hyperchromic effect) [30].
In the other hand, the adsorbed phenol molecules on the relative high surface area of the synthesized ZnO NRs shows an immediate expected decrease (see Figure 6), to reach the minimum after 15 hours due to the high kinetic of degradation of phenol which minimizes the total concentration of phenol.

This interpretation can be confirmed by the clear change in colours between the pure phenol solutions and those with the ZnO NRs dipped in. A pink colour was observed for the pure phenol solutions due to the weak n→π transitions at 434 nm (R-bands) stretching into the visible region in the p-benzoquinone molecule formed in relatively high concentration in the medium [26, 28], Figure 8.

FIG. 4 Comparative photodegradation of phenol with different concentration with and without ZnO NRs under UV light of λ=365 nm, phenol concentration=10 ppm.

FIG. 5 Comparative photodegradation of phenol with different concentration with and without ZnO NRs under UV light of λ=365 nm, phenol concentration=20 ppm.

FIG. 6 Comparative UV-vis spectrum of phenol 5 ppm degradation over ZnO NRs versus time under λ=365 nm.

FIG. 7 Proposed mechanism of phenol photodegradation [37], and its intermediates leading to complete mineralization into CO₂ and H₂O by ring opening mechanism as proposed in Figure 7.

FIG. 8 Comparative phenol solution colour between pure phenol and phenol having ZnO NRs dipped in after 10 hours of irradiation with UV light λ=365 nm.
4.3 Photocatalytic Kinetic Model

The photocatalytic degradation of phenol was observed to follow the Langmuir-Hinshelwood kinetic model [31]. The initial concentration of phenol affects primarily the degradation rate. The photocatalytic degradation of phenol over ZnO NRs under UV irradiation follows the pseudo-first-order kinetics as shown below:

\[ r = -\frac{dc}{dt} = k_{obs} \]  \hspace{1cm} (2)

A simple integration of this equation (with the same conditions for \( C=C_0 \) at \( t = 0 \), with \( C_0 \) being the initial concentration in the bulk solution and \( t \) the reaction time) gives the expected relation:

\[ \ln \left( \frac{C_0}{C} \right) = k_{obs} \times t \]  \hspace{1cm} (3)

The apparent pseudo-first-order rate constant \( (k_{obs}) \), is related to the concentration of phenol. The values of \( k_{obs} \) can be obtained simply by analysing the linear curve in the plot of \( \ln \left( \frac{C_0}{C} \right) \) vs. \( t \). Figure 9.

As shown in Figure 9 phenol with the lowest concentration gave higher \( k_{obs} \) value compare to the phenol with concentration 20 ppm because at low concentration, the competition for reactivity and catalytic sites on the surface of ZnO was not high as there were only a few phenol molecules in lower concentration. The degradation rate of 5 ppm was about 3 times higher than the degradation rate in 20 ppm of phenol solution. This indicates more rapid and easier photodegradation at lower concentration. This observation shows the significant effect that the initial concentration of phenol had on the rate of degradation. Moreover, the percentage of photodegradation between samples irradiated at \( \lambda=254 \text{ nm} \) and 365 nm shows a ~90% of transformation after 15 hours at \( \lambda=254 \text{ nm} \) (with an apparent degradation rate \( k_{obs}= 0.0023 \)). This value is approximately the double of phenol removal at \( \lambda=365 \text{ nm} \) as shown in Figure 10.

![FIG.9 Comparative photodegradation kinetics of different concentration of phenol under UV light \( \lambda=365 \text{ nm} \).](image)

![FIG.10 Comparative mineralization efficiency of phenol 5 ppm over a ZnO NRs under two different UV wave length, \( \lambda=254 \text{ nm} \) and \( \lambda=365 \text{ nm} \).](image)

5. Conclusion

Phenolic components produced in petroleum refineries in addition to certain petrochemical industries are very toxic. The remove of this kind of molecules in efficient and cost effective way is very challenging. Photocatalytic degradation process used in this study seems to be a very promoting technology for a complete remove of phenol through the ZnO NRs synthesized by hydrothermal growth method on glass substrate. The photocatalytic experiments were performed under 254 and 365 nm. It was observed that the degradation kinetics follows the Langmuir-Hinshelwood kinetic model and decrease with increasing the initial concentration from 5 to 20 ppm while the use of 254 nm UV light source for 10 hours permits an almost complete remove of phenol (~90%). Coupling UV light and ZnO NRs photocatalyst allow the transformation of phenol to its intermediates such as p-benzoquinonone, catechol, and p-hydroquinone followed by a complete degradation to \( \text{CO}_2 \) and \( \text{H}_2\text{O} \). Actual studies are in processing to improve the photocatalytic degradation in the visible light region of organic pollutant molecules and microplastics.

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