Solar Photocatalytic Degradation of Phenol in Aqueous Solutions Using Titanium Dioxide

Mohamed Gar Alalm, Ahmed Tawfik

Abstract—In this study, photocatalytic degradation of phenol by titanium dioxide (TiO_2) in aqueous solution was evaluated. The UV energy of solar light was utilized by compound parabolic collectors (CPCs) technology. The effect of irradiation time, initial pH, and dosage of TiO_2 were investigated. Aromatic intermediates (catechol, benzoquinone, and hydroquinone) were quantified during the reaction to study the pathways of the oxidation process. 94.5% degradation efficiency of phenol was achieved after 150 minutes of irradiation when the initial concentration was 100 mg/L. The dosage of TiO_2 significantly affected the degradation efficiency of phenol. The observed optimum pH for the reaction was 5.2. Phenol photocatalytic degradation fitted to the pseudo-first order kinetic according to Langmuir–Hinshelwood model.

Keywords—Compound parabolic collectors, phenol, photocatalytic, titanium dioxide.

I. INTRODUCTION

PHENOL is found in the wastewater of many industries such as resins , petrochemical, paint, textile, oil refineries, food, photographic chemicals, antioxidants and flavoring agents [1]. Phenol is considered one of such high toxic pollutant that seriously causes environmental problems and harmful to human beans [2]. Because of its toxicity and low biodegradability, phenolic wastewater needs very large systems to be treated by conventional biological treatment [3]. In addition, Using activated carbon in case of high phenol concentrations needs big amount of adsorbent and leads to contaminated solid waste [4].

Advanced oxidation processes (AOPs) have been realized as particularly efficient technologies for phenol degradation [5]. In AOPs powerful reactive species like hydroxyl radicals (•OH) are generated by specific chemical reactions in aqueous solutions [6]. (•OH) is able to destroy even the most recalcitrant organic molecules and convert them into relatively benign and less persistent end products such as CO_2, H_2O and inorganic ions [7]. Among AOPs processes, heterogeneous photocatalysis using artificial or solar irradiation have been recognized to be effective for the degradation of several types of phenolic compounds [8].

In the heterogeneous UV/TiO_2 technique, the ultraviolet light ($\lambda < 400nm$) are utilized as an energy source and TiO_2 playing as a semiconductor photo-catalyst [9]. TiO_2 is distinctive with high surface area, good particle size distribution, high chemical stability, and the possibility of using sunlight as a source of irradiation [10]. In recent years, solar photocatalytic mineralization of organic pollutants utilizing the interaction between ultraviolet irradiation and semiconductors catalysts became ubiquitous [11].

This study aims to evaluate the removal of phenol from aqueous solutions by solar photocatalytic reaction. A reactor based on compound parabolic collectors (CPCs) technology was used to employ the UV irradiation from solar light.

II. MATERIALS AND METHOD

A. Chemicals

Phenol and intermediate ring compounds such as catechol, hydroquinone, and p-benzoquinone were purchased from Merck (Germany) with purities ≥ 99% and used as received. The TiO_2 in Nano powdered scale (p25) was obtained form from Acros.

B. Photocatalysis Experiments

Photocatalysis experiments were carried out using compound parabolic collectors reactor placed in Borg Alarab City, Egypt (Latitude 30°52', Longitude 29°35') on the roof of environmental engineering department. The photo-reactor module is ($0.36m^2$) and consists of six borosilicate tubes with diameter 1 inch and length 75cm mounted on a curved polished aluminum reflector sheet with radius of curvature 9.2cm. The reactor is connected from both the inlet and outlet with a tank containing the raw solution and provided with stirrer to avoid precipitation of solids and to ensure the homogeneity of feedstock. The solution was continuously recirculated in closed cycle. A schematic diagram of the experimental set-up is shown in Fig. 1.

The reactor was fed with 4L of the 100 mg/L phenol solution, and the pH was adjusted by few drops of H2SO4, or NaOH. Then the TiO_2 was added. To evaluate the adsorption of phenol into the catalysts, the first 30 minutes was only adsorption process by mechanical mixing in the tank without turning on the recirculation pump. The solar irradiation was measured by Met one Portable Weather Station (Model Number 466A) installed in the same location. The normalized illumination time (t30w) was used to compare between photo-catalytic experiments instead of exposition time (t). The normalized illumination time was calculated by the following equations [12]:

$$t_{30w,n} = t_{30w,n-1} + \Delta t_n \left(\frac{UV}{30}\right)\left(\frac{V_i}{V_t}\right) \tag{1}$$

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$$\Delta t_n = t_n - t_{n-1} \qquad (2)$$

where t_n: the experimental time for each sample, UV: the average solar ultraviolet radiation (W/m^2) measured during $\Delta t n$, t30W: the normalized illumination time, which refers to a constant solar UV power of 30W/m^2 (typical solar UV power on a perfectly sunny day around noon), V_t: the total reactor volume and V_i: the total irradiated volume.
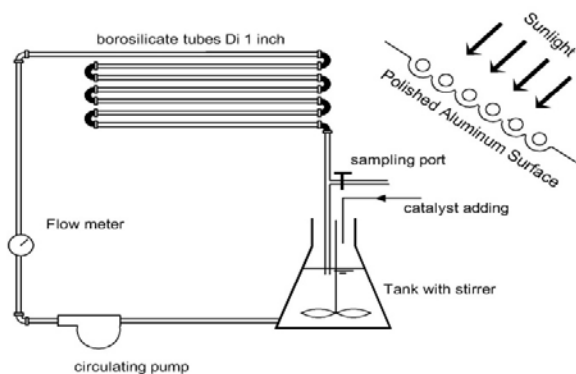

Fig. 1 Schematic diagram of the solar compound parabolic collectors' reactor

C. Analytical Methods

Phenol and oxidation intermediate ring compounds (catechol, hydroquinone and p-benzoquinone) were quantified by Shimadzu HPLC by C-18 phenomenex reverse phase column, degasser (20A5), pump (LC-20AT), and prominences Diode Array Detector (SPD-M20A). The samples were filtered by micro syringe filters (0.2 µm). The mobile phase was a mixture of ultrapure water/methanol/ acetic acid with volumetric percent ratio of 79.2:19.8:1.0. The flow rate of the mobile phase was 0.8 ml/min. The monitoring was at wave lengths of 270, 276, 290 and 245nm for phenol, catechol, hydroquinone and p-benzoquinone, respectively.

III. RESULTS AND DISCUSSION

A. Effect of Irradiation Time

The effect of irradiation time on photocatalytic degradation efficiency of phenol by TiO$_2$ is shown in Fig. 2. It could be observed that only 6% of phenol was removed during 30 minutes of dark agitation inside the tank. This result is attributed to the low adsorption of phenol on TiO$_2$ surface [13]. After turning on the circulation pump the degradation rate was relatively high as 59% degradation of phenol was achieved at the first 30 minutes of irradiation. The degradation rate was then decreased because of the consumption of TiO$_2$. After 150 minutes of irradiation the maximum degradation of phenol was achieved, which was 94.5%. This decreasing in reaction rate was due to the consuming of TiO$_2$ in the first 30 minutes.

Phenol oxidation process is accompanied with evolution of several aromatic intermediates such as benzoquinone, catechol (benzene-1,2-diol), hydroquinone (1,4-Dihydroxybenzene) [14]. As revealed from Fig. 2, the main intermediates are

hydroquinone and catechol, while benzoquinone was slightly appeared. The formation of hydroquinone and catechol can be attributed to the activation of phenol molecules by reaction with an OH radical [15]. The •OH radical attacks the phenyl ring of the phenol yielding catechol, 1,2,3-benzenetriol and hydroquinone, then the phenyl rings in these compounds disintegrate to give malonic acid, then short-chain organic acids such as, maleic, oxalic, acetic, formic 3-hydroxy propyl carboxylic acid, 2-hydroxy propanal, 2-hydroxy-ethanoic acid glycol acid, finally CO$_2$ and H$_2$O. H• produced during the attack of bonds by •OH is reported to be an important active free radical in the degradation process. During the process, H+ or H• is scavenged by oxygen to form HO$_2$• radicals, which eventually convert to •OH radicals. Therefore, the principal reaction leading to organics decomposition would be the one with •OH radicals [8]. In TiO$_2$ photocatalysis, hydroquinone gradually increased in the first 60 minutes to reach 16 mg/L, while the maximum formation of catechol was 10.5 mg/L after 30 minutes. With the decreasing of phenol concentration, the aromatic intermediates are also oxidized into carboxylic acids and CO$_2$. Finally, carboxylic acids generated from the oxidation of all aromatics, can be converted into CO$_2$ [16].
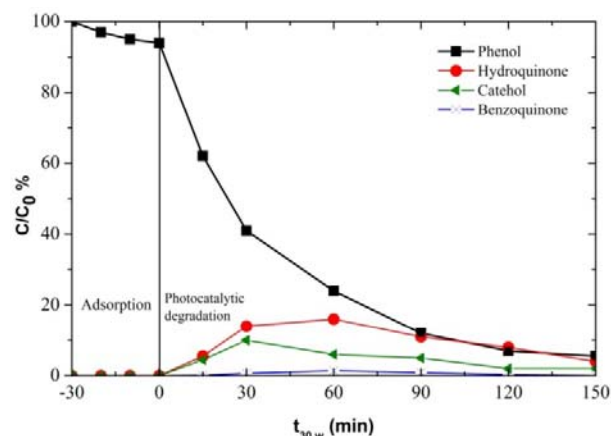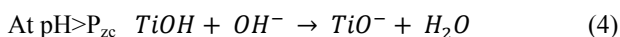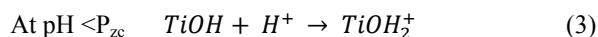

Fig. 2 Effect of irradiation time on phenol degradation and formation of intermediates, initial phenol concentration = 100 mg/L, initial pH = 5.2, TiO$_2$ dosage = 2.0 g/L

B. Effect of pH

The solution pH has a significant influence on both of adsorption to TiO$_2$, and photocatalytic degradation [17]. Therefore, the effect of initial pH was investigated in acidic and alkaline conditions. The results of pH effect are presented in Fig. 3. It could be seen that the degradation of phenol is generally enhanced in acidic solutions. The optimal solution pH was 5.2 in which 94.5% degradation of phenol was achieved after 150 minutes of irradiation. Further rising of the initial pH led to a decrease in degradation efficiency of phenol. These results correspond closely to other similar reported work [18].

The effect of pH on degradation of organic matter assisted by the semiconductor oxides is influenced by the acid–base equilibrium governing the surface chemistry of metal oxides in water as shown in the following reactions:

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At pH <P_{zc} $TiOH + H^+ \rightarrow TiOH_2^+$ (3)

At pH>P_{zc} $TiOH + OH^- \rightarrow TiO^- + H_2O$ (4)

where P_{zc} is the zero point of charge of the semiconductor [19]. It is defined as the pH at which the surface of an oxide is uncharged. The point of zero charge of the TiO_2 is reported to be about 6.25 [9]. The effect of pH on the photo-oxidation activity could be explained in terms of electrostatic interaction between the active semiconductor sites and the substrate molecules [20]. The interaction could be expected to affect the encounter probability of the resulted hydroxyl radical with the molecules. It is stated that the overall reaction would be improved or restrained depending on whether attractive or repulsive forces prevail, respectively [11]. At pH of 5.2, the electrostatic attraction force between phenol molecules and positively charged TiO_2 resulted in maximum oxidation activity, and thus led to high degradation efficiency of phenol. At higher pH the phenol molecules have negative charges, which led to repulsion with TiO_2 particulates and decrease the photocatalytic activity [21]. Besides, adjusting the pH by NaOH is reported to create a competition on adsorption on the surface of TiO_2 between the Na+ ions and OH− ions with the phenol anions, which resulted in lower photocatalytic degradation efficiency [13].
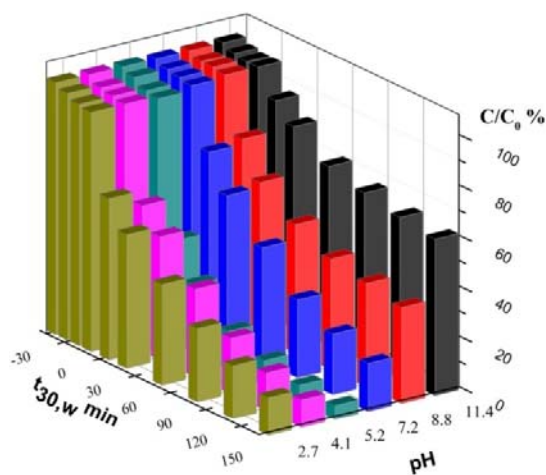

Fig. 3 Effect of pH on photocatalytic degradation of phenol, TiO_2 dosage = 2 g/L

C. Effect of Catalyst Loading

The effect of Dosage of TiO_2 dose on phenol degradation is shown in Fig. 4. The results revealed that photocatalytic degradation efficiency is improved with increasing the dosage of TiO_2. This improvement can be attributed to the increasing of active sites by providing bigger amount of catalyst, which is the semiconductor in the reaction [21]. Consequently, the formation of electron hole pairs on the surface of semiconductor and the high reactive hydroxyl radicals increased, which cause the oxidation of phenol into other intermediates [22]. The optimum dosage of TiO_2 was 2 g/L which achieved a 94.5% degradation of phenol in 150 minutes of irradiation. Increasing the dosage more than 2 g/L reduced

the degradation efficiency due to the increasing of turbidity in the solution, which detracts the amount of light reaching the semiconductor active sites [8]. Furthermore, increasing the catalyst loading may cause agglomeration of particulates, which decreases the active sites on the semiconductor surface [23].
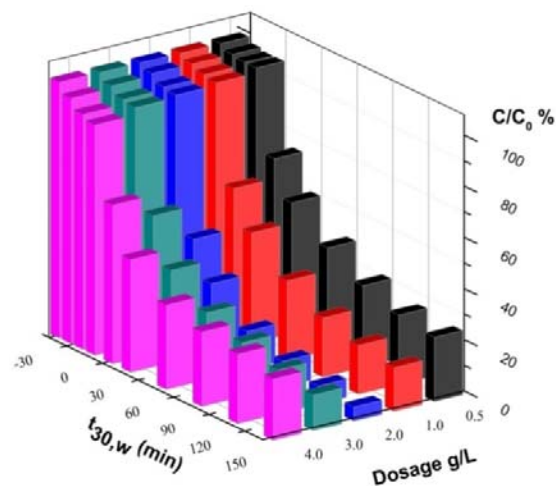

Fig. 4 Effect of catalyst loading on photocatalytic degradation of phenol, pH=5.2

D. Degradation Kinetics

The Langmuir–Hinshelwood model is usually used to describe the kinetics of photocatalytic degradation of organics in aqueous solutions [24]. It basically relates the degradation rate (r) and reactant concentration (C) in water at time t, which is expressed by the following equation [25]:

$$r = -\frac{dC}{dt} = \frac{K_r K_{ad} C}{1 + K_{ad} C} \tag{5}$$

where kr is the rate constant and Kad is the adsorption equilibrium constant. In Photocatalysis where the adsorption is relatively weak like and/or the reactant concentration is low, (5) can be simplified to the pseudo- first order kinetics with an apparent first-order rate constant kapp [24]:

$$\ln\left(\frac{C_o}{C}\right) = K_r K_{ad} t = K_{app} t \tag{6}$$

where C0 is the initial concentration of phenol. Fig. 5 shows the linear relation of Ln(C0/C) with irradiation time. Kapp was calculated for TiO_2 photocatalysis and found to be 0.017.. Correlation coefficient (R2) was also calculated was also calculated and found to be 93.1%.

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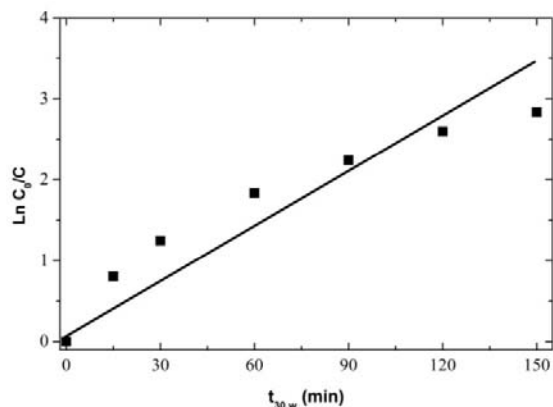Vol:8, No:2, 2014

Fig. 5 Kinetic analysis of photocatalytic degradation of phenol

IV. CONCLUSIONS

In this work, solar photocatalytic degradation of phenol using nano scale titanium dioxide as a semiconductor was investigated. The photocatalytic degradation of phenol by TiO₂ achieved 95.5% degradation of phenol in 150 minutes of irradiation. The photocatalytic activity was enhanced in acidic conditions and the optimum pH for was 5.2. The dosage of TiO₂ highly influenced the degradation of phenol and the optimum dosage was 2.0 g/L for initial phenol concentration of 100 mg/L. The photocatalytic degradation of phenol by TiO₂ followed the pseudo-first order kinetic according to Langmuir–Hinshelwood model.

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