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Utilization of nano size TiO_2 for degradation of phenol enrich water by solar photocatalytic oxidation

Tarek S. Jamil[a], Tarek A. Gad-Allah[a], Mohamed E.M. Ali[a,*], Maggy N.B. Momba[b]

[a] *Water Pollution Control Department, National Research Center, 33 El-Behouth St., Dokki, P.O. Box 12311, Cairo, Egypt*
Tel. +202 33371479; email: alienv81@yahoo.com
[b] *Department of Environmental, Water and Earth Sciences, Tshwane University of Technology, Arcadia Campus, Private Bag X680, Pretoria 0001, South Africa*

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ABSTRACT

Photocatalytic processes using TiO_2 provides an interesting route to destroy hazardous organic contaminants in water such as phenol. Usage of TiO_2 in presence of solar irradiation is considered as cost-effective technique. The solar photocatalytic degradation of phenol enrich water over prepared TiO_2 has been studied. The catalyst was characterized by several techniques such as X-ray diffraction, gravimetric-differential thermal analysis, and Fourier transformation infra red spectroscopy. The results showed that the nanoparticle prepared from TiO_2 can be used as an effective photocatalyst for phenol removal under solar radiation. Photocatalytic activity was mainly attributed to its size 19.6 nm and in turn large amount of surface hydroxyl species. Influence of pH, catalyst loading, and hydrogen peroxide dose were investigated during this study. At optimum dose of 0.50 g/L TiO_2 and pH value of 8, phenol removal was about 72% of initial concentration of 50 ppm, which was achieved within 120 min of solar irradiation time. In presence of hydrogen peroxide, the removal was increased up to 78% within 90 min. It was found that the photocatalytic degradation of the phenol enrich water obeys the pseudo-first-order kinetic reaction within degradation process. The mechanism of oxidation as well as the intermediate compounds formed was detected by GC/MS.

Keywords: Phenol; Nanoparticle TiO_2; Mechanism; Solar treatment; Photocatalysis

1. Introduction

Recently, the application of heterogeneous photocatalytic water purification processes has gained wide attention due to its efficiency in degradation and mineralization of recalcitrant organic compounds such as phenol under UV and visible light. Moreover, titania has contributed in this scenario compared to other semiconductor photocatalysts because it is inexpensive, naturally inert, and photostable [1].

Titanium dioxide (TiO_2) has been one of the most suitable photocatalyst for environmental application

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*Corresponding author.

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because of its biological and chemical inertness, strong oxidizing power, nontoxicity and long-term stability against photo and chemical corrosion [2,3]. However, TiO_2 can be activated only under UV light of wavelengths <387 nm irradiation due to its large band gap of 3.2 eV. The solar spectrum usually contains about 5% UV light. Owing to this innate limitation, the solar energy cannot be utilized efficiently in the photocatalytic process [4,5]. The photocatalytic activity of TiO_2 usually depends on a competition between the following two processes; the ratio of the transfer rate of surface charge carriers from the interior to the surface to the recombination rate of photo-generated electrons and holes. If the recombination of photo-generated electrons and holes occurs too fast (<0.1 ns), then there is not enough time for any other chemical reaction. Comparing with other semiconductor, the surface charge carriers of TiO_2 are relatively long-lived (around 250 ns), allowing the electrons or holes to travel to the crystallite surface. It is on the TiO_2 surface that different types of radicals are formed, the most common radical is hydroxyl radical $^{\cdot}OH$, which is responsible to carry out other chemical reactions on the surface of TiO_2 [6].

Generally, phenols are harmful organic pollutants in water discharged into the environment causing unpleasant taste and odor of drinking water [7]. Phenol is both a man-made chemical and a natural product. It is found in nature, in some foods, in human and animal wastes, and in decomposing organic material. The largest single use of phenol is as an intermediate in the production of phenolic resins. It is also used in the production of caprolactam (which is used in the manufacture of nylon 6 and other synthetic fibers) and bisphenol A (which is used in the manufacture of epoxy and other resins). It is also known that chlorination of natural waters (disinfection process) produces chlorinated phenols [1].

2. Materials and methods

2.1. Preparation and characterization of the photocatalysts

TiO_2 powder used in this study was synthesized by the conventional sol–gel process. $TiCl_4$ was first dissolved in an ethano0l/water (volume ratio of 4:1) solution, and ammonia was then introduced into the solution until pH reached to 7.5 to induce precipitation. The resulted gelatinous precipitate was filtered and washed with deionized water to reduce [Cl^-] below 5×10^{-4} M, as determined by titration against standard solution of silver nitrate, and then kept at 80˚C for several h in air to remove excess ammonia. The resulted powder was then dried and calcined to get the catalyst. The calcination process involved purging the reactor with the gas for 1 h, heating the powder at a rate of 40˚C/h to 450˚C. Finally, the powder was calcined at 450˚C for 4 h.

2.2. Characterization

Crystal structure of the prepared powdered TiO_2 was determined using X-ray diffraction (XRD). The XRD patterns were collected at room temperature by Philips Powder Diffractometer using Cu-Kα radiation and scan rate of 2˚/min. Thermal analysis was conducted by STERAM Labsys^{TM} TG-DSC apparatus with heating rate 5˚C/min, while IR spectra was obtained from FTIR-6300-Jasco spectrometer. The specific surface areas were determined by the single-point BET method using Flow Sorb 2300 apparatus (Micromeritics). Scanning electron microscopy (SEM) was performed using Philips microscope model 505, operating at 25 kV on specimens upon which a thin layer of gold or carbon had been evaporated.

2.3. Photocatalytic activity

All solar photocatalytic experiments were carried out under similar conditions on sunny day of summer (April–May) under clear skies. The concentrated parabolic solar collector configuration was used to perform heterogeneous photocatalysis oxidation of phenol in water under solar irradiation in a total recirculation loop with a feed tank by a peristaltic pump. The solar reactor consists of one UV transparent glass tube with 1.5 m long and internal diameter of 40 mm as a reaction chamber.

Photocatalytic oxidation was carried out using suspensions of commercial, pure, and doped TiO_2 with phenol as a model for persistent organic pollutants. Firstly, the suspensions were magnetically stirred in the dark for 30 min to attain adsorption–desorption equilibrium between phenol and TiO_2. Then, phenol and the catalyst, at definite concentrations, were continuously fed to the solar reactor from the feed tank by means of a peristaltic pump. The solution flow rate, maintained constant for all of the runs, was 60 L/h. Samples were taken at regular time intervals from the solar reactor and the first were centrifuged to get rid off the residual catalyst, and then were analyzed immediately. The concentration of the phenol in the filtrate was measured according to direct photometric method [8]. Analysis of phenol and its by-products are carried out using high-performance liquid chromatography-ultraviolet detection (HPLC/UV) (Agilent 1100 HPLC system) and GC/MS, Varian 4500. A reversed-phase ODS C18 column was used at

25°C. The mobile phase was obtained with methanol and water and the flow rate was 1.0 mL min^{-1}. The mobile phase was changed from 100% water to 0% within 30 min. Detection wavelengths were used 210, 230, 2,544, and 280 nm.

Different reaction conditions have been investigated following the previous procedure. The conditions include catalyst concentration, initial pH, phenol concentration, and hydrogen peroxide dose.

3. Results and discussion

3.1. Characterization of photocatalyst

The TGA pattern of the prepared TiO_2 calcined at 450°C is represented in Fig. 1(a). TGA curve (solid line) indicated a weight loss of 0.5% at 165°C resulting from the evaporation of residual adsorbed water and moisture from the surrounding medium. This appeared as an endothermic peak in the DTA curve (dotted line) over the temperature range from 80 to 250°C. An exothermic peak was observed during the dynamic heating in the vicinity of 290 and 400°C in the DTA curve. XRD patterns were used to determine the phase structure and crystalline size of the prepared sample and to compare it with the commercial one (Fig. 1(b)). Anatase phase of prepared TiO_2 was confirmed by (1 0 1), (0 0 4), (2 0 0), (1 0 5), and (2 1 1) diffraction peaks (card number 84–1,286) leading to expected high photocatalytic activity according to [9]. The crystallite size is determined from the broadening of the corresponding X-ray spectral peaks by the Scherer's equation [10]. The surface area of prepared TiO_2 was too much higher than that of commercial TiO_2 since their surface areas were 59 m^2/g and 15 m^2/g for the prepared TiO_2 and commercial TiO_2, respectively. The Fourier transformation infra red spectroscopy (FTIR) spectrum of the nano-synthesized powder is shown in Fig. 1(c). The main peaks appearing in the range 400–700 cm^{-1} correspond to Ti–O and Ti–O–Ti stretching vibrations [11,12].

3.2. Photodegradation of phenol

The scheme of the photocatalytic degradation phenol over TiO_2 was stated by Gaya and Abdullah, 2008 [13], as shown in Fig. 2. Photoholes have great potential to oxidize phenol directly or indirectly via the combination with hydroxyl radical predominant in aqueous solution [12,14].

Simultaneous presence of solar irradiation and TiO_2 (0.5 g/L) achieved phenol removal of 45.21% within 120 min at pH 6.5. Table 1 summarizes the obtained pseudo-first-order reaction rate constants (k_0) and phenol removal at 120 min reaction time (φ_{120}) using different catalyst dose. It is clear that the prepared TiO_2 has higher activity than commercial one which can be attributed to its nanostructure and large surface area. The optimum concentration of both TiO_2 for efficient solar photodegradation of phenol was 0.50 g/L. The calculated pseudo-first-order rate constants for the solar photodegradation along with the efficiencies of phenol removals after 120 min at different TiO_2 loading are listed in Table 1. The phenol removal was observed to be faster in alkaline pH than in acidic pH range, this was attributed to negative surface of the TiO_2 with OH^- ions which acts as an efficient trap for the photogenerated holes and

Table 1
Pseudo-first-order rate constants of phenol degradation using different doses of commercial and prepared TiO_2 [pH 6.5, C_{phenol} = 50 ppm]

Catalyst loading (g/L)	Commercial TiO_2		Prepared TiO_2	
	k_0, min^{-1}	φ_{120}	k_0, min^{-1}	k_0, min^{-1}
0.5	0.003	45.46	0.0068	72.1
0.75	0.002	35.21	0.0052	63.5
1	0.003	39.91	0.0048	52
1.25	0.001	19.84	0.0032	41
1.5	0.001	16.47	0.0021	37

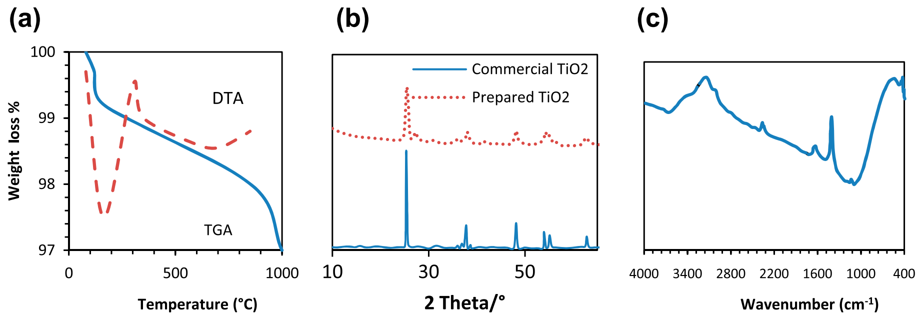

Fig. 1. Characterization of nano-prepared TiO_2 (a) TGA, (b) XRD, and (c) FTIR.

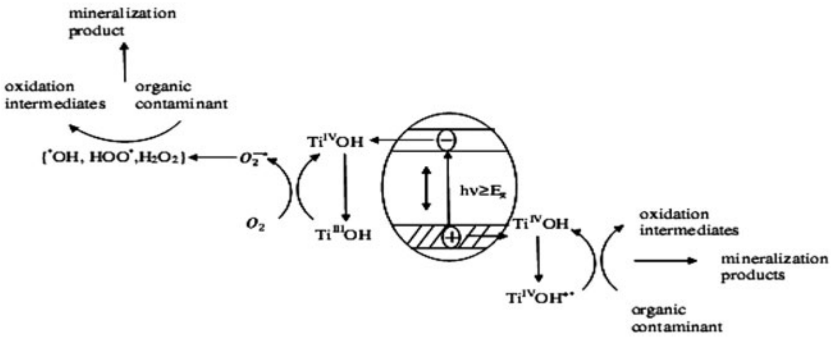

Fig. 2. Conceptual diagram for the primary processes involved in photomineralization of organic compounds [13,17,18].

produce hydroxyl radicals Reaction (1). The pseudo-first-order rate constants reported in Tables 2 and 3.

$$OH^-_{surface} + h^+_{vb} \leftrightarrow OH_{surface} \qquad \text{Reaction (1)}$$

The addition of hydrogen peroxide to the heterogeneous system inhibits the electron hole recombination, it was an acceptor of photogenerated electrons from the conduction band, and thus it promotes the charge separation which leads to increase of phenol removal up to more than 90% at 20 mM H_2O_2. Studying mechanism of phenol degradation by GC/MS showed presence of some intermediates such as catechol, muconic acid, oxalic acid, maleic acid, and their corresponding aldehydes which was in accordance with Grabowska et al. [12].

Table 2
The pH Effect on the calculated pseudo-first-order rate constants and removal of phenol [TiO_2 = 0.50 g/L and C_{phenol} = 50 ppm]

	Commercial TiO_2		Prepared TiO_2	
pH value	k_0, min^{-1}	φ_{120}	k_0, min^{-1}	φ_{120}
3	0.0009	8.78	0.0032	43.1
5	0.001	16.79	0.0039	50.6
6	0.004	21.48	0.0066	70.5
8	0.003	32.00	0.0068	72.1
10	0.002	39.45	0.0076	74.7

Table 3
Pseudo-first-order rate constants and removal percentages after 180 min at different H_2O_2 doses [TiO_2=0.50 g/L, pH 10 and C_{phenol} = 50 ppm]

	Commercial TiO_2		Prepared TiO_2	
H_2O_2 dose	k_0, min^{-1}	φ_{120}	k_0, min^{-1}	φ_{120}
0	0.004	45.21	0.0066	70.3
10	0.005	34.12	0.0073	73.9
20	0.009	54.07	0.0087	77.9
30	0.004	29.92	0.0065	68.0
40	0.002	24.6	0.0053	62.0

3.3. Pathway of phenol degradation

The mechanism of phenol photocatalytic destruction by studying intermediates of phenol qualitatively and in some cases quantitatively was investigated by Sobczynski et al. [15]. Phenol is converted to benzoquinone and catechol over TiO_2 under sunlight. The

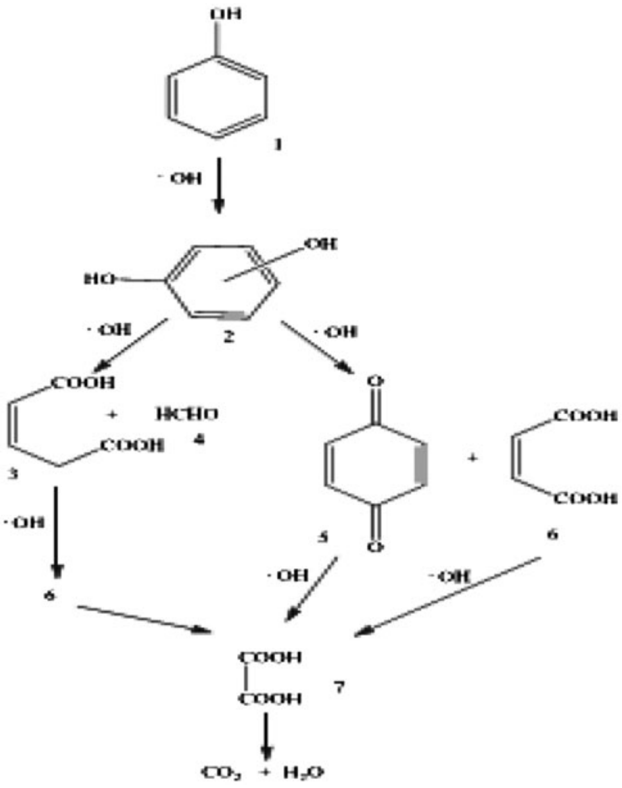

Fig. 3. Probable degradation mechanism for phenol [16].

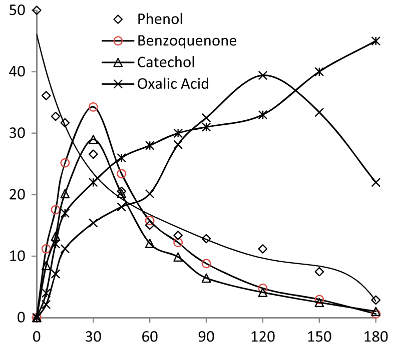

Fig. 4. By-products formation during degradation of phenol by TiO_2 sunlight/H_2O_2.

ring-opening products judged was formed by the appearance of the peak at the retention time 1.5 min, at the early stages of the decomposition process, at the same time as benzoquinone and catechol. The conversion of phenol to catechol is likely to be more advantageous for the complete mineralization of phenol rather than conversion to benzoquinone or hydroquinone because catechol decomposed to oxalic acid, acetic acid, formic acid, and then to CO_2 and water [12]. Complete degradation was already achieved after 3 h of sunlight irradiation only with TiO_2 and H_2O_2. The generated hydroxyl radicals attack phenol molecule leading to the formation of dihydroxy benzene. Further degradation proceeds through the cleavage of dihydroxy benzene. Ring opening of hydroquinone results in the formation of oxalic acid. Decarboxylation of oxalic acid further leads to the formation of formic acid, carbon dioxide, and water molecule. This mechanism, as shown in Fig. 3, was in accordance with Devi and Rajashekhar [16]. The formation of some by-products was followed by HPLC as shown in Fig. 4. Benzoquinone and catechol concentrations are increased till 30 min, and then their concentration starts to decrease due to ring rapture. Oxalic acid concentration was increased up to 120 min, and then starts to decrease due to its degradation to formic acid; then completes mineralization to carbon dioxide and water. On the other hand, concentration of formic acid increases gradually till the end of the experiment.

4. Conclusion

Photodegradation of phenol showed higher removal by nano-prepared TiO_2 than that of commercial in presence of solar energy at pH 7, 0.5 g/L TiO_2, and 20 mM H_2O_2 due to the nano size, crystal structure, crystallinity, and large amount of surface hydroxyl groups. The reaction showed to obey pseudo-first-order kinetic. Studying the degradation mechanism showed presence of aldehydes and organic acid as intermediates.

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