Original Research

Effect of H_2O_2 Addition on Phenol Removal from Wastewater Using TiO_2/Al_2O_3 as Photocatalyst

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Abstract

The photocatalytic oxidation of phenol in water in the band reactor with supported TiO_2 catalysts was investigated. Modified anatase/Al_2O_3 catalysts were used as the photocatalysts. The main aim of these studies was to determine catalytic activity of TiO_2/Al_2O_3 and V-TiO_2/Al_2O_3 in the removal of phenol from water. The effectiveness was measured in the configurations: $TiO_2/UV/O_2/H_2O_2$, $TiO_2/O_2/H_2O_2$, $TiO_2/UV/O_2$, and TiO_2/O_2. It was found that 2 hours of water treatment is enough to obtain a significant COD reduction, and that prolonging treatment time to 8 hours does not result in total phenol removal.

Keywords: photocatalysis, TiO_2/Al_2O_3, phenol, Advanced Oxidation Processes, wastewater treatment

Introduction

The primary use of phenol is in the production of phenolic resins, which are the basis for various industries. Phenol is considered to be very toxic to humans, reported to be lethal in a dose of 1 g, with symptoms including loss of coordination, paralysis, convulsions, and coma. Phenolic compounds are stable and show a tendency to bioaccumulate [1]. In respect of the common presence of phenol in water and wastewater, the methods for its removal are widely tested [2]. Traditional oxygen processes in the biological treatment are not sufficient to remove phenol because it is toxic for the activated sludge and the biological membrane of bed. Various organic and some inorganic compounds can be rendered harmless by using advanced oxidation processes (AOPs).

AOPs are based on the generation of highly reactive OH* radicals that react quickly and non selectively with most organic and some inorganic compounds, leading to its complete mineralization into CO_2, water and simple inorganic acids or its transformation into less toxic products. *OH can be generated in different ways, depending on pollutant and treatment conditions: chemically (H_2O_2/O_3, O_3/OH^-, Fe^{2+} or Fe^{3+}/H_2O_2), photochemically (H_2O_2/UV, O_3/UV) and photocatalytically (mainly TiO_2/UV) [2-6].

A harmless alternative to AOP technology for the removal of organic pollutants is heterogeneous photocatalysis, which works only at room temperature and atmospheric pressure [7]. During the process, an illuminated semiconductor absorbs light and generates active species, which leads to complete oxidation of organic components [6]. Many factors influence photodegradation: semiconductor type, its surface, light intensity, solvent, temperature, pH, and substances present in the solution. Catalysis is applied into the decomposition of most organic compounds containing halogens, nitrogen, and sulphur [5-6].

One of the most efficient, non-toxic, and cheap catalysts is recognized TiO_2 [8]. Photocatalytic activity of TiO_2 is

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influenced by surface area, surface orientation, crystal structure (anatase or rutile) and surface hydroxyl group density [2]. TiO_2 is used typically in the form of powder. In case to avoid the problems with the separation after the process has completed it can be immobilized on the reactor's walls or on the support. But the activity of supported TiO_2 catalysts is limited by the inevitable reduction of overall surface area due to catalyst immobilization [8].

Before planning the reactor there was the problem with the proper form of catalysts. TiO_2 in the suspended form needs to be mixed adequately and separated after process. Solution could be the supported TiO_2. It was indicated [9] that the high effectiveness of Acid Brown 14 oxidation over TiO_2/Al_2O_3 is ascribed to the adsorption properties of support Al_2O_3. In order to prevent recombination or decrease the rate of recombination, the factor close to the catalyst surface can be applied. This incorporates the more effective adsorption places located close to a catalyst's surface. h^+ generated in this way by oxidants (*OH) can reach them before the intermediate products would yield to further reaction, which takes place in the presence of strong adsorbent. The activity of catalysts can be enhanced by a catalyst's modification with e.g. transition metal addition or by combination with other semiconductors.

The effect of photocatalytic oxidation can be improved using the addition of external oxidants, e. g. H_2O_2 and O_3, but the effect is not obvious and depends on many factors. H_2O_2 is one of the cheapest oxidants with high oxidation power that is water soluble and thermally stable. It is easy to use, the only final products during oxidation are O_2 and H_2O, and UV illumination can be applied [10].

Direct photolysis, in comparison with the other chemical techniques, is a selective method. It is less effective because the compound must absorb UV radiation, but the absorbance is not complete and the reaction rate is negligible [11]. In the presence of UV irradiation the photolysis of H_2O_2 onto 2 *OH is observed because of H_2O_2 weak absorption of UV radiation according to equations 1-4.

$$HO–OH + h\nu \rightarrow 2 \ *OH \qquad (1)$$
$$*OH + H_2O_2 \rightarrow H_2O + HO_2* \qquad (2)$$
$$*OH + HO_2* \rightarrow H_2O + O_2 \qquad (3)$$
$$2HO_2* \rightarrow H_2O_2 + O_2 \qquad (4)$$

The photolysis rate of H_2O_2 is dependent on pH and increases in basic conditions:

$$2H_2O_2 + 2*OH \rightarrow H_2O + HO_2* \qquad (5)$$
$$2HO_2* \rightarrow \ H_2O_2 + O_2 \qquad (6)$$

But too high H_2O_2 addition causes the process to hinder because the surplus H_2O_2 captures the radicals (7) [12]:

$$H_2O_2 + *OH \rightarrow HO_2* + H_2O \qquad (7)$$

Irradiation favours the radical reactions but H_2O_2 initiates the chain reactions that run after the irradiation has finished [13].

The mechanisms of phenol oxidation are complicated. The main products observed are catehol and hydroquinone, and negliglible amounts of pirogalol, 1,2-trihydroksobenzene and hydroksybenzochinone [14].

Experimental Procedures

Photoreactor

Photoreactions were conducted in the band reactor of our construction [7]. Two tubes were placed below the UV lamp (254 nm, 50 Hz) (Fig. 1). The intensity of UV light is 1.68-2.20 mW/cm^2 measured by Radiometer VLX254 (Vilber Lourmat, 254 nm). In the reactor the bands are the main mixing system and enable the counter-current contact of the reagents. The mixture of oxygen (3 dm^3/h) and nitrogen (37 dm^3/h) was pumped into the reactor at room temperature because the aeration is usually used to prevent or hinder the charge carriers' recombination [6].

Photocatalyst

To prevent problems with filtration after the experiments as the catalysts were typed, γ-Al_2O_3-supported TiO_2 catalysts modified with V addition were prepared according to [15] by the Double Impregnation Method [16] or Classical Impregnation Method. γ-Al_2O_3 supports (INS, Puławy) with total surface area 56.2 m^2/g, after heating in 150ºC, were impregnated in $TiCl_4$ for 10 min. at room temperature. Then they were dried in 150ºC catalyst and calcinated for 3 h at 600ºC. The TiO_2/Al_2O_3 catalysts were then treated in two ways. In DIM method TiO_2/Al_2O_3 was firstly impregnated in chelating agent - EDTA and then in proper solution of V_2O_5 with NaOH. In the CIM method the EDTA impregnation stage was omitted. After impregnation and drying, all studied catalysts were calcinated for 3 h at 600ºC. Physicochemical characteristics were determined by BET method for total surface area, X-ray diffraction (XRD) for crystalline structure and X- ray fluorescence (XRF) for catalyst composition.

Photocatalytic Studies

Experiments of organic water pollutant removal were conducted in the band reactor described above. As the
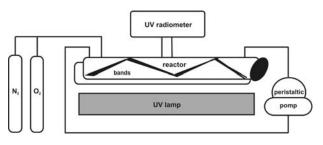
Fig. 1. Scheme of apparatus for photooxidation of organic compounds in water.

Table 1. Physicochemical properties of studied catalysts.

Catalyst	Ti content [wt.%]	V content [wt.%]	total surface area [m²/g]	impregnation method
Ti1	6.69	-	75.37	
Ti2	3.34	-	93.96	
Vc	6.82	0.54	91.96	CIM – 10 min.
Vd	5.34	4.40	71.30	DIM – 8 min.

model contaminants used solutions of phenol prepared to have a COD value ca. 3,000 mg O_2/dm^3 that is typical for real wastewater and simultaneously is exceeding the norms what may indicate highly concentrated (according to COD) wastewater [17].

As the oxidizing agents were typed oxygen (from air) and H_2O_2, the effectiveness was measured in a few configurations: $TiO_2/UV/O_2/H_2O_2$, $TiO_2/O_2/H_2O_2$, $TiO_2/UV/O_2$, and TiO_2/O_2. The sample was taken back after 115 minutes, assuming that by volumetric flow 1.3 dm^3/h the whole sample would be pumped out. The next stage was the analysis of organic compound concentrations using COD method with bichromate method [18].

Results and Discussion

The catalysts were examined in the Analytical Laboratory of the Faculty of Chemistry UMCS in Lublin to determine the total surface area – BET method, TiO_2 content – XRF method and V by AAS method (Table 1). Although the time of impregnation was similar, it was incorporated into catalyst during impregnation with chelating agent much more V (4.40%) than using the classical method (0.54%).
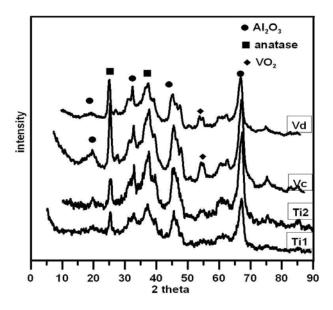
All XRD spectra of studied catalysts are similar (Fig. 2). Peaks with higher intensity (peaks by 2 theta = 20, 33 and 67) are connected with support Al_2O_3. TiO_2 is present in a form of anatase (peaks by $2\theta=25$) and V as VO_2 ($2\theta=54$).

Novel M-anatase/Al_2O_3 catalysts are effective in oxidation of organic water pollutants and they enable significant (at least 60% reduction) of COD [7, 15, 16]. As the photocatalysts were chosen Al_2O_3-supported anatase catalysts differ in Ti content and are modified with V (Fig. 3).

All studied catalysts enable significant removal of phenol, at least in 50% of cases. It was observed 70% reduction of COD of waste containing phenol over Ti1 and at least 60% over Ti2. Photocatalytic oxidation proceeds most effectively, with almost 90% reduction of COD, over Ti1 catalyst. A decrease in TiO_2 content from 6.69 wt.% to 3.34 wt% caused almost two times worse COD reduction in the range of 78-80%.

The studies of photocatalytic oxidation with H_2O_2 addition were conducted, taking into the account the effect of H_2O_2 during wastewater photooxidation. The effect of H_2O_2 on photooxidation of organic compounds in water is not clear.
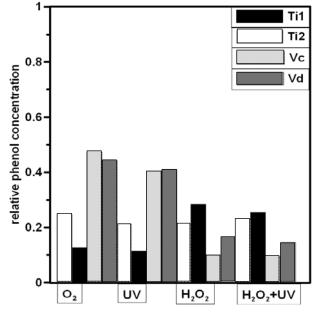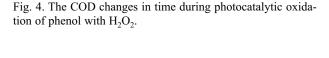

Fig. 2. XRD spectra of studied catalysts.

Fig. 3. COD changes during phenol removal O_2 – aeration, UV – UV irradiation, H_2O_2 – H_2O_2 addition, H_2O_2/UV – addition of H_2O_2 during UV irradiation.

Fig. 4. The COD changes in time during photocatalytic oxidation of phenol with H_2O_2.

UV irradiation of water with H_2O_2 addition generates more 2 radicals *OH from H_2O_2 decomposition. Hydrogen peroxide is an active electron scavenger preventing recombination of charge carriers and enhancing the creation of other radicals *OH and $*O_2^-$ on the catalyst's surface, too. The effect of H_2O_2 addition to photooxidation over V-TiO_2/Al_2O_3 is not obvious and depends on the type of compound. Generally, mineralization is increased in the presence of H_2O_2. Phenol oxidation is proceeded directly by h^+ or by *OH (mainly) [19]. Illias et al. [20] indicate that H_2O_2 addition during aeration of phenolic wastes does not cause significant changes in phenol removal.

Photooxidation of phenol over Ti1 catalyst is as effective as photooxidation with H_2O_2, which indicates that H_2O_2 does not play a significant role during photooxidation and may even retard treatment. Over Ti2 catalysts the results were worse – at least 60% COD reduction. Oxidation over catalysts with higher Ti content proceeds worse than over this with smaller Ti content, which may indicate that oxidation of phenol can be retarded using H_2O_2 and higher values of Ti. Oxidation over Ti2 is independent of the H_2O_2 addition.

Modification of the catalyst with V addition did not enable us to obtain better results during photooxidation and the treatment was significantly worse: an observed 40-50% COD reduction. But those catalysts were sensitive to the presence of H_2O_2 and the results were better than over unmodified catalysts. The method of catalyst preparation may influence photooxidation. Although the catalysts possess different V content, the COD reduction is similar and differs only in 5%, but all results are significant min. 85% COD reduction. Modification of TiO_2/Al_2O_3 catalysts with the incorporation of V and the addition of H_2O_2 deepens the treatment of phenolic wastewaters, but only at about 15% of what is economically not justified.

The COD changes in time (Fig. 4) indicate that it is not economically justified to conduct the treatment more than 2 hours. The most significant COD reduction was observed after 2 hours, and the results do not change significantly. 5-10% COD changes may suggest desorption of phenolic residues or it is just statistical error. Only over Ti1 does the oxidation proceed differently. After 2 hours treatment there was observed only 50% reduction of COD, and prolonging the time to 5 hours enabled deeper oxidation – to 80%. Exceeding the time to 8 hours did not result in total phenol removal.
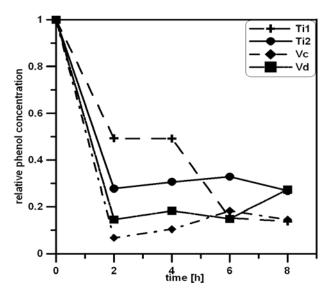
Conclusions

According to obtained results of photocatalytic oxidation of phenol in water, it may be concluded that:

• The most efficient method for removal of phenol is photocatalytic oxidation, with H_2O_2 over V-TiO_2/Al_2O_3, but the effect of treatment was better than over unmodified catalysts only at about 10-15%

• It is economically unjustified to introduce any modifier agents into catalysts during photooxidation of phenol over TiO_2/Al_2O_3.

• It is economically unjustified to use additionally any oxidizing agents such as H_2O_2 during photoxidation of phenolic waste using TiO_2/Al_2O_3, because it may even retard oxidation.

• The H_2O_2 addition is important and deepens the photooxidation of phenol, but only over V-modified catalysts.

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