Effect of H₂O₂ Addition on Phenol Removal from Wastewater Using TiO₂/Al₂O₃ as Photocatalyst

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Abstract

The photocatalytic oxidation of phenol in water in the band reactor with supported TiO₂ catalysts was investigated. Modified anatase/Al₂O₃ catalysts were used as the photocatalysts. The main aim of these studies was to determine catalytic activity of TiO₂/Al₂O₃ and V-TiO₂/Al₂O₃ in the removal of phenol from water. The effectiveness was measured in the configurations: TiO₂/UV/O₂/H₂O₂, TiO₂/O₂/H₂O₂, TiO₂/UV/O₂, and TiO₂/O₂. 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, TiO₂/Al₂O₃, 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 CO₂, 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 (H₂O₂/O₃, O₃/OH⁻, Fe²⁺ or Fe³⁺/H₂O₂), photochemically (H₂O₂/UV, O₃/UV) and photocatalytically (mainly TiO₂/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 TiO₂ [8]. Photocatalytic activity of TiO₂ is

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influenced by surface area, surface orientation, crystal structure (anatase or rutile) and surface hydroxyl group density [2]. TiO₂ 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 TiO₂ 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. TiO₂ in the suspended form needs to be mixed adequately and separated after process. Solution could be the supported TiO₂. It was indicated [9] that the high effectiveness of Acid Brown 14 oxidation over TiO₂/Al₂O₃ is ascribed to the adsorption properties of support Al₂O₃. 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. H₂O₂ and O₃, but the effect is not obvious and depends on many factors. H₂O₂ 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 O₂ and H₂O, 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 H₂O₂ onto 2 *OH is observed because of H₂O₂ weak absorption of UV radiation according to equations 1-4.

\[
\begin{align*}
\text{HO–OH} + \text{hv} & \rightarrow 2 \text{*OH} \\
\text{*OH} + \text{H}_2\text{O}_2 & \rightarrow \text{H}_2\text{O} + \text{HO}_2^* \\
2\text{HO}_2^* & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\end{align*}
\]

The photolysis rate of H₂O₂ is dependent on pH and increases in basic conditions:

\[
\begin{align*}
2\text{H}_2\text{O}_2 + 2\text{OH}^- & \rightarrow \text{H}_2\text{O} + \text{HO}_2^* \\
2\text{HO}_2^* & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\end{align*}
\]

But too high H₂O₂ addition causes the process to hinder because the surplus H₂O₂ captures the radicals (7) [12]:

\[
\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{HO}_2^* + \text{H}_2\text{O}
\]

Irradiation favours the radical reactions but H₂O₂ initiates the chain reactions that run after the irradiation has finished [13].

The mechanisms of phenol oxidation are complicated. The main products observed are catechol and hydroquinone, and negligible amounts of pirogual, 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/cm² 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 dm³/h) and nitrogen (37 dm³/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-Al₂O₃-supported TiO₂ catalysts modified with V addition were prepared according to [15] by the Double Impregnation Method [16] or Classical Impregnation Method. γ-Al₂O₃ supports (INS, Pulawy) with total surface area 56.2 m²/g, after heating in 150ºC, were impregnated in TiCl₄ for 10 min. at room temperature. Then they were dried in 150ºC catalyst and calcinated for 3 h. In DIM method TiO₂/Al₂O₃ was firstly impregnated in chelating agent - EDTA and then in proper solution of V₂O₅ 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
model contaminants used solutions of phenol prepared to have a COD value ca. 3,000 mg O₂/dm³ 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 H₂O₂, the effectiveness was measured in a few configurations: TiO₂/UV/O₂/H₂O₂, TiO₂/O₂/H₂O₂, TiO₂/UV/O₂, and TiO₂/O₂. The sample was taken back after 115 minutes, assuming that by volumetric flow 1.3 dm³/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, TiO₂ 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%).

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

Table 1. Physicochemical properties of studied catalysts.

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 Al₂O₃. TiO₂ is present in a form of anatase (peaks by 2θ=25) and V as VO₂ (2θ=54).

Novel M-anatase/Al₂O₃ 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 Al₂O₃-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 TiO₂ 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 H₂O₂ addition were conducted, taking into the account the effect of H₂O₂ during wastewater photooxidation. The effect of H₂O₂ on photooxidation of organic compounds in water is not clear.

![Fig. 2. XRD spectra of studied catalysts.](image)

Fig. 2. XRD spectra of studied catalysts.

![Fig. 3. COD changes during phenol removal O₂ – aeration, UV – UV irradiation, H₂O₂ – H₂O₂ addition, H₂O₂/UV – addition of H₂O₂ during UV irradiation.](image)

Fig. 3. COD changes during phenol removal O₂ – aeration, UV – UV irradiation, H₂O₂ – H₂O₂ addition, H₂O₂/UV – addition of H₂O₂ during UV irradiation.
UV irradiation of water with H$_2$O$_2$ addition generates more 2 radicals *OH from H$_2$O$_2$ 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$_2$O$_2$ addition to photooxidation over V-TiO$_2$/Al$_2$O$_3$ is not obvious and depends on the type of compound. Generally, mineralization is increased in the presence of H$_2$O$_2$. Phenol oxidation is proceeded directly by h$^+$ or by *OH (mainly) [19]. Illias et al. [20] indicate that H$_2$O$_2$ 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$_2$O$_2$, which indicates that H$_2$O$_2$ 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$_2$O$_2$ and higher values of Ti. Oxidation over Ti2 is independent of the H$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_3$ catalysts with the incorporation of V and the addition of H$_2$O$_2$ 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$_2$O$_2$ over V-TiO$_2$/Al$_2$O$_3$, 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$_2$O$_3$.

- It is economically unjustified to use additionally any oxidizing agents such as H$_2$O$_2$ during photooxidation of phenolic waste using TiO$_2$/Al$_2$O$_3$, because it may even retard oxidation.

- The H$_2$O$_2$ addition is important and deepens the photooxidation of phenol, but only over V-modified catalysts.

**References**


Fig. 4. The COD changes in time during photocatalytic oxidation of phenol with H$_2$O$_2$.
16. CZECH B., NAZIMEK D. Advanced Oxidation Processes in water and wastewater treatment, Przemysł Chemiczny, 8-9, 1005, 2006 [In Polish].