

Influence of water temperature on the photocatalytic activity of titanium dioxide

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Abstract In this study, it was shown that a possible explanation of increasing photocatalytic activity with temperature may be the fact that with increasing water temperature, the amount of hydroxyl radicals in water also increases, because the ionic product of water increases with an increase in temperature. For measurements of the amount of hydroxyl radicals, the fluorescence technique was used. Terephthalic acid was used as a hydroxyl radical scavenger. After inducing of TiO_2 , positive holes in the valence band may react with OH^- ions and produce $\bullet\text{OH}$ radicals, a strong oxidizing agent.

Keywords Photocatalysis · Ionic product of water · Hydroxyl radicals · Temperature

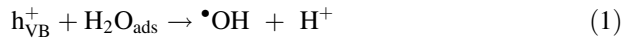
Introduction

The photocatalyst, for example, titanium dioxide (TiO_2) absorbs light with suitable wavelength in photocatalysis. An electron from the valence band is transferred to the conduction band and creates negative electron (e^-) and positive hole (h^+). The positively charged hole reacts with chemisorbed OH^- groups or water adsorbed on the surface of the photocatalyst to create $\bullet\text{OH}$ radicals and hydrogen cations (Eq. 1) or reacts with hydroxyl groups to create $\bullet\text{OH}$ radical (Eq. 2). Simultaneously, negative electrons react with oxygen to create the anion radical superoxide (Eq. 3).

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Photocatalysis is very often used for water cleaning, namely to decompose organic contaminants present in water [1].



Hoffmann et al. [2] postulated that in the presence of O_2 , hydroxyl radicals could be also generated by the reduction of dissolved oxygen by photo-electrons.

In this study, commercial TiO_2 —anatase form (Police Chemical Company, Poland) was used as photocatalyst. At different temperatures (20, 30, 40, 50, and 60 °C), the amount of produced $\bullet\text{OH}$ radicals was measured using the fluorescence technique described by Ishibashi et al. [3]. This fluorescence technique is also used by other researchers for detecting OH radicals, for example by Yu et al. [4] for the characterization of mesoporous TiO_2 powders obtained by hydrothermal surface fluorination treatment or by Tryba et al. [5] to find the relationship between the crystallinity of TiO_2 and the photocatalytic activity. Eremia et al. [6] suggested that the fluorescence method using terephthalic acid to observe the generation of hydroxyl radicals is rapid, efficient, and highly sensitive, and the apparatus used in that kind of measurements is quite simple. It is worth mentioning that there are some different other methods for $\bullet\text{OH}$ radicals determination, for example, using of $\bullet\text{OH}$ radicals scavengers such as: salicylic acid [7], diethanolamine [8], *n*-butanol [9] or using electron spin resonance (ESR) spectroscopy [10, 11]. Yang et al. [13] observed the formation of hydroxyl radicals during the reduction of molecular oxygen by Fe(II)-EDTA.

The role of hydroxyl radicals in the organic pollutant decomposition process was studied by Peiró et al. [14], Vione et al. [15] and Palmisano et al. [16]. Peiró et al. [14] concluded that during phenol decomposition, $\bullet\text{OH}$ radicals were the species involved in the oxidation process carried out in the presence of O_2 . It was also found that the phenol molecules reacted with hydroxyl radicals giving rise to phenoxy radicals. Vione et al. [15] studied the role of $\bullet\text{OH}$ radicals in photodestruction process of phenol and benzoic acid. Both degradation processes depended on the presence of hydroxyl radicals in reactive solution. Nevertheless, phenol oxidation occurred by means of $\bullet\text{OH}$ radicals, while benzoic acid molecules were decomposed on the surface of TiO_2 by means of adsorbed hydroxyl radicals. Palmisano et al. [16] investigated the selectivity of hydroxyl radicals in the partial oxidation of aromatic compounds: nitrobenzene, cyanobenzene, benzoic acid, phenol, 4-chlorophenol, *N*-phenylacetamide, phenylamine and 1-phenylethanone. They concluded that in the case of pollutants containing an electron donor group, it is possible to observe the OH radicals attack obtaining two kinds of substitution in ortho- and para-positions.

The main aim of described studies was to present one of trapping routes of positively charged holes created during TiO_2 excitation. An increase in water temperature cause an increase in the ionic product of water (OH^- , H_3O^+ anions), which is correlated with the increasing amount of $\bullet\text{OH}$ radicals in aqueous solution.

Experimental

Commercial TiO₂—anatase form (Police Chemical Company, Poland) with the specific surface area of 222 m²/g was used as the tested photocatalyst.

The yield of generated •OH radicals was measured using the fluorescence technique described in detail by Ishibashi et al. [3] using a fluorescence spectrophotometer (F-2500 Hitachi, Japan). The solution containing photocatalyst and terephthalic acid was irradiated at different temperatures (20, 30, 40, 50, and 60 °C) for 90 min (samples were taken every 10 min). 0.02 g of the photocatalyst was added to 100 mL of terephthalic acid solution with a concentration of 830 mg/L (5×10^{-4} M). The •OH radicals are generated by means of UV–Vis light illumination (6×20 W UV–Vis lamps, Philips, radiation intensity 154 W/m² of UV and 100 W/m² of Vis) react with terephthalic acid molecules to produce highly fluorescent 2-hydroxyterephthalic acid which can be easily measured using simple fluorimeters. The use of terephthalic acid was also made due to the formation of only one isomer in the reaction [7, 17]. According to Ishibashi's paper, the intensity of the peak attributed to 2-hydroxyterephthalic acid was known to be proportional to the amount of •OH radicals. Phenol decomposition with concentration of 10 mg/L at different temperatures (20, 30, 40, 50, and 60 °C) was conducted to determine the photocatalytic activity of TiO₂ at different range of temperatures. The phenol degradation was carried out for 5 h under UV–Vis light illumination. The mineralization rate of phenol and its derivatives after 5 h of UV–Vis irradiation was also estimated using TOC (Total Organic Carbon) analyzer (Jena, Germany).

Results and discussion

Fig. 1 presents the amount of 2-hydroxyterephthalic acid (fluorescence intensity) produced in terephthalic acid solution in the presence of photocatalyst during 90 min of UV–Vis light irradiation at different temperatures. It is possible to observe that with the time of irradiation, the concentration of 2-hydroxyterephthalic acid increases because higher amounts of hydroxyl radicals formed during UV–Vis exposition react with terephthalic acid molecules to create 2-hydroxyterephthalic acid. Fig. 2 presents the amount of 2-hydroxyterephthalic acid produced at different temperatures, for example, after 20, 30, and 40 min of UV–Vis light illumination in comparison to ionic product of water at different temperatures. The values of ionic product of water at different temperatures are presented in Table 1 [12]. The ionic product of water increases with temperature rise what is correlated with the increase of hydroxyl anions concentration in water. In aqueous solution, the created holes in the TiO₂ valence band are trapped by hydroxyl anions present in water, thereupon hydroxyl radicals are formed. The rise of hydroxyl anion concentration with increasing temperature conduces the hole trapping process with higher efficiency. The higher concentration of hydroxyl ions, the higher the amount of the trapped holes, thus the higher the amount of •OH radicals and 2-hydroxytepephthalic acid. It is possible to conclude that the use of TiO₂ under elevated temperature could impact on increase of photocatalytic activity of TiO₂.

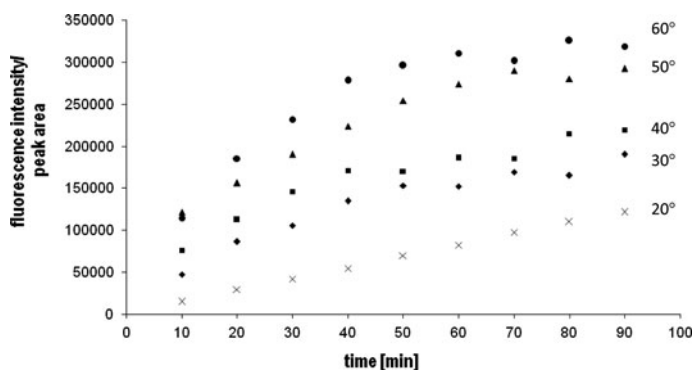


Fig. 1 The amount of 2-hydroxyterephthalic acid (fluorescence intensity) produced during 90 min of UV–Vis light irradiation. 0.02 g of TiO₂ photocatalyst was placed in 100 ml of the water solution of terephthalic acid (5×10^{-4} M) at different temperatures: 20, 30, 40, 50, and 60 °C

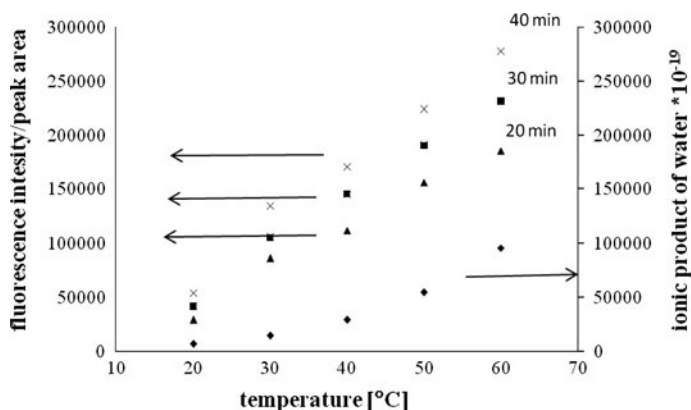


Fig. 2 The amount of 2-hydroxyterephthalic acid at different temperatures after 20, 30, and 40 min of UV–Vis light irradiation in comparison to ionic product of water at different temperatures

Table 1 The ionic product of water at different temperatures

Temperature [°C]	$K_w \cdot 10^{-14}$
20	0.6814
30	1.469
40	2.918
50	5.474
60	9.614

To prove that elevated temperature affects $\bullet\text{OH}$ radical formation and photocatalytic efficiency, an experiment with phenol decomposition under UV–Vis light irradiation at different temperatures was also conducted. First, the influence of different temperatures onto phenol and terephthalic acid adsorption on the surface of used TiO₂ was tested. Each adsorption experiment was repeated twice to check the stability of titanium dioxide surface with regard to adsorption abilities of TiO₂. The

adsorption in the darkness was carried out for 1 h, nevertheless, the concentration of phenol and terephthalic acid was checked after 30 min and 1 h of stirring. For terephthalic acid, no changes in concentration after 30 min and 1 h were observed whilst for phenol, the concentration decreased insignificantly and after 1 h of stirring in the darkness (from 1.15 to 0.34% for TiO_2 stirred at 20 and 60 °C, respectively). It was accepted that there is no influence of temperature on the adsorption rate of phenol and terephthalic acid. As can be seen from Fig. 3, the decomposition rate of phenol and derivatives rises with temperature increase. Moreover, the mineralization rate after 5 h of UV–Vis light irradiation is presented in Fig. 4. At 20 °C, the mineralization amounted to 44.3% while mineralization at 50 and 60 °C amounted 90.4 and 91.4%, respectively. As it can be noticed, the efficiency of phenol and by-product decomposition carried out at 50 and 60 °C is almost the same value. It could be presumed that the temperature of 50 °C is an optimal temperature for phenol degradation under UV–Vis illumination.

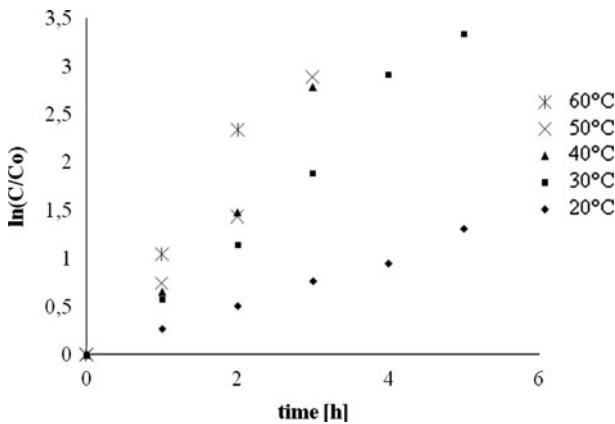


Fig. 3 The rate of phenol decomposition during 5 h of UV–Vis light irradiation at different temperatures

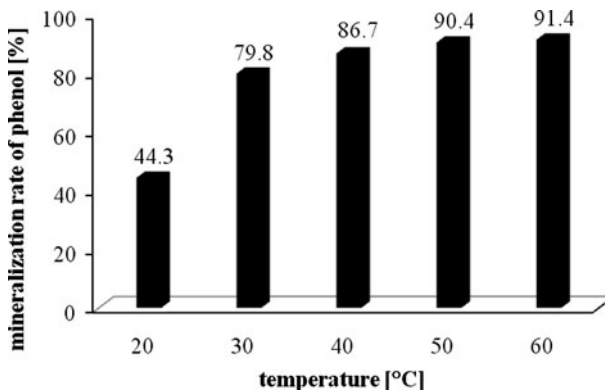


Fig. 4 Mineralization rates of phenol at different temperatures after 5 h of UV–Vis light exposition

It should be mentioned that there is no linear dependence between phenol decomposition and hydroxyl radical formation because of the presence of the phenol derivatives in the tested solution. During the UV–Vis exposure, it was possible to detect phenol, benzoquinone and hydroquinone as co-products of phenol decomposition. Part of the OH radicals was used to oxidize phenolic mentioned co-products. The reaction between phenol molecules and superoxide radicals could not be eliminated but it is very well known the reaction rate constant of phenol with $\bullet\text{OH}$ radicals highly exceeds the reaction rate constant of phenol with $\text{O}_2^{\bullet-}$.

Conclusion

In this study it was found that an increase of aqueous solution temperature in the presence of excited TiO_2 leads to improvement of the efficiency of phenol and by-products decomposition. It was proved that efficiency improvement is correlated with the increase of the ionic product of water, which rises with temperature, thereby rises the concentration of hydroxyl ions. In that situation, OH ions could rapidly react with positively charged holes from the surface of excited titania forming higher amount of hydroxyl radicals which can easily oxidize phenol and by-product molecules. The temperature of 50 °C was found to be the optimal for phenol photodestruction.

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