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Photocatalytic Treatment of a Synthetic Wastewater

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Abstract. This work aimed at investigating the photocatalytic treatment of a synthetic wastewater using UV light (254 nm, 6 W), TiO₂ catalyst and H₂O₂ in a batch recycle annular photoreactor. The total volume of the solution was 250 mL while the irradiated volume in the annular photoreactor with 55.8 mL. Each experiment lasted 120 min and samples were sent for Total Carbon and HPLC analysis. The stock wastewater had initial total carbon 1118 mg L⁻¹. The effect of the presence of phenol in the wastewater on total carbon (TC) removal was also studied. It was shown that the photocatalytic treatment was effective only when initial TC was decreased to 32 mg L⁻¹, whereas the optimum TiO₂ concentration was 0.5 g L⁻¹, leading to a TC removal up to 56%. For the same initial carbon load, the optimum H₂O₂ concentration was found to be 67 mg L⁻¹ resulting in 55% TC removal. Combining, however, TiO₂ and H₂O₂ did not lead to better performance, as 51% TC removal was observed. In contrast, when initial carbon in the wastewater was partially substituted by phenol, the combination of catalyst and hydrogen peroxide was beneficial. Specifically, when 10 ppm of phenol were added keeping the same initial TC concentration, UV/TiO₂ treatment resulted in 46% TC removal and 98% phenol conversion, whereas using additionally H₂O₂ led to 100% phenol conversion after 45 minutes and 81% TC removal.

1. Introduction

Water pollution and lack of clean drinking water are among the most significant problems worldwide. The industrial growth and rise in population have resulted in high demand for resources, whereas the release of toxic materials and wastes to the environment has posed a risk to natural ecosystems and human health. The disposal of wastewaters in the environment is a major concern. Therefore, it is essential to make sure that disposed water is appropriately treated so that it has minimal impact on aquatic life and the environment.

One of the ways to deal with such problems is to introduce wastewater treatment technologies. A variety of methods for water treatment are implemented or under development. Wastewater treatment is the procedure that eliminates the presence of various contaminants, chemicals, and bacteria, before further water usage or discharge. There are three main steps of treating wastewater: preliminary, secondary and tertiary treatment. The preliminary and secondary treatment technologies are based on physical and chemical processes, however, when wastewater contains hazardous compounds, these remediation techniques are not enough. Advanced Oxidation Processes (AOPs) are among the most effective ways to deal with toxic refractory organic compounds.

AOPs is a term used to describe an oxidation mechanism that degrades organic carbons by means of generated hydroxyl radicals (\bullet OH). These radicals are highly reactive as well as non-selective for almost all electron-reach organic compounds, which makes them very efficient in water treatment



processes [1]. Photocatalytic treatment belongs to AOPs, and there are many studies related to various types of AOP techniques applied for the degradation of toxic compounds [1-18]. However, more research is required as reclamation of water becomes more important day after day.

This paper focuses on photochemical and photocatalytic treatment methods, which differ in the source of $\bullet\text{OH}$ radicals, for the treatment of a synthetic organic wastewater. Firstly, the photocatalytic treatment using UV and TiO_2 as photocatalyst was investigated. Then, the efficiency of UV/ H_2O_2 process with the same initial total carbon concentration was evaluated for comparison purposes. The combined UV/ H_2O_2 / TiO_2 process was also examined. Finally, the effect of the presence of phenol in the wastewater was investigated keeping the same load of initial total carbon.

2. Materials and Methods

2.1. Reagents

All experiments were conducted using a synthetic wastewater with the following composition: 1.6 g L^{-1} glucose ($\geq 97.5\%$), 0.48 g L^{-1} peptone, 0.16 g L^{-1} ammonia hydrogen carbonate ($\geq 99\%$), 0.08 g L^{-1} sodium hydrogen carbonate ($\geq 99\%$), and 0.08 g L^{-1} potassium hydrogen carbonate ($\geq 99.7\%$) were purchased from Sigma Aldrich and 0.32 g L^{-1} lab lemco from Oxoid. The initial concentration of the stock solution was 1118 mg L^{-1} . Phenol was supplied by Sigma Aldrich. The concentration of hydrogen peroxide supplied by Skat-Reactiv used was 37.6% (w/w). Titanium (IV) oxide (P-25, $\geq 99.5\%$ purity) was used as a photocatalyst and supplied by Sigma Aldrich. Only deionized water was used.

2.2. Experimental Setup

All experiments were performed in batch recycle reactor with the ultraviolet lamp of 6 W, which produced ultraviolet light of 254 nm (Figure 1). The active volume of a cylindrical vessel of the reactor was 55.8 mL, and the total volume of the solution was 250 mL.

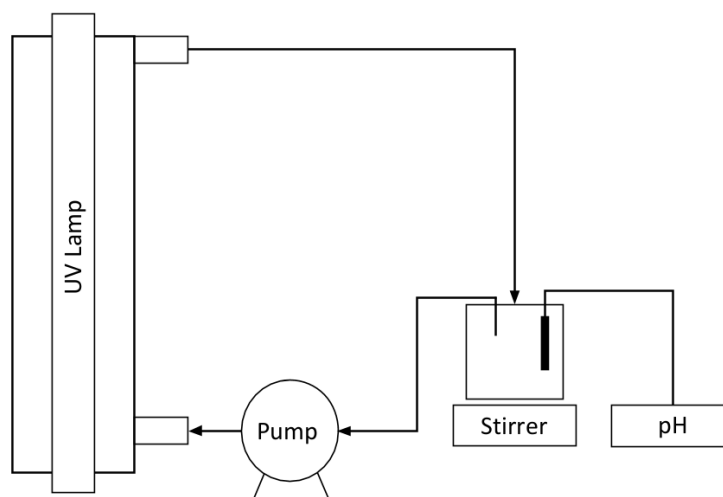


Figure 1. Schematic presentation of a batch reactor.

The solution was continuously circulated using a peristaltic pump at a rate of 175 mL min^{-1} . The part of the solution, which was not irradiated directly by UV-lamp, was continuously mixed by a magnetic stirrer. The pH measurements were conducted via pH electrode LE409 by Mettler Toledo. Each sample was taken at specific time intervals and proceeded further to total carbon (TC) and High-Pressure Liquid Chromatography (HPLC) analysis.

2.3. Analytical Methods

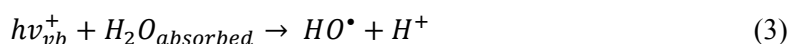
The process lasted for 120 min, and for the experiment employing UV and catalyst, samples were taken at every 30 minutes time interval. For H_2O_2 runs, samples were withdrawn every 15 minutes for

the first hour, and then every 30 minutes. Periodically, pH value was recorded, and samples (8 mL) were withdrawn from the reactor by pipette, filtrated from the catalyst and stored in 20 mL glass vials. Samples were then diluted with distilled water in 8/10 range for TC analysis. For the experiments containing phenolic compounds, one additional mL of sample was withdrawn, and after filtration, it was stored in 2 mL glass vials sent for HPLC analysis. The total carbon concentration in samples was determined using Multi N/C 3100 equipment. For quantifying phenol, an Agilent 1100/1200 HPLC was used.

3. Results and Discussion

3.1. UV/TiO₂ Photocatalytic Process

When TiO₂ surface is irradiated by UV light, it gets excited and generates a pair of electrons and holes in the conduction (e_{cb}^-) and valence band ($h\nu_{vb}^+$) with reductive and oxidative capacity, respectively. The hole adsorbs the surrounding water molecules and gets oxidized to form a hydroxyl radical [19, 20].



OH[•], H₂O and O₂ react with electrons and holes on the surface of catalyst leading to the generation of hydroxyl radicals. The generation of hydroxyl radical is a cyclic process and initiates the series of reactions on the TiO₂ surface [3]. Studies have shown that the most critical factors of a photocatalytic reactor configuration are light distribution and the total surface area of irradiated catalyst per unit volume within the reactor [20, 21, and 22].

To determine the effect of initial TC concentration on process efficiency, total carbon concentration varied between 30-500 mg L⁻¹ with fixed catalyst load (1 g L⁻¹). As it is shown in Figure 2, TC removal values of practical significance were achieved only when initial TC was decreased to 32 mg L⁻¹. Lower TC concentrations were not used, as that would not be justified from the economical point of view. The efficiency of the photocatalytic process increases with rising in pollutant concentration as it follows first order kinetics [18]. Nevertheless, above the optimum range, excess concentration of pollutants has a negative impact on process efficiency. It is evident that as the amount of catalyst loaded in the reactor remains the same, the active sites on TiO₂ surface are also fixed. Thus, higher pollutant concentrations decrease the photocatalytic degradation rate due to the shortage of generated reactive species [18].

The effect of TiO₂ on total carbon removal ([TC]₀=32 mg L⁻¹) was also investigated by varying the initial amount of loaded catalyst in the range of 0.1-1 g L⁻¹. The amount of loaded catalyst also affects process efficiency, as it is directly proportional to the overall photocatalytic reaction rate [3, 19]. At some point, reaction losses the linear dependency on TiO₂ and the process starts to deteriorate [3]. When the amount of catalyst transcends the saturation level, it leads to a high turbidity state. Excess TiO₂ particles generate light screening effect, which decreases the surface area of catalyst that is exposed to UV light. Additionally, it also impedes the penetration of UV light due to strong scattering of light photons [3, 21, 22]. It is obvious that there was no significant deviation in TC removals obtained for TiO₂ concentration in the range of 0.5-1 g L⁻¹ (Figure 3). Thus, 0.5 g L⁻¹ was selected as the optimum amount of catalyst with obtained total carbon removal 56%.

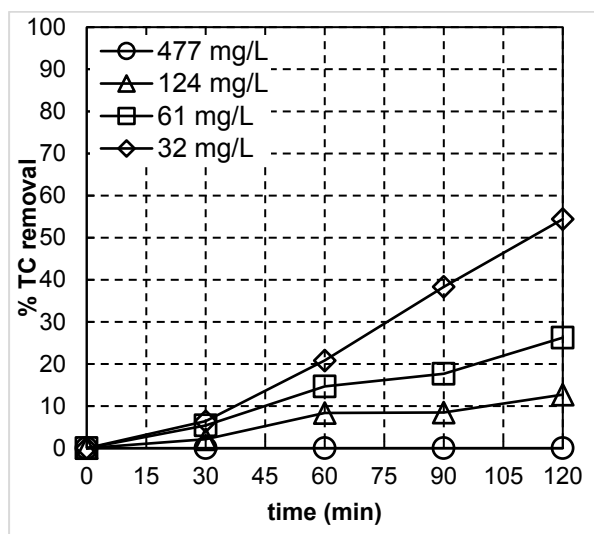


Figure 2. Effect of initial TC concentration ($[\text{TiO}_2]_0=1 \text{ g L}^{-1}$).

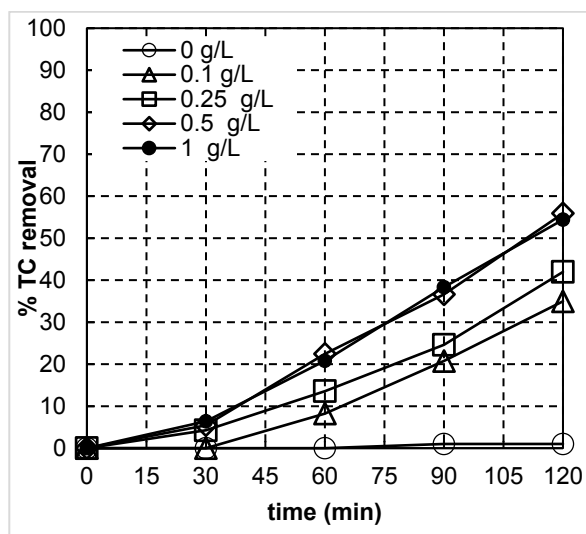


Figure 3. Effect of TiO_2 loading ($[\text{TC}]_0=32 \text{ mg L}^{-1}$).

3.2. UV/H₂O₂ Process

Hydrogen peroxide is an efficient oxidizing agent as when exposed to UV light it forms HO_2^- anions, which in turn generate hydroxyl radicals. These $\cdot\text{OH}$ radicals react almost immediately with most organic compounds and form degradation products. Some compounds can be mineralized towards CO_2 and H_2O . Additionally, pollutants may go through photolysis by direct absorption of irradiated UV light. The effect of H_2O_2 was investigated with a concentration range from 27 to 266 mg L^{-1} and fixed initial TC (32 mg L^{-1}) for comparison purposes with photocatalysis. Increasing hydrogen peroxide concentrations resulted in higher TC removals achieved (Figure 4). It was decided to use 67 mg L^{-1} concentration of H_2O_2 (55% TC removal) in photo-Fenton experiments. As it is shown in Figure 5, initial pH of solution decreased rapidly after the start of the process, which implies that organic pollutants were transformed to organic acids. As process progressed, formed organic acids seemed to have degraded slowly to CO_2 , as indicated by the increasing values of pH.

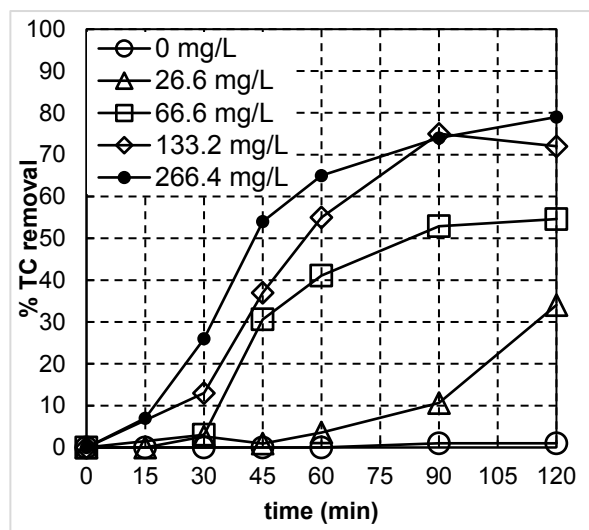


Figure 4. Effect of H_2O_2 concentration on TC removal ($[\text{TC}]_0=32 \text{ mg L}^{-1}$).

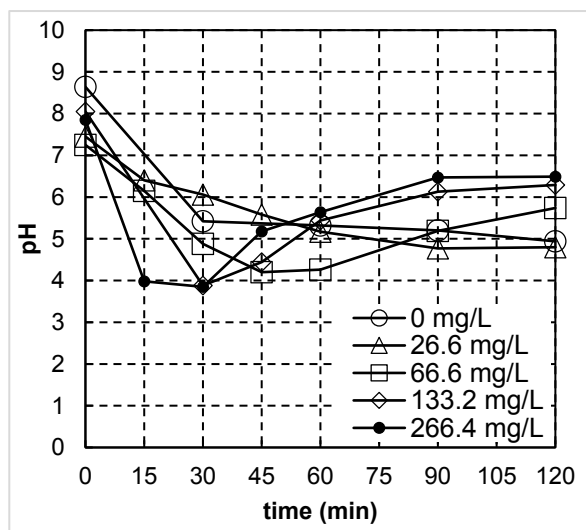


Figure 5. Effect of H_2O_2 concentration on pH ($[\text{TC}]_0=32 \text{ mg L}^{-1}$).

3.3. UV/H₂O₂/TiO₂ Process

The UV/H₂O₂/TiO₂ process efficiency was evaluated in terms of TC removal during the treatment of the synthetic wastewater with/without phenol. For the first scenario, namely without any phenol, the concentration of H₂O₂ (67 mg L⁻¹), initial TC (32 mg L⁻¹) and TiO₂ loading (0.5 g L⁻¹) were kept at the optimum values, and their combination was examined. As it is obvious in Figure 6, combining TiO₂ and H₂O₂ did not lead to a higher efficiency, as 51% TC removal was observed.

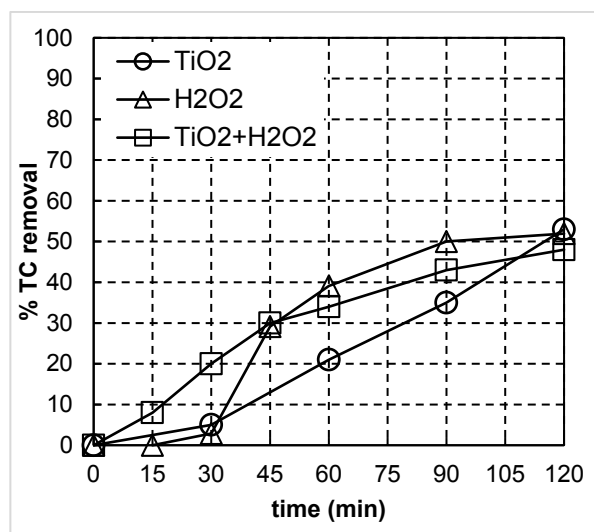


Figure 6. Effect of TiO₂ and H₂O₂ combination on TC removal ([TC]₀=32 mg L⁻¹, [TiO₂]₀=0.5 g L⁻¹, [H₂O₂]=67 mg L⁻¹).

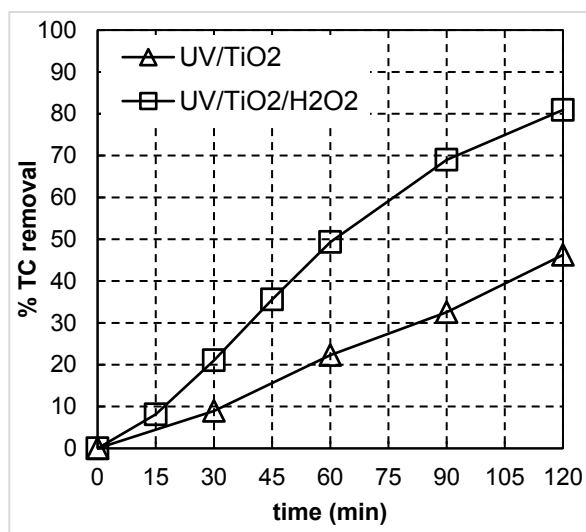


Figure 7. Degradation of 10 ppm Phenol with UV/TiO₂ and UV/TiO₂/H₂O₂ ([TC]₀=32 mg L⁻¹, [TiO₂]₀=0.5 g L⁻¹, [H₂O₂]=67 mg L⁻¹).

In contrast, when some organic carbon was substituted by phenol (keeping the same initial TC), the combination of hydrogen peroxide with titanium dioxide resulted in a better performance, achieving more than 81% TC conversion, whereas UV/TiO₂ resulted only in 46% of TC removal (Figure 7). Dixit also investigated the UV/H₂O₂/TiO₂ process on phenol and resulted in remarkably higher degradation rate compared to UV/H₂O₂ or UV/TiO₂ [22]. In the case of UV/H₂O₂/TiO₂ process, UV photons coupled with catalyst and hydrogen peroxide increases degradation rate, by forming more active radicals, thus increasing the degradation of difficult aromatic rings [22].

4. Conclusion

In this work, the photocatalytic process using TiO₂ as photocatalyst in the presence/absence of H₂O₂ was applied for the treatment of a synthetic wastewater containing mainly organic carbon. The main conclusions obtained are the following:

- During the photocatalytic treatment of the wastewater with TiO₂, TC removals practically important were obtained only when the initial TC was decreased to 32 mg L⁻¹.
- Taking into account TC removal, 0.5 g L⁻¹ was the optimum TiO₂ concentration for treating the wastewater with initial TC 32 mg L⁻¹.
- Increasing hydrogen peroxide concentrations resulted in higher TC removals achieved.
- Removal of total carbon was not enhanced after combining TiO₂ and H₂O₂.
- In contrast, the combination of H₂O₂ and TiO₂ remarkably increased the degradation of phenol and TC removal when initial carbon was partly substituted by phenol.

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