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Effects of hydrogen peroxide in a fluidized bed photocatalytic reactor for wastewater purification

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Abstract

There have been a number of studies indicating that hydrogen peroxide can enhance photocatalytic oxidation of organics by TiO_2, which is known to have relatively low quantum yield. There are also studies that reported negative effect of adding hydrogen peroxide to a photocatalytic system. In this study, various combinations of TiO_2 and hydrogen peroxide were investigated in a fluidized bed reactor in order to analyze the effect of their combined use versus single applications. A new composite photocatalyst that integrates titanium dioxide with an adsorbent zeolite supported on glass beads was implemented for the use in the photoreactor. Phenol was used as a model contaminant and 254 nm UV lamps were used for irradiation. Overall, the outcome of the experiments pointed to the advantageous use of the combination of photocatalysis with hydrogen peroxide over their individual use. Moreover, it was found that photocatalytic oxidation of phenol can be promoted with relatively small amounts of H_2O_2 (no more than one-fifth of what would be required stoichiometrically). When all reasonable combinations were explored, it was found that the outcome depended on the ratio between H_2O_2 and titania loading. The series with lower H_2O_2 and higher catalyst loading showed synergetic behavior for the process of phenol degradation but the rate of degradation decreased with further addition of H_2O_2. In the other series with higher H_2O_2 and lower catalyst loading, phenol degradation was found to continuously increase with the increase of H_2O_2. The combination of the lowest catalyst loading (0.21 g/l) with 20% H_2O_2 showed superior performance for phenol degradation in this reactor. Results of this study open new research window for a more complex approach to photocatalytic experiments where photocatalysis can be combined with hydrogen peroxide.

Keywords: Photocatalysis; Fluidized bed reactor; Hydrogen peroxide; TiO_2

1. Introduction

Heterogeneous photocatalysis has become an attractive alternative treatment method for decontamination of organics from wastewater due to its ability to mineralize organic compounds completely without generating harmful byproducts [1–4]. Conventional water treatment methods rely on transferring contamination from one medium to another (carbon adsorption transfers pollutant from liquid to solid media, gas stripping transfers pollutant from liquid to gas media). But photocatalysis overcomes the drawbacks of conventional methods as it does not produce any harmful byproducts. Photocatalysis utilizes ultraviolet light ($\lambda < 380$ nm) to activate photocatalyst. Importantly, the semiconductors used as photocatalyst can be activated by sunlight which makes it economically competitive in some cases.

Many semiconductors such as TiO_2, ZnO, CdS, ZnS and WO_3 have been studied for the role of photocatalysts, and TiO_2 was found to be one of the most promising agents for removal of refractory compounds and xenobiotics [5]. Degussa P25 (commercial TiO_2) was found to be the most effective photocatalyst (which contains 70–80% anatase, with the rest being rutile phase). TiO_2's chemical inertness, non-photocorrosivity, and non-toxic character, coupled with its ability to create a highly reactive oxidant (hydroxyl radical) upon excitation with UV radiation, makes TiO_2 highly suitable for applications in wastewater treatment. Degradation of organic compounds or microorganisms can be achieved by oxidation (using photogenerated holes) and the removal of toxic metals can be achieved by using photogenerated electrons in a reduction process.

However, large-scale application of photocatalysis in wastewater treatment facilities is still limited due to the scarcity of economically viable reactor designs [6]. Although slurry-type reactors have shown higher degradation efficiency, the extra step of separation of nano-size particles makes it a

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questionable choice for scaling up. Application of a supported catalyst eliminates the need for separation but presents another challenge related to efficient mass transfer. Fluidized bed reactors with supported catalysts provide an opportunity to escape mass transfer limitations.

There are number of studies intended to further increase efficiency of degradation of organics by combining photocatalysis with hydrogen peroxide or ozone [7]. Hydrogen peroxide is considered to be environmentally friendly as it is composed only of oxygen and hydrogen atoms and under appropriate conditions can yield water or hydroxyl ions [7]. A great number of reports of hydrogen peroxide addition to TiO_2 photocatalysis for degradation of organic pollutants in water are published [8–10]. Most of the reported studies are based on 350–380 nm UV lamps.

Many research groups have investigated the effect of hydrogen peroxide on photocatalytic degradation of organic contaminants under the optimized catalyst loading conditions. Photocatalytic oxidation of eosin Y dye using hydrogen peroxide and TiO_2 was studied by Poulios et al., in a batch slurry reactor [11]. They observed that the degradation rate was enhanced by a factor of 2 with the inclusion of hydrogen peroxide. Beneficial effects of the addition of hydrogen peroxide were also reported for the photocatalytic oxidation of dissolved organic matter in the effluent of a cellulose and paper mill industry [12].

However, others reported a negative effect of adding hydrogen peroxide for degradation of some organic pollutants. Chun and Park reported slight inhibition of trichloroethylene degradation rate by addition of hydrogen peroxide [8]. Similarly, Dillert et al. reported the inhibitory effect of hydrogen peroxide addition for the degradation rates of 2,4,6-trinitrotoluene and 1,3,5-trinitrobenzene at various initial pH values compared to those of the UV ($\lambda > 320$ nm)/TiO_2 system [13]. The authors hypothesized that this effect could be due to competition of hydrogen peroxide with the nitroaromatic contaminants for conduction band electrons. But in general, the rates of heterogeneous systems (UV/TiO_2/hydrogen peroxide) were higher than those of the homogeneous systems (UV/hydrogen peroxide) [14].

Most of the previous photocatalytic studies on the effect of hydrogen peroxide reported the existence of the optimum concentration of hydrogen peroxide. Mengyue et al. found that 6 mM hydrogen peroxide enhanced photocatalytic degradation of monocrotophos and parathion by approximately four times but further increase to 8 and 10 mM concentrations reduced that rate [9]. Kumar and Davis investigated the effect of various concentration of hydrogen peroxide (from 0 to 100 mM) for degradation of 2,4-dinitrotoluene (DNT) at the same initial concentration in a batch slurry reactor [14]. They observed 10% increase of the degradation rate at hydrogen peroxide concentration 1–10 mM but the rate decreased after more addition of H_2O_2. Degradation rate of DNT at 100 mM H_2O_2 was almost equal to rate in the absence of hydrogen peroxide. Haarstrick et al. studied photocatalytic degradation of 4-chlorophenol and *p*-toluenesulfonic acid in a fluidized bed photocatalytic reactor operated in a batch mode [10]. They suggested 2 mM hydrogen peroxide concentration was optimum based on hydrogen peroxide cost and initial concentration of pollutants.

In brief, the role of hydrogen peroxide on the photocatalytic degradation of various organic contaminants was found either positive or negative. Most studies reported that hydrogen peroxide could increase the reaction rates or cause inhibition depending on its concentration in the solution. The results from all these reports suggest that the effect of hydrogen peroxide is a function of radiation properties (i.e. wavelength, intensity), solution pH, physicochemical properties of the contaminant, type of catalyst and the oxidant to contaminant ratio.

So far to the best of our knowledge, most of the studies explored the effect of H_2O_2 after optimizing the process of photocatalysis alone and did not explore other combinations with hydrogen peroxide. In this research, various combinations of catalyst loading and hydrogen peroxide were explored for degradation of phenol in a fluidized bed reactor. Phenol was used as a model pollutant because it is a known water contaminant in itself and in addition, the phenol moiety is one of the essential functional groups of steroidal estrogens that are found in sewage water. These results will provide a strategic approach to the combined use of photocatalyst and hydrogen peroxide and help to move forward with scale up.

2. Experimental setup

2.1. Reactor design

A cylindrical reactor with a multi-lamp arrangement was used for this study. The geometry of the reactor allowed the option of inserting an additional UV lamp at the axis. The cylinders were fabricated from quartz to allow for maximum UV transmission into the reaction zone from the inside and outside. Top and bottom parts of the reactor were made from anodized aluminum. The bottom portion of the reactor was conical to allow water to enter as a jet and then be distributed through the distributor. The photocatalyst particles were retained by a 425 μm nylon mesh screen held between steel plates with 58 holes of 5 mm diameter. An external multi-lamp arrangement was provided by a Rayonet [New England Nuclear] lamp system enclosed by a reflector. There are two sampling ports at the top and bottom of the reactor to collect samples for analysis. Detailed design of the second-generation lab reactor and its positioning within the Rayonet multiple lamp arrangement are shown in Figs. 1 and 2, respectively. Low pressure Hg UV lamps of 40 W each were used in the reactor.

The complete system setup consists of the photoreactor and water recirculation line that includes a pump and a storage tank. Water is moved by a pump from the tank to the bottom of the reactor and up to complete the circulation loop. The total volume of the recirculation system is 59 l. The pump is a Goulds NPE, 90 V, 3.5 A, close coupled, end suction, single stage centrifugal pump with the flow regulator. A pressure gauge has been installed to keep track of pressure build up in the reactor in the event of screen clogging caused by fine particles generated during the process. All the connections from the pump to the photoreactor and tank are made from flexible 1.905 cm Tygon hoses.

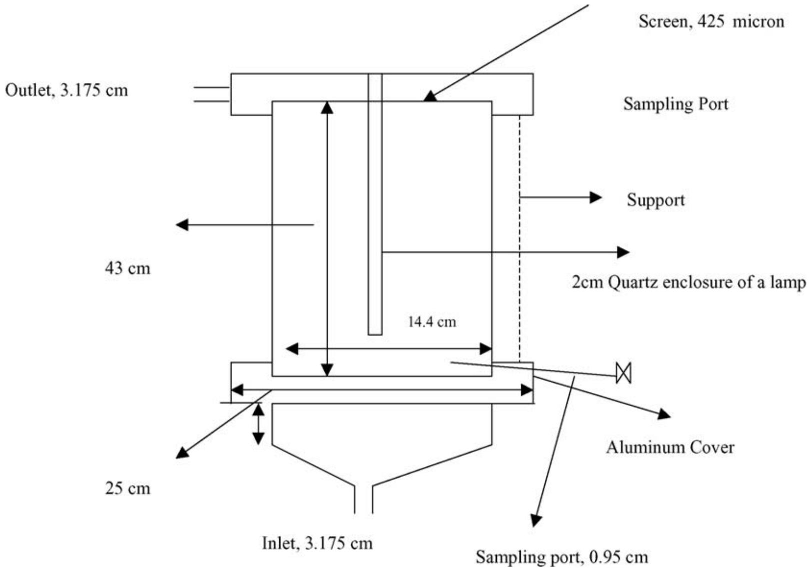

Fig. 1. Schematic diagram of fluidized bed reactor.

2.2. Integrated photocatalyst adsorbent (IPCA) and the "golf ball" concept

Fine TiO_2 powders present separation problems in slurry-type reactors leading to system complications and additional expenses. As a result, a number of efforts have been made to support TiO_2 on fixed or mechanically manageable supports. In a fluidized bed reactor, the particle size must be larger than the low micron size range of TiO_2 powders for retention of the solids in the reactor.

In our case, a mixture of TiO_2 and high silica zeolite (used as an adsorbent) were supported on a porous carrier in a configuration described as the "golf ball" concept. According to this idea, the photocatalyst and the adsorbent were impregnated into the caverns of sintered porous glass beads (SIRAN^{TM}, Jeager Biotech Engineering). The purpose of the glass beads with pore diameters up to 120 μm was to provide indentations (visualized as the dimples on a golf ball) into which TiO_2 (approximately 20 μm) and zeolite (approximately 40 μm) could penetrate for protection from mechanical attrition during fluidization. The composite created in this way was called integrated photocatalyst adsorbent (IPCA).

In the process of synthesizing the initial IPCA material, Degussa P-25 TiO_2 and Silicalite I (S-115, Zeolyst International) were attached directly to the glass beads by mixing the components into a slurry in 40% colloidal silica binder. Laboratory scale evaluation of such an IPCA has been reported and the process optimized [15]. Larger quantities were required for experiments in the photoreactors described here and the current preparation is given below.

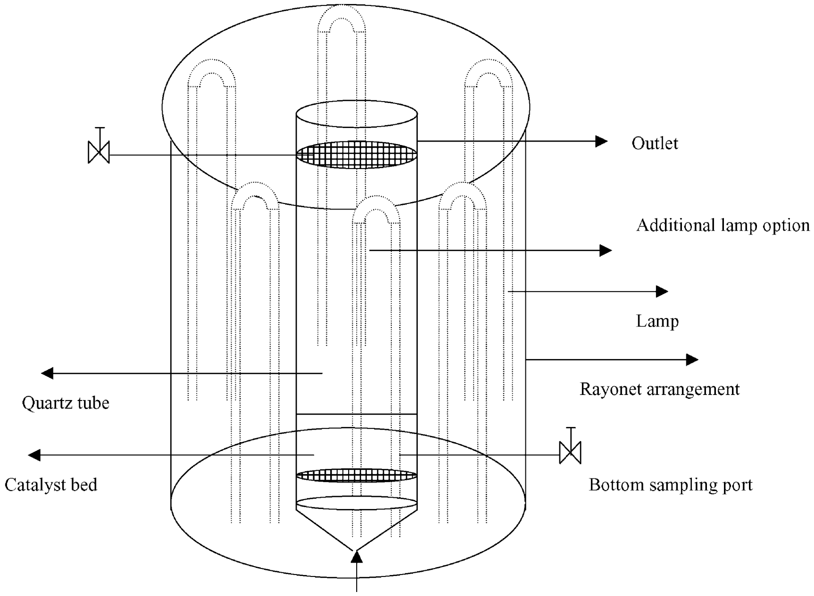

Fig. 2. Setup of the reactor in a Rayonet multi-lamp system.

Loading of TiO_2 onto the zeolite was the first stage of the manufacturing process and was performed before attaching the components to the porous glass beads (pre-treatment). Pretreatment of titania and zeolite powders involved sonication and calcination procedures where the two components were first slurried together in water, sonicated, dried at 120 °C, and then heated at 450 °C. This led to firm attachment of TiO_2 to the zeolite. Sonication was done in an aquasonic bath (model P250D) at 60 °C for 1 h. Thermal pre-treatment of the components was done in a muffle furnace (Hotpack Inc.) for 8–12 h.

2.3. Experimental procedures

Initially, a certain amount of phenol was introduced in the storage tank and then passed through the reactor for an hour in the dark to allow for saturation of the IPCA material. Afterwards, the lamps were turned on and the process was initiated (no new phenol was added to the system). Hydrogen peroxide was introduced at the initiation of irradiation. The process of phenol degradation was monitored using HPLC. The instrument had a reversed phase C_{18} column operated under the following conditions: the wavelength of the UV detector was set at 224 nm; a 50:50 mixture of CH_3CN and H_2O was used as an effluent with 1.0 ml/min flow rate. Analytical results were calibrated using a series of standard solutions corresponding to a range of concentrations used in the experiments.

3. Results and discussions

3.1. Effect of catalyst loading on reactor efficiency

Performance of the photocatalytic reactor was analyzed first with respect to the amount of the photocatalyst used alone (without hydrogen peroxide). As shown in Fig. 3, phenol degradation initially increases with the increase of TiO_2 loading (until loading of 1.61 g/l) but then it starts to decrease (loading of 2.14 g/l). It can also be seen from Fig. 3 that after 2.5 h of irradiation, phenol degradation was almost the same for loadings of 1.07 and 1.61 g/l. Decrease of the degradation rate observed at higher catalyst loadings might be attributed to a more pronounced effect of scattering of UV light by the catalyst particles inside the reactor, which results in the UV loss for the catalyst particles appeared at larger distances from the UV source.

For the next round of experiments, the most effective (1.07 g/l) and the least effective (0.21 g/l) photocatalyst loadings were chosen to analyze how hydrogen peroxide might affect phenol decomposition.

3.2. Effect of hydrogen peroxide addition to the photocatalytic system

If hydrogen peroxide was used alone, 14 moles of it would be required for complete degradation of 1 mole of phenol as per stoichiometry of the reaction (1):

$$C_6H_5OH + 14H_2O_2 \rightarrow 6CO_2 + 17H_2O \qquad (1)$$

In our experiments where 10 ppm phenol solution was used in a 59 l reactor, it would require 13.5 ml of 30% hydrogen peroxide solution for complete degradation by hydrogen peroxide alone. Since hydrogen peroxide was applied to the existing photocatalytic system, only fractions of the amount required stoichiometrically were used. The amounts varied from 1 to 20% of stoichiometrically required, which corresponds to 135 μl and 2.7 ml accordingly (in the 59 l reactor).

Effect of hydrogen peroxide addition at the catalyst loading of 1.07 g/l is shown on Fig. 4. Interestingly, addition of 1% hydrogen peroxide resulted in the highest degree of degradation. Degradation of phenol was almost doubled with the addition of this miniscule amount of hydrogen peroxide compared to the case where photocatalysis was used alone. With further increase of hydrogen peroxide, the rate started to decrease and at 20% addition of hydrogen peroxide, degradation rate was almost equal to the rate of photocatalysis applied alone.

Replicate experiments were conducted in all the trials to ensure reproducibility of the results but to simplify the presentation in Fig. 4, error bars were only presented for the trials with

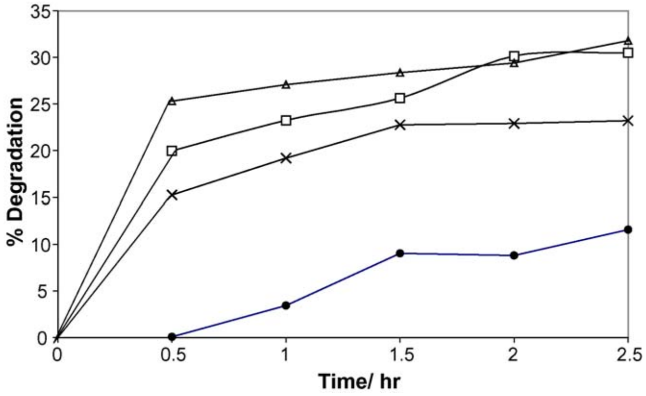

Fig. 3. Photocatalytic degradation of phenol at different catalyst loadings (initial concentration of phenol: 10 ppm, volumetric flow rate of contaminated water: 27 lpm, wavelength of UV lamps: 254 nm, no. of lamps used: 9, fluence rate: 5 mW/cm^2). (●) 0.21 g/l TiO_2, (□) 1.07 g/l TiO_2, (△) 1.66 g/l TiO_2 and (×) 2.14 g/l TiO_2.

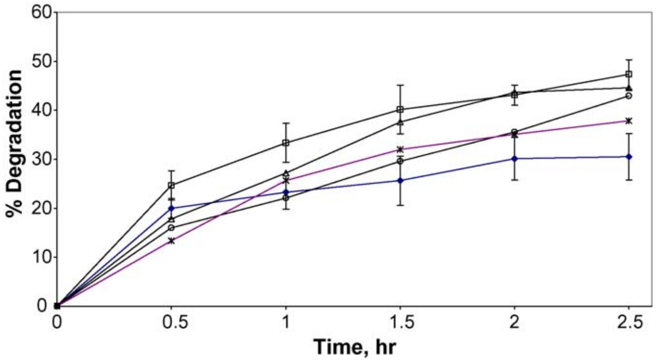

Fig. 4. Effect of hydrogen peroxide at the catalyst loading of 1.07 g/l (initial concentration of phenol: 10 ppm, volumetric flow rate of contaminated water = 27 lpm, wavelength of UV lamps = 254 nm, no. of lamps: 9, fluence rate: 5 mW/cm^2). (●) No H_2O_2, (□) 1% H_2O_2, (△) 5% H_2O_2, (*) 15% H_2O_2 and (○) 20% H_2O_2.

no H_2O_2 and 1% H_2O_2. Results of these series of experiments varied within ±5%.

It is known that hydrogen peroxide can enhance the reaction of phenol degradation by providing additional hydroxyl radicals either through trapping of photogenerated electrons (Eq. (2) and (3)) or/and through photolysis at 254 nm (Eq. (4)). As reported, hydroxyl radial can be generated when hydrogen peroxide traps photogenerated electrons [16]. This trapping would also help suppress recombination of electron–hole pair produced at the activated catalyst surface. Hydrogen peroxide can also absorb the light at 254 nm and decompose to produce $OH^{\bullet}$ radicals, which would lead to the increased rate of phenol degradation [7]:

$$TiO_2 \xrightarrow{UV} h^+ + e^- \tag{2}$$

$$H_2O_2 + e^- \rightarrow OH^- + OH^{\bullet} \tag{3}$$

$$H_2O_2 \overset{UV<300\,nm}{\longleftrightarrow} 2OH^{\bullet} \tag{4}$$

Earlier studies of degradation of pulp and paper mill effluents by our group suggested that common explanation that H_2O_2 acted simply as an alternate electron acceptor could not be sustained in some cases. The rate enhancement in solutions that had received 1% H_2O_2 addition persisted long after all of the initial H_2O_2 was exhausted and an addition of more H_2O_2 at that time had no accelerating effect. It appears that H_2O_2 plays a role in initiation of radical chain reactions that persist after the initial dose of H_2O_2 has been consumed [17]. A similar phenomenon was observed in this study in the case of 1.07 g/l loading, where very small addition of H_2O_2 affected the rate significantly.

Next, we explored the effect of hydrogen peroxide addition to the catalyst loading of 0.21 g/l as shown in Fig. 5. In contrast with the effect of hydrogen peroxide on the system with larger 1.07 g/l catalyst loading, phenol degradation was found to continuously increase with the increase of hydrogen peroxide in the case of the smaller loading (0.21 g/l). It appears that in the latter case, hydrogen peroxide acted as the dominant degrading agent. Apparently, lower light absorbance by TiO_2 allowed H_2O_2 to function as a UV absorber to produce $OH^{\bullet}$ radicals according to Eq. (4). Based on spectrophotometric measurements, we have estimated that if the solution were clear and free of particles scattering the light, roughly 38% of 254 nm light would be adsorbed in the reactor path length of 14 cm by 20% hydrogen peroxide. From previous research on the supported titania catalyst, it is known that if the loading of the supported photocatalyst is equal or greater than 0.5 g/l, over 95% of the light would be absorbed by the photocatalyst [18]. If the loading of the catalyst is less than 0.5 g/l, we expect light absorbance by H_2O_2 to make a contribution. This fact might explain why phenol degradation was found to continuously increase with the increase of hydrogen peroxide in the case of 0.21 g/l titania loading.

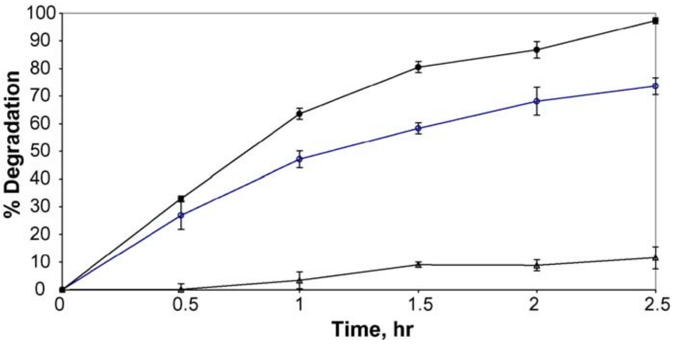

Fig. 5. Effect of hydrogen peroxide at the catalyst loading of 0.21 g/l (initial concentration of phenol: 10 ppm, volumetric flow rate of contaminated water: 27 lpm, wavelength of UV lamps: 254 nm, no. of UV lamps: 9, fluence rate: 5 mW/cm^2). (△) No H_2O_2, (◯) 1% H_2O_2 and (●) 20% H_2O_2.

3.3. Analysis of single effects of photocatalysis and hydrogen peroxide versus their combination

Individual contributions of UV, TiO_2 and hydrogen peroxide as well as their combined effects on phenol degradation are shown in Fig. 6. There was almost no degradation of phenol by 20% hydrogen peroxide with no UV and catalyst. UV alone also showed insignificant degradation rate. Irradiation of 20% hydrogen peroxide notably improved phenol degradation. Almost 70% degradation was observed within 2.5 h of irradiation in this case. However, addition of a small amount of the photocatalyst (0.21 g/l) to 20% hydrogen peroxide showed superior performance for phenol degradation; almost 98% of phenol was found to be degraded within 2.5 h irradiation.

Thus, combined effect of relatively small amounts of hydrogen peroxide and the photocatalyst was found to be the most efficient means of degrading phenol in a fluidized bed photocatalytic reactor. In this study, the amount of hydrogen peroxide was still low (20% hydrogen peroxide is equivalent to 2.7 ml of 30% hydrogen peroxide solution in a 59 l reactor) compared to what would be required stoichiometrically. Thus from economic considerations, combination of the photocatalysis and hydrogen peroxide offers an efficient solution for organic pollutant removal from wastewater. Further study with other organic pollutants will hopefully lead to a more efficient combination to

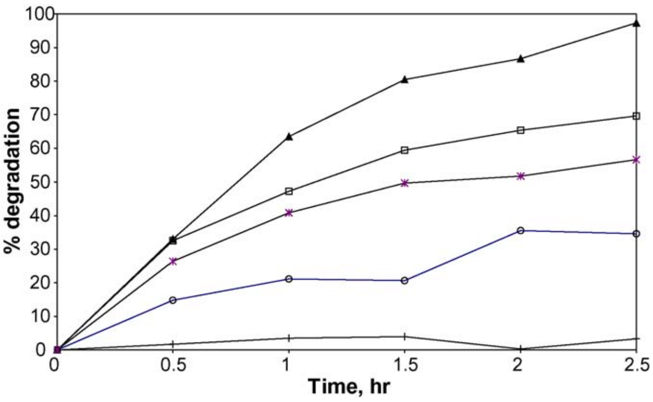

Fig. 6. Comparison of effect of single parameter and effect of combination of parameters (initial concentration of phenol: 10 ppm, volumetric flow rate of contaminated water = 27 lpm, wavelength of UV lamps = 254 nm, no. of lamps: 9, fluence rate: 5 mW/cm^2). (+) 20% H_2O_2 only, (◯) UV only (no catalyst), (*) UV + 1% H_2O_2 + 1.07 g/l TiO_2, (□) UV + 20% H_2O_2 + no catalyst and (△) UV + 0.21 g/l TiO_2 + 20% H_2O_2.

design a fluidized bed photocatalytic reactor with the potential for commercialization.

4. Conclusions

Effect of H_2O_2 addition on phenol degradation in the photocatalytic fluidized bed reactor was exploited in this research. Laboratory optimized integrated photocatalyst adsorbent was used as the supported photocatalyst. Overall, it was found that addition of hydrogen peroxide to the photocatalytic system was beneficial and it was demonstrated that the desired enhancement can be achieved with small doses of hydrogen peroxide, which is promising from economic perspective since it requires miniscule consumption of the non-recyclable agent, H_2O_2.

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