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Research Article

Use of a UV/H_2O_2 process for posttreatment of a biologically treated composting leachate

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Abstract: This research was conducted to investigate the efficacy and feasibility of a UV/H_2O_2 process as a posttreatment step for complete treatment of a biologically treated composting leachate. This study was an experimental study and was conducted during April to September 2013. Leachate samples from the effluent of a multistep biological treatment system were used for further treatment by the UV/H_2O_2 process. The effectiveness of the pH values (2–10), H_2O_2 concentrations (0.5–4 g/L), and reaction times (15–75 min) were evaluated to determine optimum operational conditions. The highest removal efficiencies were 90%, 92%, 90%, and 88% for chemical oxygen demand (COD), biochemical oxygen demand₅ (BOD₅), total organic carbon (TOC), and total suspended solids (TSS) respectively, at the optimum operation conditions (pH 4, 3 g/L H₂O₂ concentration, and 75 min reaction time). The UV/H_2O_2 was found to oxidize preferably COD and BOD₅ of the leachate samples and, as a consequence, a decrease in the organic loads of the leachate was observed after oxidation treatment. The UV/H_2O_2 process proved to be a feasible posttreatment method for a biologically treated composting leachate and effectively reduced the organic loads.

Key words: Composting leachate, biological treatment, UV/H₂O₂ process, organic loads

1. Introduction

One of the main problems associated with composting is the formation of leachate containing any material that was extracted from or suspended or dissolved in the compost pile [1]. These leachates may migrate from the refuse and contaminate surface and ground waters, which may affect human health and the aquatic environment [2]. Treatment of the leachate is often complicated and expensive in order to comply with the effluent standards prior to discharge, resulting in a challenge for environmental engineers. The treatment of the leachate is studied necessarily by alternative physical, biological, and chemical treatment technologies [3–5]. Biological treatment is the most economically efficient method for the removal of biodegradable organic compounds [6]. As the volatile fatty acid content decreases with leachate age, the biological treatments become less effective because of the presence of biorefractory compounds. In such a situation, after a biological stage, further treatment is necessary to remove the biorefractory material [7]. Advanced oxidation processes (AOPs) are one of the most common types of treatment and are particularly interesting because they can remove nonbiodegradable organic compounds, eliminate color, and reduce the organic load or toxicity without any production of residues [5,8]. AOPs are based on the generation of hydroxyl free radicals to enhance a high degradation rate of organics in

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an aqueous system. Among AOPs the UV/H_2O_2 processes have been efficiently used as a chemical process for wastewater treatment and pretreatment [9].

A wide variety of UV/H_2O_2 applications have been reported, such as degradation of persistent organic pollutant (POPs) in water [10], oxidation of pharmaceuticals in wastewater [11], decolorization of textile dye in water [12], removal of organic matter from water [13], and degradation of pesticides from aqueous solution [14]. Among them, applications of UV irradiation for the treatment of leachates have been recently reported and different conditions for these processes have been studied [15]. Shu et al. [15] achieved 72% and 65% color and COD removal efficiencies by combining UV irradiation with hydrogen peroxide for landfill leachate. By UV-TiO₂, Jia et al. [5] found respectively 60%, 70%, and 97% removal of COD, DOC, and color for landfill leachate. Moreover, de Morais et al. [16] demonstrated significant enhancement of BOD₅/COD from 0.13 to 0.37 to improve leachate biodegradability by applying UV irradiation along with 3000 mg/L H₂O₂. However, these results were obtained with landfill leachate, which is inherently different from composting leachate due to the aerobic conditions of the process and the use of fresh and young wastes.

As far as we know, there are no studies published on the use of UV/H_2O_2 for the treatment of leachates from composting processes. Therefore, the objective of the present study was to examine the utilization of UV/H_2O_2 as a posttreatment method for further treatment of composting leachate previously treated by biological processes. The efficiency of this process was evaluated in terms of reduction of organic matter loads.

2. Materials and methods

2.1. Leachate samples

The leachate samples were collected from a multistep biological treatment system that was operating on a pilot scale for treatment of the composting leachate from the Isfahan municipal solid waste composting site, Isfahan, Iran. This biological treatment system had four steps consisting of an anaerobic migrating blanket reactor (AMBR), anaerobic sequencing batch reactor (ASBR), sequencing batch reactor (SBR), and SBR along with membrane biological reactor (SBR/MBR). Part of the last stage effluent of the biological treatment system (SBR/MBR process) was used to apply to the UV/H_2O_2 process. The characterizations of the raw leachate used in the biological treatment system and the SBR/MBR effluent used in the UV/H_2O_2 process are shown in the Table.

Parameter	Raw leachate	SBR/MBR
		process effluent
COD (g/L)	99.23 ± 6.65	0.58 ± 0.004
BOD ₅ (g/L)	65.5 ± 4.3	0.22 ± 0.002
BOD_5/COD	0.66 ± 0.03	0.39 ± 0.01
pH	5.89 ± 0.4	8.4 ± 0.3
Electrical conductivity (mS/cm)	19.61 ± 3.3	2.63 ± 0.6
TDS (g/L)	9.81 ± 1.6	1.31 ± 0.3
Color	Yellow	Gray

Table. Characterizations of the raw leachate and the SBR/MBR process effluent.

2.2. Experimental setup and procedures

The experiments were carried out in a 1000-mL closed batch reactor. The photoreactor was a glass jar in which an ultraviolet lamp with a quartz sleeve was placed. Ultraviolet radiation was provided by a 254-nm

medium-pressure mercury vapor lamp (150 W, Arda, France). A stirrer (90-402, Labinco, Netherlands) was used during the UV exposures to provide adequate mixing. The entire reactor was kept in an ice chamber, where the temperature was maintained at 25 \pm 1 °C. All the experiments with UV irradiation were carried out in dark conditions to avoid external light interference.

2.3. Analytical methods

For the UV/H₂O₂ experiments, leachate samples from the effluent of the SBR/MBR process were used for treatment. The initial pH of the sample was adjusted to the desired value from 2 to 10 in constant concentration of H₂O₂ (2 g/L) and irradiation time (30 min) to determine the optimum pH. Then adequate amounts of H₂O₂ were first added to the sample from 0.5 to 4 g/L when the pH was the optimum and irradiated for 30 min. Finally the effect of irradiation time was evaluated during the optimum conditions of pH and H₂O₂ for determination of the reaction time.

2.4. Material and analysis

Hydrogen peroxide (30%, w/w) was analytical reagent grade (Merck, Germany). Double distilled water was used to prepare experimental solution. The pH was adjusted to desired values with 1 N H₂SO₄ and 1 N NaOH and measured by pH-meter (E520, Metrohm-Herisau, Switzerland). Total organic carbon (TOC) analysis was conducted with the combustion-infrared method using a TOC Analyzer (TOC-VCSH, Shimadzu, Japan) and in accordance with the Standard Method [17]. In addition, chemical oxygen demand (COD) and other analysis were conducted in accordance with the Standard Method [17]. BOD₅ was measured using the respirometric method by measuring oxygen pressure decrease using Oxitop bottles (IS6, WTW, Germany). It is important to note that during this work, since acidic and alkaline pH can affect microbial activity, BOD₅ measurements were done after neutralizing the pH of the samples as recommended in Standard Methods [17]. All experiments were carried out at room temperature in triplicate and the results were averaged.

3. Results and discussion

3.1. Leachate characterization

Characterizations of the raw leachate and the effluent of the SBR/MBR process are shown in the Table. The fresh leachate collected from the composting site presented very high levels of COD and BOD₅, whereas the ratio of BOD₅/COD was around 0.66, which corresponded to a high level of biodegradability of the organic matter. The SBR/MBR effluent also showed that further treatment was needed to achieve the discharge standards and biological treatment only was not adequate for leachate treatment.

3.2. Effect of pH

The effect of pH values on the UV/H₂O₂ process was also studied using different pH values from 2 to 10 to determine the optimal pH. Figure 1 shows that there was strong dependence of the COD and BOD₅ removal rates on the solution pH and maximum removal of COD and BOD₅ was 60% and 67%, respectively, at pH 4. Although the results regarding the effect of pH suggested that COD and BOD₅ removal was low at pH values below and above 4, the removal rate was lower in the alkaline medium compared to the acidic medium (Figure 1). This can be explained on the basis that in alkaline medium the oxidizing species hydroperoxy anion (HO₂⁻) is also formed (HO₂⁻ anion is the conjugate base of H₂O₂). This HO₂⁻ anion can react with both the OH[•]

radical as well as H_2O_2 molecules, thus consequently lowering the removal rate [18,19].

$$H_2O_2 + HO_2^- \rightarrow H_2O + O_2 + OH^{\bullet}$$
$$OH + HO_2^- \rightarrow H_2O + O_2^-$$

Results from previous studies indicated that UV/H_2O_2 operates with great efficiency in low pH values [16,20]. Results from De Morais et al. [16] suggested that UV/H_2O_2 showed the best performance in low pH values and high concentrations of H_2O_2 during landfill leachate treatment.



Figure 1. Effect of the initial pH on COD and BOD₅ removal during the UV/H₂O₂ process (Experimental conditions: H₂O₂ [2 g/L] and reaction time [30 min]).

3.3. Effect of addition of H_2O_2

The effect of addition of H_2O_2 (0.5–4 g/L) on photochemical degradation was investigated. The results obviously indicated that removal efficiency was significantly influenced by H_2O_2 concentration. As seen in Figure 2, the removal rate of COD and BOD₅ increased with increasing H_2O_2 concentration. At low concentration, H_2O_2 cannot generate enough hydroxyl radicals and the removal rate is limited [10]. Degradation is due to the reaction of hydroxyl radicals generated by hydrogen peroxide in solution upon irradiation by UV light [18].

$$H_2O_2 + hv \rightarrow 2OH^{\bullet}$$

As shown in Figure 2, addition of $0.5-3 \text{ g/L } \text{H}_2\text{O}_2$ increased degradation from 36% to 73% for COD and from 46% to 76% for BOD₅ during the 30 min reaction time and pH 4. In a study on removal of organic matter by UV/H₂O₂, the results suggested that higher H₂O₂ concentration led to better TOC removal efficiencies [13]. Results from Shu et al. [15] showed that a higher hydrogen peroxide dosage promoted more significant decolorization and COD removal of MSW landfill leachate during the UV/H₂O₂ process. Their results also demonstrated that with the maximum dosage of 4-UV lamps and 232.7 mM of hydrogen peroxide concentration, the color and COD removal were 72% and 65% for original leachate in 300 min reaction time. In our study, a further increase in the H₂O₂ concentration from 3 g/L slowed down the degradation rate of both COD and BOD₅. It can be concluded that further increases in the initial H₂O₂ concentration caused an inhibition in the UV/H₂O₂ performance because H₂O₂ itself acts as an *OH*[•] scavenger [18,21,22].

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2 + H_2O$$

$$OH + HO_{2\bullet} \rightarrow O_2 + H_2O$$

Thus, it is very important to optimize the applied H_2O_2 dose to maximize the treatment performance of the UV/H_2O_2 process.



Figure 2. Effect of the initial H_2O_2 on COD and BOD₅ removal during the UV/ H_2O_2 process (Experimental conditions: pH [4] and reaction time [30 min]).

3.4. Effect of reaction time

Reaction time is another critical factor to control the oxidation. The effect of reaction time during the UV/H₂O₂ process was investigated in optimum pH and H₂O₂ concentration. As shown in Figure 3, COD removal was enhanced by increasing the reaction time and a 90% maximum removal rate was achieved after 60 min. This phenomenon can be related to more opportunity of the OH^{\bullet} radicals to practice. As can be seen, COD removal was negligible after 60 min and was almost constant after this time. Shu et al. [15] investigated the effect of reaction time on COD removal during UV/H₂O₂ treatment. Their results indicated that the removal rate was only 40% after 20 min reaction time and this rate increased to more than 80% when the time was increased to 120 min and almost was constant after 120 min. The same results were also shown for BOD₅, TOC, and TSS and were removed more after increasing the reaction time. The BOD₅ was removed 52% after 15 min and its removal rose to 92% when the time was increased to 75 min (Figure 3). The TOC removal increased from 46% in 15 min reaction time up to 90% after 60 min and was constant after this time (Figure 4). TSS showed a lower removal rate than other parameters and its maximum removal was 88% after 75 min reaction time (Figure 4). Other studies on leachate treatment with UV/H₂O₂ have shown the same results [15,16]. Results from a study on landfill leachate treatment using UV/H₂O₂ showed the same results as our study. In that study removal of COD and TOC increased 15% and 17% when the radiation time was increased by 30 min [16].

4. Conclusions

Leachate from the composting process of MSW has been characterized in terms of organic loads. The values for both COD and BOD₅ were extremely high while the BOD₅/COD ratio was 0.66; therefore it can easily be treated by biological processes. The use of UV/H₂O₂, given the high biodegradability of composting leachate, can be proposed as a posttreatment after biological treatment to treat remaining slowly biodegradable COD. Hence, the treatment scheme reported in Figure 5 (i.e. biological treatment \rightarrow UV/H₂O₂ treatment) shows that UV/H₂O₂ can be an effective method for posttreating the investigated leachate. In fact, the COD and BOD₅ data in Figure 5 show that, by means of UV/H_2O_2 , it is possible to achieve COD and BOD₅ removal efficiencies as high as 90% and 92%, respectively. The results revealed that control of pH value was essential to obtain efficient COD and BOD₅ removal in this process. The optimal pH was 4. Furthermore, the UV/H_2O_2 system is significantly affected by H_2O_2 concentration and reaction time and it is necessary to obtain the optimal conditions. The results of the present study have clearly delineated that UV/H_2O_2 provides a promising technique for complete treatment of a biologically treated composting leachate and could effectively reduce organic matter.



Figure 3. Effect of the reaction time on COD \blacksquare and BOD₅ \blacksquare removal and concentration during the UV/H₂O₂ process (Experimental conditions: pH [4], H₂O₂ [3 g/L]).



Figure 4. Effect of the reaction time on TOC ■ and TSS ■ removal and concentration during the UV/H₂O₂ process (Experimental conditions: pH [4], H₂O₂ [3 g/L]).



Figure 5. COD and BOD₅ concentrations of raw leachate and treated leachate before and after UV/H_2O_2 treatment.

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