PERFORMANCE OF H₂O₂ - AERATED BIOFILTER IN TREATMENT OF WASTEWATER CONTAINING HUMIC ACID

Le Van Tuan*, Huynh Xuan Toan, Nguyen T. Thao Nguyen, Dang T. Thanh Loc

Department of Environmental Science, College of Sciences, Hue University, 77 Nguyen Hue street, Hue city, Vietnam

*Email: lenntuan@gmail.com

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ABSTRACT

This work presents the results of adding H₂O₂ into a modified aerated biofilter (ABF) for treatment of refractory organic constituents in wastewater. The activated sludge, taken from wastewater treatment system of Hue Beer Company, was long-time cultured in laboratory with beef extract-peptone solution. The synthetic wastewater was prepared from solutions of glucose, ammonium acetate, sodium bicarbonate, potassium dihydrogen phosphate, sodium chloride, potassium chloride, calcium chloride and magnesium sulphate. As a refractory organic compound, humic acid (HA) was added into the wastewater; and parameters of chemical oxygen demand (COD) and color were measured to estimate the treatment performance. The experiments were conducted in continuous mode to observe the effects of H₂O₂ concentration (25–100 mg/L) and hydraulic retention time (HRT: 24–18 hours; according to organic loading rate, OLR: 0.51–0.67 kg-COD/m³/d) on the aerated biofilter system, under identical treatment conditions (COD: 505 ± 10 mg/L, HA concentration: 25 mg/L, pH: 7.0 ± 0.2, temperature: 25 ± 3.0 °C, and air flow rate: 1.0 ± 0.1 L/min). At the concentration of H₂O₂ 50 mg/L and HRT of 24 hours, the ABF reactor yielded highest treatment efficiency (95 % COD and 74 % color). Consequently, H₂O₂ could be used to improve the effectiveness of activated sludge process in treatment of wastewater containing refractory organic compounds.

Keywords: H₂O₂, activated sludge, aerated biofilter, humic acid, wastewater.

1. INTRODUCTION

Humic acid (HA) is known as a major extractable component of soil humic substances. It has a wide range of distribution in molecular weight and non-biodegradability. The dark brown color caused by HA is normally found in many water effluents (i.e. leachate, domestic, palm oil mill effluent, etc.) [1]. The presence of HA in water has received much public attention due to color pollution and toxic disinfection by products formed from chlorination processes [2].

In treatment of wastewater by conventional activated sludge process, sufficient provision of oxygen for aerobic microorganisms plays an important role on organic removal efficiency. In fact, the transfer rate of oxygen from gas phase to liquid phase is normally limited by using of
normal aeration equipment. Therefore, high energy-consumption is required for the oxygen supply. Hence, using other supplemental oxygen sources (i.e. H$_2$O$_2$) has attracted attention from many researchers [3 - 6].

H$_2$O$_2$ is normally used in a single-stage of chemical oxidation process to treat refractory organic pollutants by transforming them into biodegradable substances [7]. Adding H$_2$O$_2$ in the aerobic biological treatment processes would be improved the treatable ability for a couple of reasons. Firstly, H$_2$O$_2$ could be used as an oxygen source for activated sludge. Secondly, the common presence of Fe$^{3+}$ in wastewater (i.e. leachate) could be formed the Fenton’s reagent.

The wastewater treatment based on H$_2$O$_2$ - advanced oxidation processes (AOPs, i.e. H$_2$O$_2$/Fe$^{3+}$, H$_2$O$_2$/UV, H$_2$O$_2$/O$_3$ and so forth) have shown the effective reduction of organic contaminants and color. The AOPs can increase the biodegradable fraction of organic constituents in wastewater. However, the weakness of the AOPs is the fact that it requires too much chemicals and complex operation [8]. In this study, adding H$_2$O$_2$ into a modified aerated biofilter would be expected not only to improve treatment efficiency of refractory organic compound but also to reduce amount of sludge waste by a simple operating system.

2. MATERIALS AND METHODS

2.1. Activated sludge and synthetic wastewater

Activated sludge was taken from wastewater treatment system of Hue Beer Company. The activated sludge (mixed liquor suspended solids, MLSS: 8950 ± 100 mg/L) has been cultured long-time (> 1 year) in the laboratory of Department of Environmental Science, College of Sciences, Hue University. Subtraxts used for the sludge were prepared from beef extract-peptone solution of 5 mL/L, sodium bicarbonate of 21 g/L (5 mL/L), and mixed salt solutions (NaCl, KCl, CaCl$_2$ and MgSO$_4$) (0.75 mL/L). It was then added every 48 hours.

Each liter of synthetic wastewater (WW, “medium”) was prepared from solutions of 2.5–10 mL-glucose (30 g/L) (according to COD values ranging from 125 mg/L to 500 mg/L), 5 mL ammonium acetate (20 g/L), 10 mL sodium bicarbonate (50 g/L), 2.5 mL potassium dihydrogen phosphate (7.2 g/L), 1 mL mixed salt solutions (NaCl, KCl, CaCl$_2$, MgSO$_4$) [9] and tap water (already being aerated in more than 24 hours). As a refractory organic compound, pure humic acid (Wako, Japan) (HA, 25 mg-HA/L) was added into the wastewater (WW/HA). Thus, dissolving the HA in diluted water at room temperature is not possible [2]. In this study, HA of 1000 mg was dissolved in 1 L of NaOH 0.1 N and was used as a stock solution [1].

2.2. Experimental setup

All experiments were performed in a system consisting of a modified aerated biofilter tank (ABF) with a continuous inflow of synthetic wastewater (WW or WW/HA). The influent wastewater was prepared 18 L per time. The main components of the designed laboratory setup are the ABF tank, an influent wastewater tank, a sedimentation tank, an air pump (Heibao Aquarium, HP–2800), a peristaltic pump (RP–2000 EYELA), an air flow meter, an air bubbles diffuser, a pH meter (ECO Testr pH–2) and an oxygen meter–thermometer (HACH Sensor–156). The ABF tank was a columnar clear acrylic plastic tank (10 L) with a working – liquid volume of 6 L. Inside the reactor, tiny polyethylene strings (dry weight: 32.3 g) prepared in net type were used as biomass carrier and were fixed in the middle part (3 L) of the reactor. The peristaltic pump was used for controlling wastewater flow rate and the wastewater was pumped
Performance of \( \text{H}_2\text{O}_2 \)-aerated biofilter in treatment of wastewater containing humic acid

to a distribution pipe of the reactor. The air nozzle was placed at the bottom of the net of biofilter for supplying air (Figure 1). For starting-up, the activated sludge (SS: 2700 mg/L) was added into the ABF reactor and all substrates used for the activated sludge were seeded into the reactor working volume. The system was aerated and was stabilized during 48 hours so that the activated sludge fully attached into the biomass carrier. For each of changing operation, the system was run at least 24 hours before sampling. Phase 1: The “start-up phase” lasted 37 days by continuous feeding into reactor with the synthetic wastewater (without \( \text{H}_2\text{O}_2 \) and HA). Phase 2: the synthetic wastewater (WW/HA) was continuous introduced during next 91 days for acclimation of the system, of which 49 running days to observe the effects of \( \text{H}_2\text{O}_2 \) concentration (0–100 mg/L) and 53 days to observe the effects of HRT 24–18 hours, according to OLR: 0.51–0.67 kg-COD/m³/d.

![Experimental setup](image)

2.3. Analysis methods

Samples were analyzed for such parameters as pH, DO, COD, SS, VSS and OUR; following the standard methods of APHA (1999) [10]. The existence of \( \text{H}_2\text{O}_2 \) has a positive error on COD\text{Cr} analysis [11]. Following Talinli and Anderson method (1991), our screening tests showed that in \( \text{H}_2\text{O}_2 \) concentration range of 0–300 mg/L, 1 mg \( \text{H}_2\text{O}_2 \) was equivalent to 0.35 mg COD. According to DO data series, OUR value (mg-O\text{2}/L/h) was absolute value of the SLOPE. The Koch method was applied to isolate and to calculate the number of aerobic bacteria colonies by using Winogradski medium with glucose carbon source. UV-VIS spectrophotometry (GENESYS 10S UV-VIS, USA) analysis was used to determine the de-colorization capacity via the average of absorbance values (from 240 to 540 nm) of the WW/HA samples.

3. RESULTS AND DISCUSSION

3.1. Characteristics of the activated sludge

The concentrations of activated sludge cultured for long-term were 8.95 ± 0.1 g/L and 3.96 ± 0.08 g/L as MLSS and MLVSS, respectively, with the MLVSS/MLSS ratio of about 0.44 ± 0.03. The sludge was developed well and stably. Aerobic bacteria isolation was carried out in two times. After incubating medium at 36 ± 1°C in 3 days, the number of colonies counted was
4.3×10^5 CFU/mL (5.6 log[CFU/mL]). The OUR value of the activated sludge was around 4.3 mg-O_2/L/h [12]. Microscopic observation evidenced that there are many groups of microorganisms (e.g., “chlorophyta”, “protozoa”, “fungi”, “rotifer”, etc.) in the sludge at beginning - Figure 2(a-d) and after 128 days operation - Figure 2(e-h). Interestingly, the color of some microorganisms was changed into dark-brown color caused by HA. After 128 days (in total time) running, the concentration of activated sludge in the ABF reactor was still stable at ~2700 mg-SS/L. However, the VSS/SS ratio was increased nearly twice (0.84 ± 0.02). It should be noted that sludge waste was not found in the sedimentation tank during all operations.

![Image](image1.png)

Figure 2. Some microorganisms observed in the activated sludge samples.

3.2. Start–up phase

At the start-up phase, three experimental runs were operated by using the synthetic wastewater (without H_2O_2 and HA) (Figure 3). The influent COD concentrations were increased stepwise from 135 to 505 mg/L, corresponding to OLR from 0.13 to 0.51 kg-COD/m^3/d. After 4-days, the system reached the high percentages of COD removal efficiency (>90 %) for all experimental operations. In addition, the COD values of the Eff-1 (□) and the Effl-2 (△) were the same during this phase. That indicated organic compounds in the wastewater were mostly removed by the ABF tank.

3.3. Effect of H_2O_2 concentration

The H_2O_2 concentration presented a significant impact on the activated sludge. In previous research, at batch mode testing, the suitable condition of using H_2O_2 with the aerobic biological treatment in order to increase benefit of H_2O_2 and overcome its inhibition to microorganisms were recorded at lower than 100 mg-H_2O_2/L [12]. In this study, the effect of H_2O_2 concentration (0–25–50–100 mg/L, according to runs: HO-0, HO-25, HO-50, HO-100) on the treatment of synthetic wastewater containing humic acid (WW/HA) at the concentration of COD ~518 mg/L was investigated (Figure 4). Addition of H_2O_2 did not significantly affect the COD removal. It was noticed that at the H_2O_2 concentration of 50 mg/L, 95 % removal of COD was reached. Again, the COD values of the effluent (1) and the effluent (2) were the same.
3.4. Effect of hydraulic retention time or organic loading rate

Adding \( \text{H}_2\text{O}_2 \) in a aerated biological system, long HRT may be adverse to microorganisms due to the longer exposure to \( \text{H}_2\text{O}_2 \). In this study, four experimental runs with changes in HRT from 24 hours to 18 hours (according to OLRs: 0.51–0.67 kg-COD/m\(^3\)/d) were carried out to check the influence of HRT (Figure 5 and Figure 6) under identical treatment conditions (HA: 25 mg/L, \( \text{H}_2\text{O}_2 \): 50 mg/L, COD: ~518 mg/L). An increase in HRT from 18–24 hours resulted in a higher percentage of COD removal from 86.4 ± 4.4 % to 93.8 ± 1.9 %, respectively (Figure 5b) and of color removal from 48.5 % to 74.2 %, accordingly (Figure 6b).

UV-VIS spectrophotometry (GENESYS 10s Uv-Vis, USA) results obtained (from 190 – 1100 nm) for four samples (including: 1) synthetic wastewater – WW/COD-500 mg/L, 2) humic acid (25 mg/L) and distilled water – HA 25 mg/L, 3) synthetic wastewater and HA (25 mg/L) – HO-0/lff, and 4) the effluent after 43 days of running – HO-0/Eff-1) showed clear changing absorbance values below the wavelength of 540 nm (Figure 6a). Moreover, in the range of wavelengths between 190 and 240 nm, clear synthetic wastewater (WW/COD-500 mg/L) also have high absorbance values. Therefore, the average of ranging wavelengths 240–540 nm (~300 absorbance values) was used to determine the color of influents and effluents. Addition of \( \text{H}_2\text{O}_2 \) did not clearly affect the COD removal but enhanced color removal. Under identical treatment conditions (HA: 25 mg/L, \( \text{H}_2\text{O}_2 \): 50 mg/L, COD: ~518 mg/L, HRT: 24 hours), the color removal reached 74.2 % which is better than without using \( \text{H}_2\text{O}_2 \) (58.2 %).

![Figure 3. Star-up phase: stepwise increasing the influent COD concentrations.](image)

![Figure 4. Effects of \( \text{H}_2\text{O}_2 \) concentration on the treatment of WW/Ha.](image)

![Figure 5. Effects of hydraulic retention time on COD removal.](image)
4. CONCLUSIONS

H$_2$O$_2$ could be used to improve the effectiveness of activated sludge process. Adding H$_2$O$_2$ into the modified aerated biofilter was to improve treatment efficiency of refractory organic compound (humic acid) and was to reduce amount of sludge waste. The activated sludge used for preparing the ABF was developed well and stably in the range of H$_2$O$_2$ concentration 25–100 mg/L. There was many groups of microorganisms in the sludge after 128 days operation. Remarkably, the color of some microorganisms was changed into dark-brown color caused by HA. Existence of H$_2$O$_2$ did not clearly affect the COD removal but enhanced the color removal. At the concentration of 50 mg-H$_2$O$_2$/L and HRT 24 hours, the ABF reactor yielded highest treatment efficiency (95 % COD and 74 % color).

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