

마이크로버블 오존 고도산화를 이용한 축산폐수 혐기소화 배출수의 COD와 색도의 제거

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Removal of COD and Color from Anaerobic Digestion Effluent of Livestock Wastewater by Advanced Oxidation Using Microbubbled Ozone

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축산폐수 혐기소화 유출수 중의 생물학적 난분해성 유기물의 분해를 위하여 오존 기반의 고도산화 기술을 적용하였다. 배출수의 COD 및 색도는 각각 9200~9500 mg/L 및 0.384 (400 nm)이고 1/10 희석하여 실험에 사용하였다. 공급 오존은 버블의 크기가 13 μm 인 마이크로버블 오존과 105 μm 인 일반 오존버블과의 차이를 고찰하였다. 마이크로버블 오존을 사용함으로써 오존의 용해도와 라디칼 생성량이 증가되었고 일반 오존버블에 비하여 COD 및 색도의 제거효율이 각각 85% 및 26% 향상되었다. 마이크로버블을 포함한 O_3/UV , $\text{O}_3/\text{H}_2\text{O}_2$, $\text{O}_3/\text{UV}/\text{H}_2\text{O}_2$ 의 조합을 비교한 결과 오존 단독 처리에 비하여 색도 제거율이 5~10% 정도 증가되었으며, 오존에 비하여 UV나 H_2O_2 의 색도제거에 대한 기여가 크지 않음을 알 수 있었다. 반면 COD에 대해서는 $\text{O}_3/\text{UV}/\text{H}_2\text{O}_2$ 적용시 오존 단독에 비하여 2배 이상 제거율이 증가하였으며 UV보다는 H_2O_2 의 기여도가 더 컸다. 한편 마이크로 오존의 사용시 증가된 용존오존 및 라디칼 활성으로 인하여 오존 공급을 중단한 후에도 UV 또는 H_2O_2 를 적용함으로써 추가적인 COD 분해 효과를 지속적으로 유지할 수 있었다.

Ozone-based advanced oxidation was applied for the treatment of anaerobic digestion effluent of livestock wastewater. Initial COD and color value were 930 mg/L and 0.04, respectively, and the 1/10-diluted wastewater was used for the study. The treatment characteristics were compared between the conventionally generated ozone (105 μm) and microbubbled ozone (13 μm). The use of microbubbled ozone improved the removal of chemical oxygen demand (COD) and color by 85% and 26%, respectively, compared with the conventionally bubbled ozone. The application of microbubbled O_3/UV , $\text{O}_3/\text{H}_2\text{O}_2$, $\text{O}_3/\text{UV}/\text{H}_2\text{O}_2$ combinations resulted in 5~10% higher color removal than ozone alone, which implies that the contribution of UV or H_2O_2 is not significant in color removal. On the other hand, COD removal could be increased two folds compared with ozone alone through $\text{O}_3/\text{UV}/\text{H}_2\text{O}_2$ combination. The contribution of H_2O_2 was bigger than UV for COD removal with microbubbled ozone. Due to the enhancement of dissolved ozone and radical activity, the microbubbling enabled us to additional COD removal even after stopping ozone supply in the presence of UV or H_2O_2 .

Keywords: ozone, livestock wastewater, advanced oxidation, microbubble, COD, color

1. Introduction

The treatment of livestock wastewater is important due to its high-strength loads of organic compounds, although the amount is relatively small compared to municipal wastewater and other industrial wastewaters. Some organic constituents of livestock wastewater are very persistent, often remaining even after a series of biological treatments.

Chemical oxidation process using strong oxidation agents is a good

option for removing non-biodegradable organic compounds including antibiotics from biologically-treated effluent[1-3].

As a chemical oxidation agent, ozone (O_3) has a high oxidation potential (2.07 Volt) and selectively conducts oxidation reactions with a number of organic or inorganic compounds. Especially advanced oxidation processes (AOPs), in which couples other chemical or physical agents with ozone, can generate the hydroxyl radical ($\cdot\text{OH}$, oxidation potential = 2.8 V) that non-selectively reacts to a number of contaminants, making it a proficient candidate for the destruction of non-biodegradable, toxic and harmful contaminants[4,5].

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Table 1. Characteristic of the Anaerobic Digestion Effluent of Livestock Wastewater

Items	Range
pH	8.0~8.4
Alkalinity (mg/L)	8600~9190
COD _{cr} (mg/L)	9210~9540
TOC (mg/L)	3170~3400
NH ₃ -N (mg/L)	2440~3060
T-P (mg/L)	54.0~59.9
SS (mg/L)	1080~1140
Color (400 nm)	0.384

It is known that ozone effectively removes both color and odor from water and gas stream[6,7], and it produces less byproducts compared to chlorine-based oxidation[8,9]. However, ozone alone is somewhat ineffective for general COD removal because its degradation of carbon-carbon covalent bonds is not so high[10,11]. Therefore, application of ozone is often coupled with hydrogen peroxide (H₂O₂) or ultraviolet (UV) irradiation in order to utilize radical oxidation[1,12,13].

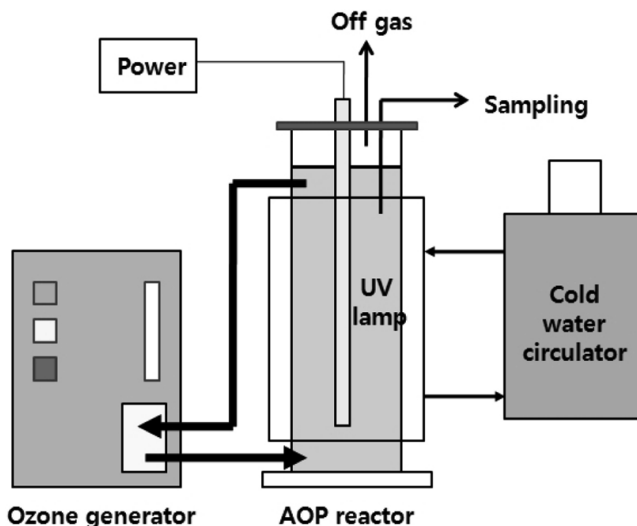
The performance of ozone-based AOP is inherently limited by the low solubility of ozone (0.21~0.24 v/v at 20 °C) and fast escaping of gaseous ozone out of the water, which subsequently results in low rate of gas-liquid mass transfer of ozone between ozone bubbles and water body. Therefore, it is important to increase contact time in ozone-based AOPs to achieve a high performance of wastewater treatment. The extension of residence time of ozone in reactor can be accomplished by two ways. One is to increase ozone-water contact frequency in the aspect of reactor design; such as using long-tubular reactors or multi-compartment contactors. Another approach is to reduce ozone bubble size. Smaller ozone bubbles last longer in water before floating to the surface because the rising velocity is a function of bubble diameter especially in independent floating (or settling) environment. Also the use of smaller size of gas bubble increases the specific surface area of bubbles which in turn improves mass transfer rate and the dissolved concentration of the gaseous components.

In this study, the use of ozone bubble of smaller size was applied to the oxidative removal of COD and color in a livestock wastewater, and the comparison with conventional ozonation was discussed. Here we utilized so-called microbubbled ozone, in which 'micro' represents the size within a few tens of micrometers, while conventional ozone bubbles are in the range from a few hundreds of micrometers to a few millimeters. The removal of COD and color was carried out by different combinations of ozone, UV and H₂O₂ to choose an effective ozone-based AOP combination.

2. Materials and Methods

2.1. Wastewater

A sample of livestock wastewater was collected from anaerobic digestion effluent in a local piggery farm in Ansung, Korea, followed by storage at 4 °C to minimize substrate decomposition. The character-

**Figure 1. Experimental set-up of microbubble ozone-based AOP system.**

istics of the wastewater are summarized in Table 1. Large-sized solids were excluded for experiments by a gravity settling. The obtained supernatant was used in the oxidation experiments after 1/10 dilution.

2.2. Ozone Generation

The ozone generator (Model HIO-600) provided from HaeSung Engineering, Inc. (Suwon, Korea) was used in the study to produce micro-sized ozone bubbles. Micro-sized ozone bubbles are generated through a specialized liquid-gas micro-mixing pump and introduced to circulating water through an in-line ventury nozzle. The conventional size of ozone was produced using the same ozone generator by adjusting pumping power and nozzling condition. The experimental setup of the microbubbled AOP system which was used in this study is shown in Figure 1.

2.3. Advanced Oxidation

A closed, cylindrical acrylic reactor with a total volume of 1.2 L (height, 43 cm; diameter, 6 cm) was used as an oxidation reactor (Figure 1). A water jacket was equipped outside of the reactor in order to keep the reactor temperature constant at 20 °C. One 15 W mercury low-pressure ultraviolet lamp (LPUV) was placed vertically in the center of the reactor. H₂O₂ dose was 100 mg/L when it is needed. The reactor was filled with 1-L working volume of livestock wastewater which was circulated through the ozone generator at a uniform speed of 2.5 vvm. Oxidation was carried out with ozone alone and with three combinations of oxidation agents; O₃/H₂O₂, O₃/UV, and O₃/H₂O₂/UV.

2.4. Analyses

The size of generated ozone bubble was analyzed through image-capturing by the Micro-Vision Inspection System (Model ICS-305, SomeTech Vision, Inc., Korea).

The chemical oxygen demand (COD) was analyzed using premixed digestion solution containing K₂Cr₂O₇ as an oxidation agent along with other premade reagents (HACH COD Digestion Kit 21259-15). Analyses

Table 2. Comparison between Microbubbling and Conventional Bubbling of Ozone

Items	Ozone supply	
	Microbubbling	Conventional bubbling
Ozone generation rate	8.0 g/h ± 0.1	
Ozone flow rate	2.5 L/min ± 0.04	
Ozone bubble size	13 μm ± 2.5	105 μm ± 34
Dissolved ozone (ppm)	4.2 ± 0.2	2.0 ± 0.3
Ozone floating velocity	< 1.6 mm/sec	> 5 mm/sec

were conducted by the manufacturer’s instructions with HACH DR4000 spectrophotometer. The quality of the wastewater sample was analyzed according to the Standard Methods[14]. For color value, optical density at 400 nm was measured using a UV-Vis spectrophotometer by following the platinum-cobalt standard method. The Indigo method was used in order to monitor dissolved ozone concentration[15].

To quantify radical activity which was produced during AOP, a dyeing substance ABTS (2,2'-azion-bis-(3-ethylbenzotriazoline-6-sulfonic acid)) was used. When attacked by radicals including hydroxyl radical, ABTS transforms and the oxidized form displays absorbance change [16].

3. Results and Discussion

3.1. Characteristics of Microbubbled Ozonation

Table 2 shows the comparison between microbubbled ozone and conventional ozone bubble produced by pressurized sparging in distilled water. Ozone bubble size generated by conventional pressurized sparging was in the range of 70~140 μm and its floating velocity is greater than 5 mm/sec according to Stokes Equation for independent settling[17],

$$v_s = \frac{g}{18\mu}(\rho_s - \rho_f)d^2 = \frac{g\rho_f}{18\mu}(S-1)d^2 \quad (1)$$

where v_s is the settling (or floating) velocity of bubble, g is the gravitational acceleration, ρ_s is the density of bubble, μ and ρ_f are the viscosity and density of fluid, and d and S are the diameter and specific gravity of the bubble, respectively. It means that it takes approximately 3 min for 100 μm ozone bubble to escape 1 m depth of water.

The microbubble ozone generator produced ozone bubbles of reduced size to 13 μm. The floating velocity of 13 μm of ozone bubble is estimated as less than 1.6 mm/s according to Eqn. 1, and it takes more than 10 min to escape from 1 m depth of water. Thus, it can be said that the 13 μm ozone bubbles can have more than tripled gas-liquid contact time and the duration of oxidation, compared to the conventional-sized ozone bubbles.

Figure 2 shows the changes of dissolved ozone concentration when ozone was supplied by conventional ozone generator and microbubbled ozone generator to the reactor containing distilled water. In order to compare the saturated level of dissolved ozone and its residual behav-

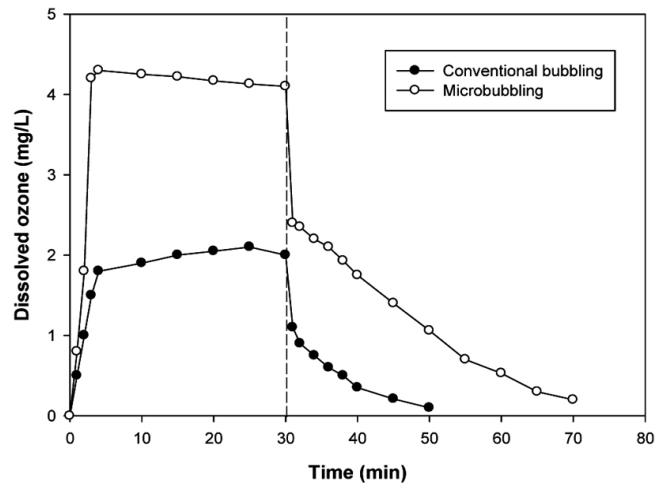


Figure 2. Comparison of dissolved ozone concentrations between conventional bubbling and microbubbling. Ozone supply was stopped after 30 min of saturation (dashed line).

ior, ozone was supplied for initial 30 min until saturation and then the supply was stopped. The level of dissolved ozone became saturated within 3 min after continuous bubbling and was not changed significantly if the temperature was maintained constant. By supplying ozone continuously, the dissolved ozone level was kept around 2 ppm by conventional generator and 4.2 ppm by microbubble generator. These results indicate that the enhanced duration of retention and increased specific interfacial area of microbubbles can increase dissolved ozone concentration.

Upon turning off the conventional ozone generator at 30 min, the level of dissolved ozone was gradually evaporated out of the water and became almost zero after 25 min. Meanwhile, in the case of microbubble ozone supply, dissolved ozone concentration was remained above 2 mg/L for another 20 min after turning off and lasted up to 40 min. This is because floating velocity of microbubble ozone decreased due to the smaller bubble size, and so it is expected that the ozone-water contact time and consequent oxidation performance will be enhanced by utilizing ozone bubbling of reduced size.

3.2. Change of Radical Activity

To demonstrate the possible enhancement of oxidation performance with microbubbling, the radical activities in distilled water were compared in Figure 3 where the scale of activity is the relative extent of oxidation for ABTS by radicals. It is seen that the oxidation power by radical is lowest and dropped rapidly after turning off ozone supply when the conventional bubbling was used. With microbubbling, the disappearance of radical activity was much gradual and thus maintained for a long time at a level higher than the conventional bubbling. The overall radical oxidation power by microbubble ozone was more than two-folds higher than the conventional one. This result was similar to that of the saturated dissolved ozone concentration as shown in Figure 2, but the duration of residual period for oxidation activity is much longer than that of dissolved ozone. This implies that the produced radicals can remain longer in water and able to perform oxida-

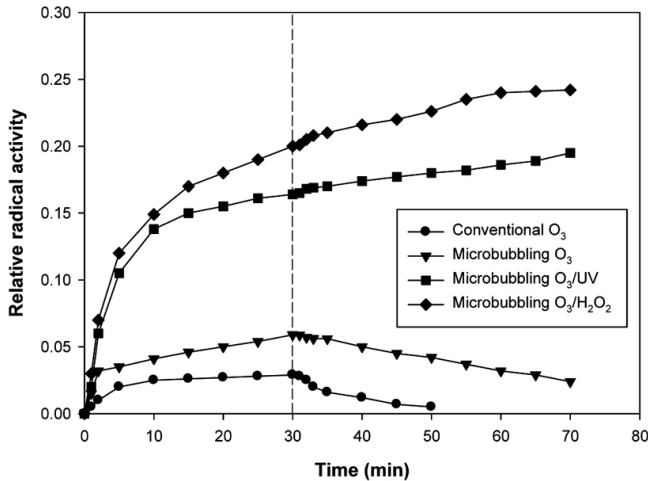


Figure 3. Comparison of radical oxidation activities between conventional bubbling and microbubbling of ozone. Dashed line represents the time of ozone-off.

tion even though dissolved ozone disappears from the water.

Figure 3 also compares the relative radical activities (or oxidation power) produced by O_3 alone, O_3/UV and O_3/H_2O_2 when ozone was supplied through the microbubble generator. The oxidizing power by O_3/H_2O_2 increased rapidly, and more than four times and ten times higher radical activity were obtained after 10 min than by O_3 alone. It is noted that the radical activity in O_3/H_2O_2 treatment was increasing further even after ozone supply was stopped. O_3/UV showed a similar tendency as O_3/H_2O_2 , but the overall radical activity was about 80% of O_3/H_2O_2 . This result implies that the free radicals (probably hydroxyl radical) are being produced further from the interaction between H_2O_2 or UV and residual ozone although there was no more ozone supply to the reactor.

This observation suggested that, during the combined application of O_3 and other oxidation agents such as H_2O_2 or UV, a continuous supply of ozone may not be always necessary to achieve a desired treatment goal. There could be a possibility of managing two-step application where micro-sized ozone is supplied until saturation first, disconnect the ozone supply, and then oxidation is continued in the presence of H_2O_2 or UV.

3.3. Removal of COD and Color in Livestock Wastewater

Figure 4 compares the removal of COD and color of livestock wastewater by ozone alone produced from the conventional and microbubble generators. COD removal by microbubbled ozone was only 24% for 80 min, indicating that the COD organics in livestock wastewater is persistent to by ozone alone. The color removal was above 90% after 35 min of treatment, indicating that color removal by ozone is efficient compared to the COD removal. By conventional bubbling, COD and color removal were only 53% and 82% of those by microbubbling, respectively.

It has been known that ozone alone is less effective for general COD removal because ozone does not easily react with carbon-carbon covalent bonds[10,11]. Therefore, application of ozone is often coupled

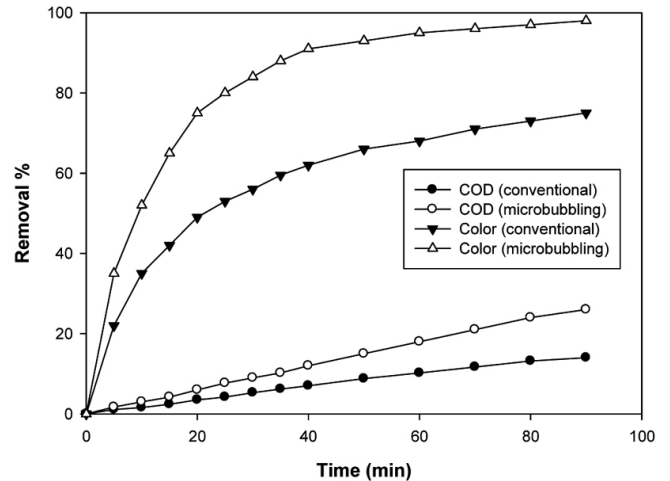


Figure 4. Removal of COD and color of anaerobic digestion effluent by ozone alone through conventional bubbling and microbubbling. Initial COD and color value were 930 mg/L and 0.04, respectively.

with hydrogen peroxide (H_2O_2) or ultraviolet (UV) irradiation in order to utilize radical oxidation, which ultimately results in increased removal of non-biodegradable COD and color[1,12,13].

Figure 5 shows the results obtained by the applications of O_3 , O_3/UV , O_3/H_2O_2 , and $O_3/UV/H_2O_2$, using microbubbled ozone. For 80 min or treatment, ozone removed 22% of COD, O_3/UV 33%, O_3/H_2O_2 39%, and $O_3/UV/H_2O_2$ 56%, respectively. The combination of O_3/H_2O_2 a little better than O_3/UV for COD removal in the present experimental condition. Although the application of $O_3/UV/H_2O_2$ was best, overall COD removal was not satisfactory. It is noted that the COD values have been corrected to avoid the overestimation problem in COD measurement by H_2O_2 [18,19].

On the contrary, over 90% of color was removed in 90 min in all the types of the AOP combination as well as in ozone alone. From the fact that the color removal performance by ozone-based AOP combinations (O_3/UV , O_3/H_2O_2 , $O_3/UV/H_2O_2$) was similar to that of ozone alone, it was regarded that UV or H_2O_2 did not make significant contributions to the color removal from the livestock wastewater and thus ozone alone is sufficient if the purpose of AOP is to remove color only[20].

3.4. Removal of COD and Color by Two-Step Application

In order for taking advantages of extended duration of radical activity in microbubble ozone system (as shown in Figure 3), the two-step application of oxidation agents was investigated by separating ozonation step and UV and/or H_2O_2 step. Figure 6 shows the results of the two-step application of the ozone-based AOP. In the first step, the ozone was supplied by circulating the wastewater through the microbubble ozone generator for 80 min. Then ozone supply was turned off and, in the second step, UV irradiation and/or H_2O_2 was applied for additional 100 min.

The COD removal rates for the first 80 min in Figure 6 are same as those in Figure 5. In the second stage (after 80 min), the COD removal by O_3/UV and $O_3/UV/H_2O_2$ is continuing even after disconnect-

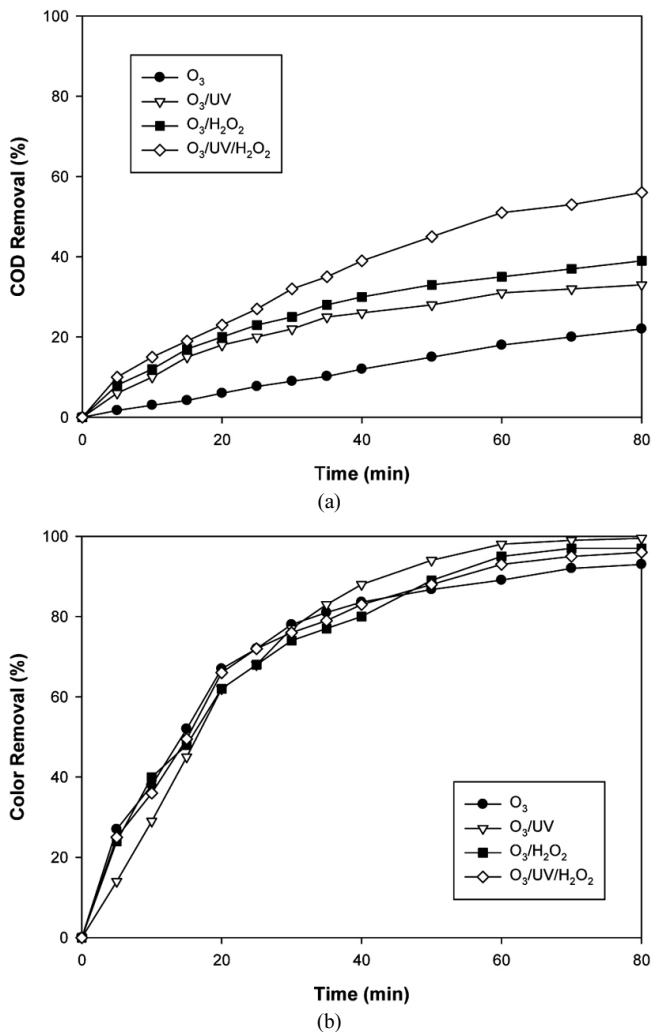


Figure 5. Removal of (a) COD and (b) color by application of different combinations of AOPs with microbubbled ozone.

ing the ozone supply, while further COD removal was insignificant in the cases of O_3 and O_3/H_2O_2 . The total COD removal at 180 min (after 120 min of ozone off) reached near to 52% and 91% by O_3/UV and $O_3/UV/H_2O_2$, respectively. As discussed earlier with Figure 3, the increase of COD removal in the absence of ozone supply after 80 min is through the oxidation by radicals which were produced during ozonation.

The two-step application of ozone-based AOP could be beneficial in saving the power cost to maintain the continuous supply of ozone throughout the whole treatment period, by turning off the ozone generation and utilizing the residual radicals for extended oxidation. For the treatment of livestock wastewater used in this study, the two-step application of $O_3/UV/H_2O_2$ AOP was successful to remove more than 90% of COD by allowing additional oxidation for more than 100 min after microbubbled ozonation for initial 80 min.

4. Conclusions

The use of ozone bubbles of reduced size, which were produced

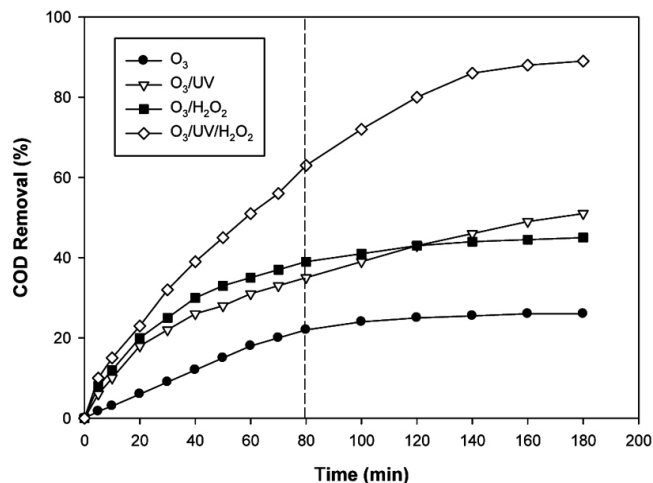


Figure 6. COD removal from anaerobic digestion effluent by two-step application of microbubbled ozone-based AOP.

from a microbubble generator, was beneficial to extend the residence time of dissolved ozone in the reactor and to prolong the ozone-water contact time. Also the residual oxidation power (or radical activity) was able to maintain even though the ozone supply was stopped. These features of microbubbling enabled us to investigate the feasibility of two-step applications of AOP agents, where ozone was saturated first and then UV or H_2O_2 was introduced after disconnecting ozone supply. In two-step application, the secondary use of UV/ H_2O_2 increased the amount of residual radicals and served for further oxidation. Up to 99% of COD could be removed by applying O_3 and H_2O_2 for 100 min after saturating the wastewater with O_3 by microbubbling for initial 80 min.

Acknowledgements

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