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Removal of recalcitrant organic substances in livestock wastewater using ozonation and an electrochemical process

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ABSTRACT

This study examined the effectiveness of an ozone (O_3) system from an existing livestock wastewater treatment plant installed with a dissolved O_3 flotation unit and suggested a method for future improvement in terms of an effective removal of recalcitrant organic substances. An optimum O_3 dose was proposed by selecting an O_3 dose yielding a maximum value of biochemical oxygen demand/chemical oxygen demand (BOD_5/COD_{Mn}). The peroxone (O_3/H_2O_2) process was found to be no different of efficiency from the O_3 alone process due to the high alkaline content of the wastewater in which all hydroxyl radicals ($OH^•$) are scavenged. In this study, an electrochemical process was found to be promising in decreasing the recalcitrant organic substances and the removal efficiency of them was not affected by the timing of ozonation, i.e., as a final step.

Keywords: Livestock wastewater; Biodegradability; BOD_5/COD_{Mn}; Ozone; Electrochemical process

1. Introduction

A high concentration of recalcitrant substances in livestock wastewater (LWW) has been considered troublesome because of their strong resistance to the common oxidation process. One of the reasons that it is difficult to address refractory issues of LWW is the lack of information on wastewater characteristics and reports on successful treatment of LWW using an effective oxidative method in connection with other conventional processes, including biological processes [1–3].

A promising candidate for LWW treatment is the combination of ozonation or advanced oxidation processes (AOPs) and biological processes because oxidation in wastewater containing high nondegradable contaminants could convert these contaminants into biologically assimilable organic compounds [4,5]. Ozone (O_3) plays the role of disinfectant and oxidant in wastewater treatment. The O_3 has been known to have considerable effect on the removal of recalcitrant organic substances, taste and odor substances in water due to relatively high oxidizing power (potential difference = 2.07 V) [6]. However, it is known that the organic substances with double bond or negative charge are oxidized earlier by O_3 and the ozonation of compounds that do not have a strong nucleophilic structure (e.g., chlorinated solvents and pesticides) is very difficult [7]. Therefore, in order to generate greater oxidation power, AOP should be applied which uses the oxidation power of hydroxyl radicals ($OH^•$; potential difference = 2.80 V) generated when O_3 is decomposed [8].

AOPs based on O_3 include O_3/high pH, O_3/UV (ultraviolet radiation), O_3/AC (activated carbon), and peroxone (the combination of O_3 and hydrogen peroxide (H_2O_2), O_3/H_2O_2) [9]. Among them, the O_3/H_2O_2 process

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is one of the AOPs in the spotlight because H_2O_2 is cheap and can be easily applied to the existing O_3 processes [10]. Furthermore, AOPs using electrolysis are also being actively researched these days. Electrolysis is regarded as a clean technology that can remove contaminants without adding any chemical oxidants unlike other AOPs because it dissolves contaminants through direct oxidation by electrodes and indirect oxidation by oxidants generated through electrode reaction [11].

Here, we aimed at selecting an optimum O_3 dose considering biodegradability index for a full-scale plant in South Korea which has treated LWW and evaluating the chemical oxygen demand (COD_{Mn}) removal performance of an O_3 contactor in operation. The main processes of this plant were bio-ceramic sequencing batch reactor (BCS) with improved microbial carrier, dissolved O_3 floatation (DOF) containing a flocculation/floatation basin followed by an ozonation basin (ozone is injected through two gas dissolve tanks (GDT)), and biological filter (BF) for up-flow anaerobic and aerobic layers (Fig.1). As AOPs to further reduce the COD_{Mn} content in the final effluent, lab-scale and full-scale experiments were conducted to determine the applicability of the O_3/H_2O_2 and electrochemical oxidation process (Table 1). Again after the determination of applicability, the process connecting ozonation and electrochemical oxidation was simulated to observe the change in the removal efficiency of COD_{Mn}. Moreover, the removal mechanism of organic matters in the two oxidation processes was examined through fluorescence analysis.

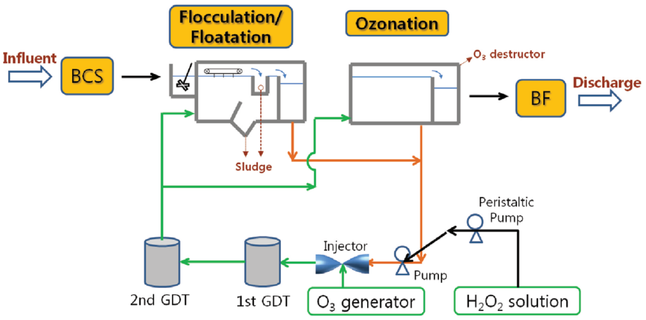

Fig. 1. Schematic diagram of the full-scale LWW treatment plant (BCS: Bio-ceramic sequencing batch reactor; GDT: Gas dissolve tank; BF: Biological filter).

Table 1
Experiment scale of the performed processes.

Performed AOPs	Experiment scale	Section	Figure
Ozonation	Lab-scale	3.2.1	Fig. 3
Ozonation	Full-scale	3.2.2	Fig. 4
Ozonation	Lab-scale	3.2.3	Fig. 5
Peroxone	Full-scale	3.3.1	Fig. 6
Electrolysis	Lab-scale	3.3.2	Fig. 7
Ozonation and electrolysis	Lab-scale and Full-scale	3.4	Fig. 9

2. Material and methods

For the O_3 and O_3/H_2O_2 experiments in the lab-scale, samples were taken from the process units of the LWW treatment plant and were shipped to the laboratory. The samples were collected in 20 L water bottle without headspace and light, and refrigerated upon receipt and stored at 4°C darkroom. The lab-scale O_3 alone and O_3/H_2O_2 processes were carried out in a semi batch reactor (Pyrex, 1 L) equipped with a semi continuous H_2O_2 injecting system that has a peristaltic pump (Fig. 2a). O_3 gas was generated from the corona discharger of an O_3 generator (LAB2B, Ozonia) and bubbled into the 1 L Pyrex reactor through a stainless steel diffuser. O_3 concentration was determined at 10 mg/L·min by titrating 2% KI solution with 0.1 N $Na_2S_2O_3$ according to the Standard Methods [12]. For the O_3/H_2O_2 experiment, diluted H_2O_2 of reagent grade (35 wt.% in H_2O, Sigma-Aldrich, USA) was continuously injected through a tip of tubing into the reactor along with continuous O_3 bubbling.

The electrochemical process was performed in a 1 L Pyrex batch reactor equipped with Pt/Ti grid-shaped undivided cells (30 mm × 30 mm, electrode specific working area = 500 mm^2) provided by Samsung DSA Co. (Korea). The anode and cathode were both made of the same material and were placed horizontally in parallel in the reactor with a gap of 2 mm. The electrical energy was applied in the range of 0–38 Wh (current: 5.0 A, voltage: 7.2–7.6 V) by a DC power supply (ODA Technology, Korea). The water temperature was maintained at 25 ± 1°C by circulating cooling water in a water jacket during the electrochemical process (Fig. 2b).

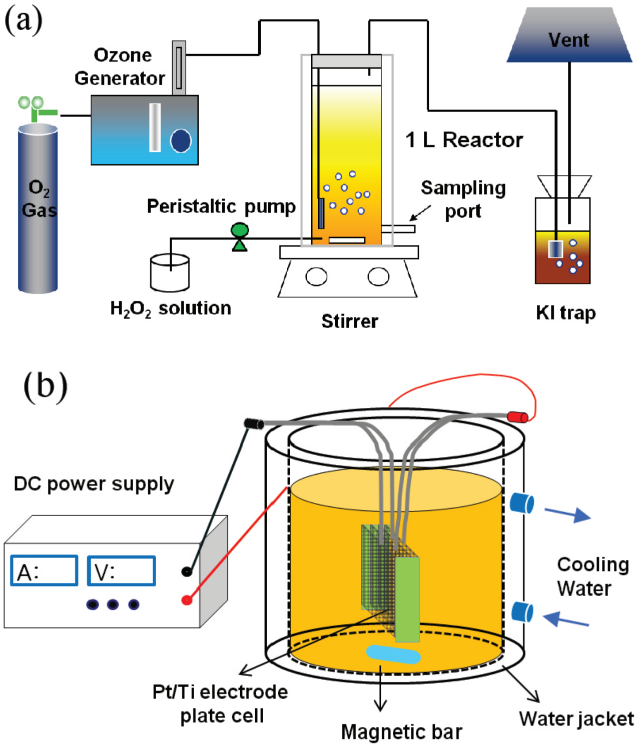

Fig. 2. Scheme of the apparatus for lab-scale (a) O_3 and O_3/H_2O_2 process and (b) electrochemical process.

The COD_{Mn} was determined using commercially available test kits (Hach Company, Hach method 8000 with DR-4000 spectrophotometer) and the biochemical oxygen demand (BOD_5) was examined using a procedure that was based on the standard method [12]. The color of the treated wastewater after each run was measured as Pt-Co color units by a HACH DR-2500 spectrophotometer at a wavelength of 456 nm. Several other parameters including dissolved organic carbon (DOC) content (TOC analyzer; Shimadzu, Japan), UV_{254} (UV absorbance at 254 nm), and pH (pH meter; Thermo Scientific, USA) were measured using Standard Methods [12]. It is generally accepted that the absorbance of natural waters at UV wavelengths around 250 nm is caused primarily by aromatic structures [13]. The specific UV absorbance (SUVA) is the ratio of UV light absorbance of wavelength, (usually 254 nm) to the concentration of DOC in the water, so that this parameter is generally used for analytical method of aromatic compounds.

3. Results and discussion

3.1. Evaluation of the full-scale plant

The livestock wastewater treatment plant (LWWTP) (Boeun, Republic of Korea) has treated 80 m^3/d of LWW containing more than 90% swine wastewater. The flow order of treatment process is as follows: raw LWW, pre-treatment (screen, press, and cyclone), sequencing batch reactor embedded bioceramics (BCS), DOF, BF, active carbon filtration, and discharge. Table 2 shows the results of long-term monitoring data from the five sampling points (raw LWW, BCS effluent, DOF effluent, BF effluent, and discharge) in the LWWTP. There were no seasonal changes in the water quality factors during the monitoring period, and BOD_5 and COD_{Mn} in the source LWW were 39,000 mg/L and 20,000 mg/L at the maximum. The pre-treatment process (solid-liquid separation and screening) before BCS removed 44% or more of the concentration of each water quality factor. After BCS, COD_{Mn} was maintained at high concentration compared to other water quality factors. DOF removed 80% or more of COD_{Mn}, SS, and TP. The remaining TN and TP after this were removed 40% or more by BF. Among the effluent water quality standards defined by the Ministry of Environment, the other water quality factors except for COD_{Mn} satisfied the effluent standard. However, COD_{Mn} in the final effluent sometimes exceeded the effluent standard (50 mg/L) due to high variations in the concentration of recalcitrant organic matters. Thus, the DOF process introduced to remove refractory CODs is not doing its part and requires improvement.

3.2. Selection of optimum O_3 dose

3.2.1. COD removal by O_3 dose

To determine the optimum O_3 dose for the DOF process of the full-scale plant, the correlation between the initial COD_{Mn} (COD_0) concentration of pre-treated wastewater (influent into the ozonation basin of DOF system) and the O_3 dose was identified through a lab-scale experiment and the biodegradability of the wastewater by O_3 was measured. Fig. 3 shows the COD_{Mn} removal trend after O_3 injection in excessive quantities by regarding the wastewater prepared in different concentrations of COD_{Mn} as the effluent of the floatation basin of DOF system. Large differences were found in the O_3 dose required to treat the wastewater to the same concentration of COD_{Mn} from different COD_0. The target concentration of effluent from the O_3 contractor considering the performance of BF (after DOF system) was 80 mg/L. To determine the O_3 dose to satisfy this condition, approximately 750 mg/L of O_3 was required for 244 mg/L of COD_0, approximately 490 mg/L for 154 mg/L of COD_0, and approximately 180 mg/L for 99 mg/L of COD_0. This result suggested that the greater the variation breadth of

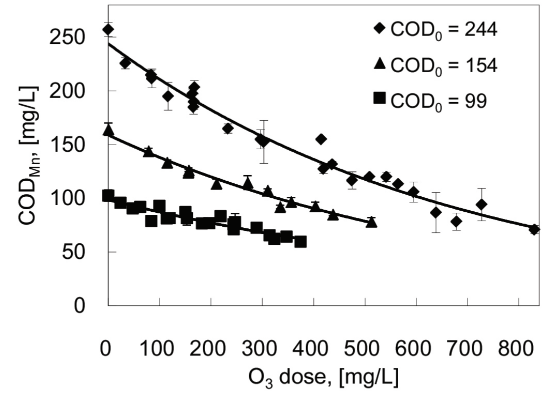

Fig. 3. COD_{Mn} reduction by ozonation (O_3 injection rate = 10 mg/L·min, pH 6.2–7.7, temperature = 25 ± 1°C, initial concentration of COD_{Mn} (COD_0) = 244, 154, and 99 mg/L).

Table 2
Average value of major water quality parameters during the monitoring period (units: mg/L except coliforms for CFU (colony forming unit)/mL)

Parameters	Raw LWW	BCS eff.	DOF eff.	BF eff.	Discharge
COD_{Mn}	17,000 ± 3,000	800 ± 170	139 ± 20	83 ± 22	49 ± 21
SS	29,000 ± 7,000	660 ± 120	48 ± 6.0	3 ± 0.7	2 ± 0.4
TN	5,000 ± 1,000	90 ± 29	31 ± 2.0	15 ± 2.0	14 ± 2.0
TP	600 ± 120	33 ± 4.0	2 ± 0.5	1.3 ± 0.3	1 ± 0.2
BOD_5	31,000 ± 8,000	–	–	–	2 ± 0.7
Coliforms	50,000 ± 12 ,000	–	–	–	≤ 30

the COD_{Mn} concentration of the floatation basin effluent was, the more difficult it was to reduce COD_{Mn} using the O_3 only process. From the slope decline of COD_{Mn} removal rate in Fig. 3, more O_3 should be required to reduce the same concentration of COD_{Mn} when the COD_0 concentration of the wastewater was lower; it was an inefficient design to locate the O_3 only process at the rear end in terms of COD_{Mn} reduction in the case of LWW.

3.2.2. Selection of the optimum O_3 dose considering BOD_5/COD_{Mn}

The optimum O_3 dose, for the complex process of a serial type that connects the O_3 process as a pre-treatment of the biological digestion process (BF), means the concentration at the maximum biodegradability of the target wastewater. Factors representing biodegradability include BOD_5/COD_{Cr}, BOD_5/DOC (dissolved organic carbon), and BDOC (Biodegradable DOC)/DOC in addition to BOD_5/COD_{Mn} [14], but BOD_5/COD_{Mn}, the most common parameter, was set as the index for evaluating biodegradability as it corresponds with the purpose of this study. Thus, BOD_5/COD_{Mn} was calculated from COD_{Mn} and BOD_5, and the optimum O_3 dose considering this value was selected and the correlation between the COD_0 and the optimum O_3 dose was analyzed.

The effective O_3 dose in the DOF system was optimized by measuring the change of BOD_5/COD_{Mn} for the effluent of floatation basin in the full-scale plant. The optimum O_3 dose was the O_3 dose corresponding to the maximum value of BOD_5/COD_{Mn} (Fig. 4(a)). Maximum values of BOD_5/COD_{Mn} and corresponding optimum O_3 doses were estimated from three data sets as follows; 0.35 and 420 mg/L for 244 mg/L of COD_0, 0.35–0.4 and 360 mg/L for 154 mg/L of COD_0, and 0.15–0.17 and 120 tmg/L for 99 mg/L of COD_0, respectively. By the relation between optimum O_3 dose and COD_0 for ozoantion, the higher O_3 dose are needed as COD_0 are increased (Fig. 4(b)). This logarithmic trend shows that excessive dose of O_3 would be inefficient in terms of biodegradability, and ozonation for relatively lower COD_0 would be meaningless to the following biological treatment step.

The principle by which O_3 oxidizes organic matters into biodegradable substances is typically known as series-parallel reaction [15]. The overall series-parallel reaction combines a few series reactions with O_3 as the reactant and the parallel reaction that is established in the inclusion or equivalent relations between the organic substances of the reactant and the product. To express organic substances as COD and BOD terms, the conceptual reaction formula of (1), (2), and (3) can be established:

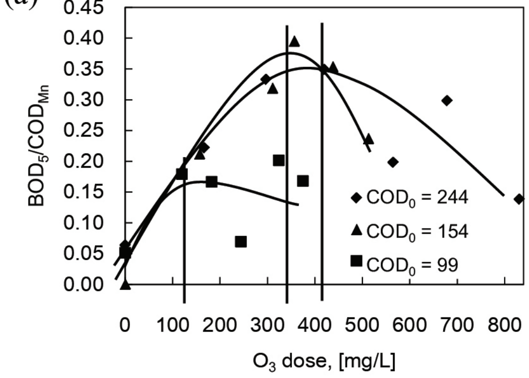

Fig. 4a. Optimization of O_3 dose considering the value of BOD_5/COD_{Mn}. (a) Variation of BOD_5/COD_{Mn} by ozonation.

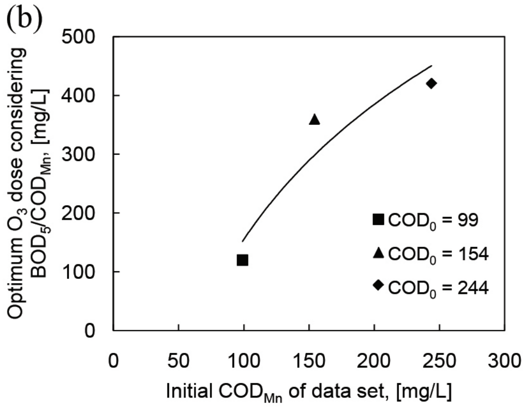

Fig. 4b. Optimization of O_3 dose considering the value of BOD_5/COD_{Mn} (b) plot of COD_0 vs. optimum O_3 dose.

$$COD_{total} + O_3 \rightarrow \text{Products} \quad (1)$$

$$COD_{NBD} + O_3 \rightarrow \text{Products} + BOD_{formed} \quad (2)$$

$$BOD_{formed} + O_3 \rightarrow \text{Products} \quad (3)$$

The above expressions assume that there is no initial BOD in the system. The COD_{total} is a COD measurement that contains COD_{NBD} and BOD_{formed}. The COD_{NBD} is a non-biodegradable COD. The BOD_{formed} is an oxidation product of COD_{NBD} by O_3. The products refer to the intermediate oxidation products of organic substance that can be measured with COD or BOD or to the CO_2 generated by the complete oxidation of organic substances. Actually, the mechanism by which conversions between organic substances by oxidation will be complex and it is difficult to establish stoichiometric relations between the items unless COD, BOD, and products are analyzed by common methods. Expression (1) shows the path of the complete oxidation of COD_{total} by reaction with O_3 or the path of conversion to BOD. In expression (2), COD_{NBD} is completely oxidized by O_3 or converted to BOD. The BOD_{formed} is oxidized by O_3 because it is also an organic substance like COD (expression (3)). As expressions (2) and (3) suggest, it is impossible for all CODs to convert to BODs because O_3 reacts with COD and BOD with no differentiation. Therefore, the concentration of BOD increases along with the O_3 dose, and starts to decrease after the peak concentration of O_3.

3.2.3. Changes in DOC, UV_{254}, $SUVA_{254}$, and color by O_3 dose

Change in the DOC, UV_{254}, $SUVA_{254}$, and color of the samples used for measurement of COD_{Mn} in the previous experiment are shown in Fig. 5. Even though DOC decreased

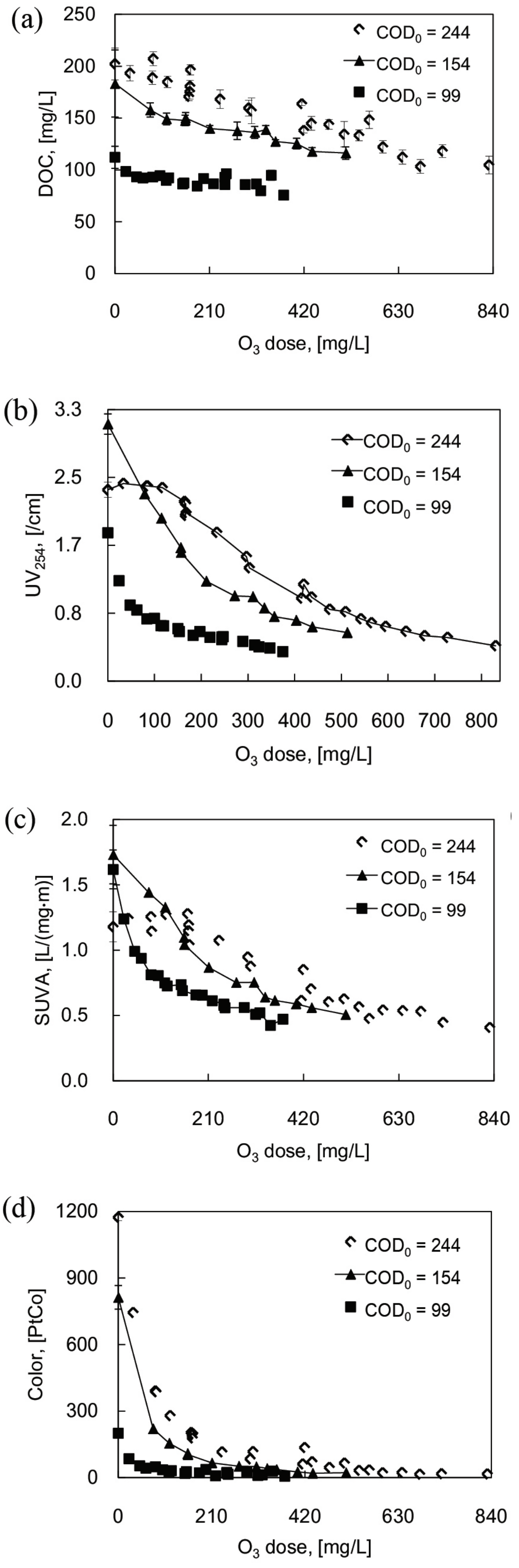

Fig. 5. Abatement of (a) DOC, (b) UV_{254}, (c) $SUVA_{254}$, and (d) color by ozonation (O_3 injection rate = 10 mg/L·min, pH 6.2–7.7, temperature = 25 ± 1°C).

as the O_3 dose increased, high concentration of O_3 seems to be required until complete oxidation like the case of COD_{Mn}. The correlation coefficient was not so high enough to determine the exponential or linear reduction trends of DOC, but the removal rate of DOC was slower than COD_{Mn} which suggests that some of the dissolved organic substances have slow reactivity with O_3. The initial UV_{254} of the formulated wastewater was not proportionate to the COD_0 and DOC. The UV_{254} of each data set decreased up to 70% by the increase of O_3 dose. Considering the fact that O_3 reacts well with humic substances, the reduction of UV_{254} after 150 mg/L or higher O_3 dose in case of 244 mg/L of COD_0 appears to be due to the interference effect of non-aromatic substances that absorb UV_{254}. As $SUVA_{254}$ is dependent on the UV_{254} formation, the $SUVA_{254}$ value of the 244 mg/L COD_0 increased until the O_3 dose of 180 mg/L and then decreased. The $SUVA_{254}$ of other two data sets were removed by 70% or more by the increase of O_3 dose. Color quickly reacted to O_3 compared to other measurement factors. The colors of three data sets were removed 80% or more at the O_3 dose of 210 mg/L and up to 90% could be removed by the increase of O_3 dose. This experiment confirmed that O_3 reacts well with the chromophores of organic substances [16].

3.3. Application of advanced oxidation process

3.3.1. Removal of COD_{Mn} by O_3/H_2O_2

Fig. 6 shows COD_{Mn} removal by O_3 alone and removal by the O_3/H_2O_2 process. With an increase in the O_3 dose, COD_{Mn} decreased, but the removal rates were slow in both the O_3 and O_3/H_2O_2 processes; enhancement of COD_{Mn} removal was not observed by adding H_2O_2. The UV_{254} removal rate was fast, but no enhancement was observed in the O_3/H_2O_2 process. The negative enhancement of COD_{Mn} removal by the O_3/H_2O_2 process was due to the high concentration of bicarbonate and carbonate ions (alkalinity = 1500 mg/L as $CaCO_3$), which scavenged all $OH^\bullet$.

3.3.2. Removal of COD_{Mn} by electrochemical oxidation

The electrochemical oxidation process was applied with the LWW as the electrolyte and the COD_{Mn} removal by the increase of electrical energy was measured (Fig. 7a). The experiment results showed reduction of COD_{Mn} in the three data sets by the supply of electrical energy. The COD_{Mn} removal and removal rate of the data sets were compared between one another when the electrical energy supply was increased to 38 Wh. The case of 310 mg/L COD_0 showed the removal of about 100 mg/L of COD_{Mn} and the removal rate of 32%. 71 and 40 mg/L of COD_{Mn} were removed with 45% and 55% removal rate in case of 158 and 88 mg/L of COD_0, respectively. The measurement results showed a reversal of the COD_{Mn} removal and removal rate (%) according to electrical energy supply. In the design where constant current is supplied to electrolyte, the voltage decreases when electric conductivity is high. However, because the higher the initial concentration is, the higher the electric conductivity becomes, the electrical energy required to supply the same current decreased. In this experiment, however, the difference in the electric conductivity according to COD_0 was a decrease of only 0.2–0.3 mS/cm when the

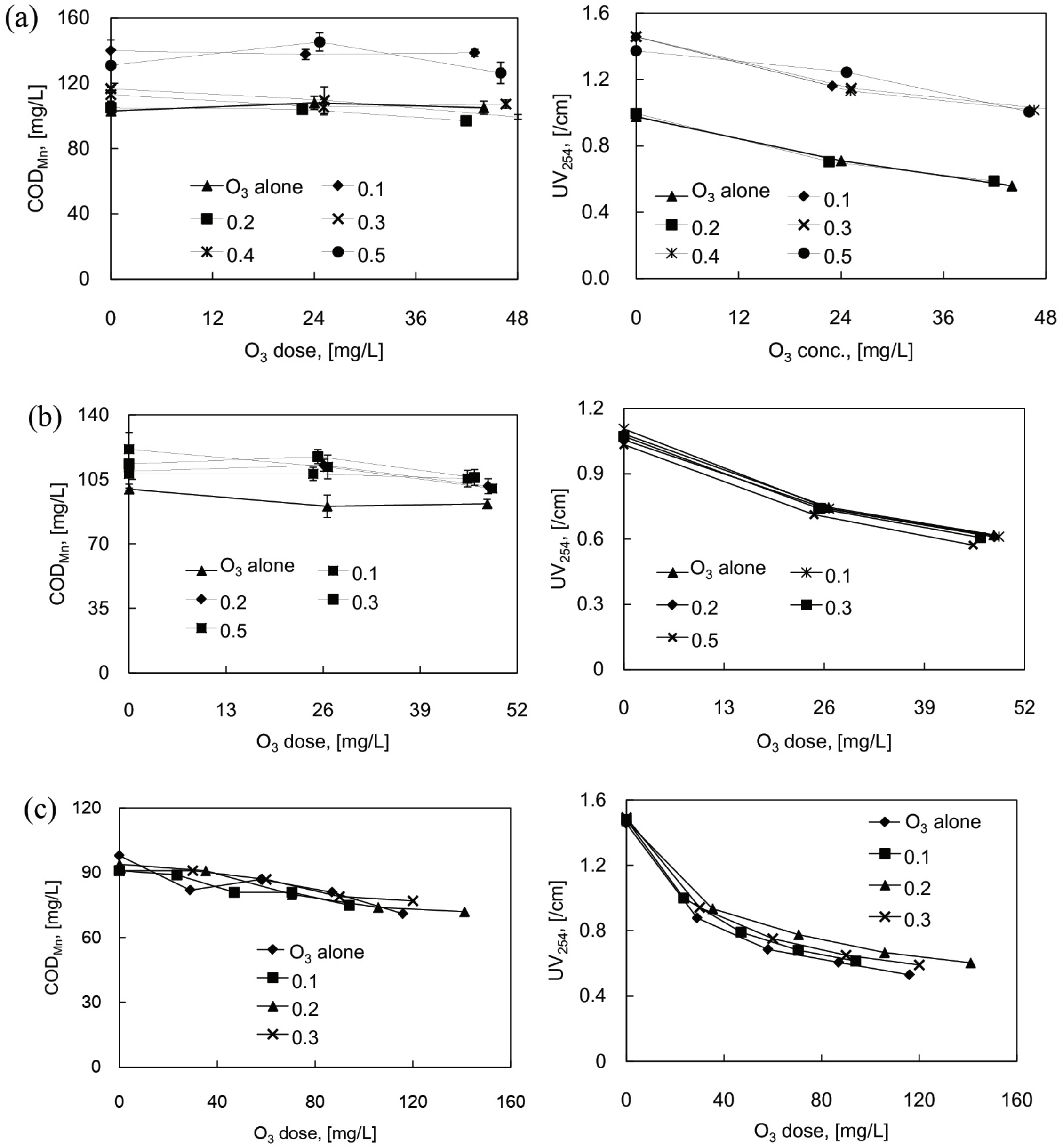

Fig. 6. Abatement of COD_{Mn} and UV_{254} by O_3/H_2O_2: [Sample] Floatation effluent for test (a) and (b), BF effluent for test (c); pH: adjusted to pH 6 for test (a), adjusted to pH 8 for test (b), originally pH 8 for test (c); Temperature: 30 ± 1°C for test (a) and (b), 25 ± 1°C for (c); O_3 injection rate = 4 mg/L·min; H_2O_2 injection weight ratio: by numbers of legends in each figure.

COD_{Mn} became lower from the criterion of 8.8 ± 0.1 mS/cm which is the electric conductivity of the 310 mg/L COD_0 case; thus, the change in the COD_{Mn} removal rate according to the electrical energy supply was not obvious. Fig. 7b reconfirms the differences between the three data sets by illustrating the COD_{Mn} percent removal rate according to increased electrical energy supply and the COD_{Mn} concentration removed from the COD_0 concentration. As can be seen from the formation of 88 mg/L of COD_0, the COD_{Mn} removal rate is relatively fast if the initial COD_{Mn} concentration is low but the quantity removed from the COD_0 becomes relatively smaller. This result has different aspect from COD_{Mn} removal rates of ozonation tests in the present study; in case the same amount of O_3 was dosed, the COD_{Mn} removal rates were independent of the concentrations of COD_0. Because the Pt/Ti electrode as anode has lower oxidant generation rate than the IrO_2 and RuO_2 electrodes, and among the generated oxidants, the generation rate of free chlorine is higher than those of O_3 and $OH^•$ [17], it is difficult to say that the oxidant generated from the electrode removed COD_{Mn}. Therefore, it appears that the oxidation path where the organic substances on the anode surface provide anodes to electrons is a superior reaction than other indirect oxidation reactions.

Furthermore, although an electrolysis followed by O_3 process was performed, it was observed that the

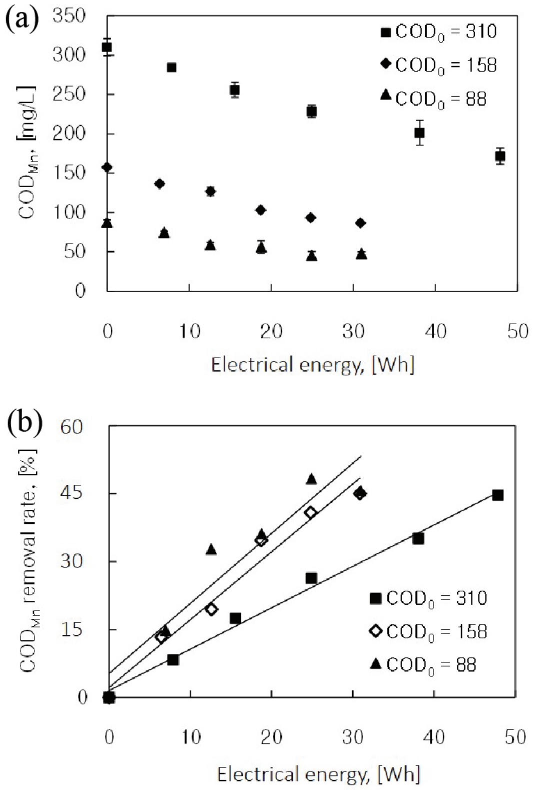

Fig. 7. Abatement of COD_{Mn} by electrochemical oxidation: (a) COD_{Mn} reduction by electrochemical oxidation and (b) relationship of electrical energy versus COD_{Mn} removal rate in percent.

electrochemical oxidation had no effect on the COD_{Mn} removal capacity of ozonation (data not shown). The electrolysis followed by O_3 data set was in the same domain as the result of the O_3 only experiment, which suggested that the electrochemical oxidation had not pre-treatment effect from the aspect of reaction speed. The O_3 followed by electrolysis process had no synergistic effects, either.

3.4. Organic substance removal mechanism of O_3 and electrochemical oxidation

To estimate the target recalcitrant organic substances in the LWW treated by O_3 and electrochemical oxidation, a fluorescence scanning and excitation-emission matrix (EEM) was used with the final discharge of BF effluents. The EEM is widely used to provide information about the provenance, relative contributions and properties of compound classes that constitute organic matter [18,19]. Some previous studies have characterized the EEM by three regions as follows: humic acid-like region (excitation/emission ranges of 300–400 nm and 310–520 nm, respectively), protein-like region (excitation/emission ranges of 250–300 nm and 310–390 nm, respectively), and fulvic acid-like region (excitation/emission ranges of 240–310 nm and 390–520 nm, respectively) [18,20] (Fig. 8). In this study, the EEM of treated LWW shows higher intensities in the humic acid-like and fulvic acid-like regions compared to the protein-like region, indicating that humic and fulvic acids are the main organic species in LWW (Fig. 8).

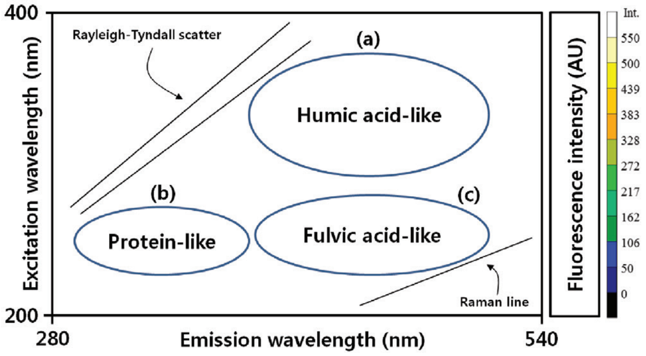

Fig. 8. Excitation-emission matrix (EEM) of LWW effluent: (a) humic acid-like region; (b) protein-like region; and (c) fulvic acid-like region.

Fig. 9a shows the EEM for the ozonated BF effluent. (a1) is the EEM of the undiluted BF effluent while (a2) and (a3) are the EEMs after O_3 injection. COD_{Mn} decreased from 58 mg L^{-1} at first to 33 mg L^{-1} and UV_{254} from 0.8 cm^{-1} to 0.24 cm^{-1} after O_3 injection. The variations of DOC concentration between samples were great, but 2 mg L^{-1} of DOC was removed. No protein-like peak appeared, and humic-like peak and fulvic-like peak decreased with O_3 injection. Due to the long sampling interval, change of the peaks in other domains by O_3 injection [21] could not be observed in this experiment. Fig. 9b shows the EEM changes by electrochemical oxidation. (b1) is the EEM of the BF effluent sample that is identical to (a1), but the difference is that there are noise peaks at excitation 405 nm and emission 340 nm. (b2) and (b3) are the EEMs after electrical energy supply as with the ozonation case. COD_{Mn} decreased from

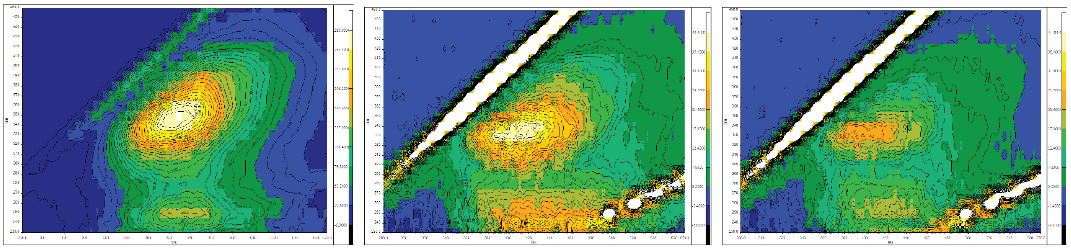
(a1) (a2) (a3)

Fig. 9a. EEM spectra of BF effluent treated by (a) ozonation process: (a1) 0 mg O_3/L; (a2) 150 mg O_3/L; (a3) 180 mg O_3/L.

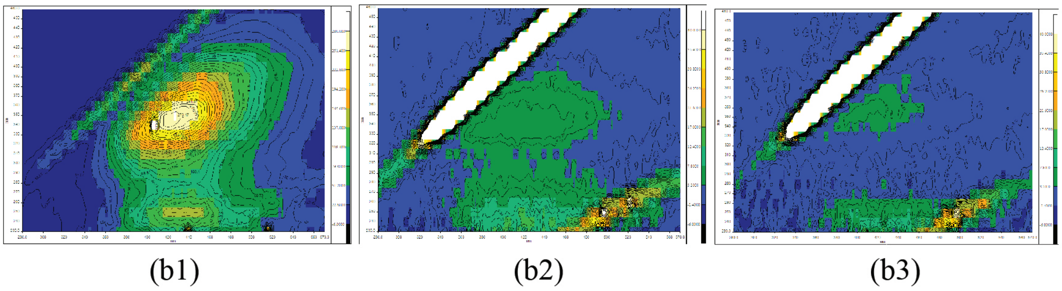
(b1) (b2) (b3)

Fig. 9b. EEM spectra of BF effluent treated by (b) electrochemical process: (b1) 0 Wh; (b2) 19 Wh; (b3) 38 Wh.

58 mg L^{-1} to 22 mg L^{-1} at 38 Wh. UV_{254} did not decrease to 0.7 cm^{-1} or lower even after the electrical energy supply of 38 Wh. It is estimated that the maintenance of UV_{254} is because the byproducts of the electrochemical oxidation absorb the ultraviolet rays of 254 nm. As the maximum absorption wavelengths range from 200 to 350 nm depending on the type of combined chlorine [22], there is sufficient possibility of interference at 254 nm. Therefore, it may be a false-positive analysis to state that the UV_{254} value obtained from the measurement of a sample after the electrochemical oxidation of wastewater containing chlorine ions represent a human substance.

4. Conclusions

Since the $OH^{\bullet}$ associated O_3/H_2O_2 AOP was ineffective in applying high alkaline wastewater, an electrolysis process was applied prior to and after O_3 application. In both cases, electrochemical processes were found to be promising in reducing COD_{Mn}, and effectiveness did not change regardless of ozonation. When electrochemical oxidation is used in livestock wastewater, mixed oxidants (free or combined chlorine, O_3, and reactive oxygen species) are readily generated *in situ*, and the formation of these reactive species might be favorable for oxidation in LWW water that contains a high level of background electrolytes. A change in water characteristics after electrolysis was observed by measuring the excitation-emission matrix spectrum. Decreases in the humic-like peaks and fulvic-like peaks in the BF effluent by ozonation and electrochemical oxidation were observed.

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