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Development of Landfill Leachate Treatment SystemUsing Ozone Oxidation and Moss

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Abstract: The landfill pollution presents a serious environmental problems. In a landfill leachate, many chemicals may be present, i.e., organic carbon, nitrogen and heavy metals. It is hoped to develop the cost-effective and sustainable disposal method. We investigated, the landfill leachate treatment using ozone oxidation and moss. The landfill leachate contained 397 mg L^{-1} COD_{Mn} and 26.5 mg L^{-1} Zn^{2+} concentration. The copper moss, *Scopelophila cataractae* could not grow in the landfill leachate. The pretreatment of the landfill leachate by ozone oxidation was carried out for 45 min. Using the landfill leachate pretreatment by ozone oxidation, *S. cataractae* could grow. COD_{Mn} and Zn^{2+} concentration decreased and reached the minimum value, 154 and 2.3 mg L^{-1}, previously.

Key words: Landfill leachate, moss, ozone oxidation, heavy metal, bioaccumulation

INTRODUCTION

The landfill leachate pollution presents a serious environmental problem (Schwedt, 2001). As many landfill sites are located in mountain area, it may happen that treated leachate is used for drinking water source. In a landfill leachate, many chemicals may be present, i.e., organic carbon, nitrogen and heavy metals (Joseph and Gina, 2000; Carmen *et al*., 2003; Rodriguez *et al*., 2004; Laitinen *et al*., 2006; Oyoh and Evbuomwan, 2008). A landfill will continue to produce contaminated leachate and this process could last for 30-40 years. Therefore, it is hoped to develop the cost-effective and sustainable disposal method.

Ozone is one of the chemical reagents capable of oxidizing a variety of organic compounds in aqueous solution and ozone oxidation treatment requires no post-treatment because the ozone degrades into oxygen itself (Nakamura *et al*., 1989). The present study describes, the effective treatment method of the lignin in a pulp wastewater, 2, 4-dichlorophenol, 2, 4-Dichlorophenoxy acetic acid (2, 4-D) and 2, 4, 5-trichloro- phenoxyacetic acid (2, 4, 5-T) (Nakamura *et al*., 1997, 2004; Daidai *et al*., 2007). However, the production of ozone requires a high cost and it can not discover the heavy metals. On the other hand, a kind of moss, fire moss can absorb and accumulate heavy metals in the cell wall (Oda and Honjyo, 1995; Bates, 2000). We have been investigating a novel treatment of waste water contaminated with copper by a moss (Kobayashi *et al*., 2006). It was reported that 100 mg L^{-1} Cu^{2+} concentration in the model waste water was removed completely by *Scopelophila cataractae*. It seems that the treatment using a moss were cost-effective and sustainable because it was growing only to carbon dioxide and sunlight. If the moss after the treatment of landfill leachate could be exchanged useful materials, i.e., bioethanol or biogass, the treatment system using a moss would be more cost-effective and sustainable. We investigated the biomass such as a bamboo or bagasse exchanged methane or ethanol using a steam explosion and fermentation methods (Kobayashi *et al*., 2004; Asada *et al*., 2005).

The previous studies, i.e., ozone oxidation treatment of wastewater, treatment of wastewater using a moss and biomass utilization were carried out separately. The advantage of ozone oxidation treatment was the degradation of many chemicals, but the disadvantages were high-cost and an almost impossible treatment of metals. The advantages of the treatment using a moss were low-cost, sustainable and a possible treatment of organic materials and/or metals, but the disadvantages were possible treatment of the specific species of

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materials, low concentration. Since, landfill leachate contains low concentration of undegrable organic materials and metals, it suggested that the treatment combined the ozone oxidation process and the process using a moss was effective for cost-effective and sustainable system.

In this research, therefore, the landfill leachate treatment using ozone oxidation and moss was investigated. The physico-chemical characteristics of the landfill leachate were measured. The effect of the ozone oxidation time on growth of *S. cataractae* was examined. The landfill leachate treatment using ozone oxidation and moss was carried out.

MATERIALS AND METHODS

Landfill leachate: Leachate samples were collected in November 2006 from some landfill cell at Kanazawa city, Japan. This cell had been in use since 1983. The sample volume was 18 L. This solution was measured COD, TOC, pH and concentrations of Cu^{2+}, Pb^{2+} and Zn^{2+}. It was used the treatment by ozone oxidation and moss.

Ozone oxidation: Ozone gas was generated from dry air by an ozone generator (MO-5A, Nippon Ozone Co. Ltd., Japan). The mixture of ozone and air was introduced into the reactor at a constant flow rate of about 0.4 $m^3\ h^{-1}$. The concentration of ozone in the feed was 15 g m^{-3}. The volume of reactor was 2 L (working volume 1 L) (Daidai *et al*., 2007).

Incubation of moss: The moss, *Scopelophila cataractae*, was used in this study. The treatment operation of landfill leachate by moss was carried out using the suspended cultivation system flowing air (Kobayashi *et al*., 2006). About 0.5 g protonema as dry weight was transferred to 100 mL of landfill leachate in 150 mL test tube for plant culture. The cap had two narrow glass tubes for aspiration and exhaust. The aspirating air was sterilized by membrane filter and the flow rate was 1.0 L min^{-1}. The test tubes with the caps were placed in rotary shaker (BR-30 L, TAITEC Co. Ltd., Koshiya, Japan) and incubated, while shaking at 50 rpm at 25°C under continuous illumination (4590 L×) supplied by five fluorescent lights.

Analysis: The value of pH was determined using a pH meter (HM-26S, Thoa Denpa Kogyo Co. Ltd., Tokyo, Japan). The values of COD_{Mn} and BOD_5 were carried out by the standard analytical method described in Japan Industrial Standards No. K 0400-20-10 and K 0400-21-10. The TOC was analyzed by a TOC analyzer (TOC-V_{CSN}, Shimadzu Co. Ltd., Japan). The Cu^{2+}, Pb^{2+} and Zn^{2+} concentrations were determined by ICP (inductively coupled plasma) emission spectrometry (OPTIMA 3300 XL, Perkin Elmer, USA) (Kobayashi *et al*., 2007). The dry weight of mosses was measured after drying at 80°C for 24 h (Kobayashi *et al*., 2006).

RESULTS AND DISCUSSION

Table 1 gives the main physico-chemcal parameters analyzed for the landfill leachate. The values of COD_{Mn} (397 mg L^{-1}) and of TOC (189 mg L^{-1}) reveal a relatively high organic load. But the values of BOD_5 (15.1 mg L^{-1}) and of BOD_5/COD_{Mn} ratio (0.038) were low. In generally, BOD_5/COD_{Mn} ratio decreased rapidly with the aging of the landfill (Renou *et al*., 2008). This is due to the release of the large recalcitrant organic molecules from the solid wastes. According to numerous researchers, three types of leachates can be classified by landfill age: young, intermediate, old (stabilized) (Poznyak *et al*., 2008). Consequently, old landfill leachate is characterized by its low BOD/COD ratio (Renou *et al*., 2008). These results indicated that the landfill in this study is old. This is unsurprising because this landfill closed on 1983 before 25 years. The heavy metal concentrations were relatively low, except for Zn^{2+} (26.5 mg L^{-1}). Some researchers reported that landfill leachates contain a lot of zinc (Safari and Bidhendi, 2007; Oygard *et al*., 2004). From results in Table 1, removal of COD_{Mn} and Zn^{2+} were examined using ozone oxidation and moss.

At first, the treatment of the landfill leachate carried out using moss only. Figure 1 shows the time courses of COD_{Mn}, TOC, Zn^{2+} concentration and dry weight of mosses on the treatment of the landfill leachate by moss, *S. cataractae*. The Zn^{2+} concentration decreased rapidly for about 10 days and after then did gradually. This reason seems to be that in the concentration mechanism of heavy metal from a solution by a biomass, two processes, adsorption on the cell surface and incorporation into the cells have been observed (Kondoh *et al*., 1998). The minimum value of Zn^{2+} concentration was 4.5 mg L^{-1}. The values of COD_{Mn}, TOC and dry weight of mosses were constantly. It seems that the moss, *S. cataractae* could not growth because

Table 1: Physico-chemical characteristics of the landfill leachate

Parameters	Values
pH	7.71
COD_{Mn} (mg L^{-1})	397
BOD_5 (mg L^{-1})	15.1
BOD_5/COD_{Mn}	0.038
TOC (mg L^{-1})	189
Cu^{2+} (mg L^{-1})	ND[a]
Pb^{2+} (mg L^{-1})	ND[a]
Zn^{2+} (mg L^{-1})	26.5

[a]Not Detected

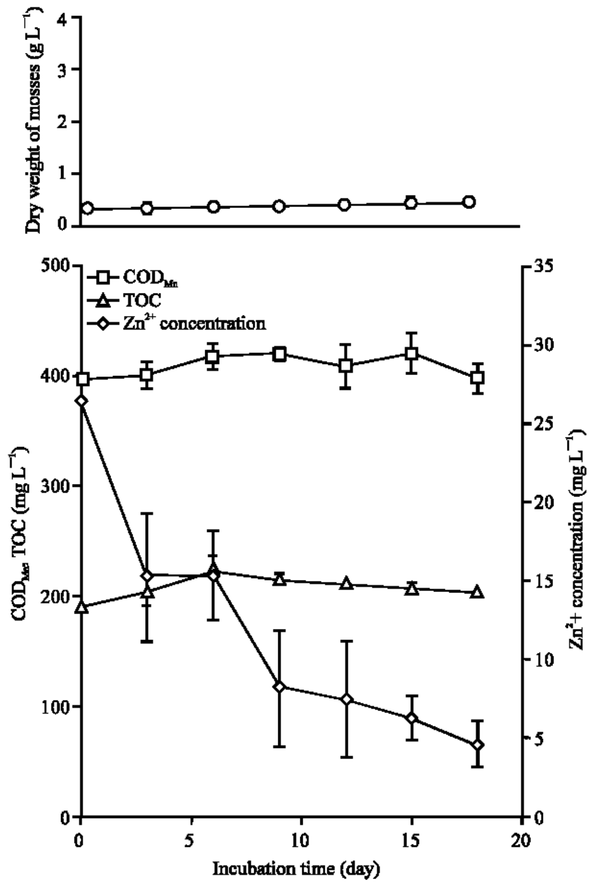

Fig. 1: Time courses of COD_{Mn}, TOC, Zn^{2+} concentration, dry weight of mosses on the treatment of the landfill leachate by moss. These data were the mean values and standard deviations corresponding to 3 time experiments

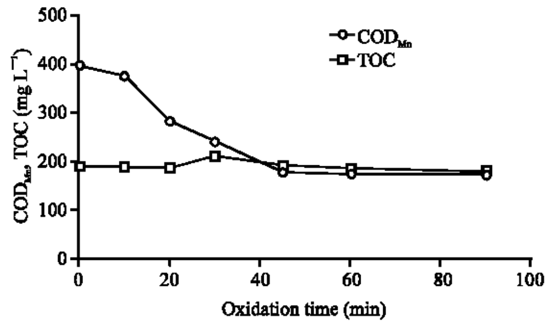

Fig. 2: Change of COD_{Mn} and TOC in the landfill leachate by ozone oxidation

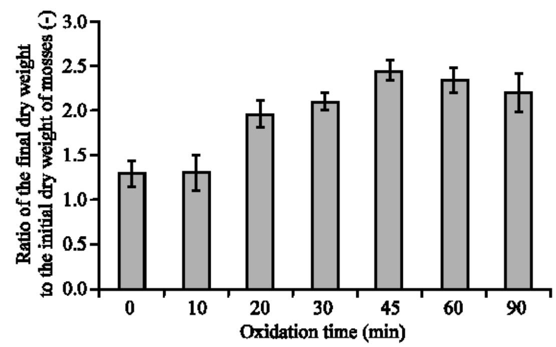

Fig. 3: Effect of ozone oxidation time on the growth of mosses. These data were the mean values and standard deviations corresponding to three-time experiments

components of COD_{Mn} and TOC could not degrade by the moss. From these results and the value of BOD_5/COD_{Mn} ratio in Table 1, the landfill leachate was characterized difficult-to-treat, hard COD compounds.

The degradation of organic matter, using various treatments as electrochemical oxidation (Bueno and Bertazzoli, 2005), membranes (Osturk *et al*., 2003), advanced oxidation (Lopes and Zamora, 2005), ozone oxidation (Monje and Velasquez, 2004) will obligatorily depend on the chemical make-up of the present organics and the ambient conditions (Poznyak *et al*., 2008). Ozone may be used in the beginning (pre-ozonation) and the main objective is the decomposition of large organic molecules (Kerc *et al*., 2003) in order to increase the effectiveness of the following treatment steps such as biodegradation. Referring to the previous study presented above, the ozone oxidation as pre-ozonation was carried out. Figure 2 shows, the change of COD_{Mn} and TOC in the landfill leachate by ozone oxidation. The COD_{Mn} decreased gradually with the increase of oxidation time and then reached almost constant value after 45 min oxidation time. The TOC was hardly decreased by ozone oxidation. It seems that some components of COD_{Mn} could not be converted into carbon dioxide and water directly by ozone oxidation and that some other was converted into small organic molecules, i.e., malonic acid and oxalic acid (Nakamura *et al*., 1997; Pozntyak *et al*., 2008). It thought that the small organic molecules are enhance or inhibit for the growth of moss, *S. cataractae*. Figure 3 shows the ratio of the final dry weight to the initial dry weight of moss on the various ozone oxidation time. The maximum value of the ratio was 2.45 at 45 min oxidation time. These results suggest that the small organic molecules converted from the landfill leachate by ozone oxidation could degrade by moss, *S. cataractae*.

Figure 4 shows the treatment of the landfill leachate using ozone oxidation and moss. The ozone oxidation time was 45 min from the results as shown in Fig. 2 and 3. The

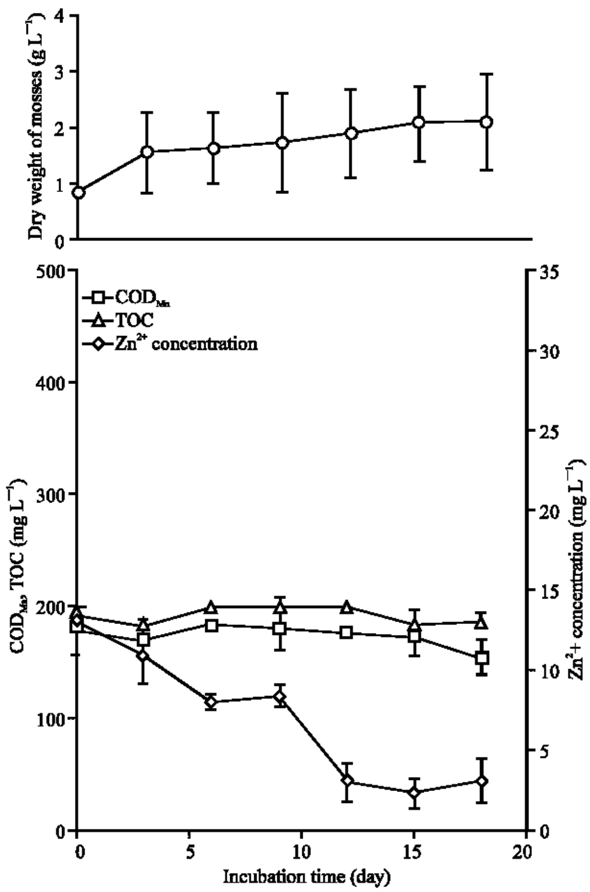

Fig. 4: The treatment of landfill leachate using ozone oxidation and moss. These data were the mean values and standard deviations corresponding to three-time experiments

dry weight of mosses increased and Zn^{2+} concentration decreased rapidly. The initial Zn^{2+} concentration on the incubation was not the landfill leachate data (26.5 mg L^{-1}), but 13 mg L^{-1}. The reason why a part of Zn^{2+} became metal oxide, i.e., Zn $(OH)_2$ and/or ZnO, by ozone oxidation and be deposited (Muruganandham *et al.*, 2007; Salem *et al.*, 2008). The final Zn^{2+} concentration was 2.3 mg L^{-1}. The value of COD_{Mn} and TOC decreased gradually and reached their minimum value of 154 and 186 mg L^{-1}, respectively. Since, COD and Zn of the environmental quality standard in Japan are 160 and 2 mg L^{-1}, respectively, it was found that the treatment using ozone oxidation and moss was the efficient method for hard landfill leachate. Future study will be focused on utilization of a moss after the treatment of landfill leachate as a biomass, i.e., production of bioethanol and/or biogass (methane), for the establishment of more cost-effective and sustainable system.

CONCLUSION

The landfill leachate was treated using ozone oxidation and moss treatment. The following findings were obtained:

- The landfill leachate contained 397 mg L^{-1} COD_{Mn}, 15.1 mg L^{-1} BOD_5, 159 mg L^{-1} TOC, 26.5 mg L^{-1} Zn^{2+}. Since, the landfill leachate was old, BOD_5/COD_{Mn} ratio was very low
- On the treatment of t he landfill leachate by moss only, Zn^{2+} could remove to 4.5 mg L^{-1} from 26.5 mg L^{-1} but COD_{Mn} and TOC could not remove
- The values of COD_{Mn} and Zn^{2+} concentration reached to 154 and 2.3 mg L^{-1} from 397 and 26.5 mg L^{-1}, respectively by the treatment using ozone oxidation and moss, it was found that this method was the efficient treatment of hard landfill leachate

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