Removal Characteristics of Ammonia in Peat Biofilter Seeded with Night Soil Sludge

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ABSTRACT

Ammonia is a typical odorous gas emitted from various industrial areas, night soil and waste water treatment plants. To treat the gas, biological deodorization methods are attracting attention, because they have the advantages of lower maintenance and operation cost and converting to N02- and N03- which react with ammonia chemically. Biofilters are reactors in which a polluted gas stream is passed through a porous packed bed carrier on which pollutant-degrading microbial cultures are naturally immobilized. Deodorization mechanisms in biofilter are principally by dissolution of the odorous gas in water, contacting with microorganisms, then oxidation by microorganisms. Peat has been proven as an excellent carrier because it possesses a large specific surface area, a high water retention capacity, and provides nutrients to microorganisms. Thus, good living conditions for microorganisms are given. So far the removal capacity of ammonia by biofilter was relatively lower. In this study, in order to improve biological removal rate of ammonia gas in peat biofilter, peat was seeded with night soil sludge, to foster ammonia oxidizing bacteria by gradual increase in ammonia load. The load of ammonia was initially supplied at 0. 13 g-N/d/kg-dry peat and gradually increased up to 3.48 g-N/d/kg-dry peat by changing space velocity from 65 to 350 h-' or inlet of ammonia concentration from 28 to 220 ppm. Complete removal of ammonia was observed up to maximum load at 2.8 g-N/d/kg-dry peat, which was higher than reported previously, ranged at 0.17 - 0.38 g-N/d/kg-dry peat. By controlling the pH in the peat biofilter, the removal ratio was observed at an average of 95%for 110 days. At the highest load, the kinetic analysis was conducted. The maximum removal rate of ammonia, V., obtained was I 1. 4 g-N/d/kg-dry peat and saturation constant, K, was 226 ppm.

INTRODUCTION

Offensively odorous substances emitted from various industrials, night soil or waste water treatment plants, are causing many problems. For treatment these gases, physical and/or chemical methods have been popularly used, such as activated carbon adsorption, combustion, acid-alkali treatment etc. Although their efficiency is generally satisfactory, maintenance and operation costs of these methods are high and thus biological methods have attracted attention as a more economical alternative. In addition, biological methods generally have the specific advantage that the pollutants are not concentrated in another phase but converted to harmless or much less harmful oxidation product.

The biological deodorizing methods are referred to biofilter which has been used as an efficient and practical technology to control odors. Biofilter is now the most commonly used for odor control technology in Europe and Japan. Biofilters are reactors in which a polluted gas stream is passed through a porous packed bed carrier on which pollutant-degrading microbial cultures are naturally immobilized. Deodorization mechanisms in biofilter are principally by dissolution of the odorous gas in water, contacting with microorganisms, then oxidation by microorganisms. In case of ammonia gas, the ammonia removal principles by biofilter are dissolution ammonia in water phase and nitrification process which is the oxidation of ammonium via nitrite to nitrate by nitrifying bacteria.

We had investigated that the ammonia removal by peat biofilter as a new biological deodorizing system was principally by physical and chemical adsorption with functional of humic substance of the peat. However, the adsorption capacity of peat is low, and the removal achieved by adsorption process will last only a short time because the functional groups of humic substances binding ammonia become saturated. On the other hand, the disadvantages of peat which is naturally acidic and has no nitrification capacity, should be improved by both neutralization with $Ca(OH)_2$ and seeding with nitrifying bacteria.

The removal capacity of ammonia by peat biofilter reported by some authors is low and no such data about removal kinetic of ammonia have been reported. In order to find the maximum removal capacity of ammonia, peat was seeded with night soil sludge, and ammonia load was introduced by gradual increase. In this study, characteristics of ammonia removal by the peat biofilter were investigated and the removal kinetic analysis was conducted.

MATERIALS AND METHODS

Peat used. Peat moss A (Takahashi Peat Moss Co. Ltd., Hokkaido, Japan) was used in this study. The characteristics of peat were 36.07 % C, 4.21 % H, 1.61 % N, 0.31 % S, 23.9 % 0 and 33.9 % ash. Of the nitrogen, NH_4-N, Org-N, NO_x-N, and total N are 0.32, 14.34, 0.13, 14.89 g-N/kg dry peat, respectively. The pH of peat is initially at 4.10. After neutralization with 37 g-$Ca(OH)_2.2H_20$/kg-dry peat, fibrous peat was seeded with night soil sludge (10 g-MILSS(mixed liquor suspended solid)/kg-dry peat), the pH changed to 7.42. As a reference, only neutralized fibrous peat was prepared. The properties of night soil sludge of Kanagawa, Japan, used for inoculation were as follows: pH 6.63, MLSS 2.92 gl^{-1}, NH_4^+ 15 ppm, $N0_2^-$ 10 ppm, $N0_3^-$ 150 ppm and light brown color.

Ammonia gas.

Ammonia gas was generated from ammonia solution of 0.05 - 1.5 N using an ammonia generator (Fig. 1) and diluted by air. A 25% of ammonia solution was purchased from Wako Pure Chemical Industries Ltd., Japan.

Experimental apparatus.

Figure I shows a schematic diagram of a laboratory-scale biofilter. The glass columns of 5 cm inner diameter and 50 cm height were used. After measurement of moisture content of the peat, a 54 g-dry peat seeded with night soil sludge was packed to the column to a height of 18 cm. It was compacted to 14 cm within two weeks. Another column was used for control experiment which contained 54 g of peat without seeding with night soil sludge. Detailed experimental conditions are summarized in Table 1. Aqueous ammonia solution in a 3 liter bottle was fed into the top of an ammonia generator column, using a peristaltic pump. The ammonia gas generator column (5 cm outer diameter of PVC) was packed with glass beads, through which air was passed in the counter current flow. The air, which contained a specific concentration of ammonia, was then supplied to the biofilter columns. Inlet ammonia concentration was changed by controlling the air flow rate, concentration of ammonia solution, and rotating speed of peristaltic pump. Thus, load of ammonia into the biofilter was changed by controlling inlet concentration and space velocity or gas flow rate. 40 ml water was sprayed manually on the peat bed in the columns every 2 days to maintain moisture content of the bed at about 70%. All experiments were done at temperature of 24-28 °C. Peat biofilter was maintained at pH 6 - 8 by adding 40 ml of I % $Ca(OH)_2.2H_20$, 0. I % Na_2C0_3, or 0. 01 N HCI.

Table 1. Experimental conditions of peat biofilter seeded with night soil sludge for ammonia removal

Characteristics	
Packing material	Peat moss A
Packing dry weight (g)	53.8
Packed volume (*l*)	0.275
Packing density (g-dry peat /*l*)	196
Packing height (cm)	14
Initial moisture content (%)	70
Initial pH	7.42
cell number (cells/kg-dry peat)[a]	6.77×10^7
Supplied gas	NH_3
Inlet concentration (ppm)	28 - 220
Flow rate (*l* / min)	0.1 - 1.5
Space velocity (h^{-1})	65 - 350
Load (g-N/d/kg-dry peat)	0.1 -'1 - 3.48

[a] counted, two weeks after kinetic data were taken.

Bacterial count.

Two weeks after kinetics data were taken, the cell number of nitrifying bacteria was counted by NWN method. About 10 g wet weight of peat bed was homogenized in 90 ml of AL medium at 10,000 rpm for 10 minutes (EX-3, Nihon Seiki Ltd., Tokyo Japan). The homogenized solution was diluted with AL medium, then 0.5 ml of the suspended solution with different dilution ratios were transferred to 4.5 ml AL medium in 18 cm test tubes, and incubated at 30 (C at 120 spm for 2 weeks in the dark room. At the end of the incubation period, each tube was scored by adding an indicator (2.2 g of diphenylamine in 100 ml of concentrated H_2S0_4) to test the presence of nitrate and/or nitrite. A blue color reaction indicates that these end products are formed, and the tube is scored positive. The absence of a blue color is scored negative. AL medium contained 2.5 g $(NH_4)_2S0_4$, 0.5 g KH_2P0_4, 50 $MgS0_4.7H_20$, 4 mg $CaCI_2.2H_20$, and 0.1 mg FE-EDTA per liter, at pH 8.0-8.2.

Analysis.

Moisture content of peat was determined by drying for more than 8 hours at 80 (C in an oven. The initial pH of peat was determined as follows. Ten g-wet of peat was homogenized with 90 ml of distilled water. After 30 minutes gravitational settling, pH value of the homogenized solution was measured. Inlet and outlet ammonia concentrations in biofilter were analyzed by ammonia gas detection tubes (Gastec, Japan). The lower detection limit of the tubes was 0.25 ppm. To test the presence of nitrate and/or nitrite in the effluent, a merckoquant test strip for nitrate and nitrite (Merck KGAA, Germany) was used.

RESULTS AND DISCUSSIONS

Ammonia removal.

The experiment was carried out under the same initial condition as that of ammonia removal by peat in a previous paper. The peat was seeded by 10 g MLSS/kg-dry peat and inlet concentration was supplied at 40 ppm of ammonia, at space velocity (SV) of 50 h^{-1} and at load of 0.13 g-N/d/kg-dry peat. Togashi *et.al.* estimated that the maximum safe inlet ammonia loading should be about 70% of the nitrifying capacity of the seeded peat (0.18 g-N/d/kg-dry peat). It was equal to about 0.13 g-N/d/kg-dry peat. This condition was maintained for the first 34 days, then the load was gradually increased by changing SV and inlet concentration of ammonia.

Time course of ammonia removal by peat biofilter seeded with night soil activated sludge, during the 110 days, is shown in Fig. 2a. The removal ratio of ammonia was calculated from inlet and outlet concentrations of ammonia as shown in Fig. 2b. Complete removal of ammonia was observed during the first 20 days. This result agreed with the previous paper where the removal of ammonia by peat was achieved by the adsorption process with the functional groups of humic substances in the peat acting as active centers. However, in the previous paper with an inlet concentration at an average 40 ppm and at ammonia loading, 0.16 g-N/d/ kg-dry peat, complete removal was achieved throughout until 101 days experiment. After complete removal of ammonia, removal ratio decreased to about 85% (Fig. 2b) and increased again, then acclamation period occurred. Complete removal of ammonia was observed for the first 28 day and the 34th day, then the load was increased (Fig. 2c) by changing, SV to 130 h^{-1} (Fig.2d). After several days fluctuation on removal ratio, complete removal was observed again (Fig.2b), then load was increased again up to 3.48 g-N/d/kg-dry peat by changing SV and inlet concentration of ammonia (Fig.2c and d).

After the kinetic analysis was conducted at 59th day, load was increased, but the removal ratio decreased. Then, the load was reduced, and the next acclamation period occurred again. Then, kinetic study was applied at 72nd day for the second time. After that, the removal ratio decreased (Fig. 2b), even when load was decreased to 1.8 g-N/d/kg-dry peat (Fig.2c). This suggests that the nitrifying bacteria was in the death phase, because the high removal capacity was not recovered after several weeks.

For the entire 110 days experiment, the peat biofilter performed at an average of 95% ammonia removal ratio. In contrast, ammonia removal using wood bark by Weckhuysen *et.al.* showed at an average of 83% removal ratio of ammonia where the inlet concentrations were at 4-16.5 ppm. A peat biofilter with down flow by Hartikainen, *et.al.* showed that the removal ratio was about 80 % for an inlet concentrations of 20-65 ppm. Another biological method for ammonia removal is a rotating biological contactor that showed about 60% by Vis and Rinzema.

pH control.

Initial pH of peat biofilter was 7.42, then the pH of effluent changed, after introducing of ammonia. It was maintained at 6 - 8, because the pH range for growth of autotrophic nitrifying bacteria, *Nitrosomonas* sp. and *Nitrobacter* sp. are 5.8 - 8.5 and 6.5 - 8.5, respectively. Figure 2e shows the change of pH in the effluent. At first, pH decreased to about 6 and 40 ml of 1% $Ca(OH)_2$ was sprayed into the column and pH increased to about 7, then decreased again. However, after 4 times of spraying $Ca(OH)_2$ solution, it caused a deposit at the top of the column. This might cause the pressure drop in the column, and then the neutralizing solution was changed to a 1 % Na_2C0_3 solution, to eliminate this disadvantage. After spraying 40 ml of I % Na_2C0_3 solution, pH was increased to 9.16, then 40 ml of 0.1 N HCI solution was sprayed two times more, and then pH of effluent was controlled. Treatment with Na_2C0_3 solution enhanced the nitrification capacity. This result agrees with the treatment of spraying $KHCO_3$ solution ($C0^3H$) which develops the nitrification.

Togashi *et.al.* showed that the pH of peat did not fall below 6.95. It might be because the constant load of 0. 16 g-N/d/kg-dry peat or at constant inlet concentration of 40 ppm ammonia introduced to the column maintained the nitrification and neutralization of NO_x with NH_3. On the other hand, Hartikainen, *et.al.* maintained pH at 4.0 to 6.0 by addition of Na_2C0_3 solution (0.1 M or 0.01 M), because the inoculated peat with sludge had a good nitrification at pH 6.0 but none at pH 4.0. However, both of that experiments had a low removal capacity.

Bacterial count.

In two weeks after kinetic data were taken, the cell number counted by MPN method as nitrifying bacteria was 6.77 x 10^7 cells/kg-dry peat. When the effluent was tested by Merckoquant test strips, $N0^{2-}$ and $N0^{3-}$ were detected. No production of $N0_2$by gas detection tubes was observed. Suggesting that no denitrification in packed bed was occurred.

Ammonia removal capacity.

Figure 3. shows the removal capacity of the biofilter bed which was calculated from the inlet and outlet ammonia gas concentrations (Fig. 2a) for a period 110 days, as a function of the load of ammonia to the bed. The solid line indicates that the removal capacity is equal to the load; hence a 100 % removal ratio is observed. The maximum load to guaranteed 100% removal was 2.8 g-N/d/kg-dry peat and the maximum removal capacity was 5.3 g-N/d/kg-dry peat (Fig. 3). The maximum capacity of ammonia removal by peat biofilter has been reported, are 0.18 g-N/d/kg-dry peat, 0.17 g-N/d/kg dry peat, 0.38 g-N/d/kg-dry peat. The maximum removal capacity obtained here is higher than any previous data reported. This is mainly because of different sources of nitrifying bacteria, the pH control, treatment with Na_2C0_3 solution, and gradually increasing of load.

Determination of the kinetic parameters.

In order to determine the kinetics of biological removal, the experiment was carried out by increasing the load of ammonia to certain level on 59^{th} and 72^{nd} day. In the deodorization kinetic analysis of ammonia by peat biofilter, a Michaelis-Menten type equation was assumed and the removal efficiency was evaluated. By assuming plug air flow in the biofilter column, the following equation was obtained.

Where C : concentration of odor compound (ppm)

l : length of column (m)

V_m : maximum removal rate (g-N/d/kg-dry peat)

K_s : saturation constant (ppm)

S_a : cross section of column (M^2)

F : gas flow rate (m^3/d)

L : height of peat packed (m)

SV : space velocity (d^{-1}) = $F/S_a.L$

α : conversion coefficient (kg-dry peat/g-N)

Conversion coefficient a defined by equation 3 was used to convert unit of 1concentration to ppm.

Where T : temperature ((C)

W : dry weight of peat (kg)

v : volume of peat (m^3)

Equation 4 was obtained by integrating equation 2 under the condition of $C = C_o$ at $l = 0$, $C = C_e$ at $1 = L$. ,

The kinetic experiment was carried out by changing the inlet concentration of ammonia up to 260 ppm and flow rate up to 3,0 *l*/min or SV up to $500h^{-1}$. From the linear relation between C_{ln} and C_{ln} /R, V_m and Ks, were assessed from the slope and the intercept, respectively as shown in Fig. 4. The maximum removal rate, V_m, obtained was 11.4 g-N/d/kg-dry peat and saturation constant, Ks, obtained was 226 ppm.

CONCLUSSION

Ammonia removal characteristics by peat biofilter seeded with night soil sludge was investigated and better than previously reported by some authors. The removal ratio of ammonia was observed at an average of 96.5 % for 110 days experiment, and the maximum removal capacity of peat biofilter was 2.8 g-N/d/kg dry peat. The maximum removal rate of ammonia, V_m, obtained was 11.4 g-N/d/kg-dry peat and saturation constant, K_s, obtained was 226 ppm.

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