Research article

Fundamental Study on Nitrogen Removal from Paddy Drainage Using Clinker Ash

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Abstract Clinker ash is a kind of coal ash produced by the burning of coal at thermal power plants. Recycling of clinker ash is highly desirable since most of it goes to landfills at present. Because of its porous solid, clinker ash has high potential as a means of purifying contaminated water. On the other hand, nitrogen outflow by paddy drainage has become a major problem in Japan. Therefore, this study examines the effectiveness of a filtering system using clinker ash for removing nitrogen from paddy drainage. A column experiment was conducted in the laboratory to examine the nitrogen removal function of clinker ash. Four types of filtering materials were prepared as the test samples. The Sample I consisted only of clinker ash; the Sample II and the Sample III were a mixture of clinker ash and paddy soil in the ratios of 3:1 and 1:3 respectively; and the Sample IV was comprised of paddy soil only. Each sample was poured into PVC columns (44 mm in diameter; 350 mm in length). A solution prepared with NH_4-N at a concentration of 10 mg/L and C/N of 12 was fed to the columns at a flow rate of 100 to 200 mL/d for 121 days. During the experiment, the columns were kept saturated at a room temperature of 24.4±1.3℃ and illuminated at 544±192 lux. The study showed that clinker ash has the effect of removing nitrogen. However, it also found that clinker ash's removal function is compromised when a large amount of paddy soil is mixed with clinker ash. In order to remove nitrogen from paddy drainage by using clinker ash, only a relatively small amount of paddy soil should be mixed with clinker ash.

Keywords nitrogen removal, clinker ash, paddy drainage, filtering system

INTRODUCTION

Water contamination due to agricultural activity is a global issue (Garnier et al., 2010). During Japan's rapid economic growth from the 1950s to 1970s, pollution issues relating to water contamination surfaced across the country. The Water Pollution Law was introduced in 1970 as a countermeasure, and other laws and regulations followed in subsequent years. These days, water contamination from point sources, such as factories and residential wastewater, has ameliorated thanks to regulatory efforts; however, nitrogen and phosphorous water contamination arising from farmland and other non-point sources is not yet sufficiently resolved (Mishima. 2007).

Many studies have reported nitrogen removal efforts on paddy fields, which account for 60% of farmland in Japan (Ichino et al., 1998; Feng et al., 2004). It has also been reported that nitrogen runoff from paddy fields is related to river water contamination, and paddy fields are thus identified as a source of water pollution. In particular, discharge of high-concentration nitrogen is noted to occur in paddy fields immediately after fertilizers are used (Yoshinaga et al., 2007).

Approximately 20% of Japan's total energy is provided by coal-fired thermal generation. In 2003, thermal generation produced a total of 7,470,000 tons of coal ash, which is roughly categorized into clinker ash and fly ash. Fly ash constitutes the majority of coal ash and is recycled as construction material. Although as much as 220,000 tons of clinker ash is generated each year, most of it ends up in landfills; thus recycling of clinker ash is an important issue to address (JETA et al., 2005). Since the surface of clinker ash has numerous pores of 1-20 μm in diameter (Fig. 1) and has a large specific surface area, it has good potential as a water purification material.

Nitrogen discharge from paddy drainage divided into seepage, surface runoff, denitrification and vaporization. Especially, it is easy to take measure regarding with decrease of nitrogen concentration in seepage and surface water using filtering system. In this study, a column experiment was conducted using clinker ash as a filtering material in order to illustrate the nitrogen removal performance of clinker ash when used against paddy field wastewater.

METHODOLOGY

A column experiment was conducted in the laboratory to examine the nitrogen removal function of clinker ash as shown in Fig. 2. Four types of filtering materials were prepared as test samples. Table 1 shows characteristics of each filtering material before the experiment. Sample I consisted only of clinker ash; Sample II and Sample III were a mixture of clinker ash and paddy soil in the ratios of 3:1 and 1:3 respectively; and Sample IV consisted of paddy soil only. Mixture samples were assumed to be degraded by paddy soil.

The coefficient of permeability was 6.23×10^{-2}cm/s in Sample I, and 1.20×10^{-4}cm/s in Sample IV. A rise in the ratio of paddy soil decreased the coefficient of permeability. While no amount of nitrogen was detected from Sample I, 181.4×10^{-5}kg/kg was found in Sample IV. The higher the ratio of paddy soil was, the greater the amount of nitrogen.

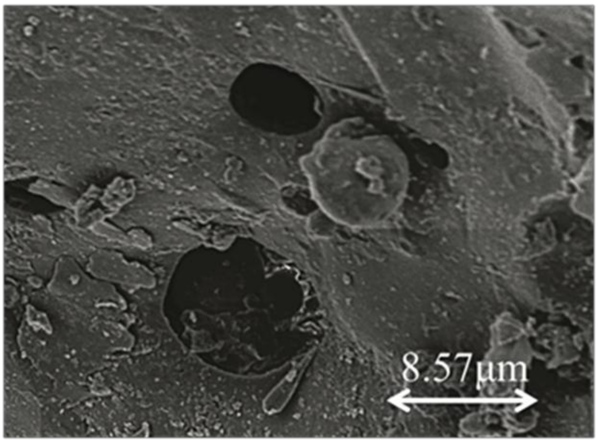

Fig. 1 Photomicrograph of clinker ash

Each sample was poured into a PVC column (44 mm in diameter; 350 mm in length). A test solution prepared with NH_4-N at a concentration of 10 mg/L and C/N of 12 was fed to the columns at a flow rate of 100 to 200 mL/d for 121 days. The drainage tube was lifted in the column upper part to make it a saturation state. During the experiment, the columns were kept saturated at the room temperature of 24.4±1.3 ℃ and illuminated at 544±192 lux. Water samples were taken every day for the first 31 days. The sampling interval was then changed to once every 2 days until the 60th day, when it was again changed to once every 4 days until the 121st day.

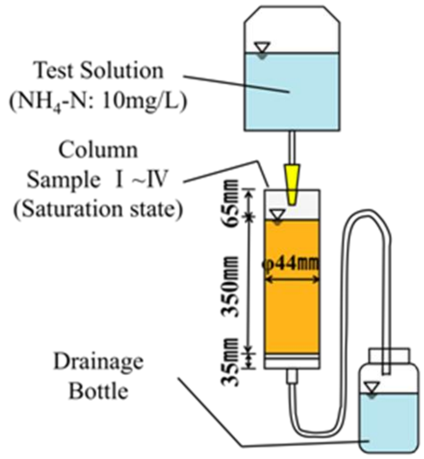

Fig. 2 Schematic diagram of column experiment

Parameters used to measure the water quality were total nitrogen (T-N), nitrate nitrogen (NO_3-N), nitrite nitrogen (NO_2-N), and ammonium nitrogen (NH_4-N); these were analyzed using ultraviolet spectrophotometry in accordance with the Japanese Industrial Standards (JIS). The quantities of nitrogen and carbon were each measured using the CN coder (SUMIGRAPH NCH-22F : Sumika Chemical Analysis Service, Ltd.) before and after the column experiment.

RESULTS AND DISCUSSION

Fluctuation of outflow nitrogen concentration as a function of time and cumulative flow

Fig. 3 shows the relationship between the number of days elapsed and the T-N concentration (C_{out}) in the outflow. Fig. 4 plots the relationship between the cumulative flow of the solution and the C_{out} in the outflow. The volume of the solution passing through during the experiment period of 121 days varied from sample to sample, due to the differences in the coefficient of permeability.

Samples I and II recorded the lowest nitrogen concentrations at 2.21 mg/L (1st day: 0.42 L) and 3.24 mg/L (5th day: 1.27 L) respectively. From then on the concentration rose gradually, stabilizing at approximately 7 mg/L. Samples I and II both recorded lower concentrations of nitrogen than that in the incoming solution throughout the experiment period, consistently demonstrating the presence of a water purification mechanism.

Table 1 Physical and chemical properties of samples

Sample	Proportion CA: soil	Soil texture	Coefficient permeability (cm/s)	Dry density (g/cm^3)	Void ratio	T-C (x10^{-5} kg/kg)	T-N (x10^{-5} kg/kg)	C/N ratio
Sample I	1:0	S	6.23×10^{-2}	0.94	1.34	441.1	0.0	ND
Sample II	3:1	LS	1.50×10^{-2}	0.96	1.34	620.1	31.0	20.0
Sample III	1:3	CL	3.17×10^{-4}	0.99	1.50	1259.6	128.5	9.8
Sample IV	0:1	LiC	1.20×10^{-4}	1.03	1.55	1497.0	181.4	8.3

Samples III and IV, on the other hand, recorded the highest nitrogen concentrations, at 67.40 mg/L (3rd day: 0.25 L) and 98.72 mg/L (3rd day: 0.20 L), respectively. The concentrations gradually decreased, with Sample III stabilizing at 11 mg/L and Sample IV at 16 mg/L. These values were higher than those in the inflow, evidencing that Samples III and IV had no nitrogen cleansing effect. The above results demonstrate that the ratio of clinker ash and paddy soil is related to the performance of the mixture as filtering material.

Nitrogen balance in each column

The nitrogen balance in each column during the 121 days was calculated by using Eq. (1) and (2):

$$L_{out} = L_{in} + SD - SP \quad (1)$$

$$SP = P_{soil} + P_{vac} \quad (2)$$

Where L_{out} is nitrogen discharge (mg), L_{in} is nitrogen supply (mg), SD is nitrogen discharge from soil (mg), SP is nitrogen removed (mg), P_{soil} is nitrogen adsorbed (mg), and P_{vac} is microbial decomposition of nitrogen compounds (mg), obtained by a subtraction based on (2).

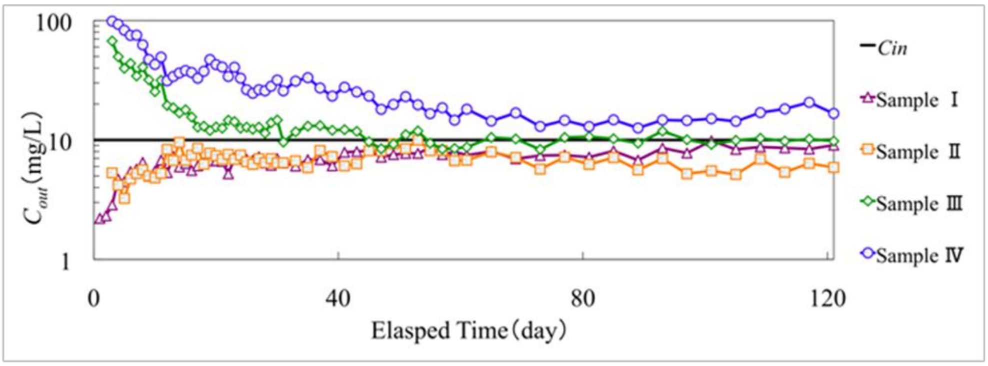

Fig. 3 Relationship between days lapsed and C_{out}

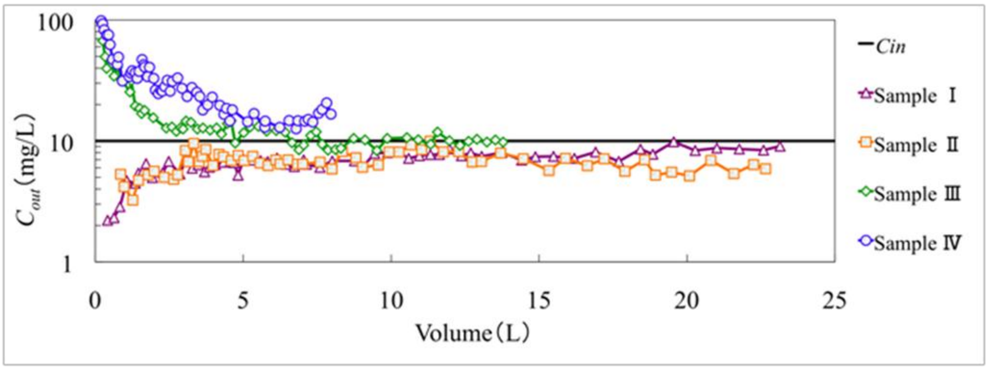

Fig. 4 Relationship between cumulative flow and C_{out}

Table 2 shows the nitrogen balance in each column. The ratios of effluence (L_{out} /L_{in}) of Samples I and II were respectively 0.74 and 0.64. This illustrates that when the nitrogen solution passes through a column containing a larger proportion of clinker ash, the concentration decreases by 26 to 36%. The values of P_{soil} and P_{vac} in Sample I were 43 mg and 17 mg, while those in Sample II were 69 mg and 10 mg. From these it is inferred that nitrogen adsorption and microbial decomposition occurred in Samples I and II.

Table 2 Nitrogen balance

Sample	L_{out} (mg)	L_{in} (mg)	SD (mg)	SP (mg)	P_{soil} (mg)	P_{vac} (mg)	Ratio of effluence L_{out}/L_{in} (-)
Sample I	169	229	0	60	43	17	0.74
Sample II	145	224	0	80	69	10	0.64
Sample III	183	135	83	35	0	35	1.36
Sample IV	195	77	165	47	0	47	2.52

Samples III and IV, on the other hand, recorded ratios of effluence of 1.36 and 2.52 respectively, demonstrating that nitrogen in the columns was released into the outflow. *SD* values of Samples III and IV were respectively 83 mg and 165 mg; it is assumed that nitrogen in the paddy soil in the column was discharged.

CONCLUSION

The column experiment confirmed that nitrogen is removed by nitrogen adsorption of clinker ash and microbial decomposition. It was further demonstrated that when the ratio of paddy soil to clinker ash rises in the mixture, the nitrogen removal mechanism fails to materialize, and the nitrogen contained in paddy soil is discharged. Thus, it is necessary to pay close attention to the mixture ratio between clinker ash and paddy soil when developing a water purification system using clinker ash.

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