

ASSESSING REUSE OF AGRICULTURAL AND FOOD RESIDUES FOR NITRATE ATTENUATION IN POROUS MEDIA

Kazuya Inoue¹, Saki Matsuyama¹ and Tsutomu Tanaka¹

¹ Graduate School of Agricultural Science, Kobe University, Japan

ABSTRACT: Nitrate pollution in groundwater is related to surplus nitrate fertilizers and animal waste disposal. As high nitrate concentration leads to health concern, mass reduction of nitrate in a contaminated site is important. From the perspective of recent reuse streams, this paper assessed the potential of agricultural and food residues such as rice husk, rice straw and used coffee as a nitrate attenuation material in porous media. Under saturated flow conditions, column experiments were carried out in silica sand with a mixture of residues. KNO₃ or NaCl solutions were injected into columns and were analyzed using temporal moment approaches to characterize the mobility of nitrate and chloride ions. The results showed that the mixture of rice straw leads to the increase of the retardation factor. The results also revealed that the use of rice husk and used coffee decreases the mass of both anions, whereas the rice straw has little effect on attenuation of these anions.

Keywords: Reuse, Agricultural and food residues, Nitrate, Column experiments, Attenuation

1. INTRODUCTION

Many different chemical and physical forms of nitrogen fertilizers exist and the nitrogen in most farm-grade fertilizers is also readily available. Man-made nitrogen fertilizers became widely used not only in Japan and the United States but also around the world, providing an inexpensive source of nitrogen and other plant nutrients that resulted in huge increases in agricultural productivity [1]. In the past century, the global nitrogen cycle has been increasingly affected by nitrogen fixation for agricultural activities, which now exceeds the amount that occurs naturally. Both groundwater and surface water can be contaminated by excess nitrate as a result of agricultural activities. Human exposure to nitrate and nitrite is mainly from the ingestion of food and drinking water [2]. Therefore, public water utilities are required to maintain nitrate levels below a Maximum Contaminant Level of 10 mg/L nitrate-nitrogen that was instituted to protect against methemoglobinemia, to which infants are especially susceptible. In addition to methemoglobinemia, a range of other health effects have been associated with ingesting nitrate-contaminated drinking water, including various cancers, neural tube defects and thyroid conditions [3],[4].

In associated with agricultural activities, large amounts of agricultural wastes are discharged, for example, from the harvesting of rice, instant coffee manufacture and field preparation [5]. Rice husk

and rice straw are the main agro-industrial residues from the rice milling industry. Coffee is also one of the largest agricultural products that are mainly used for beverages. According to the U.S. department of Agriculture, the world's coffee production in 2012/13 is forecast at a record 151 million bags, up almost 7 million from the previous year [6] and large amount of spent coffee grounds are discharged. Although part of them as well as rice husk and rice straw is reused as compost or biodiesel [7], most of these are burned as a waste, which results in production of carbon dioxide, the green house gas. Thus, it is necessary to develop new technologies enabling to reuse agricultural residues for useful purposes.

This paper assessed the potential application of agricultural residues including rice husk, rice straw and spent coffee grounds for retarding and attenuating nitrate in porous media. Some quantity factors such as the dispersivity, the retardation factor, the mass recovery fraction and the degradation rate constant were identified using temporal moment approaches based on a time series of leachate concentration of nitrate or chloride ions. Additionally, quantity parameters for assessing the potential use of agricultural residues were also discussed.

2. MATERIALS AND METHODS

2.1 Materials

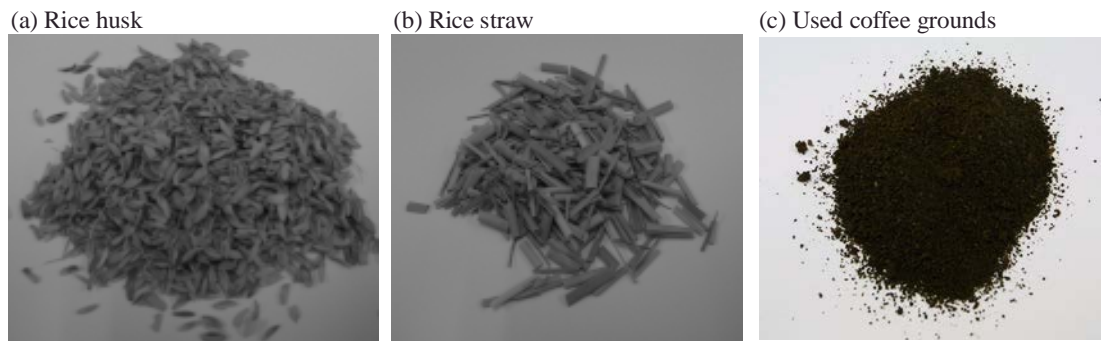


Fig. 1 Images of agricultural residues and food residue used in column experiments: (a) rice husk, (b) rice straw and (c) used coffee grounds.

Table 1 Physical properties of agricultural and food residues mixed with silica sand.

Residues	Weight ratio (%)	Porosity (-)	Hydraulic conductivity (cm/s)
Rice husk	0.95 – 2.6	0.44 – 0.47	0.10 – 0.11
Rice straw	1.0 – 2.2	0.45 – 0.46	0.053 – 0.11
Used coffee	2.3 – 8.9	0.46 – 0.56	0.070 – 0.10

In this study, as a soil material, silica sand with a low uniformity coefficient of 1.25 was selected in order to reflect a relatively high hydraulic conductivity fields such as tea garden, sugar cane field and maize field. Silica sand of interest had 0.050 cm, 2.68 g/cm³ and 0.11 cm/s of physical properties such as the mean particle size, the particle density and the hydraulic conductivity, respectively. Since silica sand was washed and dried at 110 °C repeatedly, there were no microbes onto the soil surface.

In this study, two types of agricultural residues such as rice husk and rice straw were employed, which were taken from the paddy field after the harvest. In addition, Lion Coffee’s “Hawaii coffee” used coffee grounds were used throughout as one food residue in order to compare the degree of nitrate attenuation among agricultural residues. Images of these residues are shown in Fig.1. As shown Fig.1, the length of artificially chopped rice straw was adjusted in approximately 5 mm length. All residues were dried at 110 °C before column experiments.

2.2 Experimental Setup

Column experiments under the saturated condition were carried out at room temperature (18

± 2 °C) under an air atmosphere. The soil columns were constructed of acrylic cylinders having 5 cm of inner diameter and 30 cm length and also had filter meshes attached to the top and bottom.

In column experiments, the weight ratios of rice husk, rice straw and used coffee to the total weight of silica sand were varied in order to examine the effect of the amount of residues on the degree of nitrate transfer. From the practical viewpoint, the weight of silica sand equivalent to the column height of 1.5 cm, 2.1 cm and 3.4 cm was replaced with residues of concern. These soils with one of the residues were completely saturated with deionized water before packing to avoid the entrance of air and were filled into the column in increments of 2.5 cm, homogeneously. Each layer was compacted with a rammer to adjust the porosity prior to packing the next layer. In Table 1, physical properties of each residue mixed with silica sand are listed. The porosity was estimated in each experiment indirectly from the measurements of the total weight of residue and silica sand filled in the column. The hydraulic conductivity was measured using the discharge rate of water from the column under a hydraulic gradient and the sectional area of the column.

2.3 Experimental Procedure

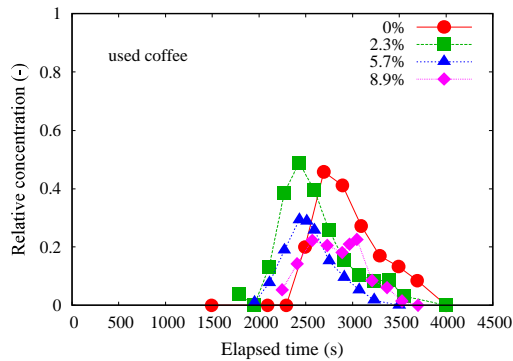


Fig.2 Representative BTCs for nitrate ion in used coffee columns

After packing, deionized water was applied to the column up to a specific level controlled by constant head reservoirs at the top and bottom of the saturated media, while maintaining the saturated condition of porous media. Steady saturated flow field was established in the column when fluctuations in the observed drainage rate from the bottom reservoir became negligible. A volume of 40 cm³ of KNO₃ solution or NaCl solution was applied to produce a pulse input with an initial concentration of 1.5×10⁻⁴ g/cm³ of nitrate-nitrogen or NaCl.

Despite of the condition of the weight ratio of residues, pore water velocities were set to approximately 0.012 cm/s under the control of the hydraulic gradient. Pore water samples at the end of the column were taken at specific intervals using a fraction collector to measure experimental breakthrough curves (BTCs). Nitrate ion in the pore water samples was analyzed by capillary electrophoresis (G1600A, Agilent technologies, USA). The basic anion buffer and a fused silica capillary with 104 cm in length and 5 cm internal diameter were obtained from Agilent technologies. The temperature-controlled cartridge for fused silica was set at 15 °C. On the other hand, electrical sensors were used to measure the voltage readings of electrical sensors using a calibrated relationship between the specific concentration of NaCl solution and the corresponding voltage via a data logger.

3. QUANTIFYING PARAMETERS

3.1 Temporal Moments

Consider a sorbing and degradable chemical moving through a homogeneous medium at a steady, uniform, flow rate. Assuming linear,

equilibrium sorption and first-order kinetic degradation for the solute, the governing transport equation can be written as :

$$R \frac{\partial c}{\partial t} = \alpha v \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - \lambda c \quad (1)$$

where c is the concentration of solute, x is the coordinate, t is the time, R is the retardation factor estimate, v is the average pore water velocity, α is the dispersivity, and λ is the degradation rate constant [8].

Temporal moment analysis is a useful approach to characterize experimental BTCs without solving solute transport model [9]. The normalized temporal moment μ_n at a location x , is defined as :

$$\mu_n = \frac{\int_0^\infty t^n c(x,t) dt}{\int_0^\infty c(x,t) dt} \quad (2)$$

In this study, the dispersivity, the degradation rate, the mass recovery fraction and the retardation factor were identified using temporal moment approaches based on a BTCs of nitrate or chloride ions as quantity factors reflecting the effect of agricultural and food residues. Representative BTCs as a function of the elapsed time for nitrate ion under different weight ratios of mixed used coffee are shown in Fig.2.

3.2 Transport Parameter Identification

The dispersivity from temporal moments was calculated as [9] :

$$\alpha_L = \frac{\xi_p}{2} \frac{\mu_2}{\mu_1^2} \quad (3)$$

where ξ_p is the distance between the source and the observation location. The retardation factor was expressed as [10],[11] :

$$R = \frac{(\mu_1 - 0.5t_0) \sqrt{v_p^2 + 4\alpha_L v_p \lambda}}{x} \quad (4)$$

where t_0 is the pulse duration. In all experiments, t_0 was set to 30 seconds to reflect the injection situation of solute.

The mass fraction of solute was used to estimate the mass recovery fraction (MRF) [8] :

$$MRF = \frac{\int_0^\infty Q(L,t)c(L,t) dt}{\int_0^\infty Q(0,t)c(0,t) dt} \quad (5)$$

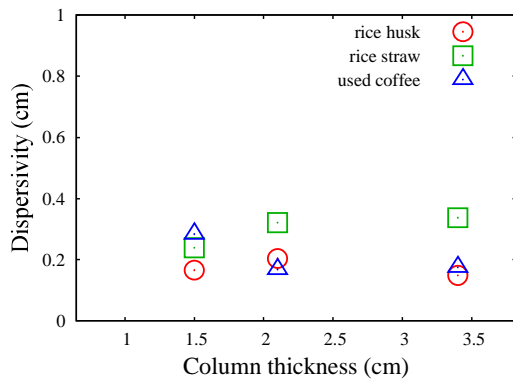


Fig.3 Relation between the column thickness of residues and the dispersivity for nitrate ion

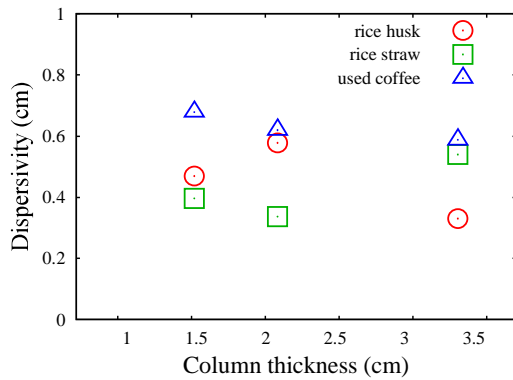


Fig.4 Relation between the column thickness of residues and the dispersivity for chloride ion

where Q is the volumetric flow rate and H is the length of the soil column. The degradation rate constant was also calculated by [7] :

$$\lambda = \frac{1}{\mu_1} \ln\left(\frac{1}{MRF}\right) \quad (6)$$

Prescribed solute source conditions in column experiments was designed to clarify the transient concentrations of nitrate and chloride ions and to effectively provide the parameter identification relevant to solute transport using temporal moment approaches.

4. RESULTS AND DISCUSSION

4.1 Dispersivity of solutes

From the practical viewpoint, larger dispersion of solute is the consequence of significant mixing

or dilution in field. The dispersivity is one of the solute transport parameters that characterizes solute dispersion in porous media [12]. The results of the dispersivities in rice husk, rice straw and used coffee, which were identified based on Eq.(3),

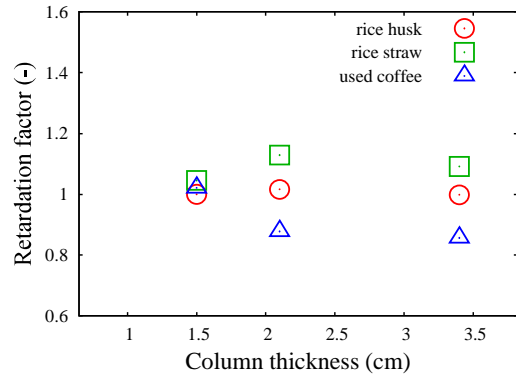


Fig.5 Relation between the column thickness of residues and the retardation factor for nitrate ion

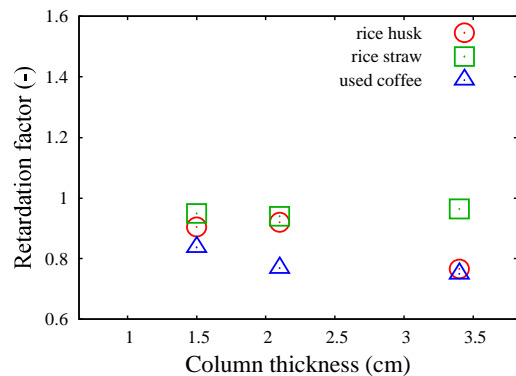


Fig.6 Relation between the column thickness of residues and the retardation factor for chloride ion

in nitrate and chloride ions are shown in Figs. 3 and 4, respectively, as a function of column thickness of each residue. In the column having only silica sand, the values of the dispersivity for nitrate and chloride are 0.16 cm and 0.32 cm, respectively. The mixture of rice husk and rice straw provides an increase tendency of the dispersivity for nitrate ion, while the opposite tendency is shown in used coffee as well as chloride ion. The dispersivity in nitrate ion exhibits lower values than that in chloride ion. This feature reflects that each anion has its own degree of solute spread with respect to mixed agricultural and food residues. The difference of the dispersivity between the anions or the agricultural residues may appear in the outcome of the retardation factor.

Table 2 Results of the mass recovery fraction and the degradation rate.

Column thickness (cm)	Nitrate ion		Chloride ion	
	MRF (-)	λ (hr ⁻¹)	MRF (-)	λ (hr ⁻¹)
<i>Rice husk</i>				
1.5	0.77	0.43	0.44	1.6
2.1	0.95	0.072	0.71	0.50
3.4	0.73	0.50	0.44	1.7
<i>Rice straw</i>				
1.5	1.0	0.	1.0	0.
2.1	1.0	0.	1.0	0.
3.4	1.0	0.	1.0	0.
<i>Used coffee</i>				
1.5	1.0	0.	0.53	1.0
2.1	0.59	0.76	0.59	0.86
3.4	0.56	0.76	0.61	0.65

4.2 Retardation of solutes

In order to quantify the degree of the variation of anion mobility, the retardation factor was employed as a measure and estimated using Eq.(4). The relation between the column thickness of residues and the retardation factor for all residues are shown in Figs.5 and 6, in terms of nitrate and chloride ions, respectively. As seen in Fig.5, the retardation factor in rice husk remains constant value of about 1.0 despite of the mixture of rice husk. This means that no retardation or no sorption occur in porous formations. The retardation factor in rice straw becomes slightly larger than the value of 1.0, indicating that the mobility of nitrate ion decreases during the transport in porous formations. Therefore, from a viewpoint related to the application of rice straw in a field, it is expected that nitrate decomposition by microbes may occur and contribute to the reduction of nitrogen mass in porous media during a transport with retarded velocity.

On the other hand, the results of the nitrate mobility exhibit below the unity in used coffee grounds. This implies the solute transport velocity becomes larger than the seepage velocity in columns filled with used coffee grounds. On average, the used coffee grounds contain up to 15% oil, although the amount of oil in the coffee source depends on its types [13]. It is inferred that surface hydrophobicity of used coffee provides the increase of the velocity of nitrate and results in the lower values of the retardation factor. Rice husk

also has the surface hydrophobicity and may affect the variation of the retardation factor in chloride ion. As a whole, the degree of retardation in nitrate ion is larger than that in chloride ion, indicating that the mobility of chloride ion is higher than that in nitrate ion. At a microscopic level, it is inferred that the degree of reaction between the anion and the surface of residues having a variety of surface structure is substantially different.

4.3 Mass Recovery Fraction and Degradation of Solutes

The change of mass balance is of interest and of significance during a course of transport associated with the mixture of agricultural and food residues. As another quantity of anion transfer, Table 2 summarizes the results of the mass recovery fraction (MRF) and the degradation rate (λ), which were estimated from Eq. (5) and Eq.(6), respectively.

As shown in Table 2, in all experimental cases, values of MRF are less than 1 and the corresponding degradation rate appears as non-zero values. In Table 2, up to 44% and 56% attenuation of the total mass in nitrate can be seen in nitrate and chloride ions, respectively. This implies that part of nitrate or chloride ions may be strongly adsorbed onto the surface of rice husk or used coffee and may be trapped within pores. This is because rice husk and used coffee have a

relatively high surface area [14]. From a practical viewpoint, the degradation of solute mass in a cropland is expected to attenuate the impact on water quality in soils as well as in groundwater. Therefore, the use of agricultural and food residues in soils has a potential to the attenuation of nitrate and chloride ions.

5. CONCLUSIONS

In the present study, the reuse of agricultural and food residues in order to retard and attenuate the impact of nitrate or chloride ions in porous media was assessed through column experiments under saturated flow conditions. Temporal moments associated with observed breakthrough curves were used to quantify the dispersivity, the retardation factor, the mass recovery fraction and the degradation rate. The increase of the mixture of rice husk and rice straw resulted in the slight increase of the dispersivity, while the opposite tendency was shown in used coffee columns. Remarkably, the mobility of anions showed the increase tendency in used coffee columns. Moreover, rice husk and used coffee were found to have a property to decrease the mass balance in both anions. These findings may be attributed to the nature of nitrate and chloride ions having its own degree of solute spread associated with mixed residues.

6. ACKNOWLEDGEMENTS

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Corresponding Author: Kazuya Inoue
