Removal of Nutrients, Organic Matter and Heavy Metals from Paddy Field Drainage by Charcoal

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ABSTRACT

This study examined the ability of charcoal to remove organic matter, nutrients and heavy metals from agricultural drainage. Water treatment equipment containing wood charcoal was installed in a test paddy field. Concentrations of total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP) and heavy metals (Cr, Fe, Zn and Pb) in water samples taken before and after passing through the equipment were analyzed. The equipment was installed simply at the outlet in the test field and removed environmental load substances during a contact time of more than one hour. The reduction rates of TOC and TN ranged from 20 % to 40 %. The reduction rate of TP ranged from 20 % to 90 %. The reduction rates of metals (Cr, Fe, Pb) ranged from 23 % to 62 %. These results suggest that charcoal can be used in water treatment equipment to treat paddy field drainage water.

Keywords: charcoal; contact time; paddy drainage, water treatment equipment

INTRODUCTION

There is concern over the deterioration of water quality due to environmental load substances discharged from agricultural areas. The drainage water from farmland contains dissolved organic matter (DOM) and nutrients. In particular, the agricultural discharge water partly includes recalcitrant organic matter derived from the leaves and stems of plants, which is known to increase chemical oxygen demand (COD) in lakes. The average biochemical oxygen demand concentration (BOD) of total river designated types in Japan in 2007 was 1.5 mg/L, and the average COD of total lakes 3.3 mg/L (Ministry of the Environment, 2008). The percentage achievement was 90.3% for rivers and 50.3% for lakes in 2007 (Ministry of the Environment, 2008). Shiratani et al. (2004) reported that the average nitrogen concentration was calculated at 5.5 mg/L in drainage water from upland fields with fertilizer based on literature data. The DOM tends to combine with heavy metals in the soil or water (Evans, 1989; Kaschl et al., 2002; Wada, 2003), forming complex substances that could contaminate water bodies. Therefore, to conserve the environment of watersheds, such runoff loads from farmland should be removed before they flow out and diffuse into drainage canals.

In this study we focused on wood charcoal as an adsorbent to remove these

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environmental loads since it has recently been attracting attention as a water treatment material. Wood charcoal has a large specific surface area and contains a large number of pores, and so is able to absorb a large amount of substances.

Several studies have been carried out on the adsorption properties of wood charcoal for extracting benzene, iodine, heavy metals and DOM. Hitomi et al. (1993) reported that charcoal carbonized at high temperatures could adsorb benzene vapor and iodine in the gas or liquid phase. Pulid-Novicio et al. (1998) reported that charcoal could adsorb mercury from a solution that included certain heavy metals: mercury, cadmium, zinc and lead. Miura et al. (2007a) examined the adsorption characteristics of charcoal with regard to DOM and reported that charcoal carbonized at high temperatures could adsorb it efficiently.

There have been other studies on using wood charcoal to treat and purify river water (Yatagai et al., 1995; Sakai et al., 1995; Abe, 1994; Arafune et al., 1991). For example, Arafune et al. (1991) performed water purification experiments by placing wood charcoal on the bottom of a river. Sakai et al. (1995) reported on a purification experiment using an up-flow charcoal bed contact treatment plant to investigate its application to the direct purification of river water.

Thus, the adsorption properties of charcoal may be useful for purifying agricultural drainage water, but there have been few such reports to date. In this study, in order to develop a technology to reduce loads from farmland, water treatment equipment containing wood charcoal was devised to enable the charcoal to remove organic matter, nutrients and heavy metals in the drainage from a paddy field, and its effects were investigated *in situ*.

MATERIALS AND METHODS

Test paddy field

The experiment on water treatment for paddy field drainage was conducted in a paddy field at our institute, the National Institute for Rural Engineering of Japan. The area of the field is 1,050 m² (70 m×15 m), and it has an inlet and an outlet. The field was fallow during the experiment. The inflowing water volume was controlled between 1.0×10^{-4} and 3.0×10^{-4} m³s⁻¹ to keep the paddy water depth at approximately 100 mm.

Adsorbent

Wood charcoal (simply called “charcoal” hereafter) was used as the adsorbent for purifying the surface drainage water. The charcoal was made from cedar forest thinnings, which were carbonized at 1,050°C. The charcoal, which was produced in a carbonization factory of a forestry cooperative in Japan, was ground to the consistency of sawdust. The physical properties of the charcoal are shown in Table 1. The specific surface area (surface area of charcoal particles per mass) and pore volume were analyzed using the Brunauer-Emmett-Teller (BET) method. Previous laboratory experiments showed that this charcoal successfully removed DOM in solution with an adsorption rate of 87% within 24 hours (Miura et al., 2007a), and the adsorptive capacity for DOM was equivalent to that of commercial granular activated carbon that is widely available in Japan (Miura et al., 2007b).

Table 1 -Physical properties of the wood charcoal used.

Carbonization temperature (°C)	Specific surface area (m ² g ⁻¹)	Mean pore diameter (nm)	Pore volume (mL g ⁻¹)	Mean particle diameter (mm)
1,050	224.0	2.7	0.12	1.6

Fig.1 - (a) Structure and (b) Sketch of the drainage water treatment equipment

Water treatment equipment using charcoal

The structure of the water treatment equipment is shown in Fig. 1(a). The equipment was 50 cm long, 50 cm wide and 10 cm deep, and consisted of acrylic plates and three nylon net bags (NB90, $\phi 155 \mu\text{m}$, Sogo Laboratory Glass Works Co., Ltd., Japan) containing the charcoal. The water treatment equipment was designed so that the field drainage water was in contact with the charcoal for enough time to remove the loads. The contact time was determined by the inflow rate based on the results of preliminary experiments. Two acrylic-plate partitions divided the interior space of the equipment and were set 16 cm apart at alternate ends of the space. The equipment was thus designed so that paddy drainage water would flow through the equipment in a zigzag pattern, as indicated by the arrows in Fig. 1(b). The nylon net bags containing charcoal were placed one each in the three longitudinal spaces formed by the partitions. In order to reduce clogging of the equipment by biological waste suspended in the drainage water and to ensure the smooth flow of drainage water through the equipment, the volume of charcoal in the nylon net bags was varied from the inlet to the outlet in the equipment. Thus, the filling rate of charcoal in nylon net bags was 50% close to the inlet, 70% in the middle of the course and 90% close to the outlet (Fig. 1 (a)). The total volume of charcoal used in the equipment was 16.8 L (2.7 kg). As shown in Fig. 1 (b), the equipment was installed across the outlet of the field.

Sampling and analysis

The water was sampled once or twice a day (morning/afternoon) nearly every day at locations before and after the drainage water passed through the equipment, as labeled by the IN and OUT points in Fig. 1 (b). Concentrations of total organic carbon (TOC),

total nitrogen (TN), total phosphorous (TP) and heavy metals (chromium = Cr, iron = Fe, lead = Pb and zinc = Zn) in the water samples were analyzed in the laboratory. In this report we analyzed and discussed mainly total elements including dissolved matters, since the removal mechanism was considered to be both adsorption and filtration because of the structure of this equipment. TOC and TN were analyzed by using a TOC analyzer (TOC-V, Shimadzu, Japan), DOM was less often analyzed by using a spectrophotometer (UVmini-1240, Shimadzu, Japan), TP by the persulfate decomposition method and molybdenum by the blue absorption metrical method. The heavy metals were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS, ELAN DRC II, Perkin Elmer, Canada) after total degradation by microwaves. The concentrations of heavy metals were analyzed in sample water collected after 16 days. The flow rates of inflow water and outflow water in the field were measured twice a day, and meteorological data was obtained from a nearby laboratory. Daily data obtained by averaging the morning and afternoon data were used for evaluating the water treatment properties.

The performance of the water treatment equipment was evaluated by the following methods. Firstly, the relationship between the removal rate for TOC, TN, TP, and heavy metals (Cr, Fe, Pb, Zn) and the contact time between the drainage water and the charcoal was analyzed. Secondly, the correlations of the reduction rate, which means removal ratio among the substances, were investigated to identify the effect of interaction among them on the removal characteristics.

RESULTS AND DISCUSSION

Relationship between removal rate and contact time

An optimum contact time between the charcoal and field drainage water in the equipment to achieve efficient removal of loads was investigated. Miura et al. (2007a) reported that in the batch test, the DOM adsorption phenomenon began immediately after charcoal contacted with sample water, and then the initial stage was rapid with the rate becoming gradually lower, and the removal rate was 41% for 15 minutes, 62% for an hour and 87% for 24 hours. In this field experiment, we assumed that the contact time of more than an hour could give valid adsorption efficiency in consideration of flow path length and flow speed, since the drainage was running water. We adjusted the flow rate of field drainage into the equipment to give a contact time of more than one hour. The inflow rate was controlled between 0.07×10^{-4} and $0.6 \times 10^{-4} \text{ m}^3 \text{ s}^{-1}$ in the first 15 days, and at approximately $0.03 \times 10^{-4} \text{ m}^3 \text{ s}^{-1}$ from the 16th day to the end of the test.

Table 2 -Concentrations of TOC, TN, TP, Cr, Fe, Pb, and Zn in the water treatment equipment.

	(mg/L)													
	TOC		TN		TP		Cr		Fe		Pb		Zn	
	IN	OUT	IN	OUT	IN	OUT	IN	OUT	IN	OUT	IN	OUT	IN	OUT
Mean	5.33	4.19	0.56	0.42	0.05	0.02	0.39	0.22	155.43	53.25	0.36	0.24	8.42	7.15
Max.	6.68	5.43	0.74	0.61	0.24	0.05	0.70	0.88	465.57	339.13	0.81	0.77	15.55	14.61
Min.	4.02	3.06	0.45	0.29	0.01	0.01	0.17	0.12	28.11	4.27	0.17	0.08	3.60	2.91
SD	0.70	0.53	0.07	0.06	0.04	0.01	0.15	0.16	112.92	78.46	0.17	0.17	2.93	3.00
CV	0.13	0.13	0.12	0.15	0.74	0.54	0.39	0.72	0.73	1.47	0.46	0.71	0.35	0.42

SD: Standard deviation. CV: Coefficient of variation

The water qualities of inflow water (IN) and outflow water (OUT) of the equipment are shown in Table 2. The number of samples we analyzed were $n=78$ for TOC, TN and TP, and $n=24$ for heavy metals. All the mean concentrations decreased from IN to OUT. The results revealed that the equipment could remove TOC, TN, TP, Cr, Fe, Pb and Zn. Regarding the variations in concentration, the coefficient of variation (CV) in TOC and TN was 0.12 and 0.13 at IN, and 0.13 and 0.15 at OUT, respectively. These variations did not significantly change before and after passing through the equipment. The coefficient of variation in TP was 0.74 at IN and 0.54 at OUT, which were larger than those of TOC and TN. In addition, the CV of TP at OUT was smaller than that at IN. The results showed that the behavior of TP differs from that of TOC and TN in the equipment.

The CVs in heavy metals were larger than those of TOC, TN and TP. Especially, the CV of Fe changed from 0.73 at IN to 1.47 at OUT. The results also suggested that the equipment was able to remove TOC and nutrients more stably than heavy metals.

The relationships between the reduction rate of water quality concentration and contact time are shown in Figs. 2, Figs. 3 and Table 3. The reduction rate was defined as the percentage of the concentration difference at IN and OUT ($IN - OUT$) to that at IN. The reduction rates of TOC and TN ranged from approximately 20% to 40% (approximately 24.7% and 29.0% on average, respectively in TOC and TN) when the contact time was longer than one hour (Fig. 2(a)). The reduction rate for DOM averaged 46% in measured data (not shown). The reduction rate for DOM was larger than that of 20% reported by Arafne *et al.* (2001). The reduction rates of TP ranged from 20 to 90% (approximately 60% on average) (Fig.2 (a)). We could obtain little or no analytical values for the dissolved portion of nutrients because of the test field being without fertilizers.

Additionally, as shown in Fig.3 (a), it seems that the removal mechanism between TOC and TN are related to each other, since variations for both TOC and TN were very similar. In spite of the short contact time (less than an hour), the reduction rate was dominantly high just after starting the test (2nd-3rd days) (Fig.3 (a)). That is considered to be the reason for the high adsorption rate attributed to the pure surface of charcoal.

The reduction rate of TOC in this test was lower than that of the batch test because the TOC average concentration of this drainage water (5.33 mg/L) was lower than the initial TOC in the previous batch test (14.4 mg/L) (Miura *et al.* 2007a). This is because charcoal that has the adsorption characteristics obeying the Freundlich equation (Miura *et al.* 2007a) indicated a high reduction rate at the higher initial concentration in a short period of time.

Moreover, the reason for the higher reduction rate of TP is assumed to be because the soil particles to which the phosphorus was attached were mostly trapped in the nylon net bags. It is known that TP is mainly transported together with soil particles (Suzuki *et al.*, 2005) and Fe in soil.

These results showed that a contact time of longer than one hour was needed for the equipment to achieve a significant removal rate of TOC, TN and TP. However, as the

standard deviation (SD) in TP was larger than those of TOC and TN (Table 3) and the reduction rate of TP was distributed over a wide range (Fig. 2(a)), it is not clear whether the equipment worked stably at a high removal rate in TP.

On the other hand, the reduction rates of the heavy metals Cr, Fe, Pb, and Zn ranged between 11.2% and 61.8% on average when the contact time was longer than one hour (Table 3). Although the mean reduction rate of Fe was the highest among the heavy metals on average, Fe contained in the soil might be removed with soil particles. Furthermore, it was suggested that this water treatment equipment could not remove Zn because the mean reduction rate of Zn was low and SD of Zn was high. Additionally, the removal mechanism of heavy metals seems to be uncorrelated with respect to one another (Fig.3 (b)).

Fig. 2 - Relationship between water contact time and concentration decreasing rate of (a) TOC, TN and TP, and (b) Cr, Fe, Pb, and Zn.

Fig. 3 - Variations of reduction rate for (a) TOC, TN and TP, (b) Cr, Fe, Pb, and Zn, and diurnal variations of contact times during field test.

Table 3 - Mean and standard deviation (SD) of the concentration reduction rate with a contact time of longer than one hour.

	TOC	TN	TP	Cr	Fe	Pb	Zn
Mean	24.7	29.0	60.3	40.6	61.8	23.4	11.2
SD	4.0	3.9	18.5	24.6	53.2	58.2	30.4

SD: Standard deviation

Table 4 - Correlation coefficient among IN concentrations of TOC, TN, TP, Cr, Fe, Pb, and Zn.

	TOC	TN	TP	Cr	Fe	Pb	Zn
TOC	----	----	----	----	----	----	----
TN	0.55 **	----	----	----	----	----	----
TP	0.36	0.48 **	----	----	----	----	----
Cr	0.11	0.13	0.39	----	----	----	----
Fe	0.36	0.47	0.72 *	0.55 *	----	----	----
Pb	0.43 *	0.38	0.34	0.53	0.43 *	----	----
Zn	-0.05	0.16	0.39	0.20	0.48 *	0.46 *	----

*means $p < 0.05$, ** means $p < 0.01$

Table 5 - Correlation coefficient among OUT concentrations of TOC, TN, TP, Cr, Fe, Pb, and Zn.

	TOC	TN	TP	Cr	Fe	Pb	Zn
TOC	----	----	----	----	----	----	----
TN	0.71 **	----	----	----	----	----	----
TP	0.26	-0.01	----	----	----	----	----
Cr	-0.34	-0.41	0.15	----	----	----	----
Fe	-0.04	-0.02	0.75 *	0.33	----	----	----
Pb	-0.34	-0.56	0.19	0.37	0.12	----	----
Zn	-0.30	-0.18	0.35	0.15	0.25	0.20	----

*means $p < 0.05$, ** means $p < 0.01$

Table 6 - Correlation coefficient among reduction rates of TOC, TN, TP, Cr, Fe, Pb, and Zn.

	TOC	TN	TP	Cr	Fe	Pb	Zn
TOC	----	----	----	----	----	----	----
TN	0.88 **	----	----	----	----	----	----
TP	0.04	0.25	----	----	----	----	----
Cr	-0.06	0.21	0.54 *	----	----	----	----
Fe	-0.16	0.11	0.42 *	0.50 *	----	----	----
Pb	-0.14	0.56 *	0.60 *	0.46 *	0.09	----	----
Zn	0.19	0.10	0.19	0.29	0.10	0.35	----

*means $p < 0.05$, ** means $p < 0.01$

In summary, the equipment could remove TOC, TN, TP, Cr, Fe and Pb in the field drainage when the contact time was longer than one hour. In addition, it is thought that the removal is filtration at the portion of inlet and outlet and at the boundary of nylon nets bags with charcoal, and is adsorption when drainage water contacts the surface of charcoal because of the structure of this equipment.

Relation of removal ability among substances

As the removal ability of a substance may be affected by other substances, we investigated the correlation of reduction rates among substances. The correlation coefficients of the concentration at IN and OUT, and the reduction rates among TOC, nutrients and metals are shown in Table 4, 5 and 6.

The correlation coefficient between TOC concentration and TN concentration at IN was 0.55 and was significant at the 1% level ($n = 78$, $p < 0.01$) (Table 4). Similarly, that of OUT was 0.71 (Table 5). Moreover, there was a high correlation coefficient between the TOC reduction rate and the TN reduction rate, and it was significant at the 1% level ($n = 78$, $p < 0.01$) (Table 6). These results indicated that there was a high relationship for the concentration variations between TOC and TN before and after passing through this water treatment equipment. Moreover, the correlation of concentration in Table 4 and 5 was reflected in the correlation of reduction rate in Table 6. These results suggested that the equipment might remove both TOC and TN.

There were a high correlation between TP concentration and Fe concentration at IN and OUT, respectively (Table 4 and 5). The correlation coefficient between the TP reduction rate and the Fe reduction rate was quite a high value (Table 6). These suggested that TP was removed with soil particle and Fe in soil. Although the correlation coefficients of the Cr reduction rate to the Fe reduction rate and the Pb reduction rate were significant at the 5% level ($n = 24$, $p < 0.05$), the mutual removal mechanism for these metals was not clear in these results. Zn removal was not correlated with the removal of any substances.

On the other hand, the correlation coefficients of the TOC reduction rate to heavy metal reduction rates were not significant at the 5% level.

CONCLUSIONS

Water treatment equipment containing wood charcoal as an absorbent was designed, and its ability to remove organic matter, nutrients, and heavy metals in a test paddy field was investigated. The following results were obtained:

- (1) The TOC, TN, TP, Cr, Fe and Pb in the drainage from the paddy field were significantly removed by the equipment when the drainage contact time with the charcoal absorbent was longer than one hour.
- (2) The reduction rates of TOC and TN ranged from 20% to 40% (approximately 24.7% and 29.0% on average, respectively).
- (3) The removal efficiency and the concentrations at IN and OUT for TOC had high correlations with that of TN.
- (4) The reduction rate of TP ranged from 20% to 90% (approximately 60% on average).
- (5) The reduction rates of metals (Cr, Fe, Pb) ranged from 23.4% to 61.8%.
- (6) The removal efficiency and the concentrations at IN and OUT for TP had significant correlations with that of Fe.

In order to understand the mutual removal mechanism for water quality items, we need to discuss the removal properties based on major factors such as initial concentration of water quality item at IN, chemical property for charcoal and heavy metals in soil and water, and so on. Since heavy metals are known to be transported in water combined with DOM, the removal of heavy metals linked with DOM needs to be studied further.

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