Practical Use of Charcoal as a Remediation Material for Cadmium-polluted Soil

Asa Miura¹*, Eisaku Shiratani²

¹Department of Science and Mathematics Education, University of Fukui, Japan
²National Institute for Rural Engineering, Tsukuba city, Japan

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Abstract The purpose of this study is to examine the practical usage of charcoal as a biomass remediation material for cadmium (Cd) polluted soil in the environment. In the field application of this material, it is necessary to consider handling methods and the environmental impact of the used materials. The following types of experiments were conducted in this study: (1) heavy metals competitive removal in solution, (2) condition of Cd re-elution from Cd-adsorbed charcoal in solution, and (3) Cd re-elution from Cd-adsorbed charcoal left in columns of soil and charcoal for long periods. The competitive removals depended on the concentrations of heavy metals. All heavy metals included in the low-level concentration were removed by charcoal efficiently. Although 65–100% of the Cd adsorbed by the charcoal was desorbed by strongly acidic water (pH 1.5), 0.8–1.6% was desorbed by water with a pH of 4.5, equivalent to the pH of acidic rain. The Cd re-elution rates from columns by both acidic and distilled water were low immediately after beginning the experiments and were not detected after two and three months. Therefore, these three experiments demonstrated the possibility of simultaneously removing two or more heavy metals by using the charcoal, processing the contaminated charcoal by using strong acids, and allowing the contaminated charcoal to stay in the environment safely for long periods.

Keywords Competitive Adsorption, Heavy Metals, Rainfall Intensity, Re-elution, Used Charcoal

1. Introduction

Environmental pollution in Asia has increased along with economic development. During periods of high economic growth, farmland in Japan was contaminated by cadmium (Cd), which is a toxic heavy metal that has diffused in the soil. The soil in several regions in Japan still contains unhealthy levels of this metal. Generally, farmlands are located near industrial land that houses refineries; therefore, Cd concentrations in the agricultural areas in Japan are higher than those in other countries. That is, toxic heavy metals are included in products themselves and in byproducts. If improper disposal methods, such as illegal waste-dumping or mixing into domestic garbage, are followed, heavy metals could leach into the environment. Toxic heavy metals are dissolved into ions by precipitation and can be discharged into underground water, rivers, or oceans. In particular, because Cd is easily absorbed by crops, this toxin can enter the human body and bioaccumulate via oral intake of contaminated plants.

To ensure a stable supply of safe foods, it is important for proper farmland standards to be observed and for the health of water/soil environments to be maintained. The Cd concentration is regulated by the Japanese temporal standard. In addition, countermeasures unrelated to the government standards have been adopted. These include water management methods in wet-rice cultivation, technical methods such as the soil dressing method, and phytoremediation [1, 2]. Soil-washing technology has also been further studied [3]. In Japan, new, effective technical methods have been discussed for reducing the Cd concentration in agricultural crops. Current methods for removing heavy metals from solution have been studied. One method involves the use of ion exchange resins [4], whereas another involves the creation of solid-state compounds by ferritization of solutions with high-levels of heavy metals [5-7]. However, because these methods are neither cost effective nor practical, other techniques should be considered.

The development of environmental remediation material with a low environmental impact is one such measure. In this technique, charcoal can be used as a biomass remediation material for Cd-polluted soil in the environment. Recently, some research on metal adsorption from water or soil by biomass has been observed [8-10]. These reports have shown that biochar derived from various materials, such as plant residuals, animal fecal material, and sludge, retain the metals adsorption capacity.
Wang et al. [11] reported on the repair of heavy metal-contaminated soils with charcoal derived from bamboo, rice hulls, and animal excreta, but when these biochar were applied to the site, problems, such as varying properties with time and the environmental impact of charcoal, have not been discussed. Xu et al. [12] have discussed the adsorption and desorption of charcoal to Cd in paddy soils. However, it was not assumed that the construction would be carried out on the actual site, and no experiments have been conducted in consideration of weather conditions, such as rainfall.

In our previous study, we proposed a method for enabling the control of Cd adsorption in farmland soil by using charcoal to protect crops from Cd contamination; the effects were observed by crop cultivation experiments [13]. In the present study, several considerations are addressed in greater detail that must be discussed before this method is adopted for practical use. These factors include competitive adsorption of heavy metals, re-elution from materials containing Cd, and re-elution into the environment due to rainfall when such materials are applied to soil and remain for lengthy periods. In this study, such considerations were investigated and discussed by conducting three laboratory experiments.

2. Materials and Methods

2.1. Adsorbent

Charcoal was used as the remediation material in the present study because its heavy-metal-adsorption ability was confirmed in our previous experiments [13]. This charcoal was created using thinned cedar wood (Cryptomeria japonica) carbonized at 1050°C to produce granules with diameters of 1–5 mm. The pH level of the charcoal is 8.2. The physical properties of the charcoal are shown in Table 1.

2.2. Laboratory Experiments

2.2.1. Competitive Removal of Heavy Metals (Experiment 1)

Metal ions are adsorbed at same site on the adsorbent if the charge number of the ions is the same. Thus, Cd, lead (Pb), copper (Cu), and zinc (Zn) were prepared in aqueous solutions at the following concentration levels: low (0.02–0.5 mg L⁻¹), high (1–10 mg L⁻¹), and medium (0.5–5 mg L⁻¹). Each prepared 100 mL solution was stirred with acidic water (pH level of 6.8), for 1 h. Preliminary experiments revealed no correlation between contact times and Cd re-elution event. The re-elution events from the charcoal depended on the pH level rather than stirring time, which explains the relatively short stirring time. After 1 h, the samples were immediately filtered using funnels to begin experiment 2 and were analyzed by atomic emission spectrophotometer (Thermo Fisher Scientific K.K., iCAP6300Duo View).

2.2.2. Cd re-elusion (Experiment 2)

Investigation of Cd concentrations re-eluted from charcoal is necessary if such charcoal that contains traces of Cd remains in the environment for a lengthy period. Two types of used charcoal were employed in Experiment 2. The first originally held Cd to determine its adsorption level, and the second held a mixture of Cd and Cu, also to measure adsorption. To prepare the used charcoal, 3 g samples were washed by distilled water were placed in a bottle containing 300 mL of solution containing 1 mg L⁻¹ of Cd and in another bottle containing both 1 mg L⁻¹ of Cd and 10 mg L⁻¹ of Cu. The solutions in the bottles were stirred continuously at 125 rpm for 24h at 25°C ±1°C. The solutions were then separated into solid and liquid components through funnels. The separated charcoal grains were dried at 80°C in a dry oven for 24 h. Thus, the concentrations of the charcoal using Cd and Cd/Cu were made using 0.98 mg Cd per 1 g of charcoal and 0.97 mg Cd and 9.94 mg Cu per 1 g charcoal, respectively.

Each type of charcoal was stirred with acidic water prepared at pH levels of 1.5, 3.5, 4.5, and 5.5, in addition to distilled water (pH level of 6.8), for 1 h. Preliminary experiments revealed no correlation between contact times and Cd re-elution event. The re-elution events from the charcoal depended on the pH level rather than stirring time, which explains the relatively short stirring time. After 1 h, the samples were immediately filtered using funnels to begin experiment 2 and were analyzed by atomic emission spectrophotometer (Thermo Fisher Scientific K.K., iCAP6300Duo View).

2.2.3. Column Experiment (Experiment 3)

Investigation of Cd re-elution affected by rainfall intensity or soil moisture is necessary if the charcoal is applied to the soil. Column experiments were conducted as shown Figure 1. A 1cm, 7 g layer of charcoal was placed in columns between two 9 cm layers of soil. We used commercial vegetable cultivation soils in the column experiments. Glass beads were placed at the bottom of column to prevent soil particles from mixing into the water sample. Cd adsorption by the charcoal in this experiment was conducted by a similar method as that in Experiment 2. A 10g sample of charcoal was stirred into a 60 mg L⁻¹ Cd solution at 125 rpm for 24h at 25°C ±1°C, and the separated solid Cd-adsorbed charcoal (used charcoal) was employed for the column experiments. 5.94 mg of Cd was adsorbed onto the charcoal layer in the column. Drops of water were applied to the soil surface from top of the column. The flow volumes assumed two patterns for rainfall intensity, 10 mm h⁻¹ and 100 mm h⁻¹, as shown in Table 2. The samples were collected once per
day during three successive days. Two column equipment sets were prepared according to the respective rainfall intensities. Moreover, samplings under soil moisture conditions were alternately conducted between nonsaturation and saturation conditions for each rainfall intensity condition. Cd concentrations in the samples were analyzed using an atomic emission spectrophotometer (Thermo Fisher Scientific K.K., iCAP6300Duo View).

### Table 1. Physical properties of charcoal used as adsorbent in this study.

| Carbonized temperature (°C) | Mean particle diameter (mm) | Mean pore diameter (nm) | Pore volume (ml·g⁻¹) | Specific surface area (m²·g⁻¹) |
|-----------------------------|-----------------------------|-------------------------|----------------------|-------------------------------|
| 1,050                       | 1.41                        | 2.7                     | 0.12                 | 224                           |

![Figure 1. Diagram of column used in Experiment 3.](image)

### Table 2. Physical properties of charcoal used as adsorbent in this study.

| Rainfall intensity (mm h⁻¹) | Conditions of soil layers          |
|-----------------------------|-----------------------------------|
| [ Flow volume of drops ] (mL h⁻¹) | a. | b. |
| 10                          | Nonsaturation | Saturation |
| [ 42 ]                      |               |
| 100                         |               |
| [ 392 ]                     |               |

### 3. Results and Discussion

#### 3.1. Competitive Removal of Heavy Metals (Experiment 1)

Each concentration level of the initial solution for Experiment 1 was prepared as shown Table 3. The competitive removal rates of the heavy metals from the mixed solutions by the charcoal depended on the concentrations of heavy metal ions in the solutions. All ions were effectively removed from the solution containing low-level of heavy metals ions; however, not all the ions were removed from the high-concentration solution. These results are shown in Figures 2 (a) and (b).

After the charcoal was in contact with the solutions containing low-level heavy metal ions for 0.25h, the removal rate for all types of heavy metals was 80% (Figure 2(a)). After 48h, removal rates for heavy metals exceeded 90%. Thus, the charcoal efficiently removed the heavy metals in the low-level concentration.

In the case of the high-level solution, the removal rate for all heavy metals was less than 7% 12h after beginning the experiment (Figure 2 (b)). The removal rates for Cu and Pb rose to 10% after 24h, which was maintained through 48h. Those for Cd and Zn were 0% after 48h. Moreover, the types of heavy metals mixed in the high-concentration solution were reduced from four elements (Cd, Pb, Cu, and Zn) to two (Cd and Cu). These results indicated that the removal effectiveness of the two heavy metals by charcoal differed from that of the four. The removal rates for both Cd and Cu were more than 95% at 24h. Further competitive removal experiments should be conducted to consider the differences in concentration patterns.
The charcoal removed all four heavy metals from the solution with low-level concentration. Conversely, the removal effects of charcoal varied in the high-level solution depending on the types of heavy metals contained in the solution.

The heavy metals removal rates from the solution with medium-level concentration were also determined (Figure 2 (c)). The removal rates for both Cu and Pb were approximately 30%, which is a larger percentage than that observed with the high-level concentration. Cd was removed slightly, and Zn was not removed at all. These results suggest that threshold solution levels exist for adsorbing all four elements by charcoal.

It is possible for metal ions with equivalent charges to be adsorbed on the same adsorbent between metal ion scramble sites. Machida et al. [14] reported that Cu and Pb were competitively adsorbed on the activated carbon from the mixed solution. The decrease in adsorption rate in highly concentrated solutions may be attributed to the area occupied by the heavy metals molecules adsorbed on the charcoal adsorption sites. It was reported that heavy metals in solution form hydrates with diameters of 10–18 Å [15, 16]. Higher concentrations of heavy metals contained in the solution result in a larger amount of heavy metal ion molecules. Therefore, the concentration of the adsorption solution may be a reason for the decrease in adsorption rate. Moreover, it is considered that the occupied area and the electrostatic repulsion between the heavy metals remarkably influence this decrease. These results indicate that simultaneous adsorption of multiple heavy metals is expected when the heavy metal concentration in the solution is low. Conversely, cases of high concentration should consider the adsorbed volume by charcoal per 1 g and the combination of heavy metal type and multiple heavy metal concentration. To approach practical application in the presence of several heavy metals, the concentration of heavy metals in solution should be determined to enable to Cd adsorption.

Table 3. Initial concentrations of solutions in experiments 1 (Unit: mg L⁻¹)

| Concentration level | Cd | Cu | Zn | Pb |
|---------------------|----|----|----|----|
| Low                 | 0.2| 0.2| 0.5| 0.02|
| High                | 1  | 10 | 10 | 2  |
| Medium              | 0.5| 5  | 5  | 1  |

3.2. Cd re-elution (Experiment 2)

The concentrations of Cd and Cu in the re-elution water from two types of the used charcoal are shown in Figures 3 (a) and (b). Water with a pH of 1.5 could remarkably elute Cd from both pollutant charcoals. In particular, the Cd re-elution rate was higher from the used charcoal with Cd/Cu (Figure 3 (b)) at nearly 100% from that with Cd at 65% (Figure 4(a)).

The Cd re-elution rates decreased dramatically for both the charcoal types used, when in contact with water having a pH of 3.5 or more. The re-elution rate for Cd was 7–8%, and that for Cu was approximately 0.1%. Increasing the pH level resulted in decreased Cd re-elution rates, which indicates that used charcoal cannot be re-eluted unless exposed to strongly acidic water. Water at pH of 4.5 (equivalent to acidic rain) yielded re-elution rates of 0.8–1.6% from both types of charcoal. The Cd re-elution rate with distilled water was approximately 1%.

The results of Experiment 2 showed similar characteristics for heavy metal elution by water with a pH of less than 2 from ferrite products used to treat polluted with heavy metal ions [7]. Moreover, these results nearly corresponded with those reported by Fujiwara et al. [17] in which a re-elution test was conducted with bamboo charcoal adsorption of Zn by strongly acidic water. In that experiment, the Zn re-elution rate was 90% for water with a pH of 2 and less than 20% for that with a pH of 4, indicating a remarkable decrease. Such acidic treatment can re-elute heavy metals ions of hydroxide heavy metals remaining in the adsorbent [5, 6]. The similar results obtained in Experiment 2 indicated that the mechanisms for heavy metal re-elution from charcoal were similar to those of ferrites. Moreover, the acidic treatment may have caused changes in the surface charges of the used charcoal. Machida et al. [18] reported that heavy metals ions present in solutions with large pH ranges are altered by the pH level of the solution, as are their formations. The surfaces of activated carbon are altered by the pH of the solution in a similar manner. Therefore, it is considered that the surfaces of the used charcoal in this study and the formation of heavy metal ions in the solution were altered by the pH of the solution, thereby changing the adsorption/desorption rates.

The results obtained in Experiment 2 suggest that even if the charcoal were in contact with acidic rainfall, the potential of re-elution from the used charcoal after use in situ would not be likely. On the contrary, the charcoal used as an adsorbent to Cd in situ may be disposed of after separation of the heavy metals by acid treatment for detoxification.
3.3. Column Experiments for Application to Soil (Experiment 3)

The elution water from the columns was sampled every 24h for 3 consecutive days immediately after starting Experiment 3. The Cd re-elution rates per 100 mL volume in sample water for rainfall intensities of 10 mm h\(^{-1}\) and 100 mm h\(^{-1}\) are shown in Figures 4 (a) and (b), respectively.

Regardless of soil water conditions, all rates of Cd re-elution from the used charcoal were less than 0.1% (Figure 4). The re-elution rates under nonsaturated conditions were higher than those under saturated conditions (Figures 4 (a) and (b)). That is, the magnification ratio of the rate of Cd re-elution in the nonsaturation case was approximately twice that of saturation with 10 mm h\(^{-1}\) rainfall intensity and approximately 7 times that with 100 mm h\(^{-1}\) rainfall intensity. Therefore, Cd was not easily eluted under saturation conditions by higher rainfall intensity or under the nonsaturated conditions by lower rainfall intensity. These indicate that Cd can be accumulated in the environment if a considerable amount is re-eluted from nonsaturated soil by a rainfall of high intensity.

Moreover, the elution water from the same columns after 1 month were sampled every 24h for 3 consecutive days; results are shown in Figure 5. We have examined the cases of rainfall intensities for nonsaturated soil because of the concern of Cd re-elution under such conditions. The results indicated that the Cd re-elution rates were less than those observed after starting Experiment 3 for both rainfall intensities (Figures 5 (a) and (b)). Additionally, it was confirmed that the re-elution water sampled after two and three months did not contain Cd (Figures 6 (a) and (b)).

According to the results of Experiment 3, it is believed that the oxidation–reduction potential was lowered under saturation conditions. Therefore, it is considered that the form of Cd re-eluted from charcoal in soil pore water could form compounds such as cadmium sulfide (CdS), which could lead to a decrease in the aqueous Cd state in sample water [2]. Moreover, it is believed that Cd re-elution from charcoal was suppressed because the re-eluted Cd from charcoal was re-adsorbed onto the soil grains.

A three-month monitoring period indicated a gradual decrease in Cd re-elution, which amounted to 0% by the end of the period. Therefore, concerns about the release of accumulated elution into the environment are resolved.
Figure 4. Elution rate from used charcoal measured immediately after beginning Experiment 3 relative to rainfall intensities of (a) 10 mm h\(^{-1}\) and (b) 100 mm h\(^{-1}\).

Figure 5. Elution rate from used charcoal measured one month after beginning Experiment 3 relative to rainfall intensities of (a) 10 mm h\(^{-1}\) and (b) 100 mm h\(^{-1}\).

Figure 6. Elution rate from used charcoal measured two and three months after beginning Experiment 3 relative to rainfall intensities of (a) 10 mm h\(^{-1}\) and (b) 100 mm h\(^{-1}\).
4. Conclusions

In this study, charcoal was examined for practical usage in the field as a remediation material for Cd contamination by conducting three evaluation experiments. The results are summarized in the following points:

1. In the presence of Cd in solution along with multiple heavy metals, a simultaneous adsorption of all such heavy metals was observed, if the solution has a relatively low concentration level. Further, the selective adsorption characteristics of the charcoal depend on the combination of types and concentrations of heavy metals contained in the solution.

2. If the pH level of the solution in contact with the used charcoal is more than 3.5, the re-elution rate is suppressed to 10% or less. Thus, it is suggested that the heavy metal re-elution rate can decrease if the solution is directly exposed to rain water of 6–7 pH or acidic rain of 4.5 pH. The normal processing of used charcoal is possible after contact with a strong acid with a pH of less than 1.5 to separate the heavy metals from the charcoal.

3. If the charcoal remains in environmental soil for a lengthy period, the Cd re-elution rate is less than 0.1%, according to the column experiment results, and the contaminant was not detected after two and three months. Therefore, it is suggested that even if the used charcoal were to remain in the environment for a long period, concerns of environmental recontamination by Cd re-elution from used charcoal are allayed.

The results of these evaluation tests of charcoal in this study validate its practical application. As topics for future research, the shape of the charcoal to be utilized must be determined, and the possibility of utilization in places other than agricultural land should be examined. A future goal is to achieve the construction of a regional resource recycling system. Local biomass resources to be discarded as waste should be treated as environmental materials used to restore regions such as agricultural, mining, and manufacturing areas. Therefore, it is expected that charcoal utilization will be employed in Japan and in other countries as a countermeasure for similar pollution problems.

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