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Adsorptivity of heavy metals Cu^{II}, Cd^{II}, and Pb^{II} on woodchip-mixed porous mortar

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HIGHLIGHTS

- Woodchip-mixed porous mortar (WPM) was developed.
- Cation exchange capacity of WPM is twice as large as that of wood chips.
- WPM can adsorb 23 times the amount of Cd^{II} as can wood chips.
- Speciation of Cu, Cd, and Pb adsorbed to WPM allows control of elution behavior.
- WPM maintains high adsorptivity for Cu, Cd, and Pb even after immersion for 1 year.

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ABSTRACT

Here, we developed a woodchip-mixed porous mortar (WPM) by mixing wood chips obtained from thinned Japanese cedar wood with porous mortar aggregates and evaluated the adsorption properties of the heavy metal ions Cu^{II}, Cd^{II}, and Pb^{II} on the WPM. The cation-exchange capacity (CEC) of cup-shaped WPM was approximately twice as large as that for wood chips. The saturation adsorption capacity of WPM for the heavy metal ions Cu^{II}, Cd^{II}, and Pb^{II}, determined by passing an aqueous solution of heavy metal ions, was 6, 23, and 7 times as much, respectively, as wood chips alone. Furthermore, the elution behavior of heavy metal ions adsorbed by WPM was studied by fractionation, wherein the metal speciation was divided into five classes by a sequential extraction method. The leached percentage of Fractions 1 and 2 combined, corresponding to the more easily eluted species of Cd^{II}, was higher than those of Cu^{II} and Pb^{II}. Finally, we found that the immersion of flat WPM in pure water and 3% sodium chloride for 1 year did not degrade the sample, which maintained its high adsorption capacity for heavy metal ions.

1. Introduction

With the revitalization of industrial activities over recent years, scrap wood has emerged as a major form of waste that is discharged into Japan's environment, with approximately 1500 t generated annually. Scrap wood can be classified as: (1) wood chips and bark generated from sawmills, (2) residual wood materials such as packaging materials generated from plants, (3) discarded wood materials generated in the construction of new buildings and the demolition of existing structures, and (4) unused wood chips generated from the thinning and felling that is related to forest maintenance [1].

To make use of this scrap wood, a multistage (cascade) procedure has been recommended in which wood waste is first put to one use and then the remainder is used for another purpose. For example, disassembled scraps from lumber products and wood scraps are converted into chips, which are then used to manufacture particle board [1] and bark compost [2,3]. In addition, such scraps could be carbonized for use in controlling moisture under the floors of houses, eliminating odors in a room, or adsorbing hazardous chemical substances [4]. The remaining degraded materials can then be converted into pellets [5] and fuels such as bioethanol [6], completing the multistage recycling process.

In this context, one approach to effectively utilizing unused wood waste is to convert it into an adsorbent for heavy metal environmental pollutants. For example, the application of aspen and maple sawdust as heavy metal adsorbents has been investigated, utilizing the metal adsorption properties of lignin and cellulose contained in the wood [7–12].

We have investigated the heavy metal ion adsorption properties of wood chips generated from the wood waste of Japanese cedar

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grown in Gunma Prefecture. Wood chips and sawdust have large surface areas and numerous sites capable of forming complexes with heavy metal ions, such as phenolic hydroxyl groups and aromatic carboxyl groups in lignin, which is one of the principal components of wood. There have been reports on the use of industrial wastes for adsorption of heavy metals. These include the woody biomass of peat and activated char [13], rice hulls, wheat husks, straw [14–19], brewer's yeast [20], brewer's refuse [21], and coffee beans [22–25]. As these technologies have low environmental loads and allow industrial wastes to be returned to the earth, they are useful for cleaning soil that is heavily contaminated with heavy metals. However, direct spraying of the waste makes it difficult to recover post-adsorption, presenting problems to the multistage procedure described above.

In this study, we developed a woodchip-mixed porous mortar (WPM) for utilization near an area in Gunma Prefecture (Fig. S1 in Supplementary Material), where it has been used on walking trails in hot spring resorts and in filters for acidic hot springs, to achieve easier collection of waste that adsorbs heavy metals. We fabricated cylindrical WPM and determined its cation exchange capacity (CEC), adsorption ratio, and saturation adsorption capacity for Cu^{II}, Cd^{II}, and Pb^{II} ions. Furthermore, to predict the potential elution of heavy metal ions adsorbed by WPM, the sequential extraction method [26] was used to identify five classes of heavy metal ions based on the ease with which they were leached out. We then determined the abundance ratio of each fraction to predict the speciation of heavy metal ions adsorbed by the WPM. Finally, a flat WPM plate was immersed in pure water and aqueous sodium chloride for an extended period of time (1 year), resulting in the leaching of calcium ions. The variations in the adsorption properties of WPS for heavy metal ions within the immersion period were investigated.

2. Experiments

2.1. Reagents

Water purified with a water distillation apparatus (ASK-2DS, Iwaki) was used to prepare aqueous solutions and to test the adsorption of heavy metal ions. All reagents were purchased from Wako Pure Chemical Industries. All stored solutions containing metal ions were acidified with nitric acid to pH < 1. Separate stock solutions were prepared by measuring a precise amount of copper (II) sulfate pentahydrate, cadmium (II) acetate dihydrate, and lead (II) acetate such that they contained 1×10^{-4} M of each heavy metal ion. The pH was adjusted using 0.1 M solutions of sodium hydroxide and nitric acid. Stock solutions of 0.1 M barium chloride dihydrate, 0.2 M magnesium sulfate heptahydrate, and 10 mg L^{-1} lanthanum nitrate hexahydrate were prepared for use in determining the CEC of the WPM samples.

2.2. Adsorption of heavy metal ions by wood chips

Japanese cedar wood chips generated in forest maintenance operations were supplied by Gunma Prefecture's Forestry Cooperative and sifted with a sieve to collect particles with a diameter less than 5 mm as test specimens. For the heavy metal ion adsorption tests for wood chips, 50 mL of solution containing 2×10^{-6} to 1×10^{-4} M of heavy metal ions and 0.1 g of wood chips was added to a 100 mL Erlenmeyer flask. The flask was sealed with a stopper and immersed in a temperature-controlled water bath (thermoregulated water bath, Iwaki CTR-330, Iwaki) at 30 °C for 60 min and stirred with a magnetic stirring bar. The filtrate of the mixture was then collected and analyzed by a polarized Zeeman effect flame atomic absorption spectrophotometer (AAS; Z-5310, Hitachi) to determine the concentration of heavy metal ions. 0.01 M 3-morpholinopropanesulfonic acid was added as a buffer to the solution, and the pH was adjusted within the range of 2.0–7.0 by a portable pH meter (F-22 pH meter, Horiba).

To determine the saturation adsorption capacity of wood chips for heavy metal ions, Eq. (1) for a Langmuir adsorption isotherm was modified to Eq. (2), in which $1/q_e$ on the left-hand side was plotted against $1/C_e$, yielding a linear plot that was extrapolated to intersect the y-axis and provide the intercept:

$$q_e = \frac{Q^0 b C_e}{1 + bC_e} \tag{1}$$

and

$$\frac{1}{q_e} = \frac{1}{Q^0 b} \cdot \frac{1}{C_e} + \frac{1}{Q^0} \tag{2}$$

where q_e is the amount of the heavy metal adsorbed per unit weight of the adsorbent (mol g^{-1}), C_e is the equilibrium concentration of the heavy metal bulk solution (mol L^{-1}), Q^0 is the monolayer adsorption capacity (mol g^{-1}), and b is the constant related to the free energy or net enthalpy of adsorption ($b \propto e^{-\Delta H/RT}$). Accordingly, Q_0 calculated from Eq. (2) indicates the saturation adsorption capacity.

2.3. Preparation of WPM

River sand (particle size: 0.2–1.0 mm), wood chips (maximum particle size: 5 mm), cement, and tap water were mixed, stirred, and fed into a mold for fabrication into a flat plate 300 × 300 × 60 mm in size using a vibration press. This mixture was cured at ambient temperature to form the WPM. Subsequently, 100-mm-long and 50-mm-thick flat plates were cut after the water content of the cement reached approximately 30%. The chemical compositions of the cement were determined by X-ray fluorescence analysis. The compositions were 60% Ca, 23% Si, 5.0% Al, 2.2% S, 2.0% Fe and 1.9% Mg. The flat WPM plate was then cut into a filter cup 10 cm in both diameter and height (Fig. S1). The tested materials were sand:woodchip:cement in the ratios of 4:0:1, 0:4:1, and 2:2:1, as mentioned in Supplementary Materials. Control samples composed of concrete only (sand and cement), of cement and wood chips, and of sand, cement, and wood chips were defined as Samples 1, 2, and 3, respectively.

2.4. Cation exchange capacity

The CEC values of the samples were determined based on the Standard for Soil Quality Testing (ISO 11260) recommended by the Japanese Geotechnical Society. The details are described in Section 2 in the Supplementary Material.

2.5. Adsorption of heavy metals by WPM

A sample was placed on the experimental apparatus illustrated in Fig. S2. Five hundred milliliters of 1×10^{-5} M heavy metal ion solution, prepared by mixing aqueous Cu^{II}, Cd^{II}, and Pb^{II} solutions, was introduced to the top of the sample such that the aqueous solution was allowed to pass through. The filtrate was collected, and the concentration of heavy metals was determined by AAS. The heavy metal absorption ratio was calculated using Eq. (3):

$$\text{Adsorption ratio}\ (\%) = \left(\frac{C_0 - C_r}{C_0}\right) \times 100 \tag{3}$$

where C_0 is the initial concentration of heavy metal and C_r is the concentration of heavy metal remaining in solution after passing through the WPM test samples.