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Adsorption Behavior of Heavy Metals on Biomaterials

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We have investigated adsorption of Cd(II) and Pb(II) at pH 2−6.7 onto the biomaterials chitosan, coffee, green tea, tea, yuzu, aloe, and Japanese coarse tea, and onto the inorganic adsorbents, activated carbon and zeolite. High adsorptive capabilities were observed for all of the biomaterials at pH 4 and 6.7. In the adsorption of Cd(II), blend coffee, tea, green tea, and coarse tea have comparable loading capacities to activated carbon and zeolite. Although activated carbon, zeolite, and chitosan are utilized in a variety of fields such as wastewater treatment, chemical and metallurgical engineering, and analytical chemistry, these adsorbents are costly. On the other hand, processing of the test biomaterials was inexpensive, and all the biomaterials except for chitosan were able to adsorb large amounts of Pb(II) and Cd(II) ions after a convenient pretreatment of washing with water followed by drying. The high adsorption capability of the biomaterials prepared from plant materials is promising in the development of a novel, low-cost adsorbent. From these results, it is concluded that heavy metal removal using biomaterials would be an effective method for the economic treatment of wastewater. The proposed adsorption method was applied to the determination of amounts of Cd(II) and Pb(II) in water samples.

KEYWORDS: Plant materials; Cd(II); Pb(II); blend coffee; tea; green tea; coarse tea; zeolite; activated carbon; yuzu; aloe; chitosan

INTRODUCTION

In the field of aquatic environment, the study of toxic metals has been known to cause severe health problems to animals and human beings (*1*). The removal of heavy metals from river water, lake water, and wastewater is a crucial issue of concern to health. Several methods have been proposed for the removal of heavy metals (e.g., ion exchange, filtration, coagulation and adsorption). Materials including ion-exchange resin, membrane filters, hafnium hydroxide, activated carbon (*2*), chelating resin, and porous polymer beads have been employed in these methods; however, these materials are expensive (*3*, *4*).

Recently, the use of cheap agricultural wastes such as rice straw (*5*), bark (*6*), Japanese green tea (*7*), wool, and coconut husks have been highlighted as potential adsorbents for metal removal from wastewater. Minamisawa et al. (*8*, *9*) have used chitin and chitosan for the adsorption of metals such as Cu, Co, Au, and Mn ions. Chitin is universally present in the exoskeletons of arthropods and manufactured in large scale from crab and shrimp shell wastes. Chitin and chitosan are nontoxic and readily biodegradable and hence are environmentally acceptable. Y. Orhan and Buyukbungor (*10*) and G. Macchi (*11*) have reported that Turkish coffee, used coffee after extraction of coffee brew, and nut and walnut shells were useful for heavy metal removal. However, these agricultural materials have to be chemically treated prior to use as adsorbents, which proves costly. In a previous paper (*12*), we demonstrated that Cu(II) and Cd(II) were almost completely removed from aqueous solution by use of roasted coffee beans that had been pretreated simply by washing with water and drying. Thus, roasted coffee beans offer potential as a new low-cost material for the removal of heavy metals. For example, in Japan, coffee beans in the form of green beans are consumed at the rate of about 39000 tons/year, and the demand for coffee surpasses that of citrus fruit or Japanese tea. The used coffee grounds, green tea, tea, and coarse tea left after preparation of these beverages is almost completely disposed of as waste.

Herein, we report the adsorption of Cd(II) and Pb(II) onto various adsorbents including chitosan, activated carbon, coffee bean, zeolite, green tea, tea, yuzu, aloe, and coarse tea, to

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discover cheap and tractable biomaterial adsorbents that exhibit high efficiency in the removal of heavy metals.

EXPERIMENTAL PROCEDURES

Materials. Coffee beans from KEY Coffee Ltd. (Japan), KIMITSU chitosan Grade-F powder from Kimitu Chemical Industries (Japan), green tea, tea, coarse tea, epidermis powder from yuzu (citrus junos), and aloe (Aloe aruborescens) from Shizen Chiyuryoku Lab. (Japan), natural zeolite from Tochigi-pre. (Japan), and activated carbon powder from Wako Pure Chemicals (Japan) were employed as adsorbents.

Green tea, tea, and coarse tea were used after extracting with hot water and air-drying. Blend coffee was prepared from four coffee beans: Brazil, Columbia, Guatemala coffees from the arabica species, and Indonesia robusta coffee from the robusta species. The beans were treated at five roasting temperatures and times as follows: light roast (190∼215 °C for 10 min), medium roast (190∼215 °C for 15 min), city roast (200∼230 °C for 15 min), full city roast (200∼240 °C for 15 min), and French roast (200∼250 °C for 18∼20 min). The preparation procedure of coffee beans is described in a previous paper (*13*).

Aqueous solutions of Cd(II) and Pb(II) were prepared by diluting standard solutions (1 g L^{-1} in 0.1 M HNO_3; Wako Pure Chemicals) and were used for atomic absorption spectrometry. All other reagents were either analytical or extra-pure reagent grade.

Adsorption Experiments. Adsorption experiments were carried out by batch method. A 1-g amount of each adsorbent (coffee, green tea, tea, coarse tea, yuzu, aloe, chitosan, activated carbon, and zeolite) was added to 200 mL of 10 mgL^{-1} Cd(II) or Pb(II) nitrate solution. These metal solutions had been adjusted to pH 2, 4, or 6.5−6.7 with diluted nitric acid or ammonia water. The suspension was stirred for 24 h on a magnetic stirrer and separated by a membrane filter with pore size 0.45 μm. The amount of adsorption of Cd(II) and Pb(II) onto the adsorbents was determined by measuring the concentration of metals in the resulting filtrate on an SAS 7500 Seiko instrument (Japan) atomic absorption spectrophotometer. IR spectra were recorded with a Jasco FT/IR-420 Fourier transform infrared spectrophotometer (Japan) by KBr method.

Adsorption experiments using sample solutions of river water, experimental wastewater, and rainwater were performed as follows: The sample solutions were filtrated with a membrane filter (pore size, 0.45 μm) to remove suspended particles, and the filtrate was acidified to pH 1 with nitric acid and stored in a polyethylene bottle. A 1-g sample of coffee or activated carbon was added to the sample solution (500 cm^3), and the mixture was adjusted to pH 5.5 with aqueous ammonia then stirred for 24 h on a magnetic stirrer. Cd(II) or Pb(II) ions were also added to the sample solutions as an internal standard to determine the metal recovery. After separation of the adsorbents from the mother solution by membrane filter, the adsorbent was carefully transferred into a test tube with stopper. The adsorbed heavy metals were dissolved with 5.0 cm^3 of 0.1 mol dm^{-3} acetic acid by stirring with a test tube mixer, and the adsorbent was removed from suspension by filtration. The amount of adsorption of Cd(II) and Pb(II) onto the adsorbents was determined by measuring the concentration of metals in the resulting filtrate by atomic absorption spectrophotometry.

RESULTS

Effect of pH on Adsorption Behavior. The effect of pH on the adsorption behavior of Cd(II) and Pb(II) onto nine types of adsorbents is shown in **Figures 1** and **2**, respectively. **Figure 1** indicates that chitosan is effective in the uptake of Cd(II) ion over a restricted pH range and that several biomaterials exhibited considerable adsorption over the pH range 4−6.7.

The Pb(II) in aqueous solution (**Figure 2**) was almost completely removed at pH 2 by an aloe and at pH 4 by several other biomaterials. Thus, Pb(II) was demonstrated to be powerfully adsorbed onto these biomaterials at comparatively low pH; whereas adsorptivity of Cd(II) varied widely over the neutral region, depending on adsorbent, but was most effective at pH 6.7. The optimum working pH range for adsorption of Cd (II)

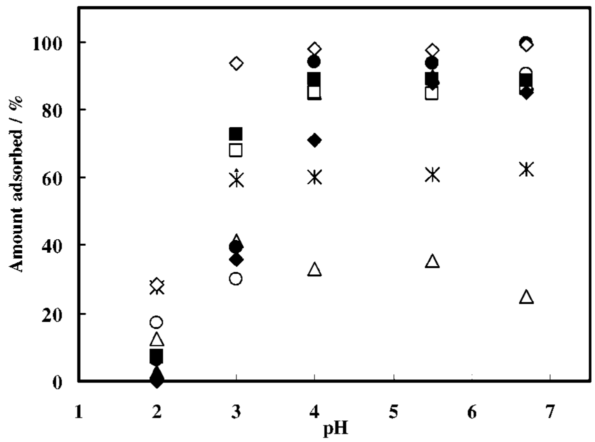

Figure 1. Effect of pH on the adsorption of Cd(II) onto the adsorbent. Sample solution of 200 mL containing Cd(II) of 2 mg was adjusted to various pHs with diluted nitric acid or ammmonia water. The suspension with the adsorbent of 1 g (▲, coarse tea; △, aloe; *,yuzu; □, green tea; ○, chitosan; ■, tea; ●, coffee; ◇, zeolite; ◆, A. C.) was stirred for 24 h at room temperature.

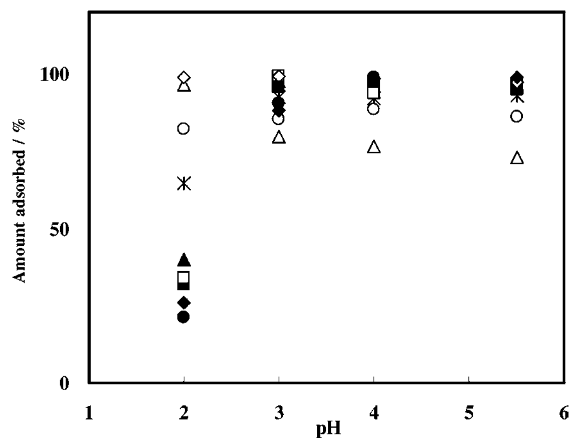

Figure 2. Effect of pH on the adsorption of Pb(II) onto the adsorbent. Sample solution of 200 mL containing Pb(II) of 2 mg was adjusted to various pHs with diluted nitric acid or ammmonia water. The suspension with the adsorbent of 1 g (▲, coarse tea; △, aloe; *,yuzu; □, green tea; ○, chitosan; ■, tea; ●, coffee; ◇, zeolite; ◆, A. C.) was stirred for 24 h at room temperature.

onto biomaterials was, therefore, set at pH 6.7 for every solution. The pH of the metal ion solution thus significantly affects the degree of metal adsorption. The Pb selectivity of aloe is conspicuous, and the selective removal of Pb(II) is possible at lower pH than it is for other biomaterials. The Pb(II) ion solutions were prepared at pH 2 for aloe and at pH 4 for the other biomaterials.

Comparison of Adsorbents. Figures 3 and **4** depict the time courses for adsorption of Cd(II) at pH 6.7 and Pb(II) at pH 2 and pH 4 on the biomaterials. Adsorption of Cd(II) and Pb(II) proceeds rapidly on most materials and reaches an adsorption ratio of over 80% after 20 min, after which equilibrium is established in about 40 min. Adsorption ratios of coffee and coarse tea were greater than those of activated carbon (A. C.) and zeolite, especially; in the case of Cd(II), absorbance ratios for coffee and chitosan exceeded 90% before 20 min. The amount of Cd(II) adsorbed increased in the following order: coffee and chitosan (97%) > coarse tea, tea, and green tea (87−91%) > A. C., zeolite (80−85%) > yuzu (58%) > aloe (24%).

From **Figure 4**, it is apparent that metal adsorption of Pb(II) onto biomaterials progressed very rapidly, reaching over 95%

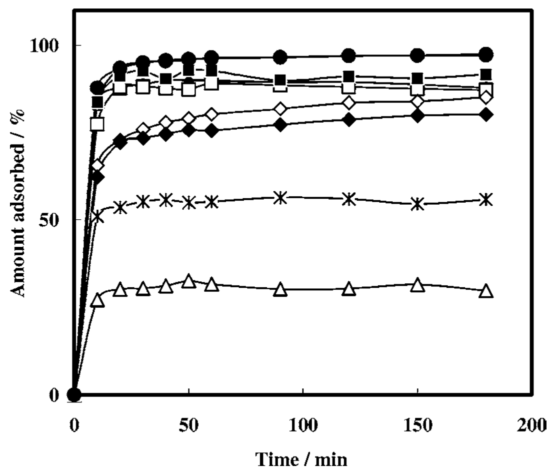

Figure 3. Time-course of Cd(II) adsorption at pH 6.7 on the biomaterials. The adsorption experiments were carried out by a batch method. A 1-g sample of each biomaterial (▲, coarse tea; △, aloe; *,yuzu; □, green tea; ○, chitosan; ■, tea; ●, coffee; ◇, zeolite; ◆, A. C.) was added to 200 mL of sample solution containing Cd(II) 10 mg L^{-1} adjusted at pH 6.7 with ammonia water. The suspension was stirred for 180 min at room temperature.

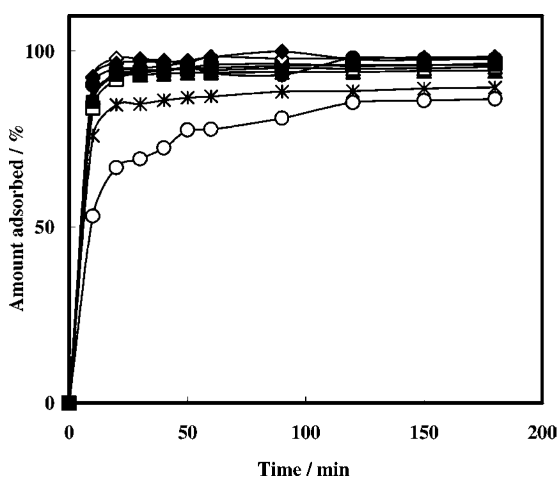

Figure 4. Time-course of Pb(II) adsorption at pH 4 on the biomaterials. The adsorption experiments were carried out by a batch method. A 1-g samlple of each biomaterial (▲, coarse tea; △, aloe; *,yuzu; □, green tea; ○, chitosan; ■, tea; ●, coffee; ◇, zeolite; ◆, A. C.) was added to 200 mL of sample solution containing Pb(II) 10 mg L^{-1} adjusted at pH 4 with ammonia water. The suspension was stirred for 180 min at room temperature.

after 10−20 min for coffee, tea, aloe, and coarse tea along with the nonbiomaterials A. C. and zeolite. Adsorption of Pb(II) onto chitosan and yuzu was 10% less than that of other biomaterials.

Adsorption Isotherms. The adsorption isotherms of Cd(II) were investigated with regard to biomaterials using an electrolyte solution at the optimum pH = 6.7. Adsorption capacities (q), the amount (mg) of adsorbed metal per weight (g) of biomaterials, were determined from eq 1 (*12*)

$$q = (C_0 - C)/W \tag{1}$$

where C_0 and C are the initial and the final metal concentrations of the solution (mg/200 mL), respectively, and W is the amount (1.0 g/200 mL) of biomaterial.

The Langmuir and Freundlich's adsorption isotherms are generally applicable in the case of monomolecular adsorption of a single species from a liquid phase to a solid phase (*14*).

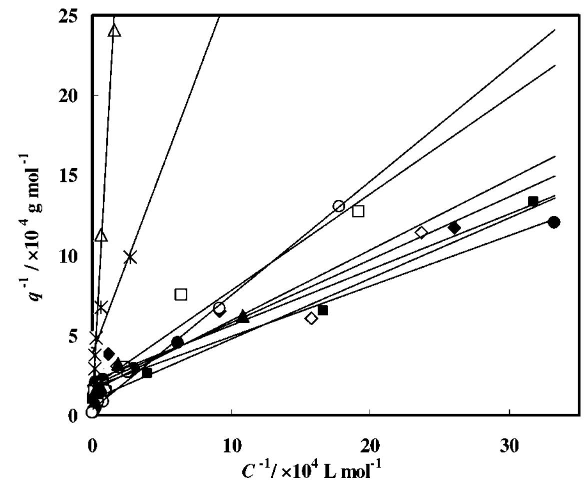

Figure 5. Langmuir plots for Cd(II) adsorption at pH 6.7 on the biomaterials (▲, coarse tea; △, aloe; *,yuzu; □, green tea; ○, chitosan; ■, tea; ●, coffee; ◇, zeolite; ◆, A. C.). Units for q and c are mol · g^{-1} and mol · L^{-1}, respectively.

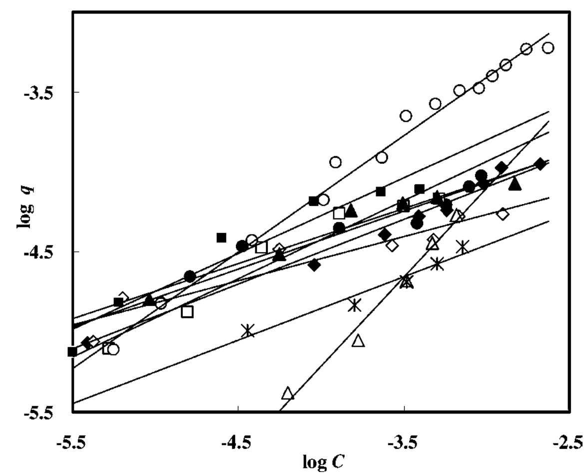

Figure 6. Freundlich plots for Cd(II) adsorption at pH 6.7 on the biomaterials (▲, coarse tea; △, aloe; *,yuzu; □, green tea; ○, chitosan; ■, tea; ●, coffee; ◇, zeolite; ◆, A. C.) Units for q and c are the same as those in **Figure 5**.

Langmuir and Freundlich adsorption isotherms can be expressed by eqs 2 and 3, respectively.

$$\frac{1}{q} = \frac{1}{b} + \frac{1}{bKc} \tag{2}$$

$$q = kc^{1/n} \tag{3}$$

where q is the amount adsorbed (mol·g^{-1}), c is the residual amount of solute in solution (M), K is the adsorption equilibrium constant (L·mol^{-1}), b is the maximal adsorption capacity, and k and $1/n$ are arbitrary parameters. The Langmuir (2) and Frendlich (3) adsorption isotherms of Cd(II) and Pb(II) ions on several biomaterials are shown in **Figures 5** and **6** and **Figures 7** and **8**, respectively. The parameters obtained from both isotherms are also summarized in **Table 1**. The Langmuir and Frendlich adsorption isotherms exhibit an approximately linear relationship for all biomaterials. The value of K is large, and $1/n$ is 0.1−0.5, indicating that the adsorbents employed have a high adsorptive capability (*8*, *9*).

The adsorption ability (k) for Cd(II) increased in the following order: aloe > chitosan > tea > green tea > A. C. > coffee > coarse tea > coarse tea > yuzu > zeolite. The maximal

Table 1. Adsorption Parameters for Cd(II) and Pb(II) Adsorptions on the Biomaterials

	Cd(II) pH 6.7				Pb(II) pH 4			
	parameters							
	Langmuir		Freundlich		Langmuir		Freundlich	
adsorbents	K/L mol^{-1}	b/mol g^{-1}	k/mol g^{-1}	$1/n$	K/L mol^{-1}	b/mol g^{-1}	k/mol g^{-1}	$1/n$
coffee	5.48×10^4	5.76×10^{-5}	1.06×10^{-3}	0.36	4.14×10^4	7.98×10^{-5}	7.45×10^{-3}	0.53
coarse tea	3.46×10^4	6.55×10^{-5}	9.46×10^{-4}	0.34	4.52×10^4	1.02×10^{-4}	3.65×10^{-3}	0.46
tea	2.61×10^4	1.01×10^{-4}	4.09×10^{-3}	0.47	1.93×10^3	8.61×10^{-4}	3.32×10^{-3}	0.42
green tea	2.92×10^4	5.67×10^{-5}	3.33×10^{-3}	0.48	6.10×10^4	1.16×10^{-4}	3.83×10^{-3}	0.43
A. C.	4.55×10^4	5.53×10^{-5}	1.31×10^{-3}	0.4	4.15×104	$1.0^3 \times 10^{-4}$	1.68×10^{-3}	0.38
zeolite	6.18×10^4	4.63×10^{-5}	3.62×10^{-4}	0.27	6.73×10^3	9.96×10^{-4}	5.79×10^{-2}	0.61
yuzu	1.62×10^4	2.67×10^{-5}	5.38×10^{-4}	0.39	2.94×10^4	6.60×10^{-5}	2.55×10^{-3}	0.48
chitosan	4.43×10^3	3.16×10^{-4}	5.79×10^{-2}	0.72	1.57×10^4	1.16×10^{-4}	3.76×10^{-2}	0.71
aloe	69.38	9.28×10^{-4}	0.17	1.11	1.29×10^4	8.60×10^{-5}	3.98×10^{-3}	0.51

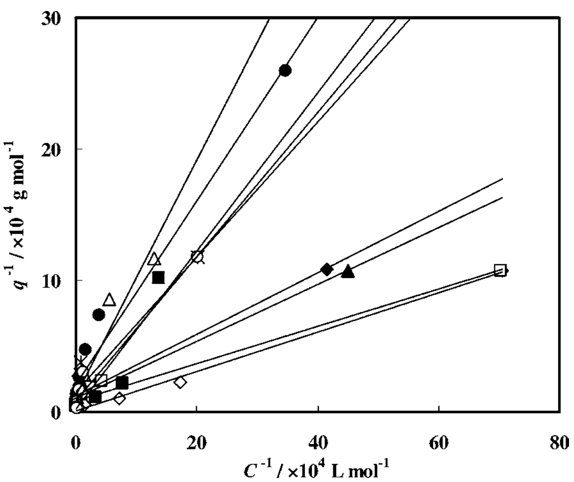

Figure 7. Langmuir plots for Pb(II) adsorption at pH 4 (at pH 2 for Aloe) on the biomaterials (▲, coarse tea; △, aloe; *,yuzu; □, green tea; ○, chitosan; ■, tea; ●, coffee; ◇, zeolite; ◆, A. C.). Units for q and c are mol•g^{-1} and mol•L^{-1}, respectively.

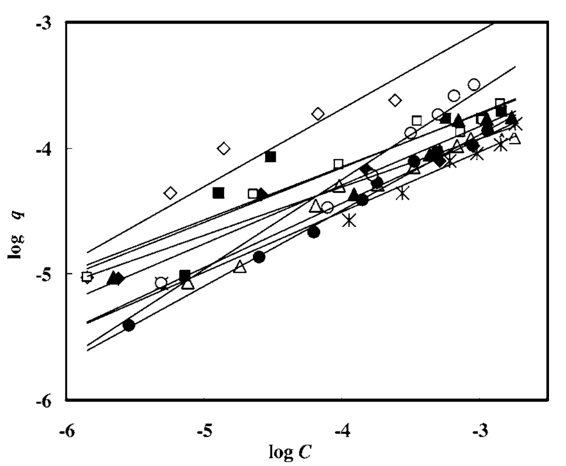

Figure 8. Freundlich plots for Pb(II) adsorption at pH 4 (at pH 2 for Aloe) on the biomaterials (▲, coarse tea; △, aloe; *,yuzu; □, green tea; ○, chitosan; ■, tea; ●, coffee; ◇, zeolite; ◆, A. C.). Units for q and c are the same as those in **Figure 7**.

adsorption amount capacity (b) of biomaterials increased in the following order: aloe > chitosan > tea > coarse tea > coffee > green tea > A. C.> zeolite > yuzu. In regard to cadmium adsorption, the adsorbents with both large k and b values were coffee, tea, and green tea. Chitosan and aloe have large b and k values but very large $1/n$ values. Thus, coffee, tea, and green tea were effective adsorbents for Cd ion removal.

For Pb(II) adsorption, the b values for all materials and the $1/n$ values for all materials besides aloe and zeolite were similar to the values for Cd(II) adsorption. The maximal adsorption amount capacity (b) for Pb(II) increased in the following order: zeolite > tea > chitosan, green tea > A. C., coarse tea > aloe > coffee > yuzu. It is particularly interesting that the b values of coffee, green tea, coarse tea, A. C., yuzu, and tea were 1.3−8.5 times those for Cd(II). Coffee, coarse tea, zeolite, and yuzu also display large values for the other parameters for Pb(II). With regard to chitosan and aloe, adsorption parameters for Cd(II) were larger than those for Pb(II), but both $1/n$ parameters were highest among the biomaterials. The 1/n is an indication of the affinity between adsorbent and adsorbate. Its value is 0.1−0.5, indicating that the adsorbents employed have a high adsorptive capability. Thus, for Pb ion removal, it was clarified that coffee, tea, coarse tea, and green tea of the plant biomaterials in comparison with activated carbon (A. C.) and zeolite of inorganic material were effective adsorbents.

The adsorption behavior of the plant biomaterials varies considerably, and the materials can be divided into three basic groups: (A) coffee, (B) tea, coarse tea and green tea, and (C) aloe, yuzu, and chitosan. Group A displayed good adsorption parameters for both Cd(II) and Pb(II) adsorption, although it displayed only moderate b values. The adsorption behaviors of group B were affected by pH in comparison with the other groups, and the adsorption parameters were better for Pb(II) than for Cd(II). In group C, although the adsorption rate was comparatively slow, for chitosan and aloe, the amount of Cd(II) adsorbed was remarkably larger than that of Pb(II). In addition, only the adsorbents of group C efficiently adsorbed the metals under pH 2−3.

Characterization of Biomaterials. In the present work, it was found for the first time that adsorbents prepared from plant materials such as coffee, coarse tea, tea, green tea, yuzu, and aloe have a large adsorptive capability for removing Cd(II) and Pb(II) ions. The adsorption ability of the biomaterials was above or equivalent to that of zeolite, chitosan, and activated carbon. The three patterns of adsorption behavior described above suggest the biomaterials contain different active components, and thus IR absorption spectrophotometry was performed to characterize these components.

Figures 9−11 show the IR absorption spectra of coffee (A), tea (B), and yuzu (C), respectively. The absorption bands at 3400, 2950, and 2850 cm^{-1} are assigned to O−H bonds of macromolecular association, $-CH_2$- bonds, and O−H stretching vibrations, respectively. The doublet peak at 2920−2880 cm^{-1}, which appeared strongly for coffee, may be due to the C−H stretching vibrations of methylamine, $N-CH_3$. The sharp peak observed at 1740 cm^{-1} for coffee and yuzu is considered to be

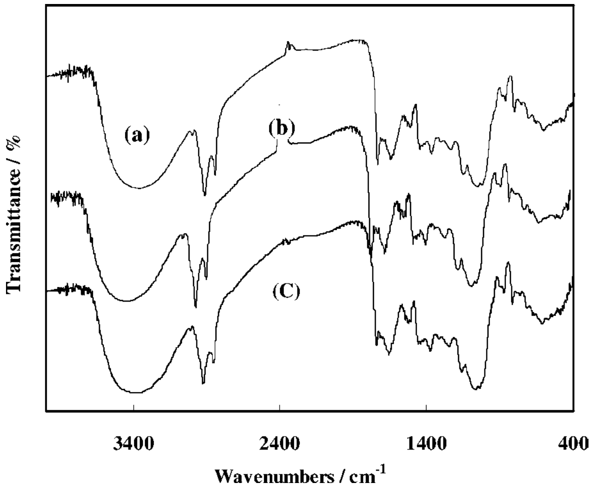

Figure 9. FT-IR spectra of (**a**) metal-free coffee bean, (**b**) Cd(II), and (**c**) Pb(II) adsorbed coffee beans were recorded with a Jasco FT/IR-420 Fourier transform infrared spectrophotometer (Japan) by KBr method.

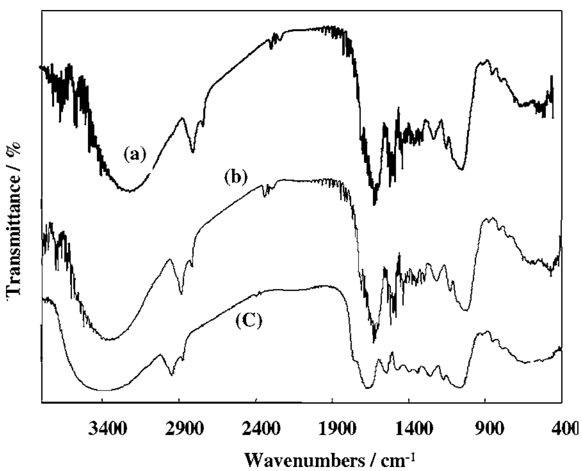

Figure 10. FT-IR spectra of (**a**) metal-free tea, (**b**) Cd(II), and (**c**) Pb(II) adsorbed tea were recorded with a Jasco FT/IR-420 Fourier transform infrared spectrophotometer (Japan) by KBr method.

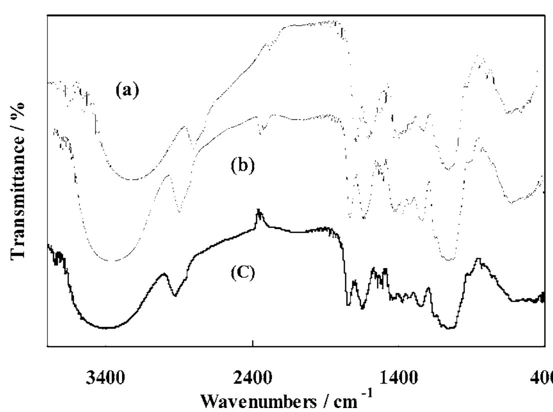

Figure 11. FT-IR spectra of (**a**) metal-free yuzu, (**b**) Cd(II), and (**c**) Pb(II) adsorbed yuzu were recorded with a Jasco FT/IR-420 Fourier transform infrared spectrophotometer (Japan) by KBr method.

due to a C═O bond of a carboxylic acid or its ester. The strong peak that appears at 1660−1650 cm^{-1} for all biomaterials is the C═O stretching vibration of a carboxylic acid that exists in an intermolecular hydrogen bond. All the absorptions at 3400, 2950, 2850, 1740, and 1660−1650 cm^{-1} shifted to higher wavenumber with adsorption of Cd(II) and Pb(II) and were nonmultiply divided (*21*) compared with those of metal-free biomaterials. From these findings, it is presumed that the heavy metal ion is incorporated within the biomaterial or inorganic material through interaction with the active groups OH, COOH, and NH_2.

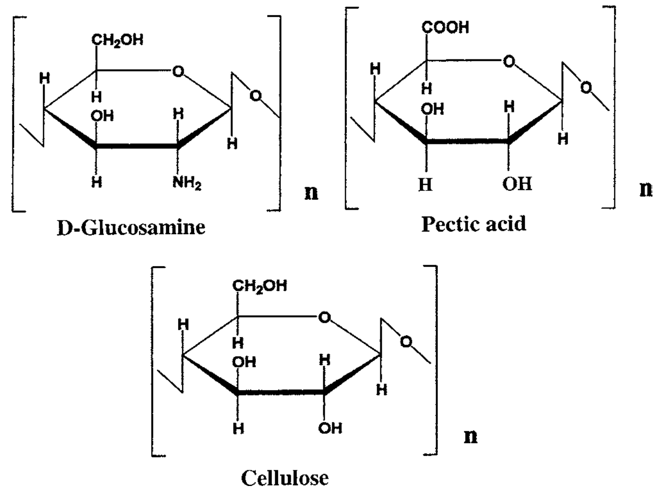

Figure 12. Chemical structure of the adsorbents derived from the plant derivation.

DISCUSSION

Relationship between the Adsorption Behavior and Adsorbent Components. The three patterns of adsorption onto plant biomaterials are attributable to the active components of these biomaterials. **Figure 12** shows the chemical structure of the biomaterials. The plant biomaterials consist essentially of cellulose. The tea, coarse tea, and green tea also contain catechin along with amino acids and caffeine (*16*, *17*). Coffee is composed of cellulose and alkaloids such as trigonelline, quinolinic acid, tannic acid, nicotinic acid, and caffeine (*18*).

The IR spectra of the tea species' display O−H bonds of macromolecular association, consistent with cellulose, and the $-CH_2-$ bond, O−H, and NH_2 groups observed are consistent with catechin. The coffee IR spectum reveals COOH groups and indicates hydrogen bond formation between carboxylic OH, $N-CH_3$, and phenolic OH groups, which are derived from the cellulose, proteins, and alkaloids in the coffee. These biomaterials seem to be acting as acid-type ion exchangers, because adsorption of Pb(II) and Cd(II) onto tea, coarse tea, green tea, and coffee hardly progressed under pH 2−3 (*16*, *17*).

On the other hand, adsorption of heavy metals onto yuzu, aloe, and chitosan did proceed at pH 2−3. The adsorption behavior of yuzu and aloe was similar to that of chitosan, a poly-D-glucosamine, which is prepared by deacetylation of the natural polymer chitin (*19*, *20*), which can be extracted from crustacean shells. Since chitosan is easily dissolved in acidic solution (*21*, *22*) the adsorption of metal ions onto chitosan may be due to the interaction with the amino group of the 2-amino-2-deoxy-D-glucose (glucosamine) unit. Thus, chitosan exhibits adsorptive activity at low pH (*23*).

The yuzu and aloe employed in this work contain D-glucosamine and pectic acid and are also highly soluble in acid. Pectic acid is an acidic polysaccharide with a carboxyl group, mainly found in citrus and seaweed. Chitosan, in contrast, is a basic polysaccharide with a primary amine. The absorption at 1740 cm^{-1} of yuzu, aloe, and chitosan (*24*), due to C═O and N−H bonds, clearly differs from that of coffee or tea. The interaction of the carboxyl group of pectic acid with the heavy metal leads to coordination between the pyranose ring oxygen and the metal ion, and a stable chelate comprising five rings is formed (*25*). Though the IR absorption of all biomaterials shifted

Table 2. Adsorptive Characteristics of Coffee Beans in Natural Water and Wastewater

sample (500 cm^3)	Cd(II)					Pb(II)				
	added amt μg	found μg	recovery %	RSD[a] %	A.C[b]	added amt μg	found μg	recovery %	RSD[a] %	A.C[b]
river water[c]	0	N. D.		3.2 (n = 3)	N.D	0	N. D.		3.5 (n = 3)	N.D
	1	0.98	98			1	0.97	97		
	5	4.92	98			5	4.97	99		
rainwater[d]	0	N. D.		3.8 (n = 3)	N.D	0	N. D.		4.4 (n = 3)	N.D
	1	1.01	101			1	0.99	99		
	5	4.97	99			5	5.01	100		
experimental wastewater[e]	0	14.2		4.2 (n = 3)	14.3	0	18.6		3.6 (n = 3)	18.5
	5	19.6	101			5	23.5	102		
	15	29.2	99			15	33.6	100		

[a] Relative standard deviation. [b] Activated carbon. [c] Kitakamigawa, Morioka Iwate, Japan. [d] Saginumadai, Narashino, Chiba, Japan. [e] Tokyo College of Medico-PharmacoTechnology, Tokyo, Japan.

to higher wavenumber after adsorption of the heavy metal (*26*), the degree of shift for the Pb(II) and Cd(II) adsorbed onto yuzu was more remarkable than that for the biomaterials, and the amount of Pb(II) adsorbed was considerably higher than that of Cd(II). Metal adsorption on yuzu and aloe occurred over a wide pH range, from a strongly acidic to a neutral solution.

These results suggest that biologically active components such as catechin in tea, the alkaloid components in coffee beans (*13*, *27*), and D-glucosamine and pectic acid in yuzu or aloe contribute to the adsorption of Cd(II) and Pb(II). The effect on the adsorption of heavy metals of these components seems greater than that of the biomaterial matrix cellulose.

Application to Determination of Cd(II) and Pb(II) in Water Samples. To investigate the metal adsorption capability of biomaterials in environmental water samples, the Cd(II) or Pb(II) content after addition of the adsorbent materials to river water, experimental wastewater, and rainwater was determined. **Table 2** gives the adsorptive characteristics of coffee residue compared to activated carbon. Cd and Pb were not detectable in the original river water and rainwater samples by means of atomic absorption spectroscopy, and thus each metal was added. The coffee residue adsorbent was found to almost completely recover the metals in the natural water samples. In the case of the experimental wastewater containing relatively large amount of Cd and Pb, both metals were adsorbed effectively, and the amounts of metals adsorbed were similar to the amounts adsorbed by activated carbon. The known amounts of Cd(II) and Pb(II) added to the sample solutions were nearly quantitatively recovered by the coffee residue. The method described here has the advantages of simplicity, rapidity, and a high concentration factor on the preconcentration procedure and is applicable to the determination of the amounts of Cd(II) and Pb(II) in wastewater samples.

Conclusion. The biomaterial residues derived from plants by extraction with hot water were found to effectively adsorb heavy metals from aqueous solution. Cd(II) and Pb(II) were removed rapidly from aqueous solutions containing these metals. The adsorption capacity of the plant biomaterials was comparable to that of chitosan, activated carbon, and zeolite, and the adsorption behavior was affected by the variety of plant and the pH. Chitosan, yuzu, and aloe dissolved easily in acidic solution (pH 2−4) and hence gave a high adsorption ratio for Cd(II) and Pb(II), respectively. Among the biomaterials investigated, coffee had the highest complexation ability with these heavy metals.

These results demonstrate the great potential of plant biomaterial residues, which are currently discarded and could provide a convenient and low-cost adsorbent of heavy metals. The heavy metal removal technique using such biomaterials would be an effective method for the economic treatment of wastewater.

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