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Removal of cadmium and copper by vegetable biomass treated with hydrochloric acid

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ABSTRACT

Food waste is discharged abundantly, and while some of it is reused, most is incinerated. The recycling of soybean waste and wheat bran as vegetable biomass needs to become established, and the ability to remove Cd^{2+} and Cu^{2+} by vegetable biomass needs to be estimated. The estimations performed here revealed that the amounts of Cd^{2+} and Cu^{2+} adsorbed onto untreated vegetable biomass were larger than those adsorbed onto defatted biomass. This indicates that the adsorption of Cd^{2+} and Cu^{2+} onto vegetable biomass may depend on fat content. On the other hand, the elution percentage of vegetable biomass increased as the concentration of hydrochloric acid increased. The elution is due to the degradation of protein in the biomass by the acid. The amounts of Cd^{2+} and Cu^{2+} adsorbed decreased as more than 0.10 mol/L of the concentration of hydrochloric acid increased. Cd^{2+} and Cu^{2+} are adsorbed on vegetable biomass by their adsorption onto protein. The amounts of Cu^{2+} adsorbed onto soybean waste and wheat bran in a binary-solution system are larger than those in a single-solution system. However, less Cd^{2+} was adsorbed onto wheat bran in the binary system than in the single one. These results indicated that the amount of Cu^{2+} adsorbed increases in the presence of Cd^{2+}. Either the adsorption of Cd^{2+} onto wheat bran is inhibited by Cu^{2+} or the adsorptions of Cd^{2+} and Cu^{2+} onto the biomass were affected by each other.

1. Introduction

It is well known that Cd^{2+} is found in vegetables, fruits, seafood, meats and especially rice. Because the Japanese eat a lot of rice, they consume more Cd^{2+} than do Europeans or Americans. The standard level of Cd^{2+} in tap water is strictly regulated in many countries to be less than 0.01 ppm, above which it may damage the kidneys. For example, it has caused itai-itai disease in the past. On the other hand, Cu^{2+} is a mineral that is naturally found in the human body and is a necessary microelement. Its standard level in tap water is less than 1.0 ppm. It participates in hematopoietic functions, mainly the synthesis of hemoglobin. Too little may cause hemolytic anemia, and too much may lead to fractures or hepatocirrhosis.

A Japanese law for food recycling and reuse, enacted in April 2001, mandates the utilization of food waste as compost, fodder, soil revised material, and so on. The discharge quantity of soybean waste (bean curd lees) in Japan is about 700 thousand t/year, whereas the amount of wheat produced in the world is about 589 million t/year. Removal of Cr^{6+} from aqueous solution using wheat bran was reported [1]. The adsorption mechanism of Cr^{6+} was in the initial stages sorption was due to the boundary layer diffusion whereas in the later stages sorption was due to the intraparticle diffusion. Some soybean waste is composted and used as fertilizer for agriculture, but most of it is incinerated, releasing carbon dioxide and thus contributing to global warming. More appropriate recycling and reuse of vegetable biomass will be important for sustainable development.

Technological uses for and methods of recycling vegetable biomass include, for example, the adsorption of heavy metals onto vegetable biomass [2–6], the removal of heavy metals by seaweed [7,8], and its decomposition into usable compost by microbes [9,10]. The adsorption of Cd^{2+} and Cu^{2+} onto cassava [11] and oceanic alga [12] has been reported. However, there has been no report on the adsorption of Cd^{2+} and Cu^{2+} onto vegetable biomass treated with hydrochloric acid. Fat and protein in the vegetable biomass treated with acid were decomposed. If the fat and protein are related to the Cd^{2+} and Cu^{2+} adsorption, the adsorption ability of Cd^{2+} and Cu^{2+} onto them must change.

In this study, the adsorption abilities of Cd^{2+} and Cu^{2+} onto soybean waste and wheat bran treated with hydrochloric acid are estimated for the development of recycling and reuse technologies.

2. Experimental

2.1. Materials

$Cd(NO_3)_2$ and $Cu(NO_3)_2$ (Wako Pure Chemical Industries Co., Ltd.) were used for the standard solutions of Cd^{2+} and Cu^{2+}, respec-

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tively. The soybean waste and wheat bran were purchased from Nissin Falma Co., Ltd. Three grams of vegetable biomass was treated with 17 mL of 0.01, 0.1, and 1.0 mol/L hydrochloric acid at 121 °C for 20 min, filtered through a 3G3 glass filter, and dried at 121 °C for 24 h.

2.2. Components of vegetable biomass

The carbon, hydrogen and nitrogen contents of soybean waste, which were analyzed by the auto element analyzer 2400II (PerkinElmer, Japan), were 46.4, 6.9 and 5.0%, respectively. Those of wheat bran were 42.7, 6.6 and 3.7%, respectively. The amount of carbon contained in soybean waste was greater than that contained in wheat bran. A Soxhlet fat extraction apparatus for extraction with ether was used to measure crude fat content [13]. A biomass sample accurately weighed to 5.0 g was placed in a cylindrical paper filter, and diethyl ether was poured into the flask. Extraction was performed for about 6 h. The flask was dried at 98–100 °C for about 1 h, left to cool in a desiccator, and weighed. The crude fat content was calculated using Eq. (1).

$$F = (A - B) \times \frac{100}{5} \tag{1}$$

where F is the crude fat content (%), A is the weight (g) of the flask after fat extraction and drying, and B is the weight (g) of the flask before fat extraction.

Crude protein content was calculated using the semi-micro Kjeldahl method [14]. First, 0.02 g of a precisely weighed sample was placed in a decomposition flask, and then 0.5 g of a decomposition promoter (K_2SO_4:$CuSO_4 \cdot 5H_2O$ = 10:1), 3 mL of concentrated sulfuric acid, 1 mL of 30 w/v% hydrogen peroxide solution, and 25 mL of 30 w/v% sodium hydroxide solution were added. Then steam distillation was started, and 100 mL of distillate was taken as the sample solution. A solution prepared by adding 15 mL of 4 w/v% boric acid solution and a few drops of bromcresol green and methyl red were used for the adsorbing solution. The test solution was titrated with 0.025 mol/L sulfuric acid solution, and a blank test was performed using distilled water. Crude protein content was calculated using Eq. (2)

$$P = 0.7003 \times (a - b) \times \frac{100}{M} \times 6.25 \tag{2}$$

where P is the crude protein content (%), a is the sulfuric acid titer (mL) required in the main experiment, b is the sulfuric acid titer (mL) required in the blank experiment, M is the sample weight (mg), and 6.25 is the nitrogen coefficient.

2.3. Amounts of Cd^{2+} and Cu^{2+} adsorbed onto vegetable biomass

In the single-solution system, adsorbents were added to solutions of $Cd(NO_3)_2$ or $Cu(NO_3)_2$ of different concentrations at a ratio of 50 mg to 50 mL. In the binary-solution system, binary solutions of the two compounds at desired concentrations were used. The liquids were shaken at 100 rpm at 25 °C for 24 h and passed through a membrane filter. We confirmed that the adsorption of Cd^{2+} and Cu^{2+} onto vegetable biomass became the equilibrium adsorption for 3 h. Moreover Singh et al. reported the Cr^{6+} adsorption onto wheat bran became the equilibrium adsorption for 2 h [1]. The concentrations of Cd^{2+} and Cu^{2+} were determined by an inductively coupled plasma-atomic emission spectrometer (ICP-AES) (ICP7000, Shimadzu). The amounts adsorbed were calculated by Eq. (3) using the initial and equilibrium concentrations:

$$X = (C_0 - C) \times \frac{50}{1000} \times \frac{1}{W} \tag{3}$$

Table 1
Components of soybean and wheat bran.

Samples	Crude fat content (%)	Total nitrogen (%)	Crude protein content (%)
Soybean	13.7	4.1	25.6
Wheat bran	2.3	3.0	19.0

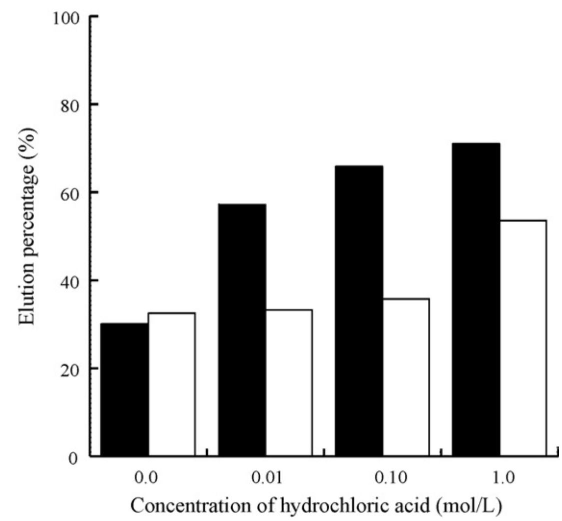

Fig. 1. Elution percentage from vegetable biomass treated with hydrochloric acid. ■: soybean waste, □: wheat bran.

where X is the amount adsorbed (μg/g), C_0 is the initial concentration (μg/L), C is the equilibrium concentration (μg/L), and W is the adsorbent weight (g).

3. Results and discussion

3.1. Components of soybean waste and wheat bran

Table 1 shows the crude fat content, the total nitrogen and the crude protein content of the vegetable biomasses. Those of soybean waste are larger than those of wheat bran. The measured crude fat content and the crude protein content of soybean waste were 6.0 and 1.3 times those of wheat bran, respectively.

Fig. 1 shows the elution percentages from soybean and wheat bran treated with hydrochloric acid. In both cases the percentage increased with an increasing concentration of hydrochloric acid because of protein degradation—that is, pectin elution—in the vegetable biomass. The elution percentage from soybean waste was larger than that from wheat bran, because the crude fat content, the total nitrogen and the crude protein content of soybean waste were larger than those of wheat bran.

3.2. Amounts of Cd^{2+} and Cu^{2+} adsorbed onto soybean

Fig. 2 shows the amounts of Cd^{2+} and Cu^{2+} adsorbed onto untreated soybean waste in single and binary-solution systems. The amounts of Cd^{2+} and Cu^{2+} adsorbed were greater in the binary-solution system than in the single-solution system. In the binary-solution system, more Cd^{2+} than Cu^{2+} was adsorbed onto the soybean waste. Khaodhiar et al. [15] examined the adsorption of copper and chromate onto iron-oxide-coated sand in both a single and a binary-solution system. Chromate adsorption increased in the presence of copper by the combination of electrostatic effects and possible surface–copper–chromate ternary complex formation. It is generally assumed that Cd^{2+} adsorption is not influenced by the existence of Cu^{2+} because both ions are cations. However,

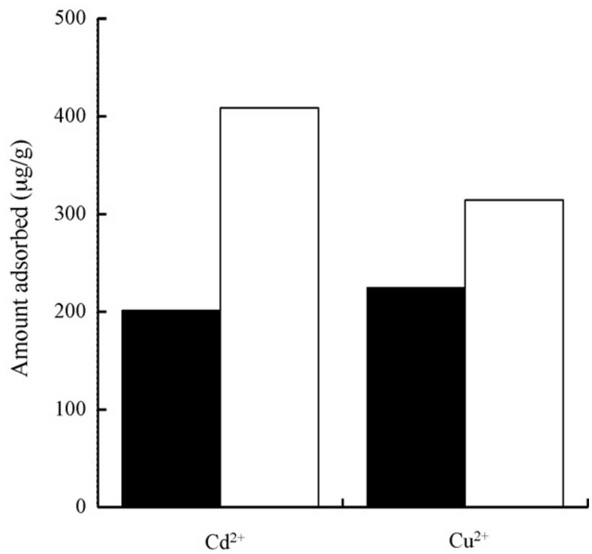

Fig. 2. Amount of Cd^{2+} and Cu^{2+} adsorbed onto untreated soybean in single- and binary-solution systems. Conditions: initial concentration 500 µg/L; temperature 25 °C. ■: single-solution system; □: binary-solution system.

the amount of Cd^{2+} and Cu^{2+} adsorbed in the binary-solution system was greater than that in single-solution system; this behavior may indicate that Cd^{2+} and Cu^{2+} interact with each other.

Fig. 3 shows the adsorption isotherms of Cd^{2+} and Cu^{2+} onto untreated and defatted soybean waste in a single-solution system. The amounts of Cd^{2+} and Cu^{2+} adsorbed onto defatted soybean waste were smaller than those adsorbed onto untreated soybean waste. This indicated that the Cd^{2+} and Cu^{2+} also may adsorb onto the fat in soybean waste. Pan et al. [16] reported that fatty acid was adsorbed from water by a metal(copper)-chelated resin adsorbent. In other words, the metal interacted with the fatty acid.

Fig. 4 shows the amounts of Cd^{2+} and Cu^{2+} adsorbed onto soybean waste treated with hydrochloric acid. In the single-solution system, the amount of Cd^{2+} adsorbed onto soybean waste decreased as the concentration of hydrochloric acid increased. Meanwhile, the amount of copper adsorbed onto soybean waste

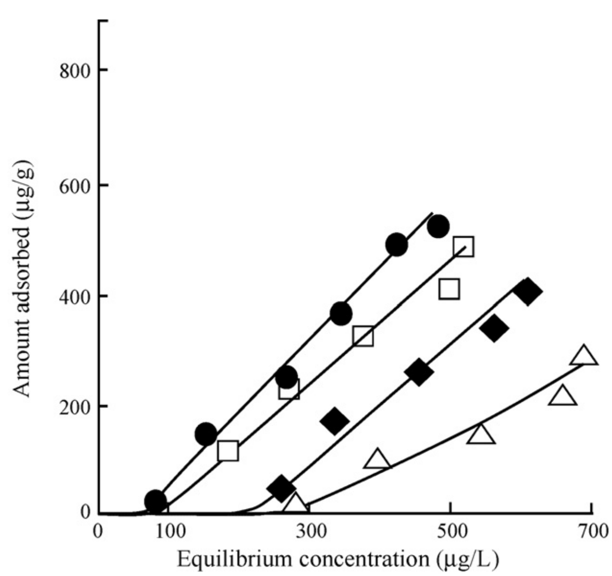

Fig. 3. Adsorption isotherms of Cd^{2+} and Cu^{2+} onto untreated and defatted soybean waste in a single-solution system. Conditions: initial concentration 50–1000 µg/L; temperature 25 °C. ●: Cd^{2+} (untreated); □: Cd^{2+} (defatted); ♦: Cu^{2+} (untreated); △: Cu^{2+} (defatted).

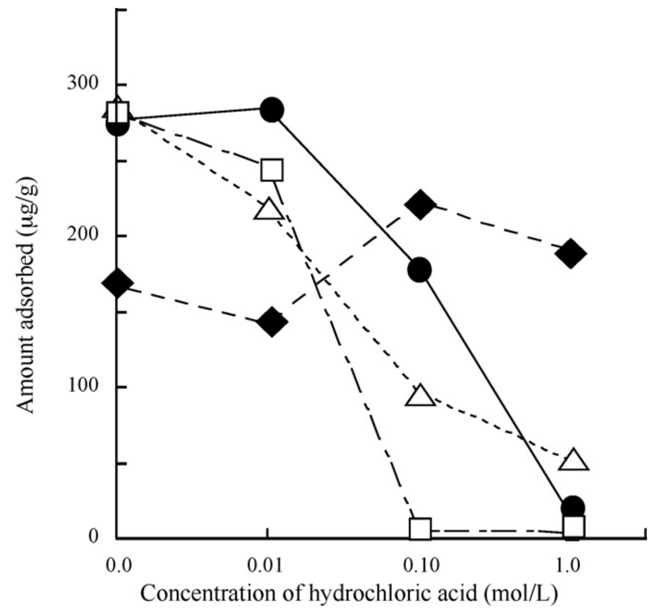

Fig. 4. Amount of Cd^{2+} and Cu^{2+} adsorbed onto soybean waste treated with hydrochloric acid in single- and binary-solution systems. Conditions: initial concentration 500 µg/L; temperature 25 °C. ●: Cd^{2+} (single); □: Cd^{2+} (binary); ♦: Cu^{2+} (single); △: Cu^{2+} (binary).

was highest at treatment with 0.1 mol/L hydrochloric acid. In the binary-solution system, the amounts of Cd^{2+} and Cu^{2+} adsorbed onto soybean waste treated with 1.0 mol/L hydrochloric acid decreased as the concentration of hydrochloric acid increased. Soybean bran treated with hydrochloric acid did not adsorb Cd^{2+}.

In both the single and binary systems, the amount of Cd^{2+} adsorbed onto soybean waste treated with hydrochloric acid decreased as the acid concentration increased. Especially, in the binary system, soybean waste treated with 0.1 or 1.0 mol/L hydrochloric acid did not adsorb Cd^{2+}. This result indicated that the adsorption of Cd^{2+} may be interrupted by Cu^{2+} [17–20], or that the hydrochloric acid treatment may degrade the protein structure of the vegetable biomass. Less Cu^{2+} was adsorbed onto acid-treated soybean waste in the binary system than in the single system. The amount adsorbed onto soybean waste decreased as the acid concentration increased, because the degradation of the protein structure increased. More was adsorbed onto soybean waste treated with 0.01 mol/L hydrochloric acid in the single system than in the binary system. This indicated that, when the concentration of hydrochloric acid is lower, the protein structure does not change, and Cu^{2+} may adsorb onto soybean waste more easily by the existence of Cd^{2+}.

3.3. Amounts of Cd^{2+} and Cu^{2+} adsorbed onto wheat bran

Fig. 5 shows the amounts of Cd^{2+} and Cu^{2+} adsorbed onto untreated wheat bran in single- and binary-solution systems. The amount of adsorbed Cd^{2+} was greater in a single-solution system while that of adsorbed Cu^{2+} was greater in a binary-solution system. The amounts of Cd^{2+} and Cu^{2+} adsorbed onto wheat bran in the binary system were one-half and twice those in the single solution, respectively. The amount of Cd^{2+} adsorbed onto the wheat bran in the single system was larger than that of Cu^{2+}, while that in the binary system was smaller. Moreover, the amount in the single system was larger than that in the binary system because of the existence of Cu^{2+}.

Fig. 6shows the adsorption isotherms of Cd^{2+} and Cu^{2+} onto untreated and defatted wheat bran in a single-solution system. The

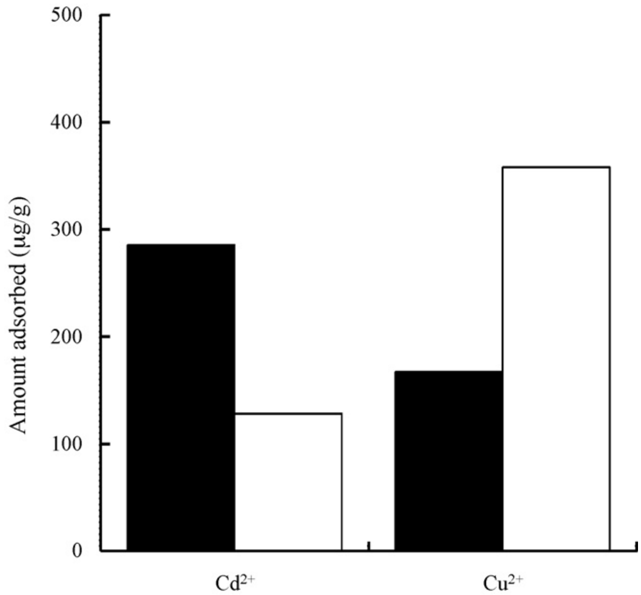

Fig. 5. Amount of Cd^{2+} and Cu^{2+} adsorbed onto untreated wheat bran in single- and binary-solution systems. Conditions: initial concentration 500 μg/L; temperature 25 °C. ■: single-solution system; □: binary-solution system.

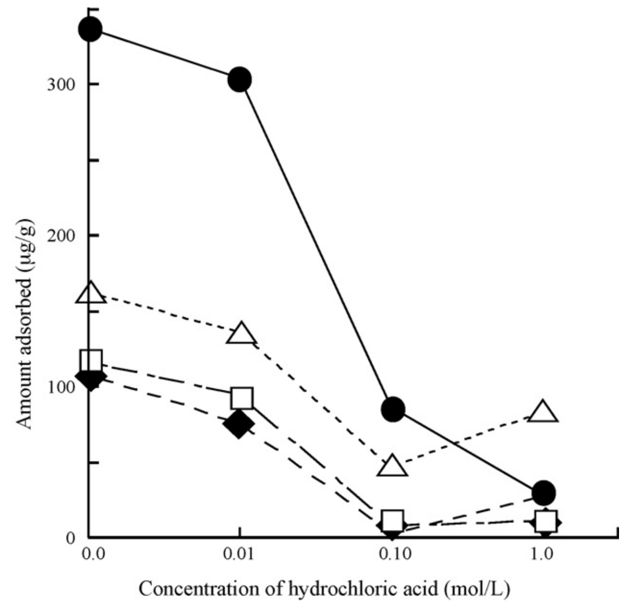

Fig. 7. Amount of Cd^{2+} and Cu^{2+} adsorbed onto wheat bran treated with hydrochloric acid in single- and binary-solution systems. Conditions: initial concentration 500 μg/L; temperature 25 °C. ●: Cd^{2+} (single); □: Cd^{2+} (binary); ♦: Cu^{2+} (single); △: Cu^{2+} (binary).

amounts of Cd^{2+} adsorbed onto defatted wheat bran were similar to those adsorbed onto untreated wheat bran. That of Cu^{2+} adsorbed decreased by the removal of fat. It is thought that the fat in vegetable biomass may be involved in Cd^{2+} or Cu^{2+} adsorption.

Fig. 7 shows the amounts of Cd^{2+} and Cu^{2+} adsorbed onto wheat bran treated with hydrochloric acid. The amount of Cd^{2+} adsorbed decreased with the increasing acid concentration, in both the single and binary-solution systems. The amount of Cu^{2+} adsorbed in the binary-solution system was greater than that in the single-solution system, because the adsorption of Cd^{2+} was inhibited by the existence of Cu^{2}. The interaction of Cu^{2+} with wheat bran was greater than that of Cd^{2+}.

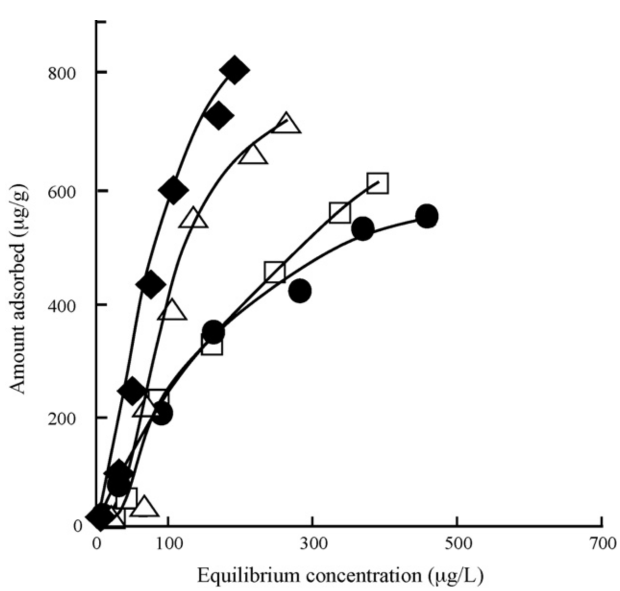

Fig. 6. Adsorption isotherms of Cd^{2+} and Cu^{2+} onto untreated and defatted wheat bran in a single-solution system. Conditions: initial concentration 50–1000 μg/L; temperature 25 °C. ●: Cd^{2+} (untreated); □: Cd^{2+} (defatted); ♦: Cu^{2+} (untreated); △: Cu^{2+} (defatted)

In general, adsorption of a variety of solutes in solutions onto adsorbates can be properly expressed by the Freundlich equation [21]:

$$\log X = \frac{1}{n}\log C + \log k \quad (4)$$

where X is the amount of solute adsorbed by the unit amount of adsorbent, C is the equilibrium concentration of solute, and n and k are constants. When $\log X$ is plotted against $\log C$, the constant $1/n$ is given by the slope of the straight line and k is given by the intercept on the ordinate. The constant $1/n$ indicates the affinity between the adsorbate and adsorbent, or the adsorption intensity, and k is associated with adsorption capacity [22]. It is generally accepted that, when $1/n$ is in the range of 0.1–0.5, the adsorbate readily adsorbs on the adsorbent, and that, when $1/n > 2$, there is little likelihood of adsorption [23].

The Freundlich equation was fitted by linear regression to the adsorption isotherm data presented in Figs. 3 and 6 to estimate the constants k and $1/n$ for each case. The results are shown in Table 2. The resultant Freundlich isotherms fitted the experimental data with correlation coefficients ranging between 0.815 and 0.983. This suggests that Cd^{2+} and Cu^{2+} adsorption onto adsorbents proceeds through monomolecular adsorption on heterogeneous surfaces. Adsorption of Cd^{2+} and Cu^{2+} onto the vegetable biomass was characterized by $1/n$; a smaller $1/n$ indicated a weaker affinity between the Cd^{2+} or Cu^{2+} and the vegetable biomass. The constant

Table 2
Freundlich constants for adsorption isotherms of Cd^{2+} and Cu^{2+}.

Adsorbents	Adsorbates	Freundlich constants		r
		$1/n$	$\log k$	
Untreated soybean	Cd^{2+}	1.73	−1.84	0.969
Defatted soybean	Cd^{2+}	1.24	−0.68	0.983
Untreated soybean	Cu^{2+}	2.42	−4.05	0.949
Defatted soybean	Cu^{2+}	3.05	−6.17	0.954
Untreated wheat bran	Cd^{2+}	0.85	0.56	0.983
Defatted wheat bran	Cd^{2+}	1.07	0.11	0964
Untreated wheat bran	Cu^{2+}	1.50	−0.35	0.949
Defatted wheat bran	Cu^{2+}	1.63	−0.92	0.815

$1/n$ for Cd^{2+} and Cu^{2+} adsorption on soybean waste was larger than that on wheat bran. The constant $1/n$ for Cd^{2+} and Cu^{2+} adsorption on untreated soybean waste was larger and smaller than that on defatted soybean waste, respectively. The interaction between the biomass surface and Cd^{2+} or Cu^{2+}, except for the Cd^{2+} adsorption onto untreated soybean waste, was increased by the removal of fat in vegetable biomass. Cd^{2+} or Cu^{2+} may strongly adsorb onto defatted biomass.

4. Conclusion

The adsorption abilities of Cu^{2+} and Cd^{2+} onto vegetable biomass treated with hydrochloric acid were investigated. The adsorption of Cu^{2+} and Cd^{2+} onto vegetable biomass depended on the protein and fat structure. When hydrochloric acid excessively degrades the protein structure in the vegetable biomass, Cu^{2+} and Cd^{2+} cannot adsorb onto the biomass, but Cd^{2+} and Cu^{2+} may interact with the fatty acid in solution. The amounts of Cd^{2+} and Cu^{2+} adsorbed onto the vegetable biomasses in the binary system were less than and greater than those in the single system, respectively. Vegetable biomass can be utilized for the removal of Cd^{2+} and Cu^{2+} from solutions. After adsorption of Cd^{2+} and Cu^{2+}, vegetable biomass may be thermal recycle.

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