

Biosorption and preconcentration of lead and cadmium on waste Chinese herb Pang Da Hai

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Abstract

The biosorption behavior of the solid waste Chinese herb Pang Da Hai (seeds of *Sterculia lychnophera* Hance) was studied as a sorbent for trace lead and cadmium. The solid waste Chinese herb Pang Da Hai has good sorption and desorption properties for Pb and Cd. The sorbed waste Chinese herb Pang Da Hai was both easily eluted with $0.1 \text{ mol l}^{-1} \text{ HNO}_3$ and easily digested with concentrated HNO_3 . The extent of adsorption depends on pH, metal concentration, substrate concentration and the presence of interfering ions. The adsorption capacities were found to be 27.1 and 17.5 mg g^{-1} for Pb and Cd. The relative standard deviation of the metal uptake experiment was found to be less than 10% for Pb(II) and Cd(II) using $100 \text{ } \mu\text{g l}^{-1}$ of metal ions and 20 mg substrate. Based on above, an ecofriendly and low cost method for Cd and Pb preconcentration and determination with flame atomic absorption spectrophotometry was developed. The method was validated by the analysis of a standard reference material (GBW 08301). The results agree with those quoted by manufactures. It was used for 90-fold preconcentration of Cd and Pb from tap water and river water samples followed by flame atomic absorption spectroscopic (FAAS) determination with satisfactory results.

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1. Introduction

As the number of ecological and health problems associated with environmental contamination continues to rise, the determination of heavy metal ion at trace level in environment samples is becoming great importance. Flame atomic absorption spectroscopy (FAAS) is the most widely used technique for such determinations because of simplicity and low initial and running cost. However, this technique suffers from lack of sensitivity for the ultra-trace metal concentrations usually encountered in environmental samples. Therefore, sample preconcentration is becoming an essential treatment step before flame atomic absorption determination. For this purpose, there are many methods have been developed, including liquid–liquid extraction [1,2], coprecipitation [3–5], ion-exchange [6,7], chelating resins [8–12] and solid-phase extraction [13]. These methods

have advantages of high selectivity, sensitivity and fast speed of operation, but they have also obvious disadvantages of their high cost and causing second pollution to the environment. Therefore, seeking methods that are friendly to the environment and low cost is becoming more and more important. The biosorption methods have been paid great attention and concern recently for this purpose [14–17]. One of those is the use of natural materials as possible media for metal preconcentration and separation from heavy-metal-containing waste streams and sludges. Until now, wool, rice straw [18], saw dust [19], peat moss [20], tea leaves [21], coffee powder [22,23], alfalfa sprouts, tomato root and stems of cattail [24], human hair [25] as biosorbents have been studied. Chinese herbs have been widely used since ancient times and the wastes were discarded on the whole. There will be more and more amount of wastes of Chinese herb produced with the modernization of Chinese herbs.

It was therefore thought worthwhile to investigate the sorption characteristics of waste Chinese herbs for metal ions. Several kinds of them were studied and the results showed that the

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solid wastes of Pang Da Hai (PDH) (seeds of *Sterculia lychnophora* Hance), which is widely used as Chinese herb, is a good biosorbent for heavy metal ions, especially for Pb(II) and Cd(II). The effect of pH, metal concentration, substrate concentration and the presence of interfering ions were studied. Equilibrium studies were performed with isotherm modeling. The potential application of PDH for metal ion preconcentration and determination were also investigated. Data were compared with a standard reference material (GBW 08301). The results agree with those quoted by manufactures.

2. Experimental

2.1. Apparatus

A Shimadzu AA-6800 atomic absorption spectrometer (Kyoto, Japan) equipped with L233 series single element hollow cathode lamps and an air–acetylene burner (Hamamatsu Photonics Co. Ltd.) was used for the determination of metals. The instrumental parameters were those recommended by the manufacturer. The wavelengths (nm) selected for the determination of the analytes were as follows: Cd 228.8 and Pb 216.7. A model pH-3C pH-meter (Shanghai Lida Instrument Factory, China) was used for the pH adjustment. A model DZD-3 multifunctional shaker (Changzhou Aite Technologies Co. Ltd., China) was used for the equilibration for the metal ion sorption measurement.

2.2. Chemicals and solutions

Doubly de-ionized (DDI) water (18 M Ω cm) was purified with a Milli-Q system (Millipore, USA). Unless otherwise stated, all reagents used were of analytical grade and all solutions were prepared with DDI water. Standard labware and glassware were used throughout and repeatedly cleaned with HNO₃ and rinsed with DDI water, according to a published procedure [26].

Stock solutions (1.0 g l⁻¹) of the elements were prepared by dissolving appropriate amounts of nitrate salts in 1.0% (v/v) HNO₃ and further diluted daily prior to use. The reference material (GBW 08301) was obtained from Institute for Environmental Certified Reference Materials of SEPA (Beijing, China).

The following buffer solutions were used for a preconcentration procedure: H₃PO₄/NaH₂PO₄ buffer for pH 2.0 and 3.0; CH₃COOH/NaCH₃COO buffer for pH 4.0 and 6.0;

NaH₂PO₄/Na₂HPO₄ buffer for pH 7.0; Na₂B₄O₇/NaOH buffer for pH 8.0–9.0. The ionic strength of the solutions was maintained at a constant level by using 0.10 mol l⁻¹ KNO₃ stock solution.

2.3. Sorbent preparation

PDH used in these studies were purchased from the drug store and have been ground into granular form. These ground PDH and 10-fold (w/w) water which are kept in small pot were brewed on electric furnace for 1 h. After that the PDH was removed from the pot and was subjected to successive sieving. Samples of 60–80 mesh size were used in the following experiments. The PDH waste was then dispersed in acid solution (0.1 mol l⁻¹ HNO₃) for about 2 h, then filtered and washed with DDI water. This process of dispersing, cleaning and filtering was repeated, when necessary, to remove any metal ions and acid adhering to PDH. The acid-washed PDH were dried in the oven at 110 °C.

2.4. Preconcentration procedure

The metal ion uptake by PDH was studied by adding a known quantity of the pretreated waste PDH to metal ion solutions having various initial metal concentrations of sample solution.

The containers used were polyethylene beakers or bottles of 150 ml capacity. The mixture was adjusted to appropriate pH using buffer solution and shaken for prefixed time followed by decantation or filtration (when necessary) and metal analysis performed using FAAS. The difference between the initial metal concentration and the concentration taken after equilibration with the substrate is taken as the concentration of metal adsorbed by the wastes. The detailed conditions are listed in Table 1.

To further check the preconcentration results, the sorbed waste PDH was digested with concentrated HNO₃, then evaporate to near dryness and the residue was immersed with 0.01 mol l⁻¹ HCl. The amounts of sorbed lead and cadmium were determined by FAAS. The blank values of the studied lead and cadmium remained in the acid-washed PDH were measured by ICP-AES.

Metal concentrations were 10–20 times greater than those of natural water levels to allow easy determination used in most of these studies.

Table 1
Conditions for preconcentration procedure

Parameter	Conditions ^a				
	Metal ion solution (mg l ⁻¹)	Equilibrium time (h)	Amount of PDH (mg)	Temperature (°C)	pH
pH effect	0.05	1.5	20	25	3.0–9.0
Sorption kinetics	0.05	5/60–2	20	25	6.5
Temperature effect	0.05	1.5	20	15–45	6.5
Amount of PDH	0.05	1.5	5–40	25	6.5
Sorption capacity	0.025–0.5	24	20	25	6.5
Selective experiment	0.0125–0.05	1.5	20	25	6.5

^a With 50 ml final volume.

2.5. Sampling procedure

A portion (50–100 mg) of the certified sediment sample was accurately weighed into a 50 ml container (or beaker) and aqua regia (12 ml concentrated hydrochloric acid and 4.0 ml of concentrated nitric acid) was added to the sample. The container was covered with a watch glass and the mixture was evaporated on a hot plate at 95 °C almost to dryness. Then 8.0 ml of aqua regia was added to the residue and the mixture was again evaporated to dryness. After cooling, resulting mixture was filtered through a 0.45 μm Millipore cellulose nitrate membrane. The sample was diluted to 10 ml with DDI water and was analyzed by the preconcentration procedure given above.

The tap water was acidified to pH 2.0 with 2.0 mol l⁻¹ HNO₃, neutralized and then buffered to the desired pH.

The surface river water samples were collected in pre-washed polyethylene bottles from dirty region of Fen River (Taiyuan, China) and Sanggan River (Datong, China) in July 2005. The bottles were cleaned with DDI water, dilute nitric acid and DDI water, in sequence. The samples were immediately filtered through a 0.45 μm Millipore cellulose nitrate membrane, acidified to pH 2.0 with 2.0 mol l⁻¹ HNO₃ and stored in pre-cleaned polyethylene bottles.

3. Results and discussion

3.1. pH effect

Fig. 1 demonstrated that the lead and cadmium adsorption by Chinese herbs is pH dependent. The optimum pH ranges for metal adsorption were 5.0–8.0 for Pb and 6.0–8.0 for Cd. So pH 6.5 was selected for the recommended procedure. Since the cell walls of Chinese herbs contain significant amounts of acidic functional groups, the optimum pH range would likely fall under weakly acidic conditions. Also at low pH, the complex formed via interaction between metal ions and acidic functional groups is expected to be destabilized since the values of conditional stability constants decrease with pH. As a result, the metal ions were desorbed into solution. Another explanation is that there is competition of hydrogen ion for surface active sites which lead to minimum or negligible metal ion uptake at low pH.

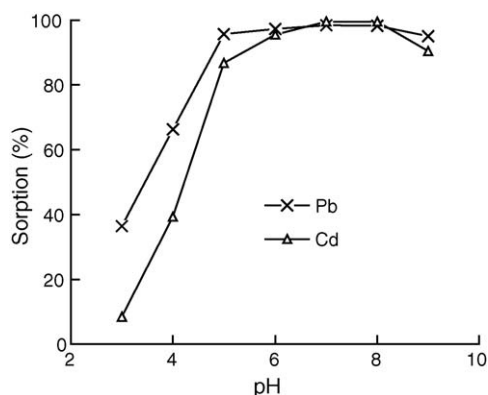


Fig. 1. The effect of pH on lead and cadmium sorption.

3.2. Kinetics of sorption and desorption

Generally speaking, the uptake of heavy metal ions by PDH has often been observed to occur in two stages: an initial rapid uptake due to surface adsorption on the PDH, and a subsequent slow uptake due to diffusion of the metal ions into the inner of PDH. Surface adsorption is a physicochemical phenomenon. The cell walls of many plants consist of polysaccharides, proteins and lipids, and therefore offer a host of functional groups capable of binding to heavy metals. These functional groups, such as amino, carboxylic, sulfhydryl, phosphate and thiol groups, differ in their affinity and specificity for metal binding. The equilibrium amount of a metal ion bound onto PDH surface would be determined by the relative affinity of the sites for metal ions present and the residual concentrations of these metal ions not taken up in the solution. The surface-bound metal ion is then transported into the inner through the diffusion. Since a fixed cell biomass offers a finite number of surface binding sites, the initial uptake, being surface adsorption, would be expected to show saturation kinetics with increasing metal ion concentration.

Adsorption, together with membrane transport model, is evident from Fig. 2, the metal adsorption rate is high at the beginning, but plateau values are reached in 80 min. The slow equilibration means that this sorbent cannot be used for fast flow-through column methods. Note that there are several parameters which determine the biosorption rate, especially metal distribution at the equilibrium, such as stirring rate; structural properties of the biosorbent (e.g. protein and carbohydrate composition and surface charge density, topography and surface area); amount of sorbent; properties of the ions under study; initial concentration of ionic species; and the presence of other metal ions, which may compete with the ionic species of interest for the active biosorption sites. Therefore, it is difficult to compare the biosorption rates reported.

Desorption rates are much faster than sorption rates. Desorption of Pb and Cd with 0.1 mol l⁻¹ HNO₃ is fast and almost complete in 5 min. Desorption with 0.1 mol l⁻¹ HCl was as efficient as HNO₃ and has no distinct advantage. On the other hand,

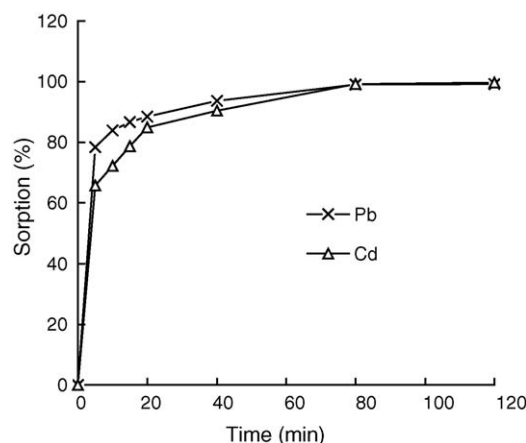


Fig. 2. Effect of equilibration time on sorption of lead and cadmium on PDH sorbent.

Table 2
Desorption of lead and cadmium

Eluent (mol l ⁻¹)	Recovery (%) ^a									
	Pb(II)					Cd(II)				
	1	2	3	4	5	1	2	3	4	5
HCl (0.1)	97.6	97.4	97.2	96.6	96.0	99.8	99.2	98.6	98.2	97.4
HNO ₃ (0.1)	98.3	98.0	97.7	97.3	96.8	99.6	99.0	98.4	98.1	97.1
EDTA (0.1, pH 8.0)	98.5	98.1	97.4	96.7	96.1	99.6	99.1	98.3	97.8	97.2

^a Results are averages from triplicate measurements.

desorption with 0.1 mol l⁻¹ EDTA (pH 8) was both quantitative and efficient in desorbing both metals from the sorbent. From Table 2, it can be seen that recycling the sorption desorption process five times showed little memory effect. However, for trace work it is advisable to use a fresh sorbent sample for each test.

3.3. Effect of temperature

The effect of temperature on the biosorption of lead and cadmium onto the PDH beads was studied between 15 and 45 °C at pH 6.5. It was observed that temperature changes between 15 and 45 °C have slightly influence on the rate of biosorption, but did not affect the biosorption capacity.

3.4. Effect of varying amount of PDH

The effect of varying the amount of substrate on the metal uptake for fixed amounts of lead and cadmium are summarized in Fig. 3. As expected, metal uptake increased linearly with an increase in substrate concentration only below 5 mg of substrate. At higher concentration, the line gradually curved off and should level off at much higher substrate concentrations.

3.5. Effect of varying metal concentration

The adsorption of lead and cadmium was found to follow Langmuir adsorption isotherm as exemplified by Fig. 4. From the Langmuir isotherm (Eq. (1)) the adsorption capacity for lead

and cadmium can be evaluated as follows:

$$q = \frac{bq_m c}{1 + bc} \quad \text{or} \quad \frac{1}{q} = \frac{1}{q_m} + \frac{1}{bq_m c} \quad (1)$$

where q is the metal concentration in the solid phase (mg g⁻¹) at equilibrium, c the metal concentration in the liquid phase at equilibrium (mg l⁻¹), q_m the maximum adsorption capacity (mg g⁻¹) and b is the constant related to the energy of chemisorption.

By plotting $1/q$ versus $1/c$, the intercept of the graph yields $1/q_m$. Hence, the q_m values are 27.1 and 17.5 mg g⁻¹ for lead and cadmium. It can be seen, the adsorption capacity of PDH calculated for lead and cadmium appears equivalently or higher than those obtained by waste tea leaves (1.63 mg g⁻¹ for cadmium) [27] and rice husk (11.4 mg g⁻¹ for lead and 21.36 mg g⁻¹ for cadmium) [28].

3.6. Effect of common ions

The effect of cations and anions possibly existed in real water samples was studied. The results show in Table 3 that the tolerance limits of the investigated electrolytes or cations are in considerable remounts.

3.7. Substrate digest

In general, the chelating resin is inert to acids, therefore, to analyze the analyte absorbed on it, only the dry ashing method is used. But as all known, the ashing method is less exact than the

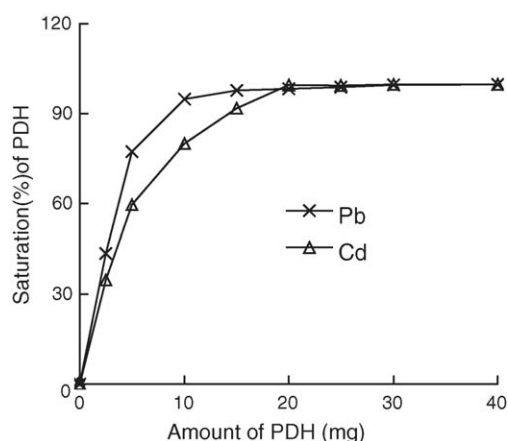


Fig. 3. The effect of amount of PDH.

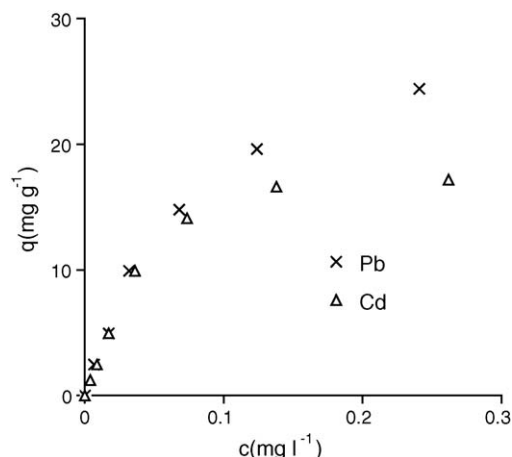


Fig. 4. The adsorption isotherm of lead and cadmium.

Table 3
Recovery of trace lead and cadmium in the presence of common ions

Element ^a	Concentration (mg l ⁻¹)	Recovery (%) ^b					
		Pb(II)			Cd(II)		
		0.25	0.50	1.0	0.25	0.50	1.0
		95.8	96.6	98.3	97.6	98.5	99.2
Na ⁺	20	96.7	96.9	97.8	97.2	99.4	99.7
	100	96.8	97.2	98.4	98.1	99.3	98.9
K ⁺	10	97.8	98.1	98.1	98.6	99.2	99.5
Ca ²⁺	50	96.2	98.7	97.9	98.8	99.4	99.0
	200	95.6	97.7	98.9	98.4	99.3	99.3
Mg ²⁺	20	97.6	98.1	97.6	98.4	99.0	99.2
Fe ³⁺	0.50	95.9	96.6	97.5	98.4	99.1	99.4
HCO ₃ ⁻	100	95.3	96.7	97.7	98.2	99.3	99.2
SO ₄ ²⁻	100	95.2	96.4	96.1	96.6	97.3	98.5
Cl ⁻	100	97.1	98.4	97.1	98.6	99.2	99.5

^a Cations were added as their nitrate or chloride salts while anions were added as their sodium salts.

^b Results are averages from triplicate samples.

Table 4
Recovery of lead and cadmium sorbed on PDH at different temperatures

Metal ions	Recovery (%)				
	15 °C	20 °C	25 °C	35 °C	45 °C
Pb	85.2	94.6	98.4	99.8	99.3
Cd	87.3	96.7	99.6	99.7	99.8

wet digest method [29]. To contrast, the waste PDH was easily digested with concentrated HNO₃. Twenty milligrams of waste PDH sorbed of 100 µg Pb and Cd was digested with 10 ml concentrated HNO₃ at different temperature for 30 min, the results are shown in Table 4. It can be seen that the recoveries for both of Pb and Cd exceed 95% at 80 °C. This is well fitted for trace analysis of lead and cadmium in environmental samples.

3.8. Validation of the method

A reference material (GBW 08301) was used for biosorption and preconcentration method validation. As seen in Table 5, the results were compared with the certified values using a *t*-test at 95% confidence limits [30]. Good agreement was obtained between the estimated content by the proposed method and the certified values for Pb and Cd. The relative error is between 2.5%

Table 5
Determination of lead and cadmium in a certified sample (GBW 08301)

Metal ions	Method	Found by present method (µg g ⁻¹) ^a	Certified value (µg g ⁻¹)	Relative error (%)
Pb	SOL ^b	77 ± 5	79 ± 6	2.5
	SUB ^c	72 ± 7		8.8
Cd	SOL ^b	2.3 ± 0.2	2.4 ± 0.3	5.3
	SUB ^c	2.2 ± 0.4		11

^a Uncertainties expressed as 95% confidence interval with *n* = 3.

^b Determined in solution.

^c Determined on substrate.

Table 6
Determination of lead and cadmium in water samples (*n* = 3)

Origin of sample	Method	Metal ions concentration (µg l ⁻¹) ^a	
		Pb	Cd
Tap water	SOL ^b	5.27 ± 0.96	0.65 ± 0.12
	SUB ^c	9.52 ± 1.83	1.47 ± 0.04
Fen River	SOL ^b	3.22 ± 0.47	0.73 ± 0.06
	SUB ^c	7.24 ± 1.40	1.62 ± 0.14
Sanggan River	SOL ^b	4.85 ± 0.55	0.81 ± 0.03
	SUB ^c	9.27 ± 1.68	1.78 ± 0.02

^a Uncertainties expressed as 95% confidence interval with *n* = 3.

^b Determined in solution.

^c Determined on substrate.

and 11%. These results also indicate that the developed preconcentration method for Pb and Cd is not affected by potential interferences from the major matrix elements of the analyzed water sample, containing 4.6, 10, 20 and 5.1 mg l⁻¹ of K, Na, Ca and Mg.

The reproducibility of the proposed procedure was also measured using model solution. The relative standard deviations (*n* = 10) were 7.2% for Pb and 4.6% for Cd. The detection limit and the quantification limit, defined as by IUPAC [31,32] were found to be 0.096, 1.71 µg l⁻¹ for Pb and 0.032, 0.18 µg l⁻¹ for Cd, respectively.

3.9. Analysis of real samples

The proposed method was applied to concentration and determination of Pb and Cd in tap water and river water samples. The sample containing 1000 ml each of the acidified tap water and river water was firstly neutralized, then buffered to pH 6.5 and determined according to the preconcentration and determination procedure. It can be seen in Table 6 that the results for Pb and Cd were satisfactory.

4. Conclusions

From this studied work we can see that the PDH is not only a good natural sorbent for lead and cadmium with large adsorption capacity, but also can it be eluted with acids at low acidity and be easily digested with concentrated HNO₃. Use of toxic, especially carcinogenic reagent is avoided. Therefore, the method proposed is very simple, low cost and ecofriendly to nature.

Because there are great many kinds of Chinese herbs, there may be more excellent materials than Pang Da Hai to be developed. Such material may find applications for reclamation and remediation of contaminated sites. It is also very interesting to study the sorption of other metals ions and semi-metals such as mercury and arsenic which is known to easily accumulate in biomass. Work in these directions is under investigation in our laboratory.

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