Adsorption Behavior of Lead(II) in Water by Means of Fern Plant Paper

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Abstract
Nine fern plant papers and three higher plant papers were prepared, and the adsorption behavior of heavy metals (Cu, Zn, Pb, and Cd etc), especially lead(II) in water was investigated in detail. It was found that metal accumulation fern plant (Athylium yokoscense) paper and other fern plant papers had generally large capacity of lead(II) adsorption compared with higher plant papers. The results were also applied to the separation and determination of traces lead(II) in water by means of fern plant papers and atomic absorption spectrometry.

1 Introduction
The removal of toxic heavy metals from sewage, industrial and mining waste streams by using biomass materials (animal or plant materials) as solid adsorbent has received much attention in recent years.[1-3] The agricultural by-products such as wool, white of an egg, tree bark, rice straw, onion skin, peanut skins, green tea, and exoskeletons of crabs and lobsters etc. have been used by several workers from the point of view of their low cost and an effective utilization of natural resources.

Athyrium yokoscense (Fr. et Sav.) Christ is well known as a widely distributed fern growing on everywhere in Japan aside from alpine and subalpine forest zone. The dense population of the species is an anomalous vegetation always found in the vicinity of all the metal mine in Japan. These pure communities of the fern were found in the areas of heavy metals pollution resulting from lead tiles of the ruins of Kanazawa Castle,[4,5] and from mine drainage of Kakehashi River from Ogoya Copper Mine in Ishikawa Prefecture,[6] and from ore deposits of all the metal mine in Japan.[7] The root of Athyrium yokoscense was found to especially accumulate heavy metals such as copper(II), zinc(II), lead(II), and cadmium(II) in high concentration.

In this investigation, the authors have prepared papers from nine fern plants including Athyrium yokoscense collected in Kanazawa Castle, and from three kinds of higher plants, and then have ascertained their adsorption behavior of copper(II), zinc(II), lead(II), and cadmium(II), especially lead(II) in water.

The effect of various factors such as shaking time, pH, and foreign ions etc. on the adsorption of lead(II) with fern plant papers was studied by batch experiments in detail. The separation of traces lead(II) in fresh water with fern plant paper was also ascertained by solid-liquid extraction.
2 Experimental

2.1 Materials

The materials (about 3 g) of nine species of fern plant such as *Athyrium yokoscense* (*Hebinonegoza*), *Athyrium niponicum* (*Inuwarabi*), *Arachniodas standishii* (*Ryomenshida*), *Dryopteris erythrosora* (*Benishida*), *Equisetum arvense* (*Sugina*), *Gleichenia japonica* (*Urajiro*), *Matteuccia struthiopteris* (*Kusasotetsu*), *Osmunda japonica* (*Zenmai*), *Polystichum polyblepharm* (*Inode*) which were obtained from Kanazawa Castle, were dried in air over 2 days, and were treated with 1 % NaOH alkaline solution on heating at 80 °C for 2 h, followed by passing through the nylon sieve (200 mesh). Then each of the products was suspended in distilled water (150 cm³). Next the commercial available bleaching powder (NaClO including surface active agent, 3 cm³) diluted ten times, were added and agitated at 80 °C for 30 min. The bleaching agent (3 cm³ every time) was added repeatedly until the materials turn to white. The product was filtered and washed with distilled water, until the pH becomes neutral. The product suspended in distilled water was passed through the nylon sieve (200 mesh), and it was added into demineralized water in order to wash three times. Then the material was dried in an oven at 60 °C on one day. The yield of fern plant papers was 12-26 % for leaves, 15-42 % for stems, and 8-15 % for roots. Fern plant paper was purified by washing twice with 0.04 M EDTA solution (M = mol dm⁻³). Fern plant paper made of *Athyrium yokoscense* was purified three times under the same conditions. The content of lead(II) in fern plant papers after purification was 10.5 ppm for leaves and 38.4 ppm for roots in *Athyrium yokoscense*, and was negligibly small in another 8 fern plants. This purification method must be followed by acid treatment with 1 M nitric acid solution in order to exchange the functional group of the fern plant paper from sodium type to acid type. The fern plant papers can adsorb heavy metals without this treatment, however the adsorption equilibrium with this paper is slower than with the acid treated papers, and the amount of lead(II) adsorbed on an untreated paper was only about 70 % of that adsorbed on an acid treated paper.

The materials of higher plant papers such as *Edgeworthia papyrifeva* (*Mitsumata*), *Wikstroemia sikokina* (*Ganpi*), and *Broussonetia Kazinoki* (*Kozo*), are generally used for Japanese papers (*Washi*). These papers were made only from their epidermis of stems. The yield of higher plant papers was 34-48 %.

2.2 Adsorption

A 1 cm³ solution containing 200 mg dm⁻³ of each heavy metals such as copper(II), lead(II), zinc(II), and cadmium(II) was mixed with 2 mg of fern plant paper in 5 cm³ of stoppered sample bottle. The solution was adjusted to desired pH in order to adsorb heavy metals effectively, and the mixture was agitated with ultrasonic generator for 5 min, until the adsorption equilibrium was reached. The mixture was then centrifuged at 6000 rpm for 3 min (or filtered through), and the concentration of metals in the solution was determined by an atomic absorption spectrometer.

3 Results and Discussion

3.1 Effect of shaking time

There was no difference on the adsorption of lead(II) at pH 4.8 with fern plant papers made of roots, stems and leaves of *Athyrium yokoscense* when agitating for 1～7 min. The effect of agitation on the adsorption of lead(II) at pH 4.8 with papers made of leaves of fern plants, *Arachniodas standishii* and *Dryopteris erythrosora*, and with a paper made of stems of higher plant, *Broussonetia Kazinoki* gave the same results as those of *Athyrium*
yokoscense (Fig.1). These results indicate that the adsorption equilibrium of lead(II) with fern plant papers was reached within one minute with ultrasonic shaker.

Therefore, 5 min agitation in this study was enough to adsorb lead(II) with fern plant papers (Fig.2).

3.2 Effect of pH

The effect of pH on the adsorption of copper(II), lead(II), zinc(II), and cadmium(II) with fern plant paper of Athyrium yokoscense is shown in Fig.3. Similar curves obtained indicate that the selectivity of the fern plant paper is poor, and this paper cannot separate heavy metals each other. The pH-adsorption curves with papers made of roots, stems, and leaves of Athyrium yokoscense was very similar except for the amount of heavy metals adsorption.

The similarity in these curves may indicate the identity of functional group involved in these papers, and the difference of metal adsorption amount may depend on their amount. It was ascertained that only carboxyl group in hemicellulose along with pectic substances was involved in the paper made of Athyrium yokoscense from the results of IR spectrum and some coloring tests. Ruthenium red dye was used to ascertain pectic substances in papers. Sodium salt of rhodizonic acid was also used for coloring lead(II) adsorbed in all fern plant papers. The coloring site in papers described above was the same position.

From these results mentioned above, it is considered that all fern plant papers show the same adsorption behavior except for the amount of lead adsorbed. It was found that carboxyl group of hemicellulose along with pectic substances was also involved in the Japanese paper (Washi) made of higher plants.

Industrial pure cellulose powder did not adsorb any lead(II) in water. From these results, it was found that heavy metals amount adsorbed depends upon the amount of carboxyl group as functional group in plant papers. Then, it can be concluded that the fern plant papers are superior to higher plant papers as an adsorbent of lead(II) in solution.
3.3 Adsorption capacity

The adsorption of lead(II) with fern plant papers was studied by agitating the mixture of 2 mg of each fern plant papers and 1 cm$^3$ of 200 mg dm$^{-3}$ lead(II) acetate solution at pH 4.8. Amount of lead(II) adsorbed with the paper made of stems (31~49 mg g$^{-1}$) is generally higher than that with paper made of another part such as roots (20~31 mg g$^{-1}$) and leaves (15~38 mg g$^{-1}$). This result indicates that the amount of functional group in fern plant papers to adsorb lead(II) is different from each parts made of fern plant tissues. The amount of lead(II) adsorption with fern plant papers made of stems was compared with that of higher plant papers (6~15 mg g$^{-1}$). The amount of lead(II) adsorbed with fern plant paper was several times higher than that with higher plant papers. The amount of carboxyl group in fern plant papers is assumed as about 1 mmol g$^{-1}$. Consequently, the amount of functional group to adsorb lead(II) may be larger in fern plant paper than in higher plant paper. These results agree well with the fact that fern plants have generally a large amount of pectic substances along with hemicellulose containing carboxyl group, which play as a functional group of lead(II) adsorption in fern plant papers.

The amount of lead(II) adsorbed with fern plant papers made of lead(I) accumulation fern, *Athyrium yokoscense*, was not always higher than that with papers made of common fern plants.

The adsorption equilibrium of lead(II) with fern plant papers was also ascertained by using Freundlich isotherm equation. The slope of straight lines obtained was 0.6~0.7, and the results indicated that fern plant papers were comparatively favorable adsorbent for lead(II).

3.4 Determination of traces lead(II) in fresh water

First of all, effect of foreign ions which may exist in fresh water and cause interference more than 5% in the adsorption of lead(II) with fern plant papers was studied using a series of sample solutions containing 10 mg dm$^{-3}$ of lead(II) and along with various amount of foreign ions from 10 to 100 mg dm$^{-3}$. There was no interference up to 100 mg dm$^{-1}$ for magnesium(II), Cl$^-$, and CO$_3^-$, 70 mg dm$^{-1}$ for SO$_4^-$, and 50 mg dm$^{-1}$ for calcium(II).

The paper made of *Arachniodes standshii* (*Ryomensida*) without any impurity of lead(II) after purification was used for the separation of traces lead(II) in water. The mixture of 100 mg of fern plant paper and 100 cm$^3$ of lead(II) acetate solution (10 mg dm$^{-3}$) was shaken with a shaker for 30 min and was filtrated with 0.45 μm filter. Then fern plant paper was treated with 1 ml of 1.0 M nitric acid in order to release lead(II) adsorbed, followed by determining lead(II) with atomic absorption spectrometry. The recovery of 10 μg dm$^{-3}$ of lead(II) spiked was 98%, and the amount of lead(II) in water for fire prevention in Kanazawa Castle was under detection limit (1.3 μg dm$^{-3}$).

The paper was recycled at least two times after treating it with 0.1~1.0 M nitric acid solution. However the paper gradually became in powder by after several refinements with the acid solution.

References