

Cesium adsorption from aqueous solutions onto Japanese oak charcoal III: effects of water-extraction treatment

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Abstract To remove group 1 and 2 metal ions from Japanese oak (*Quercus serrata* Thunb. and/or *Quercus crispula* Blume) charcoal (OC), a water-extraction treatment was employed. The treatment was repeated 1, 4, 8, or 12 times. The amounts of four metal (sodium, potassium, magnesium, and calcium) ions eluted from non-treated and treated OC were determined using an ion chromatographic apparatus. The effects of water-extraction treatment on the ability of OC to adsorb cesium were investigated using 2.50×10^{-5} and 2.50×10^{-6} mol/L aqueous cesium chloride solutions. As for both aqueous solutions, an unexpected result was obtained in that the cesium-adsorption ability of OC decreased suddenly when the repetition of water-extraction treatments exceeded a certain threshold. We explain the results in terms of pH of the sample solutions and the point of zero charge for OC.

Keywords Cesium · Adsorption · Japanese oak charcoal · pH · Residual functional group

Introduction

The disaster at the Fukushima Daiichi nuclear power stations in 2011 widely dispersed various radioisotopes. As a result, many victims are still living in temporary dwellings because the radioactivity in their hometowns remains above the safety levels established by the Japanese government. In addition, contaminated water containing radioisotopes is produced constantly at the power stations. Two cesium nuclides, ^{134}Cs and ^{137}Cs whose half-lives are about 2 and 30 years, respectively, are the main targets for decontamination, although the pollutants contain many kinds of radioisotopes. To remove and collect these radioactive cesium nuclides, it is essential to develop an ideal adsorbent for capturing them.

Many studies have already reported the cesium-adsorption performance of synthetic zeolites and Prussian blue type complexes, but only a few reports on cesium-fixation using biochar have been published [1–3]. Advantages of biochar include its ease of large-scale production and capability to reduce its volume markedly by combustion after used as an adsorptive. Kobayashi suggested that a highly practical adsorptive for cesium may be readily developed from biochar [4].

Our attention focused on Japanese oak (*Quercus serrata* Thunb. and/or *Quercus crispula* Blume) charcoal (OC), because it is the most popular charcoal manufactured in Japan. We previously investigated several factors such as pH and specific surface area that were predicted to affect adsorption ability of charcoal in aqueous solution [5]. Moreover, we clarified that group 1 and 2 metals, whose content is not negligible in ordinary charcoal [6, 7], have blocking effects on cesium adsorption onto charcoal [8]. Furthermore, we reported that partial removal of the metals from charcoal clearly raised the amount of cesium

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adsorbed from aqueous solution [9]. Therefore, it was expected that charcoal may exhibit much higher adsorption ability when metal elements are completely removed from it.

To better understand the effects of metal removal from OC, we studied changes in the cesium-adsorption isotherm of OC after water-extraction (water-washing) treatment. However, an unexpected result was obtained; the amount of cesium adsorbed onto OC decreased drastically when the repetitions of extraction treatments exceeded a certain threshold. A likely explanation is provided for these results in terms of pH of the sample solutions and the point of zero charge (PZC) for OC.

Experimental

Materials

Charcoal used in this study was produced in Iwate Prefecture and commercially available. In previous studies [5, 8, 9], its physicochemical properties were described in detail. Small OC blocks were ground in a porcelain mortar, and then OC powder was put through a 60-mesh sieve. The powder was kept in a desiccator over silica gel after drying at 105 °C for over 24 h. From Raman spectra, it was estimated that the carbonization temperature of the OC was in the range of 600–800 °C [5]. Special-grade cesium chloride anhydride was obtained commercially.

Preparation of aqueous cesium chloride solutions

Cesium chloride anhydride was used after drying at 100 °C for 24 h. Two kinds of aqueous cesium chloride solutions (I and II) were prepared using deionized water. The initial cesium chloride concentrations of solutions I and II were 2.50×10^{-5} mol/L (Cs^+ concentration: 3.32 mg/L) and 2.50×10^{-6} mol/L (Cs^+ concentration: 0.332 mg/L), respectively.

Water-extraction treatment of OC

Charcoal (ca. 20 g) powder was added into 1000 mL of deionized water. After stirring for 24 h, the OC powder was filtered out under reduced pressure and added into 1000 mL of new water. This extraction procedure was repeated 1, 4, 8, or 12 times. OC treated by the extraction is referred to as 1WE-OC, 4WE-OC, 8WE-OC or 12WE-OC depending on the repetitions of extractions performed. The water-extracted OC was used as an adsorbent after drying at 105 °C for over 24 h.

Determination of sodium, potassium, magnesium, and calcium ions eluted from OC and *n*WE-OC (*n* = 1, 4, 8, 12)

Charcoal and *n*WE-OC powder (3.20 g) were suspended in 100 mL of deionized water in a 200 mL-Erlenmeyer flask. The flask was sealed and placed on an orbital shaker at 23 ± 2 °C for 24 h. The powder from the suspensions was filtered out through a nylon-membrane microfilter (Millex-HN filters, SLHN033NS, Millipore Ireland, Ltd.). The concentrations of sodium, potassium, magnesium, and calcium ions in the filtrate were analyzed quantitatively using an ion chromatographic apparatus (Dionex CS-3000, Nippon Dionex K. K.) in accordance with the Japanese Industrial Standard for testing methods for industrial wastewater (JIS K 0102, 2008) [10].

Determination of solid-phase cesium concentration and pH

Cesium chloride solution (100 mL) was added to powdered OC or *n*WE-OC (0.20, 0.40, 0.80, 1.60, 3.20 g) in a sealed 200 mL-Erlenmeyer flask, shaken and filtered out using the same conditions as described above. The pH of the solution after filtration was recorded using a pH meter. The concentration of cesium ions in the filtrate was determined using an ICP (inductively coupled plasma) mass spectrometer (Agilent 7700×, Agilent Technologies, Ltd.) with an internal standard method (standard isotope: ^{115}In). The ICP mass analysis was repeated three times for all samples. All of the relative standard deviations were within 2.3 %. It is reasonable that the cesium ion concentration in the filtrate was regarded as the cesium ion concentration in the liquid phase was at equilibrium. The solid-phase cesium concentration (*W*) was calculated using the decrease in mass (*m*) of cesium ions in the liquid phase and the mass (*M*) of powder adsorbent added, according to Eq. (1):

$$W = \frac{m}{M} \quad (1)$$

where the units of *m* and *M* are milligrams (mg) and grams (g), respectively.

Results and discussion

Determination of sodium, potassium, magnesium, and calcium ions eluted from OC and *n*WE-OC (*n* = 1, 4, 8, 12)

We previously reported using X-ray fluorescence analysis that relative mass percentages of potassium and calcium in OC were 30.0 and 64.2 %, respectively, while sodium and

magnesium were undetectable. However, the amounts of sodium and magnesium eluted from OC were not negligible. Therefore, it was expected that these metal ions eluted from OC compete against cesium ion for adsorption sites [9]. In this study, we examined changes in the amounts of group 1 and 2 metal ions eluted from OC and *n*WE-OC. The concentrations of sodium, potassium, magnesium, and calcium ions are summarized in Table 1.

It should be noted that the most abundant metal eluted from OC was not calcium but potassium, which have the strongest blocking effect [8], despite the fact that calcium was the primary metal element in OC. The sodium ion concentration was below 1.3×10^{-6} mol/L when the extraction-treatment was carried out 4 times or more, and the potassium and magnesium ion concentrations decreased consistently with the repetitions of treatments. The potassium and magnesium ion concentrations for 12WE-OC were about one order of magnitude lower than those for OC. The calcium ion concentration reached a maximum in 4WE-OC and the concentration for OC was approximately the same as that for 12WE-OC. Therefore, the results listed in Table 1 indicate that the total amount of the four metal ions eluted from the adsorbent significantly decreased through 12 times of the treatment, although the complete removal of blocking ions was not accomplished.

Effects of adsorbent addition on pH of aqueous cesium chloride solutions

Table 2 contains a summary of the pH values of the sample solutions used to obtain the isotherms of cesium adsorption onto OC and *n*WE-OC. The pH values of solutions I and II were 5.8. An increase in pH was observed for all of the sample solutions after adsorbent addition, but this effect was obviously inhibited by the extraction treatment. A key aspect of the results shown in Table 2 is that all of the pH values in 8WE-OC and 12WE-OC were within the range from 6.4 to 7.4, which was substantially closer to the PZC, or isoelectric point, for OC (pH = 6.70) [5].

Table 1 Concentrations of sodium, potassium, magnesium, and calcium ions eluted from Japanese oak charcoal (OC) and water-extracted Japanese oak charcoal (*n*WE-OC) after 1, 4, 8, and 12 treatments

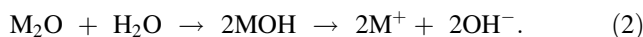
Adsorbent	Molar concentration (mol/L)			
	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
OC	7.0×10^{-6}	1.6×10^{-3}	7.7×10^{-5}	7.8×10^{-5}
1WE-OC	1.3×10^{-6}	8.4×10^{-4}	5.3×10^{-5}	1.8×10^{-4}
4WE-OC	$<1.3 \times 10^{-6}$	5.9×10^{-4}	1.7×10^{-5}	3.6×10^{-4}
8WE-OC	$<1.3 \times 10^{-6}$	3.9×10^{-4}	5.8×10^{-6}	1.7×10^{-4}
12WE-OC	$<1.3 \times 10^{-6}$	3.5×10^{-4}	4.5×10^{-6}	1.0×10^{-4}

Adsorption isotherms of cesium ions onto OC and *n*WE-OC (*n* = 1, 4, 8, or 12)

Figures 1 and 2 illustrate the adsorption isotherms of cesium adsorption onto OC and *n*WE-OC from solutions I and II, respectively. As for solution I, OC and 4WE-OC showed the higher adsorption abilities compared to those reported previously [9], suggesting that the adsorption ability of commercial charcoal is significantly different in each batch. Solutions I and II showed similar changes in the isotherms with the repetitions of water-extraction, namely, the adsorption ability of OC for cesium ions increased with the repetitions of extraction up to 4 times, but it decreased drastically after 8 times and became a little smaller after 12 times.

Although these irregular changes in isotherms seemed not to be readily explainable, it was possible to account for them on the basis of two effects of group 1 and 2 metal ions eluted from the adsorbent. The first effect is a blocking one. It is reasonable to assume that the blocking effect caused by group 1 and 2 metal ions that compete with cesium ions in occupying adsorption sites decreases greatly, because the water-extraction treatment reduces the metal ions eluted from OC.

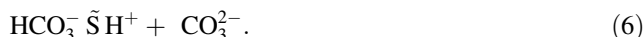
Another is regarded as an effect of increasing pH of the sample solution. From the elemental compositions [8, 9] and estimated carbonization temperatures [5], it is likely that group 1 and 2 metals mainly exist as oxides, hydroxides, or carbonates and the compounds are soluble in water. Therefore, the chemical reactions that occur when the oxides of group 1 metal (M) are dissolved in aqueous solution are as follows:



Those of hydroxides are as follows:



Those of the carbonates are as follows:



In Eq. (6), the reaction equilibrium lies extremely to the left side. Thus, oxides, hydroxides, and carbonates in aqueous solution contribute to increasing the pH. As for group 2 metal elements, the dissolving phenomena in aqueous solution are represented using the same equations, although there are few differences in coefficients and subscripts of Eqs. (2), (3), and (4).

Adsorption phenomena have been classified according to the interaction between adsorbent and adsorbate into several types. The primary interaction in adsorption for

Table 2 pH in aqueous cesium chloride solutions I and II after addition of adsorbent and stirring for 24 h

Aqueous cesium chloride solution	Mass of added adsorbent (g)	pH				
		OC	1WE-OC	4WE-OC	8WE-OC	12WE-OC
I (2.50×10^{-5} mol/L)*	0.20	9.3	8.0	8.0	6.7	6.4
	0.40	9.4	8.1	8.5	6.9	6.6
	0.80	9.6	8.2	8.4	7.1	6.7
	1.60	9.6	8.7	8.2	7.3	6.9
	3.20	9.4	8.3	8.2	7.3	7.0
II (2.50×10^{-6} mol/L)**	0.20	9.6	9.4	9.2	6.9	6.5
	0.40	9.7	9.4	9.2	7.1	6.7
	0.80	9.7	9.4	8.9	7.2	6.8
	1.60	9.6	9.3	8.5	7.4	6.9
	3.20	9.4	9.0	8.2	7.4	6.9

* pH = 5.8, ** pH = 5.8

OC Japanese oak charcoal, *n*WE-OC water-extracted Japanese oak charcoal after 1, 4, 8, and 12 treatments

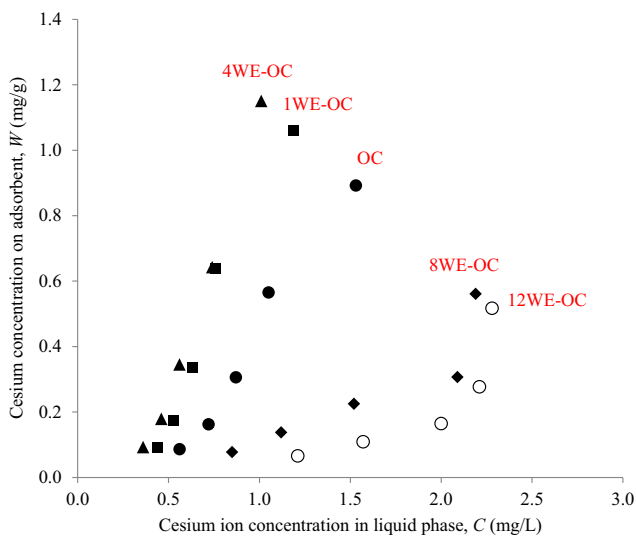


Fig. 1 Isotherms of cesium adsorption onto OC (filled circles), 1WE-OC (filled squares), 4WE-OC (filled triangles), 8WE-OC (filled diamonds), and 12WE-OC (open circles) from solution I. OC Japanese oak charcoal, *n*WE-OC Japanese oak charcoal extracted by water *n* times

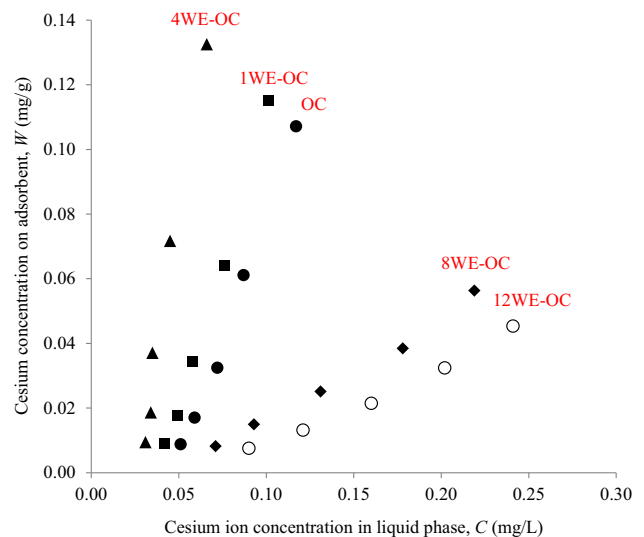


Fig. 2 Isotherms of cesium adsorption onto OC (filled circles), 1WE-OC (filled squares), 4WE-OC (filled triangles), 8WE-OC (filled diamonds), and 12WE-OC (open circles) from solution II. OC Japanese oak charcoal, *n*WE-OC Japanese oak charcoal extracted by water *n* times

group 1 metal ions such as cesium ions can be regarded as electrostatic attraction. The surface of a solid adsorbent with acidic and/or basic functional groups can be charged in aqueous solution, and the sign (negative or positive) and magnitude of the surface electrical potential are dependent upon the physicochemical properties of the adsorbent and the pH of the solution. The pH where surface electrical potential becomes approximately zero is referred to as PZC, and the potential is positive in more acidic regions and negative in more basic regions. The magnitude of the potential becomes larger as the pH of the solution moves

away from the PZC [11–15]. Accordingly, it is essential to increase the pH of the sample solution sufficiently to evaluate the inherent cesium-adsorption ability of OC. As mentioned above, this increase in pH requires sufficient elution of group 1 and 2 metals from the adsorbent, because the pH of solutions I and II are 5.8. However, these metals also possess a competing effect that hinders cesium ions from being adsorbed onto OC.

As is evident from Figs. 1 and 2, the adsorption ability of OC in the sample solution reached a maximum at a threshold of extraction treatment times and then decreased

with further extractions. The quantity and type of functional groups on the surface of the adsorbent as well as the pH of the sample solution are the dominant factors affecting the surface electrical potential [11–15]. In previous work using infrared photoacoustic spectroscopy [16], we indicated that hydroxyl and carbonyl groups remain in Japanese cedar wood and bark heat-treated under nitrogen at 600 °C. Therefore, it is likely that OC has carboxyl and phenolic hydroxyl groups as residual acidic functional groups. Thus, it can be explained that these functional groups become negatively charged by releasing a proton and then obtain the ability to capture a cation if the pH of the solution is sufficiently above the PZC, although they scarcely dissociate below the PZC. In other words, this mechanism for adsorbing cesium ions from aqueous solution can be interpreted as an ion exchange phenomenon.

Hence, it is suggested that the adsorption ability of charcoal is improved by increasing the residual acidic functional groups through lowering the carbonization temperature. Further study is necessary to evaluate the effect of carbonization temperature on adsorption ability for cesium ions in aqueous solution. In addition, demineralized OC may show high cesium-adsorption ability, if the pH of the aqueous solution can be increased by addition of alkali having no blocking effect on cesium adsorption.

It can be seen that the cesium-adsorption percentage in solution II was higher than that in solution I, by comparing the isotherms depicted in Fig. 1 with those in Fig. 2. In a previous report [9], we anticipated that the percentage increases as initial cesium concentration in solution becomes lower. These isotherms are further experimental evidence supporting our expectation.

Conclusion

In this paper, our experimental results indicated that the cesium-adsorption ability of OC in the sample solution reaches a maximum immediately after the repetitions of water-extraction treatments exceeds a threshold and decreases with further extractions. The amounts of cesium adsorbed onto OC decreased drastically when the pH of the sample solution decreased and approached the PZC of OC. A likely explanation for this interesting result is that group 1 and 2 metal ions show two important effects that compete with each other. The first is a blocking effect of group 1 and 2 metal ions competing against cesium ions for adsorption sites on OC. Another is a positive effect that dissolution of group 1 and 2 metal compounds increases the pH of the sample solution, namely, it decreases the surface electrical potential of the adsorbent. The water-extraction treatment reduces both effects. It is suggested

that residual functional groups physically and chemically play an important role in the cesium-adsorption phenomenon, and sufficiently high pH compared with the PZC of OC is essential for obtaining high cesium-adsorption ability.

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