

Factors governing cesium adsorption of charcoals in aqueous solution

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Received: 29 July 2016 / Accepted: 17 December 2016 / Published online: 10 January 2017
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Abstract Cesium adsorption by commercial charcoals was examined to elucidate the mechanisms for capturing cesium ions in aqueous solution. Changes in the adsorption ability of charcoals due to water extraction (water washing) were investigated to develop practical cesium adsorptives based on charcoal. The commercial charcoals examined included mangrove charcoal (MC) and ubamegashi (*Quercus phillyraeoides* A. Gray) bincho charcoal (BC). Data from the two charcoals were compared with those of Japanese oak (*Quercus serrata* Thunb. and/or *Quercus crispula* Blume) charcoal (OC) reported previously. Aqueous cesium chloride solution (2.50×10^{-5} mol/L) was used as a sample solution for the adsorption study. Charcoal powder was used as an adsorbent after passing through a 60-mesh sieve. The powders were characterized using methods, such as Raman spectroscopy, X-ray fluorescence spectrometry, and infrared photoacoustic spectroscopy. The results indicated that MC, which was manufactured at the lowest possible temperature and had the smallest specific surface area, possessed the greatest ability to adsorb cesium. The MC also had the great cesium-adsorption ability in weak acidic solution and maintained the ability even after lengthy extraction treatments.

Keywords Cesium · Adsorption · Charcoal · Manufacturing temperature · Functional group

Introduction

In 2011, a tsunami seriously damaged the power supply system at the Fukushima Daiichi nuclear power plant, resulting in subsequent hydrogen detonations. Significant amounts of radioisotopes were released into the atmosphere and infiltrated into the ground as a result. Decontamination work has been progressing slowly, and water is continuing to be polluted with radioactivity, with the cesium radioisotopes of ^{134}Cs and ^{137}Cs as the most important. Therefore, a high-performance adsorptive for cesium was an urgent requirement.

Studies have addressed the cesium-adsorption ability of synthesized zeolites. Recent research on Prussian blue-type complexes have been advancing rapidly. In contrast, only a few studies of biochar as a cesium adsorptive have been published [1–3] despite suggestions for its use [4].

The advantages of charcoal include its simple mass production and the ability to significantly reduce its volume by heat treatment. Japanese oak (*Quercus serrata* Thunb. and/or *Quercus crispula* Blume) charcoal (OC) was used, because it is the most popular charcoal produced in Japan, and several factors affecting its ability to adsorb cesium ions in aqueous solution were investigated. The effects of surface properties of charcoal on cesium-adsorption ability have been reported [5]. In addition, group 1 and 2 metals, which are contained in ordinary charcoal [6, 7], can prevent cesium adsorption [8]. These metals have competing effects—one exerts a blocking effect and one increases pH [9, 10]. When the pH is sufficiently high, the surface of the charcoal becomes negatively charged enough to capture cesium ions.

Part of this report was presented at the 66th Annual Meetings of the Japan Wood Research Society, Nagoya, March 2016.

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Previous studies [9, 10] have suggested that cesium adsorption of charcoal is an ion-exchange phenomenon and that the amount of acidic functional groups in the charcoal and the pH of the solution were important factors governing cesium-adsorption ability. Although some studies have focused on organic functional groups contained in charcoals made from wood or wood constituents [11–13], the roles these functional groups play in the adsorption of metals from aqueous solution are not well understood.

The present study examines the mechanisms for the capture of cesium ions in aqueous solution by charcoal, by comparing the cesium-adsorption ability of mangrove charcoal (MC) and ubamegashi (*Quercus phillyraeoides* A. Gray) bincho charcoal (BC) to that of OC reported previously [9]. The results revealed that MC, which was manufactured at the lowest temperature, possessed a strong ability for cesium adsorption, even under weakly acidic conditions, when compared with OC and BC. This unexpected adsorption behavior of MC was examined in terms of residual acidic functional groups and acidic pyrolysis products.

Experimental

Charcoals and chemicals

MC was imported from Malaysia and BC was produced in Wakayama Prefecture, Japan. Both charcoals are sold as household fuel in Japan. The OC used was described previously [5, 8–10]. The charcoals were analyzed and used as adsorbents after passage through a 60-mesh sieve and drying at 105 °C for at least 24 h. Special-grade cesium chloride anhydride (CsCl) was obtained commercially.

Water extraction

The MC or BC powder (ca. 10 g) was suspended in 500 mL of water. After stirring for 24 h, the water was removed from the charcoal powder using vacuum filtration, which was repeated 4, 8, or 12 times. The charcoal treated by the extraction is referred to as *n*WE-MC or *n*WE-BC (*n* = 4, 8, and 12) depending on the number of water extractions. The water-extracted charcoal was used as an adsorbent after drying at 105 °C for at least 24 h.

Preparation of aqueous cesium chloride solutions

The CsCl solution was prepared using cesium CsCl dried at 100 °C. The initial concentration was 2.50×10^{-5} mol/L (Cs⁺: 3.32 mg/L). The water used in this study was deionized through a column packed with ion-exchange resins.

Nonmetallic elements and ash

For MC and BC, the content of nonmetallic elements (hydrogen, carbon, oxygen, nitrogen, and sulfur) and ash were determined according to the Japanese Industrial Standard for coal and coke (JIS M 8813) [14]. Ashing of MC and BC was conducted at 1350 °C. The contents of hydrogen and carbon were calculated from the mass of water and carbon dioxide obtained by a Sheffield high-temperature method. Nitrogen and sulfur in MC and BC were quantitatively analyzed using a semi-micro-Kjeldahl and high-temperature combustion method, respectively.

Metal elements

Metal elements with atomic numbers greater than 11 in MC and BC were detected by X-ray fluorescence spectrometry using a compact spectrometer (MESA-500, Horiba, Ltd.). Charcoal powder (ca. 0.5 g) was placed in a cylindrical Teflon cell with a diameter of 20 mm. A sample chamber set in the cell was under vacuum. The X-ray irradiation was performed at room temperature, the total measurement time was 2000 s, and the X-ray tube voltages were 15 kV (1000 s) and 50 kV (1000 s). Relative mass percentages of elements to total elements detected were calculated using a standardless fundamental parameter method [15, 16] from characteristic X-ray intensities.

Raman spectra of charcoals

Raman scattering of the charcoals was recorded at ambient temperature using a Renishaw Raman Imaging Microscope System 1000 coupled with an air-cooled CCD detector. An He–Ne laser (632.8 nm) was used as an excitation source at a power of ca. 20 mW. Back-scattered Raman signals were collected through a microscope and edge filters in the range of 600–2000 cm⁻¹ with a spectral resolution of about 2 cm⁻¹. The sample powder was spread thinly on a slide glass. The Raman measurements were repeated at five different points for each sample. Wavenumber calibration was carried out using the 520 cm⁻¹ line of a silicon wafer and the 1332 cm⁻¹ line of diamond.

Raman data were analyzed using the software package GRAMS/386 (Galactic Industries, Salem, New Hampshire, USA). Raman band positions, widths, heights, and areas of the spectra corrected on baseline were calculated by curve fitting based on the Levenberg–Marquardt method. A band component was treated as a linear combination of Gaussian and Lorentzian ($f(x) = aG(x) + (1 - a)L(x)$, $0 \leq a \leq 1$); an adequate fit was not obtained for only one of the two functions. Four component bands were required to adequately fit the Raman spectra [17], although visually they seemed to exhibit only two bands.

Infrared photoacoustic (IR-PA) spectra of charcoals

The IR-PA spectra were obtained using a Jeol JIR7000 W spectrometer equipped with an IR-PA spectroscopy module (IR-PAS 1000). The spectra were obtained from 300 times accumulation with a spectral resolution of ca. 4 cm^{-1} . An aluminum thin cell (diameter: 5 mm) was filled with the charcoal powder. Photoacoustic signals were collected upon purging a cell bench with helium gas. The moving-mirror velocity was fixed at 0.16 cm/s. Carbon black was used as a reference.

Point of zero charge

The point of zero charge (PZC) for MC and BC was determined according to a previous reported method [18, 19]. Briefly, PZC was estimated from pH changes in aqueous sodium chloride solutions, upon adjustment of the pH from 2 to 12 using dilute hydrochloric acid or ammonia water, and adding demineralized MC or BC. The pH values were recorded using a pH meter (HM-25R, TOA DKK Co.)

Specific surface area

After degassing at $100\text{ }^{\circ}\text{C}$ under vacuum for 2 h, the nitrogen adsorption isotherms at liquid nitrogen temperature in the charcoal powder were recorded using a surface area analyzer NOVA 1200 (Quantachrome Co.). The specific surface area of charcoal was calculated using the isotherms obtained based on a BET multi-points method.

Sodium, potassium, magnesium, and calcium ions eluted from adsorbents

Charcoal powder (1.60 g) was added to 50 mL water. A capped 100-mL Erlenmeyer flask containing the sample solution was stirred using an orbital shaker at $23 \pm 2\text{ }^{\circ}\text{C}$ for 24 h. The powder from the solution was removed by filtration through a nylon-membrane microfilter (Millex-HN filters, SLHN033NS, Millipore Ireland, Ltd.). The filtrate (10 mL) was diluted ten-fold with water. The concentrations of sodium, potassium, magnesium, and calcium ions in the diluted solution were measured using an ion chromatographic system (Dionex CS-3000, Nippon Dionex K. K.) according to the Japanese Industrial Standard for testing methods for industrial wastewater (JIS K 0102, 2008) [20].

Absorbed cesium concentration

Aqueous CsCl solution (50 mL) containing powder adsorbent (0.10, 0.20, 0.40, 0.80, or 1.60 g) in a capped Erlenmeyer flask was shaken and then removed by

filtration through the microfilter using the same procedure as described above. The pH of the filtrate was measured using the pH meter. Cesium ion concentration in the filtrate was determined using an inductively coupled plasma mass spectrometer (ICP-MS) (Agilent 7700x, Agilent Technologies, Ltd.) with an internal standard method (standard isotope: ^{115}In). The ICP-MS measurements were repeated three times for each sample solution. All relative standard deviations were within 3.1%. The cesium ion concentration in the filtrate was regarded as the concentration of residual cesium ions in the liquid phase at equilibrium. The concentration of cesium adsorbed onto the charcoal (W) was determined by dividing the reduction in mass (m) of cesium ions in the liquid phase by the mass (M) of powder charcoal added, according to Eq. (1):

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

where the units of m and M are mg and g, respectively.

Results and discussion

The experimental data of OC and 4WE-OC have been published previously [5, 8, 9], but are presented in the figures and tables for comparison.

Nonmetallic elements and ash

Mass percentages of nonmetallic elements and ash of the three charcoals are shown in Table 1. These elements were determined using the analytical methods according to the Japanese Industrial Standard for coal and coke (JIS M 8813, 2004) [14] as described above. The calculation of the percentages was based on the dry mass of the charcoal. The percentage of carbon in MC was considerably lower than those in other charcoals, and BC had the lowest value as a mass percentage of hydrogen. Oxygen and hydrogen in MC were abundant compared to those in BC and OC. The oxygen percentage of greater than 30 suggests that MC was manufactured at relatively low temperature [12]. No

Table 1 Mass percentage of nonmetallic elements and ash

Charcoal	Mass percentage (dry basis, %)					
	C	H	O	N	S	Ash
OC*	83.86	2.36	11.86	0.45	0.04	1.32
MC	62.14	3.05	32.59	0.14	0.16	1.80
BC	78.43	0.46	19.58	0.24	0.05	1.17

OC Japanese oak charcoal, MC mangrove charcoal, BC bincho charcoal

* The mass percentage of elements and ash in OC has been published previously [8]

Table 2 Relative mass percentages of metal elements to total elements detected by X-ray fluorescence analysis

Charcoal	Element (relative mass% ^{**})										
	Mg	Al	K	Ca	Ti	Mn	Fe	Cu	Ni	Zn	Sr
OC*	ND	0.40	30.0	64.2	ND	2.21	0.45	0.09	0.09	ND	0.19
MC	ND	0.54	7.47	83.4	ND	1.77	ND	ND	0.29	ND	1.26
BC	ND	0.58	28.5	59.6	ND	6.19	0.49	1.10	0.16	0.14	0.49

OC Japanese oak charcoal, MC mangrove charcoal, BC bincho charcoal, ND not detected

* Part of the data on OC has been published previously [9]

** Relative mass percentages were calculated by dividing the mass of an element by the total mass of elements with atomic numbers greater than eleven

significant differences existed in the total percentages of carbon, oxygen, and hydrogen among the three charcoals. The percentage of ash was a slightly greater in MC than in the other charcoals.

Metal elements

Relative mass percentages of the metals contained in the charcoals were determined using X-ray fluorescence analysis, and results are listed in Table 2. However, the absolute mass percentages of metal elements should be much smaller than their relative mass percentages, because the total percentages of carbon, hydrogen, and oxygen, which are undetectable by X-ray fluorescence spectroscopy, were greater than 97 in all the charcoals.

The most abundant metal element was calcium, and the second was potassium. Other metal elements were present as trace elements except for manganese in BC.

Estimate of manufacturing temperature from Raman parameters

Figure 1 demonstrates the typical Raman spectra at room temperature of OC, MC, and BC. Table 3 contains a summary of D-band and G-band Raman parameters, and estimated manufacturing temperature (T_M) regions for the three charcoals. The T_M regions were determined using the relationship between the heat-treatment temperature and Raman parameters of the two bands obtained from Japanese cedar charcoals [17]. T_M of BC and MC used in this study were expected to be approximately 1000 °C and below 500 °C, respectively. It is generally believed that T_M of commercially available BC and MC are around 500 and 1000 °C, respectively. Thus, it would be reasonable to assume that the T_M regions of BC and MC were estimated as mentioned above.

Point of zero charge and specific surface area

As shown in Table 4, the PZC of MC was significantly less than those of OC and BC, suggesting that fundamental differences existed in the surface physical and/or chemical

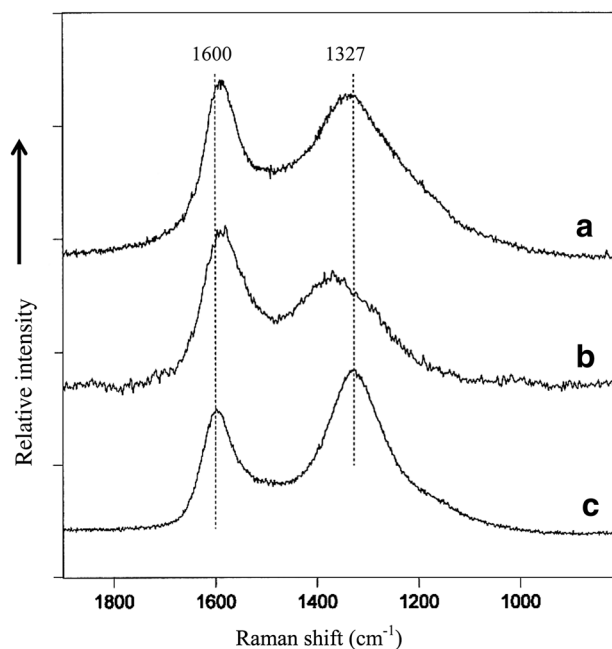


Fig. 1 Raman spectra in the 1900–800 cm^{-1} region for **a** Japanese oak charcoal (OC), **b** mangrove charcoal (MC), and **c** bincho charcoal (BC)

properties between MC and the other charcoals. The differences may be due primarily to functional groups, such as phenolic hydroxy or carboxy groups, because MC was produced at the lowest temperature and contained abundant oxygen and hydrogen compared to OC and BC (Table 1).

The specific surface area determined by the BET multi-point method increased in the order $\text{MC} < \text{BC} < \text{OC}$, and thus, no correlation was observed between specific surface area and T_M . In addition, the area of MC was smaller than those of OC and BC by at least two orders of magnitude. Thus, MC will be crucially different from OC and BC in terms of surface structure or framework at the molecular level.

IR-PA spectra of charcoals

Figure 2 shows the IR-PA spectra of the charcoals in the 3600–800 cm^{-1} region. Although the IR bands due to H_2O

Table 3 Raman parameters and estimated manufacturing temperature (T_M) region

Charcoal	D-band (cm^{-1})		G-band (cm^{-1})		Area ratio (D/G)	T_M^{**}
	Position	Line width	Position	Line width		
OC*	1338.1 ± 8.6	167.4 ± 4.4	1591.1 ± 0.6	63.4 ± 0.9	3.34 ± 0.15	$600\text{ }^\circ\text{C} < T_M < 800\text{ }^\circ\text{C}$
MC	1372.2 ± 10.3	198.1 ± 26.5	1589.1 ± 4.0	87.7 ± 3.1	1.83 ± 0.48	$T_M < 500\text{ }^\circ\text{C}$
BC	1327.7 ± 1.2	143.9 ± 14.7	1599.4 ± 1.5	65.7 ± 1.0	3.69 ± 0.83	$T_M \approx 1000\text{ }^\circ\text{C}$

OC Japanese oak charcoal, MC mangrove charcoal, BC bincho charcoal

* The outline of Raman parameters for OC has been described previously [5]

** T_M manufacturing temperature

Table 4 Point of zero charge (PZC) and specific surface area of charcoals

Charcoal	PZC	Specific surface area (BET multi-point method, m^2/g)
OC	6.70*	154
MC	4.12	<0.01
BC	6.42	8.90

OC Japanese oak charcoal, MC mangrove charcoal, BC bincho charcoal

* The PZC of OC has been published previously [5]

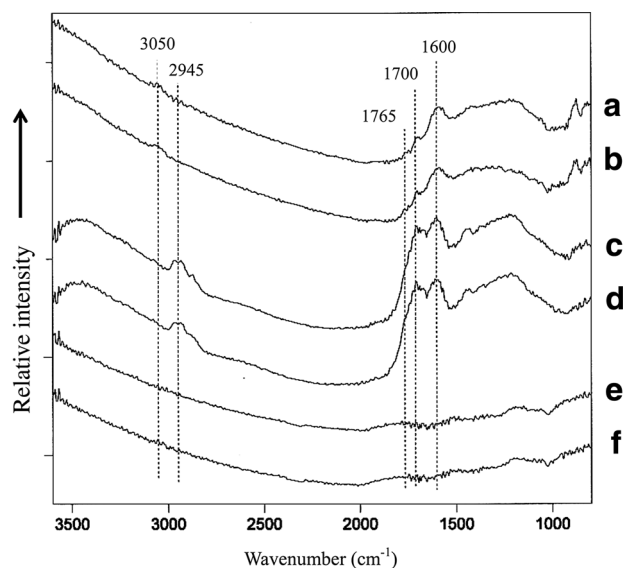


Fig. 2 IR-PA spectra in the $3600\text{--}800\text{ cm}^{-1}$ region for **a** Japanese oak charcoal (OC), **b** OC after 4 times water extraction (4WE-OC), **c** mangrove charcoal (MC), **d** MC after 4 times water extraction (4WE-MC), **e** bincho charcoal (BC), and **f** BC after 4 times water extraction (4WE-BC)

and CO_2 gas were deleted, correction of the baseline for distortion or curvature was not performed. The IR-PA spectra of charcoals made from Japanese cedar (*Cryptomeria japonica* D. Don) at various temperatures have been reported previously [21], indicating that PA

spectroscopy is an appropriate technique for obtaining IR spectra of black samples, such as charcoal.

No significant changes in the spectral profile were observed owing to the 4 times extraction of three charcoals. The IR-PA spectra of 8WE-OC, 12WE-OC, 8WE-MC, and 12WE-MC also showed no appreciable differences from the untreated charcoal.

The MC likely contains the most abundant organic functional groups among the three charcoals (Fig. 2). Few functional groups containing O or H atoms were observed on a PA spectrum of BC despite an oxygen percentage greater than 19%, and those of OC were intermediate between the two charcoals. A peak near 1600 cm^{-1} may be attributed to benzene rings and C=C bonds, and peaks and shoulders in the $1800\text{--}1650\text{ cm}^{-1}$ region are likely due to C=O double bonds in carboxy and various carbonyl groups. In the IR-PA spectra of MC and 4WE-MC, peaks near 2945 cm^{-1} and an extremely broadband at about 3450 cm^{-1} are presumably assigned to C–H stretching vibrations in saturated hydrocarbon groups and O–H stretching vibrations, respectively. A weak band at approximately 3050 cm^{-1} , observed on the IR-PA spectra of OC and 4WE-OC, would be attributed to C–H stretching vibrations in unsaturated or aromatic hydrocarbon groups.

By comparison of the IR-PA spectra of Japanese cedar charcoals [21], the T_M regions of OC, MC, and BC were estimated to be $500\text{--}600\text{ }^\circ\text{C}$, $300\text{--}400\text{ }^\circ\text{C}$, and $>700\text{ }^\circ\text{C}$, respectively. These estimates are not inconsistent with those based on Raman measurements (Table 3).

Sodium, potassium, magnesium, and calcium ions eluted from adsorbents

The concentrations of group 1 and 2 metal ions eluted from 1.60 g of charcoal into 50 mL deionized water in 24 h are given in Table 5. The rationale for calculating the maximum and minimum has been described previously [9]. Although calcium was the most abundant metal element in the three charcoals, the primary metals eluted from OC and MC were not calcium but potassium and sodium,

Table 5 Ranges of concentrations of sodium, potassium, magnesium, and calcium eluted from non-treated and treated charcoals

Adsorbent	Molar concentration (mol/L)							
	Na ⁺		K ⁺		Mg ²⁺		Ca ²⁺	
	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum
No. adsorbent (blank)	<1.3 × 10 ⁻⁶		<5.1 × 10 ⁻⁷		<8.2 × 10 ⁻⁷		<1.0 × 10 ⁻⁶	
OC*	4.8 × 10 ⁻⁵	3.6 × 10 ⁻⁵	2.8 × 10 ⁻³	2.8 × 10 ⁻³	3.3 × 10 ⁻⁵	2.6 × 10 ⁻⁵	3.0 × 10 ⁻⁵	2.1 × 10 ⁻⁵
MC	1.2 × 10 ⁻³	1.2 × 10 ⁻³	9.7 × 10 ⁻⁵	9.3 × 10 ⁻⁵	4.9 × 10 ⁻⁵	4.2 × 10 ⁻⁵	1.2 × 10 ⁻⁴	1.1 × 10 ⁻⁴
BC	5.2 × 10 ⁻⁵	4.0 × 10 ⁻⁵	3.1 × 10 ⁻⁴	3.1 × 10 ⁻⁴	8.2 × 10 ⁻⁶	0	6.7 × 10 ⁻⁴	6.6 × 10 ⁻⁴
4WE-OC*	1.3 × 10 ⁻⁵	0	1.0 × 10 ⁻⁴	9.5 × 10 ⁻⁵	8.2 × 10 ⁻⁶	0	1.7 × 10 ⁻⁴	1.7 × 10 ⁻⁴
4WE-MC	6.3 × 10 ⁻⁴	6.1 × 10 ⁻⁴	7.2 × 10 ⁻⁵	6.7 × 10 ⁻⁵	8.2 × 10 ⁻⁶	0	5.0 × 10 ⁻⁵	4.0 × 10 ⁻⁵
4WE-BC	5.2 × 10 ⁻⁵	3.9 × 10 ⁻⁵	3.1 × 10 ⁻⁵	2.6 × 10 ⁻⁵	8.2 × 10 ⁻⁶	0	1.5 × 10 ⁻⁵	5.0 × 10 ⁻⁶

OC Japanese oak charcoal, MC mangrove charcoal, BC bincho charcoal, 4WE-OC OC after 4 times water extraction, 4WE-MC MC after 4 times water extraction, 4WE-BC BC after 4 times water extraction

* The data for OC and 4WE-OC have been published previously [9]

respectively. The amount of potassium ions eluted from OC was greater than that from MC or BC by one order of magnitude. The amount of sodium ions eluted from MC was much greater than the amounts of potassium or calcium ions, and also much larger than that eluted from OC or BC. These results suggest an effect due to sea water. Specifically, mangrove forests indicate brackish water, and trees that grow there will absorb minerals from sea water.

The amounts of sodium and potassium ions eluted from OC and MC were reduced by repeating the water extraction 4 times. For BC, no significant change was observed in the elution of sodium ions, although the elution of potassium ions decreased with repeated extractions. Concentrations of magnesium ions eluted from BC, 4WE-OC, 4WE-MC, and 4WE-BC were negligible. Although the elution of calcium ions from 4WE-OC was larger than that from OC, the calcium ions eluted from MC and BC decreased clearly throughout the extraction treatments. It is noteworthy that the total elution of sodium and potassium ions, which exert much stronger blocking effects compared to magnesium and calcium ions [8], was evidently reduced by water extraction.

Adsorption isotherms of cesium ions onto adsorbents

Figure 3 depicts the plots of cesium ion concentration (C : mg/L) in aqueous solution vs. cesium concentration (W : mg/g) of the charcoal adsorbent (i.e., adsorption isotherms of cesium adsorption onto charcoals from aqueous CsCl solution).

Of the three untreated charcoals, MC possessed the greatest adsorption ability for cesium ions, followed by OC, and then BC. However, this order may not be universally true, because the entire batch of a commercial charcoal may not possess a uniform adsorption ability

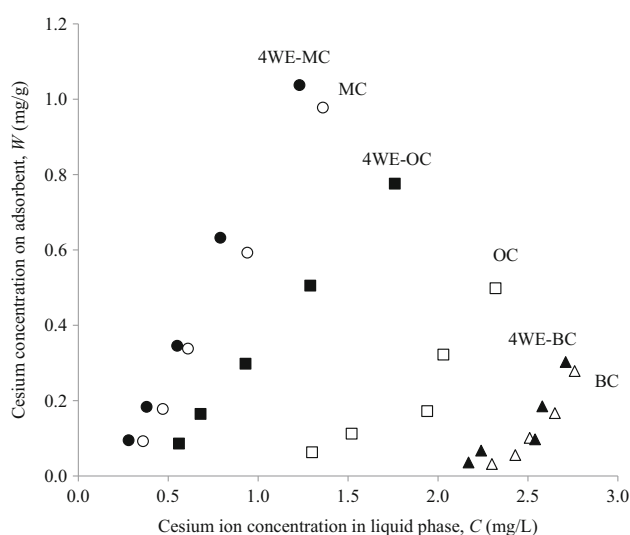


Fig. 3 Isotherms of cesium adsorption from aqueous cesium chloride solution onto mangrove charcoal (MC) (open circles), MC after 4 times water extraction (4WE-MC) (filled circle), Japanese oak charcoal (OC) (open squares), OC after 4 times water extraction (4WE-OC) (filled squares), bincho charcoal (BC) (open triangles), and BC after 4 times water extraction (4WE-BC) (filled triangles)

even when manufactured under the same conditions [9, 10]. This is further evidence that no correlation exists between cesium-adsorption ability and specific surface area. In contrast, a correlation existed between T_M and adsorption; adsorption ability increased as the T_M value decreased. In a previous report [21], IR-PA spectra indicated that charcoal manufactured at 600 °C contained a significant amount of functional groups, but few functional groups remained in the charcoal when the processing temperature was 700 °C. Accordingly, the remaining amount of functional groups plays a role in the adsorption of cesium ions.

The adsorption isotherms of 4WE-MC, 4WE-OC, and 4WE-BC indicate that extraction increased the adsorption ability of the three charcoals (Fig. 3). This increase in adsorption ability appears to be due to decreases in the total amounts of group 1 and 2 metal ions eluted from charcoal (Table 5). However, the increase for OC was much larger than those for MC and BC. As reported in a previous study [10], pH plays an important role in the cesium-adsorption ability of charcoal in aqueous solution. Thus, charcoal does not possess significant cesium-adsorption ability unless the pH of the sample solution exceeds the PZC adequately. As can be seen from Table 6, the pH values of the sample solutions containing 4WE-MC, 4WE-OC, and 4WE-BC were sufficiently larger than their respective PZC values, although they were lower than those containing MC, OC, and BC. One possible explanation for the effectiveness of extractions to increase the cesium-adsorption ability of OC is that the relatively large decrease in rate of potassium ions eluted (compared to those of MC and BC), which have stronger blocking effects than other metal ions [8], is remarkably large.

It should be noted that MC and 4WE-MC exhibited high cesium-adsorption abilities under weakly acidic conditions. This feature may be a key point for developing practical cesium adsorptives based on charcoal, because rainwater, groundwater, and soil are often weakly acidic. The pH of the sample solutions increased dramatically with the addition of OC and BC, and exceeded pH 9, but remained near 5.8 with the addition of MC. Moreover, the pH of 4WE-OC and 4WE-BC solutions increased to a value from 7 to 9, whereas the 4WE-MC solutions experienced a clear decrease in pH, with an even further decrease in the pH of the sample solutions with 8WE-MC and 12WE-MC decreased. It has been reported that the charcoal carbonized at 400 °C decreased pH of water [22].

As described previously [10], the elution of group 1 and 2 metal ions from OC was a dominant factor in increasing

the pH of sample solutions, because the metals could be contained as carbonates, hydroxides, or oxides in OC. As shown in Table 5, total elution of the four metal ions from untreated charcoal increased in the order BC < MC < OC, with 4WE-MC exhibiting the greatest total elution among the charcoals extracted 4 times. Therefore, if the chemical forms of the four metals in MC are not significantly different from those in OC and no other control factors for pH are present, pH should increase with the addition of MC or 4WE-MC. The possibility that most of the four metals exist as their chlorides in MC cannot be excluded, because the composition of trees used to make MC may be influenced by sea water, but it is unlikely that the dissolution of chlorides decreased the pH of the sample solutions.

The decrease in pH with the addition of *n*WE-MC can be explained by differences in the manufacturing processes between MC and the other charcoals. Woody materials generate considerable amounts of smoke during heat treatment for making charcoal. The smoke is sufficiently removed from OC and BC in the manufacturing processes; however, the removal of components from MC through the smoke may be incomplete. A note on the package of commercial MC usually indicates that this charcoal must be used outdoors, because its combustion often emits harmful smoke. Pyroligneous acid, known as “wood vinegar,” is obtained by cooling this smoke; this acid is strongly acid. Therefore, it is most likely that MC contains more acidic organic substances compared with OC and BC, and the elution of these substances decreases the pH of the sample solutions. The pH-decreasing effect of eluted acidic substances can be assumed to be superior to the pH-increasing effect of the eluted group 1 and 2 metal ions with respect to *n*WE-MC, and the two effects for MC are approximately equivalent to each other.

The changes in adsorption isotherms of MC by additional water extractions are shown in Fig. 4. The adsorption amounts of cesium ions onto 8WE-MC and 12WE-MC

Table 6 pH in aqueous cesium chloride (CsCl) solutions after the addition of adsorbent and stirring for 24 h

Aqueous CsCl solution	Added adsorbent (g)	pH							
		OC*	4WE-OC*	MC	4WE-MC	8WE-MC	12WE-MC	BC	4WE-BC
2.50×10^{-5} mol/L**	0.10	9.4	7.8	5.9	5.2	5.1	5.0	9.7	7.1
	0.20	9.2	8.6	5.8	5.1	5.0	4.9	10.1	7.4
	0.40	9.9	8.9	5.8	5.0	5.0	4.9	10.8	8.0
	0.80	10.1	8.0	5.7	4.9	4.9	4.8	11.1	8.0
	1.60	10.2	8.5	5.6	4.8	4.8	4.7	11.5	8.1

OC Japanese oak charcoal, MC mangrove charcoal, BC bincho charcoal, 4WE-OC OC after 4 times water extraction, 4WE-MC MC after 4 times water extraction, 8WE-MC MC after 8 times water extraction, 12WE-MC MC after 12 times water extraction, 4WE-BC BC after 4 times water extraction

* The outlines of pH values in sample solutions with OC or 4WE-OC have been described in our previous paper [8, 9]

** pH = 5.8

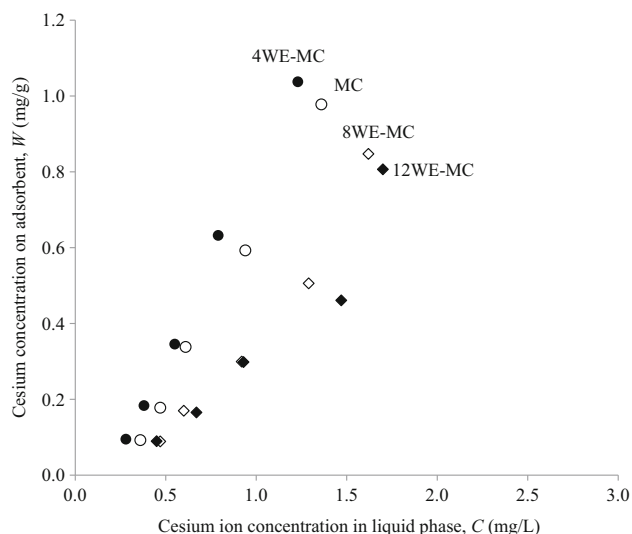


Fig. 4 Isotherms of cesium adsorption from aqueous cesium chloride solution onto mangrove charcoal (MC) (open circles), MC after 4 times water extraction (4WE-MC) (filled circle), MC after 8 times water extraction (8WE-MC) (open diamonds), and MC after 12 times water extraction (12WE-MC) (filled diamonds)

decreased, while those onto 4WE-MC increased. Similar but much larger changes were observed for OC [10]. Thus, the adsorption behavior of MC given in Fig. 4 suggests that after lengthy immersion in water, the decrease in cesium-adsorption ability of MC was much less than that of OC. This is another key factor in the development of practical adsorptives.

The amount of cesium adsorption by 8WE-MC decreased was less than that of 4WE-MC, despite the similarity in the pH of the sample solutions. In addition, the total elution of metal ions from 8WE-MC was unlikely to be greater than that from 4WE-MC. Therefore, these results suggest that factors other than pH and the level of metal ions control cesium-adsorption ability. One factor is likely to be acidic substances, which are produced during the manufacturing process, and have the ability to capture cesium ions. No noticeable differences were observed between IR-PA spectrum of MC and those of 8WE-MC and 12WE-MC. However, the decreases in cesium adsorption by 8WE-MC and 12WE-MC were due probably to the removal of the acidic substances that have the functional groups being able to capture cesium ions, such as carboxylic or phenolic hydroxyl groups from MC by the extraction treatments.

The PA spectra indicated that few organic functional groups containing H or O atoms remain in BC because of its high T_M (ca. 1000 °C). However, the cesium-adsorption abilities of BC and 4WE-BC were not negligible, as is evident from Fig. 3, which implies that cesium adsorption in aqueous solution is complicated and cannot be explained only in terms of acidic functional groups in the charcoal.

Other mechanisms for capturing cesium ions appear necessary to account for the cesium-adsorption ability of BC.

Conclusions

The experimental data collected in this study indicated that the amount of acidic functional groups contained in charcoal is a governing the ability to adsorb cesium. The results confirmed that no correlations existed between specific surface area determined using a physical method and the cesium-adsorption ability of charcoal in aqueous solution.

A notable finding demonstrated that MC possessed high cesium-adsorption abilities even in weak acidic regions, unlike OC. This study showed that practical charcoal adsorptives for cesium ions can be developed by manufacturing charcoal, such as MC, at relatively low temperatures.

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