

# Adsorption behavior of a carbonized paper sludge towards $^{137}\text{Cs}$

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**Abstract** The adsorption of  $^{137}\text{Cs}$  by a carbonized paper sludge (PSC) was studied using the original and its modified form (PFC-PSC) by impregnating with 1 % potassium ferrocyanide. The distribution coefficient of PSC decreases with increasing  $\text{Cs}^+$  concentration in  $^{137}\text{Cs}$  solutions whereas that of PFC-PSC is highest at around and lower than  $60 \text{ Bq ml}^{-1}$ . The Freundlich constant of PFC-PSC is much higher than that of PSC, suggesting that the  $^{137}\text{Cs}$  affinity of the former is higher than the latter. The pseudo second order rate constant of PSC decreases but that of PFC-PSC increases with decreasing  $\text{Cs}^+$  concentration.

**Keywords** Carbonized paper sludge ·  $^{137}\text{Cs}$  · Adsorption · Isotherm · Rate constant

## Introduction

Pulp and paper mills generate paper sludge (PS). Under the environmental protection laws in some countries, PS may not be land-filled. Generally, approximately 90 % of PS is reused in the form of ash and the balance 10 % in the original state. Most of PS ash is employed in the production of cement. And a part of it is used as antioxidant in the manufacture of iron, or road subgrade material, or industrial waste-based fertilizer in that order. The principal use

of PS in its original form is to produce foaming materials or soil fertilizer. Pyrolysis products from PS are to be used in the manufacture of soil conditioner or fertilizer. PS is also used to prepare, on a bench scale, activated carbon to remove COD [1] or phenol [2] from waste water.

Industrial activated carbon is usually made from coal (anthracite, bituminous and lignite), coconut shells, softwood and hardwood, peat and petroleum based residues. Under the Regulatory Guide 1.52, the U.S. Nuclear Regulatory Commission sets out requirements for activated carbon to be efficient in cleaning up exhaust air and gas stream containing fission product iodine isotopes, mainly  $^{131}\text{I}$ , and organic methyl iodine ( $\text{CH}_3^{131}\text{I}$ ). For this purpose, activated carbon is generally impregnated with  $\text{I}^-$ , KI or tetraethylenediamine (TEDA) prior to pyrolysis.

Caccin et al. [3] reported that amongst uranium (VI), cesium and strontium only uranium (VI) is adsorbed onto an industrial coconut shell activated carbon. On the other hand, it was found that activated carbon can only remove  $^{131}\text{I}$  but not  $^{134}\text{Cs}$  and  $^{85}\text{Sr}$  in artificially contaminated river water, and that neither  $^{131}\text{I}$  nor  $^{134}\text{Cs}$  and  $^{85}\text{Sr}$  in artificially contaminated sea water can be removed by activated carbon [4]. However, the activated carbon mentioned was not identified.

Copper ferrocyanide exchange resin [5] and potassium cobalt hexacyanoferrate (II) [6] were synthesized to separate radiocesium from fission product mixtures and to remove radiocesium from contaminated aqueous solutions, respectively. Potassium nickel hexacyanoferrate (II) was prepared to examine its uptake of radiocesium and the results showed that its cesium adsorption followed the Langmuir isotherm [7]. Nevertheless, these works did not study the kinetics of the cesium adsorption. Nickel hexacyanoferrate-pretreated laboratory-made activated carbons from rice husk and areca nut were also found to adsorb cesium according to Langmuir isotherm and their kinetics

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data are fitted well into the pseudo-second order rate model [8]. However, the kinetics of the original and nickel hexacyanoferrate-pretreated rice husk and areca nut activated carbons were not compared.

The objective of this study was to examine the adsorption of  $^{137}\text{Cs}$  in aqueous solutions onto an industrial carbonized paper sludge, both in original (PSC) and modified form which, in turn, was a PSC impregnated with 1 % potassium ferrocyanide (PFC-PSC).

## Experimental

### Materials

PSC used is produced by Doh-Ei Paper (Hokkaido, Japan). Pyrolysis conditions and characterizations PSC as well as its ability to remove  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  from radiocontaminated soil were reported earlier [9, 10]. Presently, PSC is registered as an industrial waste-based fertilizer with the Japanese Ministry of Agriculture, Forestry and Fisheries. Its relative size and scanning electron microscope (SEM) photographs are given in Fig. 1. Industrial activated carbon samples were supplied by Kuraray (Osaka, Japan) and Dainen (Himeji, Japan) Corporations.

PFC-PSC was prepared by impregnating 450 g OD (oven dry) of PSC with 450 ml of a solution containing potassium ferrocyanide (Kanto Chemicals) corresponding to 1 % (w/w) of the PSC used. After the mixture was well mixed, it was air-dried for 2–3 days and then dried at 25–30 °C for 1–2 days.

The  $^{137}\text{Cs}$  isotope was purchased from Japan Radioisotope Association in chloride form in 0.1 N HCl containing 100,000 Bq  $\text{ml}^{-1}$ .

### Procedure

Purchased  $^{137}\text{Cs}$  isotope was diluted to a solution of 103.1 Bq  $\text{ml}^{-1}$  with a cesium carrier of  $2.83 \times 10^{-3} \text{ M l}^{-1}$ . A part of this solution was further diluted to make a solution

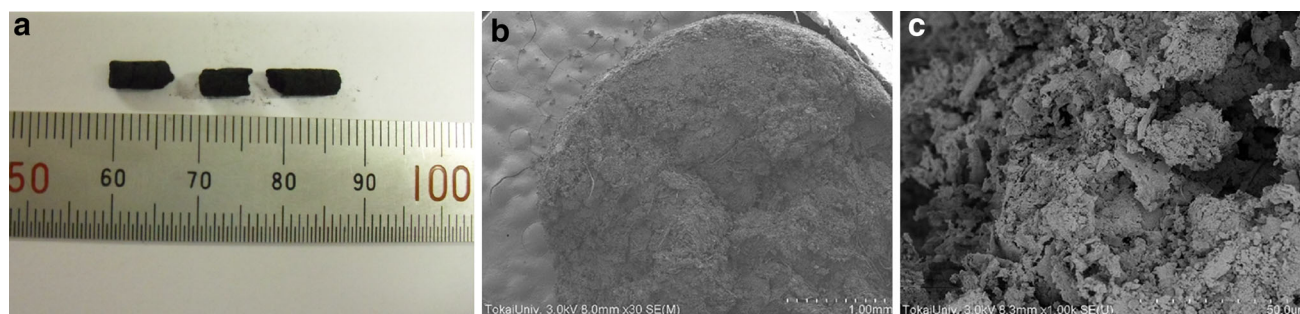
of 60.8 Bq  $\text{ml}^{-1}$ . Similarly, solutions of 30.5 and 4.6 Bq  $\text{ml}^{-1}$  were prepared from the 60.8 and 30.5 Bq  $\text{ml}^{-1}$  solutions, respectively.

32 g (OD) of PSC or PFC-PSC were placed in 175 ml Corning graduated conical tubes and 120 ml of each of the above radiotracer solutions were added. These tubes were then shaken in an agitator at 25 °C for as long as 330 h. They were taken out at different intervals, filtered on double Advantec filter papers #2 and #6, and the filtrates were analyzed for residual  $^{137}\text{Cs}$ .

The effect of acid and alkali on the pH of PSC was examined by adding 100 ml of 0.01 N HCl or 100 ml of 0.0001 N NaOH to various amounts of PSC, stirred overnight and their pH's were then measured with a glass electrode pH meter. A similar procedure was carried out to study the effect of PSC on the pH of soil by adding 100 ml of distilled water to mixtures containing various amounts of PSC and 50 g (OD) of a 2 mm screened-soil from a nearby vegetable garden. Their pH's were determined after stirring overnight.

### Analytical

Cation exchange capacity of PSC was determined based on the compulsive exchange method using barium chloride [11]. Total area, pore average diameter, pore volume of PSC, activated carbons from Kuraray and Dainen were determined with a BELSORP-mini (Osaka, Japan). Moisture was determined by drying PSC and PFC-PSC at 105 °C for 12–16 h. 1 g (OD) of PSC was added with 100 ml of distilled water, stirred overnight and titrated against 0.1 M HCl to determine its alkaline equivalence. Similarly, 1 g (OD) of PSC was added with 100 ml of distilled water, stirred overnight and its pH was measured. Carbon content was the difference in the weight of PSC, Kuraray and Dainen activated carbons before and after ashing. Ashing conditions were 850 °C and 90 min for PSC, and 950 °C and 2 h for Kuraray and Dainen activated carbons, respectively. Of the PSC components, chlorine, sulfur were determined by ion chromatography using a



**Fig. 1** Relative size in mm (a), 30X SEM (b), and 1,000X SEM (c) of PSC (SEM photographs (b) and (c) courtesy of Tokai University)

Dionex ICS-2100. Barium, cadmium and lead were determined by ICP method using a Perkin Elmer Optima 5300DV. Silica, calcium, aluminium, iron, manganese, titan, zinc, copper, magnesium were determined by the usual flame atomic method. Composition of the industrial activated carbons was supplied by each maker. Radioactivity of  $^{137}\text{Cs}$  was determined using a coaxial Ortec GMX series high purity Ge semiconductor detector and the software Gamma Studio (Seiko EG&G Ltd.).

## Results and discussion

### Characteristics of PSC

The relative size of PSC pellets is given in Fig. 1a. It is believed that this is similar to the sizes of industrial activated carbons. PSC pellets possess a lower total area, a lower pore volume and a higher pore average diameter than the corresponding characteristic of industrial activated carbon pellets made from coal by Kuraray and Dainen (Table 1). SEM photographs (b) and (c) in Fig. 1 show, respectively, the cross section and the internal structure of a PSC pellet which in turn corroborate the above results.

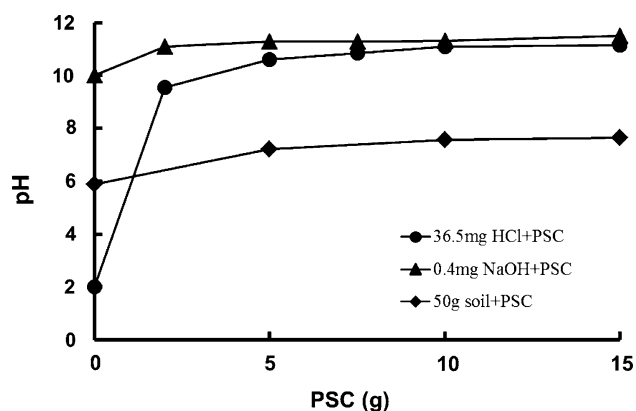
Since pH and alkaline equivalence of PSC are high, sodium hydroxide or hydrochloric acid did not affect its pH and mixing PSC with soil would only make the soil alkaline (Fig. 2).

As indicated in Table 2, the average carbon content of the industrial activated carbons employed is 90.8 % or approximately 2.9 times of that of PSC (31.7 %). Thus, the mineral content of the latter (68.3 %) is approximately 7.4 times of that of the former (9.2 %). Among the components of PSC, those with high contents are calcium, iron, magnesium, silica, and those with low contents aluminum, potassium, phosphorus, sodium, zinc, copper and sulfur. These are the nutrients for plants and vegetables. Furthermore, cadmium and lead in PSC are undetected. The

**Table 1** Physical properties of PSC and industrial activated carbons

Constituents	PSC	KrAc	DnAc
Raw materials	PS	Coal	Coal
Total area ( $\text{m}^2 \text{g}^{-1}$ )	90.9	1,014.8	973.9
Pore average $\varnothing$ (nm)	6.10	1.96	1.92
Pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	20.89	233.14	223.76
Moisture (%)	1.6		
pH	11.5		
CEC ( $\text{mEq } 100 \text{ g}^{-1} \text{ as } \text{NH}_4$ )	2.66		
Alkaline equivalence ( $\text{meq NaOH g}^{-1}$ )	1.92		

KrAc, DnAc are activated carbons from Kuraray and Dainen, respectively



**Fig. 2** Effects of hydrochloric acid, sodium hydroxide or soil on pH's of PSC

**Table 2** Composition of PSC and industrial activated carbons

Constituents	PSC	KrAc	DnAc
C (%)	31.7	92.8	88.7
Si (ppm)	9,625	514	
Al (ppm)	2,261	8,262	476
Ca (ppm)	137,115	7,010	858
K (ppm)	178	701	83
Fe (ppm)	31,536	9,301	140
Mg (ppm)	11,655	2,216	1,203
P (ppm)	189	2	
Na (ppm)	754	148	
Mn (ppm)	40	84	23
Zn (ppm)	404	10	
Ba (ppm)	89	75	
Cu (ppm)	130	44	
S (ppm)	144	3,668	
Ti (ppm)	375	304	
Cd (ppm)	ND		
Pb (ppm)	ND		

KrAc, DnAc : see footnote of Table 1

ND not detected. Detection limit of Cd and Pb: 0.01 ppm

presence of the nutrient minerals, the capability to neutralize soil and the undetection of cadmium and lead all suggest that PSC can be a good industrial waste-based fertilizer.

### Removal of $^{137}\text{Cs}$ by PSC

Shown in Fig. 3 is the removal of  $^{137}\text{Cs}$  in aqueous solution by PSC. The removal of  $^{137}\text{Cs}$  is the difference between the initial and residual  $\text{Cs}^+$  concentrations at various intervals. Observedly, the removal increased with

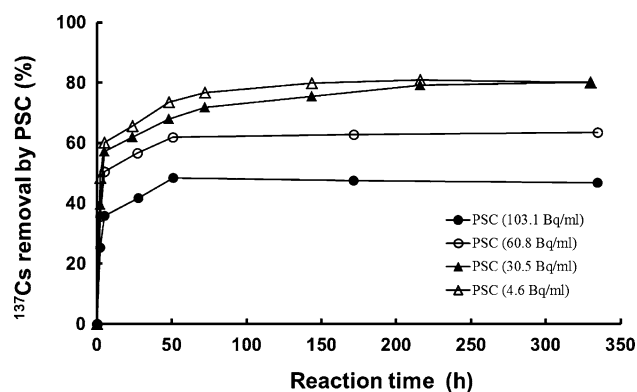


Fig. 3 Removal of  $^{137}\text{Cs}$  from aqueous solutions by PSC

decreasing initial  $\text{Cs}^+$  concentrations. However, the removal was not higher than 81 % even for a  $^{137}\text{Cs}$  solution with an initial  $\text{Cs}^+$  concentration as low as  $0.01692 \text{ g l}^{-1}$ .

For all initial  $\text{Cs}^+$  concentrations examined, the removal was fast during the first 5 h reaction and then proceeded slowly. For the solutions with  $\text{Cs}^+$  concentrations corresponding to high initial radioactivities of  $103.1 \text{ Bq ml}^{-1}$  ( $0.3768 \text{ g l}^{-1}$ ) and  $60.8 \text{ Bq ml}^{-1}$  ( $0.2265 \text{ g l}^{-1}$ ), the highest removals were 48 and 62 %, respectively, at 50 h reaction and afterwards. For the solutions with  $\text{Cs}^+$  concentrations corresponding to low initial radioactivities of  $30.5 \text{ Bq ml}^{-1}$  ( $0.1132 \text{ g l}^{-1}$ ) and  $4.6 \text{ Bq ml}^{-1}$  ( $0.01692 \text{ g l}^{-1}$ ), the removal proceeded slowly after the first 5 h reaction and attained the highest values at around 216 h reaction of 80.2 and 80.9 %, respectively. The results suggest that PSC can adsorb  $\text{Cs}^+$  of various concentrations but at different velocity and quantity.

### Removal of $^{137}\text{Cs}$ by PFC-PSC

Figure 4a shows that the adsorption of  $\text{Cs}^+$  in aqueous solution by PFC-PSC was very fast and almost attained a 100 % level at lengthened reaction times. The results were further elucidated in Fig. 4b which indicated that irrespective of  $\text{Cs}^+$  initial concentration PFC-PSC removed more than 98 % of  $\text{Cs}^+$  in aqueous solutions within the first 10 h reaction. This suggests that PFC-PSC is a stable adsorbent and can be used to remove radioactive cesium in aqueous solution at high efficiency.

### Distribution coefficient of $^{137}\text{Cs}$

In this work the distribution coefficient of  $\text{Cs}^+$  was computed according to (1) based on the literature [12].

$$K_d = \frac{A_i - A_f}{A_f} \times \frac{V}{m} \quad (1)$$

where  $K_d$  ( $\text{ml g}^{-1}$ ) is the distribution coefficient,  $A_i$  and  $A_f$  ( $\text{Bq ml}^{-1}$ ) are the respective  $\text{Cs}^+$  concentration before and

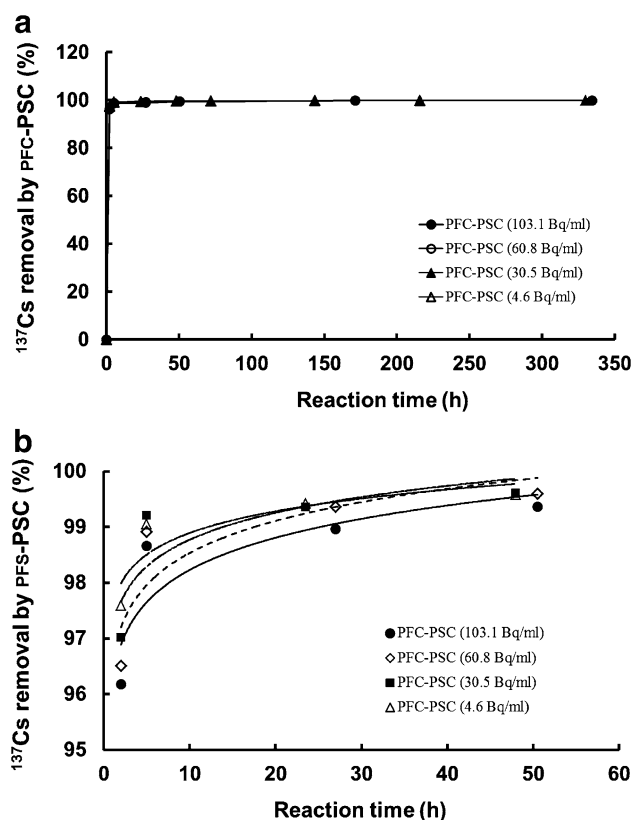


Fig. 4 a Removal of  $^{137}\text{Cs}$  from aqueous solutions by PFC-PSC. b Removal of  $^{137}\text{Cs}$  from aqueous solutions by PFC-PSC during the first 50 h

after equilibrium (the equilibrium of all the samples examined was approximately 50 h),  $V$  is the volume (ml) of the solution, and  $m$  the weight (g) of PSC or PFC-PSC.

The standard error of  $A_i - A_f$  was computed based on Eq. (2), and that of  $[(A_i - A_f)/A_f]$  on (3).

$$(A_i \pm \sigma A_i) - (A_f \pm \sigma A_f) = (A_i - A_f) \pm \sqrt{(\sigma A_i)^2 + (\sigma A_f)^2} \quad (2)$$

$$(C \pm \sigma_C) \div (A_f \pm \sigma A_f) = (C \div A_f) \pm (C \div A_f) \sqrt{(\sigma_C \div C)^2 + (\sigma A_f \div A_f)^2} \quad (3)$$

where  $C = (A_i \pm \sigma A_i) - (A_f \pm \sigma A_f)$ .

The distribution coefficients  $K_d$  and their standard errors are given in Table 3. As PSC is concerned, the values of  $K_d$  increased with decreasing  $\text{Cs}^+$  concentrations in the  $^{137}\text{Cs}$  solutions used. Although the standard errors of these distribution coefficients are approximately 1.8–2.2 % of the  $K_d$  values, the ratio of the  $K_d$  value at the concentration  $0.01692 \text{ g l}^{-1}$  to that at  $0.1132 \text{ g l}^{-1}$  is 1.43, and similarly that at  $0.1132$ – $0.2265 \text{ g l}^{-1}$  1.22, and that at  $0.2265$ – $0.3768 \text{ g l}^{-1}$  1.74. Because the ratios between  $K_d$  values are higher than 1.00, the standard errors of 1.8–2.2 % would not affect the  $K_d$  values.

**Table 3**  $K_d$  of PSC and PFC-PSC at various  $\text{Cs}^+$  concentrations

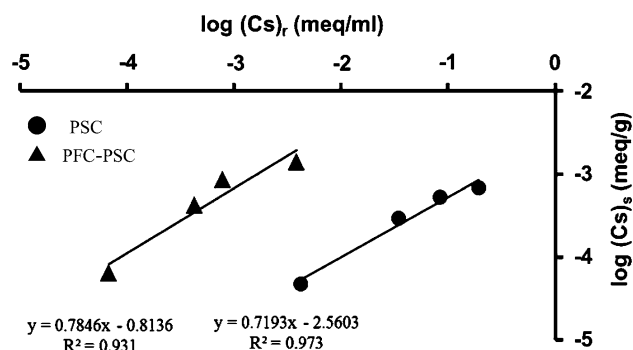
$^{137}\text{Cs}$ activity ( $\text{Bq ml}^{-1}$ )	103.2	60.76	30.45	4.560
$\text{Cs}^+$ concentration ( $\text{g l}^{-1}$ )	0.3768	0.2265	0.1132	0.01692
<b>PSC</b>				
$K_d$ ( $\text{cm}^3 \text{g}^{-1}$ )	3.53	6.13	7.46	10.6
Standard error	0.0628	0.125	0.165	0.190
<b>PFC-PSC</b>				
$K_d$ ( $\text{cm}^3 \text{g}^{-1}$ )	593.0	943.2	930.0	901.5
Standard error	10.03	19.88	19.78	21.37

Therefore, the observed relationship between  $\text{Cs}^+$  concentration and  $K_d$  values of PSC would not be altered.

Concerning the  $K_d$  of PFC-PSC, it seems there was a peak at around the  $\text{Cs}^+$  concentration of  $0.2265 \text{ g l}^{-1}$  in the  $^{137}\text{Cs}$  solution of approximately  $60 \text{ Bq ml}^{-1}$ . Similar to PSC, the standard errors of the  $K_d$  values of PFC-PSC increased with decreasing  $\text{Cs}^+$  concentrations. As the  $\text{Cs}^+$  concentrations decreased from  $0.2265$  to  $0.1132 \text{ g l}^{-1}$  and then to  $0.01692 \text{ g l}^{-1}$ , the standard errors increased from 2.1 to 2.4 % of the  $K_d$  values of PFC-PSC. On the other hand, the ratios between  $K_d$  values are 1.03 and 1.01 for the  $\text{Cs}^+$  concentration at  $0.01692$  and  $0.1132 \text{ g l}^{-1}$ , and at  $0.1132$  and  $0.2265 \text{ g l}^{-1}$ , corresponding to the  $^{137}\text{Cs}$  solutions of 4.56, 30.45 and  $60.76 \text{ Bq ml}^{-1}$ , respectively. These ratios are approximately equal to 1.00. Thus, taking into account the standard errors of 2.1–2.4 % and the ratios between  $K_d$  values of approximately 1.00, the  $K_d$  values of PFC-PSC at the  $\text{Cs}^+$  concentrations of  $0.01692$ ,  $0.1132$ , and  $0.2265 \text{ g l}^{-1}$  would be overlapped with each other. In other words, the  $K_d$  values of PFC-PSC increases as the  $\text{Cs}^+$  concentration decreases from  $0.3768 \text{ g l}^{-1}$  ( $103.16 \text{ Bq ml}^{-1}$ ) to  $0.2265 \text{ g l}^{-1}$  ( $60.76 \text{ Bq ml}^{-1}$ ) and remains almost constant afterwards. The results imply that potassium ferrocyanide may alter the distribution coefficient of the solid adsorbent PSC. Although Lalmunsiana and co-workers studied the radiocesium adsorption onto nickel hexacyanoferrate-impregnated activated carbons [8], the distribution coefficient  $s$  of these modified activated carbons were not reported.

### Freundlich adsorption isotherm

In general, the solid surface adsorption of solutes from a liquid phase is analyzed by Langmuir or Freundlich equations. The Freundlich adsorption isotherm is experimentally derived and thus empirical. Among the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models, both the Freundlich and D-R isotherms were found to better fit the sorptive removal of zinc and cadmium by a synthetic zeolite A than was the Langmuir model [13].

**Fig. 5** Freundlich isotherms of  $\text{Cs}^+$  adsorption onto PSC and PFC-PSC

According to the Freundlich equation, the logarithm of the adsorbed amount is proportional to the logarithm of the bulk concentration. In this report, the Freundlich equation is given in (4).

$$\log[C]_s = \log k + n \log[C]_r \quad (4)$$

where  $[C]_s$  is the amount of  $\text{Cs}^+$  ion adsorbed onto adsorbent PSC or PFC-PSC at equilibrium ( $\text{meq g}^{-1}$ ),  $[C]_r$  the concentration of  $\text{Cs}^+$  ion in the solution at equilibrium ( $\text{meq ml}^{-1}$ ),  $k$  and  $n$  are Freundlich constants.

The isotherm plots of the adsorption of  $\text{Cs}^+$  ion onto adsorbents PSC and PFC-PSC are showed in Fig. 5. The values of the parameters  $n$  and  $k$  for PSC and PFC-PSC derived from these linear correlations are given in Table 4. Since the  $n$  values of both PSC and PFC-PSC are lower than 1, the adsorption process of these adsorbents is non-linear. Furthermore, because the  $k$  value of PFC-PSC is higher than that of PSC, the affinity of  $\text{Cs}^+$  ion of the former is also higher than the latter. The adsorption isotherms of PSC and PFC-PSC are similar to those of Turkish bentonite, zeolite, sepiolite, and kaolinite [14].

As mentioned above, the cesium adsorption of potassium nickel hexacyanoferrate (II) [7] and nickel hexacyanoferrate-pretreated activated carbons of rice husk and areca nut [8] followed the Langmuir isotherm model and is different from the Freundlich isotherms of PFC-PSC and an activated carbon removing uranium (VI) [15]. Whether or not nickel affecting the adsorption isotherms of these nickel hexacyanoferrates requires further examination. Interestingly, the equilibrium adsorption of an industrial coconut shell activated carbon was found to be fitted by both Langmuir and Freundlich isotherm models [3].

**Table 4** Freundlich isotherm constants for the adsorption of  $\text{Cs}^+$  onto PSC and PFC-PSC

Adsorbent	$n$	$k$
PSC	0.7193	$2.752 \times 10^{-3}$
PFC-PSC	0.7846	$153.6 \times 10^{-3}$



## Adsorption kinetics

It was found that the kinetics of sorptive removals of cesium ions by nickel hexacyanoferrate-impregnated activated carbons [8] and clay minerals and zeolite [16] could be expressed by pseudo second order reaction rate equations. So was the removal of cobalt and europium ions by cerium (IV) tungstate [17]. Since the sorptive removal of  $\text{Cs}^+$  by PSC and PFC-PSC were fitted by the Freundlich isotherm as shown above, the adsorption kinetics of these adsorbents was studied using the following pseudo second order reaction rate Eq. (5).

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (5)$$

where  $q$  and  $q_e$  are the amounts of adsorbed  $\text{Cs}^+$  per gram of adsorbent at a given time  $t$  and equilibrium, respectively, and  $k_2$  is the rate constant.

Integrating and linearizing (5) yielded (6).

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Plotting  $t/q$  against  $t$  should result in a straight line with the slope  $1/q_e$  and the intercept  $1/(k_2 q_e^2)$ . The plots are showed in Figs. 6 and 7 for PSC and PFC-PSC,

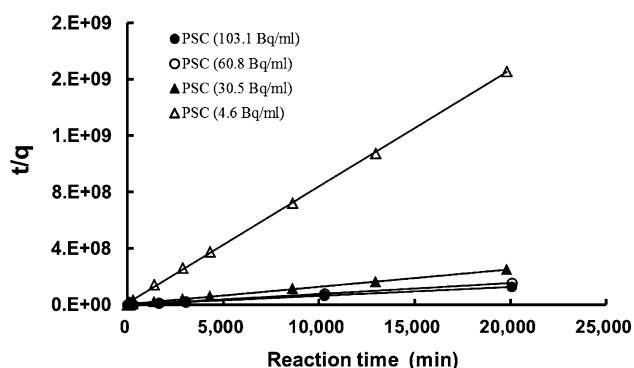


Fig. 6 Pseudo second order kinetic model for PSC

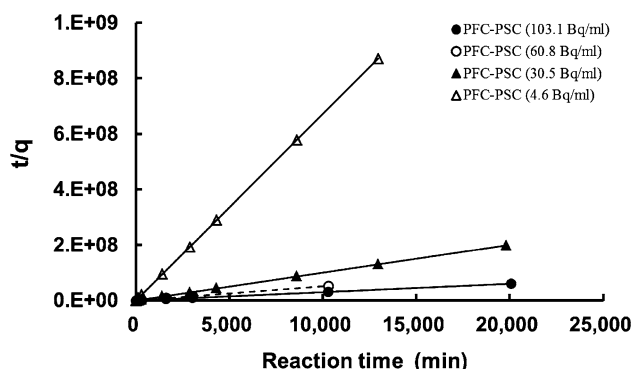


Fig. 7 Pseudo second order kinetic model for PFC-PSC

**Table 5**  $a$  and  $b$  values of the relationships between  $t/q$  and reaction time  $t$  in Figs. 6 and 7

Adsorbent	Radiocesium activity (Bq ml <sup>-1</sup> )	$a$	$b$	$R^2$
PSC	103.2	6,382.6	357,087.000	0.9998
	60.76	7,856.7	743,078.000	0.9999
	30.45	12,484	3,000,000.00	0.9989
	4.560	82,820	10,000,000.0	0.9997
PFC-PSC	103.2	3,012.8	26,348.0000	1.0000
	60.76	5,018.9	13,893.0000	1.0000
	30.45	10,043	27,214.0000	1.0000
	4.560	67,166	213,961.000	1.0000

**Table 6** Parameters of the pseudo second order kinetic models

Adsorbent	Radiocesium activity (Bq ml <sup>-1</sup> )	$q_e$ (mM g <sup>-1</sup> )	$k^2$ (g mM <sup>-1</sup> min <sup>-1</sup> )
PSC	103.2	$15.67 \times 10^{-2}$	$0.1141 \times 10^{-3}$
	60.76	$12.73 \times 10^{-2}$	$0.08307 \times 10^{-3}$
	30.45	$8.010 \times 10^{-2}$	$0.05195 \times 10^{-3}$
	4.560	$5.138 \times 10^{-2}$	$0.03788 \times 10^{-3}$
PFC-PSC	103.2	$33.19 \times 10^{-2}$	$0.3445 \times 10^{-3}$
	60.76	$19.92 \times 10^{-2}$	$1.813 \times 10^{-3}$
	30.45	$9.957 \times 10^{-2}$	$3.706 \times 10^{-3}$
	4.560	$1.489 \times 10^{-2}$	$21.08 \times 10^{-3}$

respectively. The values  $a$  and  $b$  of each relationship  $t/q = at + b$  are given in Table 5 from which the values of  $q_e$  and  $k_2$  were computed. The results are given in Table 6.

It is apparent from Table 6 that as the initial  $^{137}\text{Cs}$  concentration decreased, the adsorption rate constant of PSC also decreased whereas that of PFC-PSC increased. The results suggest that PSC's affinity for cesium is limited so that its rate constant decreases with decreasing cesium concentration. On the other hand, because the affinity for cesium of the potassium ferrocyanide group in PFC-PSC is high it is expected that its rate constant increases with decreasing cesium concentration.

Similar to the distribution coefficient discussed above, these results also suggest that potassium ferrocyanide may also alter the adsorptive kinetics of the solid adsorbent PSC.

## Conclusions

An industrial PSC and its modified form PFC-PSC were studied for their adsorptive removals of  $\text{Cs}^+$  in the  $^{137}\text{Cs}$  aqueous solutions. It was found that as the  $\text{Cs}^+$

concentration in the  $^{137}\text{Cs}$  solutions increased from  $16.92 \text{ mg l}^{-1}$  ( $4.56 \text{ Bq ml}^{-1}$ ) to  $376.8 \text{ mg l}^{-1}$  ( $103.1 \text{ Bq ml}^{-1}$ ), the distribution coefficient of PSC increased but that of PFC-PSC was highest at the  $\text{Cs}^+$  concentrations up to approximately  $226.5 \text{ mg l}^{-1}$  ( $60.8 \text{ Bq ml}^{-1}$ ) and then decreased as the  $\text{Cs}^+$  concentration was increased to  $376.8 \text{ mg l}^{-1}$  ( $103.1 \text{ Bq ml}^{-1}$ ). The Freundlich constant  $k$  of PFC-PSC is higher than that of PSC, implying that the affinity for  $^{137}\text{Cs}$  of the former is also higher compared to the latter. On the other hand, as the  $\text{Cs}^+$  concentration decreases from  $376.8 \text{ mg l}^{-1}$  ( $103.1 \text{ Bq ml}^{-1}$ ) to  $16.92 \text{ mg l}^{-1}$  ( $4.56 \text{ Bq ml}^{-1}$ ), the pseudo second order adsorption rate constant of PSC decreases but that of PFC-PSC increases. All the above results suggest that potassium ferrocyanide may alter the adsorptive characteristics of PSC and that PFC-PSC is a stable adsorbent and may be more suitable than PSC in removing radioactive cesium from aqueous solutions.

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