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Comprehensive evaluation of cesium removal by CuFC adsorption: the effects of initial concentration, CuFC dosage and co-existing ions in solution

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Abstract To use copper ferrocyanide (CuFC) more efficiently in wastewater treatment, the method of isotope carrying used in ^{137}Cs removal was investigated. A calculation model based on Freundlich isotherm was established to determine the optimum initial cesium concentration, at which the highest decontamination factor (DF) could be obtained at a certain CuFC dosage. An accurate DF prediction model was developed to describe synergistic effects of sodium and potassium. A novel index called volumetric distribution coefficient (K_{vd}) was proposed to evaluate adsorption performance in terms of DF and concentration factor.

Keywords Copper ferrocyanide · Isotope carrying · Decontamination factor · Volumetric distribution coefficient · Concentration factor

Introduction

After the Fukushima nuclear leakage accident in 2011, there has been widespread concern about the potential risk of radioactive wastewater to human and aquatic life. In the field of water pollution control, the removal of radioactive nuclides has become an area of intense research. ^{137}Cs has drawn considerable attention due to its long half-life of 30.04 years and high biological toxicity [1, 2]. Several techniques have been studied for removing cesium from radioactive wastewater, including coagulation precipitation [3], adsorption/ion exchange [4–6], membrane technology [7, 8], chemical precipitation [9], and electrochemical technology [10–13]; of these, adsorption has been considered to have good potential because of its high efficiency, easy operation and low cost [14]. Transition metal ferrocyanides (iron, cobalt, nickel, copper, and zinc) have affinity for cesium, large adsorption capacities and favorable pH adaptations; because of this, they have been studied intensively [15–18].

Based on the safety consideration and the instrument limitations, most of the experiments were carried out using stable ^{133}Cs as an analogue of radioactive ^{137}Cs in aqueous solutions [19]. From the recent reports, cesium removal rate along with the initial cesium concentration at specific adsorbent dosage showed different results. Some papers concluded that the DF was negatively related to the initial cesium concentration [20–26]. However, Vincent et al. reported the opposite conclusion in a particular cesium concentration range [27]. Therefore, it can be inferred that there exists an optimum initial cesium concentration corresponding to a specific adsorbent dosage at which the highest DF would appear. Our previous study indicated that copper ferrocyanide (CuFC) in particular has efficient adsorption and is an environmentally friendly adsorbent since the concentrations of copper and cyanide in the effluent from CuFC adsorption treatment were both below the standard in the *Guidelines for Drinking-water Quality* issued by the World Health Organization [28]. Based on these results, it is different from the conventional wastewater treatment process when we aim to use CuFC to remove ^{137}Cs from radioactive wastewater that we could

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increase the initial cesium concentration of the wastewater, i.e., add a suitable amount of ^{133}Cs into the radioactive wastewater, to obtain a favorable DF.

Most radioactive wastewaters contain co-existing non-radioactive ions at concentrations that are several orders of magnitude higher than that of the radionuclide ions [29]. Sodium and potassium are the congeners of cesium and commonly exist in wastewaters. It is useful to investigate the effects of them on the adsorption behavior of cesium. Presently, most researches investigate the interference of single sodium or potassium ion with different concentration on adsorption performance [20, 30–34], or inspect the adsorption performance of an adsorbent in a specific complicated solution, such as sea water [35] or lake water [25]. The synergistic effects of sodium and potassium with different concentration on the CuFC adsorption cesium have not yet been reported. Another problem faced by real wastewater treatment is the selection of an adsorbent and the determination of its dosage to obtain satisfactory results. Two common indices are the DF and the concentration factor (CF), which are employed to evaluate adsorption performance. However, most reports have focused on measuring decontamination performance, and there has been little attention paid to concentration performance. For application purposes, both parameters need to be considered comprehensively. Therefore, a new index is required to compare the performance of different adsorbents used in a specific process.

This research has four goals. First, we aim to ascertain a functional relationship between the DF, the initial cesium concentration and the CuFC dosage to find an optimum initial cesium concentration that could produce the highest DF at a specific CuFC dosage. Second, we investigate ^{137}Cs removal in low-level radioactivity wastewater with the stable ^{133}Cs added during the CuFC adsorption process. Third, the synergistic effects of coexisting sodium and potassium ions on cesium removal are investigated by Design-Expert optimizing software. Finally, we present a new index to evaluate the adsorption process. Generally, this paper proposes a feasible treatment for radioactive wastewater.

Experimental

Materials

The chemicals used in this research were analytical reagent grade. Sodium chloride (NaCl) and potassium chloride (KCl) were both purchased from Tianjin Kermel Chemical Reagents Co., Ltd., Tian jin, China. Stable cesium chloride (CsCl), sodium ferrocyanide ($Na_4Fe(CN)_6$) and copper nitrate ($Cu(NO_3)_2$) were purchased from Tianjin Guangfu Fine Chemical Research Institute, China. The ^{137}Cs was purchased from China Isotope & Radiation Corporation, China. Approximately 1 mCi of ^{137}Cs was dissolved in a 1000-mL volumetric flask as a stock solution, and its activity was $(4.24 \pm 0.27) \times 10^7$ Bq/L on the basis of three measurements. The ^{137}Cs solution used in this research was carrier-free. Cesium chloride was dissolved in deionized water for a stock solution of ^{133}Cs with a concentration of 100 mg/L.

Experimental equipment

A magnetic stirring apparatus (Model 79-1, Tianjin Honour instrument Co., Ltd, China) was used to mix the CuFC suspension uniformly before dosing the water sample. A thermostat oscillator (Model HNY-2102, Tianjin Honour Instrument Co., Ltd., China) was used to mix the adsorbent with the water sample at a constant temperature. A suction filtration device including a vacuum suction machine (Model AP-01P, Tianjin Honour instrument Co., Ltd, China), a flat membrane with a nominal pore size of 0.22 μm (Mixed cellulose ester, Mili membrane Co, Ltd, China) and a glass filter was used to separate the adsorbent from the mixture. The concentration of the ^{133}Cs solution and the activity of the ^{137}Cs solution were determined via an X Series inductively coupled plasma mass spectrophotometer (Thermo Electron Corporation, USA) and a Canberra high-purity germanium γ-spectrometer (Model BE 5030, Canberra Industries, USA), respectively. A Zeeman atomic absorption spectrometer (Model 180-80, Hitachi, Japan) was used to analyze the concentrations of calcium, magnesium, sodium and potassium. The concentrations of sulfate, nitrate and chloride were measured by ion chromatography (Model DX-600, Dionex Co., Ltd, USA).

Preparation of adsorbent

A 0.130 L $Na_4Fe(CN)_6$ solution with a concentration of 0.125 mol/L and a 0.124 L $Cu(NO_3)_2$ solution with a concentration of 0.375 mol/L were simultaneously dropped into 2.00 L deionized water at 0.100 mL/min under moderate stirring in a 55 °C water bath. After the reaction, CuFC was formed as sediment. The supernatant was then poured out, and the sediment was washed with deionized water eight times, after which the suspension was ready for use [36].

Experimental procedure

Effect of initial cesium concentration on DF with different CuFC dosage

The adsorption isotherm was studied based on the classical method [37, 38]. The relationship between the DF, initial cesium concentration and CuFC dosage was determined in batch experiments. The initial ^{133}Cs concentrations were 10, 100, 500, 1000 and 2500 μg/L. Six samples of a given initial cesium concentration were placed in 250-mL conical flasks, and CuFC suspensions with different dosages (from 0.01 to 0.08 g/L) were added. The samples were thoroughly mixed in the thermostat oscillator for 90 min. The experimental temperature was 25 °C. When the adsorption process was complete, the suspension was filtered, and the ^{133}Cs concentration in the filtrate was measured. Each experiment was performed twice, and the average was reported.

Effect of ^{133}Cs concentration on ^{137}Cs removal in deionized water

The ^{137}Cs activity in each sample was constant at 4.20×10^5 Bq/L. The samples were prepared by diluting the ^{137}Cs stock solution with deionized water. Then, ^{133}Cs was added to the samples at initial concentrations of 100, 500, 1000 and 2500 μg/L, respectively. The experimental procedure was the same as described in section of "Effect of initial cesium concentration on DF with different CuFC dosage". When the adsorption ended, the residual activity of ^{137}Cs in the filtrate was analyzed.

Determination of optimum initial cesium concentration in tap water

Local tap water was used, and the quality parameters are given in Table 1. The initial ^{133}Cs concentrations in the water were 10, 100, 500, 1000 and 2500 μg/L. The CuFC dosage was 0.04 g/L, the same as in our previous research [28]. The mixture was shaken for 90 min, and then, it was filtered and analyzed for residual concentration of ^{133}Cs. The experiments were conducted twice, and the averages were reported.

The synergistic effects of sodium and potassium on CuFC adsorption and a DF prediction model establishment

Considering the quality parameters of common tap water and the requirements of the Design-Expert software, the target ranges of sodium and potassium ions concentrations were selected from 10 to 100 and 3 to 10 mg/L, respectively. The initial ^{133}Cs concentration and CuFC dosage were 93.8 μg/L and 0.04 g/L, respectively. The experimental procedure was the same as described in section of "*Effect of initial cesium concentration on DF with different CuFC dosage*".

Indices used for evaluation of adsorption performance

The parameters and indices involved in this paper are presented in Eqs. (1)–(4).

$$q_e = \frac{(C_0 - C_e) \times V_{\mathrm{w}}}{m} \tag{1}$$

$$\mathrm{DF} = \frac{A_0}{A_e} \mathrm{or} \frac{C_0}{C_e} \tag{2}$$

$$K_{\mathrm{d}} = \frac{(C_0 - C_e) \times V_{\mathrm{w}}}{C_e \times m} \tag{3}$$

$$\mathrm{CF} = \frac{V_{\mathrm{w}}}{V_{\mathrm{s}}} \tag{4}$$

Here, q_e is the amount of adsorption at equilibrium (μg/g). A_0 and A_e are the initial and equilibrium activities of the radioactive nuclide (Bq/L). C_0 and C_e are the initial and equilibrium concentrations of the non-radioactive isotope (μg/L). V_{w} is the volume of water treated (L). m is the mass of the adsorbent (g). DF is the decontamination factor. K_{d} is the distribution coefficient (L/g). CF is concentration factor. V_{s} is the settlement volume of adsorbent after solid–liquid separation (L).

Results and discussion

Effect of initial cesium concentration on adsorption performance

Adsorption isotherm

Previous research has demonstrated that the adsorption process for CuFC removing cesium fits the Freundlich isotherm well [28]. Therefore, we used the model as shown in Eq. (5), and the experimental data were plotted using the linear form of Eq. (5) in Eq. (6). The linear forms of the isotherms are shown in Fig. 1. The initial cesium concentration was varied to study its effect on the Freundlich isothermal constants, which were obtained from the slopes and intercepts of the lines in Fig. 1, respectively. The isothermal constants and regression coefficient R^2 are shown in Table 2.

Table 1 Concentration of coexisting ions contained in tap water

Index	Total hardness ($CaCO_3$)	Na^+	K^+	SO_4^{2-}	NO_3^-	Cl^-
Concentration (mg/L)	224	24.0	5.40	113	2.83	43.0

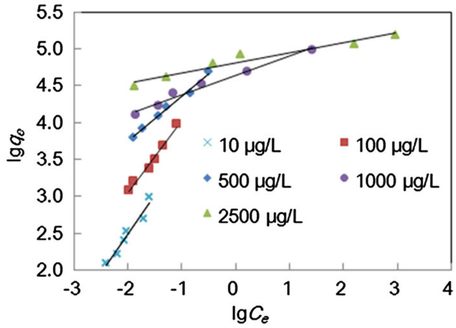

Fig. 1 Linear form of Freundlich isotherms with various initial cesium concentrations

Table 2 Freundlich isothermal constants with different initial cesium concentrations

C_0 (μg/L)	$K_f \times 10^4$ [(μg/g)(L/μg)$^{1/n}$]	n	R^2
10	4.20	0.935	0.954
100	10.1	1.03	0.984
500	9.46	1.62	0.990
1000	4.36	3.76	0.978
2500	6.47	7.46	0.951

$$q_e = K_f C_e^{\frac{1}{n}} \tag{5}$$

$$\lg q_e = \lg K_f + \frac{1}{n} \lg C_e \tag{6}$$

Here, K_f and $1/n$ are the Freundlich capacity constant ((μg/g)(L/μg)$^{1/n}$) and Freundlich intensity constant, respectively.

In Fig. 1, each line corresponds to a different initial cesium concentration. The five lines in the figure were obtained from the same dosage range of CuFC from 0.01 to 0.08 g/L. The highest CuFC dosage was set at 0.08 g/L because previous research showed that the solid–liquid separation is difficult if CuFC dosage is higher than this value. At a specific CuFC dosage, the higher the initial cesium concentration, the higher the value of lgq_e. Furthermore, the range of variation of lgq_e within the same CuFC dosage range decreased with an increase in initial cesium concentration, i.e., the slope of the adsorption isotherms (*1/n*) decreased with increasing initial cesium concentrations, which indicates that higher initial cesium concentrations are beneficial to the adsorption process and vice versa. On the other hand, the range of variation of lgC_e became larger with an increase in initial cesium concentration, which was opposite to the effect of lgq_e, and the values of lgC_e and lgq_e (i.e., C_e and q_e) at a given CuFC dosage both increased with an increase in initial cesium concentration. All variations could significantly affect the DF.

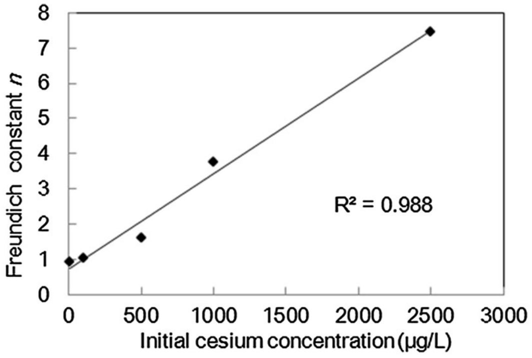

Fig. 2 Freundlich constant n varying with initial cesium concentration

Table 2 shows that K_f values varied within a range, and there was no obvious law between it and initial cesium concentration. To further study, we assume the variation in K_f was independent of C_0 and take the average value of K_f defined as K_f' in this paper. With increasing initial cesium concentration, the value of n increased linearly as presented in Fig. 2.

The relation between n and C_0 was shown as Eq. (7):

$$n = n(C_0) = 0.00270C_0 + 0.738 \tag{7}$$

Substituting K_f' and Eq. (7) into Eq. (5):

$$q_e = K_f' C_e^{\frac{1}{n(C_0)}} \tag{8}$$

Adsorbent dosage and initial cesium concentration would both have significant effect on adsorption performance. Most literatures about cesium removal employed the method of fixing adsorbent dosage and varying the initial cesium concentration to study adsorption isotherm; however, in the water and wastewater treatment field, as the pollutant concentration in the wastewater generally cannot be changed, the adsorption isotherm studies are carried out at a fixed adsorbate initial concentration and varying adsorbent dosage [37, 38]. Two methods of the adsorption isotherm study are both fixing one parameter (adsorbent dosage or initial adsorbate concentration) to investigate the effect of the other one (initial adsorbate concentration or adsorbent dosage) on the adsorption performance. Therefore, no matter what method we use, it is impossible to comprehensively describe the effect of two parameters on adsorption performance. Equation (8) could approximately represent the effects of the initial cesium concentration and the CuFC dosage on the adsorption process; the application of Eq. (8) in the CuFC adsorption process would be discussed in next section.

Effect of initial cesium concentration on the DF with varied CuFC dosages

The DF is a direct description of adsorption performance. The variation of the DF versus the initial cesium

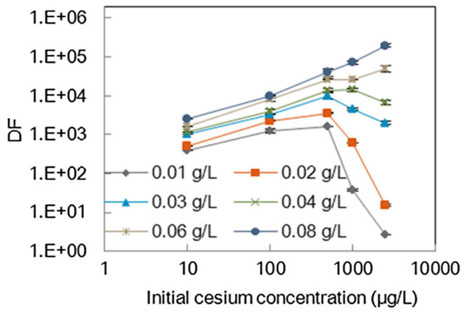

Fig. 3 Effect of initial cesium concentration on DF at various CuFC dosages

concentration at various CuFC dosages was plotted with the data in Fig. 1 and is shown in Fig. 3.

In Fig. 3, when the CuFC dosage was from 0.01 to 0.04 g/L, there was an inflection point in each curve at which a maximum DF appeared. To be similar to the CuFC dosage curves of 0.01–0.04 g/L, when the CuFC dosage was higher than 0.04 g/L, the corresponding curves should also possess a maximum DF rather than a monotonic increase. In the research, the experiments were only performed on limited initial cesium concentrations, so the real maximum DF points of every CuFC dosage might not appear at the points shown in Fig. 3, and the value might be higher. However, it is impractical to find the optimum initial cesium concentration by experimentation. Thus, this paper established a functional relationship between the CuFC dosage, C_0 and C_e by which the initial cesium concentration corresponding to the maximum DF at a specific CuFC dosage could be estimated. Substituting Eq. (1) into Eq. (8),

$$\frac{(C_0 - C_e)V_{\mathrm{w}}}{m} = K_{\mathrm{f}}' C_e^{\frac{1}{n(C_0)}} \tag{9}$$

Taking advantage of Eqs. (9) and (2), we could estimate the DF for different initial cesium concentrations in the CuFC adsorption process at a given dosage. Aiming at the six CuFC dosages studied in this paper with initial cesium concentrations from 100 to 2500 μg/L and a calculation step of 100 μg/L, the C_e could be calculated by Eq. (9). Then, Eq. (2) was used to calculate the DF at different initial cesium concentrations. Finally, the DF values were compared to find the maximum. The results are given in Fig. 4 and the calculated highest DF corresponding to the initial cesium concentration at various CuFC dosages was listed in Table 3. As shown in Table 3, the maximum DF and the corresponding C_0 were both enlarged by increasing the CuFC dosage from 0.01 to 0.08 g/L. Taking the CuFC dosage of 0.04 g/L as an example, when the initial cesium concentration was 100 μg/L, the calculated DF was only 4520; when the initial cesium concentration was increased to 1100 μg/L, as shown in Table 3, the DF reached 4.56 × 10^4 and increased by a factor of 10.

Equation (9) comprehensively considered the effect of the initial cesium concentration and CuFC dosage on the adsorption process. The optimum initial cesium concentration and the corresponding DF value could be calculated. It is unquestionable that the DF would increase with increasing adsorbent dosage at a given adsorbate initial concentration. However, the higher adsorbent dosage would pose an obstacle to the solid–liquid separation and reduce the CF, simultaneously. Therefore, in practice, the adsorbent selection and its dosage determination have to take the DF and CF into consideration simultaneously. This method offers an approach for weighing the design parameters of an adsorption process.

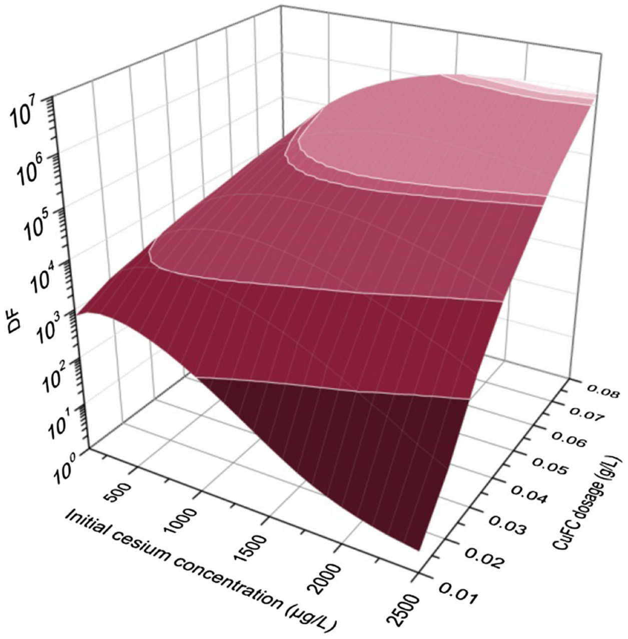

Fig. 4 Variation of DF with CuFC dosage and initial cesium concentration

Table 3 Calculated highest DF corresponding to the initial cesium concentration at various CuFC dosages

m/V_{w} (g/L)	C_0 (μg/L)	Highest DF
0.01	300	1.18 × 10^3
0.02	600	5.01 × 10^3
0.03	800	1.60 × 10^4
0.04	1100	4.56 × 10^4
0.06	1600	3.20 × 10^5
0.08	2200	2.00 × 10^6

Effect of ^{133}Cs concentration on ^{137}Cs removal in deionized water

As mentioned in section of "Experimental procedure", the activity of all samples used in this experiment was always 4.20 × 10^5 Bq/L. The concentration of ^{137}Cs was far below one microgram per liter and the ^{137}Cs solution used in this research was carrier-free. To investigate the effect of the initial ^{133}Cs concentration on ^{137}Cs removal at different CuFC dosages, ^{133}Cs with four different initial concentrations was added to the ^{137}Cs solution, and the concentration of cesium (^{133}Cs + ^{137}Cs) in water samples was approximately equal to that of ^{133}Cs. The results are shown in Fig. 5. The equilibrium activity of ^{137}Cs was significantly dependent on initial ^{133}Cs concentration at specific CuFC dosages. When the CuFC dosage was 0.01–0.03 g/L, the lowest equilibrium activities appeared at a 500 μg/L initial ^{133}Cs concentration. When the CuFC dosage was 0.04 g/L, the initial ^{133}Cs concentration at which the lowest final ^{137}Cs activity occurred was 1000 μg/L. When the CuFC dosage were larger than 0.04 g/L, the ^{137}Cs equilibrium activity decreased substantially with increased ^{133}Cs. The final ^{137}Cs activity was only 2.54 Bq/L at a CuFC dosage of 0.08 g/L and initial ^{133}Cs concentration of 2500 μg/L.

To understand the effect of ^{133}Cs concentration on the removal of ^{137}Cs, both sides of Eq. (1) were divided by C_0, then the functional relationship among the DF, q_e and C_0 could be established. As shown in Eq. (10).

$$1-\frac{1}{\mathrm{DF}}=\frac{q_e m}{C_0 V_\mathrm{w}} \tag{10}$$

From the Eq. (10), it could be concluded that when the m/V_w was a constant, the DF depends on the value of q_e/C_0. Taking an example of CuFC dosage of 0.01 g/L (The data was from the Fig. 1), the value of q_e/C_0 corresponding to the C_0 of 500 μg/L was larger than that corresponding to the C_0 of 100 μg/L. Therefore, the DF was enlarged when the C_0 increased from 100 to 500 μg/L. However, the value of q_e/C_0 was reduced when the C_0 increased from 500 to 2500 μg/L, the DF was therefore decreased. In the homogeneous solution of ^{133}Cs and ^{137}Cs, the equilibrium activity of ^{137}Cs after CuFC adsorption is dependent on the

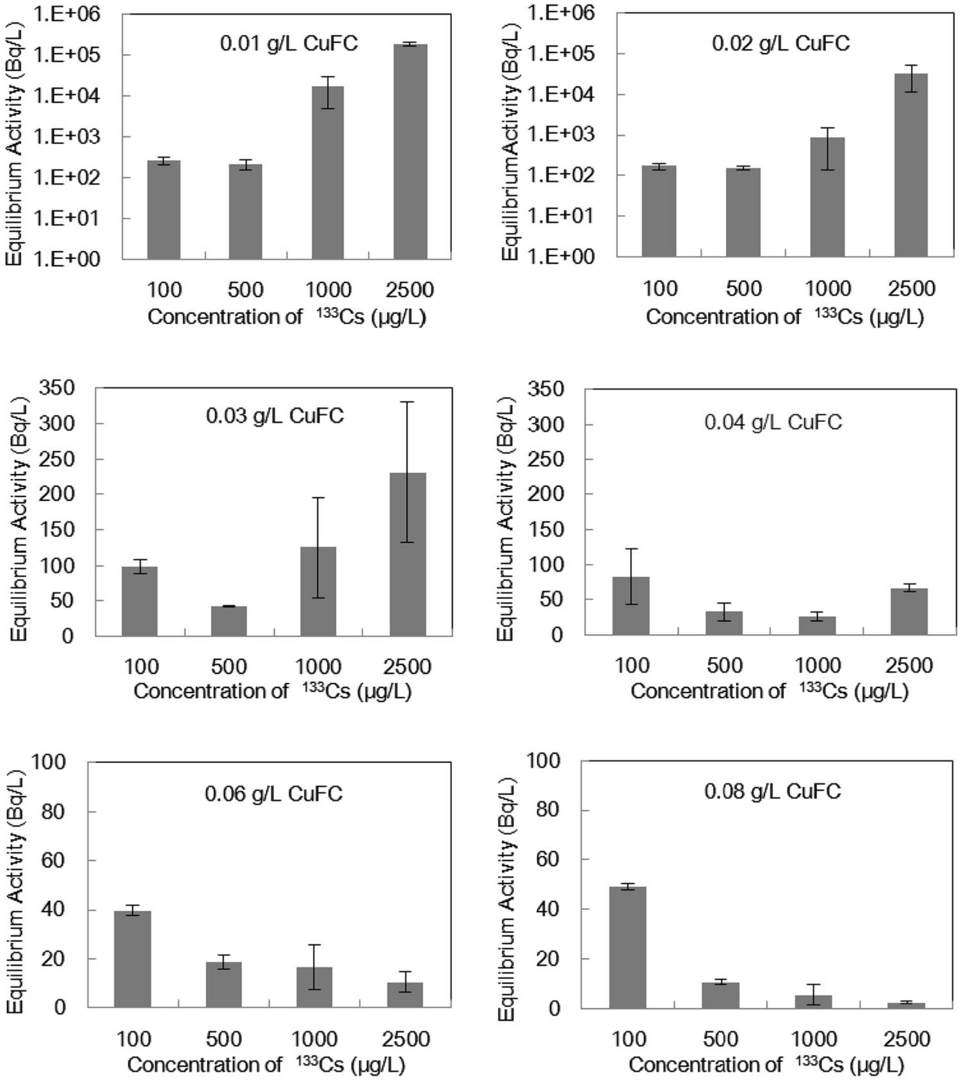

Fig. 5 Variations of equilibrium activity with CuFC dosage at different initial ^{133}Cs concentration

DF. If the DF increases, the adsorption amount of ^{137}Cs also increases and equilibrium activity of ^{137}Cs therefore decreases and vice versa.

The results indicated that a suitable initial cesium concentration obtained by adding ^{133}Cs could improve ^{137}Cs removal. The residual ^{133}Cs concentration was extremely low at the end of the adsorption process. Taking an example of an initial ^{133}Cs concentration of 1000 μg/L and CuFC dosage of 0.04 g/L, the equilibrium ^{133}Cs concentration was only 0.024 μg/L. ^{133}Cs is not considered a hazardous element by the U.S. Environmental Protection Agency (EPA) [39]. Therefore, the method is environmentally safe and could be used in radioactive wastewater treatment.

Determination of optimum initial cesium concentration in tap water

Wastewater composition can have a significant impact on the performance of an adsorbent due to the presence of competing ions [40]. The optimum cesium concentration and the highest DF in wastewater are expected to be both different from those in deionized water. It is necessary to investigate the differences in a complex water environment. This part of the experiment used local tap water containing ^{133}Cs at various initial concentrations to simulate ^{137}Cs polluted water. The results are shown in Fig. 6. When the CuFC dosage was 0.04 g/L, the optimum initial cesium concentration bringing about the highest DF was found in the tap water, which was similar to the deionized water. However, the DF value decreased markedly compared to deionized water due to the presence of alkalis and hardness substances in the water sample, as shown in Table 1. This scenario demonstrates that a suitable initial cesium concentration exists at which the DF would be the highest when aiming to remove ^{137}Cs from complicated water.

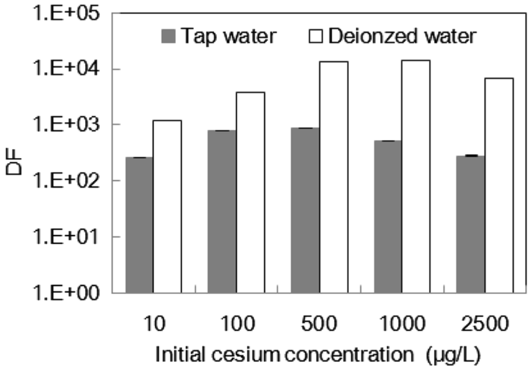

Fig. 6 Variation of the DF with initial cesium concentrations in tap and deionized water

The interference of coexisting ions is mainly due to competition with the target nuclide for binding sites [25]. The influence of sodium and potassium on the adsorption of cesium may be related to the similar chemical characteristics that result from being in the same major chemical group. The influence of calcium and magnesium on adsorption might involve in other processes except ion exchange, such as complexation or nonspecific surface adsorption [20, 41].

The synergistic effects of sodium and potassium on CuFC adsorption and a DF prediction model establishment

The literature on the synergistic effects of coexisting sodium and potassium ions on CuFC adsorption performance in water could not be found. The present research used the response surface methodology (RSM) in Design-Expert optimizing software to investigate the synergistic action of coexisting sodium and potassium ions interfering with CuFC adsorption for the removal of cesium. The design and results of the experiment are shown in Table 4.

A calculating formula was computed by entering the corresponding experimental results into the Design-Expert software. The model equation is expressed as Eq. (11), which can be used to calculate the DF under certain sodium and potassium ion coexistence conditions:

$$\begin{aligned} \mathrm{DF} = {} & 1650 - 5.17 \times X_1 - 170 \times X_2 + 0.350 \times X_1 \times X_2 \\ & + 7.19 \times 10^{-3} \times X_1^2 + 5.71 \times X_2^2 \end{aligned} \tag{11}$$

Here, X_1 and X_2 are the concentrations of sodium and potassium, respectively (mg/L).

Table 4 Design and results of the experiment

No.	Concentration (mg/L)		DF
	Sodium	Potassium	
1	60.0	6.50	648 ± 10.6
2	3.43	6.50	740 ± 29.7
3	60.0	6.50	665 ± 18.1
4	60.0	6.50	632 ± 6.5
5	100	10.0	436 ± 4.0
6	60.0	1.55	1220 ± 30.8
7	20.0	10.0	567 ± 2.0
8	60.0	11.5	361 ± 0.6
9	100	3.00	775 ± 28.5
10	20.0	3.00	1100 ± 11.5
11	60.0	6.50	657 ± 1.6
12	117	6.50	605 ± 4.0
13	60.0	6.50	618 ± 4.8

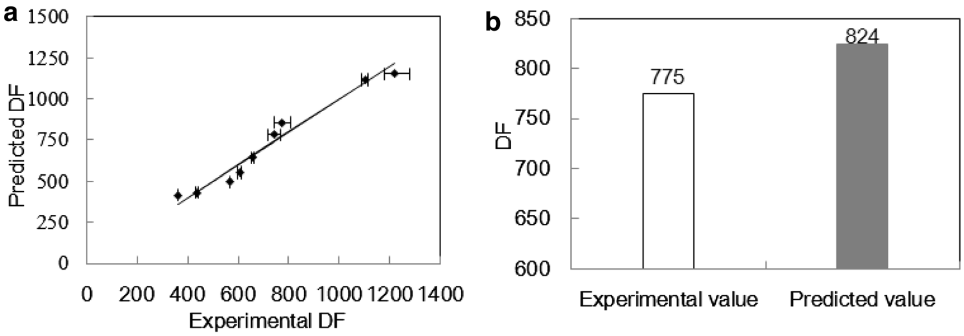

Fig. 7 Comparison of calculated and experimental DF in **a** deionized water with sodium and potassium ion added, **b** local tap water

Table 5 Comparison of the effects of sodium and potassium on the predicted DF

Concentration (mg/L)		DF
Sodium	Potassium	
60.0	1.00	1220
60.0	10.0	447
10.0	6.50	758
100	6.50	569

Analysis of variance (ANOVA) found that the signal-to-noise ratio was 18.2 (greater than 4), which was desirable and indicated an adequate signal. The *F*-value was 18.41 and the *p* value less than 0.0001, indicating that Eq. (11) was significant. Therefore, Eq. (11) can be used to predict the DF in a particular situation and quantitatively compare the inhibitory effects of coexisting sodium and potassium ions. Figure 7a is a comparison of the DF values predicted by Eq. (11) to the experimental data. The R^2 value of this experimental result from a linear regression analysis was 0.964, which indicates that the DFs predicted by the model were close to the experimental values in water containing coexisting sodium and potassium. The applicability of Eq. (11) to local tap water was also validated. The DF from the tap water was slightly lower than predicted, as shown in Fig. 7b, and the reason may be that hardness ions in the water were not taken into account.

Moreover, Eq. (11) can evaluate the competing intensity of sodium and potassium ions on the DF in the CuFC adsorption process. Table 5 summarizes the values calculated by fixing the sodium or potassium ion concentration and changing the other by a factor of 10.

Thus, Table 5 shows that the interference effect from potassium is greater than from sodium. This can be attributed to the greater similarity in Pauling's ionic radii between cesium (1.69 Å) and potassium (1.33 Å) than cesium and sodium (0.95 Å). The phenomenon also indicates that cesium adsorption might be the result of an ion exchange reaction in which cations with a similar radius and hydration energy compete more effectively with cesium for adsorption sites [25].

Evaluation of adsorption process characteristics

The distribution coefficient (K_d) is popularly used in adsorption research, and its definition is given in Eq. (3). However, the weakness of K_d is that no information about the concentration performance of an adsorbent in a process can be obtained. An index has been used in a chemical precipitation process for evaluating its decontamination and concentration characters comprehensively, and it is shown in Eq. (12) [42].

$$\mathrm{DF} \times \mathrm{CF} = \frac{C_0}{C_e} \frac{V_\mathrm{w}}{V_\mathrm{s}} \tag{12}$$

In an adsorption process, if the DF is large enough and C_0 is much greater than C_e, then Eq. (1) becomes

$$q_e = \frac{C_0 V_\mathrm{w}}{m} \tag{13}$$

The meaning of Eq. (13) is that all target elements in untreated wastewater are transferred completely into the adsorbent phase, and $C_0 V_\mathrm{w} = q_e m$. To use this expression, Eq. (12) can be written as below:

$$\mathrm{DF} \times \mathrm{CF} = \frac{q_e}{C_e} \frac{m}{V_\mathrm{s}} \tag{14}$$

Equation (14) can be observed as the ratio of $q_e m / V_\mathrm{s}$ to C_e. The meaning of the former is the concentration of the nuclide or its isotope in the settlement. Therefore, it can be

Table 6 Comparison of K_vd in different adsorption processes

No.	Adsorbent	Adsorption process	K_d	C	K_vd	Reference
1	KZnFC	Single-stage	5.46×10^2	179	9.77×10^4	[17]
2	CuFC	Single-stage	1.15×10^4	13.9	1.60×10^5	[28]
3	CuFC	Two-stage countercurrent	3.86×10^4	13.9	5.36×10^5	[28]

observed that DF × CF represents the ratio of the amount of adsorbate per volume of adsorbent settlement to the equilibrium adsorbate concentration in the wastewater treated. In this way, DF × CF can be viewed as a type of distribution coefficient. We term this the volumetric distribution coefficient (K_{vd}), and in other words, $K_{\mathrm{vd}} = \mathrm{DF} \times \mathrm{CF}$.

In Eq. (14), m/V_{s} is defined as C or settlement density related to the separation process. Equation (14) can be simplified as Eq. (15):

$$K_{\mathrm{vd}} = K_{\mathrm{d}}C \tag{15}$$

In Eq. (15), K_{d} is easily available from the literature, and C can be obtained easily by a jar test; taking CuFC as an example, the settling process was used for separation, and the value of C was 13.9 ± 0.180 g/L. Therefore, it is not difficult to obtain K_{vd}. As shown in Table 6, the values of DF and CF were influenced by both the types of adsorbents and the adsorption process. It was difficult to comprehensively evaluate the adsorption performance in terms of DF and CF separately; however, the values of K_{vd} distinctly demonstrate that CuFC is superior to KZnFC in adsorption performance and that the two-stage countercurrent adsorption process is more effective than a single-stage process.

Conclusions

1. There was an optimum initial cesium concentration that could provide the highest DF for a given CuFC dosage. A functional relationship between the DF, the adsorbent dosage and the initial cesium concentration was established. As the CuFC dosage increased, the optimum cesium concentration and corresponding DF both increased.
2. Utilizing ^{133}Cs to increase the cesium concentration to a suitable level, the equilibrium activity of ^{137}Cs could significantly decrease. When the ^{133}Cs dosage was 2500 μg/L, the ^{137}Cs equilibrium activity could decrease to 2.54 Bq/L from the initial activity of 4.20×10^5 Bq/L.
3. In a complicated water environment, such as local tap water, there was an optimum initial cesium concentration that was lower than that in deionized water. The synergistic effects of sodium and potassium ions on cesium removal were described by a DF prediction model. It was found that the interference effect from potassium ions was more severe than from sodium ions.
4. A new index was proposed that was named the volumetric distribution coefficient. It can not only evaluate an adsorbent comprehensively but also be used to compare the adsorption processes of a single given adsorbent.

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