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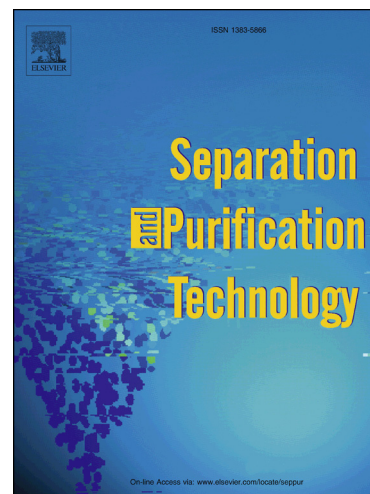
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Battery-type column for caesium ions separation using electroactive film of copper hexacyanoferrate nanoparticles

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ABSTRACT

We reported a novel and compact battery-type column using nanoparticles film of copper hexacyanoferrate (CuHCF NPs film) for sequential removal of Cs from wastewater. Different from the electrochemical deposition, chemical spray or chemical bath deposition, our film was prepared by coating water dispersed CuHCF NPs ink on the electrode surface through a simple wet process similar to ink printing. The battery-type column indicated Cs adsorption and desorption can be achieved by electrochemical redox of CuHCF NPs film, through switching the potentials between two sandwiched electrodes. Kinetic studies revealed both the static attraction and electrochemical oxidation-reduction of Fe (II/III) contributed to Cs separation. Insignificant change in the current after 100 cycles of durability test indicated the CuHCF NPs film is relatively stable, suggesting the battery-type column has a long service life for Cs removal from wastewater.

Keywords: Metal hexacyanoferrate, Electrochemical separation, Caesium, Nanoparticles film, Battery-type column.

1. INTRODUCTION

Caesium radioisotopes are among the main fission products with a very long half-lives of ~30 years for ^{137}Cs and $\sim 2 \times 10^6$ years for ^{135}Cs [1]. Typical alkaline metal ions, like Na and K, Cs can be easily incorporated into terrestrial and aquatic organisms, and represents a significant biohazard, especially to their reproductive system [2]. Due to its long half-life and bio-toxicity, its separation and removal from aquatic environments attracts particular attention especially recently after the disastrous accident at the Fukushima Daiichi nuclear power station in Japan [3]. Technologies of caesium removal from wastewater have been studied in the past few decades, including chemical precipitation, evaporation, solvent extraction, membrane processes and adsorption [4–7]. However, most of these methods have several disadvantages such as incomplete metal ion

removal and a high requirement for energy and reagents. For example, chemical precipitation and solvent extraction have low selectivity for Cs, yet generate an enormous mass of sludge or solution for disposal [8]. Similarly, evaporative methods may result in corrosion, scaling or foaming [9]. Membrane filtration also gives rise to problems such as high cost, process complexity, membrane fouling, and low permeate flux [10]. Among all above technologies, adsorption has been widely used as an attractive method for wastewater treatment because of its simplicity, economy, selectivity, and efficiency. Also, because adsorption is sometimes reversible, adsorbents can be regenerated. Transition metal (Ni, Zn, Cu, Fe, Co) hexacyanoferrates (MHCFs) are of the most frequently applied adsorbents for the treatment of radiocaesium wastewaters due to the high affinity for caesium ions and other radionuclides [11].

However, such MHCFs sorbents were usually synthesized as powder or bulk phase, which restricts its direct use as column packing for large scale Cs separation from low and intermediate-level radioactive waste effluents or contaminated water. Previous studies have focused on MHCFs associated support materials (such as polyacrylonitrile, [12] carboxylic latex [13] and mesoporous silica [14]) with suitable size and shape properties for Cs removal in columns. On the other hand, combined sorbents have been found to possess substantial disadvantages when faced with an enormous challenge of regeneration.

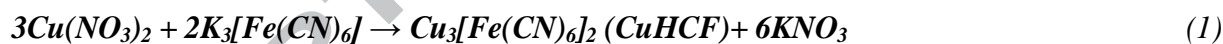
Hence, the concept of electrochemically switched ion exchange (ESIX) has been recently proposed as a promising technology using MHCFs for Cs separation. To achieve ion separation and MHCFs regeneration, MHCF were chemically or electrochemically deposited on the electrode substance [15,16] as a film. Cs adsorption and desorption can be easily controlled by switching the redox states of the MHCF films. ESIX can separate Cs without the extra chemical reagents or filtration treatment, and effective regeneration can be achieved simply. Since a satisfactory separation process should be suitable for column operations for continually dealing with the tremendous amount of wastewater, the above deposition methods for small-scale film

coating obviously could not meet the requirements for scale-up. Moreover, almost no literature referred to column technologies for ion separation by the electrochemical method.

In this study, we propose a novel and compact battery-type column using printable copper hexacyanoferrate nanoparticles (CuHCF NPs) film for electrochemical removal of caesium from wastewater. Water-dispersed nanoparticle ink of CuHCF was successfully developed and coated on the rolled sheet electrodes. The technique is straight forward and can uniformly coat the water-dispersed ink, hence it is feasible to prepare CuHCF NPs film of any size or pattern at low cost. The battery-type column compacted with two sandwiched CuHCF NPs films can achieve Cs adsorption and desorption, through switching the potentials between them. The column performance for Cs separation, film regeneration, breakthrough time, reaction kinetic, and durability property was investigated.

2. EXPERIMENTAL

The detail process for the synthesis of CuHCF NPs was described in our previous paper [17], the chemical reaction was shown as follow:



In order to prepare the water-dispersed ink, CuHCF NPs were surface capped with $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ through the successive reaction of their insoluble solid with $\text{Na}_4[\text{Fe}(\text{CN})_6]$ (Fig. 1). After centrifugation, the supernatant fluid containing redundant $\text{Na}_4[\text{Fe}(\text{CN})_6]$ was removed. MilliQ water was used to wash the CuHCF NPs ink until neutral pH was reached. Moreover, then 5% CuHCF ink was obtained for film coating by wet printing methods using a spray coater (Model HIM-01, MITSUI Electric Co., Japan). For preparation of electrode film suitable for column operation, the stainless sheet (SUS316L, thickness 25 μm) with the advantage of chemical stable, low cost, flexible shape was chosen as the electrode for film coating. Finally, the CuHCF NPs film coated electrode sheet was rolled and packed into columns for further experiments as well as Cs separation.

Cs separation was conducted in a specially designed column of 2 cm diameter and 7.5 cm length, the size of the electrode was as large as 375 cm². So the ratio of volume/surface area was 0.062 as calculated. A three-electrode set was settled in the column, in which a platinum indicator as the reference electrode, rolled stainless steel (SUS) sheet with CuHCF NPs film as the working and the pristine SUS sheet was taken as the counter electrode. The polythene filter paper (R7030, SSK Japan) was sandwiched between these two SUS sheet electrodes, and then tightly packed in the battery-type column, as described in Fig. 2.

The electrochemical analyses were conducted using a potentiostat (ALS-711B, BAS Inc. Japan). CuHCF NPs film was first pre-treated in 1 ppm NaNO₃ solution by the applied potentials +0.4 V (vs. *platinum electrode*) for 30 min, in order to discharge the residual Na⁺ caused by the fabrication and surface treatment of CuHCF. The relevant reaction was shown as follows:



After the pre-treatment, multi-potential step (MPS) technique was used for Cs loading, by stepping the CuHCF NPs film to 0.0 V, and sweeping back to +0.4 V for unloading the Cs. Adsorption and desorption can be simply controlled by switching the potentials applied to the CuHCF NPs film between 0.0 and +0.4 V. The relevant reaction was shown as follow:



Influent Cs/elutriate solution was pumped upwards through the column for Cs adsorption/desorption at a constant volumetric flow rate controlled by a peristaltic Pump (AI800, Yamaze, Japan). Effluent solution samples were collected and analysed for Cs concentration using an inductively coupled plasma mass spectrometer (ICP-MS, NexIon 300D, PerkinElmer).

3. RESULTS AND DISCUSSION

3.1. Breakthrough time

Synthesized Cs water containing 4 ppm and 6 ppm Cs was pumped into the column for the investigation of breakthrough time, respectively. The experiment was successively conducted for

2 h at a flow rate of 1.0 ml/min, room temperature. Fig. 3 indicated when Cs solution containing an initial concentration of 4.4 ppm pumped through the column, about 547.1 μg Cs can be absorbed, leading to a removal efficiency of 97.3%. Meanwhile, about 820.3 μg Cs can be removed when initial Cs concentration is 6.6 ppm, again indicating a removal efficiency of 97.1%. After 2 hours of reaction, the breakthrough time (corresponding to $C/C_0 = 0.1$) was 90 min and 100 min in the case of 4 ppm, and 6 ppm, respectively. The column did not reach the exhausted state ($C/C_0 = 0.9$) during the study.

3.2. Kinetic consideration

The kinetics of the process suggested a model that links the sorption rate with the concentration of reactants (Cs or CuHCF) and constant parameters, which might give directions to the sorption mechanism. A first-order reaction depends on the concentration of one reactant. Other reactants can be present, but each will be zero-order. While a second-order reaction depends on the concentrations of one second-order reactant or two first-order reactants. According to the kinetic data obtained from the experiments, pseudo-first-order (PFO) and pseudo second-order (PSO) models have been used to elucidate the mechanisms of adsorption and the potential rate controlling steps [18,19].

$$\log (q_e - q_t) = \log (q_e) - tk_1/2.303 \quad (4)$$

$$t/q_t = 1/k_2 \cdot q_e^{-2} + t/q_e \quad (5)$$

where q_t and q_e are the amount of adsorbed Cs (mg/g) at time t and at equilibrium time, respectively. k_1 and k_2 are PFO and PSO rate constants for adsorption.

Kinetic constants obtained from the PFO and PSO models are given in Table 1. The correlation coefficients (R^2) of the PFO and PSO models, calculated by linear regression, were 0.982 and 0.990, respectively, which means experimental data well fitted both models, referring to a combination mechanism. As shown in Fig. 4, the reaction kinetic can be divided as two steps; the first step is better fitted by the PFO model, as indicated by the red line. In the initial stage the

surface charge generated is on the active site of CuHCF NPs film. The reaction rate may only depend on Cs cations, which suggested static physical attraction might be the main force for Cs removal. The second step showed the PSO model was a better fit. As more CuHCF sites were charge compensated with the time increasing, both Cs and CuHCF determined the rate at this stage. When the electrochemical force was been applied, the chemical reduction reaction from CN-Fe(III) to CN-Fe(II) contributed to Cs adsorption.

3.3. Regeneration performance

To check the regeneration performance of CuHCF NPs film, cycle experiments of Cs uptake/elution were carried out in the battery column. In a typical run, an influent solution of CsNO₃ electrolyte was used for Cs uptake, followed by pumping 1 ppm of a NaNO₃ electrolyte for Cs elution. Each process was performed at the flow rate of 10 ml/min and repeated for five cycles. As the results indicated, Cs uptake and elution was achieved by electrochemical oxidation-reduction of CuHCF NPs film, through switching the potentials between anodes and cathodes. The average report noted when the initial Cs concentration is 100 ppm about 723.6 µg was adsorbed on the CuHCF NPs film, due to the electrochemical reduction from CuHCF(III) to CuHCF(II). For Cs desorption, 709.4 µg was detected from the elution, indicating 96 ± 2.0% of the loaded Cs can be released from the used CuHCF NPs film. This suggests the CuHCF NPs film can be successfully regenerated by a reversible oxidation reaction from CN-Fe(II) to CN-Fe(III). In contrast to the conventional method using powder or bulk MHCF sorbents [8,12,13], the effective regeneration performance suggested the battery column system can be utilized in a close circuit.

3.4. Durability investigation

The life expectancy of a sorbent is the key parameter to evaluate whether the column system is suitable for practical utilization. Thus, we carried out the cycle Cs separation using CuHCF NPs film in the battery column system. Cs adsorption and desorption process were performed for 120s

each, and repeat the process for 100 cycles. As shown in Fig. 5a, in a typical run, the equal current with opposite direction was transferred between anodes and cathodes, which resulted in a balanced state for Cs adsorption and desorption. This result also confirmed that CuHCF NPs film can be successfully regenerated by switching the potentials between anodes and cathodes. The current balanced data from the total 100 cycles (Fig. 5b) can be taken as the evidence that CuHCF NPs film is stable and efficient for Cs separation in the battery type column system.

Cyclic voltammetry (CV) records the redox responses between the films and solutions. A single redox couple characterized the CV curves, due to the electrode process represented by the reaction [20,21]:



As shown in Fig. 5c, we find that there is a slight decrease of CV area after 100 cycles Cs separation, this also indicated CuHCF film is relatively stable for Cs separation, suggesting an extended service life for sequential removal and recycle of Cs from wastewater.

For a typical electroadsorption/desorption cycle as described above, electricity consumption was only 6.827 mW/m². The developed CuHCF NPs films are also of low cost which is around 2.5 US \$/m², including the cost of CuHCF NPs ink, stainless steel sheet electrode, and separator paper. Moreover, such a system can work for Cs separation for at least 100 cycles without any significant loss. Therefore, we can tell that our battery-type column is low cost and efficient technology to separate Cs ion from wastewater.

4. CONCLUSION

A novel and compact battery-type column technology using CuHCF NPs film has been developed for sequential removal of Cs from wastewater. Two great challenges of the electrochemical column technology have been well addressed. Firstly, CuHCF NPs were successfully covered with ferrocyanide anions, so that they can be well dispersed in water and formed as ink for film coating; this makes preparation of electrode suitable for column operation

feasible. Secondly, the electrochemical column was structurally designed like the dry battery, which is compact and ease operation for continually dealing with the considerable amount of wastewater. In addition, the good performance of Cs separation and film regeneration, minimization of secondary waste, and long life expectancy of CuHCF NPs film, suggest the battery-type column system is a promising technology for Cs separation, and potentially other redox related applications.

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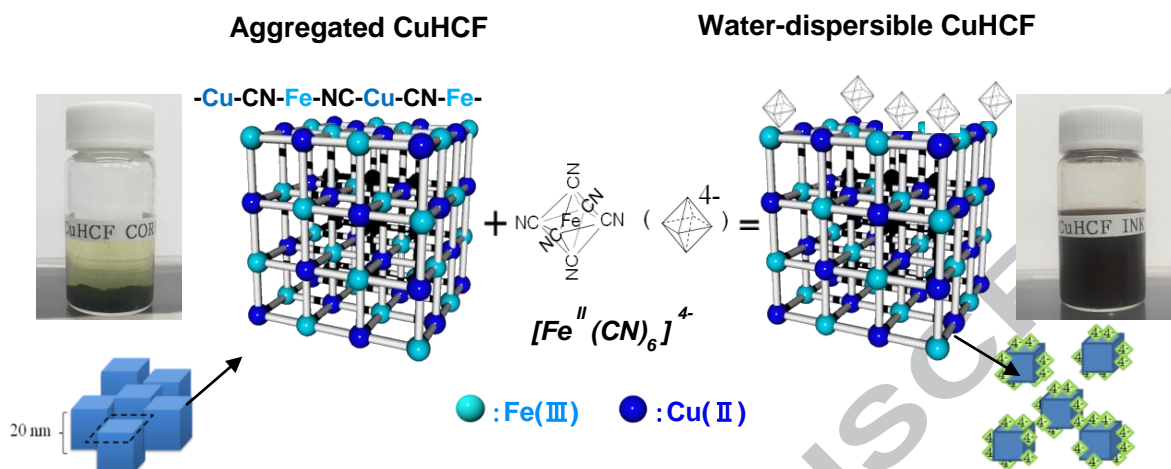


Fig. 1. The cubic framework structure of CuHCF, and its synthetic scheme for the water-dispersible by bearing negative surface-charges.

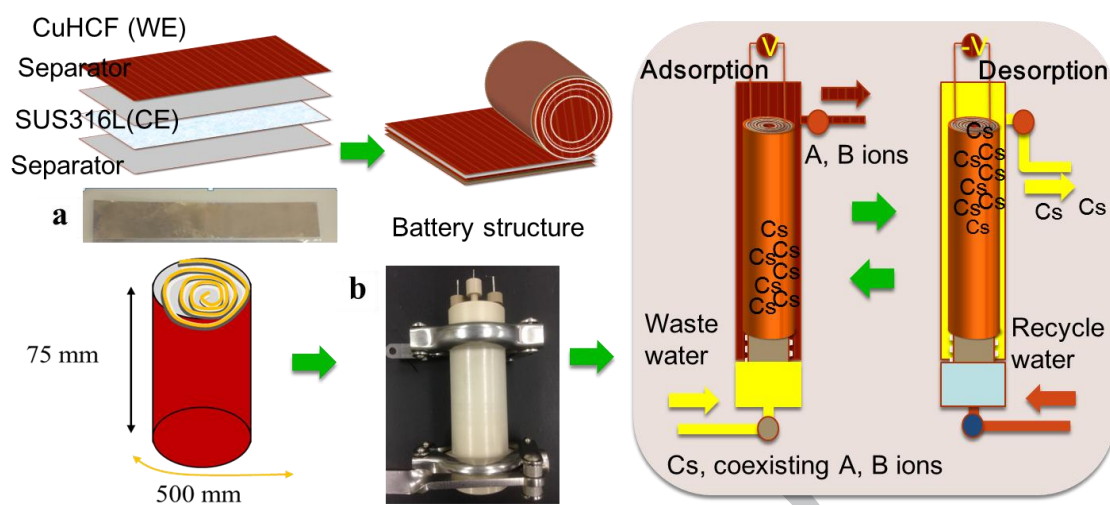


Fig. 2. A schematic view of column packing material and Cs separation experiments (a. CuHCF NPs film, b. battery-type column)

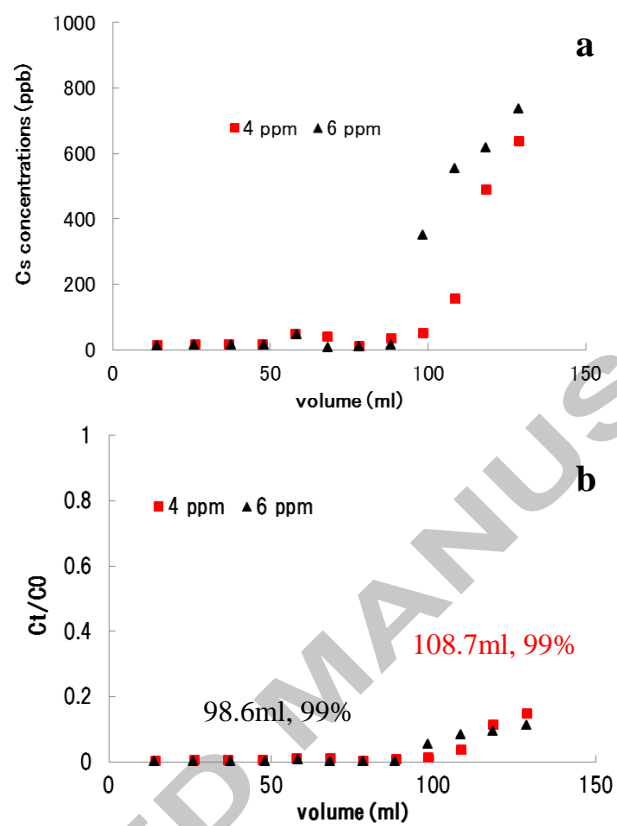


Fig. 3. (a) Cs removal efficiency in battery-type column and (b) its breakthrough curves expressed as C_t/C_0 versus volume (initial Cs concentration: 4, 6 ppm, flow rate: 10 ml/min; 1M HNO_3 and room temperature).

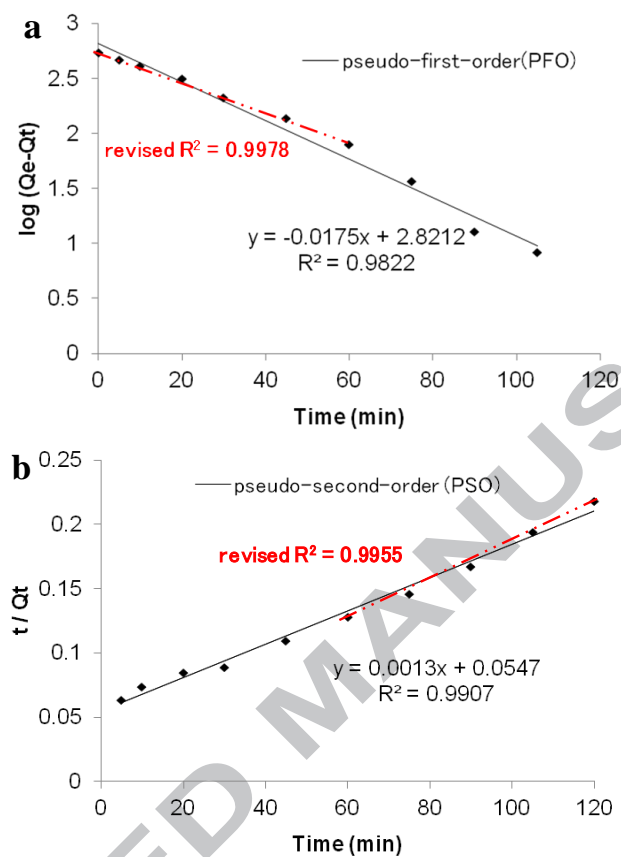


Fig. 4. Kinetic modeling of Cs adsorption on the CuHCF NPs film (a) pseudo-first-order (PFO); and (b) pseudo-second-order (PSO) (initial Cs concentration 1 ppm, equilibrium contact time 2 h, 1M HNO₃ and room temperature).

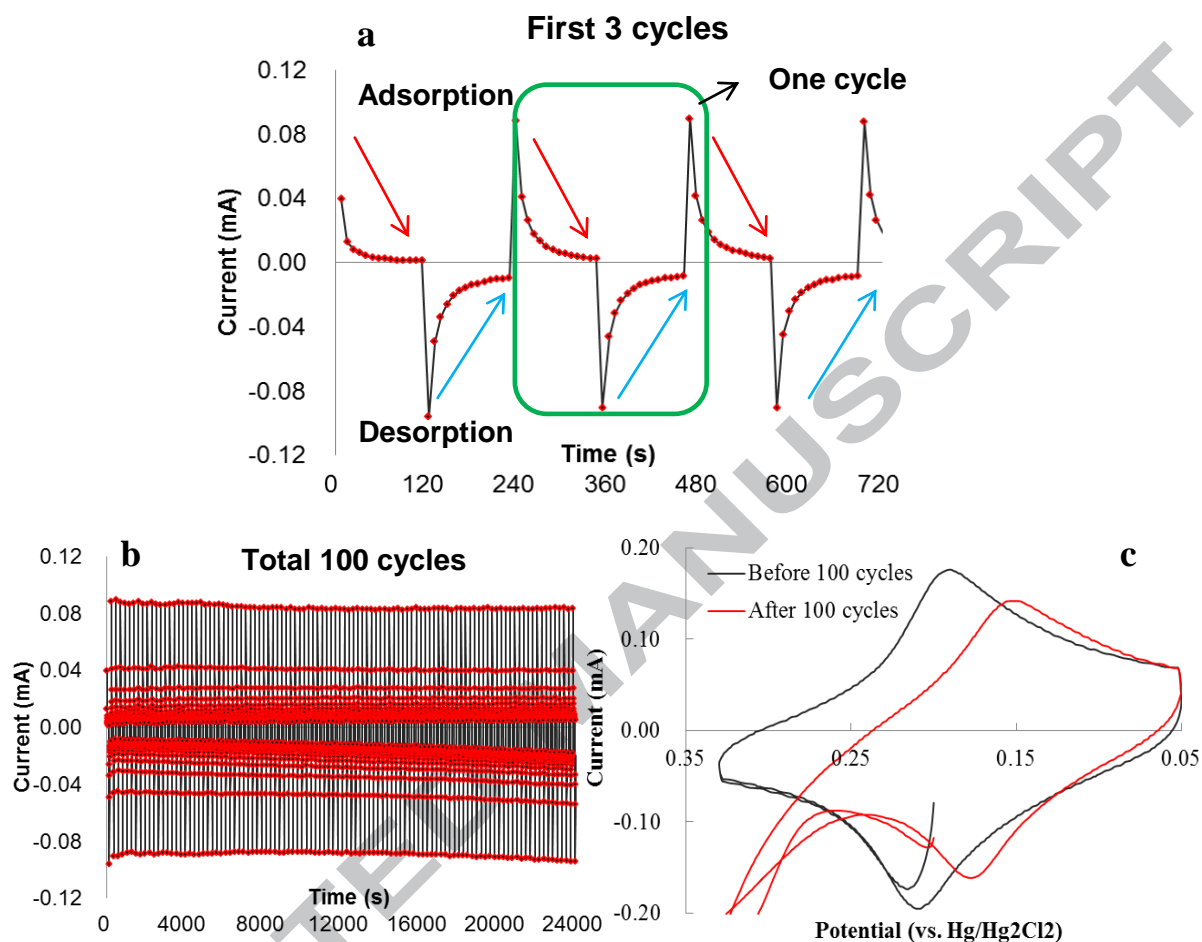


Fig. 5. Duration and stability test of CuHCF NPs film (a) current records in the first 3 cycle of Cs adsorption and desorption; (b) current records of the total 100 cycles; and Cyclic voltammetry (CV) response of CuHCF NPs film before and after 100 cycles test.

Table 1
Kinetics constant for adsorption of Caesium onto CuHCF NPs film

Pseudo-first-order (PFO)			Pseudo-second-order (PSO)			
$K_1 (\times 10^{-2})$	$Q_e (cal)$	R^2	$K_2 (\times 10^{-5})$	h	$Q_e (cal)$	R^2
4.03	662.5	0.9822	3.089	18.28	769.2	0.9907

Highlights

1. CuHCF NPs were surface-capped with $[Fe^{II}(CN)_6]^{4-}$ to be well water-dispersed as an ink.
2. CuHCF film can be simply and uniformly coated on electrodes of any size for column study.
3. A novel battery-type column using sandwiched NPs film of CuHCF was applied for sequential removal of Cs.
4. Cs separation can be simply controlled by modulating the potential of CuHCF film.
5. CuHCF NPs film is stable, even after 100 cycles of Cs adsorption and desorption.