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Recovery of cesium from residual salt lake brine in Qarham playa of Qaidam Basin with prussian blue functionalized graphene/carbon fibers composite

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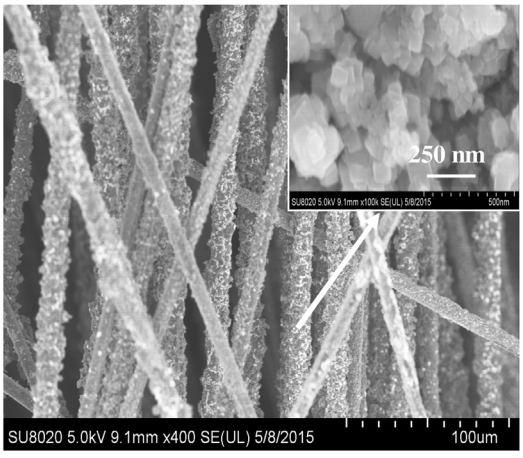
HIGHLIGHTS

- Recovery of Cs^+ from residual salt lake brine.
- Aminated graphene and carbon fibers composite support with rising specific surface area and convenient electrochemical operation.
- Prussian blue functionalized graphene/carbon fibers composite with excellent uptake for Cs^+.

GRAPHICAL ABSTRACT



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ABSTRACT

Both amination graphene and carbon fibers were cross-linked together using glutaraldehyde as composite support, then, prussian blue was electrodeposited at the surface (PB/GNs/CFs). The characterization of PB/GNs/CFs by field emission scanning electron microscopy, X-ray diffraction, fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and electrochemical techniques confirmed the correct modification. Number of cubic prussian blue particles were uniformly coated at the surface with an average size of 19.32 nm. Selective adsorption and desorption of cesium (Cs^+) were investigated at PB/GNs/CFs in aqueous solution, respectively. At the optimum conditions, PB/GNs/CFs could be used to the recovery of Cs^+ from the residual of salt lake brine which potassium was removed in Qarham playa of Qaidam Basin.

1. Introduction

Cesium, an important rare metal, is increasingly applied to energy, night-vision equipments, fiber optic telecommunication systems and catalysts [1–4]. Cesium resource is very rich in salt

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Table 1
Composition of the residual of salt lake brine in Qarham playa of Qaidam basin (pH 5.6).

Sample	Mg^{2+} g/L	Li^{+} g/L	K^{+} g/L	Na^{+} mg/L	Rb^{+} μg/L	Cs^{+} μg/L
Before recovery	1.41	0.59	0.08	1.41	23.40	12.40
*After recovery	1.35	0.53	0.067	1.11	4.40	1.80
Removal (%)	4.53	9.49	16.25	21.25	81.20	85.48

* After recovery, the concentration of ion in the residual of salt lake brine in Qarham playa of Qaidam basi.

lake brine of China, especially in Qarham playa of Qaidam basin [2,3], but cesium is at trace concentrations (0.01–1.0 mg/L), the concentrations of coexisting lithium, sodium, potassium and magnesium are thousands or even hundreds of thousands times that of cesium in the salt lake brine with close similarity in the physical and chemical properties [3]. Meanwhile, their hydration cations radii are in the order of Cs^{+} (3.25 Å), Rb^{+} (3.29 Å), K^{+} (3.3 Å), NH_4^{+} (3.3), Na^{+} (3.6 Å), Ca^{2+} (4.1 Å) and Mg^{2+} (4.25 Å) [5]. Thus the recovery of cesium is difficult from the salt lake brine. Some methods including co-precipitation [4], adsorption [2,6,7] and solvent extraction [3,8] have been used to the recovery of cesium from the salt lake brine up to now. Recently, Sun et al. synthesized faujasite-Y confined ammonium molybdophosphate using a support of natural clay by via a 'build-bottle-around-ship' approach for removing Cs^{+} in chloride solution or simulated brine [2]. Moreover, after lithium or potassium were removed from the salt lake brine of Qarham playa, and the concentrations of coexisting metal ions were sharply reduced (Table 1), it increases the possibility for the recovery of cesium from the residual salt lake brine with decreased interference [9,10]. But there is only a few reports on the study. Yang et al. reported the extraction of Rb^{+} and Cs^{+} together from the residues of salt lake brine from which potassium had been removed using a sulphonated kerosene solution of 4-*tert*-butyl-2-(α-methylbenzyl) phenol [3]. From above facts, it is obvious that the recovery of cesium has always been a challenge from the salt lake brine up to now.

On the other hand, many prior studies such as reverse osmosis, softening, coagulation/sedimentation, co-precipitation, electrodialysis/electrodriven transport, manganese oxide filtration, co-precipitation, adsorption and solvent extraction mainly focused on the removal of radioactive ^{137}cesium from nuclear wastewater [5,42]. Among these methods, adsorption was widely used to enrich and separate low-concentration Cs^{+} hitherto due to convenient and practicable [2,5]. Many adsorbents such as carbon materials (activated carbon, oxidized multiwall carbon nanotubes) [5,11,12], natural materials (zeolite, vermiculite and bentonite type et al) [5,13], biosorbents (funaria hygrometrica, betel nut shell and pinecone et al) [5,14], chemical adsorbents (manganese oxide, ammonium molybdophosphate-polyacrylonitrile) [5,2], potassium and transition metal (iron, nickel and copper et al.) hexacyanoferrates et al. [5,15–26] have been used to the removal of radioactive ^{137}cesium. In comparison with these adsorbents, only carbon materials, natural materials or biosorbents usually display poor uptake for Cs^{+}. While chemical adsorbents show much better uptake effect, especially, potassium and iron hexacyanoferrates (prussian blue, PB) [5,17–27], which become one kind of promising adsorbent for Cs^{+}. The reason is probably that the hydration radii of Cs^{+} (3.25 Å) just matches the cage size of $Fe^{III}_4[Fe^{II}(CN)_6]_3$ (PB) lattice, and nano-size PB particles with a lot of hydrophilic defect sites have supreme Cs^{+} adsorption capability by proton-elimination reaction of coordinated waters [17,18]. Recently, to improve the dispersed state, PB nanoparticles were modified at the surface of aliphalic amines, alkyl-ligand covered surface [19,20]. To enhance the adsorption capability, small size PB nanocrystal coated at poly(acrylic acid) resin, and interior hollow PB nanoparticles were fabricated with rising specific surface area [21,23]. To improve the separation, PB coated magnetic nanoparticles was prepared [5,24–26]. It is noticeable that some studies also reported the removal of Cs^{+} by electrically switched ion exchange in low pH [15,25,27]. In this method, direct oxidation and reduction of nickel hexacyanoferrates film attached to an electrode surface is used to load and unload the film with alkali metal cations. Of course, all these studies displayed much important reference value for the recovery of cesium from abundant salt lake brine. But it is necessary to further decrease the cost in terms of the practical application. The separation and regeneration of PB adsorbent after using are two key points.

In present work, prussian blue functionalized graphene/carbon fibers composite (PB/GNs/CFs) was prepared by compound electrochemical and cross linking methods. Selective adsorption and desorption of Cs^{+} were investigated at PB/GNs/CFs using various method in detail. The resulting PB/GNs/CFs was used to the recovery of Cs^{+} from the residual salt lake brines, which potassium was removed in Qarham playa of Qaidam Basin.

2. Experiment

2.1. Chemicals and apparatus

Polyacrylonitrile-carbon fibers (CFs) were obtained from Dingfeng Carbon Fibers Fabrication Company of Yixing (China, Wuxi), one truss CFs have about 3000 branches with a diameter of 7 ± 1 μm, they were snipped at 8 cm in following experiments. Ethylenediamine (EDA), *N*,*N*′-dicyclohexyl carbodiimide (DCC), polyvinylpyrrolidone (PVP), Dimethyl Formamide (DMF), glutaraldehyde (GA), $FeCl_3$, $K_3[Fe(CN)_6]$, and all other chemicals were Chemical Reagent Company of Shanghai products (China, Shanghai). The composition of residual salt lake brine was listed in Table 1 [28].

All electrochemical experiments were performed with a CH660B electrochemical workstation (Chenhua, Shanghai, China). A conventional three-electrode electrochemical system was used for all electrochemical experiments, which consisted of carbon fibers electrode, a twisted platinum wire counter electrode, and a saturated calomel reference electrode (SCE). All potentials reported are versus SCE.

Field emission scanning electron microscope (FE-SEM) images were obtained on a JSM-600 field emission scanning electron microanalyser (JEOL, Japan). X-ray diffraction (XRD) data of the samples were collected using a Rigaku D/MAX-rB diffractometer with Cu Ka radiation. Infrared spectra (IR) were measured at IR 200 (America Nicolet). X-ray photoelectron spectroscopy (XPS) were recorded using an ESCALABMK2 spectrometer (Thermo VG Scientific, East Grinstead, UK) with Mg-Alpha X-ray radiation as the source for excitation. Atomic absorption spectroscopy were performed in a AA800 spectrophotometer (Perkin Eimei, America).

2.2. Preparation of PB/GNs/CFs

2.2.1. Graphene/carbon fibers composite support preparation

CFs and graphene underwent amination, respectively, and then, amination graphene was coated at surface of amination carbon fibers using glutaraldehyde as cross linking agent by polycondensation reaction. The processes as follow: 20 trusses of CFs were dispersed in mixed acid solution of perchlorate acid and nitric acid (3:7, V/V). The mixed solution was ultrasonically agitated for 7 h to introduce carboxyl groups at the surface of carbon fibers. The carboxyl groups modified CFs were washed with double-distilled water to neutral, and dried in air (labeled as CFs-COOH). 20 trusses of CFs-COOH were put in a mixed solution of 0.3 g DCC and 30 mL