



The characterization and application of prussian blue at graphene coated carbon fibers in a separated adsorption and electrically switched ion exchange desorption processes of cesium



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ABSTRACT

Iron hexacyanoferrate/graphene/carbon fibers composite (PB/GN/CFs) was prepared by electrochemical method. Characterization of PB/GN/CFs in a separated adsorption and electrically switched ion exchange desorption processes (Ads-ESIX) of cesium ions (Cs^+) was confirmed by FE-SEM, XRD, IR, XPS and electrochemistry techniques. PB/GN/CFs displayed two quasi reversible transformations from $\text{Fe}^{\text{III}}_4(\text{Fe}^{\text{II}}(\text{CN})_6)_3$ to $\text{Fe}^{\text{III}}_4(\text{Fe}^{\text{III}}(\text{CN})_6\text{Cl})_3$, or to $(\text{NH}_4)_4\text{Fe}^{\text{II}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$ at a potential range of -0.1 – 1.2 V in pH 2, 0.1 M NH_4Cl . The recovery of Cs^+ was investigated by PB/GN/CFs using Ads-ESIX method. Cs^+ could be selectively adsorbed by PB/GN/CFs from aqueous solution in pH 7.0, and desorbed in pH 2, 0.1 M NH_4Cl . The desorption rate of Cs^+ depended on the introduction of potential at PB/GN/CFs in pH 2, 0.1 M NH_4Cl . Both H_3O^+ and NH_4^+ could play dual role of electrolyte and competitor for the desorption of Cs^+ . PB/GN/CFs could be used to the recovery of Cs^+ from the residual salt lake brine in which potassium had been removed from Qarham playa of Qaidam Basin in China.

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1. Introduction

Nowadays, the application of metal cesium are displaying an increasing tendency in new energy, metalion catalysts, night-vision equipments, telecommunication systems [1–5]. Many prior works majorly focused on the removal of Cs^+ from radioactive effluents [5–18], and less concerned about the recovery [1–4,19–21]. Among various techniques such as chemical precipitation [6], evaporation [7], extraction [8], adsorption [9] and ion exchange [10] as well as electrically switched ion exchange (ESIX) [11–20], ESIX technology is probably a promising method for the recovery of Cs^+ . Because ESIX could combine ion exchange and electrochemistry to provide a selective and reversible separation process for Cs^+ deposal, and electricity is the main driving force for Cs^+ separation. All these made ESIX a cost-effective clean-up strategy without chemical regeneration of ion exchanger. During past years nickel hexacyanoferrate has been widely used as effective electroactive ion exchangers due to its good selective adsorption for Cs^+ [11–19]. Recently copper hexacyanoferrate was successfully applied to the uptake of Cs^+ too [20]. Meanwhile iron hexacyanoferrate (PB,

prussian blue) has been widely used as adsorbent for the removal of Cs^+ from radioactive effluents due to its excellent selectivity, cheapness and nontoxicity [9]. PB has simple face-centered lattice structure in which eight water molecules exist in the unit cell, and the hydrated ions of cesium just fit the cage size of PB lattice. However, PB was hardly used in ESIX process due to only chemically stable in low pH. The properties and structural transformation of PB have not been thoroughly reported in ESIX process either.

On the other hand, the residual salt lake brine in which over 80% potassium had been removed from Qarham playa of Qaidam Basin in China, contains abundant non-radioactive ^{133}Cs resource in total with a low concentrations (0.01–0.1 mg L^{-1}) [1], and the concentrations of coexisting lithium, sodium, potassium and magnesium are ten or hundred times that of Cs^+ in the residual salt lake brine with similar physical and chemical properties [1–3,9]. The hydration radii of the cations are in the order of H_3O^+ (2.82 Å), Cs^+ (3.28 Å), Rb^+ (3.29 Å), K^+ (3.30 Å), NH_4^+ (3.30 Å), Na^+ (3.58 Å), Ca^{2+} (4.10 Å) and Mg^{2+} (4.25 Å) [9]. Although various methods including co-precipitation [21], adsorption [2,4] and solvent extraction [3] were used to the recovery of cesium from the salt lake brine. Recently extraction of Rb^+ and Cs^+ together was reported from the residues of salt lake brine using a sulphonated kerosene solution of 4-tert-butyl-2-(α -methylbenzyl) phenol [3].

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There are still some difficulties to the recovery of Cs⁺ from the residual salt lake brine in terms of economy and environment.

In this work, ethanediamine amino coating carbon fibers/graphene composite support was prepared by electrophoretic deposition to enhance the specific surface area of CFs, and improve the chemical stability of PB; then PB was electro-deposited in situ (PB/GN/CFs). A separated adsorption and electrically switched ion exchange desorption method (Ads-ESIX) was proposed for the recovery of Cs⁺ using PB/GN/CFs. The properties and structural transformation of PB/GN/CFs was characterized in the Ads-ESIX processes of Cs⁺ in detail in terms of reusing materials and saving expenditure. The recovery of Cs⁺ was investigated using PB/GN/CFs from the residual salt lake brine in which potassium had been removed from Qarham playa of Qaidam Basin in China.

2. Experimental

2.1. Chemicals and apparatus

Polyacrylonitrile-carbon fabrics (CFs) were obtained from Dingfeng Carbon Fibers Fabrication Company of Yixing (Wuxi, China), one truss CFs have about 3000 branches with a diameter of 7 ± 1 μm, they was snipped at 8 cm in following experiments, which was fixed in solution with 4 cm (0.0034 g, area ≈ 780 m²/g). Natural graphite powder was purchased from Qingdao Jin Lai Graphite Co., Ltd (Qingdao, China). Potassium ferricyanide, ¹³³cesium chloride, ferric chloride, polyvinyl pyrrolidone (PVP), ethylenediamine and N,N'-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All reagents used were analytical grade. All solutions and subsequent dilutions were prepared using doubly distilled water. The composition of residual salt lake brine was listed in Table 1 [22].

Electrophoretic deposition was performed with a DYY-2C electrophoresis apparatus (Liuyi instrument plant, Beijing, China). All other electrochemical experiments were carried out with CHI 660B electrochemical workstation (Chenhua, Shanghai, China). The three-electrode system contained a CFs (PB/GN/CFs) as the working electrode, a saturated calomel electrode and a platinum electrode as reference electrode and counter electrode, respectively. Infrared spectra were measured at IR 200 (Nicolet, America). X-ray diffraction (XRD) data were collected using a X'Pert PRO MPD diffractometer with Cu Kα radiation (PANalytical, Netherlands). Field emission scanning electron microscope (FE-SEM) images were obtained on a SU8020 field emission scanning electron microanalyser (Hitachi, Japan). X-ray photoelectron spectroscopy (XPS) experiments were performed on an ESCALAB250Xi spectrometer (Thermo, America) with Mg-Alpha X-ray radiation as the source for excitation. AA800 atomic absorption spectrophotometer was used to quantify the concentration of Cs⁺ (Perkin Eimer, America).

2.2. Preparation of materials

PB/GN/CFs could be prepared as following three steps. (1) Electrophoretic deposition of GO at the surface of CFs. Graphene

oxide nanosheets (GO) were obtained from natural graphite flakes by a modified Hummer's method [23]. 0.05 mg GO was dispersed in 50 mL DMF with sonication of 2 h to obtain a stable suspension. Then, 0.02 g CFs and a stainless steel plate (15 × 35 mm) were employed as anode and cathode with a distance of 1 cm between double electrodes. The electrophoretic deposition was performed in 25 mL GO suspension at 90 V with 10 min [24]. The resulting material was dried at 50 °C (signed as GO/CFs). (2) Amination of GO/CFs. A mixture of 0.02 g GO/CFs, 30 mL ethylenediamine and 0.3 g dicyclohexylcarbodiimide were put in a flask in oil bath at 120 °C with reflux condensation of 48 h. The material was washed by ethanol, and dried at 60 °C in vacuum (signed as GN/CFs). (3) Electrodeposition of PB at GN/CFs [25–28,41]. 0.02 g GN/CFs was immersed in 30 mL mixture including 1 mM FeCl₃, 1 mM K₃[Fe(CN)₆], 0.1 M KCl, 0.01 M HCl and 15 mg PVP (chemical etching) [28]. PB/GN/CFs could be formed by cyclic voltammetric (CV) in a potential range of -0.1–0.5 V and scan rate of 50 mV/s with 30 cycles (signed as PB/GN/CFs). The reactions as following: [Fe^(III)(CN)₆]³⁻ + e⁻ = [Fe^(II)(CN)₆]⁴⁻; Fe³⁺ + 3 [Fe^(II)(CN)₆]⁴⁻ = Fe^(III)₄[Fe^(II)(CN)₆]₃↓. The scheme could be found in Fig. 1.

2.3. Adsorption experiments

3 trusses (0.011 g) PB/GN/CFs was added into 10 mL CsCl solution (ranging from 2 to 100 mg L⁻¹) in a sealable plastic tube. PB/GN/CFs was simply used in a static mode. The concentration of Cs⁺ that remained in solution was quantified with an atomic absorption spectrophotometer. The adsorption of each sample was tested in triplicate, and averages were used to evaluate the adsorbent capabilities. The adsorption capacity at equilibrium (q_e) of Cs⁺ can be calculated by using Eq. (1), where C_0 and C_e are the initial and equilibrium concentrations of Cs⁺ (mg L⁻¹) in the solution, respectively; q_e is the amount of adsorbate adsorbed per unit dry weight of adsorbent (mg g⁻¹), V is the volume of the solution (L), and m is the dry-weight of the adsorbent (g).

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

2.3.1. Adsorption kinetics

The Lagergren pseudo-first-order model in Eq. (2) and pseudo-second-order model in Eq. (3) were used to investigate the kinetic models [29]. Where q_{e1} and q_{e2} are the amount adsorbed at equilibrium of the pseudo-first-order and the pseudo-second-order, respectively. q_t is the amount of adsorbed at time t .

$$\log(q_{e1} - q_t) = \log q_{e1} - \frac{k_1 t}{2.303} \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e2}^2} + \frac{t}{q_{e2}} \quad (3)$$

2.3.2. Adsorption isotherms

Adsorption isotherms were described using linear form of the Langmuir Eq. (4), Freundlich Eq. (5) [30]. Where K_L is the Langmuir isotherm parameter, K_F is the Freundlich isotherm parameter, q_e is the amount adsorbed at equilibrium, q_m is the maximum adsorption capacity of the adsorbent, and n is the heterogeneity parameter of the adsorbent surface.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (4)$$

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

Sample	Mg ²⁺	Li ⁺	K ⁺	Ca ²⁺	Na ⁺	Rb ⁺	Cs ⁺
Before (mg/L)	5419.6	2792.8	324.3	272.4	5.74	0.115	0.051
After (mg/L)	5411.2	2749.2	288.2	267.8	5.52	0.037	0.002
Removal (%)	1.4	1.5	11.2	1.6	3.8	67.8	96.1

^a (n = 3).

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