Colloids and Surfaces A 550 (2018) 99–107

Contents lists available at ScienceDirect

Colloids and Surfaces A

journal homepage: www.elsevier.com/locate/colsurfa

Magnetic $K_2Zn_3[Fe(CN)_6]_2$ @ Ni-P composites for highly selective cesium separation

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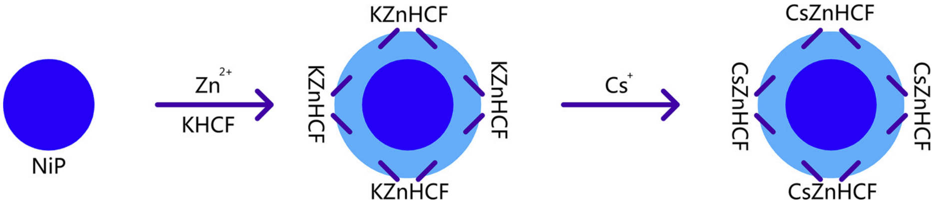
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Cesium
Adsorption
Magnetic
Hexacyanoferrate

ABSTRACT

$K_2Zn_3[Fe(CN)_6]_2$ @ Ni-P (KNiP) composites with high cesium selectivity were synthesized for the first time. Nickel phosphorus (NiP) was used as a solid base for the adsorption of $K_2Zn_3[Fe(CN)_6]_2$ (KZnHCF). The synthesized KNiP composites were characterized by SEM, TEM, XRD, VSM and BET. The characteristic results demonstrated that the composites possess a ball-shape structure, a large surface area of 305.031 m^2/g and high saturation magnetization of 2.95 emu/g. The ICP-OES analyser was used to determine the concentration of ions in this study. KNiP showed good cesium adsorption performance over a wide pH range and high selectivity for cesium over coexistent competing ions. Analysis of dynamics showed that KNiP has good adsorption performance toward cesium, with an adsorption capacity of 54.95 mg/g. Equilibrium was achieved within only two hours and the experimental data fit the Pseudo second-order model, indicating that the adsorption process was chemisorption. The adsorption process followed the Freundlich isotherm model, indicating that it mainly occured on a heterogeneous surface.

1. Introduction

Radioactive cesium (^{134}Cs and ^{137}Cs) is a fission by-product in nuclear power plants and has been involved in a number of nuclear accidents [1–4]. The removal of radioactive cesium has attracted attention since the Fukushima accident [5–8]. Cesium radioisotopes can significantly contaminate the aquatic environment due to their long half-life ($t_{1/2}$ = 30.17 years) and high radioactivity [9–11]. In addition, as member of the alkali metal family, cesium radioisotopes are mostly in the form of Cs^+, which guarantees high solubility and mobility in water and high transferability into the biosphere [8,12–14]. Once ingested by humans, cesium can be accumulated in the gut and distributed throughout the soft tissues, creating an internal hazard and resulting in diseases such as thyroid cancer [15–17]. Therefore, removal of cesium will reduce the risk of radioactive exposure during handling of nuclear wastes or in contaminated aquatic environments [17–19]. Moreover, the separated cesium ions can be used in sterilization processes, food preservation and sewage sludge treatments [20–22]. Thus, the nuclear industry and institutions must find an effective and highly selective method to separate cesium from aquatic solutions.

The three main methods for separating cesium from aqueous

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https://doi.org/10.1016/j.colsurfa.2018.04.037
Received 1 February 2018; Received in revised form 16 April 2018; Accepted 17 April 2018

environments are precipitation, solvent extraction, and ion exchange [2,22,23]. Among these methods, adsorption is the most effective way to remove cesium. Ion exchange method is a type of adsorption that leads to exchange between ions [2,14]. The cesium adsorption process has been investigated using various adsorbents [8,14,16]. Materials such as hydrous ferric oxide, dolomite, hybrid gel, titanosilicate and some biosorbents have been proved effective [2,14,20]. The preparations of these adsorbents are relatively shorter and easier, because there is no need to separate the target adsorbents from their isomers [8,14]. Furthermore, evidence has shown that most adsorbents can react instantly with target ions [16,20]. Studies under different conditions have proved that these adsorbents have strong stability under acidic or alkaline conditions [20]. Because of their low cost, strong stability and high efficiency, the ion exchange method has attracted the most attention [2,14,16]. Nevertheless, its direct use in environmental cleanup has been hampered by the low cesium selectivity and difficulty in collection.

Metal (Co, Ni, Cu, Zn) hexacyanoferrate is considered a promising adsorbent for the selective recovery of cesium from wastewater and is chemically stable over a wide pH range [7]. Metal hexacyanoferrate has a face-centered cubic lattice with octahedral transition metal ions that are coordinated by $-N{\equiv}C$ and $-C{\equiv}N$ ligands, and the alkali metal cations are in the tetrahedral sites [9]. These alkali metal cations can be replaced by cesium in aqueous environments, and because of the difference in covalent bond energy between the alkali metal cations and ferricyanide ions, these metal hexacyanoferrates have high selectivity over coexistent competing ions [9,24,25]. Among them, $K_2Zn_3[Fe(CN)_6]_2$ (KZnHCF) is often chosen as the agent in practical ion exchange applications because of its strong stability [26,27]. However, with an average diameter of ~300 μm, the KZnHCF fine powder suspending in aqueous solutions is difficult to collect, limiting its application in large scale cesium recovery [7,9]. In order to improve the mechanical properties of KZnHCF, a solid base with a larger scale is required. With an average diameter of ~5 μm, the nickel phosphides (NiP), which have a large BET surface area and good room-temperature magnetism, are an ideal base for the adsorption of KZnHCF [4,28–30]. The enormous surface area of NiP guarantees their good combination with KZnHCF, and their magnetic properties allow them to be easily collected from a large volume of water under the assistance of a magnetic field.

This study synthesized a novel adsorbent of $K_2Zn_3[Fe(CN)_6]_2$ @ Ni-P (KNiP) composites by coating NiP with KZnHCF precipitates. SEM, TEM, XRD and BET were used to characterize the composites. To evaluate the adsorption ability of the KNiP composites, experiments were conducted under different conditions.

2. Materials and methods

2.1. Materials

All reagents and chemicals used were of analytical grade and were used without further purification. Nickel chloride ($NiCl_2 \cdot 6H_2O$) and dimethyl formamide (C_3H_7NO) were purchased from Aladdin, Shanghai. Sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$), sodium hydroxide (NaOH), hydrochloric acid (HCl) and ferric trichloride ($FeCl_3 \cdot 6H_2O$) were purchased from Yuanli Chemical Co. Ltd, Tianjin. Zinc chloride ($ZnCl_2$) was purchased from Damao Chemical & Reagent, Tianjin. Potassium hexacyanoferrate ($K_4[Fe(CN)_6] \cdot 3H_2O$) was purchased from Chemical & Reagent Supply, Tianjin. Cesium nitrate ($CsNO_3$) was purchased from Special Chemical Reagents, Northern China. Potassium chloride (KCl) was purchased from Guangfu Chemical Engineering Institution, Tianjin.

2.2. Synthesis of NiP

Urchin-like NiP particles were prepared via a hydrothermal reaction at 160 °C. A mass of 3.8 g (16 mmol) of $NiCl_2$·6H2O and 0.704 g (8 mmol) of NaH_2PO_2 were added to a 100 mL volumetric flask and diluted with deionized water. The solution was then transferred to a 200 mL Erlenmeyer flask with 40 mL of DMF and mixed by an electromagnetic agitator for 20 min at room temperature. After the agitation, the 140 mL solution was separated into two 100 mL hydrothermal reactors. The reactors were placed in a pre-heated oven for 16 h at 160 °C, then cooled naturally to room temperature. The resulting precipitates were washed with deionized water and ethanol and then vacuum desiccated for 6 h.

2.3. Synthesis of KNiP

KZnHCF precipitates were subsequently formed on the surface of NiP particles as Zn^{2+}-coordinated $[Fe(CN)_6]^{4-}$ [7,8,10]. Solutions (0.1 M) of $K_4[Fe(CN)_6]$ (KHCF) and $ZnCl_2$ were prepared and slowly dropped into the solutions during the precipitation process. Nitrogen was used to avoid peptization of the KZnHCF material [18]. The mixture was stirred for 3 h to allow the complete adsorption of the metal ferrocyanide precipitates onto NiP. Then, the resulting KNiP composites were collected with a strong magnet.

2.4. Quantitative and structure analyses

The morphology and composition of the KNiP composites were analysed using an SEM&EDS model JSM-6510A instrument and a TEM model JEM-2100F instrument from JEOL, Japan. The X-ray diffraction patterns were recorded using a Philips X-ray diffractometer, model PW1710, with monochromatized Cu-Ka radiation (k = 0.154 nm, 40 kV and 25 mA). The magnetization of KNiP was measured at room temperature using a SQUID VSM. A MA-235 digital pH meter (Mettler Toledo, UK) was used for the pH measurements. The determination of the particle surface area was determined using a BET analyzer from Micromeritics Instrument Corporation, America.

2.5. Adsorption experiments

The adsorption ability of KNiP was tested and compared with other cesium adsorbents. The concentration of ions were tested by an Optima 5300DV ICP-OES analyzer from Perkin Elmer, America. ^{133}Cs (inactive cesium) was used to study the adsorption process. The adsorption capacity was evaluated using the following equation:

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

where q_e is the quantity of cesium adsorbed per unit dry weight of the adsorbent (mg/g), C_0 and are the initial and equilibrium concentrations of cesium, m is the dry weight of the adsorbent (g), and V is the volume of the solution (mL).

The removal efficiency was evaluated by the following equation:

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \tag{2}$$

where R is the removal efficiency and C_0 and are the initial and equilibrium concentrations of cesium.

To study the effect of the amount of adsorbent, different amounts of KNiP (5–50 mg) were immersed in 70 mL of 50 mg/L $CsNO_3$ solution. A mass of 20 mg of KNiP was dispersed in 70 mL of 50 mg/L $CsNO_3$ solution to investigate the influence of other factors on the adsorption process, including competing ions and pH. Salts of Na^+, K^+, Li^+, Mg^{2+} were added to adjust the concentration of these ions from 5 to 30 mg/L. The pH values ranging from 2 to 11 were adjusted by 0.1 M HCl and 0.1 M NaOH. A 50 mL volume of 5 mg/L $CsNO_3$ and 5 mg of KNiP were used to obtain the equilibrium curve of KNiP. To assess the effects of concentration, solutions with initial cesium concentrations ranging from 10 mg/L to 100 mg/L were investigated at room temperature, with a solution volume of 30 mL and 20 mg of adsorbent.