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Sorption behavior of cesium from aqueous solution on magnetic hexacyanoferrate materials

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HIGHLIGHTS

- A novel pathway of synthesizing magnetic hexacyanoferrate material was developed.
- The synthesized material can offer a high capacity for sorption of cesium.
- The material can offer a fast removal of cesium in kinetic performance.
- The fine M-PTH particle can be easily separated from wastewater for recirculation.

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ABSTRACT

The rapid development of the nuclear power plant in China leads to increasing attention to the treatment of low-level radioactive wastewater (LLRW). One of possibilities is the application of inorganic adsorbent like potassium titanium hexacyanoferrate (PTH), which can exhibit the effective adsorption of cesium. In this paper, the PTH material was optimized by means of being loaded on magnetite substrate. The synthesized material (magnetic PTH, M-PTH), with a particle size of less than 100 nm, can offer a high capacity and favorable kinetic performance, however, without difficulties of separation from the LLRW due to its magnetic characterizations. The batch experiments demonstrate that cesium sorption isotherm of M-PTH coincide well with Langmuir model. The calculated capacity amounts to 0.517 mmol/g, approximately 1.5 times the capacity of zeolite materials. The sorption process follows the pseudo-second-order sorption model. In the initial phase the rate-controlling step is intraparticle diffusion. With the Cs accumulation on the particle surface, external diffusion performs an important role together with intraparticle diffusion.

1. Introduction

Since the first nuclear power plant (NPP) went into commercial operation in 1991, China had completed 11 units in six locations with a total generation capacity of 9 GW by the end of 2007. Now the government has made the objective to build nuclear power plants with 40 GW power generation capacities by 2020. The rapid development of nuclear energy will inevitably lead to large volumes of low-level radioactive wastewater (LLRW). Removal of radioactive nuclide from the LLRW would be necessary before discharge to environment. Radioactive-cesium is the major objective to be removed in many cases, due to its high portion in the nuclides of most LLRW, the long half-life, high solubility and bioavailability. There is evidence which indicates that radiocesium continues to be recirculated in biological systems for many years following a pulse of contamination (Avery, 1996).

Most LLRW contains very trace radiocesium at concentrations far below nanogram per liter. However, inactive metal ions, like Na+, K+, etc., exist at excessive concentration of above milligram per liter, in some cases even amount to several moles per liter. Therefore, the corresponding separation technology must be selective on the trace radionuclide. The application of most ion-exchange resin is discounted because the excessive inactive metal ions in LLRW rapidly exhaust the ion-exchange sites of the resin.

One of possibilities is by means of inorganic adsorbent that can exhibit the high selectivity on trace Cs (Borai et al., 2009; Han et al., 2013; Tel et al., 2010). The additional advantages of inorganic adsorbent come from the high thermal and radiation stabilities. Inorganic sorbents include natural clinoptilolite, synthetic zeolites such as Na-Y zeolite, aluminosilicate and silica gels, transition

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metal ferrocyanides, oxyhydrates and phosphates of titanium or zirconium in spherical granules, natural pyrolusite, modified manganese dioxide and activated charcoals. (Ojovan and Lee, 2005)

Among these sorbents, zeolite has been widely applied in the treatment of LLRW, due to its high exchange capacity, possible selectivity and specificity, good resistant to radiation (El-Kamash, 2008). Zeolites even played an important role in separation of Cs from contaminated water in Fukushima nuclear accident. In the last decades various zeolites including natural clinoptilolite (NaNCl), natural chabazite (NaNCh), natural mordenite (NaNM) and synthetic mordenite (NaSM) have been investigated. It seems that natural chabazite (NaNCh) has the higher distribution coefficients as well as the highest capacity toward cesium ion (Borai et al., 2009).

Hexacyanoferrates are also promising candidates for separation of radioactive cesium from LLRW, due to its high selectivity over a wide pH range even in the presence of high salt loadings (Liu et al., 2008; Sheha, 2012). Hexacyanoferrate-based extractant (CsTreat) had even been applied to extract Cs from reverse osmosis brine, since it was hardly influenced by brine salinity (Peterskova et al., 2012). In order to optimize the adsorbent performance, many efforts had been tried to improve the hydrodynamic characteristics of this adsorbent, for example, by addition of mesoporous matrix (Chang et al., 2008; Lin et al., 2001; Sangvanich et al., 2010) or organic polymer (Someda et al., 2002; Vrtoch et al., 2011). Reducing the particle size can enhance the specific surface area and therefore improve the capacity and kinetic performance. However, this fine particle in nanoscale is hard to be separated from solution quickly. In many cases membrane technologies would be necessary like micro- and ultra-filtration. Another solution is to manufacture the magnetic microscale or nanoscale particles coated with hexacyanoferrates by means of magnetically assisted chemical separation process (Nunez et al., 1995), adsorption occurs quickly and the fine exhausted adsorbent can be separated from the LLRW easily, without the great reduction of capacity of cesium (Marmier et al., 1999). It has been reported that magnetic potassium nickel hexacyanoferrate composite was prepared based on wet-dispersion and in situ precipitation, and low coercivity of the prepared particles enabled easy filter regeneration (Ambashta et al., 2003).

In this paper, a novel pathway of synthesizing magnetic potassium titanium hexacyanoferrate (M-PTH) was developed based on wet dispersion and in situ precipitation. In the composite M-PTH, the magnetic Fe_3O_4 material coated with SiO_2 acts as porous support for hydrous titanium oxide. The high PTH loads can be achieved by means of Ti—O—Si bonds between SiO_2 layer and hydrous titanium oxide. The synthesized composite material can be easily separated from liquid by external magnetic field despite of its very fine particle size.

2. Experimental

2.1. Chemicals

All the chemicals, including hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$), sodium hydroxide (NaOH), tetraethyl orthosilicate (TEOS), sodium silicate (Na_2SiO_3), tetrabutyl titanate ($(C_4H_9O)_4Ti$), isopropyl alcohol ($(CH_3)_2CHOH$), potassium hexacyanoferrate ($K_4[Fe(CN)_6]$) were of analytical grade.

For the tests, $CsNO_3$-bearing solutions of demineralized water were used. Their cesium concentrations amounted to approximately 1.5–35 mg/L.

The inorganic sorbent was synthesized in the laboratory. The zeolite materials used in the study (clinoptilolite and mordenite) were commercially available, with the uniform particle size of 0.098–0.2 mm, considering the separation efficiency from liquid.

2.2. Synthesis of M-PTH material

The synthesis of M-PTH consists of four steps: Fe_3O_4 preparation; surface coating of SiO_2; surface coating of TiO_2; coating of the sorbent.

Fe_3O_4 preparation. 0.1–0.2 mol/L Fe^{2+}/Fe^{3} mixed solution and hydroxylamine hydrochloride were dropwise added to 0.5–2.0 mol/L sodium hydroxide solution simultaneously under stirring and nitrogen gas protection at room temperature with the pH value of 11–12. The molar ratio of total iron to hydroxylamine hydrochloride was controlled between 0.5 and 1.5. The solution was slowly heated to about 80 °C, stirred for 2–3 h, and then cooled down to room temperature. The black precipitate (Fe_3O_4) was obtained after washing and drying.

Surface coating of SiO_2. Tetraethyl orthosilicate (TEOS) was dissolved in alcoholic solvent with the volume ratio ranging from 0.005:1 to 0.05:1, named solution A. Solution B was obtained by dissolving sodium silicate into deionized water with the concentration of 1–10 g/L. The pH value was adjusted to 9–10 by hydrochloric acid. Alcoholic solvent was mixed with deionized water at a volume ratio of 2:1–5:1, named solution C. The prepared Fe_3O_4 in former step was put into 0.01–0.1 mol/L HCl with the dosage of 0.05–0.3 mg/L in ultrasonic processing under nitrogen gas protection for 5–20 min. The precipitate was washed and added to solution C with the dosage of 0.005–0.02 mg/L in ultrasonic processing under nitrogen gas protection for 10–30 min, followed by the addition of solution A (mole ratio of Fe_3O_4/Si: 2.5–3). After stirring with nitrogen gas protection for 1–2 h, 25–30% (mass percentage concentration) concentrated ammonia was added dropwise and the pH was controlled at 9–10. 5–6 h later, the precipitate was washed and added to solution B (mole ratio of Fe_3O_4/Si: 2.5–3) with pH controlled at 8–9. Surface coating of SiO_2 was completed after stirring for 1–3 h, washing and drying the precipitate (Fe_3O_4/SiO_2 composite).

Surface coating of TiO_2. 2.0–2.5 mL tetrabutyl titanate was dissolved in 100 mL isopropyl alcohol, named solution D. 80 mL isopropyl alcohol was mixed with 40 mL deionized water, named solution E. 1.0 g Fe_3O_4/SiO_2 composite was put into solution E for ultrasonic processing for 30 min, and then 3 mL concentrated ammonia was added under stirring. Solution D was added dropwise at room temperature under stirring for 5 h. The precipitate was $Fe_3O_4/SiO_2/TiO_2{\cdot}H_2O$ composite after washing and drying.

Coating of the sorbent. 1.0 g $Fe_3O_4/SiO_2/TiO_2{\cdot}H_2O$ composite was put into 50–100 mL mixture solution composing of $K_4[Fe(CN)_6]$ (0.5–1.0 mol/L) and HCl (1.0 mol/L) under stirring for 30 min every 3 h. After 20–24 h, the precipitate ($Fe_3O_4/SiO_2/K_{4-y}Ti_x[Fe(CN)_6]$ composite) was washed by deionized water, and then washed by absolute ethyl alcohol. After drying under vacuum at 60–80 °C for 10–12 h, the final product in blue-black was the M-PTH material.

2.3. Characterization of M-PTH material and analysis of water samples

The surface morphology of sorbents was investigated using a scanning electron microscope Jeol JSM-7001F. Coarse elemental analyses were carried out by energy-dispersive X-ray spectroscopy (EDX) spectra with Oxford microanalysis system connected to a scanning electron microscope Jeol JSM-7001F. Infrared spectra were obtained in the range 400–4000 cm^{-1} using a Spectrum GX FTIR system (PerkinElmer).

The concentration of Cs was analyzed by using Thermo ICP-MS XII based on the general rules for inductively coupled plasma-atomic emission spectrometry (JY/T 015-1996).