Chemical Engineering Journal 275 (2015) 262–270

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Removal of cesium from low-level radioactive wastewaters using magnetic potassium titanium hexacyanoferrate

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HIGHLIGHTS

- A synthesized sorbent can offer considerable selectivity to Cs.
- The sorbent make a good performance over a wide pH range.
- Cs sorption was test over a wide concentration range of co-existing ions.
- The kinetic performance follows the pseudo-second-order sorption model.
- Sequencing batch reactor is recommended as Cs sorption reactor.

ARTICLE INFO

Article history:
Received 8 February 2015
Received in revised form 9 April 2015
Accepted 10 April 2015
Available online 15 April 2015

Keywords:
Magnetic hexacyanoferrate
Cs
Low-level radioactive wastewater
Adsorption

ABSTRACT

The rapid development of nuclear energy in China has led to an increase in attention to the treatment of low-level radioactive wastewaters (LLRWs). One of the important contaminants is radioactive Cs. The removal of trace amounts of ^{134}Cs and ^{137}Cs can be achieved by means of a selective adsorption process. One of the possibilities is the application of potassium titanium hexacyanoferrate. In this paper, a novel magnetic potassium titanium hexacyanoferrate (M-PTH) material was prepared. The batch experiments demonstrate a selective adsorption of Cs over a wide pH range from 1 to 10. The co-existing nonradioactive ions can affect the adsorption of Cs. By increasing the Na^+ and K^+ concentration from 0.001 to 0.1 M, the distribution coefficient (K_d) of Cs drops slowly within the ranges of 7.28×10^4 to 1.10×10^4 mL/g and 1.25×10^5 to 1.49×10^4 mL/g, respectively. The adsorption isotherm coincides well with the Langmuir model. The thermodynamic study reveals an endothermic and spontaneous process. The kinetic performance follows the pseudo-second-order adsorption model, with intra-particle diffusion as the rate-controlling step. Based on the characteristics of M-PTH, a sequencing batch reactor (SBR) was considered to be suitable for the treatment of LLRWs containing radioactive Cs. Up to a total throughput of 70 batches, the decontamination factor (*DF*) can be kept at 1000. The volume ratio of treated solution and exhausted adsorbent was almost 7000.

1. Introduction

The rapid development of nuclear energy in China has led to an increase in attention to the treatment of low-level radioactive wastewaters (LLRWs). Removal of radioactive nuclides from LLRWs is necessary before discharge to the environment. Radioactive Cs is the major contaminant to be removed in many cases. For example, in the accident at Fukushima Daiichi Nuclear Power Station, a large amount of contaminated water leaked from the damaged reactors. Among the radioactive elements in the contaminated water, Cs was the major source of radiation emission [1,2].

Radioactive Cs is found in trace amounts in LLRWs, which also contain excessive amounts of other ions that are radiologically inactive; there is therefore a great need for selective separation methods. According to the regulations of the International Atomic Energy Agency, LLRWs are defined as solutions with a total radioactivity below 4.0×10^6 Bq/L. Therefore, radio-Cs occurs at concentrations far below one microgram per liter on the basis of the specific radioactivities of ^{134}Cs and ^{137}Cs. However, non-radioactive ions such as Na^+, K^+ and Ca^{2+} exist in LLRWs at excessive concentrations, far above one milligram per liter and in some cases even in amounts up to several moles per liter [3,4]. Therefore, the corresponding separation technology must be selective for trace

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http://dx.doi.org/10.1016/j.cej.2015.04.052
1385-8947/

amounts of radionuclides. Ion exchange resins can be used only for the purification of dilute solutions. In general, an inorganic adsorbent can offer selective separation of trace radioactive nuclides from high-salt solutions. In addition, the inorganic adsorbent material exhibits several superior properties such as high thermal and radiation stability [5]. Over the few past decades, various inorganic adsorbent materials have been investigated for Cs adsorption including natural materials like clay minerals, soils, sediments and rocks [6–8]; pure minerals like illite, kaolinite, montmorillonite, bentonite, magnesite, phlogopite, granite, sepiolite and goethite [9–11]; and titanate-based adsorbents like crystalline silicotitanate (CST), monosodium titanate, and peroxytitanate [12–14]. Ceric vanadate can offer an adsorption capacity of 17.3 mg/g for Cs [15]. The adsorption capacity of bentonite and montmorillonite can amount to 126.4 mg/g and 37.2 mg/g, respectively [11]. As an important inorganic adsorbent, zeolites such as natural clinoptilolite, natural chabazite, natural mordenite and synthetic mordenite have been widely applied in the removal of Cs from LLRWs [16–19]. The synthetic zeolite A can offer an adsorption capacity of 207.5 mg/g [17]. An experimental apparent capacities of natural clinoptilolite, natural chabazite, natural mordenite and synthetic mordenite amount to 168.9, 275.3, 256.7 and 222.1 mmol/g, respectively [18].

It is well known that hexacyanoferrate materials are effective adsorbents for Cs over a wide pH range. It is reported that the effective adsorption capacity of heterogeneous potassium cobalt hexacyanoferrate for Cs amounts to 46.6 mg/g [20]. Copper ferrocyanide functionalized mesoporous silica can offer an adsorption capacity of 21.7 mg/g for Cs at pH 1.1 [21]. Moreover, there are many other studies on Cs adsorption using hexacyanoferrates [22–25]. In order to optimize the adsorbents' performance, many efforts have been made to improve the materials' hydrodynamic characteristics. For example, potassium titanium hexacyanoferrate (PTH) can be easily coated on a porous support such as SiO_2. The as-prepared PTH/SiO_2 material has a large surface area and high particle strength [26]. The PTH/SiO_2 material can be further optimized by means of being loaded on a magnetite substrate [27]. In our previous work, magnetic potassium titanium hexacyanoferrate (M-PTH) was synthesized based on a wet dispersion and in situ precipitation process. The as-prepared M-PTH material, with a particle size ranging from 100 to 400 μm, can offer a high capacity and favorable kinetic performance. Due to its magnetic characteristics, the as-prepared M-PTH material can be easily separated from liquid despite its very fine particle size [5]. Since radioactive Cs is found in trace amounts in LLRWs, the corresponding separation technology must be selective. In this paper, the effects of co-existing non-radioactive ions on Cs adsorption using the as-prepared M-PTH material will be investigated by means of laboratory scale experiments.

2. Materials and methods

2.1. Chemicals and raw water

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 ($(CH_3)_2CHOH$) and potassium hexacyanoferrate ($K_4[Fe(CN)_6]$) were of analytical grade.

The inorganic adsorbent of M-PTH was synthesized in the laboratory. The zeolite materials used in the study (clinoptilolite and mordenite) were commercially available, with the uniform particle size of 0.1–0.2 mm.

In this paper, $CsNO_3$-bearing solutions of deionized water were used and the Cs concentrations were approximately 1.5–16.0 mg/L. For investigating the effects of co-existing inactive ions and pH on the uptake of Cs, the $CsNO_3$-bearing solutions were additionally spiked with $NaNO_3$, KNO_3, $Ca(NO_3)_2$, $Mg(NO_3)_2$, $Al(NO_3)_3$, $Fe(NO_3)_3$ or HCl.

2.2. Synthesis of M-PTH

The synthesis of M-PTH consists of four steps [5]:

2.2.1. Fe_3O_4 preparation

A 0.1–0.2 M Fe^{2+}/Fe^{3} mixed solution and hydroxylamine hydrochloride were simultaneously added dropwise to sodium hydroxide solution with stirring under an atmosphere of nitrogen at room temperature. The pH of the solution was kept at pH 11–12. The solution was slowly heated to approximately 80 °C, stirred for 2–3 h and then cooled down to room temperature.

2.2.2. Surface coating of SiO_2

TEOS was dissolved in an alcoholic solvent, (Solution A). Sodium silicate was dissolved in deionized water (Solution B). Alcoholic solvent was mixed with deionized water at volume ratio of 2:1–5:1 (Solution C). The prepared Fe_3O_4 was dispersed into HCl solution using ultrasonication under an atmosphere of nitrogen. The precipitate was washed and added to Solution C using ultrasonication under an atmosphere of nitrogen followed by the addition of Solution A. After stirring under an atmosphere of nitrogen, concentrated ammonia was added dropwise to the reaction mixture. The precipitate was washed and added to Solution B. Surface coating of SiO_2 was completed by washing and drying the precipitated Fe_3O_4/SiO_2 composite.

2.2.3. Surface coating of TiO_2

Tetrabutyl titanate was dissolved in isopropyl alcohol, (Solution D). Isopropyl alcohol was mixed with deionized water (Solution E). Fe_3O_4/SiO_2 composite was added to Solution E using ultrasonication and then concentrated ammonia was added with stirring. Solution D was added dropwise to the reaction mixture at room temperature with stirring. The precipitate was washed and dried to give the $Fe_3O_4/SiO_2/TiO_2{\cdot}H_2O$ composite.

2.2.4. Coating of the adsorbent

The $Fe_3O_4/SiO_2/TiO_2{\cdot}H_2O$ composite was added to a mixed solution composed of $K_4[Fe(CN)_6]$ and HCl with stirring. After 20–24 h, the precipitated $Fe_3O_4/SiO_2/K_{4-y}Ti_x[Fe(CN)_6]$ composite was washed with deionized water and absolute ethyl alcohol. After drying under vacuum, the M-PTH material was obtained.

2.3. Adsorption studies

The adsorption equilibrium of Cs was determined using a batch equilibrium technique. Samples of adsorbent (3–61 mg) were equilibrated with 40 mL of deionized water containing $CsNO_3$ at 298 K. The Cs concentrations are in the range of 4–16 mg/L. The pH values are kept at 6.5–7.5. After being shaken in a thermostatic shaker for 1 week, the supernatant was filtered using a 0.22 μm filter membrane to determine the equilibrium concentration of Cs. The adsorption kinetics experiments were conducted under static conditions in a thermostat fitted with a stirrer at 300 rpm. The adsorbent was covered with 1 L of $CsNO_3$ solution with an initial Cs concentration of 1.5 mg/L. The pH values are kept at 6.5–7.5. The samples taken equaled approximately 1% of the total volume of the original solution at certain time intervals.

The adsorption isotherms were modeled by the Langmuir relationship shown below:

$$\frac{C}{Q} = \frac{1}{Q_m}C + \frac{1}{Q_m K_L}, \qquad (1)$$