Journal of Industrial and Engineering Chemistry 67 (2018) 407–416

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Nanocomposite SiEA-KNiFe sorbent — Complete solution from synthesis through radiocesium sorption to vitrification using the sol–gel method

Dagmara Chmielewska[a,*], Małgorzata Siwek[b], Danuta Wawszczak[a], Marek Henczka[b], Bożena Sartowska[a], Wojciech Starosta[a], Jakub Dudek[a]

[a] Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland
[b] Faculty of Chemical and Process Engineering, Warsaw University of Technology, Warynskiego 1, 00-645 Warsaw, Poland

ARTICLE INFO

Article history:
Received 20 July 2017
Received in revised form 3 July 2018
Accepted 15 July 2018
Available online 9 August 2018

Keywords:
Cesium
Sorption
Batch
Column
Vitrification
Leaching

ABSTRACT

This study presents a novel complete solution starting with a synthesis of silica modified with potassium-nickel hexacyanoferrate and ethanolamine (SiEA-KNiFe) sorbent through radiocesium sorption in different process configurations and moving on to the vitrification of the spent sorbent, using the sol–gel method. The experimental data for deionized water solution, as well as seawater solution, correlates strongly with the Langmuir isotherm model. Moreover, the study also presents a method for spent sorbent solidification in the glass matrix. The cesium leaching test confirmed that spent sorbent can be stably bound in the glass matrix after radionuclide removal.

Introduction

The most significant source of radioactivity in liquid waste from the reprocessing of nuclear fuel is radiocesium. ^{137}Cs and ^{134}Cs are two radioactive cesium isotopes produced by nuclear fission of ^{235}U. They are washed out from fuel cladding flaws and penetrate the cooling water and the water in the spent fuel storage basins, or are emitted into the environment by accidental release, e.g. due to the Chernobyl nuclear accident [1] or the damage to the Fukushima Dai-ichi Nuclear Power Plant in Japan caused by the tsunami [2]. These radionuclides pose a potential threat to humans and the environment, because they exhibit high solubility and high mobility in the environment and have a long half-life: 30.1 years for ^{137}Cs and 2.1 years for ^{134}Cs. Due to its chemical similarity to potassium ions radiocesium tends to incorporate into terrestrial and aquatic organisms [3] and then bioaccumulate in human tissues. Bioaccumulation of radiocesium in the body can increase the risk of cancer because of the tissues' exposure to beta particles as well as high-energy gamma radiation. Therefore, removal of radiocesium from nuclear wastewater is still an absolutely crucial issue for human health and for environmental safety.

Different methods of radioactive product removal from water containing radioisotopes have been developed: e.g. flotation [4], membrane processes [5], biosorption [6], solvent extraction [7], ion exchange [8], and electrocoagulation [9].

A low or very low concentration of radionuclides in the liquid radioactive waste (LRW) limits the application of most of the above processes to radionuclides' separation. Therefore, the most common method used for LRW treatment is ion exchange, which is presented in this work.

The ion exchange process offers several advantages over the others. It requires simple and compact equipment and is very effective at converting low concentrations of the radioactive species, dispersed in a large volume of liquid, into a low-volume solid, which can easily be disposed of.

The need for the development of a new highly advanced sorbents is being reported. Different methods of synthesis are being developed. Novel, highly efficient resins have been synthesized and applied to different metals. The synthesis and characterization of novel chloromethylated polystyrene-g-2-adenine chelating resin to preconcentrate and detect mercury concentrations or cellulose functionalized by a thioglycolic acid regenerative microcolumn for selenium sorption have been

---

[*] Corresponding author.
E-mail address: d.chmielewska@ichtj.waw.pl (D. Chmielewska).

https://doi.org/10.1016/j.jiec.2018.07.015
1226-086X/

reported [10,11]. The selective removal of copper with polystyrene-1,3-diaminourea chelating resin can be obtained [12]. These studies have shown that the most appropriate methods for the study of such sorbents are batch and fixed-bed column sorption processes that provide information regarding selectivity, process thermodynamics and kinetics. Similar techniques have been applied in this paper.

One should remember that the major difficulty in low-level radioactive waste (LLRW) treatment is its very low radiocesium concentration in comparison to the level of competitive ions present in seawater. Thus, the sorbent must be highly selective for cesium. But, the presence of other radionuclides that are harmful to people and the environment, such as ^{90}Sr and ^{60}Co in LLRW [13], motivates the elaboration of new sorbents that are effective in multi-ion systems. Furthermore, different engineering methods can be applied to treat LLRW: columns or slurry. These methods require the application of a sorbent of the proper size distribution and morphology. Therefore, a very valuable property of the sorbent is the potential for the controlled modification of particle size and morphology to be applied in different process configurations.

Because the many important properties of the material (e.g. grain size and surface area, thermal stability, mechanical durability, and resistance to ionizing radiation) must meet requirements for LLRW processing, different matrices are used for ion exchanger synthesis. The cost of the bulk material applied is an additional factor. Therefore, silica, which is one of the most abundant materials in the Earth's crust, has become the focus of attention for many researchers [14,15]. Silanol (Si—OH) groups on the surface of silica do not show a high affinity to metal cations, due to their low acidity, but they can be easily modified with various functional groups to enhance sorption capacity [16]. Therefore, most of the developments with silica applications concern the usage of this material as a component of composites. It is mostly hexacyanoferrates that are used for silica fictionalization [17,18]. Nonetheless, composite materials containing hexacyanoferrates exhibit high selectivity for cesium and rarely provide a high affinity to other harmful radionuclides, such as ^{90}Sr and ^{60}Co. The additional modification of composite material with amino alcohol, such as ethanolamine, allows the extension of sorbent selectivity for radiostrontium and also radiocobalt. The —NH_2 amine group enhances the affinity of the ion exchanger toward radionuclides because of the free pair of electrons present on a nitrogen atom [19].

The high level of efficiency of removal of ^{60}Co from the distilled and seawater solution by silica modified with potassium-nickel hexacyanoferrate and ethanolamine (SiEA-KNiFe) sorbent, as well as the SiEA-KNiFe resistance to ionizing radiation, have already been reported [20].

Moreover, the latest accident at the Fukushima Dai-Ichi One nuclear power plant has demonstrated the lack of a sorbent as being effective for radioisotopes present in sea water in which inactive alkali ions are present in much higher concentrations.

The management of a sorbent with radiocesium bound in its matrix is highly challenging. Among the many methods of radioactive waste immobilization, vitrification is considered the best [21]. The main advantage of this method is the possibility of the incorporation of a large number of the elements into the matrix and the production of durable and small volume wastes which, in turn, prevents leaching of radionuclides to the environment [22]. Borosilicate glasses are the materials most widely applied used to form the vitreous matrix. However, some of the fission products, especially radiocesium, are volatile at temperatures much lower than that necessary for the glass to melt, which means that some of the radioactive cesium can escape from the matrix during the melting process [23]. The sol–gel methods that require low processing temperatures help to alleviate this drawback [23].

This study presents, a novel complete solution, which starts with the synthesis of silica modified with potassium-nickel hexacyanoferrate and ethanolamine (SiEA-KNiFe) sorbent through radiocesium sorption in different process configurations and continues with the vitrification of the spent sorbent, using the sol–gel method.

The application of transition metal hexacyanoferrates, which are very selective for radiocesium is described in many works [24]. However, due to very fine size of their particles and poor mechanical resistance, proper support materials are necessary before they can be employed as the sorbent [25]. Moreover, low permeability limits the use of transition metal hexacyanoferrates in the column process [26]. This work described the application of silica as the support, which is thermally and chemically stable and possesses Si—OH groups on the surface, that enables easy modification of the material to obtain highly selective for different radionuclides' sorbent. Moreover, the application of water glass as the source of silica constituting the support makes this solution very economical. Developed sorbent is based on a silica matrix that is a component of the glass used for vitrification and is compatible with the matrix, which is glass. Dry sorbent can easily be dosed to the melted base material or processed at a high temperature after the application of the sol–gel method, as demonstrated in this experiment. This is not the case when organic type ion exchangers are applied in separation process: these should be incinerated first, followed by the ashes [27,28].

In comparison to other solutions presented in the literature, the ssynthesis method of SiEA-KNiFe sorbent is simple and cheap; requires no length and complex processes; and does not involve advanced apparatus [29–31]. Additionally, the possibility of the controlled modification of particle size and morphology of the SIEA-KNIFe sorbent makes this material ideal for its application in different process configurations: slurry, column or hybrid membrane methods. Moreover, additional modification of the sorbent with ethanolamine allows the selectivity of the SiEA-KNiFe sorbent for ^{60}Co to be extended and ensures its effectiveness in multi-ion systems [20].

The adsorption capacities obtained for cesium sorption onto the SiEa-KNiFe sorbent have significantly higher values than those obtained for other sorbents based on hexacyanoferrates or aminoalcohols and, among the collations summarizing different studies [17,19,31–34]. Furthermore, the selectivity of the SiEA-KniFe sorbent remains very high ($Kd = 10^5$ ml/g), even in the presence of competitive ions, and this result is also significantly higher than the selectivity of other sorbents based on hexacyanoferrates [25,35,36].

In none of the publications have the authors cited the method of the spent sorbent utilization is proposed, while the management of a sorbent with radiocesium bound in its matrix is highly challenging. Moreover, only the elaboration of the method of radioactive waste immobilization, which ensures durable wastes and prevents the leaching of radionuclides into the environment, makes the technology complete and ready for upscaling.

Apart from its high selectivity for different radionuclides in the presence of competitive ions, the SiEA-KNiFe sorbent is characterized by thermal and chemical stability, and resistance to ionizing radiation and can be stably bound in the glass matrix after removal of radionuclide.

Materials and methods

Chemicals

All chemicals were purchased in analytical purity and were used without any further purification. Potassium haxacyanoferrate (II) trihydrate ($K_4Fe(CN)_6 \cdot 3H_2O$) and sulfuric acid (H_2SO_4) were