Research article

Effective removal of cesium from wastewater solutions using an innovative low-cost adsorbent developed from sewage sludge molten slag

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ABSTRACT

This study investigates the effective removal of cesium (Cs) from aqueous solution using sewage sludge molten (SSM) slag that has undergone the surface modification with alkali (NaOH) hydrothermal treatment. The raw and modified slags were characterised systematically using the BET method, the FESEM, the XRF, the XRD spectroscopy and the CEC analysis to understand the physicochemical changes of the materials, and its sensitivity to Cs ions adsorption. Batch adsorption experiments were carried out to investigate the effects of adsorbent dose, contact time, solution pH, different initial Cs concentrations, temperature and the effect of competitive ions on Cs adsorption. The adsorption isotherm, kinetic and thermodynamic studies were also evaluated based on the experimental results. A higher Cs removal efficiency of almost 100% (for 20–100 mg/L of initial concentration) was achieved by the modified SSM slag, and the maximum adsorption capacity was found to be 52.36 mg/g. Several types of synthetic zeolites such as zeolite X, zeolite Y, zeolite A, and sodalite were formed on surface of the modified slag through the modification process which might be enhanced the Cs adsorption capacity. Kinetic parameters were fitted by the pseudo-second order model. The adsorption isotherms data of modified slag were well-fitted to the Langmuir ($R^2 = 0.989$) and Freundlich isotherms ($R^2 = 0.988$). The thermodynamic studies indicated that the adsorption process by the modified slag was spontaneous and exothermic. In the competitive ions effect, the modified slag effectively captured the Cs ion in the presence of Na^+ and K^+, especially at their lower concentrations. Moreover, the modified slag was reused for several cycles after the successful elution process with an appropriate eluting agent ($0.5\,M\,H_2SO_4$), without deterioration of its original performance. Therefore, the SSM modified slag could be effectively used as a low-cost potential adsorbent for high Cs adsorption from wastewater.

1. Introduction

In order to attenuate the global warming effect on the environment, nuclear energy is one of the most sensible alternatives compared to the traditional limited fossil fuel based energy sources, including petroleum oil, coal and natural gasoline (Jing et al., 2016). Currently, it contributes to a considerable amount (approximately 11%) of environment friendly electricity regarding global warming to fulfil the total global demand (World Energy Needs and Nuclear Power - World Nuclear Association, 2016). However, radioactive wastes are basically generated from the nuclear power plant's operation and unforeseen accidents; hence, it is crucially important to dispose of them in a proper manner. The nuclear tragedy at Fukushima Daiichi nuclear power plant in Japan, due to the Great Earthquake on March 2011, released several types of radionuclides such as [134]Cs, ^{137}Cs, ^{131}I and ^{90}Sr into the nearby environment (Awual et al., 2014a, 2016). Among these, ^{137}Cs is considered one of the most dangerous nuclides due to its long half-life (30.17 years) as well as for its significant hazardous effect on human health. Cesium is chemically similar to sodium and potassium. Due to its high solubility and accumulation in food and water, it can be easily deposited into the human body and create thyroid cancer (Sangvanich et al., 2010). Therefore, environmental scientists are highly interested in finding a suitable technology for removing radioactive cesium from contaminated water.

A considerable effort has been employed over the years to introduce an efficient and sustainable approach for the decontamination of radionuclide cesium from wastewater. This includes solvent extraction, chemical precipitation, membrane process, electrochemical separation, ion exchange, and adsorption (Sun et al., 2012; Park et al., 2010; Danilin and Drozhzhin, 2007; Chen and Wang, 2008; Iwanade et al.,

2012). However, high amount of chemical cost, excessive installation expenditure, and operation cost are the cardinal shortcomings of these technologies for frontline applications (Ding et al., 2013).

Among the radioactive wastewater treatment technologies, the adsorption process is broadly exercised for its several advantages such as process simplicity, high removal efficiency, and availability of the low-cost adsorbents (Park et al., 2010; Ding et al., 2013; Dubourg, 1996). Moreover, adsorption and ion exchange process can be applied for the removal of radioactive cesium from low contaminated wastewater, flexible for using batch and continuous process, and a possibility for regeneration and recycling (Lee et al., 2016; Kim et al., 2014).

Over the last few years, many adsorbents have been successfully studied for radioactive cesium adsorption from wastewater such as chitosan, bamboo charcoal, potassium copper ferrocyanide composite, biomass (Lavina Lipa and Voda, 2017; Khandaker et al., 2017; Zong et al., 2017; Ofomaja et al., 2015a), etc. In comparison, with the above materials, the inorganic adsorbents (zeolites, clay and minerals, etc.) have some superior qualities in terms of chemical and mechanical strength and large ion exchange ability, which are important for wastewater treatments in the adsorption process (Kim et al., 2014). Therefore, adsorbents generated from waste materials (clay minerals, coal fly ash and blast furnace slag) have attracted more attention due to their low cost, availability and opportunity for secondary applications (Mohan and Gandhimathi, 2009; Liu et al., 2016; Tsutsumi et al., 2014; Nakamura et al., 2002).

In Japan, a large amount of sewage sludge is produced (approximately 2 million tons) each year, and these are mostly incinerated for volume reduction before using in different civil engineering purposes, including backfilling, artificial lightweight aggregates (Lin and Weng, 2001; Pan et al., 2003), etc. The incinerated sewage sludge ash contains hazardous substances, including dioxins and heavy metals. Therefore, this material would be a secondary pollutant, which can pose a threat to the environment. To overcome this problem, dewatered sewage sludge is pyrolysed at an elevated temperature ($> 1300\,°C$) in a controlled environment and the products obtained through this process is known as sewage sludge molten (SSM) slag. Considering that a large amount of energy is required to produce the aforementioned slag, disposing it through backfilling or making artificial aggregates does not constitute a viable option. Therefore, it is crucially important to explore possible economically attractive and innovative applications of SSM slag.

The SSM slag contains significant amounts of alumina, silica and many other oxides (Kikuch, 1998; Lee et al., 2017), which are a cheap source for the synthesis of aluminosilicate minerals (zeolites). The basic frame of zeolites consists of SiO_4^- and AlO_4^- tetrahedral units, which are connected with each other through oxygen atoms. The negative charge of AlO_4^- is balanced by cations such as Na^+, K^+, Ca^{2+} or Mg^{2+} that are typically present in the zeolite structure. These cations are generally exchanged with other cations through a cation exchange mechanism and have been successfully used as adsorbents for the removal of metal ions from wastewater (Avramenko et al., 2011). Therefore, there is a possibility of synthesis of zeolite minerals from the SSM slag to be used as adsorbents. Additionally, the associated low-cost cesium removal is an alternative characteristic of such applications. However, to the best of our knowledge, this material has not been used before for this kind of application.

The aim of this research is to produce synthetic zeolites from SSM slag and explore the cesium removal capacity as a new adsorbent. In this study, adsorbents were characterised by using a N_2 adsorption-desorption isotherm, a Field Emission Scanning Electronic Microscope (FESEM), an X-ray Fluorescence (XRF), an X-ray Diffraction (XRD) spectroscopy and the cation exchange capacity (CEC). Moreover, batch adsorption experiments were carried out to meticulously evaluate the adsorption behaviour at different experimental conditions such as adsorbent dose, contact time, solution pH, initial cesium concentrations, competing ions of Na^+ and K^+ and the temperature. Furthermore, adsorption kinetics, equilibriums, and thermodynamic studies were also

performed to understand the adsorption mechanism. Finally, regeneration and reusability studies were also carried out.

2. Materials and methods

2.1. Chemicals and reagents

Non-radioactive cesium chloride (CsCl, FW: 168.36 g) was obtained from Wako Pure Chemical Industries Ltd, Japan as a replacement for radioactive ^{137}Cs for safety purposes. Moreover, the chemicals, sodium chloride (NaCl), potassium chloride (KCl), sodium hydroxide (NaOH) and hydrochloric acid (HCl), used in this study were of analytical reagent grade and purchased from the same supplier.

2.2. Adsorbent

The SSM slag was collected from an undisclosed sludge melting facility located in the western part of Japan. The sewage treatment plant is comprised of a secondary activated sludge process, and the sludge is dewatered by a gravity thickener and a belt filter press. The dewatered sludge is generally pyrolysed at $1300\,°C$ and then, air-cooled. The gravel size of the slag was about 2–3 mm, which was crushed by a ball mills machine (Mixer Mill MM 400, RETSCH, Japan). The powdered form of the slag was sieved at $75\,\mu m$. This slag was identified as raw slag.

2.3. Modification of raw slag

15 g of raw slag was treated with 120 ml of 1.0 N NaOH (solid, liquid ratio = 1:8) at $120\,°C$ in a hot plate for 24 h. Then, the treated slag was washed several times with deionized water (Elix Millipore, Japan) using a vacuum filter until the pH obtained was 7.0–8.0. After that, the treated slag was oven dried at $50\,°C$ for 18 h and preserved in a desiccator. The obtained slag was identified as modified slag in this study.

2.4. Characterisation and analysis

The nitrogen adsorption-desorption isotherms were performed at $-196\,°C$ (77 K) by using the BELSORP-mini II, Japan. The Brunauer–Emmett–Teller (BET) theory was used to calculate the specific surface area (Brunauer et al., 1938) and the total pore volume. The samples were degassed at $200\,°C$ (473 K) for 6 h prior to this analysis. The morphological structure was examined by FESEM (UHR FE-SEM, Model: SU8000, HITACHI, Japan). The chemical compositions of the samples were analysed by using a XRF (EDX-7000/8000 Energy Dispersive X-ray Fluorescence Spectrometer, SHIMADZU, Japan). The XRD data of the samples were recorded from 5° and 60° using a Rigaku X-ray diffraction-meter (Rigaku, Japan) with Cu Kα radiation. The mineralogical phases were identified by using the PDXL software, and various crystalline phases were detected with the help of the JCPDS (Joint Committee on Powder Diffraction Standards) file for inorganic compounds. The cation exchange capacity (CEC) of the samples was investigated following the procedure of Hesse (1972). Briefly, 1.0 g of the samples (raw and modified slag) was shaken individually with 30 ml of 1.0 mol/L sodium acetate (CH_3COONa) for 5 min. After separating the solids by centrifugation, the procedure was repeated twice on each sample. Then, the solids were shaken three times with 30 ml of 95% ethanol (C_2H_5OH). After that, the solid samples were shaken three times with 30 ml of 1.0 mol/L ammonium acetate (CH_3COONH_4) to replace the Na^+ with NH_4^+. The three sodium extracts were collected and diluted to 100 ml. The Na^+ content of this solution was analysed by using AAS.

2.5. Cs removal studies

A 1000 mg/L stock solution of CsCl was prepared by dissolving