Thesis for the the Degree of Master of Science

Cesium Sorption Characteristics of Polysulfone Carrier with HNO_3 treated Bamboo Charcoal

by

Ni Wayan Sukma Taraning Rahayu

Department of Earth & Environmental Sciences

The Graduate School

Pukyong National University

August 2020

Cesium Sorption Characteristics of Polysulfone Carrier with HNO_3 treated Bamboo Charcoal

(질산처리된 대나무활성탄으로 조제한 폴리술폰 (polysulfone) 담체의 세슘 흡착 특성)

Advisor: Prof. Minhee Lee

by

Ni Wayan Sukma Taraning Rahayu

A thesis submitted in partial fulfillment of requirements
for the degree of
Master of Science

Department of Earth & Environmental Sciences
The Graduate School
Pukyong National University

August 2020

Cesium Sorption Characteristics of Polysulfone Carrier with HNO_3 treated Bamboo Charcoal

A Thesis

by

Ni Wayan Sukma Taraning Rahayu

Approved by:

(Chairman) Minjune Yang

(Member) Jongsik Ryu

(Member) Minhee Lee

August 28th, 2020

CONTENTS

LIST OF FIGURES

LIST OF TABLES

Study on Cesium Sorption Characteristics of Polysulfone Carrier with HNO_3 treated Bamboo Charcoal

Ni Wayan Sukma Taraning Rahayu

Department of Earth & Environmental Sciences
The Graduate School
Pukyong National University

Abstract

The cesium (Cs) sorption characteristics of a bead-type polysulfone carrier contained HNO_3 treated bamboo charcoal (BC) in water system were investigated and its Cs removal efficiency from water was also identified by various laboratory experiments and sorption model studies. Results from batch sorption experiments showed that the Cs sorption rate of the polysulfone carrier with only 5% HNO_3 treated BC was very fast and the reaction equilibrium reached within 1 hour having the Cs removal efficiency of 57.80%. The Cs removal efficiency of the polysulfone carrier in water after 24 hours reaction maintained > 69% at a wide range of pH and temperature conditions, suggesting its applicability under various water system. Batch sorption experiments were repeated for polysulfone carrier coated with two types of microorganisms (*Pseudomonas fluorescens* and *Bacillus drentensis*), which were well known for the high heavy metal removal efficiency in water. The

Cs removal efficiency for microorganism coated polysulfone carrier was increased by 19% and 18%, respectively, compared to that only polysulfone carrier without microorganisms coated. The Cs desorption rate of polysulfone carrier for 24 h was lower than 16%, showing the Cs was stably attached on HNO_3 treated BC in so much as its long-term use. The maximum Cs sorption capacity (q_m) of the polysulfone carrier calculated from the Langmuir isotherm model study was 60.9 mg/g, which was much higher than those of other adsorbents from previous studies for 1 hour sorption time. The sorption kinetic model study represented that the polysulfone carrier was well fitted to the pseudo-second-order model. Results of the Cs sorption isotherm and kinetic model study suggested that the relatively rapid sorption including precipitation on the HNO_3 treated BC surfaces in a polysulfone carrier would be one of the prevailing processes to remove Cs from water system. Results of continuous column experiments showed that the column packed with polysulfone carrier coated with microorganisms maintained more than 80% of the Cs removal efficiency during 100 pore volumes flushing suggesting that only 14.7 g of polysulfone carrier (only 0.75 g of HNO_3 treated BC included) can successfully clean-up 7.2 L of Cs contaminated water (the initial Cs concentration: 1.0 mg/l; the effluent concentration: < 0.2 mg/L). The present results demonstrated that the polysulfone carrier with HNO_3 treated BC has a remarkable potential to remove Cs from various water system.

CHAPTER I. INTRODUCTION

Radioactive waste is one kind of extremely hazardous waste because it consists of highly toxic radioactive materials. It is originated from the by-products of nuclear power generation and other utilization of nuclear technology such as radiation treatment. According to the report of the World Nuclear Association (WNA), South Korea has a 23,172 MWe of total operable nuclear reactor net capacity which is the 7th highest in the world (WNA, 2017) (Fig. 1). These various activities in nuclear power plants and in the nuclear industry have the potential for bringing serious problems of radioactive contamination into surrounding environments such as soil, groundwater, surface water, and seawater (Lee et al., 2016; Kurihara et al., 2018; Manabe et al., 2020).

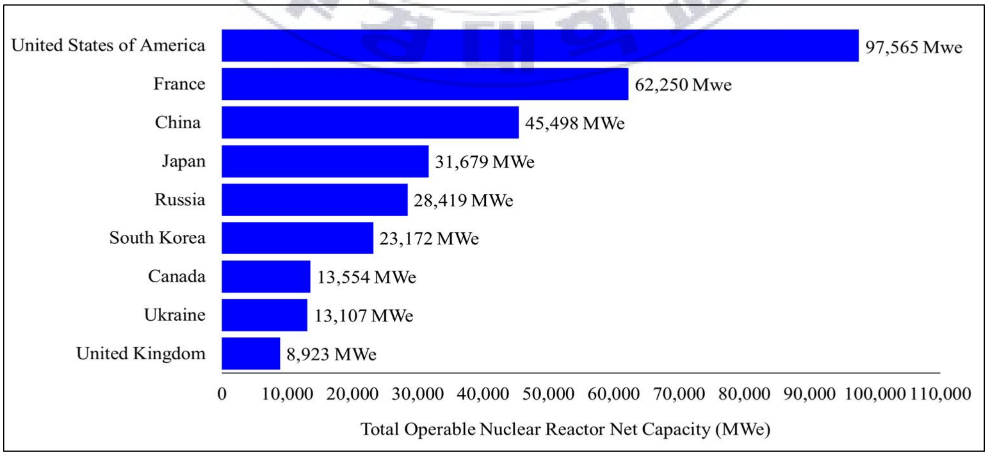


Fig. 1. Total operable nuclear reactor net capacity in the top 10 ranks (modified from WNA, 2017).

The radioactive cesium (Cs) has been known as one of the most dangerous radioactive for human health and ecosystem because it has high specific radioactivity and long half-life. The removal of radioactive Cs from wastewater is very difficult because it likes to exist as a soluble form when it is exposed to the environments (Gad and Pham, 2014; Awual et al., 2014). The Environmental Protection Agency (EPA) categorized the stable ^{133}Cs, ^{134}Cs, and ^{137}Cs as target compounds needed for cleanup activities (ATSDR, 2004). There has been increased public interest in the removal of radioactive Cs from water environments contaminated by nuclear waste. Efficient and sustainable technologies for the decontamination of radionuclide Cs from contaminated water have been developed and they include chemical precipitation, membrane process, solvent extraction, ion exchange, electrochemical separation, and adsorption (Iwanade et al., 2012; Deng et al., 2016; Alamudy and Cho, 2018; Ding et al., 2019; Tao et al., 2019; Wang and Zhuang, 2020). Among these treatment methods, the adsorption has been considered as one of the most effective removal processes due to the simplicity of the process, the high Cs removal efficiency, and the relatively low-cost (Ding et al., 2013; Zhang et al., 2018).

The adsorption in water system proceeds by (1) migrating the concentration of adsorbate to the surface of adsorbent; (2) diffusing on the external surfaces characterized by the available external surface on the adsorbent; (3) diffusing on the internal pores of the adsorbent (Fig. 2). So far, a variety of adsorbents such as clays, zeolites, metal oxides, chitosan, and activated carbon, have been studied for the Cs removal from contaminated water (Dechojarassri, et al., 2017; Wang, et al., 2018; Park, et al., 2019; Falyouna, et al., 2020). However, these adsorbents are either expensive or inefficient for practical application, showing low Cs removal efficiency at low Cs concentration conditions. Therefore, the development of more efficient and inexpensive adsorbents is necessary for the removal of Cs from water at the wide range of Cs concentration.

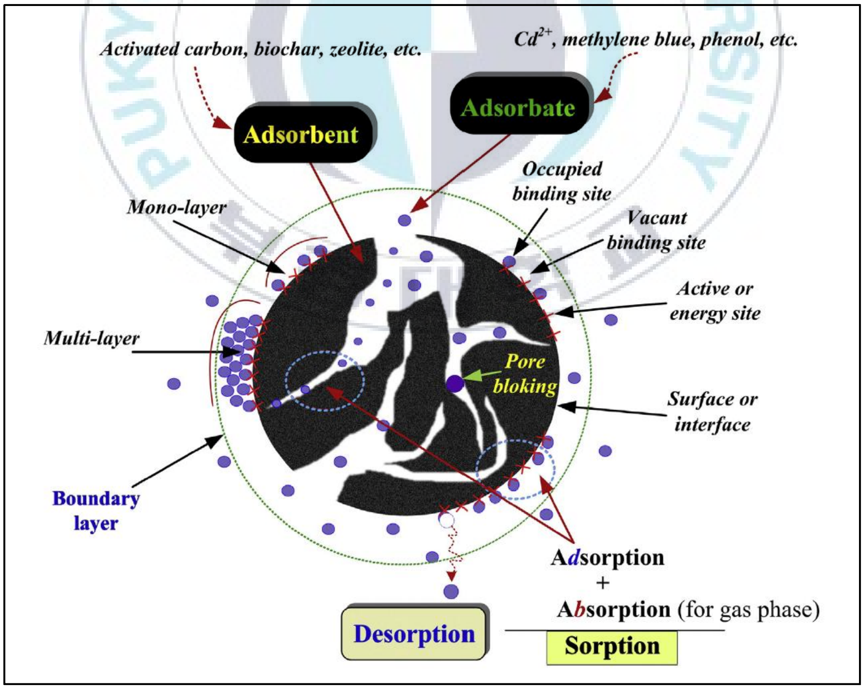


Fig. 2. Feasible sites of the adsorbent during the adsorption process (modified from Tran et al., 2017).

Bamboo charcoal (hereafter 'BC') is known as the promising adsorbent because of its many microporous structures, large surface area, high mechanical strength, and chemical stability such as acid alkali resistance and heat resistance (Lin et al., 2003). In the last few decades, BC has drawn interest to the researchers as a novel adsorbent due to its special microporous structure (Hameed et al., 2007; Wang et al., 2008). Fu et al. (2010) confirmed that 1 g of BC has almost 400m^2 surface area, thus indicating a high adsorption capacity. The BC has been applied in a variety of adsorption fields such as pharmaceutical, chemical, and metallurgical industries. According to previous studies, the adsorption using BC was considered to have a great potential for the Cs removal from water (Ahn and Lee, 2018; Khandaker et al., 2017). The surface porous structure of BC can also be improved by the chemical activation by using H_3PO_4, H_2SO_4, and HNO_3 which has significant effects on Cs adsorption performance (Khandaker et al., 2017). Previous studies for the activated BC to use an adsorbent are listed in Table 1.

Because most of the batch experiments from previous researches were performed by using the powdered form to gain the high Cs sorption capacity, it is also necessary to investigate the Cs removal efficiency for reasonable forms (sizes) of BC instead powdered form in order to easily apply in real field. There exist other application problems such as the difficulty of separation of powdered BC from water after the treatment and the low mechanical strength.

Table 1. Applications of BC as an adsorbent.

Modification	Applications	Reference
Modification with H_2SO_4	Adsorption of ammonia gas	Asada et al., 2006
Activation with carbon dioxide and steam	Adsorption of chromium nickel, and cadmium	Wang et al., 2008
Modification with H_2SO_4 and NaOH	Adsorption of chloramphenicol	Fan et al., 2010
Activation with H_3PO_4 and KOH	Adsorption of lead (II)	Lalhruaitluanga et al., 2010
BC without treatment	Adsortion of ^{131}I (radioactive)	Chien et al., 2011
Activation with $KMnO_4$ and followed by HNO_3	Adsorption of lead (II)	Wang et al., 2012
Modification with NaOH	Adsortion of arsenic	Liu et al., 2012
BC without treatment	Removal of lead, copper chromium and cadmium	Lo et al., 2012
BC without treatment	Removal of carbon dioxide	Huang et al., 2014
Activation with $ZnCl_2$ and $FeCl_3$	Removal of mercury	Tan et al., 2015
BC without treatment	Removal of cesium	Ahn and Lee, 2018
BC without treatment	Removal of uranium	Lee et al., 2018

To overcome these limitations, the effective immobilization of BC powder in the polymeric matrix can be devised and this BC carrier as an adsorbent could confer high resistance to physicochemical reactions and also provide additional advantages such as easy separation from water after the treatment and efficient regeneration. The selection of an optimal polymeric matrix for BC carrier as an adsorbent is very important for the application of immobilized BC to various water systems because the polymeric matrix directly affects the mechanical strength, rigidity and pore properties of adsorbent. Various polymeric materials such as alginate, polyacrylamide, polysulfone, and polyvinyl alcohol have been used as immobilized matrixes for heavy metal sorption processes in water (Mbareck et al., 2009; Wang et al., 2018; Godiya et al., 2019). As a thermoplastic polymer matrix, polysulfone is widely used in many applications due to its low cost, outstanding manufacturing properties, resistance over a wide range of pH, high mechanical strength, and thermal stability. The mechanical strength and good impact stability of the material is crucial for handling the adsorbent (Ding and Bikson, 2010; DeMeuse, 2014; Shokri et al., 2016; Furuya et al., 2017). Based on Bai et al (2003), the degree of mechanical strength and chemical resistance of the immobilized matrix was in the order of polysulfone > polyisoprene > polyvinyl alcohol > polyacrylamide > calcium alginate. This revealed that the polysulfone carrier is mechanically steady and chemically resistant than using all other matrices. The use of polysulfone as a polymeric matrix to immobilize BC in an adsorbent carrier for Cs removal in water system has never been attempted before even in the laboratory. In this study, the bead-type polysulfone carrier with HNO_3 treated BC was applied to the Cs removal from water in batch and continuous column experiments.

Microorganisms play significant roles in the removal of Cs owing to their good performance, low cost, and large available quantities. They can take up radioactive metals via dependent metabolism (internalization of Cs through cell wall) or independent metabolic pathways (adsorption of Cs on the surface wall) pathways (Katsenovich et al., 2013; Kang et al., 2017). In order to optimize the conditions for Cs removal efficiency of the polysulfone carrier, two kinds of microorganisms (*Pseudomonas fluorescens* and *Bacillus drentensis*) were coated on the polysulfone carrier surface and the change of Cs removal efficiency for microorganisms coated carrier was also investigated. This study would be helpful to understand the Cs adsorption mechanisms of polysulfone carrier with HNO_3 treated BC and to evaluate the possibility for the application of the polysulfone carrier to actual Cs treatment sites.

CHAPTER II. OBJECTIVES

The overall objective of this study is to develop a new effective adsorbent consisting of the bead-type polysulfone carrier, immobilizing HNO_3 treated BC and maintaining the high Cs removal efficiency. It is a novel feasibility study because this new adsorbent can have the practical benefit of lowering its manufacturing cost due to the use of a small amount of HNO_3 treated BC (only 5 wt%) and dealing with various water system due to easy production of various carrier types (in different size or shape). Several laboratory works were performed to meet the objective and they were listed below.

1. The bead-type polysulfone carrier (3 – 4 mm in diameter) with HNO_3 treated BC was manufactured and it feasibility as an available adsorbent to remove Cs from water was evaluated by several laboratory-scale experiments. Reliable evidences for the adsorption mechanisms of Cs was also provided by SEM (Scanning Electron Microscope) and EDS (Energy Dispersive X-Ray Spectrometer) analysis.

2. Batch adsorption and desorption experiment were performed at various sorption conditions (contact time, BC amount in the carrier, adsorbent

dosage, pH, and temperature) to determine the optimal Cs adsorption condition and to maintain the high Cs removal efficiency. The adsorption characteristics and mechanisms of the polysulfone carrier with 5% HNO_3 treated BC were also identified by the adsorption kinetic and isotherm model studies.

3. The continuous column experiments were also conducted by considering the kinetic effect of the Cs adsorption from water. Three different adsorbents such as original BC granules without HNO_3 treatment, polysulfone carrier having 5% of HNO_3 treated BC, and polysulfone carrier coated with microorganisms were used in column experiments. The total treated water volume and the mass of Cs removed per unit polysulfone carrier mass were calculated in continuous column experiments.

4. The effect of microorganisms (*Pseudomonas fluorescens* and *Bacillus drentensis*) coated on the polysulfone carrier surface on the Cs removal efficiency was also verified through batch and continuous column experiments.

CHAPTER III. MATERIAL AND METHODS

3.1 Design of experiments

This study was composed of systematic experiments investigating (1) the Cs sorption/desorption of polysulfone carrier with HNO_3 treated BC, (2) the Cs sorption of polysulfone carrier coated with microorganisms, and (3) the kinetic of Cs sorption, which was summarized in the schematic flowchart in Fig. 3.

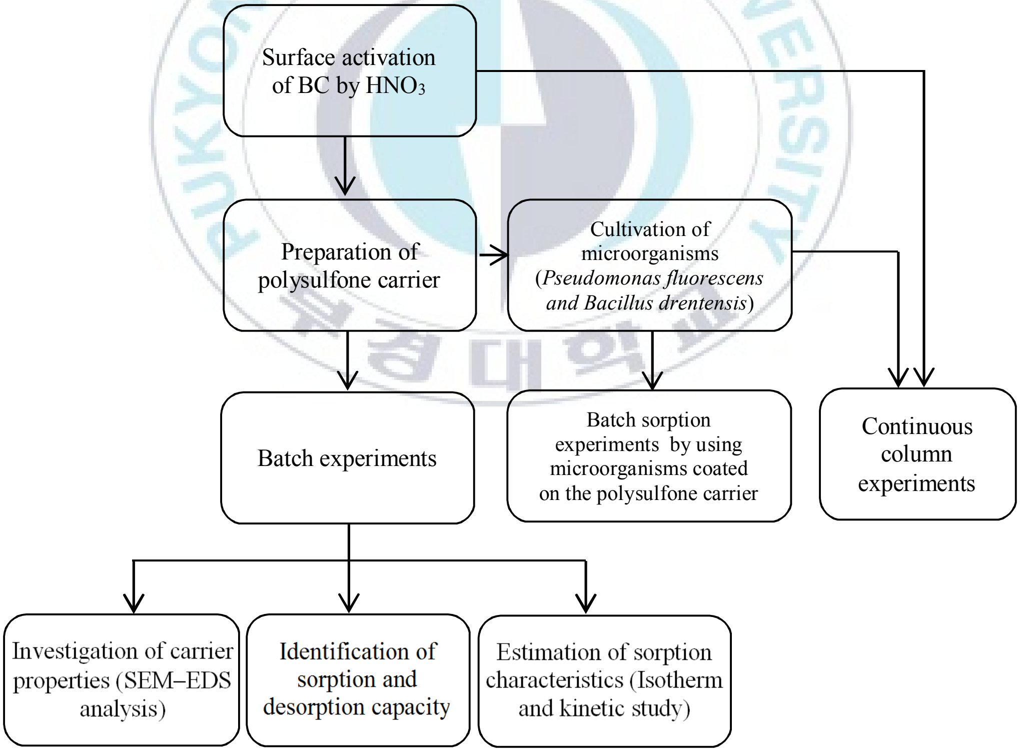


Fig. 3. Flowchart for the overall processes of the study.

3.2 Materials and chemical reagents

The Cs^{133} standard solution (1000 mg/L ± 2 mg/L in 2% w/w HNO_3), hydrochloric acid (HCl, 37.0%), *N,N*-dimethyl formamide (DMF, 99.8%), and polysulfone (Mw = 35,000 g/mol) were purchased from Sigma Aldrich Ltd.. Sodium hydroxide (NaOH, 97.0%), and nitric acid (HNO_3, 69-70%) was purchased from Daejung company and J.T.Baker, respectively. BC used in this study was purchase from GEX (Aqua Plus). The BC blocks were crushed and sieved with a 100-mesh sieve (particle diameter: < 150μm), which were stored for further experimental use.

3.3 Surface activation of BC by HNO_3

Main mechanisms of HNO_3 treatment was to activate surface oxygen as well as an acidic functional group on the surface of the adsorbent and to increase the sorption performance by the increase of pore opening. It was verified that the surface activation of BC with HNO_3 increases its Cs sorption capacity by Khandaker et al., (2017). The main reason for the Cs sorption capacity increase was the widening of the pores after the activation treatment, and there existed some enhancement in the meso/macropore region and reduction in the microporous range. This surface activation was mainly due to the transition of microporous into mesoporous on BC after a highly corrosive nitric acid activation process. For the surface activation of BC with HNO_3, 10 grams of powdered BC was mixed with 100 mL of HNO_3 solution (69-70%) and they were heated in a hot plate at 120 ℃ for 6 hours. The HNO_3 treated BC was washed several times with distilled water until the pH washed solution was stable (>pH 3) and was dried in an oven at 100 ℃ for 24 hours (Fig. 4).

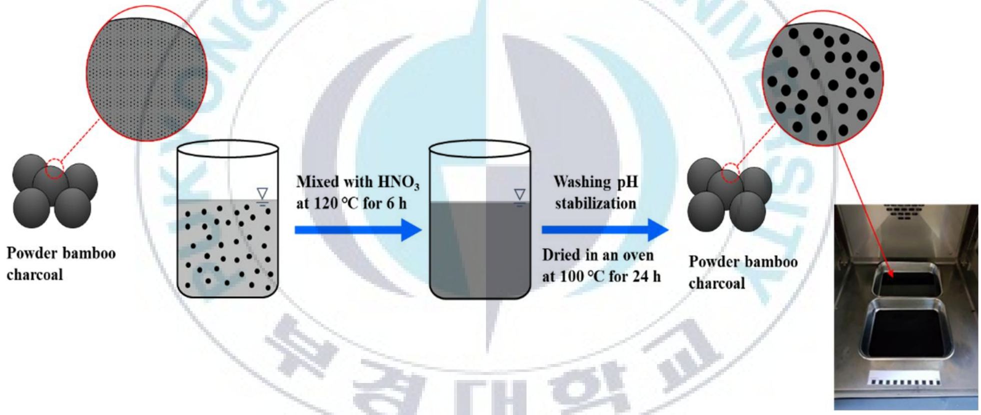


Fig. 4. Schematic process of HNO_3 treatment for BC increasing Cs sorption capacity.

3.4 Preparation of polysulfone carrier with HNO_3 treated BC

The selection of the immobilization matrix for BC is a key factor in the application of immobilized BC for the real field because the polymeric matrix determines the mechanical strength and chemical resistance of an adsorbent. Among the polymeric matrix, polysulfone has the advantages of low cost, high mechanical strength, and resistance over a wide range of pH (Shokri et al., 2016; Furuya et al., 2017). Several previous studies have revealed the potential application of polysulfone as the polymeric carrier to improve the separating performance, surface properties, the porosity as well as the easy processability (Melvin et al., 2017; Cojocaru et al., 2017; Benkhaya et al., 2020). The process of producing the polysulfone carrier with HNO_3 treated BC was as follows; ten grams of polysulfone was shaken in 90 mL of DMF (N, N-dimethyl formamide) solvent solution at 125 rpm for 16 hours at room temperature to prepare a polysulfone solution. Polysulfone solution was mixed with HNO_3 treated BC 0%, 1% (1g), 2% (2g), 5% (5g), and 10% (10g) and the mixed slurry was dropped with a constant speed into 80% of methyl alcohol solution through a syringe with a needle size of 18G to produce the uniform bead type carrier (3 – 4 mm in diameter) (Fig. 5). The polysulfone carrier were washed with distilled water for 1 hour on a rotary shaker and then dried at room temperature (22 ± 1 ℃), which was used for further batch and column experiments (Fig. 6).

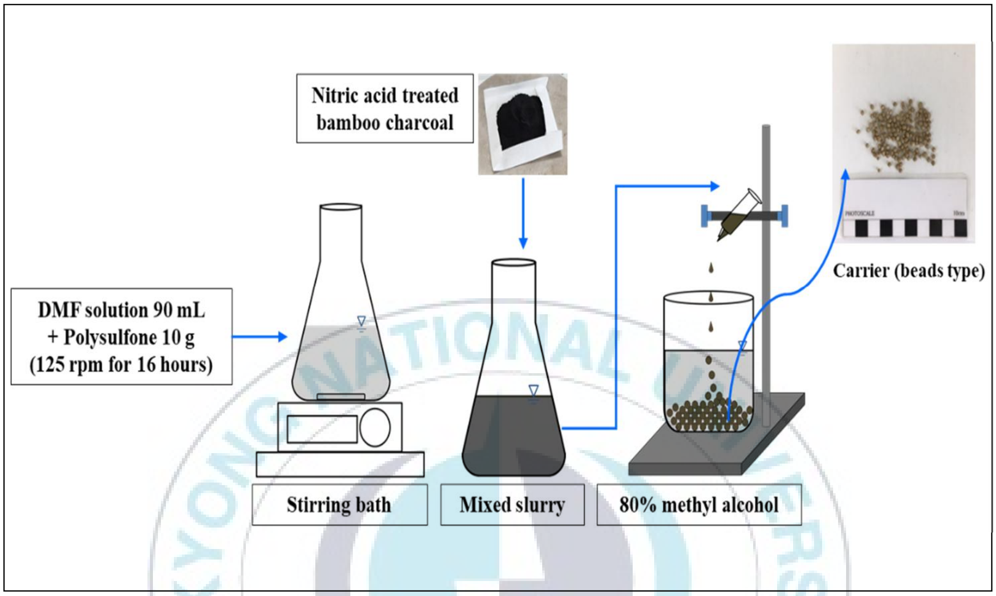


Fig. 5. Schematic to produce the polysulfone carrier with HNO_3 treated BC.

Fig. 6. Polysulfone carriers with 0, 0.5, 1, 2, 5, and 10% HNO_3 treated BC (from the far right).

3.5 Batch sorption experiments

Batch experiments were performed to investigate the Cs sorption capacity of the polysulfone carrier with HNO_3 treated BC (adsorbent) under different experimental conditions. A stock solution (1000 mg/L) of Cs^{133} was prepared prior to the experiments. The different Cs concentrated solution, which was prepared by the appropriate dilution from the stock solution, was used for batch experiments. For the sorption experiment, 0.6 g of adsorbent was added to 30 mL of Cs solution (2 wt% of adsorbent in solution) at various temperatures and reaction time conditions at 125 rpm. All batch experiments were conducted by using the polysulfone carrier having 5% HNO_3 treated BC except for a test identifying the effect of BC amount in polysulfone carrier. Each experiment was triplicated and the average value was used as the final value for the result. After the sorption reaction, the adsorbent was separated from the solution by a 0.8 μm syringe filter (16592-K, Sartorius) and stored into 15 mL polypropylene tubes prior to analyzing the Cs concentration in solution. The Cs concentration of the collected sample was analyzed using an Inductively Coupled Plasma/Optical Emission Spectrometer (ICP/OES; Optima 7000DV, Perkin Elmer) to calculate the Cs removal efficiency.

The effect of the sorption time on the Cs removal was also observed in batch experiments with different sorption time intervals (10, 30, 60, 120, and 240 minutes). A 0.6 g of polysulfone carrier was added to 30 mL of Cs solution (initial Cs concentration: 1 mg/L). The Cs concentration of the supernatant was analyzed and the Cs removal efficiency of the adsorbent (polysulfone carrier) was calculated using the following equation:

$$Removal\ efficiency\ (\%) = \frac{(C_0 - C_t)}{C_0} \text{ x } 100 \tag{1}$$

Where C_0 is initial concentration (mg/L), C_t is final concentration (mg/L). From the results of Cs concentration in solution, the equilibrium sorption time was determined. The equilibrium sorption time was applied for the following batch experiments.

To investigate the effect of BC amount in the carrier on the Cs sorption, the sorption batch experiments were performed with polysulfone carrier having different BC amounts of 0, 0.5, 1, 2, 5, and 10%. The 0.6 g of polysulfone carrier was mixed with 30 mL of the Cs solution and the mixture was stirred at 125 rpm at room temperature (22 ± 1 ℃) for 1 h. In order to find out the optimum adsorbent amount in solution, the batch experiment was duplicated with different adsorbent dosages of 0.03, 0.15, 0.3, 0.6, and 0.9 g in 30 mL of solution (0.1, 0.5, 1, 2, and 3%). Other conditions in experiment were the same as those of earlier experiments.

The pH and temperature of the solution may also affect the Cs sorption capacity and the sorption batch experiment with different pH and temperature condition was repeated, investigating their effects on the Cs removal efficiency. The initial pH of the solution was titrated from 3 to 11 by using 1 M of HCl or NaOH solution and the final pH of the solution after the experiment was measured by a pH meter (ORION Star-A211, Thermo scientific). The initial Cs concentration of the solution was 1 mg/L and other experimental conditions were the same as those of earlier experiments. Sorption batch experiments were duplicated at different temperature conditions (5, 10, 15, 20, and 30 ℃) to investigate the effect of temperature on the Cs removal efficiency.

3.6 Desorption experiments

Since the Cs is a radioactive isotope, it is crucial to observe the release Cs back to the water system after the treatment. Domestic and International radioactive waste management laws are active to prevent negative effects caused by the release of Cs from the adsorbent. Therefore, it is important to evaluate the Cs desorption capacity or rate of adsorbent used for water treatment. In this study, the desorption batch experiment was performed to quantify how much of sorbed Cs on polysulfone carrier was released after the sorption experiment. The polysulfone carrier having sorbed Cs was dried at 50 ℃ in an oven for 24 h and 0.6 g of dried polysulfone carrier was mixed with 30 mL of distilled water. The mixture was stirred at 125 rpm to lead the Cs desorption from polysulfone carrier and the supernatant was sampled by using a filtered syringe at different desorption time intervals (1, 3, 6, 12, and 24 h). The Cs amount from the carrier after the desorption experiment was determined from the Cs concentration in solution which was analyzed by ICP/OES. The desorption rate for the polysulfone carrier was calculated using the following equation:

$$Desorption\ rate\ (\%) = \frac{Amount\ of\ Cs\ desorbed\ (mg/L)}{Amount\ of\ Cs\ adsorbed\ (mg/L)} \times 100 \qquad (2)$$

3.7 Effect of microorganisms coated on the polysulfone carrier on the Cs sorption capacity

The purpose of this experiment is to investigate the effect of polysulfone carrier coated by microorganisms on the removal of Cs. Two microorganisms which were reported as good adsorbents for heavy metals were purchased from the Korean Culture Center of Microorganisms (Mao et al., 2011; Kim et al., 2017). For the experiment, *Pseudomonas fluorescens* was cultivated in nutrient agar (3.0 g beef extract, 5.0 g peptone, and 15.0 g agar), and *Bacillus drentensis* was cultivated in trypticase soy agar (17.0 g pancreatic digest of casein, 3.0 pancreatic digest of soybean meal, 5 g NaCl, 2.5 g K_2HPO_4, 2.5 g glucose, and 15.0 agar) (Fig. 7). The polysulfone carrier coated with microorganisms was prepared by adding the polysulfone carrier into the microorganism cultivated solution and leave for 24 h, to allow the microorganisms to be coated with the carrier (Fig. 8). Batch sorption experiments were repeated with polysulfone carrier coated with each microorganism (*Pseudomonas fluorescens* or *Bacillus drentensis*). The 0.6 g of polysulfone carrier coated with microorganisms was added to 30 mL of Cs contaminated solution and the mixture was stirred at 125 rpm at room temperature (22 ± 1 ℃) for 1 h. The Cs removal efficiency of microorganism coated polysulfone carrier was compared to that of only polysulfone carrier.

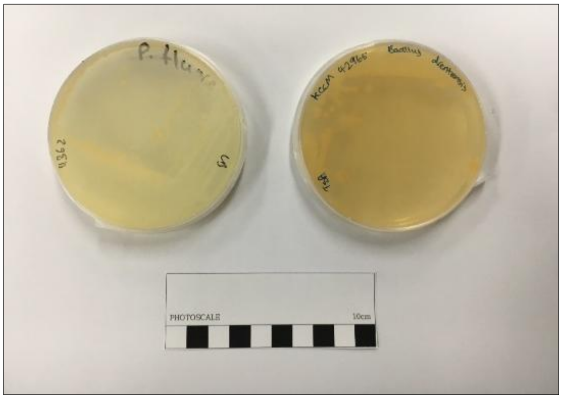


Fig. 7. Cultivated microorganisms (*Pseudomonas fluorescens* and *Bacillus drentensis*) for the sorption experiment.

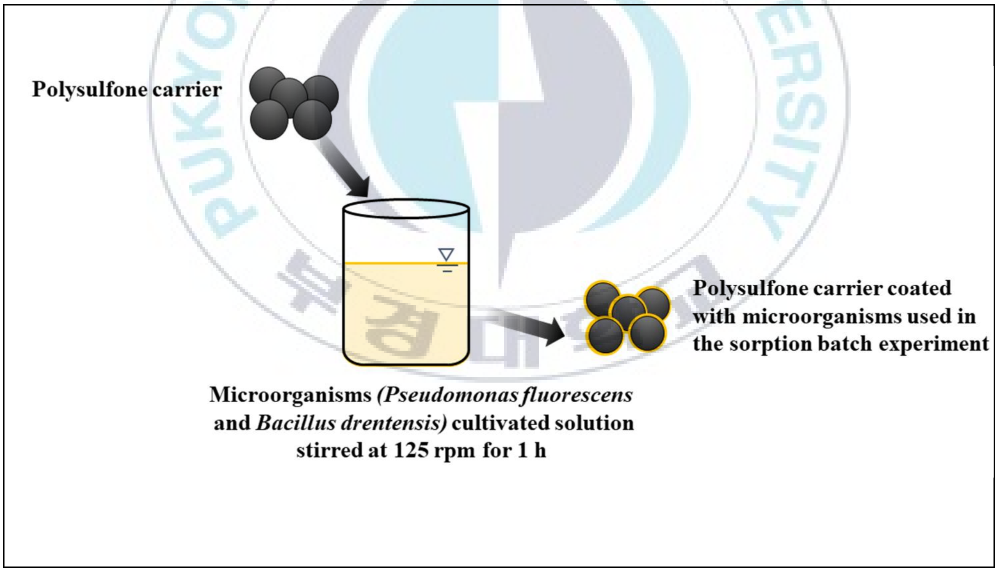


Fig. 8. Preparation the polysulfone carrier coated with microorganisms (*Pseudomonas fluorescens* and *Bacillus drentensis*).

3.8 Continuous column experiments

Since most of the previous sorption studies have been limited to batch experiments, the confirmation of the potential of adsorbents to remove Cs in a non-equilibrium condition becomes necessary to successfully design the operation process in the real field. By the continuous column experiment, this kinetic effect on the Cs removal of water treatment systems can be investigated. In this study, continuous column experiments were performed to consider the Cs removal efficiency of the polysulfone carrier in a nonequilibrium condition. A glass column (3 cm of internal diameter and 33 cm in length) was used in column experiment and the experimental setup is shown in Fig. 9. Four different adsorbents such as original BC granules without HNO_3 treatment (16 – 18 mm in diameter); polysulfone carrier having 5% of HNO_3 treated BC; polysulfone carrier coated with microorganisms (*Pseudomonas fluorescens* and *Bacillus drentensis*). A glass column was packed with 7.3 g of BC granules, representing 10 times of total BC amount in the polysulfone carrier packed column. The void spaces of this column was additionally packed with silica beads (8 – 9 mm in diameter) to maintain the constant flow in the column. The second column was fully packed with 51.4 g of BC granules (no times of total BC amount in the polysulfone carrier packed column). Two others were packed with 14.7 g of only polysulfone carrier and polysulfone carrier with microorganisms, respectively.

The column was saturated with distilled water while two pore volumes of distilled water were flushed through the column by an up-flow system at 1.5 mL/min. Then the Cs contaminated solution (initial Cs concentration: 1 mg/L) consistently flowed into the column at the rate of 1.5 mL/min for 250 pore volumes (about 18 Liters) (Fig. 9). The flushed solution was sampled from the effluent of the column at certain time intervals (from 1 h to 200 h) and its Cs concentration was analyzed by ICP/OES.

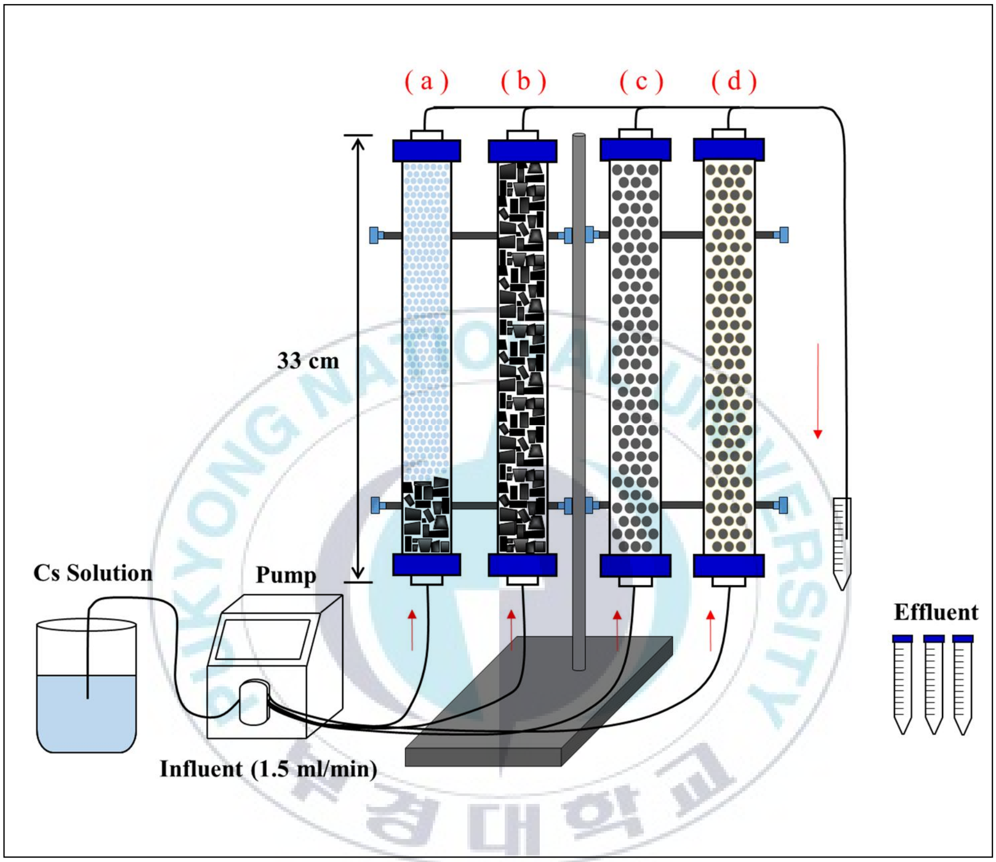


Fig. 9. Column experiments with four different adsorbents ((a) packed with 7.3 g of original BC granules; (b) packed with 51.4 g of original BC granules; (c) packed with polysulfone carrier only; (d) packed with polysulfone carrier coated with microorganisms.

3.9 SEM−EDS analysis for the polysulfone carrier

SEM (Scanning Electron Microscope; TESCAN, Czech, VEGA II LSU) and EDS (Energy Dispersive X-Ray Spectrometer; Horiba Scientific) analysis were performed to visualize the structure of polysulfone carrier and to understand its compositional characteristics after the sorption process. The SEM uses a focused electron beam of high-energy electrons to generate various signals produced by electron–sample interactions. The higher the accelerating voltage applied on the electron beam, the larger the interaction volume. In EDS, an X-ray spectrum emitted by the specimen provides both qualitative and quantitative information, allowing identification of which elements are present in the sample and the amount of each element (Girao et al., 2017). For SEM/EDS analyses for Cs adsorbed polysulfone carrier, batch experiments by using 30 mL solution with high Cs concentration (500 mg/L) were performed for 1 hour. After 1 hour reaction, the polysulfone carrier was analyzed by SEM coupled with EDS. For the analysis, polysulfone carrier granules were mounted on a stainless steel stab with a double stick tape followed by high vacuum evaporation coating with a thin layer of platinum by using a plasma sputter coater to increase the electron conduction and to improve the quality of the micrographs. All image were obtained by accelerating the voltage of 15 kV.

3.10 Study on the Cs sorption characteristics of polysulfone carrier

The Cs sorption capacity and kinetic behavior for polysulfone carrier with HNO_3 treated BC were investigated to understand the Cs sorption characteristics of polysulfone carrier in detail. For the kinetic study, sorption batch experiments at different sorption time intervals were fitted to curves of two sorption kinetic models such as the pseudo-first-order and pseudo-second-order model. The kinetic study of the sorption was processed helpful to determine the sorption rate and to understand the characteristics of the possible sorption mechanisms.

The sorption isotherm model indicates that the distribution of the adsorbed molecules between the liquid and solid phase when the sorption process reaches an equilibrium (Ho et al., 2002). Two typical sorption isotherm models (Langmuir and Freundlich isotherm model) were also used to evaluate the Cs sorption capacity of polysulfone carrier. For the sorption isotherm model study, the sorption batch experiment was repeated with different initial Cs concentration in solution. Kinetic experimental data were applied to determine the Cs sorption equilibrium time, whereas the isotherm fitting data were used to provide the maximum Cs sorption capacity for the polysulfone carrier (Fig. 10).

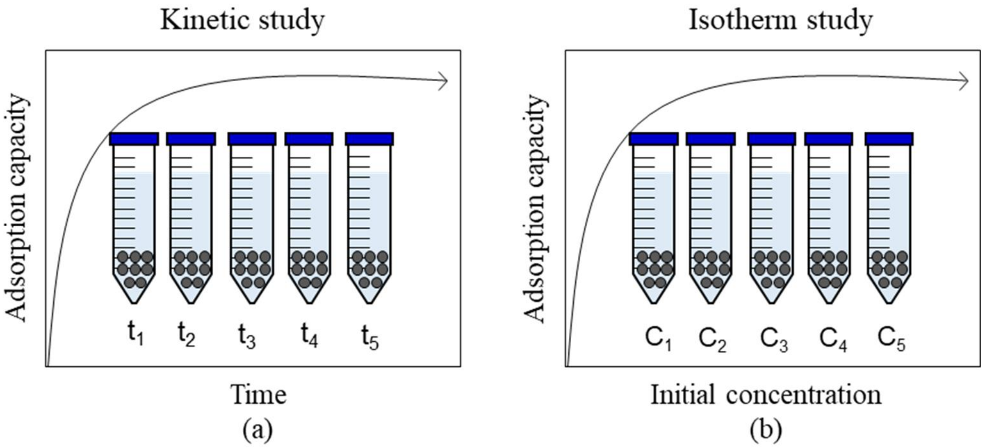


Fig. 10. Illustration of the data acquisition design for kinetic (a) and isotherm study (b).

3.10.1 The Cs sorption kinetic study

The Cs sorption rate and kinetic behavior for polysulfone carrier with HNO_3 treated BC were evaluated by the kinetic model study. The Cs sorption kinetics reflect the evolution of the sorption process versus time. Two kinetic models used to study the kinetic behavior were the pseudo-first-order model and the pseudo-second-order model. Pseudo-first-order and second-order kinetic models could generally simulate the physical and chemical sorption processes. For the kinetic experiment, 0.6 g of polysulfone carrier and 30 mL Cs contaminated solution (initial Cs concentration: 1 mg/L) were reacted for different contact times such as 10, 30, 60, 120, and 240 minutes.

3.10.1.1 Pseudo-first-order kinetic model

In the pseudo-first-order kinetic model, the Lagergren (1898) showed that the sorption capacity in equilibrium condition (q_e) and sorption rate constant (K_1) are important factors, determining the sorption capacity on the adsorbent and understanding the sorption behavior. The pseudo-first-order kinetic model assumes that the rate of occupation of the sorption site is proportional to the number of unoccupied sites (Kumar, 2006). The influence of the initial concentration of the value K_1 depend on the sorption system. The value of K_1 will decrease as the initial concentration increase. A larger sorption rate K_1 usually represents a quicker adsorption rate (Mishra and Hussain, 2018). Parameter values of pseudo-first-order kinetic model can be acquired by plotting graphs of log $(q_e - q_t)$ versus t. The obtained slope and intercept from the linear fitting are used to estimate the value of q_e and K_1 in equation (3).

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303}\right)t \tag{3}$$

where, K_1 is the rate constant of sorption min^{-1}. The q_e and q_t are the amount of Cs adsorbed (mg/g) at equilibrium and at time t.

3.10.1.2 Pseudo-second-order kinetic model

The pseudo-second-order kinetic model was applied to calculate the value of $q_{e.}$ The pseudo-second-order kinetic model is based on the assumption that the rate-limiting steps may be chemical sorption involving valence forces through sharing or exchange of electron between adsorbent and adsorbate (Kumar, 2006). The equilibrium time achieved at a shorter time as the value of K_2 increases. When its value is relatively high, the equilibrium condition is reached in a very short period. Parameter K_2 decreases with an increase in the initial concentration (Mishra and Hussain, 2018). Value of parameters for pseudo-second-order kinetic model can be determined by plotting a graph of $\frac{t}{q_t}$ versus t in equation (4).

$$\frac{t}{qt} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \qquad (4)$$

where, K_2 is the pseudo-second-order rate constant (g/mg.min). The q_e and q_t are the amount of Cs adsorbed (mg/g) at equilibrium and at time t.

3.10.2 Sorption isotherm study

The Cs sorption isotherm study of polysulfone carrier was conducted to understand the main mechanism of Cs sorption on the polysulfone carrier. The experimental sorption data were fitted to the Langmuir and Freundlich isotherm models. The Cs sorption batch experiments were conducted using 0.6 g of polysulfone carrier and 30 mL of Cs contaminated solution (initial Cs concentration range: 0 to 10 mg/L).

3.10.2.1 Langmuir isotherm

The Langmuir isotherm model is principally valid when the monomolecular layer sorption occurs on the adsorbent surface. It results from the homogeneous sorption which supports that all the sorption sites are equally capable of adsorbing pollutants irrespective of the status of the adjacent sites. The Langmuir isotherm was also applied to evaluate the maximum sorption capacity (q_m) which represents the capacity produced from the complete single layer coverage of adsorbent surface (Langmuir, 1916). The linear form of Langmuir sorption isotherm model is written as:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_{mK_L}} \tag{5}$$

where C_e is concentration of Cs in solution at equilibrium time (mg/L), q_e is the amount of Cs adsorbed (mg/g) at equilibrium, q_m is Langmuir constant related to the maximum amount of Cs sorption (L/mg), and K_L is Langmuir constant connected to the energy of sorption (L/mg).

The separation factor or equilibrium parameter (R_L) is an dimensionless constant that expresses the characteristic of Langmuir isotherm. The value of separation factor (R_L) can be used to determine whether the additional sorption is favorable or unfavorable (Ho et al., 2002; Khandaker et al., 2017). The lower value of R_L indicate the higher affinity of adsorbent to adsorbed and it can be calculated from Langmuir sorption constant in equation (6).

$$R_L = \frac{1}{(1 + K_L C_o)} \tag{6}$$

where C_o is initial concentrations of Cs solution (mg/L). The effect of separation factor on the Langmuir isotherm shape is summarized in Table 2.

Table 2. Effect of separation factor R_L on isotherm shape (Ho et al., 2002; Khandaker et al., 2017).

R_L value	Type of isotherm
(R_L> 1)	Unfavorable
(R_L= 1)	Linear
($0 < R_L$< 1)	Favorable
(R_L= 0)	Irreversible

Furthermore, the surface coverage (θ) is one of the factors that is used to understand the sorption behavior of the Langmuir isotherm. The value of surface coverage can be determined by plotting surface coverage versus initial Cs concentration. When the calculated (θ) close to 1, it indicates that the surface of adsorbent was nearly covered with a monomolecular layer for the Cs removal (Lalhruaitluanga et al., 2010; Khandaker et al., 2017). The equation for (θ) is expressed as:

$$\theta = \frac{K_L C_i}{1 + K_L C_i} \tag{7}$$

where K_L is the Langmuir constant and C_i is the initial Cs concentrations (mg/L).

3.10.2.2 Freundlich isotherm

The Freundlich isotherm model is more available to represent the heterogeneous sorption process than the Langmuir isotherm model, supporting that the proportion of the amount of adsorbate into a given mass of adsorbent is inconstant at different concentrations in solution (Freundlich, 1906). The equation for the Freundlich isotherm model is written as:

$$\log q_e = \log K_F + n \log C_e \tag{8}$$

where C_e is the equilibrium Cs concentration (mg/L), q_e is the amount of Cs adsorbed per unit mass of the adsorbent at equilibrium (mg/g), K_F is Freundlich constants that related to sorption capacity (L/mg), and n is sorption intensity. The Freundlich isotherm constants can be calculated from the slope and intercept of the linear plot between logq_e and logC_e.

CHAPTER IV. RESULTS AND DISCUSSION

4.1 Batch sorption studies for Cs

4.1.1 Estimating of the Cs sorption time

The Cs removal efficiency of polysulfone carrier at different sorption time was calculated from the results of sorption batch experiments, which was used to determine the Cs sorption equilibrium time for the further study (Fig. 11). The result showed that the Cs sorption rate was fast and the reaction reached in equilibrium within the first 240 min. The Cs removal efficiency of the polysulfone carrier was 57.80%, which was considered sufficient, compared to those of previously used adsorbent. Even the Cs removal efficiency increased with the increase of sorption time, its increasing pattern became gentle after 60 min of sorption time, representing the fast Cs sorption process of polysulfone carrier. This result suggested that the polysulfone carrier with HNO_3 treated BC have enough number of free active space, causing the fast Cs sorption at the initial stage (Qing, 2010). Rapid sorption kinetics of adsorbent is very important for its application in wastewater treatment, resulting in short operation time and low operation cost. These experimental results were used for the further sorption kinetic study.

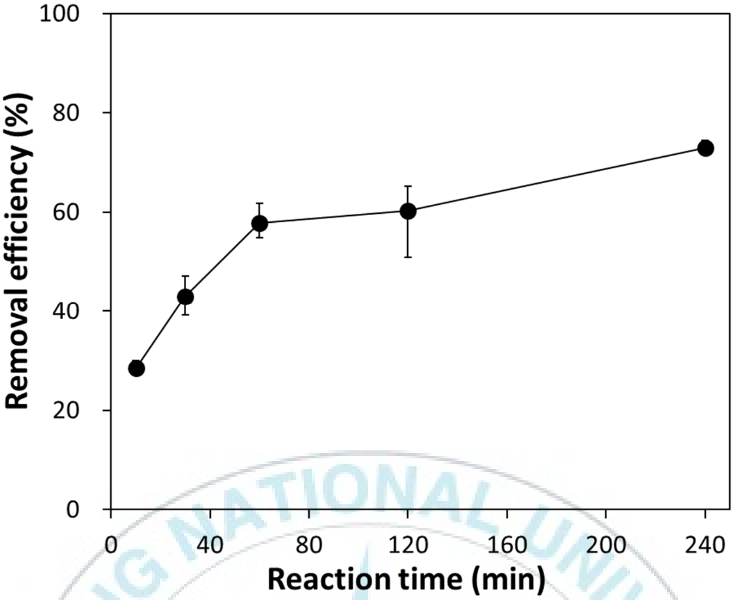


Fig. 11. Effect of different reaction times on Cs sorption.

4.1.2 Effect of BC amount in polysulfone carrier on the Cs sorption

The result of Cs removal efficiency according to different BC amount in polysulfone carrier is shown in Fig. 12. The Cs removal efficiency increased with the increase of BC amount in polysulfone carrier. For 2% of BC amount in polysulfone carrier, the Cs removal efficiency was less than 45%. However, the Cs removal efficiency increased to 62.37% and 68.45% with 5% and 10% BC in the polysulfone carrier, respectively. These results indicate that 5% BC in polysulfone carrier is enough for the Cs removal in water, thus this condition was used for further batch sorption experiments.

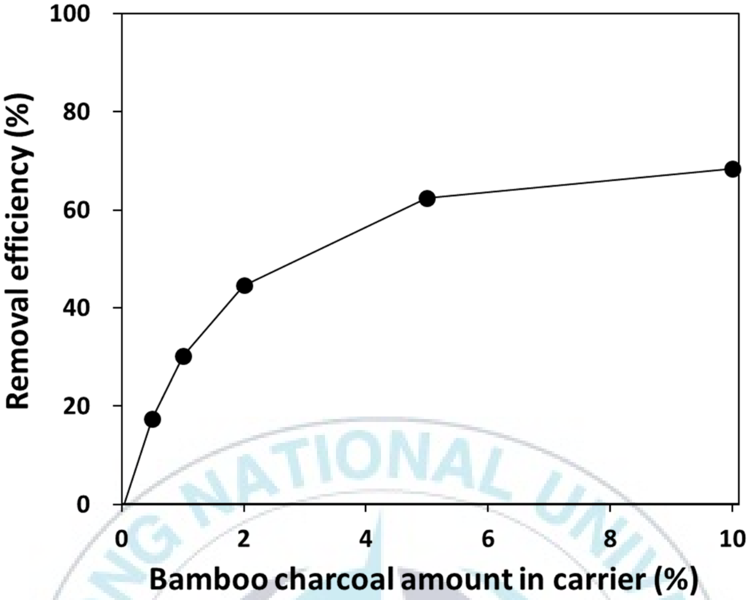


Fig. 12. Effect of different BC amount in carrier on the Cs sorption.

4.1.3 Effect of adsorbent dosages on the Cs sorption

The Cs sorption experiments were repeated with different adsorbent dosages in solution at room temperature in order to determine the optimal adsorbent dosage for the Cs removal. The change of the cesium removal efficiency by using the different doses of polysulfone carrier in solution is shown in Fig. 13. As the amount of the polysulfone carrier increased in solution, the available sites for Cs became abundant but instead relative Cs amount in solution decreased (Liu et al., 2012; Sakamoto et al., 2016). The Cs removal efficiency was greatly increased from 11.17 to 72.67% with increased adsorbent dosages (from 0 to 3%), representing that the number of active sites proportionally increased as well as the sorption rate. The Cs removal efficiency does not change significantly in the further increase of adsorbent dosages (>2%). Thus 2% of polysulfone carrier in solution was used as the optimum amount of adsorbent for the experiments.

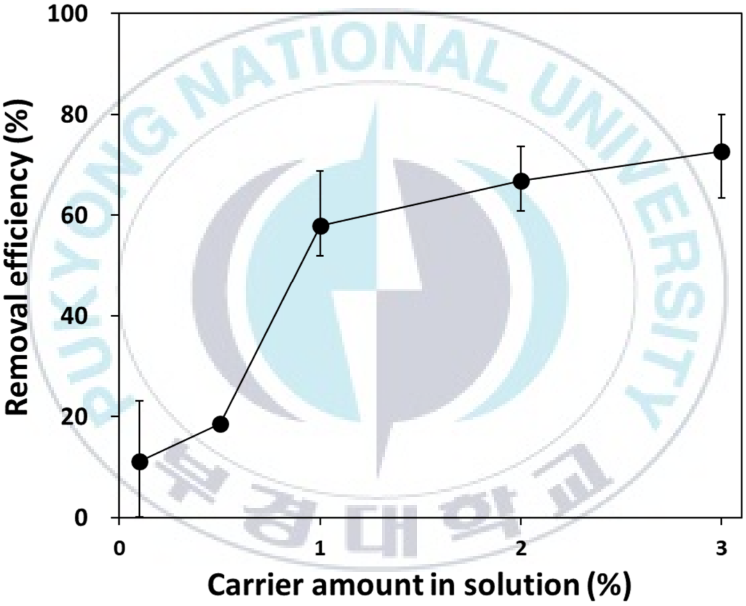


Fig. 13. Effect of polysulfone carrier dosages on the Cs sorption

4.1.4 Effect of solution pH on the Cs sorption

Many studies reported that the sorption capacity of adsorbent was dependent on the pH of the solution. The pH of the solution has greatly affected the sorption process and capacity due to its impact on the surface property of the adsorbent, the ionization in solution, and dissociation (Ghaedi et al., 2011). The effect of pH on the Cs sorption capacity of polysulfone carrier at equilibrium condition is shown in Fig. 14. The Cs removal efficiency increased from 43.47% to 54.07% with the increase of pH (from 3 to 5), and remained steady up to pH 11. The relatively high Cs removal efficiency (average of 58.14%) maintained at a wide range of pH conditions. The low removal efficiency at lower pH conditions can be related to the high concentration of H^+ ions competing with the Cs ions for the sorption site in the adsorbent (Saberi et al., 2010). However, the Cs removal efficiency of the polysulfone carrier with HNO_3 treated BC was > 40% even at pH of 3, indicating that this adsorbent is suitable for the treatment of Cs contaminated water at low pH condition.

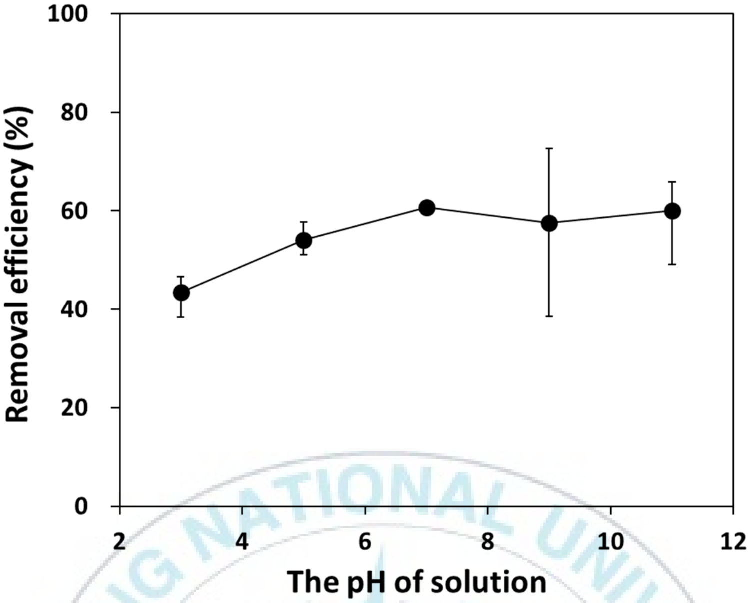


Fig. 14. Effect of solution pH on Cs sorption.

4.1.5 Effect of temperature on the Cs sorption

Temperature also can be one of the important factors for the Cs sorption capacity because it can affect the diffusion rate of the adsorbed molecules and the sorption rate. Fig. 15 represents the Cs removal efficiency of the polysulfone carrier at various temperature conditions. The result suggested that the Cs removal efficiency of the polysulfone carrier was not significantly affected by temperature. The high Cs removal efficiency (more than 69%) was maintained at the range of 5 ℃ to 30 ℃, verifying its applicability for a wide range of temperatures.

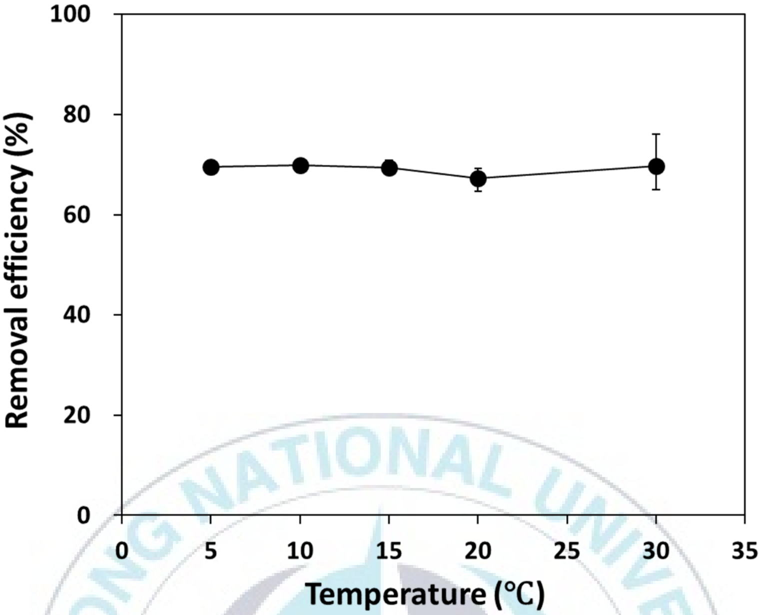


Fig. 15. Effect of temperature on Cs sorption.

4.2 Desorption experiments

The desorption characteristics are very important for the field application of the adsorbent because the desorption rate can be used as a criterion to evaluate the possibility of subsequent pollution due to the Cs release from the polysulfone carrier. The results in Fig. 16 showed that the average of Cs desorption rate for the polysulfone carrier was 14.64% for 24 h of desorption time, the polysulfone carrier with HNO_3 treated BC maintain the strong attraction force of Cs on the carrier surface. It can be ascribed that the chemical sorption is the main sorption mechanisms for Cs, which is stable to desorbed by distilled water (Chen et al., 2013).

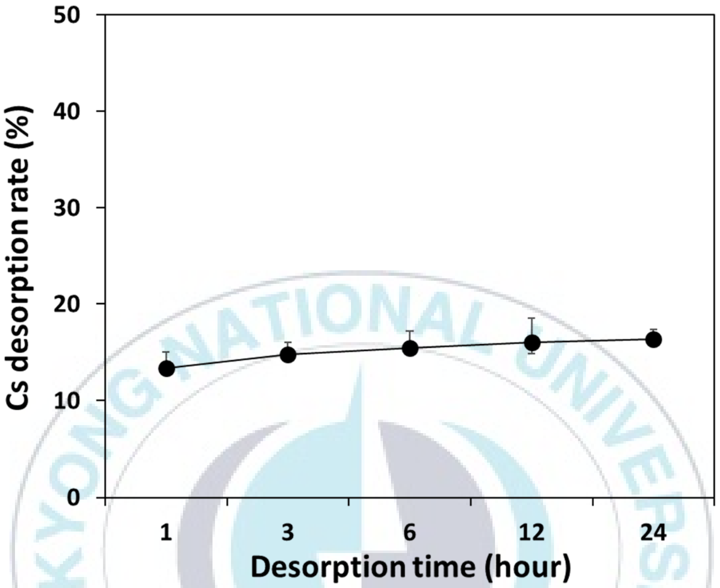


Fig. 16. The Cs desorption rate of the polysulfone carrier with HNO_3 treated BC.

4.3 Batch experiment with polysulfone carrier coated by microorganisms

Previous studies reported that microorganisms could offer a significant fraction of the reactive surface area and numerous functional groups such as phosphate, carboxyl, and amide groups to interact with radionuclides on the cell wall. These organics could be attached on the adsorbent surface through the immobilization process and finally enhanced the active sorption sites of the prepared adsorbents (Li et al., 2014). Moreover, microorganisms activities are well known to have a remarkable influence on the chemical and migration behaviors of radionuclides by altering the speciation, solubility and sorption properties (Katsenovich et al., 2013; Li et al., 2014). Results for the Cs removal efficiency from the batch experiment with polysulfone carrier coated by microorganisms are shown in Fig. 17. The average Cs removal efficiency of the polysulfone carrier without microorganisms coated was 73.83%. However, when the polysulfone carrier coated with *Pseudomonas fluroescens* and *Bacillus drentensis* were used in sorption batch experiments*,*their Cs removal efficiencies were 88.27% and 87.18%, respectively. The presence of microorganisms on the surface of polysulfone carrier increased the Cs removal efficiency by 19% and 18%, compared to that of polysulfone carrier without microorganism coated.

The higher Cs removal efficiency for microorganism coated polysulfone carrier could be ascribed to the thicker peptidoglycan framework on the cell walls which provides more functional groups accelerating in the interaction with Cs (Fang et al., 2011). In addition, the Cs immobilzation by these microorganism cells could be presumably due to the properties of an outer membrane, which permits Cs diffusion inside the cells and their uptake by the local polyphosphate bodies (Li et al., 2014). According to previous studies (Kang et al., 2017; Zhao et al., 2016), the Cs sorption by living microorganisms can be explained as a two-step process. The Cs were initially adsorbed to the surface of cells by ion-exchange and electrostatic interaction, and then the Cs entered into the cytoplasm of microorganisms across the cell membrane. These Cs immobilization mechanisms by microorganisms coated on polysulfone carrier surface led to an increase in the Cs removal efficiency.

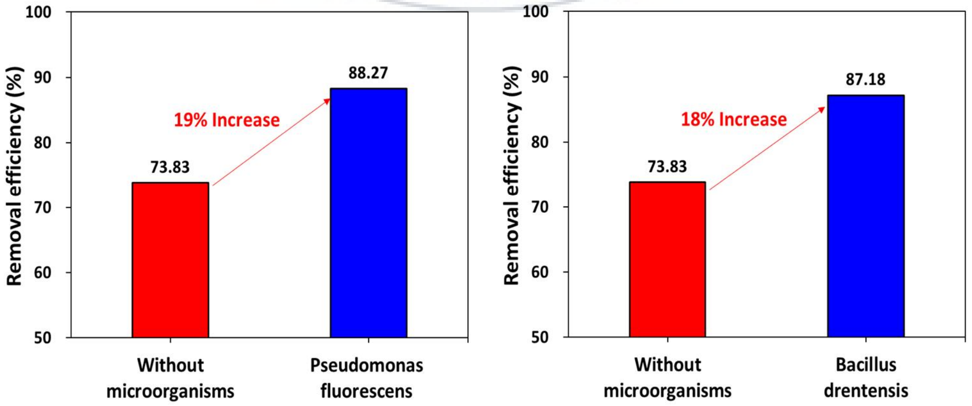


Fig. 17. Sorption result of polysulfone carrier coated with microorganisms.

4.4 Continuous column experiments

Fig. 18 shows the results of the Cs removal efficiency in continuous column experiments using four different adsorbents. In the column experiments using only BC granular as an adsorbent, both of two columns packed with 7.3 and 51.4 g of BC granules shows the low Cs removal efficiency. The Cs removal efficiency of the column experiments for 7.3 g and 51.4 g of BC granule maintained below 20% for 250 pore volumes flushing (the maximum Cs removal efficiency of the was 28%, occurred at the early stage of flushing). However, the Cs removal efficiency for the column packed with polysulfone carrier without microorganism coated maintained over 80% until 50 pore volumes of flushing and reached the lowest removal efficiency of 2% at 182 pore volumes. Different results for the Cs removal efficiency were shown in the column with the polysulfone carrier coated with microorganisms. The polysulfone carrier coated with *Bacillus drentensis* and *Pseudomonas fluorescens* showed 99% of Cs removal efficiency for 70 pore volumes of flushing in column experiments. The Cs removal efficiency of both of microorganisms coated polysulfone carrier maintained more than 80% during 100 pore volumes of flushing, suggesting that only 14.7 g of polysulfone carrier can successfully clean-up 7.2 L of Cs contaminated water (1 mg/L of initial Cs concentration). From the results of column experiments, it was investigated that the coated microorganisms positively affect the Cs removal efficiency of polysulfone carrier from solution.

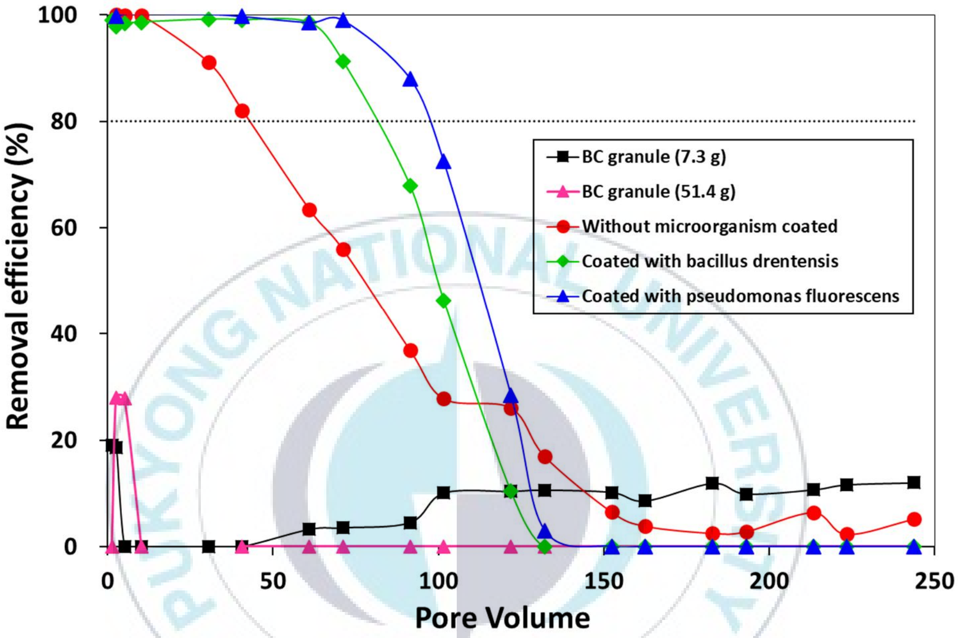
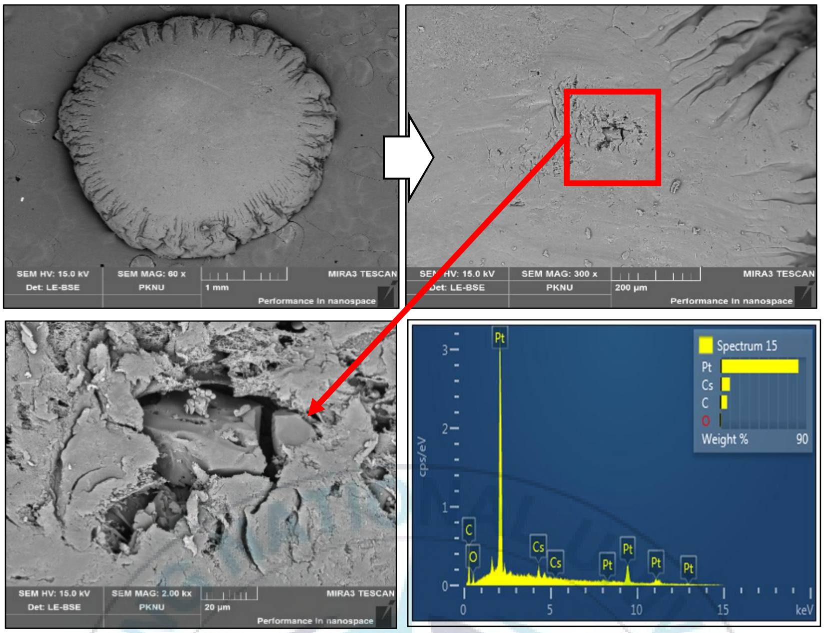


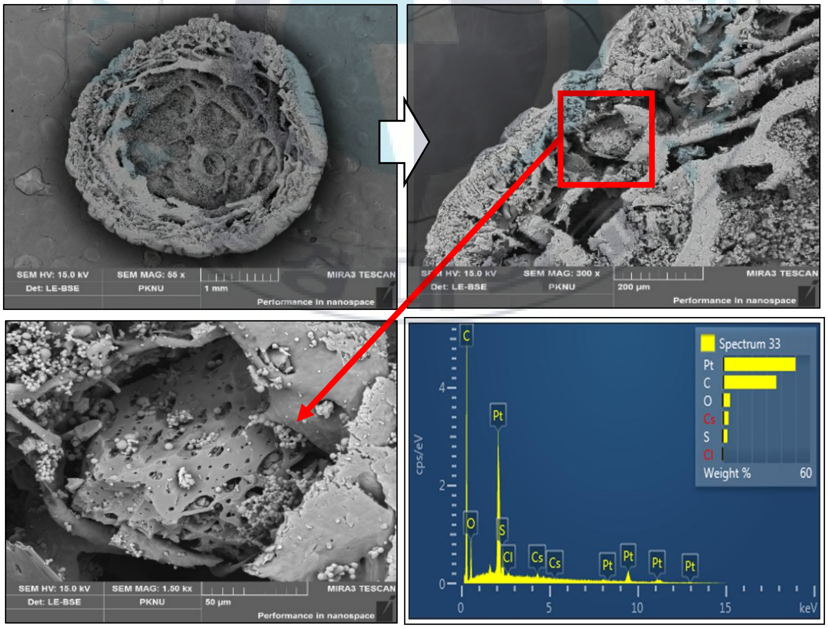
Fig. 18. Results of continuous column experiments packed with four different adsorbents (((a) packed with 7.3 g of original BC granules; (b) packed with 51.4 g of original BC granules; (c) packed with polysulfone carrier only; (d) packed with polysulfone carrier coated with microorganisms.

4.5 SEM-EDS analyses for the Cs sorbed polysulfone carrier

SEM and EDS analysis were carried out to identify the structure and compositional components of the polysulfone carrier. The outer and inner surface of polysulfone carrier were visualized by SEM analysis (Fig. 19). The SEM images of the polysulfone carrier after the sorption experiment showed that the polysulfone carrier with HNO_3 treated BC has complicated porous structures that would have contributed well to the Cs sorption sites embedded in the polysulfone carriers. The EDS analysis was performed along with SEM images to measure the Cs amount of the selected spots on the polysulfone carrier. From the EDS spectra, the adsorbed Cs amount was 10.00 and 4.08% of the total component weight on the outer and inner surface of the polysulfone carrier, respectively, indicating that the Cs was successfully adsorbed on outer and inner space of polysulfone carrier.



(a) Outer surface



(b) Inner surface

Fig. 19. Results of SEM/EDS analyses for the polysulfone carrier after the Cs sorption experiment.

4.6 Sorption kinetic study

Kinetic study of the sorption process is helpful to understand the sorption mechanism and the Cs amount sorbed on the polysulfone carrier at different sorption times (0 – 240 min) in the batch experiment was fitted to the pseudo-first-order and pseudo-second-order kinetic models. Based on the fitted plots and calculated parameters, the calculated q_e values obtained from the pseudo-first-order model does not give reasonable values. The results suggested that this kinetic model does not suitable for the Cs sorption process. The rate constant of pseudo-second-order kinetic is listed in Table 3 and the experimental results were plotted in Fig. 20. The experimental values of sorption fit well with the calculated values by the pseudo-second-order kinetic model with the correlation coefficients (R^2) 0.933 and the experimental q_e values were similar to the calculated q_e values. This suggests that the Cs sorption of the polysulfone carrier followed the pseudo-second-order kinetic model and the major sorption mechanisms of Cs is chemisorption rather than physisorption and the sorption rates were dependent on active sites and not on Cs concentration (Liu et al., 2019).

Table 3. The pseudo-second-order sorption rate constant from experimental and calculated q_e values.

Experimental value q_e (mg/g)	K_2	Calculated value q_e (mg/g)	R^2
0.039	1.090	0.036	0.9933

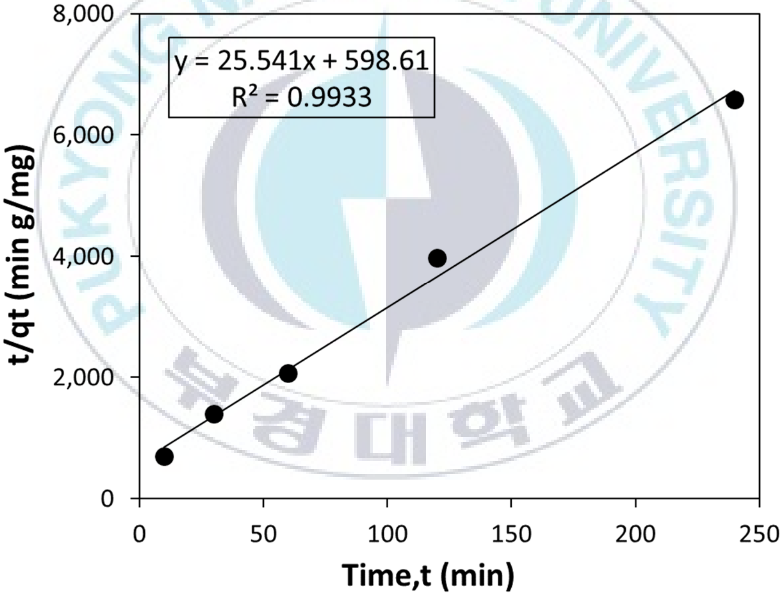


Fig. 20. Pseudo-second-order kinetic model for sorption of Cs.

4.7 Sorption isotherm study

Sorption isotherms were studied to determine the maximum Cs sorption capacity of the polysulfone carrier with HNO_3 treated BC for a wide range of initial concentration of Cs (0 to 10 mg/L) (Fig. 21). The equilibrium data were obtained from experimental results, which are fitted to the Langmuir and Freundlich isotherm models. Table 4 shows the sorption isotherm parameters obtained from these model studies. From the correlation coefficient (R^2), the Langmuir model (R^2=0.996) was better fitted to experimental results for the removal of Cs, compared with the Freundlich model (R^2=0.987). This was confirmed that mostly monolayer coverage sorption takes place on the adsorbent surface (polysulfone carrier) and the Cs was homogenously distributed on the carrier surface (Crini et al., 2007). According to the isotherm study by using the Langmuir model, the maximum Cs sorption capacity (q_m) of polysulfone carrier was determined to 60.89 mg/g.

Table 4. The average Langmuir and Freundlich isotherms parameters for the sorption of Cs.

Langmuir isotherm			**Freundlich isotherm**		
q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	n	R^2
60.89	9.175	0.996	99.289	1.415	0.987

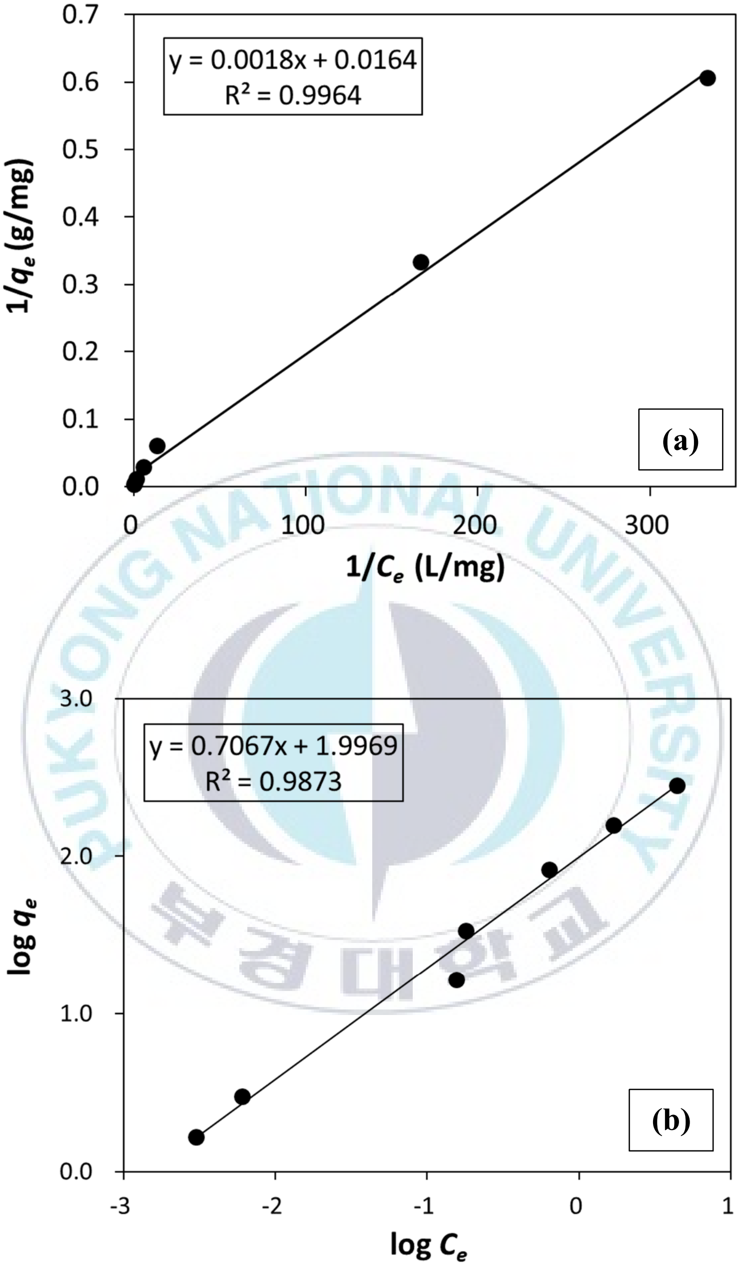


Fig. 21. Equilibrium isotherm curve fitting to two isotherm models: Langmuir model (a), and Freundlich model (b).

According to the Langmuir isotherm model, the favorability of the Cs sorption process can be explained by the separation factor (R_L). The calculated separation factor (R_L) values at different initial Cs concentrations is presented in Fig. 22(a). The values of R_L were in the range of 0 to 1 ($0 < R_L < 1$), indicating that the polysulfone carrier was favorable under a wide range of initial concentration in the sorption process. The R_L values were also on a sharp decline with the increase of the Cs initial concentration and maintained below 0.1, suggesting that the Cs sorption of polysulfone carrier was more favorable at higher concentrations. The surface coverage values (θ) increased with the increase of initial Cs concentration in Fig. 22(b). The surface coverage value (θ) was close to 1, as the Cs initial concentration was higher than 10 mg/L, representing that the adsorbent surface was closely covered with a monomolecular layer of adsorbate (Khandaker et al., 2017). The value of the exponent n in the Freundlich isotherm equation can give an indication of the favorability and capacity of the adsorbent. When the value of n is higher than 1, the adsorbent is considered to have additional potential for sorption by using mechanisms such as inner layer attraction and multimolecular layer formation. In this study, the value of Freundlich exponent n was 1.415, indicating that polysulfone carrier with HNO_3 treated BC has a possibility of the favorable Cs sorption at high Cs initial concentration range (Crini et al., 2007). Considering the higher correlation coefficient, the Cs sorption mostly follow the Langmuir isotherm model. Additionally, the Freundlich isotherm model also can be useful for understanding the Cs sorption mechanism in the situation of high Cs concentration. Results of the Cs sorption isotherm and the kinetic study suggested that relatively rapid sorption (including precipitation onto the HNO_3 treated BC surface in a polysulfone carrier) would make this one of the prevailing processes for removing Cs from the water system.

Based on the literature review, several studies have been carried out to remove the Cs using the different adsorbents material and the results in this study were compared with those found in the literature (Table 5). The present study found the maximum Cs sorption capacity was 60.89 mg/g, which was much higher than those of previous studies, verifying the great Cs sorption capacity of polysulfone carrier with HNO_3 treated BC. Thus it might be a promising adsorbent for Cs removal from water.

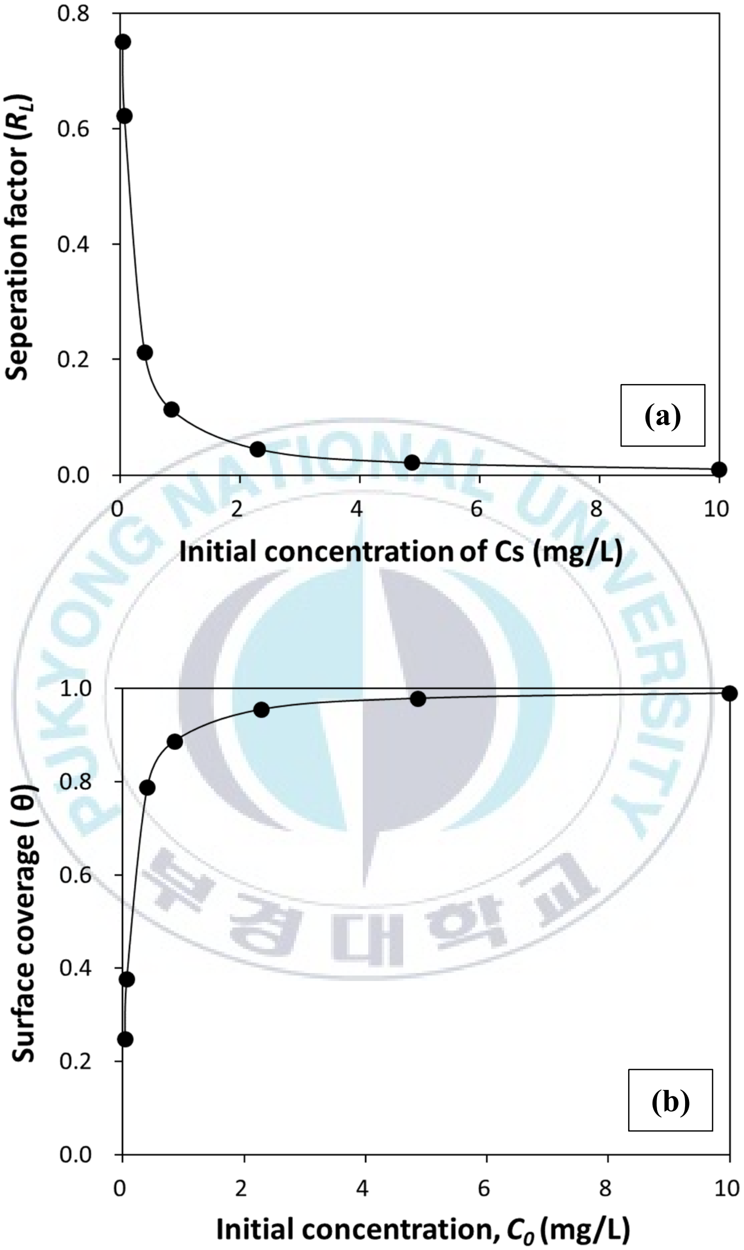


Fig. 22. Separation factor (R_L) (a) and surface coverage value (θ) (b) against initial concentration for the Cs sorption of the polysulfone carrier.

Table 5. Comparison of the Cs sorption capacities (q_m in mg/g) for different adsorbents.

Adsorbent materials	Sorption capacity (mg/g)	Reference
Cocoanut shell activated carbon	0.76	Caccin et al., (2013)
Pine cone	5.75	Ofomaja et al., (2015)
Touene-ethanol extracted pine cone	7.01	Ofomaja et al., (2015)
Immobilized nickel hexacyanoferrate-sericite beads	13.88	Jeon (2016)
Silica gel embedded phosphotungstic acid	20.80	Seaton et al., (2017)
Ammonium-pillared montmorillonite/Fe3O4	27.53	Zheng et al., (2017)
Maghemite PVA-alginate beads	28.32	Majidnia and Idris (2015)
Magnetic prussian blue/graphene oxide nanocomposites caged in calcium alginate microbeads	43.52	Yang et al., (2014)
Nitric acid modified bamboo charcoal	45.87	Khandaker et al., (2017)
Conjugate adsorbent	50.23	Awual et al., (2014a)
Polysulfone carrier with HNO_3 treated BC	60.89	(This study)
Modified hydroxyapatite	69.49	Metwally et al., (2017)
Mesoporous hybrid adsorbent	97.63	Awual et al., (2016b)
Lithium-modified montmorillonite caged in calcium alginate beads	100.25	Xia et al., (2018)

CHAPTER V. CONCLUSIONS

There is an imperative and urgent need for removing Cs from water solution due to its radioactivity, toxicity, and mobility, which may pose a serious threat to the human and ecosystem. The powdered form of HNO_3 treated BC has been recently used as an absorbent to remove Cs from water. However, there exist some limitations for its usage in the real field such as high production cost and additional treatment needed to separate from water. This study introduces a bead-type polysulfone carrier with HNO_3 treated BC as an effective and low-cost adsorbent due to the use of a small amount of HNO_3 treated BC (only 5 wt%). This adsorbent exhibited the relatively high Cs removal efficiency even in the low initial Cs concentration (1 mg/L). The findings of this study can be concluded as below:

1. The use of polysulfone polymer has excellent mechanical strength and good ability to hold strongly the HNO_3 treated BC as well as easy separation capability from water after treatment (instead of powder form). The feasibility of the bead-type polysulfone carrier for the removal of Cs could be verified through both batch and continuous column experiments. The results of SEM and EDS analyses revealed that the polysulfone carrier has the complicated porous structure and

the Cs was successfully adsorbed on the outer and inner space of the polysulfone carrier.

2. From results of batch experiments, it was investigated that the polysulfone carrier with HNO_3 treated BC is available to remove Cs within 1 hour reaction, having the high Cs removal efficiency of 57.8%. The high Cs removal efficiency (>60%) maintained at a wide range of pH and temperature conditions. Moreover, the Cs desorption rate of polysulfone carrier with HNO_3 treated BC for 24 h was <16%, suggesting that the Cs sorption stability of the polysulfone carrier is very high.

3. From results of Langmuir sorption isotherm model study, the maximum Cs sorption capacity (q_m) of polysulfone carrier with HNO_3 treated BC was 60.9 mg/g, which was much higher than those of other adsorbents in previous studies. Results from the Cs sorption kinetic model studies represented the polysulfone carrier with HNO_3 treated BC showed the pseudo-second-order kinetic model pattern, suggesting that the chemisorption is the probable mechanism for the Cs sorption.

4. The Cs removal efficiency from batch experiment with polysulfone carrier coated by two microorganisms increased by 18%, compared to that without coated microorganism. The continuous column experiments showed that the polysulfone carrier coated with microorganisms maintained more than 80% of Cs removal efficiency during 100 pore volumes flushing, suggesting that only 14.7 g of polysulfone carrier can successfully clean-up 7.2 L of Cs contaminated water (initial Cs concentration: 1 mg/L). These result indicated that the polysulfone carrier coated with microorganisms could positively affect the Cs removal efficiency of polysulfone carrier from solution

REFERENCES

Ahn, J., Lee, M., 2018. Sorption efficiency of the bamboo charcoal to remove cesium in the contaminated water system. Econ. Environ. Geol. 51, 87-97.

Alamudy, H.A., Cho, K., 2018. Selective adsorption of cesium from an aqueous solution by a montmorillonite-prussian blue hybrid. Chem. Eng. J. 349, 595-602

Asada, T., Ohkubo, T., Kawata, K., Oikawa, K., 2006. Ammonia adsorption on bamboo charcoal with acid treatment. J. Heal. Sci. 52, 585-589.

Awual, M.R., Miyazaki, Y., Taguchi, T., Shiwaku, H., and Yaita, T., 2016. Encapsulation of cesium from contaminated water with highly selective facial organic–inorganic mesoporous hybrid adsorbent. Chem. Eng. 291, 128-137.

Awual, M.R., Suzuki, S., Taguchi, T., Shiwaku, H., Okamoto, Y., and Yaita, T., 2014. Radioactive cesium removal from nuclear wastewater by novel inorganic and conjugate adsorbents. Chem. Eng. J. 242, 127-135.

Bai, R.S., Abraham, E., 2003. Studies on chromium (VI) adsorption–desorption using immobilized fungal biomass. Bioresource Technology. 87, 17-26.

Benkhaya, S., M'rabet, S., Hsissou, R., Harfi, A.E., 2020. Synthesis of new low-cost organic ultrafiltration membrane made from Polysulfone/Polyetherimide blends and its application for soluble azoic dyes removal. J. Mater. Res. Technol.

Bolsunovsky, A., Dementyev, D., 2011. Evidence of the radioactive fallout in the center of Asia (Russia) following the Fukushima nuclear accident. J. Environ. Radioact. 102, 1062–1064.

Caccin, M., Giacobb, F., Ros, M.D., Besozzi, L., and Mariani, M., 2013. Adsorption of uranium, cesium and strontium onto coconut shell activated carbon. J. Radional. Nucl. Chem. 297, 9-18.

Chen, C., Wang, J., 2008. Removal of Pb^{2+}, Ag^{+}, Cs^{+} and Sr^{2+} from aqueous solution by brewery's waste biomass. J. Hazard. Mater. 151, 65–70.

Chen, Y.G., He, Y., Ye, W.M., Sui, W.H., Xiao, M.M., 2013. Effect of shaking time, ionic strength, temperature and pH value on desorption of Cr(III) adsorbed onto GMZ bentonite. Trans. Nonferrous Met. Soc. China. 23, 3482-3489.

Chien, C.C., Huang, Y.P., Wang, W.C., Chao, J.H., Wei, Y.Y., 2011. Efficiency of moso bamboo charcoal and activated carbon for adsorbing radioactive iodine. Clean – Soil, Air, Water. 39, 103-108.

Cojocaru, C., Petronela, P.D., Airinei, A., Olaru, N., Samoila, P., Rotaru, A., 2017. Design and evaluation of electrospun polysulfone fibers and polysulfone/NiFe2O4 nanostructured composite as sorbents for oil spill cleanup. J. Taiwan. Inst. Chem. E. 70, 267-281.

Crini, G., Peindy, H.N., Gimbert, F., Robert, C., 2007. Removal of C.I. Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: Kinetic and equilibrium studies. Sep. Puri. Tech. 53, 97-110.

Danilin, L., Drozhzhin, V., 2007. Inorganic sorbents based on modified microspheres for treatment of liquid radioactive waste. Radiochemistry 49, 319–322.

Dechojarassri, D., Asaina, S., Omote, S., Nishida, K., Furuike, T., Tamura, H., 2017. Adsorption and desorption behaviors of cesium on rayon fibers coated with chitosan immobilized with Prussian blue. Int. J. Biol. Macromol. 104, 1509-1516.

DeMeuse, M.T., 2014. Polysulfones as a reinforcement in high temperature polymer blends. High Temperature Polymer Blends. 165-173.

Deng, H., Li, Y., Huang, Y., Ma, X., Wu, L., Cheng, T., 2016. An efficient composite ion exchanger of silica matrix impregnated with ammonium molybdophosphate for cesium uptake from aqueous solution. Chem. Eng. J. 286, 25-35.

Ding, S., Zhang, L., Li, Y., Hou, L., 2019. Fabrication of a novel polyvinylidene fluoride membrane via binding SiO_2 nanoparticles and a copper ferrocyanide layer onto a membrane surface for selective removal of cesium. J. Hazard. Mater. 368, 292-299.

Ding, Y., Bikson, B., 2010. Macro and meso porous polymeric materials from miscible polysulfone/polyimide blends by chemical decomposition of polyimide. Polymer. 51, 46-52.

Falyouna, O., Eljamal, O., Maamoun, I., Tahara, A., Sugihara, Y., 2020. Magnetic zeolite synthesis for efficient removal of cesium in a lab-scale continuous treatment system. J. Colloid Interface Sci. 571, 66-79.

Fan, Y., Wang, B., Yuan, S., Wu, X., Chen, J., Wang, L., 2010. Adsorptive removal of chloramphenicol from wastewater by NaOH modified bamboo charcoal. Bioresource Technology. 101, 7661-7664.

Fang, L., Wei, X., Cai, P., Huang, Q., Chen, H., Liang, W., Rong, X., 2011. Role of extracellular polymeric substances in Cu (II) adsorption on Bacillus subtilis and Pseudomonas putida. Bioresour. Technol. 102, 1137-1141.

Freundlich, H.M.F., 1906. Uber die adsorption in Losungen. Journal of Physical Chemistry, 57, 285-470.

Fu, J.W., Wen, T., Wang, Q., Zhang, X.W., Zeng, Q.F., Shu□Qing An, S.Q., and Hai□Liang Zhu, H.L. (2010) Degradation of Active Brilliant Red X□3B by a microwave discharge electrodeless lamp in the presence of activated carbon. J. Environ. Tech. 6, 1-20.

Furuya, K., Hafuka, A., Kuroiwa, M., Satoh, H., Watanabe, Y., Yamamura, H., 2017. Development of novel polysulfone membranes with embedded zirconium sulfate-surfactant micelle mesostructure for phosphate recovery from water through membrane filtration. Water Res. 124, 521-526.

Gad, S.C., Pham, T., 2014. Cesium, Encyclopedia of Toxicology. Third Edition. Elsevier, 776-778. https://doi.org/10.1016/B978-0-12-386454-3.00827-7

Ghaedi, M., Hossainian, H., Montazerozohori, M., Shokrollahi, A., Shojaipour, F., Soylak, M., Purkait, M.K., 2011. A novel acorn based adsorbent for the removal of brilliant green. Desalination. 281, 226-233.

Girao, A.V., Caputo, G., Ferro, M., 2017. Chapter 6 - Application of Scanning Electron Microscopy–Energy Dispersive X-Ray Spectroscopy (SEM-EDS). ″Compr. Anal. Chem. 75, 153-168.

Godiya, C.B., Cheng, X., Deng, G., Li, D., Lu, X., 2019. Silk fibroin/ polyethylenimine functional hydrogel for metal ion adsorption and upcycling utilization. J. Environ. Chem. Eng. 7, 102806.

Hameed, B.H., Din, A.T.M., Ahmad, A.L., 2007. Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies. J. Hazard. Mater. 141, 819-825.

Ho, Y.S., Huang, C.T., Huang, H.W., 2002. Equilibrium sorption isotherm for metal ions on tree fern. Process. Biochem. 37, 1421-1430.

Huang, P.H., Jhan, J.W., Cheng, Y.M, Cheng, H.H., 2014. Effects of carbonization parameters of moso-bamboo-based porous charcoal on capturing carbon dioxide. Sci. World J. 937867.

Iwanade, A., Kasai, N., Hoshina, H., Ueki, Y., Saiki, S., Seko, N., 2012. Hybrid grafted ion exchanger for decontamination of radioactive cesium in Fukushima Prefecture and other contaminated areas. J. Radioanal. Nucl. Chem. 293, 703–709.

Jeon, C., 2016. Removal of cesium ions from aqueous solutions using immobilized nickel hexacyanoferrate-sericite beads in the batch and continuous processes. J. Ind. Eng. Chem. 40, 93-98.

Kang, S.M., Jang, S.C., Heo, N.S., Oh, S.Y., Cho, H.J., Rethinasabapathy, M., Vilian, A.T.E., Han, Y.K., Roh, C., Huh, Y.S., 2017. Cesium-induced inhibition of bacterial growth of *Pseudomonas aeruginosa* PAO1 and their possible potential applications for bioremediation of wastewater. J. Hazard. Mater. 338, 323-333.

Katsenovich, Y., Carvajal, D., Guduru, R., Lagos, L., Li, C.Z., 2013. Assessment of the Resistance to Uranium (VI) Exposure by Arthrobacter sp. Isolated from Hanford Site Soil. Geomicrobiol. J. 30, 120-130.

Khandaker, S., Kuba, T., Kamida, S., and Uchikaawa, Y., 2017. Adsorption of cesium from aqueous solution by raw and concentrated nitric acid-modified bamboo charcoal. J. Environ. Chem. Eng. 5, 1456-1464.

Khandaker, S., Kuba, T., Toyohara, Y., Kamida, S., and Uchikaawa, Y., 2017. Development of ion-exchange properties of bamboo charcoal modified with concentration nitric acid. IOP Conf. Ser. Earth Environ. Sci. 82, 012002.

Kim, I., Lee, M., Wang, S., 2014. Heavy metal removal in groundwater originating from acid mine drainage using dead *Bacillus drentensis* sp. immobilized in polysulfone polymer. J. Environ. Manag. 146, 568-574.

Kosaka, K., Asami, M., Kobashigawa, N., Ohkubo, K., Terada, H., Kishida, N., Akiba, M., 2012. Removal of radioactive iodine and cesium in water purification processes after an explosion at a nuclear power plant due to the Great East Japan earthquake. Water Res. 46, 4397–4404.

Kurihara, O., Tsuchida, T., Takahashi, G., Kang, G.O., Murakami, H., 2018. Cesium-adsorption capacity and hydraulic conductivity of sealing geomaterial made with marine clay, bentonite, and zeolite. Soils Found. 58, 1173-1186.

Lalhruaitluanga, H., Jayaram, K., Prasad,M.N.V., Kumar, K.K., 2010. Lead(II) adsorption from aqueous solutions by raw and activated charcoals of

Melocanna baccifera Roxburgh (bamboo)—A comparative study. J. Hazard. Mater. 175, 311-318.

Langmuir, I., 1916. The constitution and fundamental properties of solids and liquids, Journal of the American Chemical Society, 38, 2221-2295.

Lee, J., Kim, T., Lee, M., 2018. The uranium removal in groundwater by using the bamboo charcoal as the adsorbent. Econ. Environ. Geol. 51, 531-542.

Lee, K.Y., Kim, K.W., Park, M., Kim, J., Oh, M., Lee, E.H., Chung, D.Y., Moon, J.K., 2016. Novel application of nanozeolite for radioactive cesium removal from high-salt wastewater. Water Res. 95, 134–141.

Li, X., Ding, C., Liao, J., Lan, T., Li, F., Zhang, D., Yang, J., Yang, Y., Luo, S., Tang, J., Liu, N., 2014. Biosorption of uranium on Bacillus sp. dwc-2: preliminary investigation on mechanism. J. Environ. Radioact. 135, 6-12.

Lin, Y.Z., Hwang G.S. and Wang I.S., 2003. Introduction to production and utilization of bamboo charcoal. Forest Tech. Report, 10 (3);31.

Liu, X., Ao, H., Xiong, X., Xiao, J., Liu, J., 2012. Arsenic removal from water by iron-modified bamboo charcoal. Water. Air. Soil Pollut. 223, 1033-1044.

Lo, S.F., Wang, S.Y., Tsai, M.J., Lin, L.D., 2012. Adsorption capacity and removal efficiency of heavy metal ions by Moso and Ma bamboo activated carbons. Chem. Eng. Res. Des. 90, 1397-1406.

Majidnia, Z., and Idris. A., 2015. Evaluation of cesium removal from radioactive waste water using maghemite PVA–alginate beads. Chem. Eng. J. 262, 372-282.

Manabe, S., Kiliyankil, A., Vipin., Kumashiro, T., Takiguchi, S., Fugetsu, B., Sakata, I., 2020. Stabilization of Prussian blue using copper sulfate for eliminating radioactive cesium from a high pH solution and seawater. J. Hazard. Mater. 386, 121979.

Mao, Y., Hu, H., Yan, Y., 2011. Biosorption of cesium(I) from aqueous solution by a novel exopolymers secreted from *Pseudomonas fluorescens* C-2: Equilibrium and kinetic studies.

Mbareck, C., Nguyen, Q.T., Alaoui, O.T., Barillier, D., 2009. Elaboration, characterization and application of polysulfone and polyacrylic acidblends as ultrafiltration membranes for removal of some heavy metals from water. J. Hazard. Mater. 171, 93-101.

Melvin Ng, H.K., Leo, C.P., Abdullah, A.Z., 2017. Selective removal of dyes by molecular imprinted TiO_2 nanoparticles in polysulfone ultrafiltration membrane. J. Environ. Chem. Eng. 5, 3991-3998.

Metwally, S.S., Ahmed, I.M., and Rizk, H.E., 2017. Modification of hydroxyapatite for removal of cesium and strontium ions from aqueous solution. J. Alloys Compd. 709, 438-444.

Mishra, A. K., Hussain, C. M. (Eds.). (2018). Nanotechnology for Sustainable Water Resources. Scrivener Publishing.

Ofomaja, A.E., Pholosi, A., Naido, E.B., 2015. Application of raw and modified pine biomass material for cesium removal from aqueous solution. Ecol. Eng. 82, 258-266.

Park, S.M., Alessi, D.S., Baek, K., 2019. Selective adsorption and irreversible fixation behavior of cesium onto 2:1 layered clay mineral: A mini review. J. Hazard. Mater. 369, 569-576.

Park, Y., Lee, Y.C., Shin, W.S., Choi, S.J., 2010. Removal of cobalt, strontium and cesium from radioactive laundry wastewater by ammonium molybdophosphate-polyacrylonitrile (AMP-PAN). Chem. Eng. J. 162, 685–695.

Qing, C., 2010. Study on the adsorption of lanthanum(III) from aqueous solution by bamboo charcoal. J. Rare. Earth. 28, 125.

Saveri, S., Nilchi, A., Garmarodi, S.R., Zarghami, R., 2010. Adsorption characteristic of 137 Cs from aqueous solution usimg PAN-based sodium titanosilicate composite. J. Radional. Nucl. Chem. 284, 461-469.

Seaton, K., Little, L., Tate, C., Mohseni, R., Roginskaya, M., Povazhniy, V., and Vasiliev, A., 2017. Adsorption of cesium on silica gel containing embedded phosphotungstic acid. Microporous Mesoporous Mater. 55-56.

Shokri, E., Yegani, R., Pourabbas, B., Kazemian, N., 2016. Preparation and characterization of polysulfone/organoclay adsorptive nanocomposite membrane for arsenic removal from contaminated water. Appl. Clay Sci. 132-133, 611-620.

Sun, B., Hao, X.G., De Wang, Z., furaGuan, G.Q., Zhang, Z.L., Bin Li, Y., Bin Liu, S., 2012. Separation of low concentration of cesium ion from wastewater by electrochemically switched ion exchange method: experimental adsorption kinetics analysis. J. Hazard. Mater. 233–234, 177–183.

Tan, Z., Niu, G., Chen, X., 2015. Removal of elemental mercury by modified bamboo carbon. Chin. J. Chem. Eng. 23, 1875-1880.

Tao, Q., Zhang, X., Prabaharan, K., Dai, Y., 2019. Separation of cesium from wastewater with copper hexacyanoferrate film in an electrochemical system driven by microbial fuel cells. Bioresour. Technol. 278, 456-459.

Tran, H.N., You, S.J, Bandegharaei, A.H., Chao, H.P., 2017. Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: A critical review. Water Res. 120, 88-16

Wang, J., Zhuang, S., 2020. Cesium separation from radioactive waste by extraction and adsorption based on crown ethers and calixarenes. Nucl. Eng. Technol. 52, 328-336.

Wang, J., Zhuang, S., Liu, Y., 2018. Metal hexacyanoferrates-based adsorbents for cesium removal. Coord. Chem. Rev. 374, 430-438.

Wang, S.Y., Tsai, M.H., Lo, S.F., Tsai, M.j., 2008. Effects of manufacturing conditions on the adsorption capacity of heavy metal ions by Makino bamboo charcoal. Bioresource Technology. 99, 7027-7033.

Wang, Y., Wang, X., Wang, X., Liu, M., Yang, L., Wu, Z., Xia, S., Zhao, J., 2012. Adsorption of Pb(II) in aqueous solutions by bamboo charcoal modified with $KMnO_4$ via microwave irradiation. Colloids Surf. A: Physicochem. Eng. Aspects. 414, 1-8.

Xia, M., Zheng, X., Du, M., Wang, Y., Ding, A., and Dou, J., 2018. The adsorption of Cs^+ from wastewater using lithium-modified montmorillonite caged in calcium alginate beads. Chemosphere. 203, 271-280.

Yang, H., Li, H., Zhai, J., Sun, L., Zhao, Y., and Yu, H., 2014. Magnetic prussian blue/graphene oxide nanocomposites caged in calcium alginate microbeads for elimination of cesium ions from water and soil. Chem. Eng. J. 246, 10-19.

Yin, C.Y., Aroua, M.K., and Daud, W.M.A.W., 2007. Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solution Sep. Puri. Tech. 52, 403-15

Zhang, J.F., Yang, L.R., Dong, T.T., Pan, F., Xing, H.F., Liu, H.Z., 2018. Kinetics-Controlled Separation Intensification for Cesium and Rubidium Isolation from Salt Lake Brine. Ind. Eng. Chem. Res. 57, 4399-4406.

Zhao, C., Liu, J., Li, X., Li, F., Tu, H., Sun, Q., Liao, J., Yang, J., Yang, Y., Liu, N., 2016. Biosorption and bioaccumulation behavior of uranium on Bacillus sp. dwc-2: investigation by box-Behenken design method. J. Mol. Liq. 221, 156-165.

Zheng, X., Dou, J., Yuan, J., Qin, W., Hong, X., and Ding, A., 2017. Removal of Cs^+ from water and soil by ammonium-pillared montmorillonite/Fe3O4 composite. J. Environ. Sci. 56, 12-24.

ACKNOWLEDGEMENT

Time flies. Here comes the end of my magister time. First of all, I would like to express my sincere gratitude to my advisor, Prof. Minhee Lee for continuous support, guide, and immense knowledge during my master research. His enthusiasm, amicability, and generosity make me feel warm in Korea. I would also like to extend my sincere gratitude to my thesis committee, Prof. Minjune Yang and Prof. Jongsik Ryu for their precious advice and comments. I would like to give appreciations to all professors in the Department of Earth and Environmental Sciences program who gave me comprehensive knowledge during the past two years.

I greatly thank Dr. Leekyung Han who always helping and encourages me. Also, I would like to thank the previous and current members of our research laboratory: Taehyoung Kim, Jinkyun Lee, Seonhee Kim, Hyunji Tak, Kyeongtae Kim, Geonwook Hwang, Danu Kim, Jihye Yang, Soyoung Jeon, Yuna Oh, and Kyounghoon Lee for their unlimited helps since the first time I arrived in Pukyong National University and the good working environment. I learned a lot working with them and also had fun every now and then. Finally, special thank goes to my dearest parents and my families. This thesis would not be completed without their love and support. Words cannot express how thankful I am to my father, my mother, my brother, and all my families.