



Rapid and selective removal of Cs⁺ from water by layered potassium antimony thiostannate

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ABSTRACT

¹³⁷Cs is radioactive and highly hazardous to human health and the environment and its efficient removal from water is still challenging. In this study, potassium antimony tin sulfide (KATS-2) was synthesized using a hydrothermal method and utilized for the first time for cesium removal from water. KATS-2 showed a high maximum ion exchange capacity (358 mg g⁻¹) and distribution coefficient (1.59 × 10⁵ mL g⁻¹) toward Cs⁺. In particular, KATS-2 showed rapid ion exchange kinetics and reached the adsorption equilibrium within 5 min with 99% removal efficiency. The adsorption was good at a wide active pH range (1–12) even in extreme alkaline conditions ($K_d = 3.26 \times 10^4$ mL g⁻¹ at pH 12). The effect of coexisting ions was also investigated, and a high selectivity toward Cs⁺ was maintained even in artificial seawater ($K_d = 3.28 \times 10^3$ mL g⁻¹). Powder X-ray diffraction and thermogravimetric analysis demonstrated that KATS-2 was chemically and thermally stable. The results showed that owing to its excellent adsorption performance as well as chemical and thermal stability, KATS-2 is a promising adsorbent for Cs⁺ removal from contaminated water.

1. Introduction

In order to meet the increasing energy demand and alleviate global warming, nuclear power has recently garnered increased attention. However, nuclear power plant water consumption is 20–83% greater than coal-fired power plants with the same capacity (Khamis and Kavvadias, 2012). Of greater concern is the resulting wastewater, with pH values ranging from extremely acidic to strongly alkaline, which contain a multitude of radionuclides (Valsala et al., 2011). ¹³⁷Cs, the main hazardous radionuclide, poses a threat to human health owing to its production of gamma rays and high-energy beta particles and its long half-life ($t_{1/2} \approx 30$ years) (Sarma et al., 2016; Rathore et al., 2017; Chaudhury et al., 2014). The coexistence of highly concentrated nonradioactive ions in wastewater makes ¹³⁷Cs separation extremely challenging; therefore, a new material with high ¹³⁷Cs selectivity needs to be developed.

Chemical precipitation, membrane separation, electro-dialysis, solvent extraction, biological treatment, and ion exchange have been utilized to remove radioactive Cs from water (Zhang and Hu, 2017; Osmanlioglu, 2018; Kim et al., 2020; Mahendra et al., 2014; Ding et al., 2017). Of these methods, ion exchange is an attractive method for Cs⁺ removal due to its simple operation, relatively low cost, and high

efficiency (Crini and Lichtfouse, 2018).

Metal sulfides have garnered significant attention as one of the selective ion exchangers for radionuclide removal from contaminated water (Sengupta et al., 2014; Ding and Kanatzidis, 2010; Zhang et al., 2020). The existence of the Lewis soft S²⁻ ligand in the metal sulfide framework gives them an innate high affinity to Lewis soft acid (Pearson, 1963). In addition, because the open accessible structures of layered metal sulfides can contribute to ion exchange, layered metal sulfides have become highly popular (Sarma et al., 2016); however, there are still issues with the existing materials. For example, Mn²⁺ to Mn³⁺ oxidation during the ion exchange process causes KMS-1 to have a less than theoretical adsorption capacity for Cs⁺ (Manos and Kanatzidis, 2009). KMS-2 (Mertz et al., 2013) and KTS-3 (Sarma et al., 2016) possess lower selectivity to Cs⁺ in the presence of high competitive ion concentrations. For FJSM-SnS (Qi et al., 2015) and InSnOS (Wang et al., 2019a), synthesis was extremely slow, Cs⁺ selectivity was low in highly alkaline conditions, and an undesirable release of organic moieties occurred due to the ion exchange (Rathore et al., 2017).

Recently, Sb³⁺ based chalcogenide has attracted significant interest because the lone-pair electrons tend to adopt asymmetric coordination geometries and often undergo self-condensation when combined with chalcogenide ions to form oligomeric chains or rings. This contributes to

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improvement in the variety of versatile chalcogenidometalates (Feng et al., 2016). Moreover, the Sb^{3+} lone-pair electrons could cause it to function as a Lewis base, therefore, binding with metal ions. Compared with Sn^{4+} , Sb^{3+} is relatively less positively charged and has a larger ionic radius; therefore, a more Lewis basic Sb^{3+} -contained layer is expected to possess a high affinity to metal ions (Wang et al., 2019b). Furthermore, the addition of Lewis basic Sb^{3+} could allow the chalcogenide structure to withstand a more basic environment (Mertz et al., 2013). However, there have been no reports for the utilization of antimony chalcogenides to remove Cs^+ from water (Hassanzadeh Fard et al., 2015).

In this study, layered potassium antimony tin sulfide (KATS) was developed utilizing a one-pot hydrothermal method, which was applied for the first time for Cs^+ removal from water. The results indicated that the KATS material could maintain its distribution coefficient over a wide pH range (1–12) and the ion exchange for Cs^+ rapidly reached equilibrium within 5 min. Furthermore, a high maximum Cs^+ exchange capacity of 358 mg g^{-1} was also achieved.

2. Materials and method

2.1. Chemicals and materials

Cesium nitrate (CsNO_3 , 99.8% metal basis) and antimony(III) oxide (Sb_2O_3 , 99%) were purchased from Alfa Aesar (USA) and Sigma Aldrich (USA), respectively. Sulfur powder (S, 99%), tin powder (Sn), potassium carbonate anhydrous powder (K_2CO_3 , 99.5%), hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH, 97%), sodium chloride (NaCl, 99.5%), potassium chloride (KCl, 99%), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 98%), and acetone ($\text{C}_3\text{H}_6\text{O}$, 99.8%) were purchased from Daejung Chemicals and Metals Co., Ltd. (South Korea). Calcium chloride (CaCl_2 , 95%) and artificial seawater were purchased from Kanto Chemical Co., Inc. (Japan) and Coralife (USA), respectively. All the chemicals were used without any further purification during the experiments.

2.2. KATS synthesis

KATS-2 was synthesized using a simple one-pot hydrothermal method. First, K_2CO_3 (3.3337 g, 24 mmol), Sb_2O_3 (0.5889 g, 2 mmol), tin powder (2.8634 g, 24 mmol), and sulfur powder (3.8867 g, 120 mmol) were mixed in a 100 mL Teflon-lined stainless-steel autoclave and $\sim 1.8 \text{ mL}$ deionized water was added dropwise. Thereafter, the autoclave was sealed well, placed in a preheated electric furnace at 200°C for 24 h, and then cooled naturally at room temperature. The resultant product was isolated by a centrifuge (Combi 514R, Hanil Scientific), washed several times with deionized water and acetone, and dried in a vacuum oven at 60°C for 18 h. The final product collected was a dark yellow powder. Other KATSs with different Sb_2O_3 dosages (1, 4, 6, and 12 mmol) were synthesized by the same procedure and named as KATS-1, KATS-4, KATS-6, and KATS-12, respectively.

2.3. Characterization

Field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDS) analyses were performed using a SUPRA 25 scanning electron microscope (SEM) with a MIRA 3 LMH In-Beam EDS detector (Zeiss). Thermogravimetric analysis was performed using a thermal analyzer system (STA6000, PerkinElmer) under nitrogen atmosphere with a $10^\circ\text{C min}^{-1}$ heating rate from approximately 25°C to 600°C for the KATS and Cs-loaded KATS analyses. The powder X-ray diffraction (PXRD) patterns were analyzed at room temperature with an Xpert 3 X-ray powder diffractometer (Malvern Panalytical) operating at 40 kV and 30 mA. X-ray photoelectron spectra (XPS) were collected by using an AXIS SUPRA X-ray photoelectron spectrometer (Kratos Analytical) with a monochromatic Al $\text{K}\alpha$ X-ray source

(1486.6 eV). Samples were analyzed with 160 and 20 eV pass energy (survey and high-resolution scans, respectively). All peaks were referenced to the $\text{C}1s$ peak signature. Inductively coupled plasma mass spectrometry (ICP-MS) (iCAP TQ, ThermoFisher Scientific) and inductively coupled plasma mass optical emission spectrometry (ICP-OES) (Optima 8300, Perkin Elmer) were used for metal ion concentration measurements (K, Cs, Sn, and Sb). Nitrogen adsorption and desorption isotherms were measured at 77 K using liquid nitrogen on an ASAP 2020 (Micromeritics) system. Samples were degassed at 333 K under vacuum for 15 h.

2.4. Adsorption

All experiments were conducted a minimum of three times. The typical experiments for Cs adsorption were carried out as follows. First, 25 mg of adsorbent and 25 mL of Cs^+ solution with a specific concentration were added in a 30 mL scintillation vial. Then, the mixture (pH = 7) was shaken in an orbital shaker (SHO-2D, Daihan) at room temperature. The adsorbent was separated by a $0.20 \mu\text{m}$ membrane filter (DISMIC cellulose acetate 25CS type, Advantec). The Cs^+ concentrations in the filtrates were analyzed by an atomic absorption spectrometer (AAS-200, PerkinElmer).

In order to determine the optimal Sb precursor dosage, Cs^+ adsorption experiments were conducted using KATSs synthesized at various Sb_2O_3 dosages (1, 2, 4, 6, and 12 mmol). The Cs^+ solution concentration was 500 ppm and it was kept in the orbital shaker for 18 h. To study the adsorption kinetics, adsorption experiments of various contact times (1, 5, 15, 30, 60, 120, 300, and 1080 min) were performed. The initial Cs^+ concentration was approximately 20 ppm. In the isotherm experiments, solutions were prepared with different Cs^+ concentrations (4.81–1097 ppm) and the contact time was 5 h.

Cs^+ ion exchange experiments at various pH values and competing ion concentrations were also performed. The required pH values (1, 2, 4, 6, 7, 8, 10, and 12) were adjusted by adding HCl and NaOH solutions into the Cs^+ solution ($\sim 20 \text{ ppm}$). The ion exchange experiments at various Na^+ , K^+ , Mg^{2+} , and Ca^{2+} concentrations were performed by dissolving the required amount of NaCl, KCl, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, and CaCl_2 , respectively, in 100 mL of Cs^+ solution ($\sim 20 \text{ ppm}$). Furthermore, to assess the Cs^+ adsorption performance in a real water environment, artificial seawater with $\sim 17.6 \text{ ppm}$ of Cs^+ was used. The contact time for the experiments was 5 h.

The adsorption capacity at equilibrium, q_e (mg g^{-1}), removal efficiency, R (%), and distribution coefficient, K_d (mL g^{-1}), were calculated based on the following equations:

$$q_e = [(C_0 - C_e) \times V] / m \quad (1)$$

$$R = [(C_0 - C_e) / C_0] \times 100 \quad (2)$$

$$K_d = [(C_0 - C_e) \times V] / (C_e \times m) \quad (3)$$

where C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the initial and final concentrations of Cs^+ in the solution, respectively; m (g) is the mass of the adsorbent; and V (mL) is the Cs^+ solution volume.

3. Results and discussion

3.1. Sb dosage effect

The Sb_2O_3 dosage effect was investigated to obtain an optimal synthesis condition for the adsorbent. Fig. S1a shows the typical appearances of the different KATSs. The colors of these powders changed from orange yellow to dark brick red with increasing Sb dosages. The chemical formulae derived from the element analysis of the KATS powders (Table S1) confirm the increasing amount of incorporated Sb to the Sn-S matrix of KATS as the Sb precursor dosage was increased in

adsorbent synthesis. To further study the structure of the as-prepared KATS adsorbents, PXRD analysis was carried out. PXRD patterns (Fig. S2) reveal that KATS-1 and KATS-2 have similar crystal structure to that of KTS-3 (Sarma et al., 2016). The crystal structure of KATS changed at higher Sb dosage with KATS-12 almost losing its crystallinity.

To test the adsorption performance of the different KATSs, a Cs^+ adsorption experiment was performed with an initial concentration of 500 ppm. Fig. 2a shows the adsorption capacity at various Sb_2O_3 dosages. As the dosage increased from 1 to 2 mmol, the Cs^+ adsorption capacity also increased, which can be attributed to the replacement of Sn by Sb while preserving the crystal structure. Increasing the Sb_2O_3 dosage further decreased the adsorption capacity. This can be explained by sample morphology. When small Sb precursor amounts were utilized (KATS-1 and KATS-2; Fig. S1b and c, respectively), the morphologies of the KATSs were similar to those of Sn-based metal sulfides, such as KTS-3 (Sarma et al., 2016) and NaTS (Zhang et al., 2019). This is caused by the replacement of some Sb atoms with Sn atoms, which are then incorporated into the Sn-S matrix, and retention of the crystal structure similar to that of Sn-based metal sulfides; however, with continued increase of the Sb_2O_3 dosage (4–12 mmol), the KATS morphology became similar to that of the Sb-based metal sulfide and the crystal structures were obviously different from KATS-1 and KATS-2 (Zhang et al., 2016). This may be attributed to the reaction between Sb and S, and because the Sb atoms blocked the Sn diffusion pathway, thereby leading to small particle formation. A similar phenomenon was also found in PbSbTe (Su et al., 2015). The destroyed layer possibly blocked the diffusion of interchangeable K^+ and caused an adsorption capacity decrease. Moreover, compared to nanoparticles, hierarchically structured 2D nanosheet materials can provide well-ordered channels for mass transfer and robust structure for stability, which can improve the adsorption performance. This elucidates the decline in the adsorption capacities of KATS powders with Sb precursor dosage of 2–12 mmol (Wang et al., 2020). The highest adsorption capacity (294.85 mg g^{-1}) was achieved with a 2 mmol Sb_2O_3 dosage; therefore, KATS-2 was chosen for further experiments.

3.2. KATS-2 characterization

FE-SEM images of KATS-2 at various magnifications (Fig. 1a and b)

demonstrated the layered morphology. The N_2 adsorption-desorption isotherms (Fig. S3a) demonstrated that KATS-2 was mesoporous adsorbent and the occurrence of the H-3 hysteresis indicated the mesopores have cylindrical and slit-shaped geometries (Gregg et al., 1967). Moreover, pore size distribution calculated from the desorption process by the Barrett–Joyner–Halenda method showed a broad pores size range of 5–61 nm, and the average pore size was 30.39 nm (Fig. S3b).

KATS-2 was also analyzed by semi-quantitative EDS (Fig. S4), which showed the presence of K, Sb, Sn, and S, and an average formula of KATS-2, $\text{K}_{1.59}\text{Sb}_{0.07}\text{Sn}_3\text{S}_{6.68}$, was obtained. To more accurately determine the atomic contents of the KATS-2 compound, ICP-OES was used to analyze the concentration of each element after dissolving the powder sample in an aqua regia solution. The chemical formula of KATS-2 derived from the results of the elemental analysis was $\text{K}_{1.29}\text{Sb}_{0.15}\text{Sn}_3\text{S}_{6.87}$. In addition, the K, Sb, Sn, and S elements were homogeneously dispersed on the KATS-2 surface, which was indicated by the elemental mapping images (Fig. 1c).

KATS-2 thermal stability was analyzed by a thermogravimetric analysis. As shown in Fig. S5a, a weight loss of 16.2% was observed, which mainly corresponds to the adsorbed water molecule loss. A similar phenomenon was also found in the other chalcogenides (Sarma et al., 2016). Furthermore, the compound can remain stable in temperatures up to 480°C with a weight loss of $\sim 16.9\%$, which reveals the excellent thermal stability of KATS-2. As shown in Fig. S5b, the PXRD patterns of the pristine KATS-2 and KATS-2 treated in solutions with various pH values for 24 h indicated that its structure was very stable over a wide pH range (4–12). After being treated in solutions with a pH of 1 and 2, the XRD patterns were very different from those of the pristine material and revealed KATS-2 decomposition under these conditions.

The XPS full survey spectra demonstrated that KATS-2 was composed of K, Sb, Sn, and S (Fig. 2b) and the high-resolution spectra are shown in Fig. S6. The two peaks centered at 292.9 and 295.7 eV are characteristic of the K^+ ions of $2p_{3/2}$ and $2p_{1/2}$, respectively (Moulder, 1992) and the 486.3 and 494.7 eV peaks are characteristic of the Sn^{4+} ions of $3d_{5/2}$ and $3d_{3/2}$, respectively (Moulder, 1992). The two peaks at 529.5 and 530.4 eV correspond to Sb^{3+} $3d_{5/2}$ and the two peaks at 538.8 and 539.7 eV correspond to Sb^{3+} $3d_{3/2}$ (Moulder, 1992). In addition, the broad band deconvolution showed two bands centered at 161.1 and

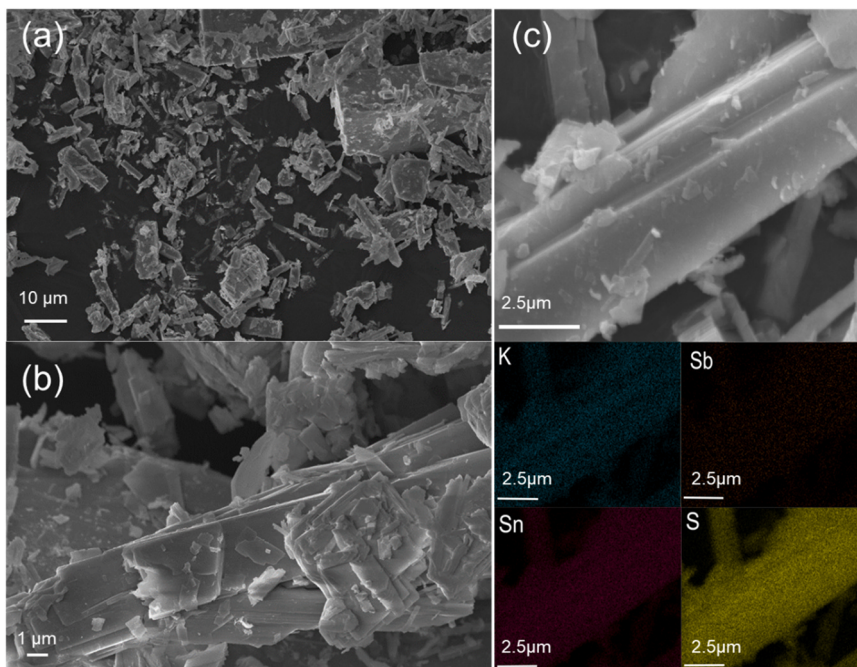


Fig. 1. (a–b) FE-SEM images of KATS-2 at two magnifications, and (c) SEM-EDS elemental mapping of KATS-2.

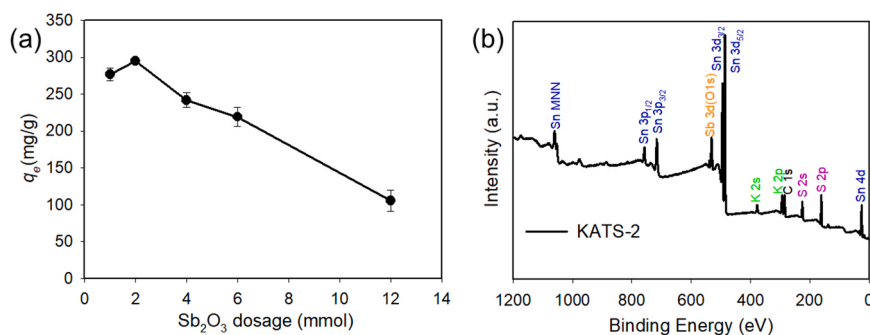


Fig. 2. (a) Cs^+ uptake capacity at equilibrium (q_e) with various Sb_2O_3 dosages; (b) XPS full survey spectra of KATS-2.

162.3 eV, which are characteristics of the $2p_{3/2}$ and $2p_{1/2}$ of the S^{2-} anion, respectively (Moulder, 1992).

3.3. Adsorption kinetics

Rapid adsorption kinetics was observed in this study. As shown in Fig. 3a, the Cs^+ concentration decreased sharply from 20 to 0.3325 mg L^{-1} in the first minute and 98% removal efficiency was achieved. Within 5 min the removal efficiency reached 99%, which was maintained for the duration of the experiment. The KATS-2 rapid removal kinetics and high removal efficiency are comparable with some metal sulfides including KMS-1 (equilibrium time, $t_e = \sim 5$ min and $R = 90\%$) (Manos and Kanatzidis, 2009), KTS-3 ($t_e = \sim 5$ min and $R = 94\%$) (Sarma et al., 2016), FJSM-SnS ($t_e = 5$ min at 65°C) (Qi et al., 2015), and InSnOS ($t_e = 5$ min) (Wang et al., 2019a), and are much faster than other adsorbents, such as Cu-BTC/KNiFC ($t_e = 45$ min) (Naeimi and Faghihian, 2017), FJSM-InMOF ($t_e = 3$ h) (Gao et al., 2018), and $\text{K}_4\text{Nb}_6\text{O}_{17}$ ($t_e = 5$ h) (Sun et al., 2014).

The kinetic data were fitted to the linear form of the pseudo-first-order and pseudo-second-order models, which are expressed by Eqs. (S1) and (S2), respectively.

The fitted results are presented in Figs. 3b and S7 and Table 1. The correlation coefficient value (R^2) and the agreement of the calculated q_e with the experimental data showed a good fitting with the pseudo-second-order model. Moreover, the large KATS-2 rate constant ($k_2 = 0.5791 \text{ g mg}^{-1} \text{ min}^{-1}$) demonstrated rapid adsorption kinetics, which can be attributed to the rapid diffusion of K^+ and Cs^+ from and into the layered KATS-2 inner channels, respectively. The rapid ion exchange kinetics of the KATS-2 implies that it is a good candidate for real applications, including nuclear power plant accidents.

3.4. Adsorption isotherms

To evaluate the KATS-2 adsorption performance, a systematic adsorption isotherm study was performed by varying the Cs^+

concentration in the solution. Langmuir, Freundlich, and Sips isotherm models were used to fit the Cs^+ adsorption data. The equations of each model are shown in Section S2, and the fitted values of each parameter are presented in Table 2.

The Langmuir isotherm refers to homogeneous adsorption, which assumes monolayer adsorption where the adsorption can only occur at fixed sites (Foo and Hameed, 2010). The Freundlich isotherm is an empirical model and can be applied to multilayer adsorption and the adsorption affinity differs based on surface sites (Blázquez et al., 2011; Violante et al., 2008). The Sips isotherm is a combination of the Langmuir and Freundlich models, which reduces to the Freundlich or Langmuir isotherms at low or high adsorbate concentrations, respectively (Pérez-Marín et al., 2007).

As shown in Fig. 4a, the KATS-2 equilibrium adsorption capacity of Cs^+ initially increased rapidly and eventually reached saturation. The Sips model showed the highest correlation coefficient ($R^2 = 0.99$) of the three models. The n_s value of the Sips model is regarded as the parameter characterizing the system heterogeneity. When this parameter approaches unity, the Sips equation reduces to the Langmuir equation. As n_s departs from unity, the adsorption system becomes more heterogeneous. In our work, the n_s value was 1.69, suggesting heterogeneous cesium uptake by KATS-2 which could be attributed to the different adsorption sites of KATS-2, the detailed explanation will be given in Cs adsorption mechanism on KATS-2 section (Do, 1998).

From the Sips isotherm model, the maximum adsorption capacity (q_m) of Cs^+ was found to be 358 mg g^{-1} , which was compared with other adsorbents (Table S2). This value was greater than that of K-MPS-1 (337.5 mg g^{-1}) (Rathore et al., 2017), KTS-3 (280 mg g^{-1}) (Sarma et al., 2016), KMS-1 (226 mg g^{-1}) (Manos and Kanatzidis, 2009), Zeolite A (207.47 mg g^{-1}) (El-Kamash, 2008), FJSM-InMOF (198.63 mg g^{-1}) (Gao et al., 2018), and $\text{K}_4\text{Nb}_6\text{O}_7$ ($166.125 \text{ mg g}^{-1}$) (Sun et al., 2014), and was significantly larger than that of commercial AMP-PAN (81 mg g^{-1}), which is currently marketed as UOP IONSIV IE-910 (Park et al., 2010). The value was lower than InSnOS (537.7 mg g^{-1}) (Wang et al., 2019a), KMS-2 (531.7 mg g^{-1}) (Mertz et al., 2013), hf-TiFC

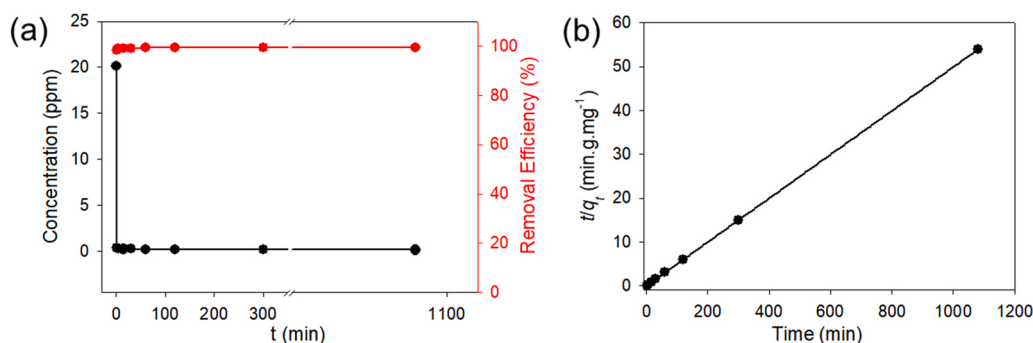


Fig. 3. (a) Cs^+ concentration and removal efficiency (%) at various times, and (b) fitting of kinetics data using the pseudo-second-order model. The solid to liquid ratio was 1 g L^{-1} and C_0 was ~ 20 ppm.

Table 1Parameters of pseudo-first-order and pseudo-second-order models for the kinetic data of Cs⁺ adsorption on KATS-2.

Pseudo-first-order			Pseudo-second-order			Experimental
k_1 (min ⁻¹)	$q_{e,cal}$ (mg g ⁻¹)	R^2	k_1 (g mg ⁻¹ min ⁻¹)	$q_{e,cal}$ (mg g ⁻¹)	R^2	q_e (mg g ⁻¹)
0.0097	0.1040	0.7779	0.5791	20.0400	1.0000	20.0357

Table 2

Parameters obtained by the Langmuir, Freundlich, and Sips isotherm models.

Model	Parameter	Value
Langmuir	q_e (mg g ⁻¹)	312
	K_L (L mg ⁻¹)	0.1491
	R^2	0.9653
Freundlich	K_F (mg g ⁻¹ (L mg ⁻¹) ^{1/n_f})	73.7745
	1/n _f	0.2389
	R^2	0.9471
Sips	q_e (mg g ⁻¹)	358
	K_S (L mg ⁻¹) ^{1/n_s}	0.2108
	n _s	1.6863
	R^2	0.9912

(454.54 mg g⁻¹) (Yang et al., 2019), MIL-101-SO₃H (453 mg g⁻¹) (Aguila et al., 2016), and FJSM-SnS (408.91 mg g⁻¹) (Qi et al., 2015); however, the KATS-2 selectivity was significantly higher than most of these adsorbents, which is discussed in detail in Sections 3.4 and 3.5.

3.5. Effect of pH

A solution's pH value is a significant factor for Cs⁺ removal from an aqueous solution. As shown in Fig. 4b, the final pH increased for the initial pH of 4 and 6 and decreased for the initial pH of 8 and 10 after KATS-2 was dispersed into the Cs⁺ solution, which indicates that KATS-2 can act not only as a proton acceptor but also as a proton donor according to the pH environment.

KATS-2 showed excellent Cs⁺ adsorption performance in a wide pH range. As demonstrated in Fig. 4b and c, the KATS-2 removal efficiency of Cs⁺ exceed 97% in the pH range of 4–12, and the K_d values ranged from 3.26×10^4 to 1.59×10^5 mL g⁻¹. This excellent performance was mainly attributed to the chemical stability of KATS-2 at these pH conditions, which was proven by the PXRD pattern as shown in Fig. S5b. Based on the results, it is posited that the addition of Lewis basic Sb³⁺ might allow KATS-2 to withstand a more basic environment (Mertz et al., 2013).

KATS-2 was very stable and showed a high K_d value (3.26×10^4 mL g⁻¹) at a pH of 12. As shown in Fig. S8, the KATS-2 K_d value toward Cs⁺ was higher than InSnOS (Wang et al., 2019a), KMS-2 (Mertz et al., 2013), MIL-101-SO₃H (Aguila et al., 2016), and FJSM-SnS (Qi et al., 2015) except hf-TiFC (Yang et al., 2019), which had higher q_m values than KATS-2. Moreover, the cesium species predicted by MINTEQ (version 3.1) at different solution pH values is shown in Fig. S9. Result of the simulation indicated that cesium exists as Cs⁺ at pH values 0–14, which is also demonstrated by previous researches (Park et al., 2010; Takeno, 2005; Alby et al., 2018). This confirms that the excellent adsorption performance of KATS-2 at pH 12 was not due to the precipitation of cesium into metal hydroxide at this pH level. In extreme acidic conditions, the KATS-2 K_d value was slightly decreased at pH ~ 2 (1.32×10^3 mL g⁻¹) and sharply decreased at pH ~ 1 (179.86 mL g⁻¹), which may be due to the competition of H⁺ with Cs⁺ and the different degrees of decomposition of KATS-2 at pH 1 and 2 (Fig. S10). Although K_d decreased, as shown in Fig. S7, it still is comparable with KMS-2 (Mertz et al., 2013), InSnOS (Wang et al., 2019a), and KTS-3 (Sarma et al., 2016), and although FJSM-SnS showed a higher K_d value in

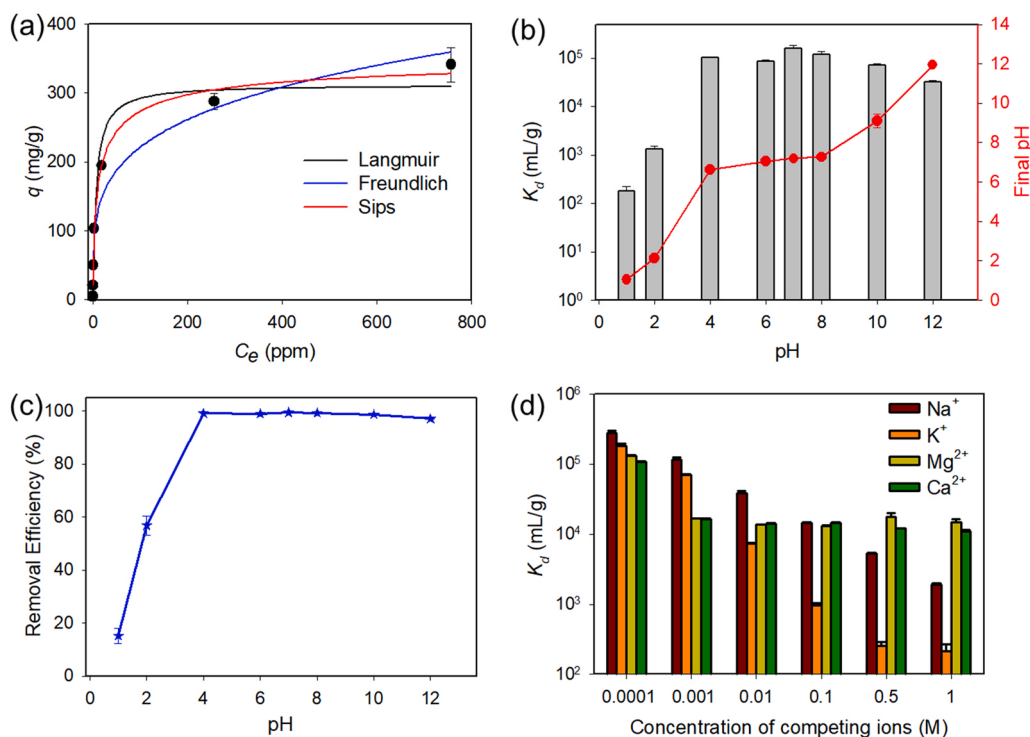


Fig. 4. (a) Adsorption isotherm for Cs⁺ and fittings by various isotherm models; variation of (b) distribution coefficient, K_d and (c) Cs⁺ removal efficiency at various pH values; and (d) distribution coefficient, K_d , at various molar concentrations of four competing ions. All the experiments above were conducted at a contact time of 5 h.

extreme acidic conditions, the release of organic moieties after the ion exchange is undesirable (Qi et al., 2015).

The favorable adsorption performance of KATS-2 over a wide pH range can be interpreted by the low point of zero charge value. A previous study showed the point of zero charges of metal sulfides were between 0.6 and 3.3 with most values below pH 2 and had a negative correlation with their electronegativities (Bebie et al., 1998). Because the electronegativities of Sb_2S_3 and SnS_2 are in the same range of most transition metal sulfides, their point of zero charges should also be around pH 2. The KATS-2 surface is negatively charged above pH 4, which facilitates cation transport in the electric layer and neutralizes the surface negative charge (Zhang et al., 2015). Thus, KATS-2 could achieve high K_d and R values at pH values of 4 and higher. This remarkable performance in a wide pH range, especially in extreme alkaline conditions, makes KATS-2 an excellent candidate for Cs^+ removal in real applications because the pH of most radionuclide wastewater is adjusted to alkaline conditions for storage tank protection (Liu and Han, 2019; Gephart, 2010).

3.6. Competing cation effects

K_d represents the adsorbent selectivity toward Cs^+ . To study the effect of coexisting ions on the KATS-2 selectivity toward Cs^+ , four metal cations commonly found in water, such as Na^+ , K^+ , Mg^{2+} , and Ca^{2+} , were chosen as the competing cations and their concentrations varied from 0.0001 to 1 M.

As shown in Fig. 4d, the K_d values were greater than $1.07 \times 10^5 \text{ mL g}^{-1}$ at a concentration of 0.0001 M and at this concentration, there is no cation effect on the Cs^+ adsorption. As the concentration increased, K_d decreased. Up to a concentration of 0.001 M, divalent ions such as Mg^{2+} and Ca^{2+} affected K_d more than the monovalent ions, which is probably due to their electrostatic effect. The ionic strength of the divalent ion solution is greater than that of the monovalent ion solution, resulting in the thinning of the electric double layer thickness. Also, the electrostatic attraction between the negative KATS-2 surface and the cations is greater for divalent ions (Kang et al., 2020).

However, when the competing cation concentration increased from 0.01 to 1 M, the K_d decrease was more noticeable for the monovalent ions because the ionic radius effect overrode the charging effect where at high cation concentrations, the compression of the electric double layer was saturated (Shaw, 1980). In particular, K^+ showed a dominant effect as K_d was 213 mL g^{-1} at 1 M. K^+ has a more similar hydrated radius (3.31 Å) with Cs^+ (3.29 Å) than the other cations, such as Na^+ (3.58 Å), Ca^{2+} (4.12 Å), and Mg^{2+} (4.28 Å) (Alamudy and Cho, 2018). The cation effect toward Cs^+ adsorption at high concentrations was in the order of $\text{K}^+ > \text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$. As shown in Table S3, the K_d toward Cs^+ determined by this study for KATS-2 was lower than that of InSnOS and hf-TiFC (Wang et al., 2019a; Yang et al., 2019); however, it was much higher than that of KTS-3 (Sarma et al., 2016), $\text{K}_4\text{Nb}_6\text{O}_{17}$ (Sun et al., 2014), and APS-4 (Chen et al., 2019).

To investigate the applicability of KATS-2 to remove cesium from real water systems, Cs^+ -spiked reproducible artificial seawater (ASW) was used as the adsorbate solution. Using ASW addresses the problem on seasonal variability in the quality and organics content of natural seawater, as ASW contains the major seawater ionic species, such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , Br^- , and NO_3^- , and it has a salinity of 3.24% similar to that of real seawater (3.5%) (Mathew et al., 2016). The concentrations of main ASW components are listed in Table S4. The K_d at this condition was high ($3.28 \times 10^3 \text{ mL g}^{-1}$), which is comparable with K-RWY (Yang et al., 2016), NaMT1 (Kim et al., 2018), and K-MPS-1 (Rathore et al., 2017), and significantly higher than FJSM-SnS and MIL-101- SO_3H (Qi et al., 2015; Aguila et al., 2016). This high selectivity toward Cs^+ is attributed to the soft S^{2-} base in KATS-2, which has a higher affinity to soft Cs^+ acid than other hard cations such as Na^+ and Mg^{2+} ; therefore, KATS-2 can selectively remove Cs^+ from real water systems.

3.7. Cs adsorption mechanism on KATS-2

Several methods were utilized to study the KATS-2 adsorption mechanism toward Cs^+ . First, ICP-MS and ICP-OES were used to determine the amount of Cs^+ adsorbed onto the KATS-2 and the amounts of K^+ , Sb^{3+} , and Sn^{4+} released from the KATS-2. In Table S5, the molar ratio of the sum of the released K^+ , Sb^{3+} , and Sn^{4+} to adsorbed Cs^+ was 1.11. This value, which is slightly higher than unity, may be due to the H^+ adsorption onto the KATS-2. The solution pH increased slightly after adsorption. Similarly, the KATS-2 SEM-EDS results (Figs. S4 and S11) also showed the increased Cs and decreased K molar ratios after adsorption. The average molar ratio of each element in the KATS-2 and Cs-loaded KATS-2 were $\text{K:Sb:Sn:S} = 1.59:0.07:3:6.68$ and $\text{Cs:K:Sb:Sn:S} = 1.56:0.17:0.08:3:6.43$, respectively.

Second, XPS was used to analyze the KATS-2 and Cs-loaded KATS-2. Comparing the two full survey spectra (Fig. 5a), the characteristic Cs^+ peaks (724.2 and 738.1 eV for $\text{Cs } 3d_{5/2}$ and $\text{Cs } 3d_{3/2}$, respectively) were newly discovered in the Cs-loaded KATS-2 (Fig. 5b) (Moulder, 1992). Furthermore, as shown in Fig. S12, the K^+ peak height in the Cs-loaded KATS-2 was significantly reduced compared to the KATS-2 peak (292.9 and 295.7 eV for $\text{K } 2p_{3/2}$ and $\text{K } 2p_{1/2}$, respectively), which indicates an ion exchange between Cs^+ and K^+ (Moulder, 1992). The binding energy of $\text{Sn } 3d_{3/2}$ and $\text{Sn } 3d_{5/2}$ did not change after adsorption. However, the main binding energy of $\text{Sb } 3d_{5/2}$ and $\text{Sb } 3d_{3/2}$ increased from 529.4 and 538.7 eV to 529.5 and 538.8 eV, which indicates a lower electron density around Sb possibly due to chemisorption of Lewis soft Cs^+ through the lone pair electron of Lewis soft base Sb^{3+} (Fig. S13a and S13b) (Pearson, 1963; Yashonath et al., 1982; Whittles, 2018). The binding energy shift of the S 2p was observed in the high-resolution spectrum (Fig. 5c). S $2p_{3/2}$ decreased from 161.11 to 161.02 eV, and S $2p_{1/2}$ decreased from 162.29 to 162.20 eV after the ion exchange, which indicates a higher electron density for S in the Cs-loaded KATS-2 (Moulder, 1992; Whittles, 2018). The substitution of less electronegative Cs for K resulted in a higher electron density for S. This phenomenon possibly demonstrated the electron transfer from Cs to S when Cs^+ was adsorbed onto the KATS-2 and the formation of Cs-S bonding. According to Pearson's hard-soft-acid-base theory, soft S^{2-} base has a higher affinity to softer acid Cs^+ compared to K^+ (Pearson, 1963). Thus, the ion exchange between Cs^+ and K^+ could result in the formation of stronger Cs-S bonding.

The PXRD patterns (Fig. 5d) showed that the Cs-loaded KATS-2 was isostructural to KATS-2, which confirmed the topotactic exchange mechanism. The main XRD peak shifted, lowering 2θ from 10.69° to 10.14° with an increasing d -spacing of 0.828–0.872 nm, respectively, after ion exchange because the Cs^+ ionic radius is larger than K^+ (Mertz et al., 2013). However, the Cs-loaded KATS-2 morphology remained the same as KATS-2 (Fig. S14). In addition, the SEM-EDS elemental mapping of Cs-loaded KATS-2 in Fig. S15 showed the new and homogeneous Cs distribution and less K distribution after adsorption, while other elements appeared unchanged. To demonstrate the thermal stability of Cs-loaded KATS-2, a thermogravimetric analysis was also executed. As shown in Fig. S16, weight loss of 9.6% was due to the adsorbed water molecules. Notably, the Cs-loaded KATS-2 remained stable in temperatures up to 488°C , which is of great significance for Cs-loaded adsorbent storage.

4. Conclusions

In this study, KATS-2 was successfully synthesized by the one-pot hydrothermal method, and for the first time, was applied for the removal of Cs^+ in water. Substitution of more Lewis basic Sb^{3+} for Sn^{4+} produced a higher affinity to Cs^+ ($q_m = 358 \text{ mg g}^{-1}$), had greater stability in extreme alkaline conditions ($K_d = 3.26 \times 10^4 \text{ mL g}^{-1}$ at pH 12), and had rapid kinetics (equilibrium time of 5 min). High selectivity toward Cs^+ was observed even at high salt concentrations and in artificial seawater ($K_d = 3.28 \times 10^3 \text{ mL g}^{-1}$). The excellent properties of KATS-2

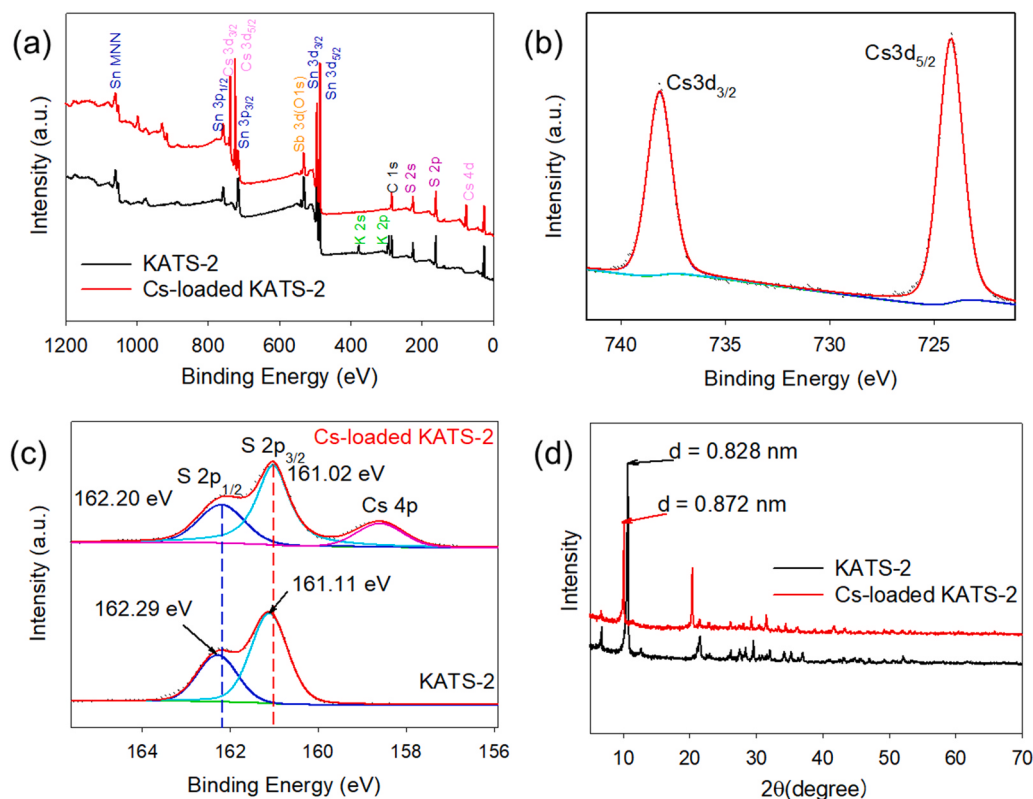


Fig. 5. (a) XPS survey spectra of pristine KATS-2 and Cs-loaded KATS-2, (b) high-resolution spectra of Cs 3d, (c) high-resolution spectra of S 2p, and (d) PXRD patterns of pristine KATS-2 and Cs-loaded KATS-2.

show promise for the application of Cs removal from water.

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CRediT authorship contribution statement

Chenyang Yang: Conceptualization, Methodology, Writing - original draft. **Kuk Cho:** Validation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Declarations of interest

None.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the

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