Effective utilization of waste cathode ray tube glass—Crystalline silicotitanate synthesis

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ABSTRACT

A novel process for crystalline silicotitanate (CST) synthesis was developed using waste cathode ray tube (CRT) panel glass as silicon source. The key trait of the process was to extract most of the silicon out of the glass for CST preparation, but leave Ba and Sr in the residue which had the potential to be employed as raw material for metallic Ba and Sr metallurgy. In the synthesis process, waste CRT panel glass was firstly treated by supercritical water (SCW)–NaOH solution for Si extraction, then sol–gel and hydrothermal treatments were used for CST preparation. 80% of Si in the glass could be extracted into the solution, while Sr and Ba were enriched in the residue in the form of Sr_2SiO_4 and $Ba_2Si_3O_8$, respectively. Sr and Ba contents in the residue were 2–3 times higher than those in the raw glass. SEM, XRD and TEM results indicated that CST was successfully synthesized. Ion exchanging experiments showed that the batch distribution coefficient of the synthesized CST to Cs^+ was up to 1.2×10^4 mL/g at pH 0.26.

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1. Introduction

In recent years, the replacement of cathode ray tube (CRT) televisions and monitors by liquid crystal display (LCD), light emitting diode (LED) panel or plasma display panel (PDP) is particularly significant, causing millions of units of waste CRT. CRT glasses contain poisonous heavy metals [1]. Lead (Pb), in particular, represents a serious threat to the environment and human health [2]. Therefore, technologies for CRT glass treatment and reutilization are urgently required, especially in China, where is the destination of more than 70% of the world's Waste Electrical and Electronic Equipment (WEEE) [3].

Thus far, many studies have been carried out on CRT glass treatments [4–21]. In previous years, CRT glass was generally cleaned, sorted and sent to glass manufacturers for new CRT glass manufacturing. Currently, due to the extreme reduction in CRT production, much attention had been attracted to the recycle of CRT glass as a secondary raw material, such as reutilization as glaze [4,5], glass ceramic [6], foam glass [7–12] and glass matrix composites [13–16]. Nevertheless, these methods paid little attention to the environmental security, since the prepared products still contain dangerous heavy metals, which should be removed or separated. Therefore, technologies for lead extraction were proposed, such as

ultrasonically enhanced leaching [19], subcritical water-aided acid leaching [20] and vacuum-aided pyro-metallurging [21]. However, these extraction methods only focused on extracting/recycling lead from lead containing CRT funnel glass. Thus far, very limited information is available on environment benign technologies for recycling Ba/Sr from Ba/Sr containing CRT panel glass. According to our recent study, this type of glass was splendid for crystalline silicotitanate (CST) synthesis.

CST ($Na_2Ti_2O_3SiO_4 \cdot 2H_2O$), with a sitinakite-like structure, jointly developed by Sandia National Laboratories and Texas A&M University [22], is a kind of useful inorganic ion exchangers for removing ^{137}Cs and ^{90}Sr radionuclides from defense wastes, since it is highly selective for Cs and Sr over a broad pH range and in the presence of competitive ions (i.e. Na, Ca) [23–29]. In addition, the cesium trapped CST can be directly immobilized to a ceramic or glass form for final disposal [30]. Therefore, CST has been recognized as the preferable choice for removing Cs/Sr from nuclear waste, and it was awarded a 1996 R&D 100 award as "one of the 100 most technologically significant product of the year" [31,32]. Thus far, many papers have been published on CST synthesis [33–35], generally using titanium isopropoxide/titanium tetrachloride as titanium source and tetraethyl orthosilicate/silicon ethoxide/colloidal silica as silicon source. However, reports on preparing CST using waste CRT glass as silicon source are considerably few.

In this paper, CRT panel glass was used as silicon source for CST synthesis. The proposed process consisted of silicon extraction from CRT panel glass, gel formation and CST preparation. The separated

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Table 1
Chemical composition of the investigated panel glass by X-ray fluorescence (XRF).

Oxide	SiO$_2$	PbO	K$_2$O	Na$_2$O	Al$_2$O$_3$	SrO
wt.%	59.42	1.16	7.88	5.72	1.92	10.4
Oxide	CaO	BaO	MgO	ZrO$_2$	Fe$_2$O$_3$	P$_2$O$_5$
wt.%	0.32	9.67	–	2.32	–	–

liquid and solid after SCW–NaOH treatment were examined, and the synthesized CST was characterized for Cs$^+$ removal.

2. Experimental

2.1. Materials

Panel glasses of PC monitor, provided by Huaxing Environmental Protection Corporation, was firstly ball-milled to powders (no more than 80 mesh), which was described elsewhere [21]. Chemical composition of the glass powder was examined by XRF and the results were presented in Table 1. Other materials used in the experiments were all analytical reagents unless otherwise mentioned.

2.2. Silicon source preparation

A stainless autoclave was employed for SCW–NaOH treatment. The autoclave was made of 316L stainless alloy with a capacity of 200 mL. The pressure inside the autoclave changed within 32–42 MPa along with the temperature varying from 573 K to 723 K. In a typical SCW–NaOH treatment process, 5 g of the panel glass powder (fixed), a certain amount of NaOH and 120 mL of distilled water were mixed in the stainless autoclave. The treatment time was varied from 1 h to 10 h, and the treatment temperature was kept at 673 K. NaOH adding amount investigated were 0 g, 1 g, 2 g, 5 g, 8 g, 10 g, 15 g and 20 g. After the treatment, the autoclave was immediately cooled using an electronic fan. Then the suspension was centrifuged at 3000 rpm for 20 min to separate the liquid and solid, and the supernatant was filtrated through 0.45 μm membranes. At last, the filtrated liquids were used as the silicon source for CST preparation.

The filtrated liquids were examined by inductively coupled plasma optical emission spectrometer (ICP-OES, OPTIMA 2000), while the residues, after the centrifugation, were dried at 378 K, digested by HNO$_3$–HClO$_4$–HF [36] and analyzed by ICP-OES. Silicon extraction rates were calculated according to the silicon content before and after SCW–NaOH treatment process. Other elements, such as Na$^+$, K$^+$, Pb^{2+}, Sr^{2+}, Ba^{2+} and Al^{3+}, were also examined to determine their distributions in the liquids and residues after the treatment. The residues were also investigated by X-ray diffraction (XRD) using the Ni-filtered Cu Kα radiation on a Rigaku D/MAX2500 diffractometer.

2.3. CST preparation

First, titanium tetrachloride was dropped into the stirring absolute ethyl alcohol. The volume ratio of TiCl$_4$:CH$_3$CH$_2$OH was 1:4. Then a homogenous yellow solution was obtained. The solution was then dropped into the strongly agitating silicon source obtained according to Section 2.2, and a gel was obtained. After lying overnight, the gel was loaded into a Teflon-lined pressure vessel. The Teflon bomb was then placed in a stainless steel vessel, sealed, and then heated in a 443 K oven for 7 days. The white solid resulting from the hydrothermal treatment was filtrated and washed with large quantities of water in an attempt to wash away sodium excess. It should be pointed out that all theses liquids were col-
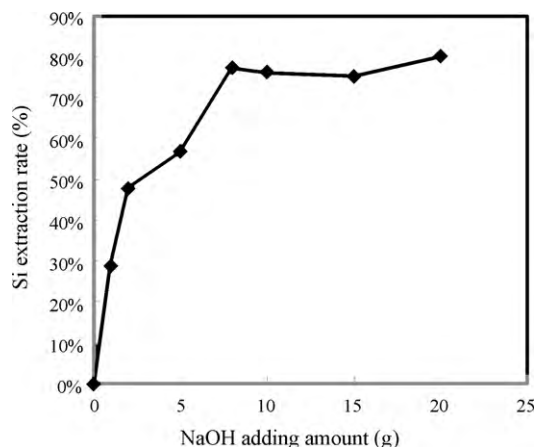

Fig. 1. Effect of NaOH amount on Si extraction percentage. Other conditions: temperature = 673 K; treatment time = 3 h.

lected and treated to fulfill the regulations before discharge. At last, the white solid was dried at 333 K. Scanning electron microscope (SEM, S-3000N), XRD, and transmission electron microscopy (TEM, H-7500) were employed to examine the surface morphology, crystalline property and particle size of the prepared CST.

2.4. Sorption experiments

The prepared CST was further characterized by sorption experiments. The purification of nuclear waste effluents using CST inorganic ion exchangers always involves column exchange, and the batch distribution coefficient (K_d) represents the maximum processing capacity in column operation [37]. Therefore, K_d was also used in this study. Under ideal conditions, K_d is calculated from Eq. (1)

$$K_d = (C_0 - C_e)/C_e \cdot V/M \tag{1}$$

where C_0 and C_e are, respectively, the initial and equilibrium concentrations of the radionuclide of interest and V/M is the solution volume to exchanger mass ratio. The distribution coefficients obtained in this study were the mean value of two experiments.

The prepared CSTs were accurately weighed (10 mg) and placed in contact with 20 mL of Cs$^+$ solution (50 ppm, pH in the range of 0–14). The solution/solid mixtures were equilibrated for 2 days on a mineralogical roller. The suspensions were then centrifuged and filtrated through 0.2 μm membranes, and the filtrates were analyzed for Cs$^+$ by an inductively coupled plasma mass spectrometer (ICP-MS, Plasma Quad 3). K_d was calculated according to Eq. (1). All samples were counted at the same geometry, and the measurement errors were around ±1%.

3. Results and discussion

3.1. SCW–NaOH treatment process

Si is generally extracted by NaOH fusion, though this method is complicated and its Si extraction rate is limited. Comparatively, SCW–NaOH process could greatly enhance the extraction efficiency, since glass network could be broken down efficiently by supercritical water, as reported by a previous study [38].

The effect of NaOH amount on silicon extraction rate by the SCW–NaOH process is shown in Fig. 1. When no NaOH was added in the SCW–NaOH system, the CRT glass powders, no more than 80 mesh, were agglomerated to a single brick and it was hard to take out from the autoclave, indicating that some mineralization process may occur. Furthermore, it can be seen from Fig. 1 that,
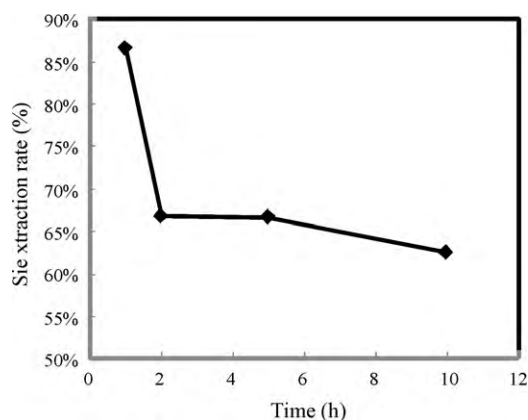
Fig. 2. Effect of treatment time on Si extraction percentage. Other conditions: temperature = 673 K; NaOH = 5 g.

when NaOH amount was between 0 g and 8 g, the silicon extraction rate increased significantly with the increase of NaOH amount, e.g. increased from 28.84% at 1 g to 77.17% at 8 g, then it reached a plateau value when NaOH adding amount was higher than 8 g. The results indicated that, when NaOH was no more than 8 g, OH$^-$ amount in the treatment system increased greatly along with the increase of NaOH, leading to a high broken efficiency of $\equiv$Si–O–Si$\equiv$ bonds, hence silicon could easily be transferred to the liquid phase and silicon extraction rate increased. When NaOH adding amount was higher than 8 g, OH$^-$ amount in the treatment system was sufficient to break $\equiv$Si–O–Si$\equiv$ bonds, leading to a slight increase of silicon extraction rate (Fig. 1).

Fig. 2 gives the effect of treatment time on silicon extraction rate by the SCW–NaOH process. When the treatment time increased from 1 h to 2 h, silicon extraction rate decreased greatly from 86.54% to 66.72%. Further extending the treatment time, the silicon extraction rate decreased slowly. This could be attributed to that, in a related short treatment time, SCW–NaOH could destroy the glass network efficiently, promoting silicon extraction. But the extracted silicon could mineralize with the extension of treatment time in the system of high pressure (about 40 MPa) and high temperature (673 K) [19], forming insoluble silicate minerals hence silicon extraction decreased.

3.2. Characterization of the liquid and residue after SCW–NaOH treatment

The composition of the filtrated liquid and the residue was analyzed, when the panel glass was treated by SCW–NaOH at 673 K for 3 h with NaOH adding amount of 5 g, and the results are given in Tables 2 and 3. Fig. 3 shows the XRD pattern of the residue.

From Table 2, it can be found that Na$^+$ concentration in the liquid was the highest, up to 23.38 g/L, followed by silicon, around 9.65 g/L, while Pb^{2+} in the solution was 2.84 mg/L. K$^+$ and Al^{3+} in the solution were supposed to come from the glass network after the network
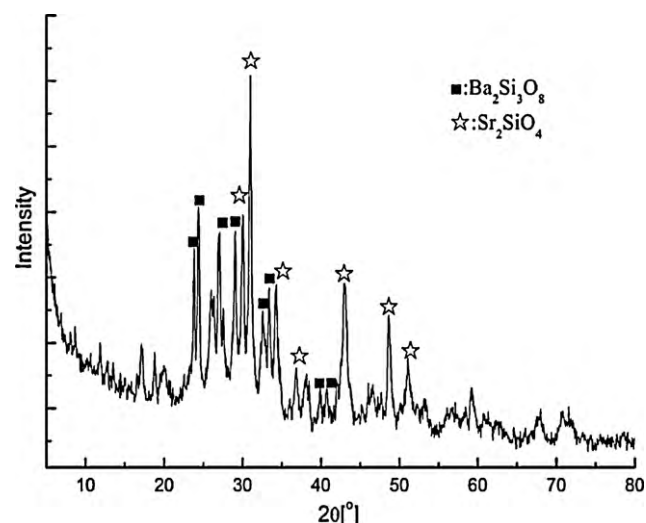

Fig. 3. XRD patterns of the residue after supercritical water–NaOH treatment. Other conditions: panel glass = 5 g, NaOH = 5 g, temperature = 673 K; treatment time = 3 h.

destruction. Pb^{2+} in the solution could be attributed to that lead oxides were slightly dissolved by OH$^-$ since lead oxides are slightly amphoteric. It can also be found from Table 2 that no strontium and barium ions can be detected by ICP-OES, indicating that, after the SCW–NaOH extraction process, Sr and Ba were not transferred to the liquid phase but enriched in the residue.

Considering the composition of the investigated panel glass, it can be seen from Table 3 that the content of PbO, Na$_2$O, Al$_2$O$_3$, SrO and BaO in the residue increased, while those of K$_2$O and SiO$_2$ decreased. SrO and BaO in the residue were about 3 times of those containing in the investigated panel glass, while SiO$_2$ in the residue decreased to 26.63% from 59.42% in the investigated panel glass. To further check the elements distribution, the mass balance analysis of Pb, Ba, Sr, Na, K, Al and Si containing in the investigated panel glass, and containing in the filtrated liquid and residue after SCW–NaOH treatment were conducted. It was found that, after SCW–NaOH treatment, about 90% of K, 50% of Al and 80% of Si were transferred from solid to liquid. From Fig. 3, it can be found that strontium and barium containing in the investigated panel glass were converted from amorphous to crystalline, mainly Ba$_2$Si$_3$O$_8$ and Sr$_2$SiO$_4$.

When the waste panel glass was treated by SCW–NaOH, most of its silicon entered the liquid phase, while Sr and Ba were enriched in the residues. Meanwhile, the silicon liquid can be used as silicon source to synthesize function materials such as molecular sieves or other chemical substances. On the other hand, BaO and SrO in the residue increased to 26.28 and 28.26 wt.% from 9.67 and 10.4 wt.%, respectively, which has the potential to be used as the raw material for metallic Ba and Sr metallurgy. To identify this possibility, studies are currently under investigation in our lab. In addition, studies are carried out to understand whether Pb containing in the residue will

Table 2
Solution composition after SCW–NaOH treatment of color panel glass (5 g glass and 5 g NaOH at 673 K for 3 h).

Element	Pb^{2+}	K$^+$	Na$^+$	Al^{3+}	Sr^{2+}	Ba^{2+}	Si
Concentration	2.84 mg/L	1.29 g/L	23.38 g/L	0.23 g/L	–	–	9.65 g/L

Table 3
Residue composition after SCW–NaOH treatment of color panel glass (5 g glass and 5 g NaOH at 673 K for 3 h).

Oxide	PbO	K$_2$O	Na$_2$O	Al$_2$O$_3$	SrO	BaO	SiO$_2$
wt.%	2.99	0.56	12.88	2.40	28.26	26.28	26.63

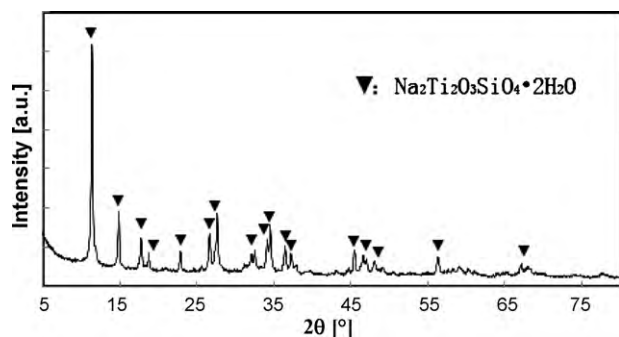**Fig. 4.** XRD patterns of the crystalline silicotitanate.
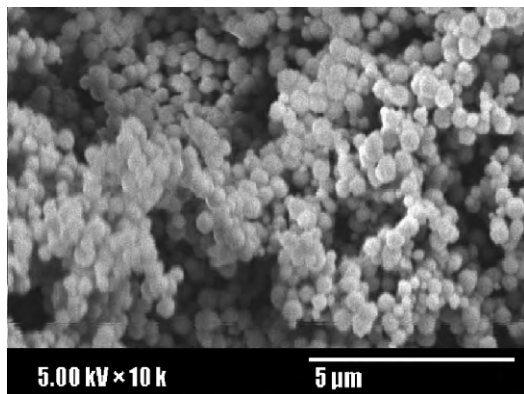
Fig. 5. SEM photographs of the synthesized CST(10,000×).

Fig. 7. TEM micrograph of the crystalline silicotitanate (300,000×).
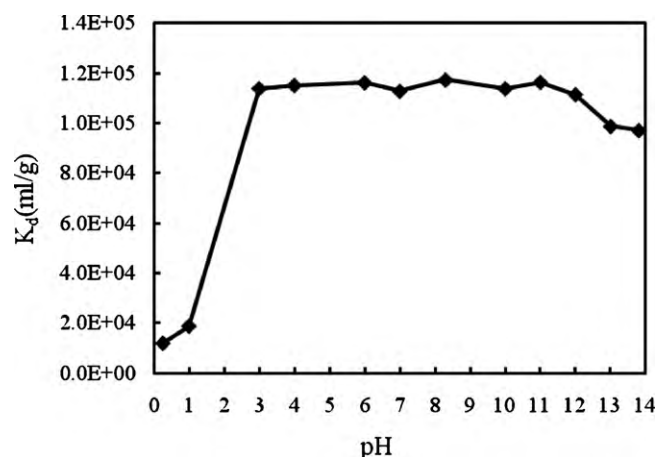
Fig. 8. Effect of pH on K_d(Cs$^+$). Other conditions: 10 mg CST in 20 mL of Cs$^+$ (50 ppm), 2 days.

affect the metallurgic process and to examine whether Pb containing in the residue will result in a secondary contamination, since PbO in the residue was enriched from 1.16 wt.% to 2.99 wt.%.

3.3. CST characterization

The filtrated liquid after SCW–NaOH treatment was used as silicon source for CST preparation. Si concentration of the filtrated liquid was about 9.65 g/L. For each preparation, 50 mL of the liquid, 5 mL of TiCl$_4$–CH$_3$CH$_2$OH were used, and CST synthesis was strictly based on Section 2.3.

Fig. 4 shows the XRD patterns of the synthesized CST. It can be found that the baseline was flat and there were no any amorphous features, indicating that the products were well crystallized. An intensive fraction peak with low 2θ value around 11° showed the crystal structure of CST, and all the peaks in the XRD patterns were well indexed to PDF 47-0591 (CST).

The synthesized product was further characterized by SEM to examine its surface morphology. From Fig. 5, it can be seen that the prepared material was fully crystallized, and the particles were
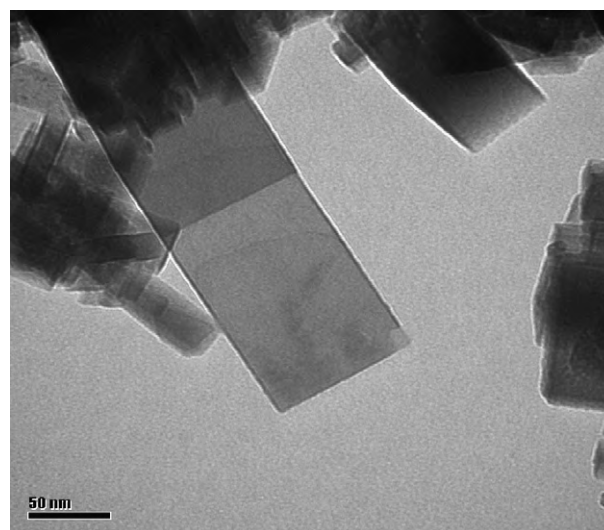
tiny, around 0.5 μm, and in ball shape. According to the TEM results shown in Fig. 6, the ball shape CST, shown in SEM pictures, was actually the secondary particles formed by the agglomeration of initial CST crystal particles, indicating that the initial CST particles were seriously agglomerated. Fig. 7 indicates that the cross-section of the synthesized CST was rectangle.

Fig. 8 illustrates the effect of pH on Cs$^+$ removal by CST at ambient temperature. It can be found that CST showed an extremely high selectivity to Cs$^+$ in the whole examined pH range, though the values of K_d were relatively lower in a strong acidic environment, e.g. only 1.2×10^4 mL/g at pH 0.26. When pH was in the range of
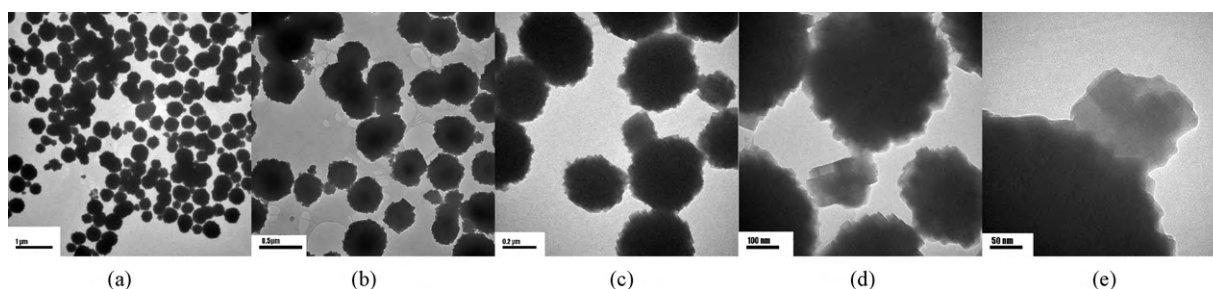

Fig. 6. TEM micrograph of the crystalline silicotitanate (a: 20,000×, b: 50,000×, c: 100,000×, d: 200,000×, e: 400,000×).

0–3, K_d was significantly increased from 1.2×10^4 mL/g at pH 0.26 to 1.1×10^5 mL/g at pH 3; and it almost kept constant when pH was in the range of 3–12. When pH value was increased to 14, K_d decreased to around 1.0×10^5 mL/g. This trend is very similar to the CSTs prepared using pure organic substances [39], but the distribution coefficient of CST prepared in this experiment using waste CRT panel glass as silicon source was about 100 times higher than those of CSTs prepared by pure organic substances [39], possibly because that the Cs^+ containing solution in this experiment was simulated, without any other competitive ions such as Na^+, K^+ and Ca^{2+}.

4. Conclusions

In this paper, CST was successfully prepared by sol–gel and hydrothermal treatment using waste CRT panel glass as silicon source extracted by SCW–NaOH process. In the extraction process, supercritical water could destroy the glass network, hence Si could efficiently transfer into the solution with an efficiency of 80%, while Sr and Ba were enriched in the residue in the form of Sr_2SiO_4 and $Ba_2Si_3O_8$.

After the extraction process, Sr and Ba contents in the residue were about 2–3 times higher than those in the original glass. The residue has the potential to be used as a raw material for metallic Ba and Sr metallurgy, and the liquid could be used as a silicon source for CST synthesis. The synthesized CST could be used as an inorganic ion exchanger for Cs^+ removal from aqueous system with a distribution coefficient of up to 1.2×10^4 mL/g.

Acknowledgements

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