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Cs and Sr removal over highly effective adsorbents ETS-1 and ETS-2†

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Engelhard titanosilicate-1 (ETS-1) and Engelhard titanosilicate-2 (ETS-2) were prepared. It was the first time their properties were studied for applications in water treatment. The performance of ETS-1 and ETS-2 in Cs and Sr removal was investigated and compared with those of ETS-4, Na-Y and Na-ZSM-5. Characterization revealed successful synthesis of ETS-1 and ETS-2, having layered structures with specific surface areas of about 120 m^2 g^{-1} and 220 m^2 g^{-1}, respectively. The compositions of ETS-1 and ETS-2 were analyzed by XRF and TGA, and the theoretical exchange capacities for monovalent cations were calculated to be 6.70 mmol g^{-1} and 8.12 mmol g^{-1}, respectively, assuming all the alkali metal cations could be exchanged. ETS-1 showed the highest Cs removal performance among the adsorbents studied, whereas ETS-2 was promising in Sr removal. In competitive removal experiments for Cs and Sr, the highest amount of Cs uptake was observed over ETS-1, though ETS-1 did not show specific selectivity to Cs removal.

1 Introduction

Due to the earthquake and the melt-down of the atomic power plants in Fukushima, Japan, in March 2011, water was contaminated with radioactive Cs and Sr. These radioactive species are harmful to human beings, and therefore it is urgently required to remove them from water.[1]

In order to remove these radioactive species, several adsorbents have been developed. For the removal of Cs, zeolites (Na-Y, ZSM-5 *etc.*),[2,3] Prussian blue,[4,5] birnessites,[6] and heteropoly acids[7] are the most commonly adopted adsorbents. For Sr removal, carbon (including active carbon and carbon nanotubes),[8,9] calixarene amide ionophores,[10] and silica-based materials[11,12] have been studied. Titanosilicate materials have been one of the main types in heavy metal removal. Among them, Engelhard titanosilicate-4 (ETS-4), Engelhard titanosilicate-10 (ETS-10),[13,14] crystalline silicotitanate,[15] AM-2,[16] AM-3 (ref. 17) and AM-4 (ref. 18) have been widely studied and they have shown high efficiencies in Cs and Sr removal.[19–22]

As titanosilicates also invented by the Engelhard Corporation, however, Engelhard titanosilicate-1 (ETS-1) and Engelhard titanosilicate-2 (ETS-2) have not attracted as much attention of scientists as ETS-4 and ETS-10. In this work, we synthesized ETS-1 and ETS-2 and for the first time they were employed as adsorbents in Cs and Sr removal. Their physicochemical properties were studied in detail, and their performance was compared with those of Na-Y, ZSM-5 and ETS-4.

2 Experimental

2.1 Reagents

Sodium silicate (52–57 wt% in water, and the molar ratio of SiO_2/Na_2O was 2.06–2.3/1), $TiCl_3$ (20 wt% $TiCl_3$ in 10 wt% HCl solution), NaOH, KOH (minimum content of KOH was 85 wt%), NaF, KF, $CsNO_3$ and $SrCl_2 \cdot 6H_2O$ were obtained from Wako Pure Chemical Industries, Ltd. Na-Y $[n(SiO_2)/n(Al_2O_3) = 5.5]$ and Na-ZSM-5 $[n(SiO_2)/n(Al_2O_3) = 23.0]$ were supplied by TOSOH Corp.

2.2 Synthesis of ETS-1, ETS-2 and ETS-4

ETS-1 was synthesized with the same method as in ref. 23. That is, 8.08 g sodium silicate (52–57 wt%), 38.1 g $TiCl_3$ (20 wt%), 11.7 g NaOH, 4.91 g KOH (>85 wt%), 2.90 g KF and 20.0 mL water were mixed in a 200 mL flask and stirred at room temperature for half an hour. Then, the mixture was transferred into a Teflon-lined autoclave and hydrothermally treated at 125 °C for 1 day or 3 days. After washing with water until there were no changes in pH (pH $\approx$ 9), the product was dried at 70 °C overnight. The ETS-1 samples obtained were denoted as ETS-1 1d and ETS-1 3d, respectively.

ETS-2 was synthesized as in ref. 23. The preparation method for ETS-2 was similar to that for ETS-1 except that the potassium-containing raw materials were replaced by sodium-containing ones. Namely, 14.7 g NaOH and 4.20 g NaF were employed for the preparation of ETS-2 instead of the 11.7 g NaOH + 4.91 g KOH and 2.90 g KF used for the ETS-1 preparation. Similarly, ETS-2 samples obtained using different

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hydrothermal treatment times were denoted as ETS-2 1d and ETS-2 3d, respectively.

15.2 g sodium silicate (52–57 wt%), 38.1 g $TiCl_3$ (20 wt%), 11.7 g NaOH, 1.39 g KF and 56.3 mL water were mixed and stirred at room temperature for half an hour, and then the mixture was hydrothermally treated at 200 °C for 7 days in a Teflon-lined autoclave. After washing and drying at 70 °C, ETS-4 was obtained.[24]

2.3 Characterization of adsorbents

The specific surface areas and pore volumes were calculated based on N_2 adsorption–desorption isotherms measured using a Belsorp-mini (Bel Japan Inc.) after pretreatment at 70 °C for 1 h. Elemental analysis of Na-Y and Na-ZSM-5 zeolites and the other adsorbents was carried out by the X-ray fluorescence (XRF) method (XRF-1800-HE-CCD-J, Shimadzu Corp.). Thermogravimetric analysis (TGA) was carried out using a Thermo plus TG 8120 (Rigaku Corp.). The characterization of crystalline phases of the adsorbents was carried out with an X-ray diffractometer (XRD, Rigaku Corp.) at room temperature, using Ni-filtered Cu Kα radiation and instrumental settings of 40 kV and 20 mA.

2.4 Removal of Cs and Sr

A typical Cs removal procedure is as follows. Into a 100 mL Erlenmeyer flask containing 50 mL of $CsNO_3$ solution (the concentration of Cs^+ was 100–1500 ppm), $SrCl_2$ solution (the concentration of Sr^{2+} was 50–750 ppm) or mixed solution of $CsNO_3$ and $SrCl_2$ (Cs^+ 1500 ppm and Sr^{2+} 300 ppm) with a pH of 5.8 was added a 0.050 g portion of the adsorbent. The adsorption was carried out at room temperature for different contact times (0.5–24 h).

Both the initial $CsNO_3$ solution and the solution after Cs adsorption were attenuated with pre-prepared KCl diluent (0.1 mol L^{-1}), and were analyzed with an atomic absorption spectrophotometer (Z-2010, Hitachi). The differences between the initial and final Cs concentrations could be ascribed to the amounts of Cs removed by the adsorbents. For Sr, the solution was analyzed by ICP (ICPS-7510, Shimadzu Corp.) after dilution with water.

3 Results and discussion

3.1 Crystalline structure

The crystalline structures of the as-prepared samples and the commercial Na-Y and Na-ZSM-5 were characterized by XRD, and the results are shown in Fig. 1. Na-Y and Na-ZSM-5 exhibited their typical diffraction peaks,[25,26] and the peaks for the as-prepared ETS-2 and ETS-4 were coincident with those reported in refs. 27 and 24. As for ETS-1, all the peaks mentioned in ref. 23 appeared in the XRD profiles, whereas there was a difference in the relative intensities of the peaks, which is probably due to the crystal growth anisotropy of different facets. Though the main diffraction peaks for ETS-2 were in similar positions to those of ETS-1, ETS-1 and ETS-2 were different materials (Fig. 1s and 2s†). ETS-2 was poorly crystallized even after 7 days' hydrothermal treatment time (Fig. 3s†). Thus, ETS-1, ETS-2 and ETS-4 were synthesized successfully. Prolonged hydrothermal treatment time had little effect on the XRD patterns of the samples.

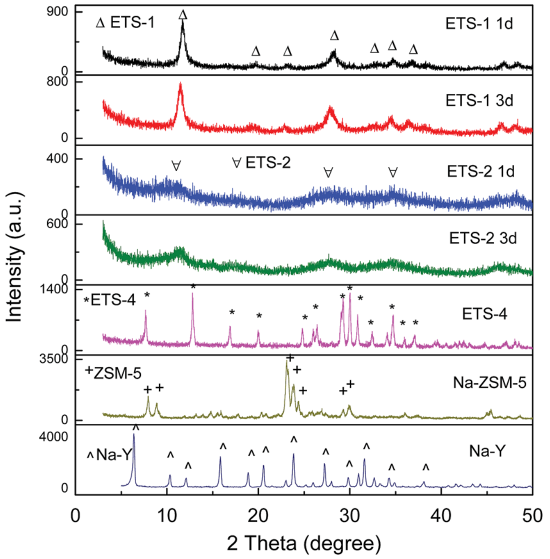

Fig. 1 XRD patterns of as-prepared ETS-1, ETS-2 and ETS-4 and commercial Na-Y and Na-ZSM-5.

3.2 Elemental analysis

The contents of Ti, Si and Na (and K) in ETS-1 and ETS-2 were analyzed by XRF and the amounts of water were obtained from TGA. The XRF results are listed in Table 1. It could be seen that there were small differences between the compositions of Ti, Si and Na (and K) with changing hydrothermal treatment time, and the differences might be within the detection errors. Converting the elemental compositions into oxides, namely TiO_2, SiO_2, Na_2O (and K_2O), gave the results in Table 2. As it is not possible to measure the amounts of water by the XRF method, the contents of SiO_2, TiO_2, Na_2O and K_2O obtained are on a dry basis. Then, the total amounts of the oxides were summed for each of the samples, and nearly 100 wt% was obtained.

TGA was employed to analyze the amounts of water in the adsorbents (Fig. 2). The weight losses mainly appeared in the range of room temperature to 300 °C, and the weights were almost stable during 300–500 °C. As stated previously, the samples were dried at 70 °C overnight, so the weight losses at temperatures lower than 70 °C might be due to the adsorption of moisture from the air. The weight losses at temperatures

Table 1 Composition of ETS-1 and ETS-2 from XRF (calibrated by standard samples)

Sample	Ti (wt%)	Si (wt%)	Na (wt%)	K (wt%)
ETS-1 1d	26.9	13.3	13.7	8.5
ETS-1 3d	29.5	12.1	13.3	7.9
ETS-2 1d	30.6	9.9	21.4	—
ETS-2 3d	27.7	11.5	21.9	—

Table 2 Composition of ETS-1 and ETS-2 from XRF and TGA

Sample	TiO_2 (wt%)	SiO_2 (wt%)	Na_2O (wt%)	K_2O (wt%)	Total (wt%)	H_2O (wt%)
ETS-1 1d	85.0					15.0
	44.8	28.5	18.5	10.2	102.0	
ETS-1 3d	85.0					15.0
	49.2	25.9	17.9	9.5	102.5	
ETS-2 1d	85.8					14.2
	51.0	21.2	28.8	—	101.0	
ETS-2 3d	87.6					12.4
	46.2	24.6	29.5	—	100.3	

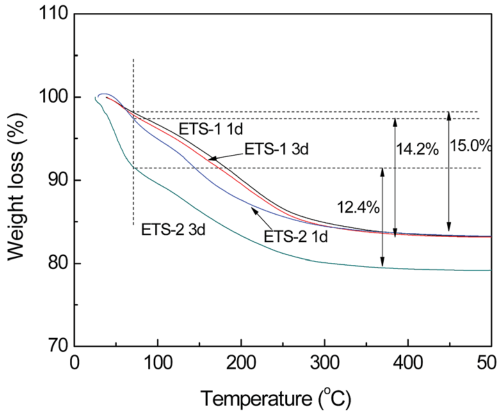

Fig. 2 TGA of water in the adsorbents.

higher than 70 °C were attributed to water existing in the adsorbents. Similar weight losses due to the water in the adsorbents were obtained for ETS-1 and ETS-2. As reported in ref. 23 and 28, titanosilicates are not thermally stable, and they undergo structural rearrangement even at 200 °C. For this reason, ETS-1, ETS-2 and ETS-4 were not calcined after drying at 70 °C in this study.

By knowing the weight percentage of every component in the sample, the molar ratio of the components of ETS-1 and ETS-2 could be calculated. As mentioned before, the small differences between the samples prepared with different hydrothermal treatment times might be due to detection errors. Therefore, the values for ETS-1 1d and ETS-1 3d were averaged to get the possible composition of ETS-1. Similar calculation was made for ETS-2 1d and ETS-2 3d. The molar ratio was $n(TiO_2) : n(SiO_2) : n(Na_2O) : n(K_2O) : n(H_2O) = 1.3 : 1 : 0.65 : 0.23 : 2.2$ for ETS-1 and $n(TiO_2) : n(SiO_2) : n(Na_2O) : n(H_2O) = 1.6 : 1{:}1.3 : 2.3$ for ETS-2. The exchange capacity was estimated by considering that all the Na and K could be exchanged, and the values were 6.70 mmol g^{-1} and 8.12 mmol g^{-1} for ETS-1 and ETS-2, respectively.

The composition of ETS-4 is known as $Na_9Si_{12}Ti_5O_{38}(OH)\cdot 12H_2O$.[29] In our case, since both Na and K salts were used as raw materials for the synthesis of ETS-4, it would lead to the partial replacement of Na by K. However, it is expected that both Na and K could be exchanged, and the exchange capacity from the known composition of ETS-4 is about 5.50 mmol g^{-1}. As for Na-Y and Na-ZSM-5, their exchange capacities could be calculated according to their $n(SiO_2)/n(Al_2O_3)$ ratios, and they were 3.87 mmol g^{-1} and 1.24 mmol g^{-1}, respectively.

3.3 Porous properties

The N_2 adsorption–desorption isotherms of the adsorbents are shown in Fig. 3 and the calculated specific surface areas and pore volumes are given in Table 3. Na-Y,[30] Na-ZSM-5 (ref. 31) and ETS-4 (ref. 20 and 32) exhibited their typical isotherms, specific surface areas and pore volumes. ETS-1 and ETS-2 showed type III adsorption–desorption isotherms and H_3 type hysteresis loops, implying they have layered structures. ETS-1 possessed a specific surface area of about 120 m^2 g^{-1} and pore volume of 0.49 cm^3 g^{-1}, whereas the specific surface area was 220 m^2 g^{-1} and pore volume was 0.35 cm^3 g^{-1} for ETS-2.

3.4 Cs removal

The performances for Cs removal over ETS-1, ETS-2, ETS-4, Na-Y and Na-ZSM-5 were investigated at room temperature and at

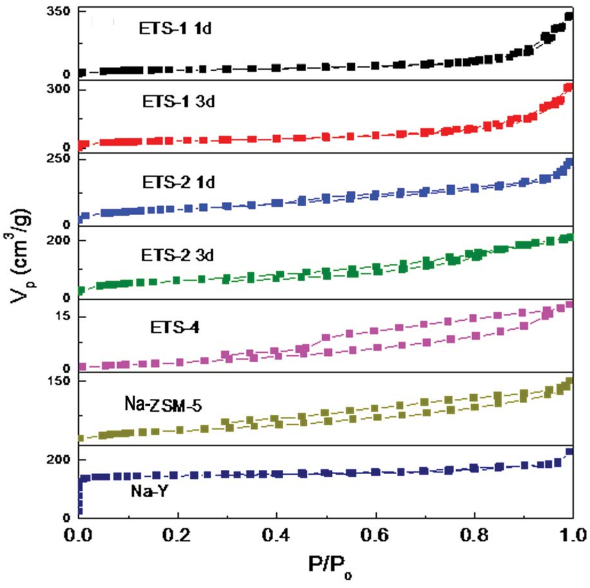

Fig. 3 N_2 adsorption–desorption isotherms of the adsorbents.

Table 3 Specific surface areas and pore volumes of as-prepared samples

Sample	Specific surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
ETS-1 1d	107	0.49
ETS-1 3d	127	0.48
ETS-2 1d	219	0.36
ETS-2 3d	228	0.32
ETS-4	13	0.03
Na-ZSM-5	217	0.21
Na-Y	486	0.35

different initial Cs concentrations, and the results are shown in Fig. 4. All the samples showed similar performance and more than 90% of Cs was removed when the initial Cs concentration was low (100 ppm). Differences between the samples emerged with an increase of the initial Cs concentration from 500 ppm to 1500 ppm. ETS-1 exhibited the highest ability for Cs removal irrespective of the hydrothermal treatment time (about 2.6 mmol g^{-1}). ETS-2, ETS-4 and Na-Y showed similar but somewhat lower performance than ETS-1 (in the range of 1.9–2.3 mmol g^{-1}) whereas Na-ZSM-5 was the poorest (about 1.4 mmol g^{-1}). The similar performance for the samples with different hydrothermal treatment time is related to the similar composition of the adsorbents. It has to be noted that due to the higher dilution ratio at higher initial Cs concentrations, bigger errors would be obtained in the values calculated for Cs removal. That is why the simulated curves were not the same for ETS-1 1d and ETS-1 3d, and also why larger Cs uptake than the capacity was obtained over Na-ZSM-5 when the initial Cs concentration was 1500 ppm.

The contact time was varied to check the Cs removal performance of the samples (Fig. 5). It could be seen that all seven samples reached an equilibrium in a short time (within 0.5 h), and then the amounts of Cs removal remained constant with increasing contact time to 24 h.

In order to get the maximum amounts of Cs removal (Q_{max}) over these samples, the Langmuir equation, $C_e/Q_e = (1/Q_{max})C_e + 1/(Q_{max}b)$, was employed to simulate the data obtained. Since the hydrothermal treatment time did not influence the properties and the performance of ETS-1 and ETS-2 for Cs removal, the values for 1d and 3d were averaged and used for the simulation of ETS-1 and ETS-2. The plots are shown in Fig. 6. All the samples fitted well to the Langmuir adsorption models (except some data with bigger errors). The maximum amounts of Cs removal could be obtained by calculating the reciprocals of the relevant slopes, and they were 2.50, 2.22, 1.79, 1.87 and 1.25 mmol g^{-1} over ETS-1, ETS-2, ETS-4, Na-Y and Na-ZSM-5, respectively. The lower exchange capacities of ETS-1 and ETS-2 than the theoretical values might result from the existence of less easily exchangeable cations,[33] though the cations in ETS-4 and ETS-10 were reported to be easily exchanged.[20,34–36]

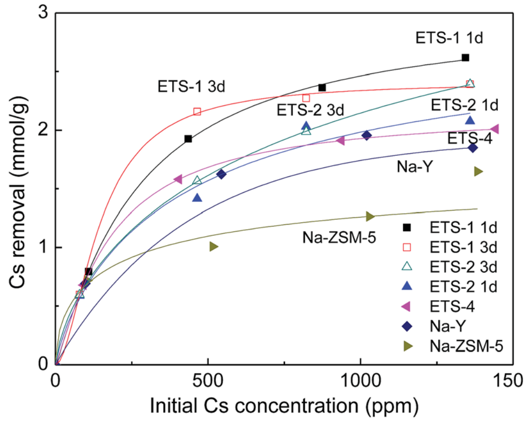

Fig. 4 Effect of initial Cs concentration on Cs removal over ETS-1, ETS-2, ETS-4, Na-Y and Na-ZSM-5. Adsorption conditions: initial Cs concentration 100–1500 ppm, solution 50 mL, pH 5.8, contact time 0.5 h, adsorbent 0.050 g.

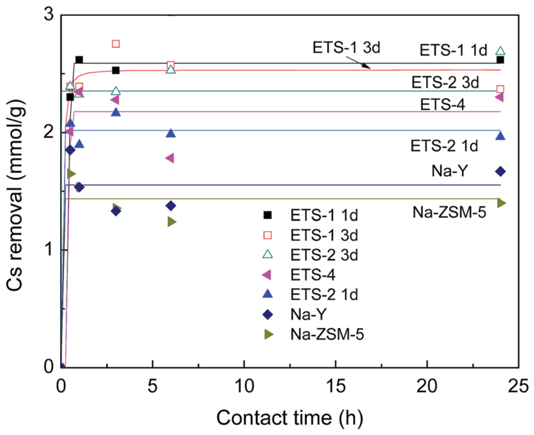

Fig. 5 Effect of contact time on Cs removal over ETS-1, ETS-2, ETS-4, Na-Y and Na-ZSM-5. Adsorption conditions: initial Cs concentration 1500 ppm, solution 50 mL, pH 5.8, contact time 0.5–24 h, adsorbent 0.050 g.

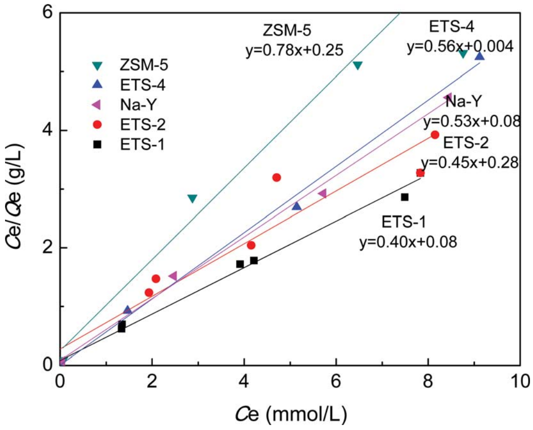

Fig. 6 Langmuir plots of Cs removal over ETS-1, ETS-2, ETS-4, Na-Y and Na-ZSM-5. Adsorption conditions: initial Cs concentration 100–1500 ppm, solution 50 mL, pH 5.8, contact time 0.5 h, adsorbent 0.050 g.

There might be two factors that relate to the performance of the adsorbents for Cs removal. One is the exchange capacities of the samples,[37] and the other is the size differences between the cations in their structures and in solution.[16] As discussed in Section 3.2, the nominal exchange capacity was in the order of ETS-2 (8.12 mmol g^{-1}) > ETS-1 (6.70 mmol g^{-1}) > ETS-4 (5.50 mmol g^{-1}) > Na-Y (3.87 mmol g^{-1}) > Na-ZSM-5 (1.24 mmol g^{-1}). For the comparison of ETS-1 and ETS-4 in Cs removal (both Na and K present), only the exchange capacity mattered, which led to the amount of Cs removal in the order of ETS-1 > ETS-4. For the comparison of ETS-2, Na-Y and Na-ZSM-5 (with only Na), also the exchange capacity was the only factor, and then the amounts of Cs uptake were in the order of ETS-2 > Na-Y > Na-ZSM-5, whereas for ETS-2 and ETS-4, both of the two factors would exert their own effects. It has been reported that the smaller the size differences between the cations in the adsorbent and in the solution, the kinetically easier it is for the exchange process to occur.[20] Compared with Na^+ (0.102 nm), the size of K^+ (0.138 nm) is closer to that of Cs^+ (0.167 nm). In this respect, the cations in ETS-4 were more easily exchanged with Cs^+ than those in ETS-2. However, ETS-2 possessed higher exchange capacity than ETS-4. Then, the mixed effects of both of the two factors resulted in their similar performance in Cs removal.

3.5 Sr removal

The exchange properties of ETS-1, ETS-2, ETS-4, Na-Y and Na-ZSM-5 were further investigated in Sr removal. Their performance at different initial Sr concentrations is shown in Fig. 7 and 8. They displayed different exchange performance even at low initial Sr concentration (50 ppm), and the difference became more obvious with increasing initial Sr concentration (Fig. 7). In addition, varying the contact time from 0.5 h to 24 h had little effect on the amounts of Sr uptake over the adsorbents studied (Fig. 8). The maximum amounts of Sr removal over the samples were also simulated by Langmuir plots, and the results are shown in Fig. 9. All the data fitted the Langmuir plots well, and the calculated maximum Sr exchange amounts were 1.52, 1.82, 0.44, 1.09 and 0.35 mmol g^{-1} over ETS-1, ETS-2, ETS-4, Na-Y and Na-ZSM-5, respectively. Then, the order of Sr removal was ETS-2 > ETS-1 > Na-Y > ETS-4 ≈ Na-ZSM-5.

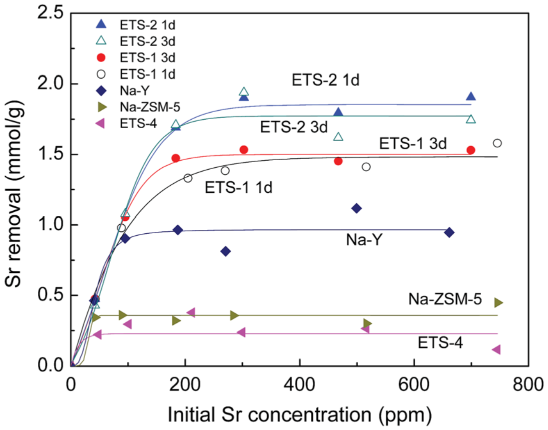

Fig. 7 Effect of initial Sr concentration on Sr removal over ETS-1, ETS-2, ETS-4, Na-Y and Na-ZSM-5. Adsorption conditions: initial Sr concentration 50–750 ppm, solution 50 mL, pH 5.8, contact time 0.5 h, adsorbent 0.050 g.

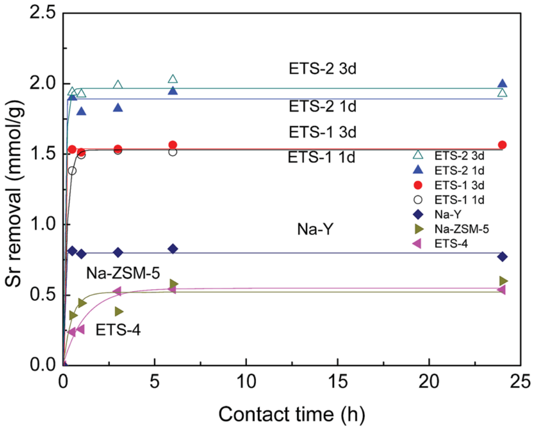

Fig. 8 Effect of contact time on Sr removal over ETS-1, ETS-2, ETS-4, Na-Y and Na-ZSM-5. Adsorption conditions: initial Sr concentration 300 ppm, solution 50 mL, pH 5.8, contact time 0.5–24 h, adsorbent 0.050 g.

The ionic radius of Sr^{2+} (0.118 nm) is smaller than those of Cs^+ (0.167 nm) and K^+ (0.138 nm), and a little larger than that of Na^+ (0.102 nm). Therefore, the Na^+ and K^+ in the structures of the adsorbents could be exchanged more easily with Sr^{2+} in the solution than with Cs^+. If so, the exchange capacity is the only factor that matters. However, compared with the trend for exchange capacity, ETS-2 (8.12 mmol g^{-1}) > ETS-1 (6.70 mmol g^{-1}) > ETS-4 (5.50 mmol g^{-1}) > Na-Y (3.87 mmol g^{-1}) > Na-ZSM-5 (1.24 mmol g^{-1}), ETS-4 showed somewhat lower performance for Sr removal.

There have been several studies on the removal of Sr over ETS-4,[19,20] and Na-ETS-4 was reported to be effective in Sr removal, which was totally different from our case. Probably the preparation method, raw materials employed and hydrothermal

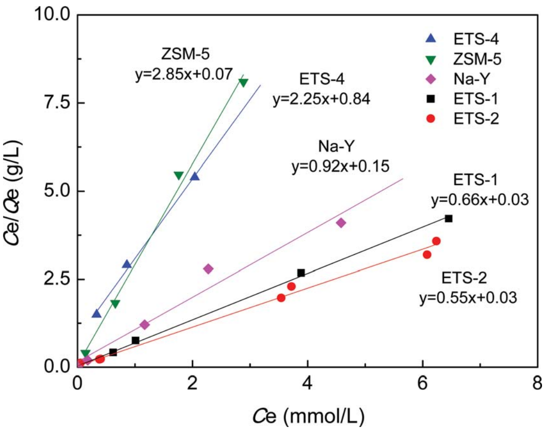

Fig. 9 Langmuir plots of Sr removal over ETS-1, ETS-2, ETS-4, Na-Y and Ns-ZSM-5. Adsorption conditions: initial Sr concentration 50–750 ppm, solution 50 mL, pH 5.8, contact time 0.5 h, adsorbent 0.050 g.

Table 4 Cs and Sr competitive removal over ETS-1, ETS-2, ETS-4 and Na-ZSM-5[a]

	Exchange capacity (mmol g^{-1})	Cs uptake (mmol g^{-1})	D_{Cs}	Sr uptake (mmol g^{-1})	D_{Sr}	D_{Cs}/D_{Sr}
ETS-1 1d	6.70	1.83	0.22	0.60	0.22	1.0
ETS-1 3d	6.70	1.65	0.20	0.36	0.14	1.4
ETS-2 1d	8.12	0.61	0.07	1.29	0.77	0.1
ETS-2 3d	8.12	0.38	0.04	1.18	0.67	0.1
ETS-4	5.50	1.53	0.17	0.12	0.04	4.8
Na-ZSM-5	1.24	1.31	0.15	0.02	0.005	29.3
Na-Y	3.87	0.84	0.08	0.67	0.24	0.4

[a] Adsorption conditions: initial Cs 1400 ± 100 ppm, initial Sr 280 ± 20 ppm, solution 50 mL, pH 5.8, contact time 0.5 h, adsorbent 0.050 g.

treatment conditions would affect the exchange properties of ETS-4.

3.6 Competitive removal of Cs and Sr

In order to selectively remove Cs or Sr, a competitive removal experiment was carried out, and the results are given in Table 4. It could be seen that for ETS-1, D_{Cs}/D_{Sr} of about 1.0 was obtained, indicating no special selectivities towards Cs or Sr. In contrast, for ETS-2 and Na-Y, D_{Cs}/D_{Sr} values were about 0.10 and 0.35, respectively, which implies that ETS-2 and Na-Y could selectively remove Sr instead of Cs. On the other hand, the values of D_{Cs}/D_{Sr} were much higher than 1.0 for ETS-4 and Na-ZSM-5, and this means that these two samples could selectively remove Cs. In spite of the high selectivity to Cs over ETS-4 and Na-ZSM-5, the amounts of Cs removed were lower than for ETS-1 (1.65–1.83 mmol g^{-1}). That is to say, no matter with or without the presence of Sr, ETS-1 proved itself as a better adsorbent than ETS-4 and Na-ZSM-5 in Cs removal. In addition, ETS-2 was a promising adsorbent for Sr uptake.

4 Conclusions

Layered ETS-1 and ETS-2 were synthesized successfully. The specific surface areas and the theoretical exchange capacities for ETS-1 and ETS-2 were about 120 and 220 $m^2 g^{-1}$, and 6.70 and 8.12 mmol g^{-1}, respectively. Both ETS-1 and ETS-2 exhibited better performance in the removal of Cs and Sr, compared with ETS-4, Na-Y and Na-ZSM-5. ETS-1 was effective in Cs removal whereas ETS-2 showed more promise for Sr uptake.

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