

Selectivity modification by ion memory of magnesio-silicate and magnesium alumino-silicate as inorganic sorbents

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Abstract

Synthetic magnesio-silicate and magnesium alumino-silicate as inorganic ion exchange materials with the formula $\text{MgSi}_{5.59}\text{O}_{12.18} \cdot 5.93\text{H}_2\text{O}$ and $\text{MgAl}_{2.32}\text{Si}_{5.2}\text{O}_{14.88} \cdot 18.23\text{H}_2\text{O}$, respectively, have been found to be suitable for the removal of Cs^+ , Co^{2+} and Eu^{3+} ions with the selectivity sequence $\text{Eu}^{3+} > \text{Co}^{2+} > \text{Cs}^+$. Samples of Cs-, Co- and Eu-loaded were prepared and thermally treated at 850 °C in a furnace for the creation of specific cavity. Surface area, IR and X-ray diffraction patterns of the products were conducted. Surface area values of OMS, OMAS, TMS, TMAS, ETMS and ETMAS were measured and indicated an increasing in the surface area values for the TMS and TMAS samples and decreasing in the ETMS and ETMAS samples. Desorption studies in nitric acid medium were carried out and reloading of the eluted solids with the studied cations were conducted and the data show an ion memory behaviour for the eluted solids. Finally, the rate of Cs^+ ion sorption on OMS, OMAS, ETMS and ETMAS was studied. The diffusion coefficients calculated indicated that the diffusion of Cs^+ ion is high for the ETMS and ETMAS samples compared to the OMS and OMAS samples.

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Keywords: Selectivity; Ion memory; Magnesio-silicate; Magnesium alumino-silicate; Inorganic sorbent

1. Introduction

Understanding the origin of selectivity in inorganic ion exchangers is still somewhat limited. However, it is of great importance to increase this understanding in order to be able to design selective materials for the effective separations of radioactive nuclides in variable conditions. By slightly altering the composition or dimensions of the three-dimensional framework structure of an ion exchange material through cation substitution, exchangers with more desirable properties may be developed. Several factors typically simultaneously affect the

ion exchange properties of inorganic ion exchangers (elemental composition, acidity, water content and hydration of exchanging ions) must be conducted in order to be able to make definite conclusions on the origin of selectivity. High selectivity for sodium ions was observed using niobium oxide [1] and tantalum acid show high selectivity for lithium ion [2]. Gupta et al. reported the removal of some heavy metals from aqueous solutions using different adsorbents [3–10]. Kinetics of mercury adsorption from waste water using activated carbon has been reported by Mohan et al. [11].

In our laboratories [12,13] and literature [14–27] the evaluation of the ion exchange properties of various synthetic inorganic ion exchange materials indicated that, most of inorganic ion exchanger loss its capacities or great extent of its capacities when treated at high temperature. So in this work we attempt to overcome of these problems by thermal treatment of the exchangers in the loaded form at high temperature to construct the material by keeping ionic bonding for exchangeable ions in framework of coordination bonding. If this is done, then the product will show high selectivity just as to be retained in ion memory after exchanging particular ion with other ion to maintain fundamentally original structures.

Abbreviations: MS, magnesio-silicate; MAS, magnesium alumino-silicate; OMS, original magnesio-silicate; OMAS, original magnesium alumino-silicate; TMS, treated magnesio-silicate at 850 ± 2 °C; TMAS, treated magnesium alumino-silicate at 850 ± 2 °C; ETMS, exchange treated magnesio-silicate; ETMAS, exchange treated magnesium alumino-silicate; Cs-TMS, Cs-treated magnesio-silicate; Co-TMS, Co-treated magnesio-silicate; Eu-TMS, Eu-treated magnesio-silicate; Cs-TMAS, Cs-treated magnesium alumino-silicate; Co-TMAS, Co-treated magnesium alumino-silicate; Eu-TMAS, Eu-treated magnesium alumino-silicate.

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2. Experimental

All chemicals used were of analytical reagent purity grade and used without further purification.

2.1. Synthesis of ion exchangers

Magneso- and magnesium alumino-silicate ion exchangers were prepared as reported earlier [28] by drop wise addition of equimolar solutions (0.25 M) of magnesium chloride or mixture of magnesium chloride and aluminum chloride to sodium metasilicate with volumetric ratio equal to unity. The mixed solutions were immediately hydrolyzed in deionized water and the precipitates formed were kept in the mother solution overnight. Then filtered and washed with 0.1 M HNO₃ to remove reagents adherent with the precipitates. The precipitates were rewashed for several times by distilled water to remove NO₃⁻ ion and the final products were dried at 50 °C, cracked into fine particles by immersed in near boiling water, dry, ground, sieved and store at room temperature.

2.2. Loading of the ion exchange materials

Loading of MS and MAS ion exchange materials was carried out by contact 0.1 g of the solid with 200 ml of 0.1 M CsNO₃ or Co(NO₃)₂ and 0.01 M Eu(NO₃)₃ solutions, under through stirring for 4 h. In another set of identical experiments, the Cs-, Co- and Eu-nitrate solutions were also spiked with corresponding radioactive isotopes, ¹³⁴Cs, ⁶⁰Co and ^{152>154}Eu, respectively, for convenience in analysis. At equilibrium the solid was separated and the metal ion concentrations in the solids and solutions were measured by counting the solids and solutions radiometrically using NaI(Tl) Scintillation counter of the type Sealer Ratemeter SR7, England.

2.3. Thermal treatment

MS and MAS ion exchange materials before and after loading were thermally treated at 850 ± 2 °C. The solids produced were characterized using IR, surface area and XRD measurements.

2.4. Surface area measurements

Surface area values of the QMS, OMAS, TMS, TMAS, ETMS and ETMAS ion exchange materials were measured using BET-technique as an adsorption phenomenon of nitrogen gas of NOVA A 3200, Quantachrome Corp., USA.

2.5. X-ray diffraction studies

The XRD patterns of the powdered QMS, OMAS, TMS, TMAS, ETMS and ETMAS ion exchange materials were obtained using A Shimadzu X-ray diffractometer model XD-D1, Cu K α radiation tube source ($\lambda = 1.5406 \text{ \AA}$).

2.6. Infrared studies

The IR spectra of OMS, OMAS, TMS, TMAS, ETMS and ETMAS ion exchange materials were obtained using BOMEM-FTIR spectrometer and KBr disk method.

2.7. Desorption studies

The ETMS and ETMAS ion exchange materials were subjected to desorption process using different nitric acid concentrations. 0.5 g of the ETMS and ETMAS solids were packed in a glass column of 5 mm internal diameter and 30 mm height. The effluent was allowed to percolate through the solid at flow rate of 1 ml/min. and the effluent samples were collected and the activity of ¹³⁴Cs, ⁶⁰Co and ^{152>154}Eu were continuously measured using NaI(Tl) scintillation counter.

2.8. Kinetic studies

The radius of the particle of the sieved fractions was determined by measuring the diameter of 100 particles with an optical microscope. The particles were assumed to be spherical and a mean equivalent radius was calculated.

The rate of adsorption of Cs⁺ ion in OMS, OMAS, ETMS and ETMAS ion exchange materials was studied by batch experiment techniques. 0.05 g of the solid was added to 5 ml of 0.1 M CsNO₃ in a shaker thermostat adjusted at 25 ± 1 °C. After the adjusted interval time, the solid was separated immediately from the solution and the extent of the sorption was determined.

3. Results and discussion

The prepared MS and MAS ion exchange materials were prepared as reported earlier [28] and the skeletal structure of both materials were elucidated using different tools, IR, XRD, XRF, DTA and TGA analyses. The formula of synthesized materials MS and MAS were found to MgSi_{5.59}O_{12.18}·5.93 H₂O and MgAl_{2.32}Si_{5.2}O_{14.88}·18.23H₂O, respectively.

The loading of MS and MAS ion exchange materials by Cs⁺, Co²⁺ and Eu³⁺ ions were carried out at 0.1 M for CsNO₃ and Co(NO₃)₂ and 0.01 M Eu(NO₃)₃ and *V/m* ratio 200 ml/g. The capacity of these solids for the corresponding ions were calculated and tabulated in Table 1. The data in Table 1 showed that MS has a higher capacity for Co²⁺ and Eu³⁺ ions and lower capacity for Cs⁺ ion compared to MAS and the overall capacity sequence is Eu³⁺ > Co²⁺ > Cs⁺. This sequence may be attributed

Table 1
Capacity of OMS, OMAS, TMS and TMAS for Cs⁺, Co²⁺ and Eu³⁺ ions at 25 ± 1 °C

Ion exchanger	Form of ion exchanger	Capacity (meq./g)		
		Cs ⁺	Co ²⁺	Eu ³⁺
Magneso-silicate (MS)	OMS	0.55	1.14	1.39
	TMS	0.029	0.041	0.048
Magnesium alumino-silicate (MAS)	OMAS	0.77	1.06	1.09
	TMAS	0.03	0.04	0.045

Table 2
Surface area values of OMS, OMAS, TMS, TMAS, ETMS and ETMAS ion exchangers

Form of ion exchanger	Surface area (m ² /g)
OMS	178.47
TMS	225.51
Cs-TMS	68.59
Co-TMS	88.22
Eu-TMS	52.02
OMAS	83.46
TMAS	160.58
Cs-TMAS	31.51
Co-TMAS	42.0
Eu-TMAS	22.71

to the increase of electrostatic interaction of multivalent cation compared to the monovalent ones [29]. When the solids thermally treated at 850 °C the capacity are decreased from 0.55 to 0.029 meq./g for Cs⁺ ion, 1.14–0.041 meq./g for Co²⁺ ion and 1.39–0.048 meq./g for Eu³⁺ ion on MS. Similar behaviour was observed for the capacity of TMAS ion exchanger. This decrease in capacity may be related to the loss of water molecules that act as exchangeable active site and/or an increase in crystallinity during thermal treatment at 850 °C.

The loaded samples of MS and MAS were thermal treated at 850 °C in furnace and the products were characterized by surface area, IR, XRD studies.

Surface area values of OMS, OMAS, TMS, TMAS, ETMS and ETMAS solids were measured using the standard volumetric method by nitrogen gas adsorption at 77 K and application of the BET-equation. The values of the surface area obtained were represented in Table 2 and showed a higher surface area value for MS compared to MAS. This may be related to the presence of aluminum in MAS leads to decrease of some pores present in MS and perhaps cancel of these pores.

Thermal treatment of OMS, OMAS, EMS and EMAS ion exchangers heated at 850 ± 2 °C indicated that the treatment of OMS and OMAS solids leads to increase of the surface area values to high extent. This increase may be attributed to the loss of water molecules that occupy most of the reactive pores present in the exchangers. Also, at high temperature (850 ± 2 °C) ion exchanger may be undergo to some shrinkage in the lattice structure and create a new channel with a new surface area that leads to an increase in the total surface area values. During the exchange of Cs⁺, Co²⁺ and Eu³⁺ ions on MS and MAS solids one would expect the replacement of exchangeable ions (H⁺ of H–O–H) with Cs⁺, Co²⁺ and Eu³⁺ ions. The surface area values of the ETMS and ETMAS ion exchangers are decreased compared to OMS, OMAS, TMS and TMAS ion exchange materials (Table 2) and the order has the following sequence;

TMS (225.51 m²/g) > Co-TMS (88.22 m²/g)
 > Cs-TMS (68.59 m²/g)
 > Eu-TMS (52.02 m²/g) and TMAS (160.58 m²/g)
 > Co-TMAS (42.0 m²/g) > Cs-TMAS (31.51 m²/g)
 > Eu-TMAS (22.71 m²/g).

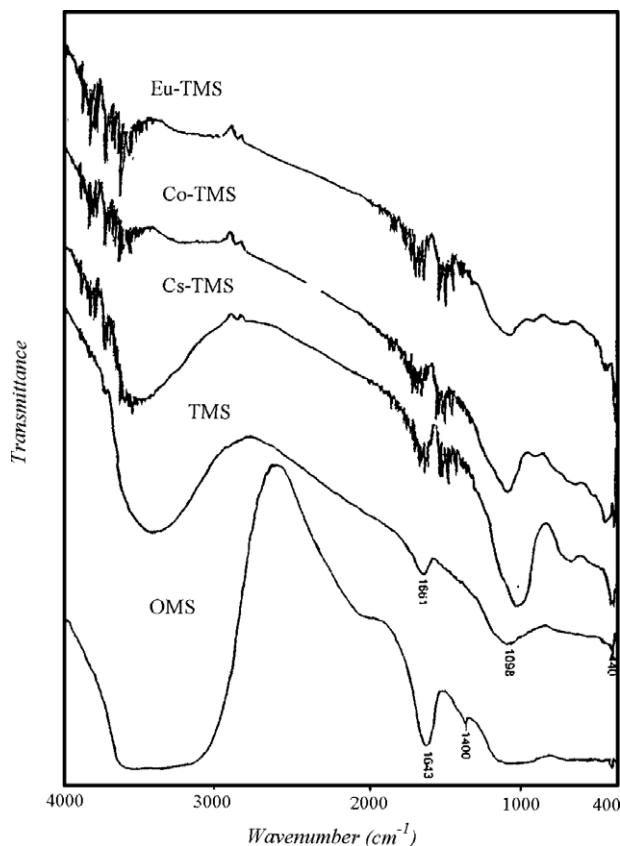


Fig. 1. IR spectra of OMS, TMS, Cs-TMS, Co-TMS and Eu-TMS.

This sequence can be explained on the basis of replacement of exchangeable ions by cation, during the exchange process the smaller ions (H⁺, H–O–H) are replaced by ions of different radius (Eu³⁺ > Cs⁺ > Co²⁺) and the surface area are reduced from 225.51 m²/g to 52.02, 68.59 and 88.22 m²/g for Eu-TMS, Cs-TMS and Co-TMS, respectively. In case of ETMAS the surface area values are decreased from 160.58 to 22.71, 31.51 and 42 m²/g for Eu-TMAS, Cs-TMAS and Co-TMAS, respectively.

IR studies of OMS, TMS, ETMS and OMAS, TMAS, ETMAS were carried out and the spectra obtained were represented in Figs. 1 and 2, respectively. The spectra in Figs. 1 and 2 represent the decrease of the strong and broad peaks in the range 3600–2800 and 1643 cm^{−1} that assigned to free water and H–OH bending and interstitial water molecules [30,31] when the OMS, OMAS, EMS and EMAS thermally treated at 850 ± 2 °C. Also, the degree of intensity decreasing is parallel to the capacity measurements, where the peak intensity related to H₂O becomes very low in case of exchange Eu-ion exchanger and lower than exchanged Co- and Cs-ion exchangers. The peaks at 860–1175 and 550–450 cm^{−1} that related to silicate (Si–O) groups [30,31] becomes more sharp and have high intensity by thermal treatment of the ion exchanger. The spectra of the treated exchange Co-ion exchangers show two small peaks at 673 and 570 cm^{−1} that may be related to the adsorption of Co²⁺ ion on MS and MAS. These peaks were appeared but shifted to lower frequency where the adsorption of atom or molecules on the surface of the ion exchanger perturbs the motion of atom or a group, causing a shift in some group vibration frequency [30], such a shift is

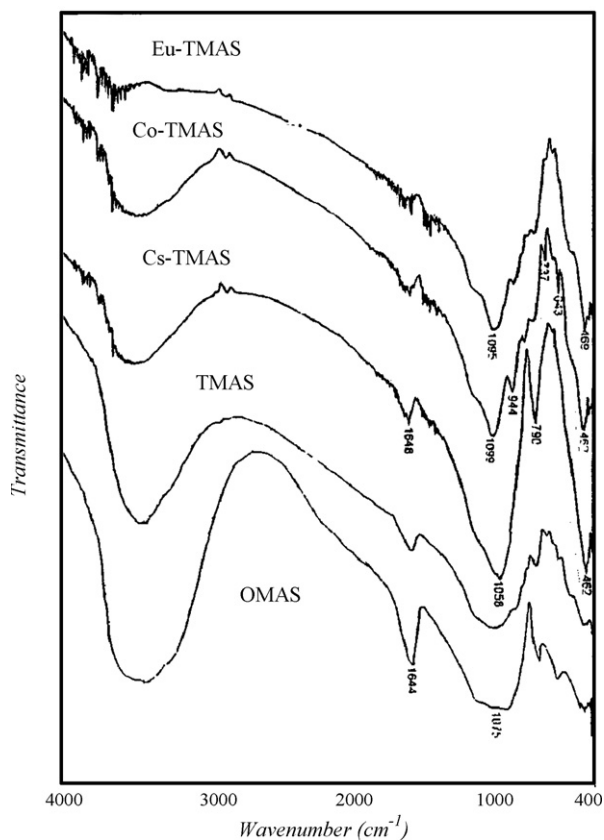


Fig. 2. IR spectra of OMAS, TMAS, Cs-TMAS, Co-TMAS and Eu-TMAS.

evidence that the deformation frequency at 2800 cm^{-1} on the hydrogen ion form is affected by chemically adsorbed ions. A small peaks at 944 cm^{-1} in spectra of treated exchange Co- and Eu-ion exchangers are appeared (Figs. 1 and 2) that may be due to M–M bond formation [30,31].

XRD patterns of OMS, TMS, ETMS and OMAS, TMAS, ETMAS are represented in Figs. 3 and 4, respectively. The patterns of all treated and all treated exchange ion exchangers revealed exactly the same diffraction as the OMS and OMAS. Therefore, no possible structure change caused in the treated and treated exchange of some cations with the exchangers and we failed to arrive to any defined conclusion except that both exchangers still exhibit amorphous character after treatment for

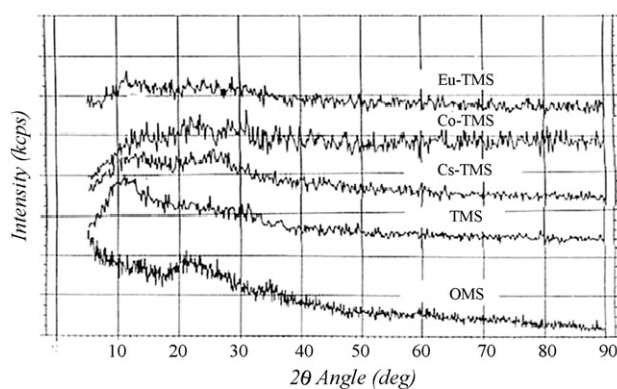


Fig. 3. XRD patterns of OMS, TMS, Cs-TMS, Co-TMS and Eu-TMS.

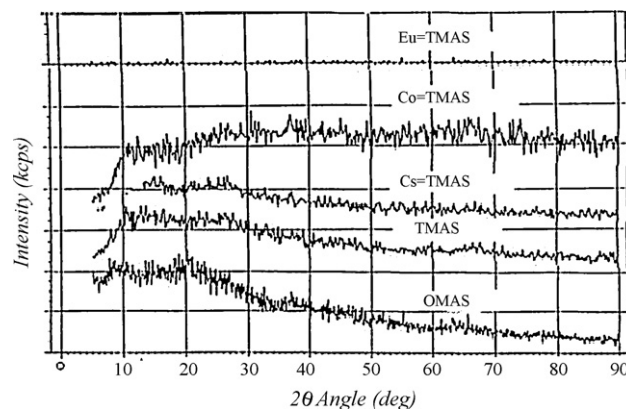


Fig. 4. XRD patterns of OMAS, TMAS, Cs-TMAS, Co-TMAS and Eu-TMAS.

Table 3

Desorption of Cs^+ , Co^{2+} and Eu^{3+} ions from ETMS ion exchanger by different concentrations of HNO_3 at $25 \pm 1^\circ\text{C}$

Form of ion exchanger	Effluent	Volume of effluent (ml)	%Recovery	%Overall recovery
Cs-TMS	0.01 M HNO_3	40	46.94	54.08
	0.1 M HNO_3	25	7.14	
Co-TMS	0.01 M HNO_3	40	15.3	23.29
	0.1 M HNO_3	25	7.99	
Eu-TMS	0.01 M HNO_3	40	29.86	69.12
	0.1 M HNO_3	30	39.26	

the original and exchanged magnesio- and magnesium aluminosilicates. Also, this result indicated the high stability of both exchangers to high temperature.

3.1. Desorption studies

For the desorption studied, samples of ETMS and ETMAS were used. The results obtained for the desorption of three sorbed cations Cs^+ , Co^{2+} and Eu^{3+} from MS and MAS are represented in Tables 3 and 4, respectively. Table 3 shows that the desorption extent of Cs^+ , Co^{2+} and Eu^{3+} ions from ETMS in 0.01 M HNO_3 is higher than those obtained by 0.1 M HNO_3 . This indicated that these sorbed ions are physically or weakly bonded with the exchanger and the other extent are trapped in pores and channel in the ETMS, so when higher concentration of HNO_3 used the small extent trapped are recovery. On the other hand,

Table 4

Desorption of Cs^+ , Co^{2+} and Eu^{3+} ions from ETMAS ion exchanger by different concentrations of HNO_3 at $25 \pm 1^\circ\text{C}$

Form of ion exchanger	Effluent	Volume of effluent (ml)	%Recovery	%Overall recovery
Cs-TMAS	0.01 M HNO_3	40	29.0	88
	0.1 M HNO_3	40	59.0	
Co-TMAS	0.01 M HNO_3	40	8.72	21.84
	0.1 M HNO_3	35	13.12	
Eu-TMAS	0.01 M HNO_3	40	25.52	94.16
	0.1 M HNO_3	60	68.64	

Table 5
Capacity of eluted ETMS and ETMAS ion exchangers for Cs⁺, Co²⁺ and Eu³⁺ ions at 25 ± 1 °C

Form of ion exchanger	Capacity (meq./g)		
	Cs ⁺	Co ²⁺	Eu ³⁺
Eluted Cs-TMS	0.33	0.31	0.087
Eluted Co-TMS	0.55	1.09	0.139
Eluted Eu-TMS	0.075	B.D.L.	B.D.L.
Eluted Cs-TMAS	0.59	0.48	0.153
Eluted Co-TMAS	0.23	0.75	0.066
Eluted Eu-TMAS	0.33	B.D.L.	0.07

B.D.: below detection limit.

desorption of the above mentioned cations from magnesium aluminosilicate show small desorption extent by 0.01 M HNO₃ (Table 4) and the major extent are recovery by 0.1 M HNO₃. This may be attributed to the strong adsorption of these cations on MAS as represented from IR spectra (Fig. 2). Tables 3 and 4 also indicated that the overall recovery percent of these cations from MAS is higher than those obtained from MS ion exchanger.

MS and MAS ion exchangers produced from the desorption studies were taken to study the ion memory of these exchangers to the previous exchangeable ions (Cs⁺, Co²⁺ and Eu³⁺) in framework of MS and MAS.

3.2. Selectivity modification and ion memory of the exchangers

The capacity and selectivity of the eluted ETMS and ETMAS for Cs⁺, Co²⁺ and Eu³⁺ ions were studied and the results tabulated in Table 5. The data in Table 5 showed that the selectivity of MS and MAS for Cs⁺, Co²⁺ and Eu³⁺ ions are modified in the direction of the exchanged form of the ion exchangers and the selectivity sequence seems to be

Cs⁺ (0.33 meq./g) > Co²⁺ (0.31 meq./g) > Eu³⁺ (0.087 meq./g) for eluted Cs-MS,
 Co²⁺ (1.09 meq./g) > Cs⁺ (0.55 meq./g) > Eu³⁺ (0.139 meq./g) for eluted Co-MS,
 Cs⁺ (0.59 meq./g) > Co²⁺ (0.48 meq./g) > Eu³⁺ (0.153 meq./g) for eluted Cs-MAS, and
 Co²⁺ (0.75 meq./g) > Cs⁺ (0.23 meq./g) > Eu³⁺ (0.066 meq./g) for eluted Co-MAS.

These results suggest that the materials can be constructed by keeping cavity for exchangeable ions in the framework of coordination bonding; the product will show high selectivity for the exchangeable ions just as to be retained in ion memory after exchanging particular ion with other ion to maintain fundamentally original structures. For the eluted treated Eu-solids, the capacity values for the studied cations is very low and have not definite selectivity that may be attributed to the higher cavity created by thermal treatment of the solid and this cavity may undergoes some shrinkage and divided into large number of small cavity that make satiric hindrance and leads to very low capacity values for the studied cations.

By comparison the data in Tables 1 and 5 we found that MS and MAS ion exchangers are loss ~94–96% from its original capacities when thermally treated at 850 ± 2 °C (Table 1), on the other hands, the eluted EMS and EMAS thermally treated at the same high temperature have capacity values relatively smaller

than its original values. This means that we can overcome the problem of the loss of capacity of the ion exchangers at high temperature by thermally treatment of the exchanged magnesio- and magnesium aluminosilicates.

3.3. Kinetic studies

As sake of brevity, the kinetic studies were performed for Cs⁺ ion on MS, MAS and ETMS and ETMAS ion exchangers. The kinetic studies were performed at very vigorous stirring condition and hence the results may be interpreted as indicating that film diffusion was not controlling in the sorption process under the operating conditions. The rate of attainment of equilibrium Cs⁺ sorption was seemed to be nearly independent of metal ion concentration. This indicated the possibility of ordinary particle diffusion control of the sorption process. Helfferich [32] introduced a numerical technique to extend the Nernst–Plank model for intraparticle diffusion controlled ion exchange to multi species systems with very fast reversible reactions at local equilibrium. This method is applicable to most reactions which are very fast compared with diffusion in ion exchanger. Hence, an approximate and simple model based on Pick's flux equations was used to analysis the rate of metal sorption. An effective diffusion coefficient for the sorption of Cs⁺ ion on the studied ion exchangers has been calculated by assuming particle control governed by Pick's second law. For practical use, applying Vermeulen's equation, fraction attainment of equilibrium (*F*) can be approximated to the following equation [33]:

$$F(t) = \left[1 - \exp\left(-\frac{D_i t \pi^2}{r_0^2}\right) \right]^{1/2}$$

where *r*₀ is the radius of the ion exchanger and *D*_{*i*} is the effective diffusion coefficient. Thus, the fraction attainment of

equilibrium depends only on the magnitude of the dimensionless time parameter, (*D*_{*i*} *t* / *r*₀²). The half time for adsorption is given by substituting *F*(*t*) = 0.5, i.e.

$$t_{0.5} = \frac{(0.03 r_0^2)}{D_i}$$

Figs. 5 and 6 show the plots of fraction attainment of equilibrium (*F*) against time (*t*) for Cs⁺ ion on MS and MAS, respectively. The calculated values of *D*_{*i*} for Cs⁺ ion sorption in MS, MAS and eluted ETMS and ETMAS are given in Table 6. The data in Table 6 indicated that the diffusion coefficient of Cs⁺ ion is high for the exchanger ETMS and ETMAS compared to MS and MAS samples. This may be attributed to the created channel and pores that preformed during the thermal treatment process and the diffusion directly proportional to the size of the eluted cations.

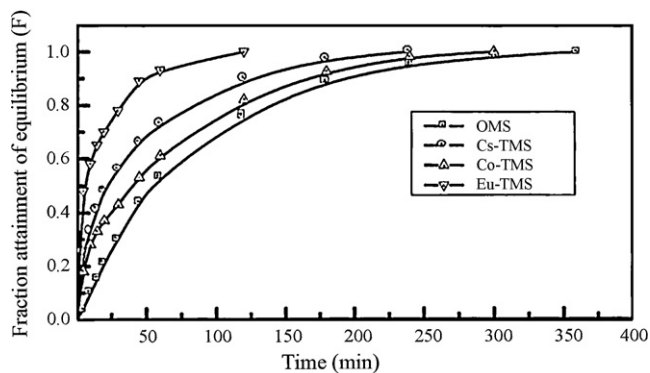


Fig. 5. Rate of Cs⁺ ion sorption on OMS, Cs-TMS, Co-TMS and Eu-TMS at 25 ± 1 °C.

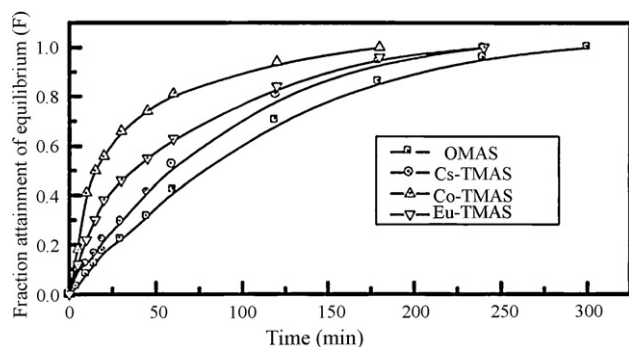


Fig. 6. Rate of Cs⁺ ion sorption on OMAS, Cs-TMAS, Co-TMAS and Eu-TMAS at 25 ± 1 °C.

Table 6
Diffusion coefficient of Cs⁺ ion in the particles of OMS, OMAS, ETMS and ETMAS at 25 ± 1 °C

Form of ion exchanger	Diffusion coefficient × 10 ⁸ (cm ² s ⁻¹)
OMS	1.11
Cs-TMS	2.78
Co-TMS	1.46
Eu-TMS	8.73
OMAS	0.85
Cs-TMAS	1.11
Co-TMAS	4.08
Eu-TMAS	1.69

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