

# Novel inorganic ion exchange materials based on silicates; synthesis, structure and analytical applications of magnesio-silicate and magnesium alumino-silicate sorbents

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## Abstract

Two novel inorganic ion exchange materials magnesio-silicate and magnesium alumino-silicate have been synthesized under identical conditions. The structure of these materials was established by chemical analysis, X-ray diffraction, thermogravimetric and differential thermal analyses, Fourier transform infrared spectroscopy and X-ray fluorescence analysis. Magnesio-silicate and magnesium alumino-silicate were found to have the formulas  $\text{MgSi}_{5.59}\text{O}_{12.18} \cdot 5.93\text{H}_2\text{O}$  and  $\text{MgAl}_{2.32}\text{Si}_{5.2}\text{O}_{14.88} \cdot 18.23\text{H}_2\text{O}$ , respectively. The structure of both sorbents was arranged and predicted according to the ChemDraw Ultra program. The ion exchange capacities of these materials for some radionuclides and heavy metals  $\text{Cs}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  were investigated and the data obtained showed that magnesium alumino-silicate has a higher capacity for these cations compared to magnesio-silicate. Distribution coefficients in nitric acid medium have been evaluated to explore the separation potentiality of magnesio-silicate and magnesium alumino-silicate for  $\text{Cs}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$  ions. Sorption isotherms for all cations were investigated and the data showed the applicability of Freundlich isotherm for all cases.

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## 1. Introduction

Synthesis of inorganic ion exchangers has studied extensively by various workers [1–4]. Excellent selectivity's on the inorganic ion exchangers have been found for a certain elements or group of elements in presence of a large amount of other bulk components [5,6]. The development of new inorganic ion exchangers with characteristic properties is still need attention and their utility in diverse fields is yet to be explored. Titanates [4–12], antimonates [13–15], molybdates [16,17], silicates [18], vanadates [19], doped silica [20] and zeolites [21] based exchangers have been reported earlier from our laboratory and in literature, but magnesio-silicate and magnesium alumino-silicate have not been reported. The idea of the present work was stimulated from the consideration the heteropolybasic acid salts show better ion exchange properties than their corresponding single salts.

In the present paper magnesio-silicate and magnesium alumino-silicate ion exchange materials were synthesized in identical conditions. Composition, chemical and thermal stabilities, IR spectra, XRD and XRF analyses were conducted. Ion exchange capacity and equilibrium distribution coefficients of metal ions on the samples prepared were determined for their selectivities and to explore the separation potential of the studied cations on the matrices.

## 2. Experimental

### 2.1. Reagents and chemicals

Sodium metasilicate (GRG, UK), magnesium chloride (El-Nasr Company, Egypt), all other reagents and chemical used were of analytical grade and used without further purifications.

### 2.2. Synthesis of magnesio-silicate sorbents

Magnesio-silicate was synthesized by dropwise addition of 0.5 M aqueous solutions of magnesium chloride to 0.5 M

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aqueous solution of sodium metasilicate (1:1) with continuous stirring in a water bath adjusted at  $60 \pm 1$  °C. The mixed solution was immediately hydrolyzed in demineralized water. Diluted ammonia solution was added to the mixture until complete precipitation attained. The precipitate formed was kept in the mother solution to overnight standing. The precipitate was washed several times with distilled water, and then washed by 0.1 M HNO<sub>3</sub> to remove impurities and Cl<sup>-</sup> ions. The precipitate rewashed by distilled water to remove NO<sub>3</sub><sup>-</sup> ions. After drying at  $60 \pm 1$  °C, solid was poured in distilled water heated at  $80 \pm 1$  °C to broken the solid and remove air trapped inside the solid, then redried at  $60 \pm 1$  °C. The obtained solid was ground, sieved and store at room temperature.

### 2.3. Synthesis of magnesium alumino-silicate sorbent

This composite was synthesized by dropwise addition of a mixture of 0.5 M aqueous solutions of magnesium chloride and aluminium chloride (1:1) (200 ml) to 0.5 M aqueous solution of sodium metasilicate (200 ml) with continuous stirring in a water bath adjusted at  $60 \pm 1$  °C. The mixed solution was immediately hydrolyzed in demineralization water. The precipitate was formed by addition of diluted ammonia solution to the mixture. After an overnight standing, the precipitate was separated and follow the same above procedure.

### 2.4. Composition of synthesized ion exchangers

The stiochiometry of the constituents in magnesio-silicate and magnesium alumino-silicate ion exchange materials were determined using Philips sequent ional X-ray spectrometer-2400. The solid samples were ground to very fine powders and then mixed with polyvinyl methacrylate as a binder to facilitate the pressing process. The mixture was pressed in a sample holder of 40 mm diameter aluminum cups and pressed on pressing machine at 20 psi to produce a sample with the diameter of 40 mm and 50 mm thickness. The concentrations of magnesium, aluminum and silicone were measured according to Super-Q quantitative application program.

### 2.5. Thermal studies

Samples of magnesio-silicate and magnesium alumino-silicate ion exchange materials (20 mg) were analyzed for DTA and TGA with sample holder made of Al<sub>2</sub>O<sub>3</sub> in N<sub>2</sub> atmosphere using a Shimadzu DTG-60/60H. The heating rate was maintained at 10 °C/min with using alumina powder as reference material.

### 2.6. Infrared spectra

The IR spectra of magnesio-silicate and magnesium alumino-silicate ion exchange materials were carried out by mixed of the solid with potassium bromide in ratio 1:5 and ground to a very fine powder. A transparent disc was formed in a moisture free atmosphere. The FTIR spectra were recorded using BOMEM-FTIR spectrometer in the range 400–4000 cm<sup>-1</sup>.

### 2.7. X-ray analysis

X-ray diffraction patterns of magnesio-silicate and magnesium alumino-silicate ion exchange materials were carried out using a Shimadzu XD-D1, X-ray diffractometer with Cu K $\alpha$  radiation tube source ( $\lambda = 1.5406$  Å) and graphite monochromator operating at 30 kV and 30 mA. The measurements were done in  $2\theta$  ranges from 5 to 90 with scan speed 2 °/min.

### 2.8. Chemical stability

Chemical stability of magnesio-silicate and magnesium alumino-silicate in water and mineral acids (HCl and HNO<sub>3</sub>) was carried out by mixing 0.1 g of the solid with 200 ml of the desired solution with continuous shaking for 7 days. The solid was filtered and the solution was analyzed for Mg, Al and Si ions by a Shimadzu ICPS-7500 spectrometer.

### 2.9. Capacity measurements

Repeated batch equilibration of 0.1 M metal nitrate solutions (Cs<sup>+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup> and Fe<sup>3+</sup>) with the solid material in V/m ratio 100 ml/g was carried out for the capacity evaluation. The mixture was shaken in a shaker thermostat at  $25 \pm 1$  °C. After over night standing the solid was separated and the concentration of the metal ions was measured. <sup>134</sup>Cs and <sup>60</sup>Co were measured radiometrically and Cu<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup> and Fe<sup>3+</sup> were measured by atomic absorption spectrometer. The capacity value was calculated by the following formula;

$$\text{Capacity} = \frac{\% \text{ uptake}}{100} C_0 \frac{V}{m} Z \text{ (meq./g)}$$

where  $C_0$  is the initial concentration of the ions in solution,  $V$  is the solution volume,  $m$  is the sorbent mass and  $Z$  is the valence of the exchanged ions.

### 2.10. Distribution and selectivity studies

The distribution coefficient ( $K_d$ ) of some radionuclides and heavy metals (Cs<sup>+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup> and Fe<sup>3+</sup>) on magnesio-silicate and magnesium alumino-silicate sorbents were determined by batch equilibration. A sample of the solid was immersed in metal nitrate solutions of 10<sup>-4</sup> M with V/m ratio 100 ml/g in 10<sup>-3</sup> M nitric acid medium. The mixture was placed in shaker thermostat adjusted at  $25 \pm 1$  °C for 5 h (time within an equilibrium was attained). After equilibrium, the solutions were separated by centrifugation and the concentration of metal ions in the exchanger and in the solution was deduced from the concentration relative to the initial concentration in the solution. The concentrations of <sup>134</sup>Cs and <sup>60</sup>Co were measured radiometrically using NaI (TI) Scintillation detector connected to an ORTEC assembly but Cu<sup>2+</sup>, cd<sup>2+</sup>, Zn<sup>2+</sup> and Fe<sup>3+</sup> ion concentrations were determined by atomic absorption spectrometer. The  $K_d$  and separation factor values were evaluated;

$$K_d = \frac{(A_o - A_{eq.}) V}{A_{eq.} m} \text{ (ml/g)}$$

where  $A_0$  and  $A_{eq}$  are the concentrations of the ions in solutions before and after equilibration, respectively,  $V$  is the solution volume and  $m$  is the exchanger mass.

### 2.11. Sorption isotherm studies

Sorption isotherms of  $Cs^+$ ,  $Co^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Zn^{2+}$  and  $Fe^{3+}$  ions on magnesio-silicate and magnesium aluminosilicate sorbents were determined over the entire concentration range  $10^{-4}$ – $5 \times 10^{-2}$  M at pH 3 and constant  $V/m$  ratio of 10 ml/g. The experiments were carried out in shaker thermostat at  $25 \pm 1$  °C. The equilibrium concentration ( $C_{eq}$ ) and amount uptake ( $W$ ) were calculated in mmol/g as follows;

$$W = \text{uptake} \times C_0 \times \frac{V}{m} (\text{mmol/g}) \quad C_{eq} = (1 - \text{uptake})C_0$$

where  $C_0$  is the initial concentration of ions (M),  $V$  is the solution volume (ml) and  $m$  is the mass of the exchanger (g).

Plot of  $C$  against  $C/W$  and/or  $\log C_{eq}$  against  $\log W/m$  were performed to obtain the required isotherm.

### 3. Results and discussion

The scope of this work is the attempt to synthesize a high chemical stable inorganic ion exchange material with high selectivity for some radionuclides and/or heavy metals. Di- and tri-components inorganic ion exchange materials magnesio-silicate (MgSi) and magnesium aluminosilicate (MgAlSi) have been synthesized with complete characterization for elucidation of the structure and the chemical formulas of the two matrices.

IR spectra of magnesio-silicate and magnesium aluminosilicate were represented in Fig. 1. From this figure we found that magnesio-silicate and magnesium aluminosilicate show strong and broad band in the range  $3600$ – $2800$   $cm^{-1}$  that assigned to free water molecules [22,23]. The sharp band at  $1645$   $cm^{-1}$  may be due to HO–H bending and interstitial water molecules. Broad and strong peaks at  $860$ – $1175$  and  $540$ – $450$   $cm^{-1}$  were

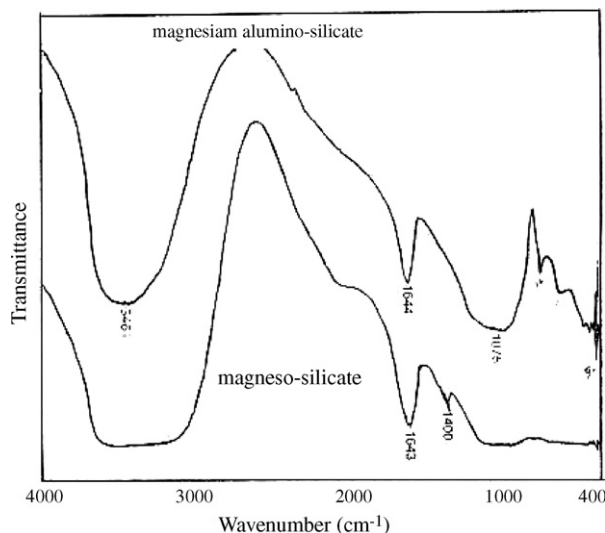


Fig. 1. Infrared spectra of magnesio- and magnesium aluminosilicates.

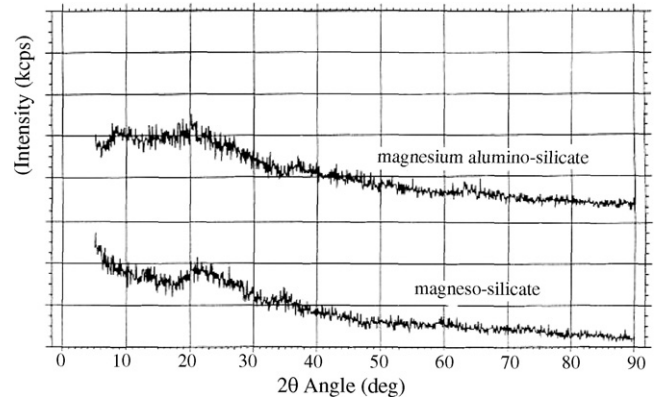


Fig. 2. X-ray diffraction patterns of magnesio- and magnesium aluminosilicates.

appeared in the spectra of both magnesio-silicate and magnesium aluminosilicate that may be assigned to presence of silicate groups [22,23]. The intensity of these peaks are increased in magnesium aluminosilicate compared to magnesio-silicate that related to the higher content of silicate group in the former solid compared to the later ones. Two medium bands at  $860$ – $920$  and  $620$ – $670$   $cm^{-1}$  were appeared in the spectrum of magnesium aluminosilicate that assigned to Al–O bond. These bands are supported by appear two weak bands at  $550$  and  $450$   $cm^{-1}$  which are related to Al–O bond [22,23].

X-ray diffraction patterns of magnesio-silicate and magnesium aluminosilicate were measured and represented in Fig. 2. Fig. 2 shows that both materials have the amorphous nature. Also the patterns of the magnesio-silicate and magnesium aluminosilicate indicated that both materials are found in one phase.

Differential thermal and thermogravimetric analyses (DTA and TGA) of magnesio-silicate and magnesium aluminosilicate are given in Figs. 3 and 4, respectively. The TGA curve of magnesio-silicate (Fig. 3) shows a sharp loss in weight up to  $150$  °C that may be attributed to the loss of water molecules. The interpretation is supported by appearance of endothermic peak in DTA curve (Fig. 3) at  $80.6$  °C. After that a continuous

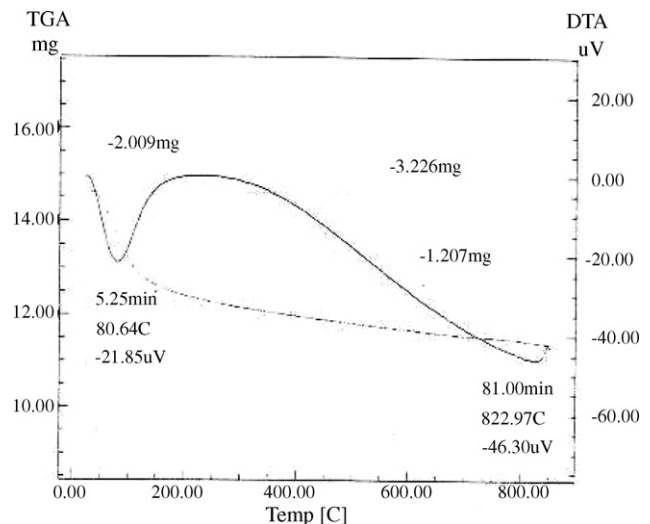
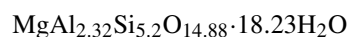
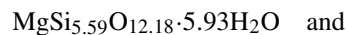


Fig. 3. DTA and TGA of magnesio-silicate.

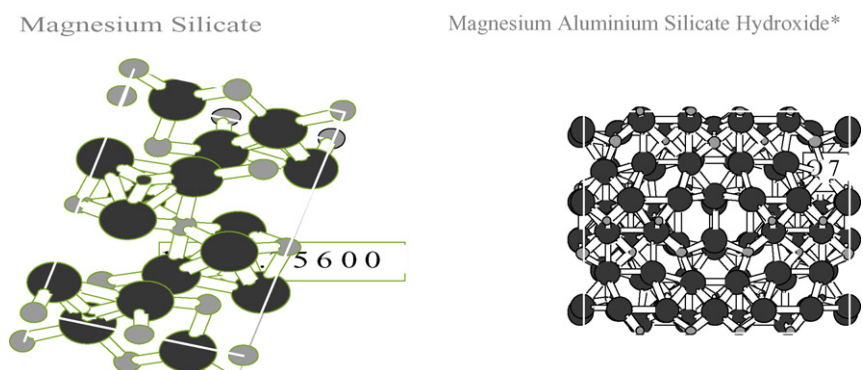
loss in weight is gradually observed up to 850 °C. This decrease in weight is reflected the decomposition reaction of material and formation of metal oxide as supported from the DTA endothermic peak at 822.9 °C. The DTA and TGA of magnesium aluminosilicate (Fig. 4) shows different behaviour than magnesio-silicate where the weight loss are decreased sharply with total weight loss equal 38.08% at 850 °C. This decrease in weight is supported from DTA endothermic peak at 75.06 °C that may be related to elimination of free water molecule in the exchanger. Another endothermic peak at 251.72 °C also may be due to dehydration reaction of magnesium aluminosilicate.

The calcinations of both materials at 850 °C were carried out and indicated that the weight loss due to ignition are equal 22.09 and 38.08% for magnesio-silicate and magnesium aluminosilicate, respectively. These values were used in calculation

silicate and magnesium aluminosilicate were assigned to  $\text{MgSi}_{5.59}\text{O}_{12.18} \cdot n\text{H}_2\text{O}$  and  $\text{MgAl}_{2.32}\text{Si}_{5.2}\text{O}_{14.88} \cdot n\text{H}_2\text{O}$ , respectively. From the loss of ignition, the number of water molecules ( $n$ ) per mole of the material was calculated and equal 5.93 and 18.23 mol for magnesio-silicate and magnesium aluminosilicate, respectively. The above formulas then rewritten as,



for magnesio-silicate and magnesium aluminosilicate, respectively. The structure modeling and the arrangement of atoms in both magnesio-silicate and magnesium aluminosilicate can predict according to ChemDraw Ultra program and represented as following;



of the number of water molecules in the exchanger using the formula [15];

$$18n = \frac{X(M + 18n)}{100}$$

where  $X$  is the percent weight loss of ignition and  $M$  is the molecular weight of the exchanger.

Analysis of the exchange materials for the elemental composition was carried out by X-ray fluorescence technique. The data obtained indicated that the percent of Mg and Si in magnesio-silicate equal 6.65 and 42.26%, respectively, and the percent of Mg, Al and Si in magnesium aluminosilicate equal 2.69, 13.87 and 16.23%, respectively. From all results obtained from IR, DTA, TGA, XRD and XRF the tentative formulas of magnesio-

The chemical stability of magnesio-silicate and magnesium aluminosilicate towards mineral acid solutions was studied and the data showed that the presence of aluminum with magnesio-silicate leads to high stability to chemical attack compared to magnesio-silicate itself. This result is agreed with the fact that the chemical stability of tri-components salt ( $\text{MgAlSi}$ ) is higher than di-components where the presence of Al inside magnesio-silicate leads to more rigid structure and more stability. Author found similar trend for lithium zirconium silicate where the solubility of lithium zirconosilicate decreased with increased the concentration of lithium in situ precipitated with zirconium silicate ion exchanger [18]. The data of chemical stability indicated that magnesio-silicate is stable in  $\text{HNO}_3$  and  $\text{HCl}$  solutions up to 2 M but magnesium aluminosilicate more stable up to 4 M acid solutions. At high concentrations of acid media (5 M) both magnesio-silicate and magnesium aluminosilicate are partially soluble.

The ion exchange capacities of magnesio-silicate and magnesium aluminosilicate for some radionuclides and heavy metals ( $\text{Cs}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$ ) were investigated and the data are represented in Table 1. Table 1 indicated that the affinity sequence for all cations is  $\text{Co}^{2+} > \text{Cd}^{2+} \sim \text{Zn}^{2+} \geq \text{Cu}^{2+} > \text{Cs}^+ > \text{Fe}^{3+}$  for magnesio-silicate and  $\text{Cd}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Cu}^{2+} > \text{Cs}^+ > \text{Fe}^{3+}$  for magnesium aluminosilicate ion exchanger. This sequence is in accordance with the hydrated radii of the exchanging ions. The ions with smaller hydrated radii easily enter the pores of the exchanger, resulting in higher adsorption [1,2]. The capacity of magnesio-silicate for cobalt ion has an exception where it show high

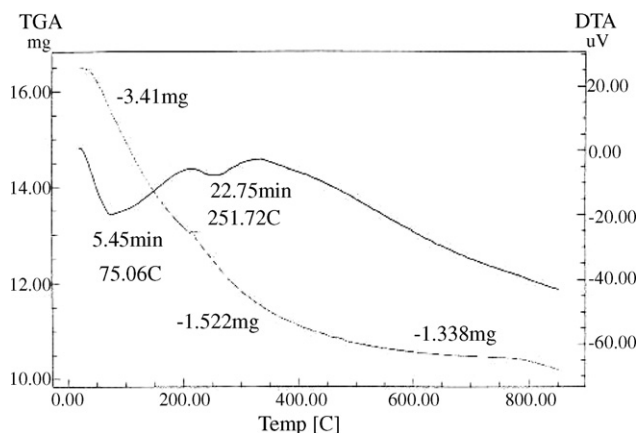


Fig. 4. DTA and TGA of magnesium aluminosilicate.

Table 1  
Capacities of magnesio-silicate and magnesium aluminosilicate sorbents for some cations at  $25 \pm 1^\circ\text{C}$

Sorbent	Cation	Capacity (meq./g)
Magnesio-silicate, $\text{MgSi}_{5.59}\text{O}_{12.18} \cdot 5.93\text{H}_2\text{O}$	$\text{Cs}^+$	0.57
	$\text{Co}^{2+}$	1.16
	$\text{Cu}^{2+}$	0.60
	$\text{Zn}^{2+}$	0.82
	$\text{Cd}^{2+}$	0.82
	$\text{Fe}^{3+}$	0.08
Magnesium aluminosilicate, $\text{MgAl}_{2.32}\text{Si}_{5.2}\text{O}_{14.88} \cdot 18.23\text{H}_2\text{O}$	$\text{Cs}^+$	0.77
	$\text{Co}^{2+}$	1.00
	$\text{Cu}^{2+}$	0.88
	$\text{Zn}^{2+}$	1.38
	$\text{Cd}^{2+}$	2.06
	$\text{Fe}^{3+}$	0.54

capacity that may be due to the higher complexing ability of cobalt with the presence in more than one oxidation states. The lower capacity of magnesio-silicate and magnesium aluminosilicate for  $\text{Fe}^{3+}$  reflects the nonselectivity of both exchangers for  $\text{Fe}^{3+}$  ion, as we shall see later in the distribution coefficient studies. Also, the data in Table 1 shows a relatively high capacity of magnesium aluminosilicate compared to magnesio-silicate for the studied cations that, may be due to the addition of Al to magnesio-silicate material increases the number of acidic sites on the surface of magnesium aluminosilicate.

Preliminary studies on the kinetic of exchange for  $\text{Cs}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$  ions on magnesio-silicate and magnesium aluminosilicate indicated that equilibrium was attained within 5 h in a shaker thermostat adjusted at  $25 \pm 1^\circ\text{C}$ .

The distribution coefficient is an important parameter to explore the separation potentiality of magnesio-silicate and magnesium aluminosilicate for  $\text{Cs}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$  ions. The distribution coefficients ( $K_d$ ) and separation factors ( $\alpha$ ) for the mentioned cations in  $10^{-3}\text{M HNO}_3$  medium were calculated and tabulated in Table 2. The data in Table 2 indicated that the distribution coefficients have the affinity sequence  $\text{Cs}^+ > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+}$  for magnesio-silicate

Table 2  
Distribution coefficients and separation factors for  $\text{Cs}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$  ions on magnesio- and magnesium aluminosilicates in  $10^{-3}\text{M HNO}_3$  medium at  $25 \pm 1^\circ\text{C}$

Sorbent	Parameter	$\text{Fe}^{3+}$	$\text{Co}^{2+}$	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Cd}^{2+}$	$\text{Cs}^+$
Magnesio-silicate, $\text{MgSi}_{5.59}\text{O}_{12.18} \cdot 5.93\text{H}_2\text{O}$	$K_d$ (ml/g)	11.73	39.43	13.66	22.71	24.68	58.95
	Separation factor $\{K_d(\text{B})/K_d(\text{A})\}$ , $\alpha$ ;		3.36	1.16	1.93	2.10	5.03
				0.35	0.58	0.63	1.49
					1.66	1.81	4.32
						1.09	2.59
						2.39	
Magnesium aluminosilicate, $\text{MgAl}_{2.32}\text{Si}_{5.2}\text{O}_{14.88} \cdot 18.23\text{H}_2\text{O}$	$K_d$ (ml/g)	29.27	98.01	34.12	57.48	73.31	77.46
	Separation factor $\{K_d(\text{B})/K_d(\text{A})\}$ , $\alpha$ ;		3.34	1.17	1.96	2.51	2.65
				0.35	0.58	0.75	0.74
					1.68	2.15	2.27
						1.28	1.35
						1.05	

and  $\text{Co}^{2+} > \text{Cs}^+ > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+}$  for magnesium aluminosilicate in  $10^{-3}\text{M HNO}_3$ . This sequence supports the sorption of metal ions in hydrated state. The separation factors for the studied cations were calculated and indicated that,  $\text{Cs}^+$  ion has a higher separation factor 5.03, 1.49, 4.32, 2.59 and 2.39 for  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  ions, respectively, on magnesio-silicate and 2.65, 0.74, 2.27, 1.35 and 1.05 for  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  ions, respectively, on magnesium aluminosilicate ion exchanger. These values indicated that  $\text{Cs}^+$  ion can easily separated from radioactive and industrial waste solutions included the above-mentioned cations.

The nature of adsorption processes for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cs}^+$  and  $\text{Fe}^{3+}$  ions on magnesio-silicate and magnesium aluminosilicate were investigated by gradual increase of the sorbate concentration and measuring the amount sorbed at each equilibrium concentration. The freundlich isotherm most widely used mathematical model, given an empirical expression encompassing the surface heterogeneity and exponential distribution of active sites and their energies was tested in the following form;

$$\log \frac{W}{m} = K + K' \log C_{\text{eq}}$$

where  $W$  is the amount uptake,  $C_{\text{eq}}$  is the equilibrium concentration,  $K$  and  $K'$  are the freundlich constants measure the adsorption intensity and adsorption capacity of the sorbent, respectively, and computed from the slope and intercept of the linear relationship.

Plots of  $\log W/m$  against  $\log C_{\text{eq}}$  linear relationships were obtained for all cases as shown in Figs. 5 and 6 for magnesio-silicate and magnesium aluminosilicate, respectively. The data in Figs. 5 and 6 show the applicability of freundlich isotherm for all cases and all of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cs}^+$  and  $\text{Fe}^{3+}$  ions are physically sorbed on magnesio-silicate and magnesium aluminosilicate. The values of adsorption capacity ( $K$ ) and adsorption intensity ( $K'$ ) for  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cs}^+$  and  $\text{Fe}^{3+}$  ions on magnesio-silicate and magnesium aluminosilicate were computed from the linear relationships in Figs. 5 and 6 and tabulated in Table 3. As seen from Table 3 the numerical values of ( $K' < 1$ ) suggest the surface of the sorbent of heterogeneous type [15].

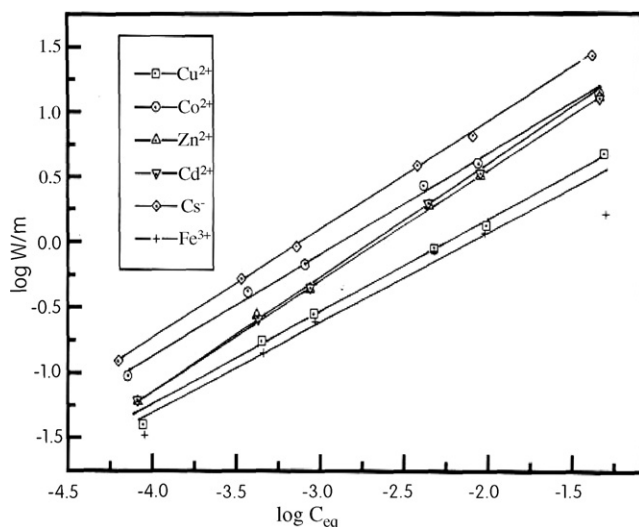


Fig. 5. Freundlich adsorption isotherms for the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cs}^+$  and  $\text{Fe}^{3+}$  ions on magnesio-silicate at  $\text{pH} = 3$  and  $25 \pm 1^\circ \text{C}$ .

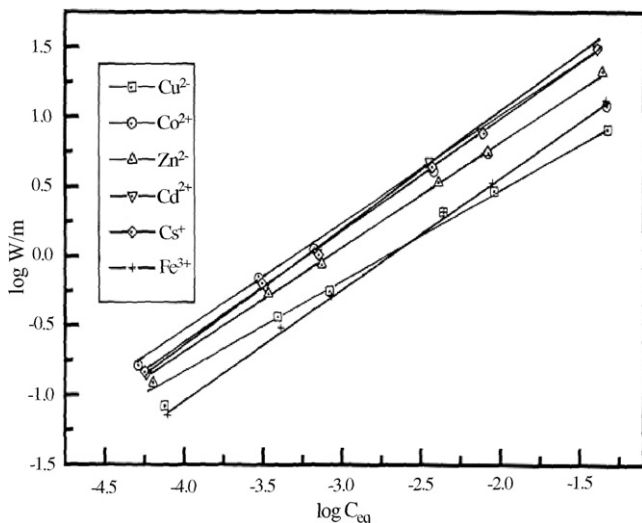


Fig. 6. Freundlich adsorption isotherms for the adsorption of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cs}^+$  and  $\text{Fe}^{3+}$  ions on magnesium alumino-silicate at  $\text{pH} = 3$  and  $25 \pm 1^\circ \text{C}$ .

Table 3

Freundlich parameters for adsorption of  $\text{Cs}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$  ions on magnesio- and magnesium alumino-silicates at  $\text{pH} 3$  and  $25 \pm 1^\circ \text{C}$

Cation	Freundlich parameter	Magnesio-silicate	Magnesium alumino-silicate
$\text{Cu}^{2+}$	$K$	0.014	0.022
	$K'$	0.86	0.68
$\text{Co}^{2+}$	$K$	0.018	0.089
	$K'$	0.83	0.59
$\text{Zn}^{2+}$	$K$	0.011	0.032
	$K'$	0.79	0.77
$\text{Cd}^{2+}$	$K$	0.011	0.035
	$K'$	0.79	0.83
$\text{Cs}^+$	$K$	0.025	0.035
	$K'$	0.86	0.86
$\text{Fe}^{3+}$	$K$	0.008	0.014
	$K'$	0.71	0.77

The numerical value of ( $K'$ ) is only reduced at lower equilibrium concentrations. From parameters ( $K^-$ ,  $K$ ) that referred to adsorption intensity and adsorption capacity, respectively, we found that ( $K^-$ ) has higher values for magnesium alumino-silicate compared to magnesio-silicate and both of them  $< 1$ . This means that the heterogeneity increased by the presence of aluminum in situ magnesio-silicate. Freundlich sorption isotherm does not predict any saturation of the solid surface thus envisages infinite surface coverage mathematically. Similar results were also reported for the adsorption of  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  ions on poly acrylamide acrylic acid impregnated with silico-titanate ion exchanger [24].

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