SYNTHESIS AND CHARACTERIZATION OF A NEW CATION EXCHANGER-MANGANESE (II) SILICATE DOPING WITH FE, CE, V AND W ELEMENTS AND THEIR USE FOR TREATMENT INDUSTRIAL LIQUID WASTES.

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Abstract

Manganese (II) silicate has been synthesized as a gel product by direct precipitation reaction. Modifying its structure by doping with iron, cerium, vanadium and tungsten elements has been carried out. These materials were characterized using X-ray, IR ,TGA-DTA and chemical stability was studied. The prepared materials show increasing in the capacities values from 2.65, 2.55, 2.22, 1.73 and 1.50 to 3.61, 3.42, 3.11, 2.68 and 2.16 (meqg^{-1}) for Co^{2+}, Cd^{2+}, Cu^{2+}, Cs^{+} and Al^{3+}, Respectively as a result of the modification by doping. pH titration data reveal monofunctional behavior. The distribution coefficients values of metal ions have been determined at different pHs. Column application was also studied.

Introduction

Significant accumulation of toxic metals in the environment and their persistent nature have been the subject of great concern in recent years due to their over increased use in various industries. The hazardous heavy metal ions that pose potential dangers to human lives from the industrial effluents include lead, mercury, cadmium, chromium, copper, zinc and nickel. The toxicities of heavy metals may be caused by the inhibition and reduction of various enzymes, complexation with certain ligands of amino acids and substitution of essential metal ions from enzymes [1,2]. Their quantification in industrial effluents, various water and biological samples is important, especially in the environment monitoring and assessment of occupational and environmental exposure to toxic metals. During the last decades inorganic ion exchangers have also found applications in the field of sensor [3-5], wastewater treatment [6-9], radiochemical separation [10] and chromatographic separation of pesticides [11,12] because of their unusual selectivity towards certain ionic species. Synthesis of two component ion exchangers by introducing tetravalent metals (Zr and Sn) into phosphate, silicate, arsenate and molybdate have been the extensively studied groups owing to their variable coordination number [13]. Inorganic ion exchangers of three components have been found to exhibit enhanced ion exchange capacity and selectivity [14–17]. In this work, modification the new ion exchanger (manganese (II) silicate) by doping with (iron , cerium , vanadium and tungsten) elements has been done , which exhibit a dramatic increasing in its sorption capacities and selectivities toward Co^{2+} , Cd^{2+} , Cu^{2+} , Cs^{+} and Al^{3+} at different pHs. The aim of this work was to study the doping effects on the ion exchange performance and physico-chemical properties of this interaction. We present in this paper the synthesis , characterization , ion exchange behaviour and application using column technique.

Experimental

Reagents and chemicals

All reagents and chemicals utilized in this work were of analytical grade purity. In all experiments, bidistilled water was used for solutions preparation, dilution and distilled water was used for washing all glasses used.

Preparation of manganese (II) silicate

Manganese silicate was prepared by drop wise addition of equal volumes of 0.5 M manganese chloride to a hot solution of 0.5 M sodium metasilicate with continuous stirring. After over night standing in mother liquor the obtained precipitate was filtered, washed thoroughly with bidistilled water by using a centrifuge (about 10^4 rpm), and dried at 60ºC. The dried product was rewashed with bidistilled water in order to remove fine adherent particles and finally air dried to produce manganese silicate (Mn-Si) in initial form.

In order to introduce variable coordination number of ions to the surface or the structure of synthetic manganese silicate, which may facilitate its binding to heavy metals or any other active compounds, iron, cerium, vanadium and tungsten were doped. Different doping forms of manganese silicate named as (Mn-Fe-Si, Mn-Ce-Si , Mn-V-Si and Mn-W-Si) which can be obtained by mixing 0.5 M of $MnCl_2$ in presence of 0.5 M Na_2SiO_3 with 0.05 M solutions of Fe $(NO_3)_3.9H_2O$, $((NH_4)_2Ce(NO_3)_6)$, $NaVO_3$, or $Na_2WO_4.2H_2O$ at 60ºC on water bath; by ratio equal (1 : 1 : 0.1), respectively. All the modified products were filtered, washed with bidistilled water and dried at 50 ºC.

The products in initial and doped forms were further treated with excess of 0.1 mol L^{-1} nitric acid solutions for complete replacement of counter ions by H^+ ions.

The excess of acid was removed by repeated washing with bidistilled water . Finally the material was dried in an oven at 50 ºC, ground, sieved then stored in dark bottle [18]. The total water contents of the samples were determined from their TG-thermograms up to 1000ºC, and or by calcinations of 1 g of the samples at the same temperature and calculate the % loss in weight.

Characterization of modified forms of manganese (II) silicate

Some physical and chemical properties of the prepared manganese silicate and its modified forms (doped forms) were characterized using different analytical techniques, using the facility and equipment in analytical service laboratory, Hot Labs Center, Atomic Energy Authority.

Powder X-ray diffraction patterns were carried out using Shimadzu X-ray diffractometer, Model XD – D1 Shimadzu, Kyoto (Japan) with a nickel filter and Cu-K_α radiation tube, the elemental analysis of the synthesized manganese silicate and its modified forms were carried out using Philips Pw-2400 sequential X-ray spectrometer, the Fourier transform infrared spectra were measured with BOMEM FT-IR spectrometer, model MB 147, product from Canada on KBr disc technique in the range 400-4000 cm^{-1}, differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) were performed at heating rate of 20 ºC / min using Shimadzu DTG-60 Thermal Analyzer Shimadzu-Kyoto-Japan. The samples measured from ambient temperature up to 1000 ºC with a heating rate of 20 deg /min.

The number of water molecules (n) per mole of the material can be calculated from Alberti equation [19];

$$18n = x\,(M+18n) / 100$$

where, x is the percent of water content and M+18n is the molecular weight of the materials.

Chemical Stability:

Chemical stability of manganese silicate was studied in water, sodium hydroxide, nitric, and hydrochloric acids by mixing of the examined sample (0. 5 g) with 50 ml of the above solutions with continuous shaking for about one week.

Titration of ion exchanger

Manganese (II) silicate in H^+-form was placed in a column that was fitted with glass wool at its bottom. A glass bottle containing 200 ml of 0.001M HCl was placed below the column, and for determination of pH, a glass electrode was placed in the solution, NaOH was poured into the column. Titration was carried out, by passing the 0.01 M NaOH solution at a drop rate of about 0.3 ml / min, and continued to a pH of about 11 [20].

Capacity of manganese (II) silicate

The capacities of different prepared forms were determined by batch experiment technique, where 0.1 g of the each solid material was equilibrated with 10 ml of 0.05 M of each Co^{2+}, Cu^{2+} Cd^{2+}, Cs^{+} and Al^{3+} chloride solutions. The mixture was shaken for 24 h at 25±1ºC. After equilibrium, the liquid phase was separated by centrifugation and replaced by the same volume of the initial solution. The procedures were repeated until no further absorption of cations occurred. The capacities were calculated from the following equation [21]:

$$\text{Capacity, meq/g} = \%\ \text{uptake} \times C_{\circ} \times V/m \times Z / 100$$

where :

$C_{\circ}$: is the initial concentration of solution , g /ml .

V : is the solution volume , ml .

m : is the weight of the exchanger, g.

Z : is the charge of the metal ion adsorbed.

Distribution Studies :

Distribution coefficient (K_d) is actually used to access the overall ability of the material to remove the ion of interest under set condition. Batch technique was followed to determine the distribution coefficient (K_d) values on both the initial and doped forms of manganese silicate as a function of different pH solutions as following:

0.1g of each exchanger were shaken at 25±1 ºC with 10 mL of solutions of 50 ppm from different studied cations. The initial pH of the solution was adjusted to pH 1 - 5.78 range with 0.1 M HNO_3. After an overnight standing (sufficient to attain equilibrium), the mixtures were centrifuged and the acidity of the solutions were determined (equilibrium pH). The distribution coefficient (K_d) values were calculated according to equation:

$$K_d = [I - F]/F \times V/m \text{ ml/g}$$

where I, F, are the initial and final concentrations of the studied ions in solution, V is the volume of solution (ml) and m is the mass of sorbent (g).

Results and discussion

It has previously shown that several silicates have different analytical and industrial application either in initial or when modified chemically [22,23]. Some account in the literature describing the synthesis, chemistry and application of manganese silicate. There are very little applications were found on the using of manganese silicate as cationic exchanger.

Manganese (II) silicate has been prepared as a gel product by direct precipitation reaction using solutions of manganese chloride and sodium metasilicate in equimolar ratio. Also it should pointed out that, there are no studies dealing with the influence of the structural modification of the manganese silicate by doping with iron , cerium, vanadium and tungsten on its ion exchange character.

The synthesis and characterization of the different forms of manganese silicates (which included elemental, infrared, X-ray and Thermogramivimetric analyses), have been studied.

Elemental analysis of the fresh samples of manganese silicate in each doped form was obtained by XRF measurements and given in Table (1). The results indicated that, the synthetic gel was changed to new modified forms.

In all the cases, the contents of SiO_2 in the samples ranged between 48.69 % and 54.61 %. Thus, variation in composition for samples obtained with different doping element was occurred as given in Table (1).

.Table (1) : Elemental composition of manganese (II) silicates and its modified forms

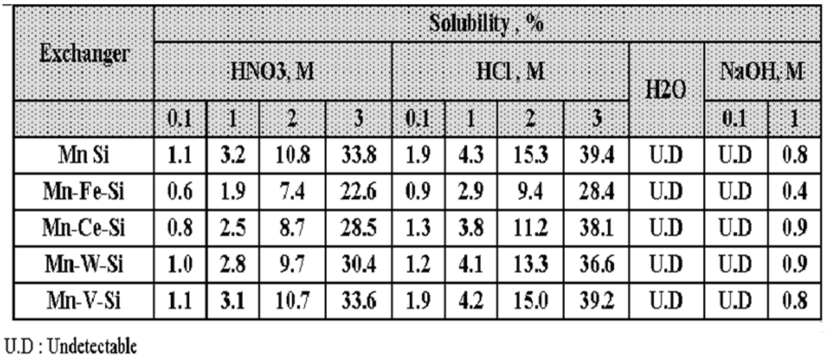
Exchanger	MnO %	SiO_2 %	Na_2O %	Water % content	V_2O_5 %	CeO_2 %	WO_3 %	Fe_2O_3 %
Mn -Si	24.81	48.69	0.50	17.76	0.00	0.00	0.00	0.00
Mn-Fe-Si	10.09	54.61	0.28	25.36	0.00	0.00	0.00	7.01
Mn-Ce-Si	14.67	53.94	0.33	22.32	0.00	5.80	0.00	0.00
Mn-W-Si	16.98	51.21	0.40	19.76	0.00	0.00	6.65	0.00
Mn -V- Si	18.92	50.66	0.44	18.09	5.79	0.00	0.00	0.00

From the data given in Table (1) it was found that, the components percentage of manganese silicates reveal variable ratios depending on the doping element which well cause change in physico-chemical properties of the products. Consequently, this change may produce an expected different behavior as ion exchange material

Chemical stability of synthetic inorganic ion exchangers plays an important role in their analytical applications. Exchangers which have a high solubility in water, alkaline as well as in acid media may not be useful for separation investigations [24,25]. It is therefore advisable to have enough guide of the solubility of an ion exchanger. In this concern, chemical stability of the prepared manganese silicate samples was investigated in water, nitric acid, hydrochloric acids and sodium hydroxide at different concentrations (0.1- 3.0 M) for nitric and hydrochloric acid and (0.1 – 1 M) for sodium hydroxide.

The results of chemical stability of the prepared materials at different conditions are presented in Table (2). Data in Table (2) indicated that , all prepared materials have reasonable good chemical stability in water , alkali and in acids up to 1 M, while are partially dissolved in the range higher than 1 M acid concentrations.

Table (2) : Chemical stability of the prepared manganese silicate samples in acid and alkaline media , (at 25 ± 1 ^{0}C) with relative errors about ± 1 %.



Exchanger	Solubility , %										
	HNO3, M				HCl , M				H2O	NaOH, M	
	0.1	1	2	3	0.1	1	2	3		0.1	1
Mn Si	1.1	3.2	10.8	33.8	1.9	4.3	15.3	39.4	U.D	U.D	0.8
Mn-Fe-Si	0.6	1.9	7.4	22.6	0.9	2.9	9.4	28.4	U.D	U.D	0.4
Mn-Ce-Si	0.8	2.5	8.7	28.5	1.3	3.8	11.2	38.1	U.D	U.D	0.9
Mn-W-Si	1.0	2.8	9.7	30.4	1.2	4.1	13.3	36.6	U.D	U.D	0.9
Mn-V-Si	1.1	3.1	10.7	33.6	1.9	4.2	15.0	39.2	U.D	U.D	0.8

U.D : Undetectable

The chemical stability of the prepared matrices follows the order:

Mn-Fe-Si >Mn-Ce-Si >Mn-W-Si >Mn-V-Si > Mn-Si.

The DTA / TGA curves of the different synthesized manganese silicates have been showon in Fig.1 (a-e).

Fig. (1a) shows one endothermic peak with maxima at $T_{m1} \approx 99.18^{\circ}C$ resulting from 12.74 % mass change. The mass loss increase slightly up to ~ 800°C to become

17.76 %. The first peak is possibly assigned to the dehydration of hygroscopic water (adsorbed on the mineral surface and called zeolitic when it occupies the central part of the channels) [26], and the second one is possibly due to the loss of constitution water, which forms part of the crystalline network and it is generally presented like hydroxyl groups [26]. Also, at this temperature, where the compound have been transformed totally into crystalline solid; energy has to be released to perform such transformation.

Different-thermogram behaviors were obtained after doping the solid (Mn-Si) with different elements, where Fig. (1b) of Mn-Fe-Si, indicated that, only one sharp endothermic peak at Tm 88.47 ºC, resulting from 15.10 % mass loss at 200 ºC which was slightly increased with heating to become 25.36 % at 800 ºC.

Fig. (1c) of Mn-Ce-Si, shows an endothermic peak at Tm 82.07 ºC corssponding to mass change equals 12.9 % follwed by mass change continous up to 800 ºC equals 22.32 %.

Fig. (1d) Mn-W-Si, shows an endothermic peak 99.18 ºC corssponding to mass change 12.74 % this loss continous up to 800 ºC to become 19.76 %.

Consequantly, Fig. (1e) of Mn-V-Si, shows an endothermic peak at Tm 107.48 ºC corssponding to mass change equals 14.31 % follwed by mass change continous up to 800 ºC equals 18.09 %.

According to the results of TG-thermograms, the trend of total water contents becomes as following;

Mn-Fe-Si (H_2O = 25.36) > Mn-Ce-Si (H_2O = 22.32) > Mn-W-Si (H_2O = 19.76%) > Mn-V-Si (H_2O = 18.09 %) > Mn-Si (H_2O = 17.76 %).

The relatively high content of bound moisture, ranging from 17.76 % in the sample undoped to 25.36 % in the sample doped with iron (Mn-Fe-Si) may be pointed to presence of Si-OH groups in the internal structure of the obtained manganese silicates [27].

Based on the literature data [28,29,30], the structural water molecules may play an important rule as exchanging sites. However, the H_3O^+ in the structure of inorganic ion exchanger (e.g hydrous metal oxide and zeolites) has important effect on the ion exchange capacity.

Infrared spectroscopy provides information on the chemical strucure of adsorbent materials. FT-IR spectra of manganese silicates are shown in Fig.2 (a-e). The spectrum of initially obtained manganese silicate which represent similtinous peaks at 3496 cm^{-1} characteristic to Mn-OH streach of manganese silicate [31,32] , an additional broadining absorbance near 3200 cm^{-1} attributed to H-bonding (of coordinated water) and a band at 1638 cm^{-1} is due to the bending mode of water ; a weak band at 1412 cm^{-1} may ascribed to hydroxyl streach of zeolitic water, while the strong band at 1032 is ascribed to Si-O streatching vibrations. Also, band at 452 cm^{-1} is due to the Mn-O vibrations.[33].

A diffractogram prepared for the samples of synthetic manganese silicate and its modified form which are dried at 50ºC showed that no peaks at all thereby suggesting an amorphous nature of manganese silicates..

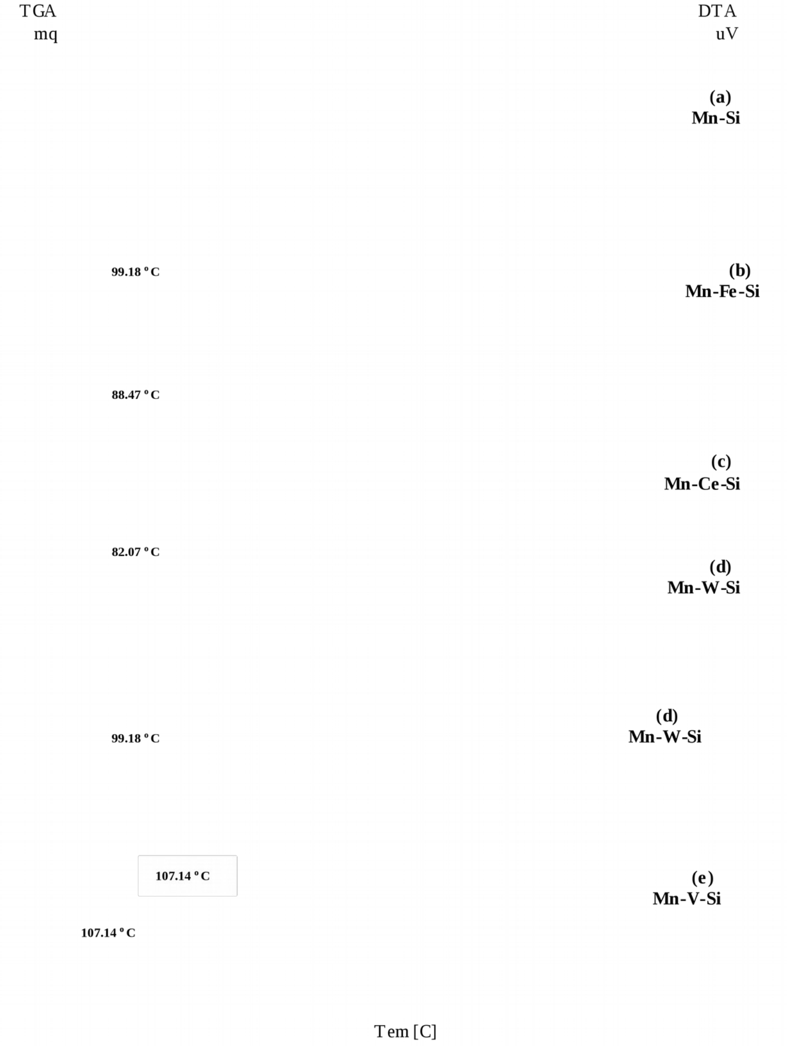


Fig. (1): DTA-DTG Thermograms of manganese silicate and its modified forms

Fig.( ): DTA-TG Thermograms of manganese silicates , where (a) undoped form & (b) doped with (Fe).

The capacities of manganese silicate doped with different elements for Co^{2+}, Cu^{2+}, Cd^{2+} , Cs^{+} and Al^{3+} ions at different pH values were determined. It is clear that, the capacity values increase with increasing pH of the solution as shown in Table (3). The prepared matrices behave as a strong cation exchanger in high pH values. At high pH the concentration of hydrogen ion in solution is small and the cations compete successfully for the exchange sites. A comparison of the capacity values of manganese silicate doped with different elements, reveal the following sequences :

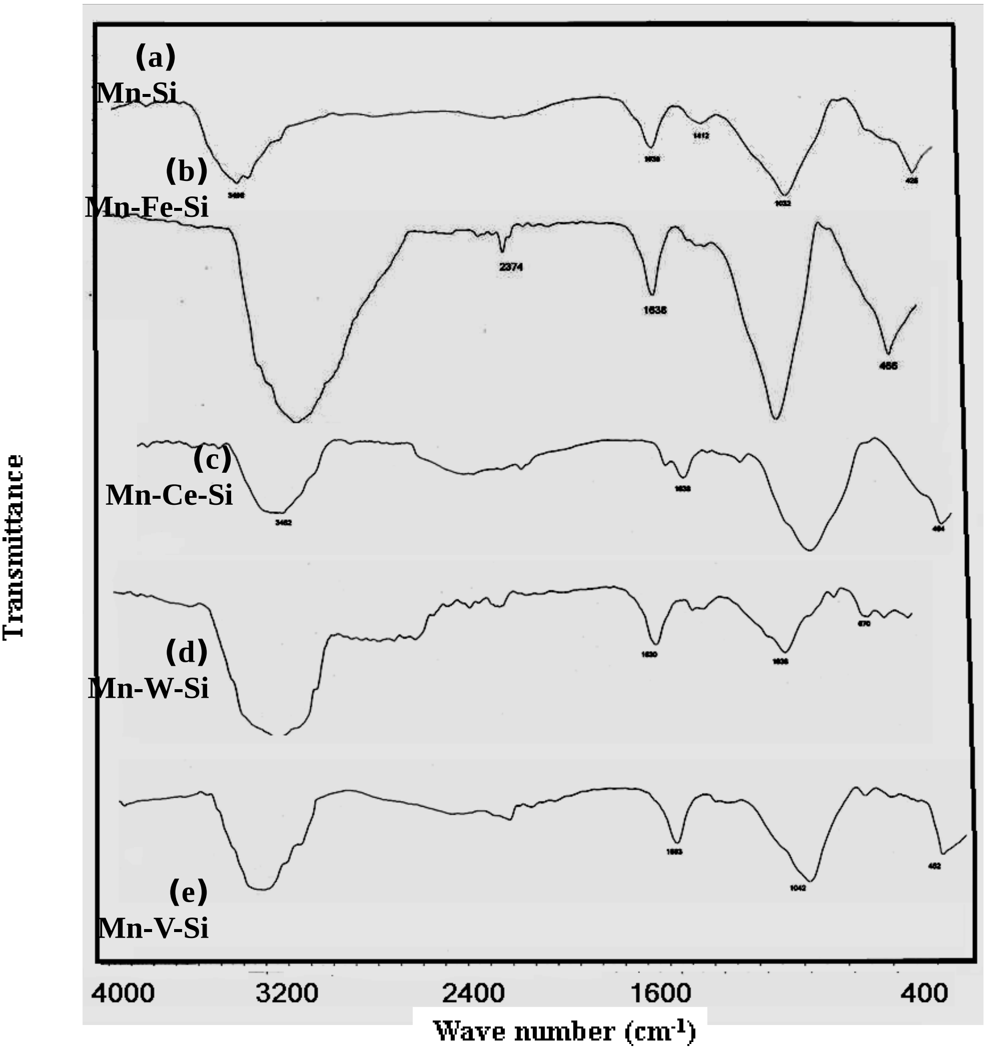


Fig. (2) : Infrared spectra of manganese silicate and its modified forms.

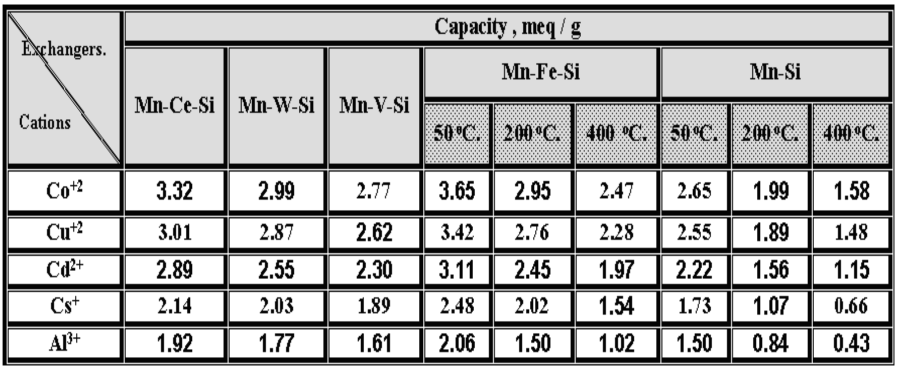
Mn-Fe-Si > Mn-Ce-Si >Mn-W-Si > Mn-V-Si >Mn-Si .

The determined capacity of the five forms of manganese silicate are in correlation with their water contents. Hence, Mn-Fe-Si has the higher value of water contents (25.36%) compared to other silicate forms , as in (Table1), and it shows the highest ion exchange capacity, as shown in (Table 3).

This result is similar with many silicate compounds [34,35] where, the water molecules may be included as exchanging sites.

On the other hand, Table (3) indicates that, the ion exchange capacity decrease as a function of increasing drying temperatures, as in case of Mn-Fe-Si which heated at (50 , 200 and 400 °C). and Mn-Si at (50 , 200 and 400 °C).

Table (3) : Capacity measurements of Co^{2+}, Cu^{2+}, Cd^{2+}, Cs^{+} and Al^{3+} metal cations on manganese silicate samples at 25 ± 1 ºC.



Exchangers. / Cations	Capacity , meq / g								
	Mn-Ce-Si	Mn-W-Si	Mn-V-Si	Mn-Fe-Si			Mn-Si		
				50 ºC.	200 ºC.	400 ºC.	50 ºC.	200 ºC.	400 ºC.
Co^{+2}	3.32	2.99	2.77	3.65	2.95	2.47	2.65	1.99	1.58
Cu^{+2}	3.01	2.87	2.62	3.42	2.76	2.28	2.55	1.89	1.48
Cd^{2+}	2.89	2.55	2.30	3.11	2.45	1.97	2.22	1.56	1.15
Cs^{+}	2.14	2.03	1.89	2.48	2.02	1.54	1.73	1.07	0.66
Al^{3+}	1.92	1.77	1.61	2.06	1.50	1.02	1.50	0.84	0.43

The pH titration curve of manganese silicate doped with iron (Mn-Fe-Si) was shown in Fig. (3). The pH titration curve shows only one inflection point indicating that mono functional and acidic character ion exchanger. However, the exchange takes place in one step under this condition, this is expected result for silicates.

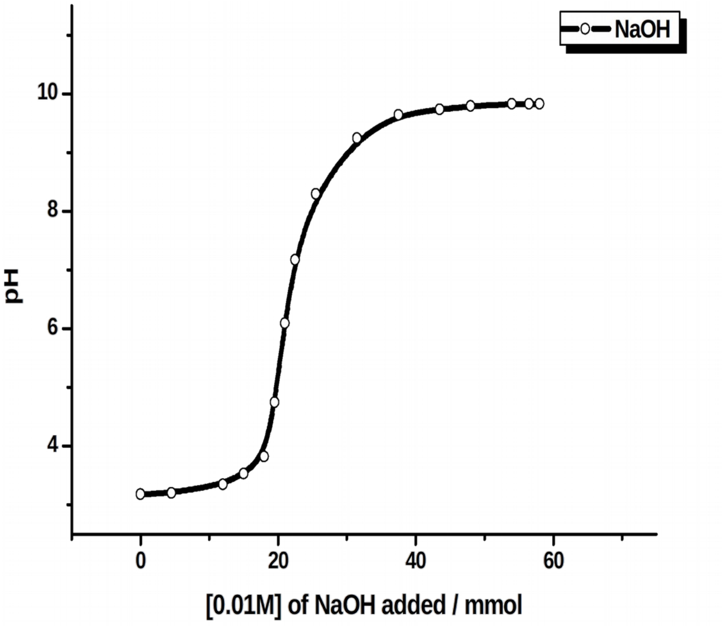


Fig. (3) : The pH titration curve of manganese silicate doped with iron (Mn-Fe-Si).

The distribution coefficient (K_d, ml / g) of Cu^{2+}, Co^{2+}, Cd^{2+}, Cs^{+} and Al^{3+} species on the different modified forms of manganese silicates was determined in aqueous media with respect to pH values lower than the pH of hydroxide formation (<6) as shown in Fig.(4).

The preliminary investigations indicated that the equilibrium time for the exchange Cu^{2+}, Co^{2+}, Cd^{2+}, Cs^{+} and Al^{3+} ions on manganese silicates were attained within 6 hrs, (sufficient to attain equilibrium) in a shaker thermostat adjusted at 25±1ºC.

In our case the relation between log K_d against pH are linear relations and the slopes are deviated than the charge, this reveals that our studied systems are non ideal ion exchange process. This deviation may be due to the prominence of a mechanism other than ion exchange, like simultaneous adsorption of anions. From the obtained results it was observed that the distribution coefficient for all the metal ions studied were increased with increasing pH (low acid concentration). The increasing of the distribution coefficient values for the studied metal ions with increasing the pH may be considered a general phenomenon for many ion exchange materials [35,36,37]. This behavior may be due to the concentration of hydrogen ion in solution is small and the cations compete successfully for the exchanging sites, thus the K_d value are increased. While, at lower pH value, there is an increase in the hydrogen ion concentration in solution which competed successfully on ionized exchange sites leading to decrease in the K_d values for all metal ions.

Generally, for the present exchangers we can concluded that, manganese silicate doped with iron (Mn-Fe-Si) shows a greater affinity for the studied ions (Co^{2+} , Cu^{2+}, Cd^{2+}, Cs^{+} and Al^{3+}) than that of initial form and the other doped forms. At the same time , the selectivity sequence for manganese silicate doped with Fe, Ce, and W follows the order; $Co^{2+} > Cu^{2+} > Cd^{2+} > Cs^{+} > Al^{3+}$.

In this concern, the selectivity sequence of manganese silicate toward the studied heavy elements can be explained in terms of electrostatic interaction between the hydrated cations and the anionic sites in the exchange. The attraction between anions and cations in ionic crystal, obeys coulombs law which demands that; for cations of equal charge a small ion be attracted with a greater force and held more tightly than a large ion, the ionic radius of Co^{2+} (0.72A°) ions are smaller than that of Cu^{2+} (0.74A°) than Cd^{2+} (0.97A°) ions, which leading to high mobility of Co^{2+} than Cu^{2+} than Cd^{2+} ions and high adsorption value obtained. While for Aluminum , the hydration energy may be the reason for its coming at the end of this sequence [38,39,40].

In contrast, the selectivity sequence of manganese silicate doped with V and undoped form reveal the order $Cu^{2+} > Co^{2+} > Cd^{2+} > Cs^{+} > Al^{3+}$. This trend may be attributed to that, the higher selectivity of Cu^{2+} ions compared to other ions, even at low pH, likely due to precipitation, while as the pH was increased, its contribution decreased and a considerable amount of cupper ions was removed by adsorption as well [41,42].

According to the data in Figs. (4), it can concluded and summarized that,

(i) all manganese silicate forms (except that vanadium doped and initial form) show the selectivity sequence ;

$$Co^{2+} > Cu^{2+} > Cd^{2+} > Cs^{+} > Al^{3+}$$

while the initial and vanadium (V) doped forms show the selectivity sequence ;

$$Cu^{2+} > Co^{2+} > Cd^{2+} > Cs^{+} > Al^{3+}$$

ii) manganese silicates doped with iron (Mn-Fe-Si) shows a greater affinity for the studied ions than the other doped forms and achieving the order ;

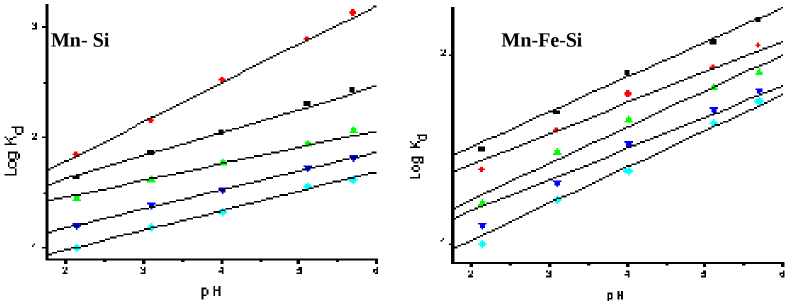
Mn-Fe-Si > Mn-Ce-Si > Mn-W-Si > Mn-V-Si > Mn-Si in the case of Co^{2+}.

Mn-V-Si > Mn-Si > Mn-Fe-Si > Mn-Ce-Si > Mn-W-Si in the case of Cu^{2+}.

(iii) all cations reveal increasing adsorption with pH increasing up to studied pH value.

The column chromatography separation is explained by plate theory. According to this theory, column is considered to be divided into a number of equal units called calculated plates. These units, although entirely hypothetical, give rise to a very useful way for the practical measurements of column efficiency.

Investigation were conducted to explore suitable conditions for quantitative loading and sorption of Co^{2+},Cu^{2+}, Cd^{2+}, Cs^{+} and Al^{3+} ions in neutral media and at 25 ºC. As far as the break through capacity of the column used, (Fig.5) shows break through capacity curves for Co^{2+}, Cu^{2+}, Cd^{2+}, Cs^{+} and Al^{3+} (50 ppm for each) on manganese silicate doped with iron (Mn-Fe-Si) column in the feed solutions. Each break through curve depicts the percent concentrations of the respective metal ion in the effluent to the feed solution (C / C_o %) vs. effluent volume (V ml) as shown in Fig. (5).



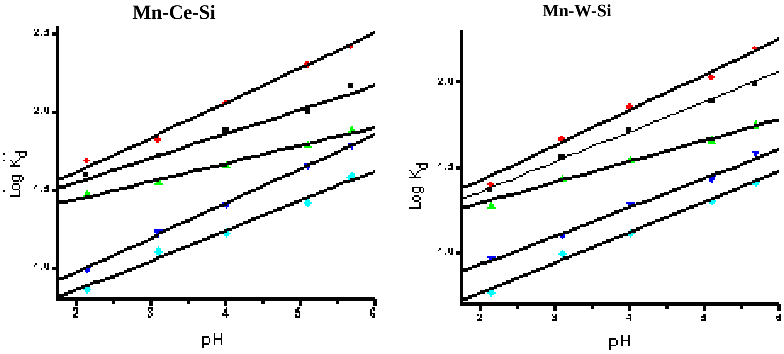


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Fig. (4): Plots of log K_d against pH for the exchange of Cu^{2+}, Co^{2+}, Cd^{2+}, Cs^{+}, and Al^{3+} ions on Mn-Si , Mn-Fe- Si , Mn-Ce-Si, Mn-W-Si and Mn-V-Si at 25±1˚C.

The corresponding uptake for the investigated cations per gram of solid is calculated using the following formula:

$$Q_{0.5} = C_0 V (50\ \%) / W \quad \text{meq / g}$$

where $Q_{0.5}$ means the break through capacity in meq / g, C_o is the initial metal concentration in mg / ml, V is the volume to break through in Cm^3 and W is the weight of the (Mn-Fe-Si) in gram. From the results presented in Fig. (5), it was found that the selectivity of the ions towards the Mn-Fe-Si is in the order ;

$$Co^{2+} > Cu^{2+} > Cd^{2+} > Cs^{+} > Al^{3+}$$

The break through capacity for all the metal ions studied are calculated from Fig. (5), and found to be 3.01, 2.02 , 2.88 , 2.01 and 1.88 meq / g for Co^{2+}, Cu^{2+}, Cd^{2+}, Cs^{+} and Al^{3+} respectively. This result agree with that of batch ion exchange capacity.

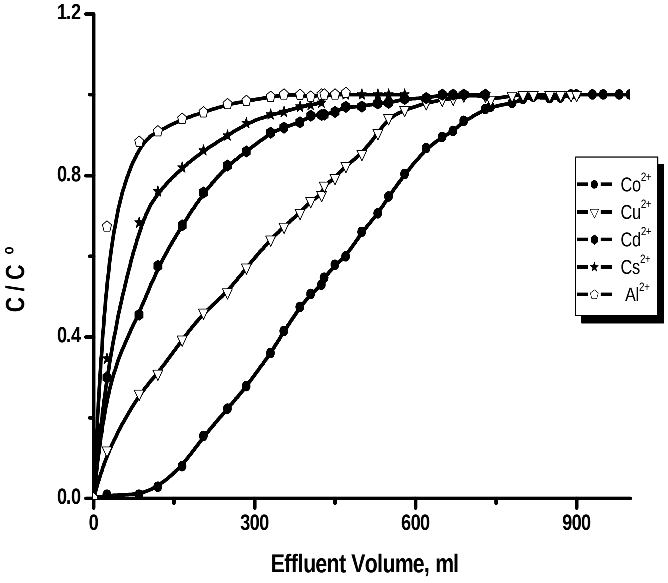

Fig. (5): Break through curves of mixture of Co $^{2+}$, Cu^{2+},Cd^{2+}, Cs^{+} and Al^{3+} ions on (Mn-Fe-Si) in neutral pH and at 25±1˚C.

On the other hand, the regeneration of an ion exchanger is an important step in order to make the ion-exchange process more economical. So, the regeneration test of the spent (Mn-Fe-Si) beads from column runs was also conducted by (0.1-2 M) HNO_3 solutions at the flow rate of 4 ml min^{-1} in the same column at 25 ºC [43,44], as shown in Fig. (6), at 0.1 M HNO_3 (~ 40 ml) sharp peak concerned to Co^{2+} ions followed by another smaller peak of Cu^{2+} below the first peak, and both overlapped with small peaks of other ions (Cd^{2+}, Cs^{+} and Al^{3+}) followed by a second moderate peaks of Co^{2+} and Cu^{2+} ions overlapped with minor peaks of other ions at 1 M HNO_3 (~120ml).

To increase the regeneration efficiency larger than 99 %, additional volume of 2 M HNO_3 was rinsed through the Mn-Fe-Si columns , as shown in (Fig.6).

As seen from the results it is clear that, the different ions can be removed from sorbent (Mn-Fe-Si) column by increasing concentration of nitric acid HNO_3 and it was found that the tail end of different ions is continuous until the volume of eluent becomes a round 220 ml which is necessary to remove the adsorbed ion completely (99%). Thus , it can expect using the column in the regeneration process.

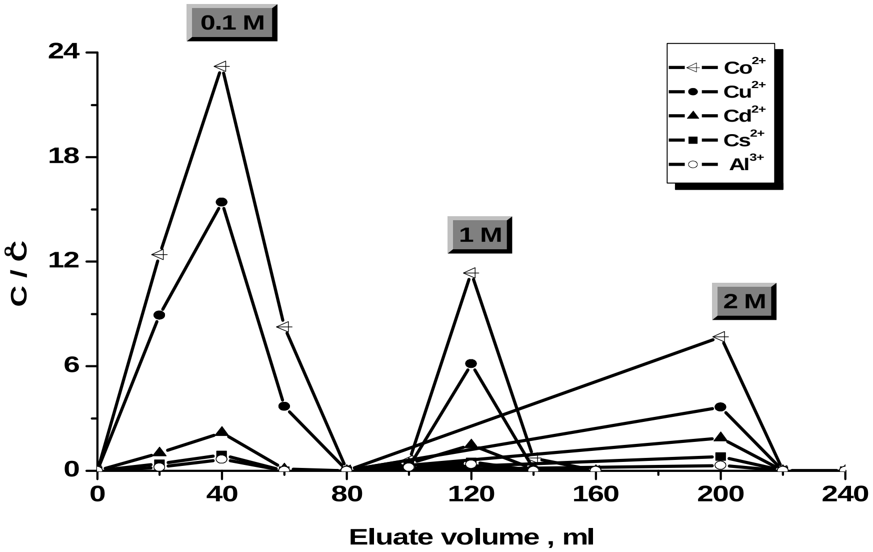

Fig. (6): Elution curves of mixture of Co^{2+} , Cu^{2+},Cd^{2+}, Cs^{+} and Al^{3+} ions with 0.1, 1 and 2M HNO_3 from (Mn-Fe-Si) (0.5 diameter x 5 Cm length and 4 ml / min. flow rate).

Conclusion

On the base of the experimental result of this investigation, the following conclusion can be drawn:

- The new inorganic cation-exchanger manganese (II) silicate was prepared by simple method (precipitation) which has high chemical and thermal stability , and its modification by doping with iron, cerium , vanadium, tungsten has been done, which exhibit a dramatic increasing in its sorption capacities and selectivities toward Co^{2+} , Cd^{2+} , Cu^{2+} , Cs^{+} and Al^{3+} at different pHs.
- Studying the log K_d against pH indicated that,

  (i) all manganese silicate forms (except that vanadium doped form and initial form) show the selectivity sequence;

  $Co^{2+} > Cu^{2+} > Cd^{2+} > Cs^{+} > Al^{3+}$

  while the initial and vanadium (V) doped forms show the selectivity sequence;

  $Cu^{2+} > Co^{2+} > Cd^{2+} > Cs^{+} > Al^{3+}$

  ii) manganese silicates doped with iron (Mn-Fe-Si) shows a greater affinity for the studied ions than the other doped forms and achieving the order;

  Mn-Fe-Si > Mn-Ce-Si > Mn-W-Si > Mn-V-Si > Mn-Si in the case of Co^{2+}.

  Mn-V-Si > Mn-Si > Mn-Fe-Si > Mn-Ce-Si > Mn-W-Si in the case of Cu^{2+}.

  (iii) all cations reveal increasing adsorption with pH increasing up to studied pH value.
- Different ions can be separated from (Mn-Fe-Si) column by 0.1 M HNO3, so we can expect using the column in the regeneration process.

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