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Unheated and Heated Batch Methods in Ion Exchange of Clinoptilolite

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Additional information is available at the end of the chapter

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1. Introduction

It is well known that natural zeolites consist of alumina and silica tetrahedra which, bound in a definite way, include crystal structure vacancies, channels and pores [1,2]. About 40 natural zeolites have been identified during the past 200 years; the most widespread are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite. More than 150 zeolites have been synthesized; the most common are zeolites A, X, Y, and ZMS-5. Clinoptilolite has the structural formula $(\text{Na,K})_6(\text{Al}_6\text{Si}_{30}\text{O}_{72}) \cdot 20\text{H}_2\text{O}$, characterized by two different rings, which are $8(3,3 \times 4,6 \text{ \AA})$ T and $10(3,0 \times 7,6 \text{ \AA})$ T on the ab-plane, and channels with rings of $8(2,6 \times 4,7 \text{ \AA})$ T on the bc-plane. As shown in Figure 1, there are exchangeable cations of Na^+ , K^+ , Ca^{2+} and Mg^{2+} through the channels

Because clinoptilolite has rings of two different dimensions, it is used in retention and separation of various gases, as an adsorbent, and as a molecular sieve. Because of its exchangeable cations clinoptilolite, which has the property of ion exchange, is used in producing biological and water filters, in retention of various heavy metal ions and radio-isotopes, in production of fillers in animal feeds, and in the horticulture and agriculture as a soil additive.[4, 5, 6]

Clinoptilolite is a material that is used in both its natural and modified forms. Both forms of clinoptilolite have widespread application but, apart from their general ion-exchange properties and the high quantities of exchangeable cations through their channels, their general properties are different [7, 8].

2. Materials and methods

2.1. Unheated batch method

Ion-exchanged forms of Na-clinoptilolite from the Bigadiç area were produced via the batch method, using solutions of 0.1N, 0.5N and 1N – with salts of Na^+ , K^+ , Ca^{2+} , Cr^{3+} , Ag^+ and 100

ml of deionized water. Five grams of 300-mesh clinoptilolite were poured into each solution and stirred gently, and then put in suspension for 72 hours at room temperature. Subsequently, the clinoptilolite-solution suspension system was filtered. After filtration, the clinoptilolite was washed eight times with deionized water at 98°C and dried at 110°C for 16h. [9, 10]

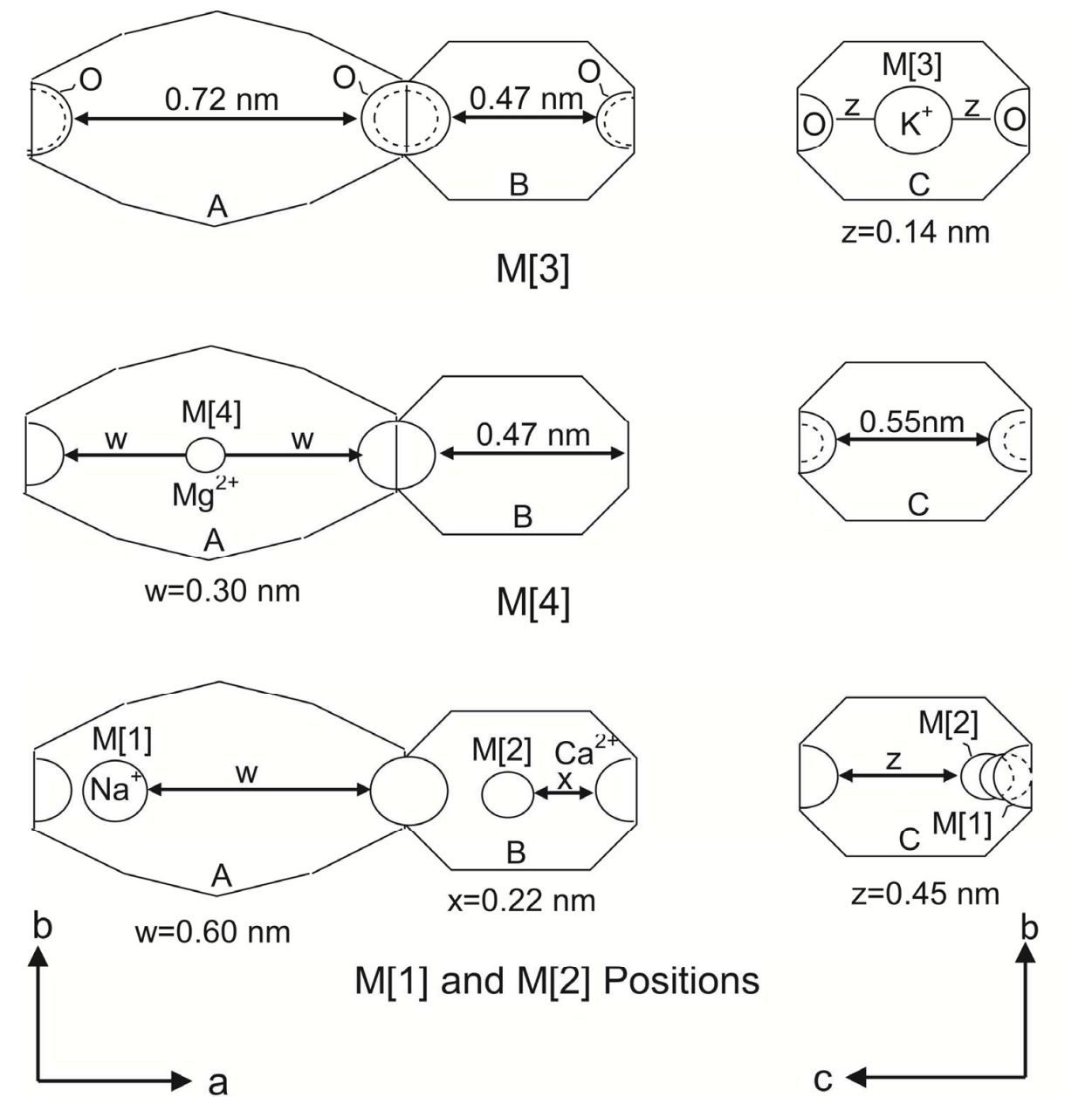


Figure 1. Cation positions in clinoptilolite.[3]

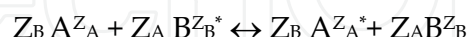
2.2. Heated batch methods

Ion exchange is conducted using a heated/cooled back magnetic stirrer system. A 100 ml solution was prepared by mixing 5 g of 300 mesh clinoptilolite with deionized water kept at 98°C for 2h.

The clinoptilolite-solution suspension system was then filtered. After filtration, the clinoptilolite was washed eight times with deionized water at 98°C and then dried at 110°C for 16 h. [11, 12]

2.3. Ion exchange

The process of ion exchange occurs between the A^{Z_A} cation in solution and B^{Z_B} cation in the zeolite, and can be formulated as follows:



where Z_A and Z_B show the valences of the cations, and A^{Z_B} and B^{Z_A} show the cations in the zeolite structure.

Ion-exchange reactions are stoichiometric, graphical representations of equilibrium concentrations of exchangeable ions in both solutions; the structure of zeolite may be ascertained from ion-exchange isotherms.

Before an ion-exchange isotherm may be obtained, equilibrium of ion exchange must be reached. In zeolites A, X, and Y with low framework densities, the equilibrium of exchange between one valence ions (such as Na^+ and K^+) is obtained in approximately one week. In zeolite structures with high framework densities, the equilibrium of exchange among high valence ions is obtained in a few months.

After the time of equilibrium is defined, this procedure could be utilized in order to plot an isotherm. Zeolites react with a solution containing ions of both A^{Z_A} and B^{Z_B} . Although the relative amounts of ions A^{Z_A} and B^{Z_B} might vary, solutions must have a constant total normality (N). According to the condition of equinormality, total ionic intensities of any solution in the system of the zeolite/solution must be constant before and after ion-exchange reactions.

The ionic intensity of any solution is

$$I = (1/2) \sum C_i Z_i^2$$

where C_i are the concentrations of opposing ions in ion-grams per liter, and Z_i are the valences of opposing ions.

Because of the distribution of A^{Z_A} and B^{Z_B} between the phases, the solution and solid phases in equilibrium must be analyzed. Thus, a plot of the equivalent fraction of ion in solution (A_s) versus equivalent fraction of the same ion in zeolite (A_z^*) isotherm may be obtained.

The ion-exchange isotherm indicates the relative preferences of any ion within the zeolite structure. Besides, the separation factor of ion A within the zeolite structure is

$$\alpha = (A_z^*/B_z^*)(m_B/m_A)$$

where A_z^* ve B_z^* are equivalent fractions of ions A and B in zeolite, respectively, and m_A and m_B are the concentrations of ions in solutions in mole/liter. The total of the equivalent

fractions of Az^* and Bz^* must equal 1. On the basis of ion selectivity, if $\alpha > Z_A/Z_B$, the zeolite prefers A^{Z_A} ions; if $\alpha = Z_A/Z_B$, the zeolite has no preference; and if $\alpha < Z_A/Z_B$, the zeolite prefers B^{Z_B} ions. [13, 14]

2.4. Ion-exchange rate

XRF analyses were conducted on 0.1N-, 0.5N- and 1N-modified forms of solid-phase Na-clinoptilolite, and especially the values of exchangeable and other cations differed greatly from values of the natural form (Table 1). The numbers of atoms in the unit cell were calculated with the knowledge that the unit cell includes 72 oxygen atoms. The numbers of atoms calculated and the following formula were used:

$$X_{\text{form}} = [1 - (A_{\text{form}} / A_{\text{natural}})] \times 100$$

where X_{form} = the ion-exchange rate of the forms and the number of atoms in the unit cell of the same form, and A_{natural} = the number of atoms in the unit cell of the natural form.

2.5. Rate of ion selectivity

The rate of ion selectivity, as termed by us, is different from the "ion selectivity" of the ion-exchanged forms; this rate is calculated from the percentages of ions in the structure, and thus is similar to the rate of ion exchange. For Na^+ , K^+ , Ca^{2+} and Mg^{2+} (exchangeable cations) forms, this quantity may be calculated using

$$\alpha_{\text{form}} = [(A_{\text{form}} / A_{\text{natural}}) - 1] \times 100$$

and for non-exchangeable cations such as Co^{3+} , Cd^+ , Cr^{3+} , Ag^+ forms using

$$\alpha_{\text{form}} = A_{\text{form}} \times 100$$

where α_{form} is the ion-selectivity rate of the ionic form, and A_{form} and A_{natural} are the numbers of atoms in the unit cells of the ion-exchanged form and the natural form, respectively.

3. Results and discussion

3.1. Rate of ion exchange

The results of chemical analyses and the numbers of atoms in the unit cells of natural and Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Co^{3+} , Cd^{2+} , Cr^{3+} and Ag^+ modified forms of clinoptilolite are given in Tables 1 and 2. As shown in the chemical formula of clinoptilolite, the numbers of atoms in the unit cell were calculated with the knowledge that the unit cell includes 72 oxygen atoms (Table 2).

Tables 3 and 4 were derived from data given in Table 2. Ion-exchange rates and the ordering of ion-exchange rate for unheated and heated methods applied to Na-clinoptilolite from Bigadiç-Balıkesir (Turkey) are given in Tables 3 and 4.

Ion-Exchange Method	Ion-Exchange Forms	Molecules												
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	Co ₂ O ₃	CdO	Cr ₂ O ₃	Ag ₂ O	H ₂ O	Σ
	Natural	69.81	11.92	0.78	3.32	1.33	1.65	0.49	-	-	-	-	10.70	100.00
UHBM	0.1N Na ⁺	68.45	11.72	0.86	2.72	1.24	2.19	0.81	-	-	-	-	11.98	99.97
	0.5N Na ⁺	68.44	11.69	0.76	1.80	1.06	4.28	1.13	-	-	-	-	10.85	100.10
	1N Na ⁺	69.05	11.79	0.83	1.53	0.96	4.22	1.66	-	-	-	-	9.96	100.00
HBM	0.1N Na ⁺	68.21	11.63	0.83	3.14	1.58	1.92	0.94	-	-	-	-	11.75	100.00
	0.5N Na ⁺	69.40	11.78	0.85	3.04	1.47	1.79	1.02	-	-	-	-	10.63	100.00
	1N Na ⁺	68.69	11.67	0.89	1.92	1.14	1.63	3.18	-	-	-	-	10.89	100.01
UHBM	0.1N K ⁺	68.94	11.77	0.85	2.71	1.23	2.72	0.42	-	-	-	-	11.37	100.01
	0.5N K ⁺	67.48	11.51	0.70	1.60	0.97	5.82	0.10	-	-	-	-	11.80	99.88
	1N K ⁺	67.86	11.60	0.69	1.47	0.96	6.64	0.13	-	-	-	-	10.67	100.02
HBM	0.1N K ⁺	68.91	11.75	0.82	3.57	1.25	1.62	0.46	-	-	-	-	11.63	100.01
	0.5N K ⁺	68.26	11.61	0.81	2.39	1.35	4.11	0.17	-	-	-	-	11.31	100.01
	1N K ⁺	67.57	11.54	0.61	0.58	0.55	8.54	0.12	-	-	-	-	10.49	100.00
UHBM	0.1N Ca ²⁺	69.49	11.86	0.84	3.38	1.29	1.62	0.57	-	-	-	-	10.95	100.00
	0.5N Ca ²⁺	70.26	12.02	0.83	3.52	1.31	1.61	0.47	-	-	-	-	9.98	100.00
	1N Ca ²⁺	69.02	11.69	0.55	4.01	1.51	1.72	0.16	-	-	-	-	11.04	99.70
HBM	0.1N Ca ²⁺	70.46	12.00	0.73	3.56	1.22	1.80	0.22	-	-	-	-	10.04	100.03
	0.5N Ca ²⁺	69.49	11.81	0.74	3.67	1.41	1.79	0.18	-	-	-	-	10.91	100.00
	1N Ca ²⁺	69.49	11.87	0.77	3.85	1.24	1.77	0.15	-	-	-	-	10.85	99.99
UHBM	0.1N Mg ²⁺	69.71	11.87	0.91	3.15	1.35	1.61	0.52	-	-	-	-	10.88	100.00
	0.5N Mg ²⁺	68.84	11.74	0.86	3.01	1.45	1.61	0.58	-	-	-	-	11.91	100.00
	1N Mg ²⁺	68.32	11.66	0.94	2.92	1.56	1.58	0.62	-	-	-	-	12.38	99.98
HBM	0.1N Mg ²⁺	67.54	11.42	0.76	3.13	1.27	1.80	0.22	-	-	-	-	13.89	100.03
	0.5N Mg ²⁺	69.62	11.84	0.79	3.15	1.79	1.80	0.22	-	-	-	-	10.79	100.00
	1N Mg ²⁺	67.98	11.56	0.74	2.96	2.26	1.72	0.27	-	-	-	-	12.52	100.01
UHBM	0.1N Co ³⁺	68.51	11.71	0.85	2.64	1.20	2.83	0.32	0.19	-	-	-	11.18	100.00
	0.5N Co ³⁺	67.63	11.56	0.84	2.55	1.15	2.67	0.37	1.69	-	-	-	11.52	99.98
	1N Co ³⁺	66.75	11.36	0.81	2.57	1.14	2.67	0.36	2.37	-	-	-	11.97	100.00
HBM	0.1N Co ³⁺	66.93	11.41	0.55	0.44	0.45	9.09	0.11	0.72	-	-	-	10.32	100.01
	0.5N Co ³⁺	64.75	10.99	0.75	3.15	1.33	1.69	0.19	5.95	-	-	-	11.19	99.99
	1N Co ³⁺	63.74	10.82	0.68	2.81	1.16	1.67	0.20	7.25	-	-	-	11.68	100.07
UHBM	0.1N Cd ²⁺	68.66	11.69	0.76	2.61	1.19	2.73	0.39	-	0.13	-	-	11.84	100.00
	0.5N Cd ²⁺	67.29	11.47	0.73	2.47	1.14	2.79	0.39	-	2.18	-	-	11.54	100.00
	1N Cd ²⁺	65.44	11.10	0.66	2.43	1.07	2.87	0.30	-	3.66	-	-	12.47	100.00

Ion-Exchange Method	Ion-Exchange Forms	Molecules												
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	Co ₂ O ₃	CdO	Cr ₂ O ₃	Ag ₂ O	H ₂ O	Σ
HBM	0.1N Cd ²⁺	69.21	11.90	0.83	2.87	2.06	1.78	0.19	-	0.61	-	-	10.66	100.11
	0.5N Cd ²⁺	67.65	11.51	0.65	2.85	1.33	1.91	0.20	-	2.30	-	-	11.59	99.99
	1N Cd ²⁺	64.45	10.92	0.52	2.33	1.11	2.08	0.18	-	5.61	-	-	12.81	100.01
UHBM	0.1N Cr ³⁺	68.39	11.65	0.88	3.28	1.27	1.65	0.56	-	-	0.65	-	11.67	100.00
	0.5N Cr ³⁺	68.76	11.74	0.79	3.00	1.25	1.66	0.55	-	-	0.98	-	11.26	99.99
	1N Cr ³⁺	68.70	11.70	0.85	2.81	1.18	2.33	0.33	-	-	0.87	-	11.23	100.00
HBM	0.1N Cr ³⁺	69.47	11.88	0.81	2.92	1.34	1.80	0.31	-	-	0.66	-	10.81	100.00
	0.5N Cr ³⁺	67.79	11.58	0.63	2.77	1.33	3.13	0.19	-	-	1.76	-	10.83	100.01
	1N Cr ³⁺	61.92	10.39	0.27	0.70	0.47	8.36	0.10	-	-	5.64	-	12.15	100.00
UHBM	0.1N Ag ⁺	69.44	11.86	0.74	2.62	1.20	2.82	0.32	-	-	-	0.22	10.79	100.01
	0.5N Ag ⁺	66.25	11.25	0.55	1.85	1.02	2.46	0.33	-	-	-	4.36	11.90	100.00
	1N Ag ⁺	63.17	10.69	0.42	1.57	0.86	2.27	0.23	-	-	-	10.57	10.22	100.00
HBM	0.1N Ag ⁺	68.04	11.51	0.47	2.49	1.26	2.25	0.20	-	-	-	0.36	13.42	100.00
	0.5N Ag ⁺	67.63	11.39	0.59	2.35	1.35	1.67	0.17	-	-	-	1.93	12.91	99.99
	1N Ag ⁺	62.21	10.51	0.16	0.84	0.52	1.34	0.12	-	-	-	10.98	13.31	99.99

UHBM: unheated batch method; HBM: heated batch method

Table 1. Chemical analyses of natural and Na⁺, K⁺, Ca²⁺, Mg²⁺, Co³⁺, Cd²⁺, Cr³⁺, Ag⁺ modified forms of clinoptilolite.

Ion-Exchange Method	Ion-Exchange Forms	Atoms												
		Si	Al	Fe	Ca	Mg	K	Na	Co	Cd	Cr	Ag	H	Si/Al
	Natural	24.60	4.95	0.21	1.25	0.70	0.75	0.33	-	-	-	-	25.15	4.97
UHBM	0.1N Na ⁺	23.98	4.84	0.23	1.02	0.64	0.98	0.55	-	-	-	--	28.00	4.95
	0.5N Na ⁺	24.40	4.92	0.21	0.69	0.56	1.95	0.78	-	-	-	--	25.80	4.96
	1N Na ⁺	24.80	4.99	0.22	0.59	0.51	1.93	1.16	-	-	-	-	23.86	4.97
HBM	0.1N Na ⁺	23.82	4.79	0.22	1.18	0.82	0.86	0.64	-	-	-	-	28.19	4.97
	0.5N Na ⁺	24.54	4.91	0.23	1.16	0.78	0.81	0.70	-	-	-	-	25.07	5.00
	1N Na ⁺	24.33	4.88	0.24	0.73	0.60	0.74	2.18	-	-	-	-	25.74	4.99
UHBM	0.1N K ⁺	24.28	4.88	0.22	1.02	0.65	1.22	0.29	-	-	-	-	26.71	4.98
	0.5N K ⁺	24.00	4.83	0.19	0.61	0.51	2.64	0.07	-	-	-	-	28.00	4.97
	1N K ⁺	23.73	4.71	0.18	0.54	0.49	2.92	0.09	-	-	-	-	24.53	5.04
HBM	0.1N K ⁺	24.15	4.85	0.22	1.34	0.65	0.78	0.31	-	-	-	-	27.19	4.98
	0.5N K ⁺	24.20	4.85	0.22	0.91	0.71	1.86	0.12	-	-	-	-	26.75	4.99
	1N K ⁺	24.54	4.94	0.17	0.22	0.30	3.96	0.08	-	-	-	-	25.42	4.97

	0.1N Ca ²⁺	24.46	4.92	0.22	1.28	0.62	0.73	0.39	-	-	-	-	25.71	4.97
UHBM	0.5N Ca ²⁺	24.89	5.02	0.22	1.34	0.69	0.73	0.32	-	-	-	-	23.59	4.96
	1N Ca ²⁺	24.33	4.85	0.22	1.51	0.79	0.78	0.11	-	-	-	-	25.96	5.02
	0.1N Ca ²⁺	24.94	5.01	0.20	1.35	0.64	0.81	0.15	-	-	-	-	23.70	4.97
HBM	0.5N Ca ²⁺	24.48	4.90	0.19	1.38	0.74	0.80	0.12	-	-	-	-	25.63	5.00
	1N Ca ²⁺	24.49	4.93	0.20	1.45	0.65	0.80	0.10	-	-	-	-	25.51	4.97
	0.1N Mg ²⁺	24.53	4.92	0.24	1.19	0.71	0.72	0.36	-	-	-	-	25.53	4.99
UHBM	0.5N Mg ²⁺	24.05	4.83	0.23	1.13	0.76	0.72	0.39	-	-	-	-	27.75	4.98
	1N Mg ²⁺	23.80	4.79	0.25	1.09	0.81	0.70	0.42	-	-	-	-	28.77	4.97
	0.1N Mg ²⁺	23.26	4.64	0.20	1.15	0.65	0.79	0.14	-	-	-	-	31.91	5.01
HBM	0.5N Mg ²⁺	24.52	4.91	0.21	1.19	0.94	0.81	0.15	-	-	-	-	25.35	4.93
	1N Mg ²⁺	23.67	4.75	0.19	1.10	1.17	0.77	0.18	-	-	-	-	29.09	4.98
	0.1N Co ³⁺	23.93	4.82	0.22	0.99	0.63	1.26	0.22	0.19	-	-	-	26.05	4.97
UHBM	0.5N Co ³⁺	23.94	4.82	0.23	0.97	0.61	1.20	0.26	0.43	-	-	-	27.20	4.97
	1N Co ³⁺	23.62	4.74	0.22	0.97	0.60	1.20	0.25	0.61	-	-	-	28.25	4.98
	0.1N Co ³⁺	24.48	4.92	0.15	0.17	0.25	4.24	0.07	0.19	-	-	-	25.18	4.98
HBM	0.5N Co ³⁺	23.29	4.66	0.20	1.21	0.71	0.77	0.13	2.33	-	-	-	26.85	5.00
	1N Co ³⁺	22.92	4.59	0.19	1.08	0.62	0.84	0.14	1.89	-	-	-	28.02	4.99
	0.1N Cd ²⁺	24.03	4.87	0.20	0.99	0.63	1.23	0.27	-	0.02	-	-	27.91	4.93
UHBM	0.5N Cd ²⁺	24.02	4.83	0.20	0.94	0.61	1.27	0.27	-	0.37	-	-	27.48	4.97
	1N Cd ²⁺	23.46	4.63	0.18	0.93	0.57	1.31	0.21	-	0.61	-	-	29.82	5.07
	0.1N Cd ²⁺	24.46	4.96	0.22	1.09	1.09	0.80	0.13	-	0.10	-	-	25.13	4.93
HBM	0.5N Cd ²⁺	24.04	4.82	0.18	1.09	0.70	0.87	0.14	-	0.38	-	-	27.48	4.99
	1N Cd ²⁺	23.22	4.64	0.14	0.90	0.60	1.00	0.13	-	0.95	-	-	30.78	5.00
	0.1N Cr ³⁺	24.01	4.82	0.23	1.23	0.66	0.73	0.38	-	-	0.18	-	27.33	4.98
UHBM	0.5N Cr ³⁺	24.20	4.87	0.21	1.13	0.66	0.74	0.38	-	-	0.27	-	26.44	4.97
	1N Cr ³⁺	24.32	4.88	0.22	1.07	0.62	1.05	0.23	-	-	0.08	-	26.52	4.98
	0.1N Cr ³⁺	24.49	4.93	0.22	1.10	0.70	0.81	0.21	-	-	0.18	-	25.42	4.97
HBM	0.5N Cr ³⁺	24.15	4.86	0.17	1.06	0.71	1.42	0.13	-	-	0.50	-	25.74	4.97
	1N Cr ³⁺	22.68	4.48	0.07	0.28	0.26	3.90	0.07	-	-	1.63	-	29.68	5.06
	0.1N Ag ⁺	24.58	4.95	0.20	0.99	0.63	1.27	0.22	-	-	-	0.04	25.48	4.97
UHBM	0.5N Ag ⁺	23.94	4.79	0.15	0.72	0.55	1.13	0.23	-	-	-	0.83	28.69	5.00
	1N Ag ⁺	24.30	4.85	0.12	0.65	0.49	1.11	0.17	-	-	-	2.11	26.23	5.01
	0.1N Ag ⁺	23.55	4.70	0.12	0.92	0.65	0.99	0.13	-	-	-	0.07	30.99	5.01
HBM	0.5N Ag ⁺	23.70	4.71	0.17	0.88	0.71	0.75	0.11	-	-	-	0.35	30.18	5.03
	1N Ag ⁺	23.20	4.62	0.05	0.34	0.29	0.64	0.09	-	-	-	2.13	33.12	5.02

Table 2. Numbers of atoms in the unit cells of natural and Na⁺, K⁺, Ca²⁺, Mg²⁺, Co³⁺, Cd²⁺, Cr³⁺, Ag⁺ modified forms of clinoptilolite.

Ion-Exchange Method	Ion-Exchange Forms	Ions				
		Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Fe ³⁺
UHBM	0.1N Na ⁺	-	-	18.40	8.57	-
	0.5N Na ⁺	-	-	44.80	20.00	-
	1N Na ⁺	-	-	52.80	27.14	-
HBM	0.1N Na ⁺	-	-	5.60	-	-
	0.5N Na ⁺	-	-	7.20	-	-
	1N Na ⁺	-	1.33	41.60	14.29	-
UHBM	0.1N K ⁺	12.12	-	18.40	7.14	-
	0.5N K ⁺	78.79	-	51.20	27.14	9.52
	1N K ⁺	72.72	-	56.80	30.00	14.29
HBM	0.1N K ⁺	6.06	-	-	7.14	-
	0.5N K ⁺	63.63	-	27.20	-	-
	1N K ⁺	75.76	-	82.40	57.14	19.05
UHBM	0.1N Ca ²⁺	-	2.67	-	2.67	-
	0.5N Ca ²⁺	3.03	2.67	-	1.43	-
	1N Ca ²⁺	66.67	-	-	-	-
HBM	0.1N Ca ²⁺	54.55	-	-	8.57	4.76
	0.5N Ca ²⁺	63.64	-	-	-	9.52
	1N Ca ²⁺	69.70	-	-	7.14	4.76
UHBM	0.1N Mg ²⁺	-	4.00	4.80	-	-
	0.5N Mg ²⁺	-	4.00	9.60	-	-
	1N Mg ²⁺	-	6.67	12.80	-	-
HBM	0.1N Mg ²⁺	57.58	-	8.00	-	4.76
	0.5N Mg ²⁺	54.55	-	4.80	-	-
	1N Mg ²⁺	45.45	-	12.00	-	9.52
UHBM	0.1N Co ³⁺	33.33	-	20.08	10.00	-
	0.5N Co ³⁺	21.21	-	22.40	12.85	-
	1N Co ³⁺	24.24	-	22.40	14.29	-
HBM	0.1N Co ³⁺	78.79	-	86.40	64.29	28.57
	0.5N Co ³⁺	60.61	-	3.20	-	4.76
	1N Co ³⁺	57.57	-	13.60	11.43	9.52
UHBM	0.1N Cd ²⁺	18.18	-	20.80	10.00	4.76
	0.5N Cd ²⁺	18.18	-	24.80	12.85	4.76
	1N Cd ²⁺	36.36	-	25.60	18.57	14.29
HBM	0.1N Cd ²⁺	60.61	-	12.80	-	-
	0.5N Cd ²⁺	57.58	-	12.80	-	14.29
	1N Cd ²⁺	60.61	-	28.00	14.29	33.33

Ion-Exchange Method	Ion-Exchange Forms	Ions				
		Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Fe ³⁺
UHBM	0.1N Cr ³⁺	-	2.67	1.60	5.71	-
	0.5N Cr ³⁺	-	1.33	9.60	5.71	-
	1N Cr ³⁺	30.30	-	14.40	11.43	-
HBM	0.1N Cr ³⁺	36.36	-	12.00	-	-
	0.5N Cr ³⁺	60.61	-	15.20	-	19.05
	1N Cr ³⁺	78.79	-	77.60	62.86	66.67
UHBM	0.1N Ag ⁺	33.33	-	20.80	10.00	4.76
	0.5N Ag ⁺	30.30	-	42.40	21.43	28.57
	1N Ag ⁺	48.48	-	48.00	30.00	42.86
HBM	0.1N Ag ⁺	60.61	-	26.40	7.14	42.86
	0.5N Ag ⁺	66.67	-	29.60	-	19.05
	1N Ag ⁺	72.73	14.67	72.80	58.57	76.19

Table 3. Ion-exchange rates for Na⁺, K⁺, Ca²⁺, Mg²⁺, Co³⁺, Cd²⁺, Cr³⁺, Ag⁺ modified forms compared to natural clinoptilolite.

Ion-Exchange Method	Ion-Exchange Forms	Ordering of Ion-Exchange Rate
UHBM	Na ⁺	Ca ²⁺ >Mg ²⁺
HBM	Na ⁺	Ca ²⁺ >Mg ²⁺
UHBM	K ⁺	Na ⁺ > Ca ²⁺ > Mg ²⁺ > Fe ³⁺
HBM	K ⁺	Na ⁺ > Ca ²⁺ > Mg ²⁺ > Fe ³⁺
UHBM	Ca ²⁺	Na ⁺ >K ⁺ >>Mg ²⁺
HBM	Ca ²⁺	Na ⁺ >Mg ²⁺ >Fe ³⁺
UHBM	Mg ²⁺	Ca ²⁺ > K ⁺
HBM	Mg ²⁺	Na ⁺ >Ca ²⁺ >Fe ³⁺
UHBM	Co ³⁺	Na ⁺ > Ca ²⁺ >Mg ²⁺
HBM	Co ³⁺	Na ⁺ > Ca ²⁺ >Mg ²⁺ >Fe ³⁺
UHBM	Cd ²⁺	Ca ²⁺ >Na ⁺ > Mg ²⁺ >Fe ³⁺
HBM	Cd ²⁺	Na ⁺ > Ca ²⁺ >Mg ²⁺ >Fe ³⁺
UHBM	Cr ³⁺	Na ⁺ > Ca ²⁺ >Mg ²⁺ > K ⁺
HBM	Cr ³⁺	Na ⁺ > Ca ²⁺ > Fe ³⁺ >Mg ²⁺
UHBM	Ag ⁺	Na ⁺ > Ca ²⁺ > Fe ³⁺ >Mg ²⁺
HBM	Ag ⁺	Na ⁺ > Ca ²⁺ > Fe ³⁺ >Mg ²⁺ > K ⁺

Table 4. Ordering of ion-exchange rate for unheated and heated methods for Na-clinoptilolite from Bigadiç-Balıkesir (Turkey)

The order of ion-exchange rate of Na^+ and K^+ forms is constant under both unheated and heated conditions. On the other hand, high ion-exchange rates occur under the effects of heating. The ion-exchange rate order of Ca^{2+} , Mg^{2+} , Co^{3+} , Cd^{2+} , Cr^{3+} and Ag^+ forms changes upon heating, plus Fe^{3+} is leached from the structure. Although iron occurs as Fe^{3+} in the general order, Fe^{2+} was depleted instead of Fe^{3+} because Fe^{3+} cannot be depleted from the structure of clinoptilolite. Generally speaking, the ion-exchange process acts more on the surface of clinoptilolite than on its inner sites.^[15]

Generally, the ion-exchange rate of the cations increases with increase in normality via application of both unheated and heated batch methods. Ion-exchange rates increase via the heating method compared to the unheated one. Forced-ion exchange occurs using the heated batch method as compared to natural ion exchange via the unheated method. The ion exchange of cations is controlled by cation valence, cation radius, ionization potential and the location of cations within pores.

The weak connection of the +1 valence of the Na^+ cation to the structure of 10T is related to its low ionization potential, resulting in leaching -with a high ion-exchange rate- from its structure (Figure 1). The Mg^{2+} cation exhibits low depletion due to its having symmetrical binding to the structure of 8T, despite having the lowest ionization potential. Ca^{2+} is more depleted than Mg^{2+} because of the unsymmetrical binding of Ca^{2+} to the structure, although the ionization potential of Ca^{2+} is higher than that of Mg^{2+} . The K^+ cation is strongly bound between the 8T and 10T structures; therefore, it is only slightly depleted.

Exchangeable Cations	Ionic Radii (Å)	Ionization Potential (eV)
Na^+	0.99	5.13
K^+	1.37	4.34
Ca^{2+}	1.00	6.11
Mg^{2+}	0.57	7.64
Cr^{3+}	0.62	6.77
Ag^+	0.79	7.57
Co^{3+}	0.55	7.88
Cd^{2+}	0.78	8.99
Fe^{+2}	0.63	7.90
Fe^{3+}	0.49	7.90

Table 5. Ionic radii and ionization potentials of exchangeable cations. ^[16]

Ion-Exchange Method	Ion-Exchange Forms	Ions							
		Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Co ³⁺	Cd ²⁺	Cr ³⁺	Ag ⁺
UHBM	0.1N Na ⁺	66.67	-	-	-	-	-	-	-
	0.5N Na ⁺	136.36	-	-	-	-	-	-	-
	1N Na ⁺	251.52	-	-	-	-	-	-	-
HBM	0.1N Na ⁺	93.94	-	-	-	-	-	-	-
	0.5N Na ⁺	112.12	-	-	-	-	-	-	-
	1N Na ⁺	560.61	-	-	-	-	-	-	-
UHBM	0.1N K ⁺	-	62.67	-	-	-	-	-	-
	0.5N K ⁺	-	252.00	-	-	-	-	-	-
	1N K ⁺	-	289.33	-	-	-	-	-	-
HBM	0.1N K ⁺	-	4.00	-	-	-	-	-	-
	0.5N K ⁺	-	148.00	-	-	-	-	-	-
	1N K ⁺	-	428.00	-	-	-	-	-	-
UHBM	0.1N Ca ²⁺	-	-	2.40	-	-	-	-	-
	0.5N Ca ²⁺	-	-	7.20	-	-	-	-	-
	1N Ca ²⁺	-	-	20.80	-	-	-	-	-
HBM	0.1N Ca ²⁺	-	-	8.00	-	-	-	-	-
	0.5N Ca ²⁺	-	-	10.40	-	-	-	-	-
	1N Ca ²⁺	-	-	16.00	-	-	-	-	-
UHBM	0.1N Mg ²⁺	-	-	-	1.43	-	-	-	-
	0.5N Mg ²⁺	-	-	-	8.57	-	-	-	-
	1N Mg ²⁺	-	-	-	15.71	-	-	-	-
HBM	0.1N Mg ²⁺	-	-	-	-	-	-	-	-
	0.5N Mg ²⁺	-	-	-	34.29	-	-	-	-
	1N Mg ²⁺	-	-	-	67.14	-	-	-	-
UHBM	0.1N Co ³⁺	-	-	-	-	19	-	-	-
	0.5N Co ³⁺	-	-	-	-	43	-	-	-
	1N Co ³⁺	-	-	-	-	61	-	-	-
HBM	0.1N Co ³⁺	-	-	-	-	19	-	-	-
	0.5N Co ³⁺	-	-	-	-	233	-	-	-
	1N Co ³⁺	-	-	-	-	189	-	-	-
UHBM	0.1N Cd ²⁺	-	-	-	-	-	2	-	-
	0.5N Cd ²⁺	-	-	-	-	-	37	-	-
	1N Cd ²⁺	-	-	-	-	-	61	-	-
HBM	0.1N Cd ²⁺	-	-	-	-	-	10	-	-
	0.5N Cd ²⁺	-	-	-	-	-	38	-	-
	1N Cd ²⁺	-	-	-	-	-	95	-	-
UHBM	0.1N Cr ³⁺	-	-	-	-	-	-	18	-
	0.5N Cr ³⁺	-	-	-	-	-	-	27	-
	1N Cr ³⁺	-	-	-	-	-	-	8	-

Ion-Exchange Method	Ion-Exchange Forms	Ions							
		Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Co ³⁺	Cd ²⁺	Cr ³⁺	Ag ⁺
HBM	0.1N Cr ³⁺	-	-	-	-	-	-	18	-
	0.5N Cr ³⁺	-	-	-	-	-	-	50	-
	1N Cr ³⁺	-	-	-	-	-	-	163	-
UHBM	0.1N Ag ⁺	-	-	-	-	-	-	-	4
	0.5N Ag ⁺	-	-	-	-	-	-	-	83
	1N Ag ⁺	-	-	-	-	-	-	-	211
HBM	0.1N Ag ⁺	-	-	-	-	-	-	-	7
	0.5N Ag ⁺	-	-	-	-	-	-	-	35
	1N Ag ⁺	-	-	-	-	-	-	-	213

Table 6. The ion-selectivity rates of Na⁺, K⁺, Ca²⁺, Mg²⁺, Co³⁺, Cd²⁺, Cr³⁺ and Ag⁺ modified forms of clinoptilolite compared to natural clinoptilolite.

3.2. Rate of ion selectivity

Table 6 shows the ion-selectivity rates of Na⁺, K⁺, Ca²⁺, Mg²⁺, Co³⁺, Cd²⁺, Cr³⁺ and Ag⁺ modified forms compared to natural clinoptilolite. Entrance of the cation into the structure depends on the ion-selectivity rate, that is, the ion-selectivity coefficient of cations. The rate of ion selectivity is controlled by cation valence, cation radius, ionization potential, pore size and location of the cation within the pore. Entrance of the cation into the structure increases with increasing normality and heating (Table 6). Monovalent cations such as K⁺, Na⁺ and Ag⁺ predominantly enter the structure of Na-clinoptilolite; these cations have relatively low ionization potentials. These cations are followed by other cations, such as Ca²⁺, Mg²⁺, Co³⁺, Cd²⁺ and Cr³⁺.

Selectivity Order	References
Pb ²⁺ >NH ₄ ⁺ >Ba ²⁺ >Cu ²⁺ >Zn ²⁺ >Cd ²⁺ >Co ²⁺	[19]
Pb ²⁺ >Cd ²⁺ >Cs ²⁺ >Cu ²⁺ >Co ²⁺ >Cr ³⁺ >Zn ²⁺ >Ni ²⁺ >Hg ²⁺	[20]
Pb ²⁺ >Ag ⁺ >Cd ²⁺ >Zn ²⁺ >Cu ²⁺ >Na ⁺	[21]
Pb ²⁺ >Cu ²⁺ >Cd ²⁺ >Zn ²⁺ >Cr ³⁺ >Co ²⁺ >Ni ²⁺	[22]

Table 7. Global experimental ion-selectivity order for modified clinoptilolite.

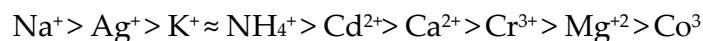
The ordering of ion-selectivity rates via application of unheated and heated methods is as follows:

Unheated: K⁺>Na⁺>Ag⁺>Co³⁺>Cd²⁺>Cr³⁺>Ca²⁺>Mg²⁺

Heated: Na⁺>K⁺>Co³⁺>Ag⁺>Cr³⁺>Cd²⁺>Mg²⁺>Ca²⁺

The ordering rate obtained via the unheated batch method is consistent with the results given in the global literature; conversely, this order changes upon heating via application of the heated batch method.

Moreover, the order of the ion-selectivity rates, namely



was also determined for the Gördes Na-clinoptilolite.^[17, 18] Other results are given in Table 7.

4. Conclusions

1. Rates of ion exchange and ion selectivity increase with increase in normality via application of both unheated and heated methods.
2. Entrance of heavy metals into and depletion of exchangeable cations from the zeolite structure is controlled by cation valence, cation radius, ionization potential, pore size and location of the cation within the pore.
3. The rates of ion exchange and ion selectivity are higher in application of the heated batch method than in the unheated one.
4. Forced ion exchange occurs via application of the heated batch method as compared to natural ion exchange via the unheated method due to the rates of ion exchange and ion selectivity.
5. The order of ion-selectivity rate for the modified forms, except for the exchangeable cations, is $\text{Ag}^+ > \text{Cd}^{2+} > \text{Cr}^{3+} > \text{Co}^{3+}$; this finding is consistent with Ag^+ , Cd^{2+} , Cr^{3+} and Co^{3+} cation adsorption from wastewater, as determined worldwide.
6. Na-clinoptilolite adsorbs cations such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Co^{3+} , Cd^{2+} , Cr^{3+} and Ag^+ . Ion-exchangeable cations such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , 8T and 10T structures and negative structure also exhibit adsorptive capacity with respect to other cations.
7. Heavy-metal cation retention in large volumes of water (such as in rivers) requires application of the unheated batch method. In contrast, heavy-metal cation retention in small volumes of water (such as in the laboratory) over shorter time periods requires application of the heated batch method.

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