



Adsorption of sulfur dioxide on natural clinoptilolite chemically modified with salt solutions

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ABSTRACT

Various ion exchange forms of preliminary partly decationised zeolite (hydrogen forms) were obtained by indirect modification with metal salt solutions, as well as by direct treatment of natural clinoptilolite taken from Bulgarian deposits. Direct modification leads to a higher extent of samples enrichment with corresponding ion. Independently of the conditions, the alkaline and alkaline earth metal ions (especially sodium and calcium) were inserted to a greater extent, while the transitional metals—at a comparatively lower extent. The cationic forms of clinoptilolite were used for adsorption and desorption experiments. The breakthrough adsorption curves and the concentration curves at temperature-programmed desorption were obtained and compared. The breakthrough and saturation times, the adsorption capacity, the distribution coefficient, the adsorbed SO_2 , the portions desorbed as SO_2 and SO_3 , respectively, as well as the not desorbed portion of SO_2 , were determined using these curves. It was established that a definite quantity of undesorbed SO_2 has remained in the zeolite forms modified with transitional metal cations. This statement was proved not only by the comparison between the adsorbed and desorbed quantities, but also by three-cycle adsorption–desorption experiments for the Cu^{2+} -form. The results demonstrate a decrease in the capacity for each following cycle in an extent similar to the undesorbed SO_2 quantity. It was not observed a visible difference in the values of the distribution coefficients for adsorption on identical cation forms, directly or indirectly obtained. However, the breakthrough time of the samples obtained by ion exchange of the hydrogen form was longer in all cases. Definite quantities of desorbed SO_3 were registered for all forms, except for the natural clinoptilolite and the samples enriched with alkaline and alkaline earth metal cations.

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1. Introduction

It is well known that zeolites consist of aluminum and siliceous tetrahedrons, which bound in a definite way, form a crystal structure with vacancies, channels and pores. The electronegative charge of the alumino-silicate framework is compensated by alkaline or alkaline earth metal cations, which depending on their size, charge and the synthesis conditions, can occupy various geometric sites. They could be fully or partially substituted by other alkaline, alkaline earth or transitional metal cations without destruction of the crystal framework, i.e. ion exchange is possible. Literature is abundant of publications on ion exchange.

The investigations on the ion exchange can be classified according to the following zeolites applications:

Ion exchange for the treatment of drinking and wastewaters [1–12], demineralization of sea water or water softening [13], as well as for uptake and utilization of heavy metals [13,14]. In these cases the

investigations are directed to determination of: the capacity of the material applied [1–4,15–18]; the working conditions, e.g. the concentration of the cation to be removed in the solution [18,19], of the another present cations in the aqueous solution [7,9,17,20–23], anions [7,9,24,25] or organic substances (e.g. phenol [20]); the effect of the temperature [4,8,26]; zeolite particle size [3,9]; contact time [10] or the volumetric flow rate for dynamic experiments [26]. Special attention is paid to the influence of the solution pH [3,8,9,20,27], concerning the possibility of precipitation of sediment in the zeolite pores [3,14,20,24,27], which leads to unstoichiometric removal and blockage of zeolite pores [18,24]. The possibility of desorption and zeolite application in a cyclic process, e.g. for Ni removal was also studied [14]. There are also investigations on the kinetics of cation exchange [1,2,12,28]. When the uptake of more than one cation on the zeolite is examined, the investigations include comparison of the ion exchange capacity and as a result the original selectivity orders of zeolite removal are obtained [1,2,9,15,17,29–32]. These orders are useful as they allow to predict the zeolites behaviour at competitive ion exchange. The order of the cations is defined on the basis of the ion radii of the exchangeable cations [30,31], of the specific hydration energy [33], the presence

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of impurities, etc. Important criteria are zeolite electronegativity (determined by the Si/Al ratio), as well as the cation charge [22,29,34].

Ion exchange for improvement of zeolite adsorption [35–43] and separation capability [37,44–47] or for catalyst production [48,49]. The aim of the investigations is to determine how the ion exchange could change the total pore volume [37,41,49] and pore size so that the zeolite could then adsorb molecules with various kinetic diameters [40,41], i.e. to change the molecular-sieve activity. The changes of the content and sites in the zeolite lattice, occupied by the cations, are especially important for some molecules which are specifically adsorbed. It also allows the adsorption of molecules with different polarity and the application of the zeolite in catalytic processes [50].

Ion exchange for evaluation of zeolite structure and properties: the available sites for the cations, the presence and type of lattice water [42,51,54], zeolite thermostability [21,45,52], determination of the values of the thermodynamic constants [15,16,36,41,53].

The investigations cited are mainly conducted in a batch reactor and sometimes in a column [8,20,22,29,55,56]. As though the cation content of the synthetic zeolites could be preliminarily set, natural zeolites are generally used for ion exchange. The latter are heteroionic, i.e. they contain different quantities of exchangeable Na^+ , K^+ , Ca^{2+} and Mg^{2+} . The ion exchange with preliminary obtained monoion zeolite forms as sodium [2–4,7,9,11,16,19,20,50], potassium [9,15], calcium [5,9], hydrogen [35,40,42,57] or some other [3,6,9], is preferred in some cases to the direct application of natural zeolites. The advantage of using mono-ion forms is the possibility to avoid competitive effects [2]. Moreover, literature cites that the preliminary treatment of zeolites with NaCl solutions significantly improves their ion exchange capacity [11,58].

The influence of the cations in the cation lattice on SO_2 adsorption is also discussed in some publications [35–38,40,59–62]. Some authors state that the adsorption capacity to SO_2 and the diffusivity are determined by Na^+ quantity in the samples. As bigger is the ratio of the exchangeable cations ($(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+)/(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ + \text{Na}^+)$), the higher are the diffusion coefficient and the quantity of SO_2 adsorbed at 25 and 150 °C [60,61]. The comparative analysis of the data obtained with different zeolites proved that the influence of the cation nature is not identical. Natural zeolites initially treated with HCl, then modified with solutions, containing Li^+ , K^+ , Na^+ , Ca^{2+} and Mg^{2+} are applied for the purification of flue gases, containing NO, CO, CO_2 and SO_2 [35]. The experimental results showed that the Li, K and Mg forms were the most effective for SO_2 removal. To combine the advantages of the wider pores obtained as a result of an acid modification, and high- Na^+ concentration, necessary for the specific adsorption of the polar SO_2 molecule, the so called recationisation of the sodium synthetic mordenite was suggested [40]. The recationised forms demonstrated higher quantity SO_2 adsorbed when compared to the primary zeolite. Another study proposed that the adsorption capacity of SO_2 depended on the cation electronegativity and polarization activity, thus the following order of SO_2 adsorption on enriched forms of natural clinoptilolite from Turkey was determined: $\text{H}^+ > \text{Na}^+ > \text{K}^+ > \text{Ca}^{2+}$, where the calcium form practically did not adsorb SO_2 [38]. A different order for SO_2 adsorption was obtained for cationic forms of Hungarian mordenite: $\text{H}^+ > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+$ [37]. Opposed results were obtained for the synthetic zeolite Y, exchanged with hydrogen cations, alkaline and alkaline earth metal cations. The following order for the adsorption capacity for SO_2 was determined: $\text{HY} < \text{AEY} < \text{AY}$ [36]. In the monograph of Smola and Keltsev [59] data for the adsorption of SO_2 on various forms of erionite and synthetic zeolites Y and A are cited. The values of the adsorption capacity at 350 °C decreases in the order:

- For erionite: $\text{Zn} > \text{initial form} > \text{Cu} > \text{Mn} > \text{Mg} > \text{Cd} > \text{Ti} > \text{Ba}$.
- For Y zeolite: $\text{Cu} > \text{Pb} > \text{Zn} > \text{Cd} > \text{Na} > \text{H}$.
- For A zeolite: $\text{Mg} > \text{Zn} > \text{Na}$.

The adsorption at higher temperature forms other adsorption capacity orders to SO_2 :

- For erionite: $\text{Zn} > \text{Cd} > \text{Mn} > \text{Cu} > \text{initial form} > \text{Ti} > \text{Mg} > \text{H} > \text{Ba}$.
- For Y zeolite: $\text{Na} > \text{Pb} > \text{Cd} > \text{Zn} > \text{Cu}$.
- For A zeolite: $\text{Mg} > \text{Zn} > \text{Na}$.

The diffusivity is also determined on the basis of the dominant exchangeable cation. During the adsorption of gases, including SO_2 , on cation forms of mordenite, it was established that the diffusion resistance decreases in the following order:

natural mordenite > Na-mordenite > H-mordenite.

Thus, it could be concluded that the adsorption parameters for SO_2 depend on the zeolite type, the type of the dominant cations in the channels, the presence of impurities, etc.

The aim of the present study was the modification of natural clinoptilolite from Bulgaria with salt solutions and the examinations of the samples obtained for SO_2 adsorption and desorption from gaseous mixtures.

2. Materials and methods

2.1. Materials

The material used in the investigations is natural clinoptilolite from Bulgaria, which mineral purity and chemical content, are given in a previous study [63].

2.1.1. Zeolite modification

The zeolite modification was accomplished in a reactor at room temperature. 1.6–2 mm sieve fraction particles were used.

Two series of experiments were conducted to obtain different cationic forms of the zeolite—indirect modification of the hydrogen form and a direct modification of natural clinoptilolite.

The indirect modification was accomplished with samples preliminarily treated with 1N HCl. Dissolving of some amorphous impurities, weak dealuminization and about 25% decationisation were achieved for the obtained hydrogen forms [63]. Zeolite decationisation decreases the diffusion resistance as a result of pores entrances expansion. Then the samples were treated with aqueous chloride and nitrate solutions of: Na, K, Ca, Li, Ag, Cu, Cd, Co and Mn. To prevent salt occlusion in the pores and to facilitate zeolite washing after filtration, the samples were six-times treated with low-concentration solutions (0.5N) at liquid:solid phase ratio = 6 ml:1 g [64]. Each operation lasted 30 min followed by filtration and washing out with hot distilled water to a negative reaction for the respective anion.

The direct modification of the natural clinoptilolite was conducted with aqueous solutions of Na, K, Ca, Li, Cd, Zn, Mn, Fe(III) chlorides as well as $\text{Cu}(\text{NO}_3)_2$, AgNO_3 , $\text{Co}(\text{NO}_3)_2$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Each sample had been three-times treated with 1N solution of the respective salt for 2 h at liquid:solid phase ratio = 6:1, then filtered and washed out with hot distilled water.

2.2. SO_2 adsorption/desorption

The samples obtained were examined as adsorbents for SO_2 . Adsorption/desorption experiments were accomplished on a standard installation for dynamic investigations, described previously [65]. The main part is a thermostatic adsorption column with

Table 1
The extent of ion exchange.

Indirectly modified forms			Directly modified forms		
Cation	Metal amount in the sample after the treatment (mgequiv./gatomAl)	Excess of the same cation in the initial hydrogen form (%)	Cation	Metal amount in the sample after treatment (mgequiv./gatomAl)	Excess of the same cation in the initial natural zeolite (%)
Na ⁺	0.354	43.9	Na ⁺	0.515	54.8
K ⁺	0.346	8.9	K ⁺	0.502	40.8
Ca ²⁺	0.216	42.8	Ca ²⁺	0.339	50.6
Li ⁺	0.126		Li ⁺	0.147	
Ag ⁺	0.203		Ag ⁺	0.262	
Cu ²⁺	0.050		Cu ²⁺	0.072	
Cd ²⁺	0.030		Cd ²⁺	0.050	
Co ²⁺	0.035		Co ²⁺	0.053	
Mn ²⁺	0.052		Mn ²⁺	0.111	
			Fe ³⁺	0.063	
			Fe ²⁺	0.018	
			Zn ²⁺	0.074	

19.5 mm diameter and 500 mm height. It is possible to replace this column with the same sized desorption column. The zeolite in the desorption column can be heated at a definite rate. This column was used for the thermal activation of the samples before adsorption, as well as for the desorption experiments. The gas concentration is measured by iodine titration (part of the flow is blowing through the iodine solution with known concentration).

Zeolite thermal activation (dehydration) was performed by heating up to 360 °C at a rate of 5 °C min⁻¹ and maintaining this temperature for 4 h. Simultaneously the layer was blown with dry air to remove the water vapour and gases inside the pores.

The adsorption experiments with indirectly modified forms were accomplished at the following conditions: temperature 25 °C; bed depth 200 mm; volumetric gas flow rate 0.165 m³ h⁻¹; SO₂ concentration in a model gas–dry air mixture C₀ 0.65 vol.%. The desorption investigations with these forms were also carried out by blowing the bed with dry air (0.0764 m³ h⁻¹), heating to 360 °C at rate of 5 °C min⁻¹ and maintaining this temperature for 4 h.

The adsorption experiments with directly modified natural clinoptilolite forms were held at similar working conditions: temperature 25 °C; bed depth 200 mm; volumetric gas flow rate 0.185 m³ h⁻¹; SO₂ concentration in a model gas–dry air mixture C₀ 0.475 vol.%.

3. Results and discussion

3.1. Zeolite modification

The results obtained by treatment of the samples with aqueous solutions are presented in Table 1, Fig. 1 (for indirect modification) and Fig. 2 (for direct modification).

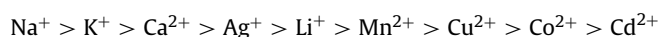
As the experiments do not aim to reach total ion exchange and as the results presented in Table 1 show only enrichment of the

samples with the corresponding cation, the following tendencies can be noticed:

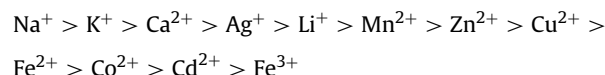
- The extent of enrichment achieved at direct ion exchange was higher than that at indirect.
- Among the present cations in the natural clinoptilolite potassium cation is the most poorly substituted. The degree of substitution of sodium and calcium cations is similar.
- The transition metal cations were enriched at a lower extent than those of the alkaline and alkaline earth metals at the treatment conditions.
- Both initial forms possess high affinity to the silver cation. It is well known that natural zeolites, and clinoptilolite in particular, exhibit very high selectivity to Ag⁺ [15,66].

For the treatment conditions the following selectivity orders of ion exchange according to the metal quantity after the treatment can be written:

- For indirect ion exchange (initial form—partially decationised natural clinoptilolite, so-called hydrogen form):



- For direct ion exchange (initial form—natural clinoptilolite):



Similar selectivity orders were obtained independently on the different extent of samples enrichment by both treatment techniques. Attempts for correlation of the above selectivity orders with some ion properties (Table 2), influencing ion exchange can turn out to be quite a complex task. For example, if the hydration energy

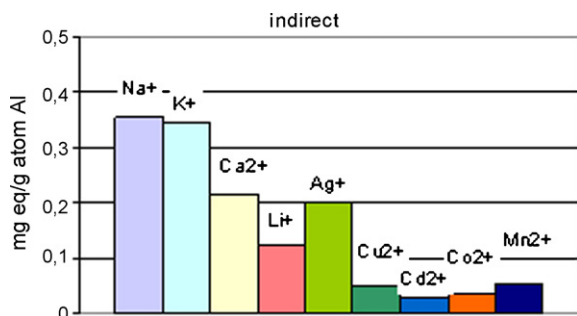


Fig. 1. Ion exchange extents at indirect treatment.

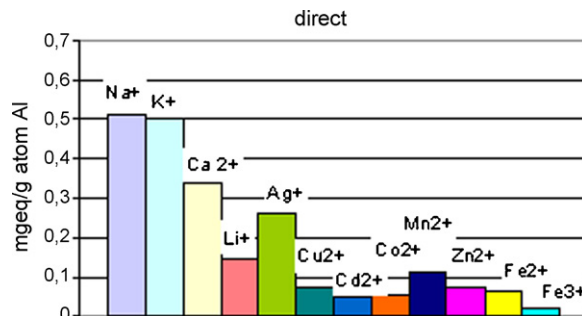
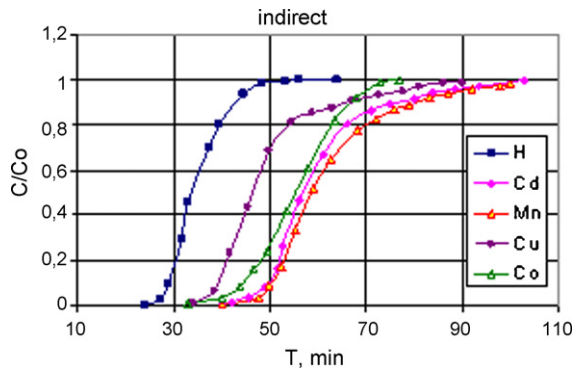


Fig. 2. Ion exchange extents at direct treatment.

Table 2

Some properties of the ion exchange resins used.

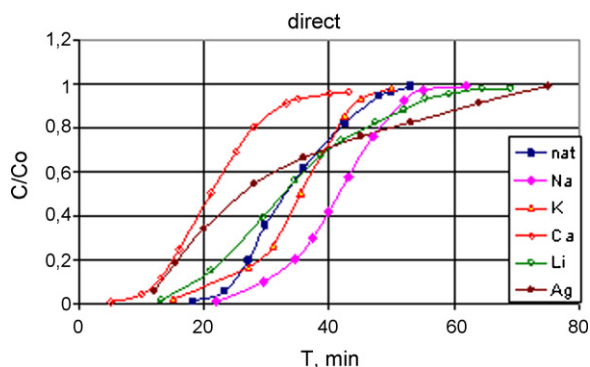
Ions	Ion radii [67] (nm)	Hydration energy [68] (kJ mol ⁻¹)	Ion potential [67] (eV)	Ions	Ion radii [67] (nm)	Hydration energy [68] (kJ mol ⁻¹)	Ion potential [67] (eV)
Na ⁺	0.098	-405.84	5.139	Cu ²⁺	0.080	-2054.34	7.726
K ⁺	0.133	-330.54	4.341	Cd ²⁺	0.099	-1778.20	8.994
Li ⁺	0.068	-506.26	5.392	Co ²⁺	0.078		7.870
Ca ²⁺	0.104	-1560.63	6.113	Zn ²⁺	0.083	-2004.14	9.394
Ag ⁺	0.113	-472.79	7.576	Fe ²⁺	0.080		7.893
Mn ²⁺	0.091	-1811.67	7.893	Fe ³⁺	0.067	-4412.07	

**Fig. 3.** Breakthrough curves for adsorption with indirectly modified forms.

and ion potential are compared, the selectivity orders will start with potassium, but its cation has comparatively large radius, thus zeolites have higher selectivity to sodium cations. Despite some deviations, it can be found that zeolites selectivity to monovalent cations decreases with an increase in their hydration energy, while such dependence was not observed for the bivalent cations. It should also be considered that in the ion exchange with natural zeolites all exchanged cations (Na⁺, K⁺, Ca²⁺, and Mg²⁺) participated as counter ions, so their properties should also be recognised. Consequently, it is very difficult for the selectivity orders to be predicted or explained.

3.2. SO₂ adsorption/desorption

The results from the adsorption experiments are presented as breakthrough curves, some of which are shown in Fig. 3 for indirectly modified forms and in Fig. 4 for directly modified forms. The breakthrough time $\tau_{0.1}$ and the saturation time $\tau_{0.9}$ (the times necessary for the gas effluent to reach relative concentrations C/C_0 0.1 and C/C_0 0.9, respectively) were accounted from the curves. The dynamic adsorption capacity, a (the relative quantity adsorbed SO₂ until $C/C_0 = 0.9$ is obtained) was determined, too. The distribution coefficients $K = a/C_0$ were also calculated to avoid errors when comparing the results obtained at adsorption experiments with dif-

**Fig. 4.** Breakthrough curves for adsorption with directly modified forms.

ferent SO₂ concentrations in the gaseous phase. The results from the desorption experiments are obtained as concentration curves for SO₂ and SO₃. Some of them are presented in Fig. 5a–c. Desorption of SO₃ was also registered for all the systems studied, except for the natural clinoptilolite and the forms indirectly modified with alkaline and alkaline earth metal cations. The adsorbed and desorbed quantities of SO₂ and SO₃ ($M_{SO_2}^{ads}$, respectively $M_{SO_2}^{des}$ and $M_{SO_3}^{des}$) were calculated by integration of the breakthrough curves of adsorption and the concentration desorption curves, as well as by the material balance. It was estimated the part being desorbed as SO₂, and SO₃, respectively, and the quantity not desorbed at all, from the total adsorbed amount of SO₂. The values obtained are presented in Table 3. The total adsorbed quantity of SO₂ was desorbed

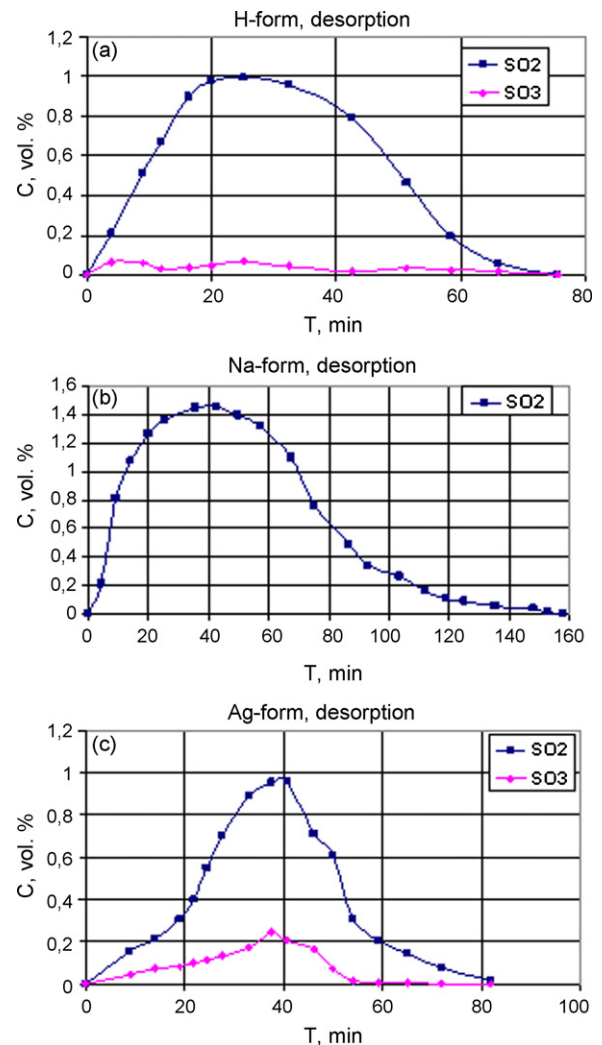
**Fig. 5.** Desorption concentration curves: (a) desorption concentration curve (H-form), (b) desorption concentration curve (Na-form), and (c) desorption concentration curve (Ag-form).

Table 3
Results from the adsorption and desorption experiments.

Forms	$\tau_{0.1}$ (min)	$\tau_{0.9}$ (min)	a (mmol g ⁻¹)	K (g g ⁻¹)	$\frac{M_{SO_2}^{des}}{M_{SO_2}^{ads}}$ (%)	$\frac{M_{SO_3}^{des}}{M_{SO_3}^{ads}}$ (%)	Undesorbed amount (%)
nat	25.0	46.0	0.725	3.187	99.86	0	0
H-form	29.0	42.5	0.791	3.409	94.79	5.2	0
Formes produced by indirect ion exchange							
Na, ind	41.0	53.0	0.989	4.355	99.57	0	0.43
K, ind	34.0	43.5	0.765	3.578	98.99	0	1.01
Ca, ind	18.7	34.5	0.714	2.381	99.49	0	0.51
Li, ind	31.0	57.0	0.892	3.750	97.11	0	2.89
Ag, ind	24.0	49.0	0.710	3.149	68.63	12.54	18.84
Cd, ind	50.0	76.0	1.188	5.563	73.62	3.81	22.6
Mn, ind	50.0	80.0	1.322	8.010	80.91	2.93	16.17
Cu ^I , ind	39.5	66.0	1.104	4.589	76.52	3.15	20.33
Cu ^{II} , ind	28.0	54.0	0.864	3.751			
Cu ^{III} , ind	24.0	51.0	0.799	3.453			
Co, ind	44.0	67.0	1.132	5.195	82.27	3.31	1.42
Formes produced by direct ion exchange							
Na, dir	29.0	51.5	0.712	4.393			
K, dir	22.0	43.5	0.606	3.765			
Ca, dir	12.5	32.5	0.379	2.342			
Li, dir	19.0	53.0	0.619	3.684			
Ag, dir	13.0	62.0	0.553	3.437			
Zn, dir	35.0	53.5	0.750	4.356			
Fe ²⁺ , dir	24.5	59.0	0.719	4.372			
Fe ³⁺ , dir	20.0	45.0	0.623	3.523			
Mn, dir	32.5	63.0	0.812	5.075			
Co, dir	34.5	64.0	0.817	5.170			
Cd, dir	34.0	61.0	0.826	5.065			
Cu, dir	25.0	61.0	0.720	4.442			

only in the case of the natural clinoptilolite and its hydrogen form. At this stage of investigation it is not possible to answer exactly if this is a catalysis during the adsorption or an oxidation during the thermal desorption. The adsorption experiments with the various modified forms of the synthetic Y zeolite displayed different behaviour [36]. The adsorption capacity of the HY form was totally restored after desorption due to the weak bonds with SO₂, while for NaY and LiY the adsorption was not completely reversible as a result of the strong interconnections with the adsorbate. Although in the present investigations some discrepancy between the adsorbed and desorbed amounts for the alkaline and alkaline earth metal cations modified forms was registered (Table 3), this conclusion could not be generalised due to the insignificant differences. Definite undesorbed quantity was left in the adsorption bed in the experiments with the forms modified with transition metal cations. This was established not only by the comparison between the adsorbed/desorbed quantities but also by conducting multi-cycle adsorption–desorption. Three adsorption–desorption cycles were carried out for the indirectly enriched with Cu²⁺ form. The obtained breakthrough curves, presented in Fig. 6, show that the

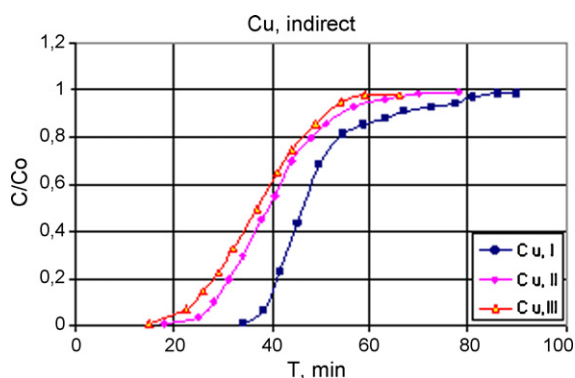


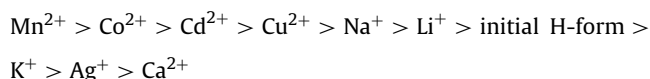
Fig. 6. Multi-cycle adsorption breakthrough curves.

curve becomes more stretched and moves to the left at each following cycle demonstrating a decrease in the adsorption capacity and an increase in the mass transfer resistance, probably due to the undesorbed gas. The data in Table 3 also indicate a decrease in the dynamic adsorption capacity at each following cycle in a relationship close to the undesorbed SO₂ quantity.

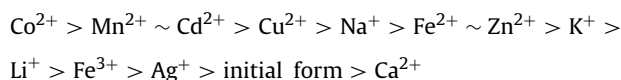
The breakthrough curves obtained for directly and indirectly modified samples were compared. Some of the results are shown in Fig. 7a and b. For all the cases the concentration curves are more stretched and moved to the left. The data in Table 3 show similar values of the distribution coefficients K for the indirectly and directly modified forms. To achieve low concentrations of SO₂ by adsorption purification of polluted gases, thus protecting the atmosphere, the indirectly modified forms will be more applicable and efficient owing to their higher breakthrough time.

From the results in Table 3, the following orders of decreasing distribution coefficients for SO₂ adsorption can be composed:

- For indirectly modified forms:



- For directly modified forms:



Although the extent of ion enrichment with Mn²⁺, Co²⁺ and Cd²⁺ cations during the indirect and direct modification is not very high, the elevated values of the distribution coefficients (respectively, dynamic adsorption capacities) of the samples containing these cations make a great impression. The adsorption capacity of the sodium form was the highest and of the potassium—the lowest, by analogy with the data for the natural clinoptilolite from Turkey [38].

It is well known that if the alkaline and alkaline earth cations in the zeolite are exchanged with some transient metal cations the

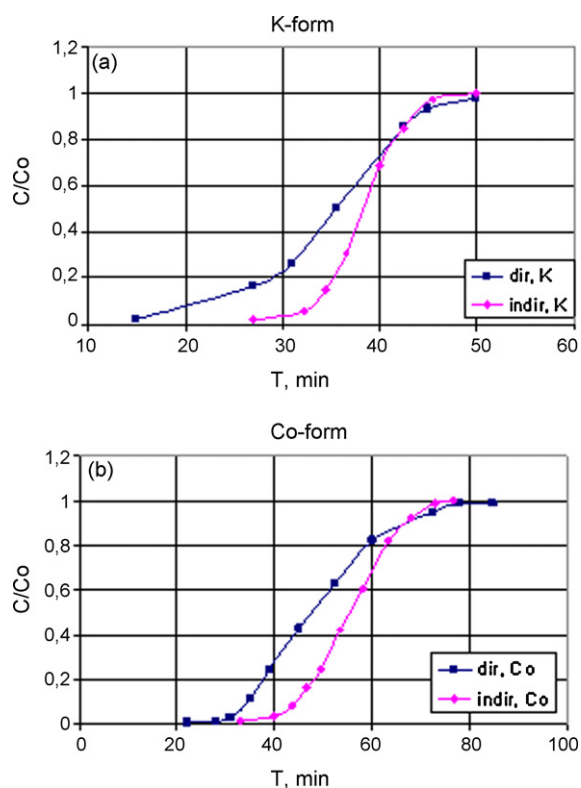


Fig. 7. (a) Breakthrough curves for indirectly and directly modified K-forms. (b) Breakthrough curves for indirectly and directly modified Co-forms.

samples colour [69]. If the colour of the metal cation is different for anhydrous or hydrous state, it means that its colour will change when heated. This phenomenon was observed during the recent investigations. A preliminary thermal activation is necessary for the effective realization of gas or vapour adsorption on zeolites, which in these work was carried out by simultaneous removal of water vapours with a gas-carrier—dry air, as it was described earlier. Some of the coloured ion exchange forms did not change their tint (e.g. reddish brown for the Mn-form) when heated at these conditions. For other forms the colour change was gradual at the bed height in the direction of the gas-carrier movement. For example, the Co-form changed its colour from red to violet-blue, the Cu-form—from heavenly blue to dark blue, and both Fe-forms (di- and trivalent) initially had a similar yellow colour that was changed gradually through the thermal activation to dark brown. An idea of applying this property in analytical chemistry, as an indicator for water vapour traces, exists [70]. It could also be useful for determination of the readiness of the respective metal form for gas or vapour adsorption.

4. Conclusions

1. It was established that a higher extent of enrichment was achieved at direct ion exchange compared to indirect.
2. At identical treatment conditions, a considerably higher extent of ion enrichment was observed for the alkaline and alkaline earth metal cations (mostly for sodium and calcium) and a lower—for the transition metal ions. The extent was high for the Ag-ions, too.
3. Independently on the different quantity of the substituted cations by both treatment methods, similar selectivity orders of ion exchange were obtained.
4. More of the obtained cation forms displayed higher adsorption capability to SO₂ compared to the natural clinoptilolite, even to

its hydrogen form. The adsorbed quantity in the samples containing transition metal ions was markedly high, while that of the calcium form—comparatively low.

5. The values of the distribution coefficients for equal indirectly or directly modified cation forms were comparable, while the breakthrough time for the indirectly produced samples was higher.
6. Definite amounts of undesorbed SO₂ were left in most of the samples at the selected conditions of programmed thermal heating. This amount was considerable for the transition metal forms, thus it led to noticeable decrease in the adsorption capacity at a multi-cycle process. For the alkaline and alkaline earth forms it could be accepted, that this quantity is within the error range, and for the natural clinoptilolite and its hydrogen form—the total adsorbed SO₂ was then desorbed.
7. All indirectly obtained cation forms, except for the natural clinoptilolite and the samples enriched with alkaline and alkaline earth metals, a definite amount of SO₃ was registered in the gas released after desorption.

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