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Adsorption of sulfur dioxide on chemically modified natural clinoptilolite. Acid modification

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ABSTRACT

Natural Bulgarian clinoptilolite from the south-eastern Rhodopes mountain was modified through treatment with hydrochloric acid with various normality, both single and repeatedly, as well as through a charring of a preliminary obtained NH_4-form. The parameters concerning the uptake of the ion-exchangeable cations (Ca^{2+}, Na^+ and K^+), as well as the uptake of aluminium from the natural material were calculated on the basis of the chemical contents. The highest extent of cations removal was attained in the case of the treatment with NH_4Cl solution, while the highest aluminium deficiency was established in the samples treated by hydrochloric acid solutions with increasing concentration. Sulfur dioxide adsorption on the obtained decationised and dealuminised samples was studied according to the frontal-dynamic method. The parameters of the breakthrough curves, namely breakthrough time, saturation time and some of the statistical moments of the curve distribution, were determined. The dynamic adsorption capacities were also specified. Comparing the momentum values it was established that as a result of the natural zeolite treatment with NH_4Cl and with low concentrated acid, the diffusion resistance decreases because of the dominant exchange of the presenting exchangeable cations in the samples with the smaller size protons and because of enlargement of the pores opening. Intensified dealuminisation was observed when more concentrated acid solutions are used. The capacity is enhanced, probably due to an increase in the total pore volume.

1. Introduction

The adsorptive purification of flue gases from sulfur dioxide has many advantages. The sorbents used have to possess high capacity persistent at multi-cycle exploitation, stability at high temperature and acid treatment, selectivity to SO_2 in the presence of other gas mixture components (especially water vapour). Some grades of highly siliceous zeolites, investigated for SO_2 adsorption, meet these requirements [1–15]. One part of the literature sources cited deals with the applicability of natural zeolites [11–15] possessing some disadvantages, mainly unstable chemical composition and impurities. However, they are widely available, low cost, and characterized with high mechanical strength. Some of them, especially the highly siliceous ones, possess higher thermal and mechanical stability compared to their synthetic analogues [16,17].

Thermal and chemical treatment could improve the industrial applicability of natural zeolites due to changes in their composition, structure and properties [17].

Zeolite heating at moderate temperature as a compulsory step before the gas adsorption results in more available adsorption space because of the "zeolite" water separation.

Acid treatment is among the most common and simple methods for zeolite modification. Hydrochloric acid solution treatment leads to decationisation (obtaining the so-called "hydrogen form" zeolites), dealuminisation and sometimes destruction of the crystal lattice. Dissolving of some amorphous materials that block the pores of natural zeolites is another consequence from the acid modification [17–20]. The effectiveness of acid treatment depends on the chemical contents, structure, mineral purity, and the working conditions. The effect of hydrochloric acid on the various grade of zeolites is different. As an example, the HCl acid modification of the natural materials mordenite and erionite conducted at similar conditions led to weak decationisation and almost no dealuminisation of mordenite, while the extent of alkaline and alkaline earth metals uptake, as well as of aluminium from erionite was more than 90% [21]. The cations content, the nature of the mineral as well as the impurities have significant influence on the effect of the acid modification of structurally identical natural zeolites [22,23]. It was observed that as a result of the treatment with HCl acid solutions with various concentrations a different extent of decationisation and dealuminisation was achieved [24]. Another group

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of investigations indicated the influence of the acid modification time [19,25], the heating of the samples before [24] and after [15,26] the treatment process, as well as the preliminary treatment with water [27] or with other chemical solutions, e.g. KOH [28] or NH_4Cl [26]. The effect of multistage zeolites acid modification was also established [18].

Low siliceous zeolites are unstable to the acid activity and the decationisation is conducted by means of other methods [29]. More often ion exchange with soluble ammonium salts (usually NH_4Cl) is the initial stage, followed by heating of the samples rich in ammonium ion to eliminate ammonia and to obtain hydrogen forms. This method of decationisation is applied also for highly siliceous zeolites. The influence of the concentration of the modification solution and the reaction time are also taken into consideration [14,19,30].

Literature reports a combined treatment method consisting in decationisation of zeolite particles with NH_4Cl solution as a first stage, followed by heating and dealuminisation of the hydrogen forms with HCl solution [26]. An alternative method with a reverse sequence of the cited procedures is also possible [25].

The changes in the zeolites chemical composition and structure as a result of the decationisation and dealuminisation steps lead to changes of the minerals properties.

Due to the limited space taken by the proton, the hydrogen forms of some HCl acid or NH_4Cl modified zeolites demonstrate higher capacity to a number of adsorbates, e.g. SO_2 [14,15,31]. The expansion of the pore opening influences the adsorption kinetics and the diffusion resistance in the zeolite hydrogen forms decreases during SO_2 adsorption [1,31]. The acidic treatment of the zeolites is also used as a stage of the blocking and deblocking of the pores to obtain a zeolite membrane for the application in the separation processes [32]. The substitution of the present alkaline and alkaline earth cations with protons or OH-ions undoubtedly would affect the molecular-sieve properties. The same effect is expected in the case of catalysis with the modified zeolites [25,26]. The type of cations changes the ionic density of the lattice [20] thus strongly influencing the adsorption of polar molecules because along with the dispersive interaction an electrostatic interaction is introduced.

The partial dealuminisation of the zeolite framework changes the microporosity. A second variety of larger size micropores is developed [26], the total micropore volume is increased and the secondary specific surface area is significantly enlarged [15,28].

The increase of the molar ratio (siliceous module) $n = SiO_2/Al_2O_3$ in the framework leads to the increase of the thermal stability [4,17] and the hydrophobicity [4]. The synthesised zeolites are attractive mainly due to their extremely high mole ratio SiO_2/Al_2O_3 (over 100), which makes them hydrophobic and increases their selectivity, e.g. to SO_2 uptake from humid mixtures [3,6], while the high thermal stability facilitates the thermal desorption [4].

Literature cites that the hydrogen forms of some zeolites (those with a high siliceous module SiO_2/Al_2O_3) exhibit higher capacity and lower diffusion resistance compared to the precursor during SO_2 adsorption. Partial dealuminisation could enlarge the pore volume thus improving the zeolite thermal stability, increasing the hydrophobicity and making the minerals more appropriate adsorbents for SO_2 from flue gases.

Natural clinoptilolite is highly siliceous zeolite with a mole ratio SiO_2/Al_2O_3 of about 10. The cations compensating the negative charge of the framework are: Na^{2+}, K^+, Ca^{2+} and Mg^{2+}. Depending on their location the quantity of some of them is dominating.

The high acid stability of the natural clinoptilolite allows both HCl acid and NH_4Cl modification. The extent of the changes depends on the cation content, on the impurities amount and content, as well as on the modification process conditions.

The aim of this study is to investigate the effect of HCl acid and NH_4Cl modification of clinoptilolite on its chemical content and adsorption behaviour towards SO_2.

2. Experimental

The material used in this study is Bulgarian clinoptilolite taken from the south-eastern Rhodopes mountain with mineral purity of 90%. The chemical analysis (Table 1) shows a prevailing content of calcium and potassium ions (Ca^{2+}, K^+). To avoid the operations: grinding, impurity separation from the zeolite, and granulation after the acid treatment, the samples were sieved and the fraction 1.6–2 mm was modified and used in the adsorption investigations. In other cases various size particles of natural material were used in the experiments of HCl acid and NH_4Cl modification [15,19,24].

2.1. *Zeolite modification*

The HCl modification of clinoptilolite was conducted following a methodology offered for a highly siliceous natural zeolite [22]. In the experiments 100 g samples were first rinsed with distilled water and were subjected to 4 h treatment at the boiling temperature of the water bath with 1500 ml acid with various normality (1, 2, 3, 4, 5, 6, 8N). Then the particles were filtered and rinsed with hot distilled water to a negative reaction for Cl^-. The samples obtained were named Series 1 including Z1H, Z2H, Z3H, Z4H, Z5H, Z6H and Z8H. Series two is a second set of materials with a single, double, threefold, fourfold and fivefold modification of the zeolite with 1N HCl acid solution was conducted. The samples obtained were named Z1H, Z1H2t, Z1H3t, Z1H4t and Z1H5t. The chemical composition of the modified forms is presented in supplementary information Table 1. The siliceous ions in highly siliceous zeolites practically were not extracted during the acid treatment [33]. On the basis of the high molar ratio SiO_2/Al_2O_3 (9.34) of the zeolite applied, it could be accepted that the SiO_2 quantity in the solid phase would not change reasonably during the treatment procedure. Thus, the composition of the samples obtained would be better represented as a relative mass concentration related to SiO_2 (supplemntary information Table 1). A similar approach was applied by other authors [25].

In addition, a clinoptilolite sample was threefold treated with 1N HCl acid solution and NH_4Cl solution at boiling temperature and constant agitation at liquid–solid phase ratio of 33:1. The duration of each operation was 90 min. After filtration and rinsing with hot distilled water to a negative reaction for Cl^-, the obtained NH_4-form was heated to 360 °C at a rate of 5 °C min^{-1}. Then the temperature was kept constant for 1 h. During this procedure ammonia is liberated and a decationised form of the zeolite—ZNH_4 (series 3) was produced. Its chemical composition is also given in supplementary information Table 1.

2.2. *SO_2 adsorption*

The samples obtained were examined as adsorbents for SO_2 removal. The experiments were conducted in a standard reactor [34] in dynamic conditions at: temperature 25 °C, diameter of the thermostated column D 19.5 mm, adsorbent bed height L 200 mm, particle diameter d 1.6–2 mm, gas flow rate in the whole column section w 0.158 m s^{-1}, fixed-bed porosity ε 0.65, SO_2 initial concentration in the model gas mixture C_0 0.7 vol.% (or 0.183 kg SO_2 m^{-3}). Dry air, preferred for flue gas modeling purposes, was used as a carrier gas [4]. The water and gases filling the zeolite pores were preliminary separated with dry air and by programmed heating of the adsorbent bed to 350 °C at 5 °C min^{-1} rate. The temperature was kept constant for 4 h.

Table 1
Chemical composition of the natural clinoptilolite (mass%).

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	Loss at ignition
mass%	64.2	11.67	1.03	7.42	0.35	2.36	3.84	0.34	8.66

3. Results and discussion

3.1. Zeolite modification

For the estimation of the extent of dealuminisation and decationisation of the treated samples, the following parameters are calculated:

$$n = \frac{SiO_2}{Al_2O_3} \quad (1)$$

$$m = \frac{N^o - N^n}{N^o} \times 100 \quad (2)$$

$$A_M = \frac{C_M^o - C_M^n}{C_M^o} \times 100 \quad (3)$$

$$Z_{cat} = \frac{\sum C_M^n}{N^n} \times 100 \quad (4)$$

where n, molar ratio of siliceous and aluminium oxides (siliceous module) [mol mol^{-1}]; m, dealuminisation extent [%]; A_M, decationisation extent related to the available gram equivalent cations for each M in the initial zeolite (M means Ca, Mg, Na or K, respectively) [%]; Z_{cat}, cation equivalent of the alkaline and alkaline earth cations [%]; N^o, gram atoms of Al in the initial clinoptilolite; N^n, gram atoms of Al in the modified sample; C_M^o, gram equivalents of the corresponding cation (M) in the initial clinoptilolite; C_M^n, gram equivalents of the corresponding cation (M) in the modified sample. The indexes used mean: o, untreated clinoptilolite; n, acid concentration for modification in the first series, or how many times modification is applied in the second series samples.

The values of the parameters calculated on the basis of Eqs. (1)–(4) are presented in supplementary information Table 2.

The quantity of Mg^{2+} in the untreated and the treated samples is relatively low, therefore, the examination of its decationisation, analogous to the other cations, would lead to incorrect conclusions. In other investigations [35,36] Mg^{2+} decationisation also is not considered even when its quantity is commensurable with that of other cations. The difficulties of their separation in the solution probably either due to occupation of difficult to access sites in the zeolite structure, or due to the fact that they are constituents of amorphous, poorly soluble impurities like $MgCO_3$ or MgOH, are outlined [36].

The results from the investigations show that a considerable amount of calcium and sodium cations migrate in the solution at once during the first treatment with 1N HCl acid, while the uptake of potassium cations for both samples series is uniform but at a lower extent. A low rate and an extent of uptake of potassium ions are established when zeolites are treated both with HCl acid and with NH_4Cl solutions [16,19,24,33,36]. The probable reason is the presence of these ions in sites which are hard to access for ion-exchange sites, and due to the larger ion radius of K^+ (0.133 nm compared to 0.098 nm for Na^+ and 0.104 nm for Ca^{2+}) their migration in the solution occurs at a lower rate.

Obviously, from the extent of decationisation related to the present gram equivalent cations in the initial zeolite A_M (supplementary information Table 2), the following selective order of uptake is formed, which assigns to both experimental series and to the NH_4Cl modified sample:

$$Ca^{2+} > Na^+ > K^+$$

It is shown that during the acid modification of various natural highly siliceous zeolites, like mordenite, erionite, and clinoptilolite, the sodium ions that are most weakly bonded to the lattice are easily removed [19,33,37,38]. According to the results published by other authors [14,35], it can be calculated that predominantly calcium ions are removed. Possibly the discrepancy stated could be due to the presence of soluble impurities, different ratio of the exchangeable ions in the natural material, as well as to the influence of the modification conditions. For example, various orders of uptake, depending on the concentration of the modification solution, were obtained when clinoptilolite was treated with NH_4Cl solution [19]. A more clear quantitative idea of the substitution of the alkaline and alkaline earth cations from the zeolite structure with protons or hydroxide ions could be withdrawn on the basis of the Z_{cat} function. Obviously, the cation deficiency is the highest for series 3, and the lowest for series 1. Consequently it could be concluded that the highest extent of decationisation is obtained for NH_4Cl modification and the lowest—for the treatment with increasing acid concentration solutions.

The extent of samples dealuminisation increases with the increase in the concentration of the acid. It is established that during the multiple treatment with 1N HCl the dealuminisation was detected even at a lower extent, while during the threefold NH_4Cl treatment no dealuminisation was registered. These tendencies could be observed also from the changes in the silicate module due to the chemical modification. The modification accomplished in this study did not lead to a high extent of decationisation and a high molar ratio SiO_2/Al_2O_3, as it was demonstrated in some other investigations at the same working conditions [22,24]. The reason might be due to the prevailing calcium ions in the material used and to the influence of the impurities. Possibly, the slight effect of the acid treatment is a result not only from equilibrium but also from kinetic factors, as the experiments were conducted with comparatively large particles, not with powdered material.

3.2. SO_2 adsorption

The obtained modified zeolite forms were tested as adsorbents for SO_2 removal by means of the breakthrough curves method. The experimental data for the first sample series are presented in Fig. 1, while those for the second series and for ZNH_4 in Fig. 2.

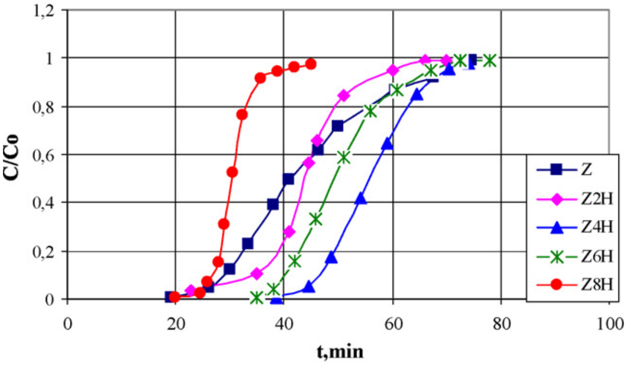

Fig. 1. Breakthrough curves for SO_2 adsorption on samples treated with various concentration HCl solutions.

Table 2
Breakthrough curve parameters.

Sample	Name	$t_{0.1}$ (min)	$t_{0.9}$ (min)	μ'_1 (min)	μ_2 (min)	η	$a_{0.1}$ (mg cm^{-3})	$a_{0.9}$ (mg cm^{-3})
Series 1								
0	Z	29.0	61.0	38.64	140.97	0.0472	51.10	73.34
1	Z1H	30.0	43.3	37.73	54.64	0.0192	59.62	74.94
2	Z2H	35.0	54.2	38.38	51.17	0.0174	66.31	72.67
3	Z3H	42.0	60.0	39.91	49.85	0.0156	63.20	74.35
4	Z4H	46.5	66.8	50.35	77.55	0.0153	79.75	93.82
5	Z5H	43.0	66.0	47.83	60.62	0.0147	75.75	89.12
6	Z6H	40.2	63.0	44.91	53.44	0.0133	74.94	83.67
8	Z8H	26.5	35.0	27.43	23.03	0.0080	49.78	51.47
Series 2								
1	Z1H	30.0	43.3	37.73	54.64	0.0192	59.62	74.94
2	Z1H2t	33.0	50.0	37.17	49.84	0.0196	62.66	69.27
3	Z1H3t	34.2	53.0	37.71	54.33	0.0181	64.13	70.56
4	Z1H4t	37.0	55.0	36.80	55.88	0.0179	68.93	71.77
5	Z1H5t	35.5	56.5	40.59	48.55	0.0197	66.47	75.96
Series 3								
1	ZNH$_4$	42.0	60.0	44.26	62.93	0.0161	56.36	83.11

Almost all of the breakthrough curves for the treated samples show higher breakthrough time and their slope is larger when compared to the natural clinoptilolite curve. This statement is true especially for the first series samples. To assess the influence of the equilibrium and kinetic factors, the following parameters were reported from the experimental curves: the breakthrough time $t_{0.1}$, the saturation time $t_{0.9}$ (the time necessary to achieve relative SO$_2$ concentrations at the fixed-bed exit $C/C_0 = 0.1$ and $C/C_0 = 0.9$, respectively); the first μ'_1 and the second μ'_2 initial and the second central μ_2 statistic moments of the breakthrough curves, as well as the reduced second central η statistic moment were determined by Eqs. (5)–(8); the dynamic adsorption capacity to breakthrough $a_{0.1}$ (Eq. (9)) and to saturation $a_{0.9}$ (Eq. (10)) were calculated. The values obtained are presented in Table 2.

$$\mu'_1 = \frac{1}{C_0} \cdot \int_0^\infty (C_0 - C) \cdot dt \tag{5}$$

$$\mu'_2 = \frac{2}{C_0} \cdot \int_0^\infty (C_0 - C) \cdot t \cdot dt \tag{6}$$

$$\mu_2 = \mu'_2 - (\mu'_1)^2 \tag{7}$$

$$\eta = \frac{\mu_2}{2 \cdot (\mu'_1)^2} \tag{8}$$

$$a_{0.1} = \frac{C_0 \cdot w_0 \cdot \varepsilon \cdot t_{0.1}}{L \cdot (1 - \varepsilon)} - \frac{\varepsilon}{1 - \varepsilon} \cdot C_0 \tag{9}$$

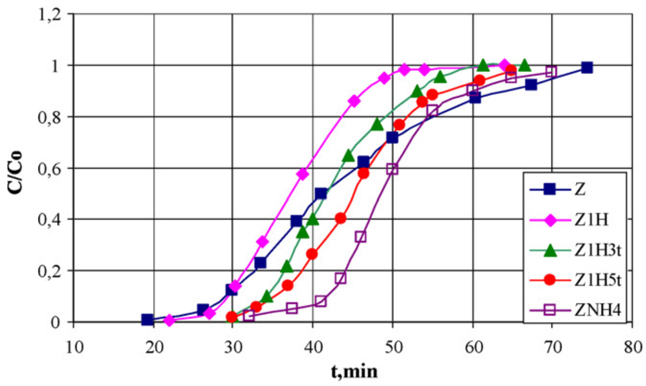

Fig. 2. Breakthrough curves for SO$_2$ adsorption on samples multiply treated with 1N HCl and NH$_4$Cl solutions.

$$a_{0.9} = \frac{C_0 \cdot w_0 \cdot \varepsilon \cdot \mu'_1}{L \cdot (1 - \varepsilon)} - \frac{\varepsilon}{1 - \varepsilon} \cdot C_0 \tag{10}$$

In Eqs. (5) and (6) C is the current SO$_2$ concentration in the gas mixture at the fixed-bed exit, and t is the current time.

The first initial moment μ'_1, which is the value of the integral of the breakthrough curve, at equal gas flow flux and bed height is a measure for the adsorption capacity. The second central moment μ_2 is a function of equilibrium and also of kinetic factors and represents the concentration curve dispersion with time at the bed exit. Often for convenience, the relative breakthrough curve dispersion, i.e. the reduced second central moment η, is used when evaluating only the kinetic parameters.

There are some interesting effects resulting from the clinoptilolite modifications made with regard to the saturation adsorption capacity $a_{0.9}$. The increase of the adsorption capacity of the ZNH$_4$ sample is about 13%. It was established that the adsorption capacity of the samples from the first series at 4, 5 and 6N HCl treatment increases but the capacity of the samples treated with 8N HCl decreases. The sample Z4H characterizes with the highest $a_{0.9}$ value (28% higher than that of the natural clinoptilolite). The dealuminisation of the same sample is 24%. Concerning the second series, there is no tendency of significant change in μ'_1, respectively in the adsorption capacity. As the series 1 and 2 differ mainly in the extent of dealuminisation, probably the outlined changes in the adsorption capacity are due to an increase of the total pore volume when more aluminium is removed. About 50% of the initial aluminium ion amount was removed when the zeolite was modified with 8N HCl solution. The tendency of adsorption capacity decrease at higher extent of dealuminisation, probably is due to a change in the ratio between the strong electrostatic and the weak Van-der Waals interaction between the zeolite surface and the polar SO$_2$ molecule. The same effects at increasing of SiO$_2$/Al$_2$O$_3$ ratio are observed more often for water vapours adsorption [6]. A partial destruction of the crystal lattice is not excluded.

The dynamic adsorption capacity to breakthrough $a_{0.1}$ is attractive from a point of view concerning the practical application of zeolites for SO$_2$ removal from flue gases, when the process is carried out to meet the required concentration. The values of $a_{0.1}$ increase to a greater extent when compared to $a_{0.9}$ (e.g. with 56% for Z4H), except for the sample Z8H. The tendency here is the same—decrease of $a_{0.1}$ after 24% dealuminisation extent.

Comparing the values of the reduced second order central moment η a sharp decrease in all samples is observed. One possible reason might be the expansion of the pore openings as a result of decationisation, i.e. formation of the so-called "open structures",

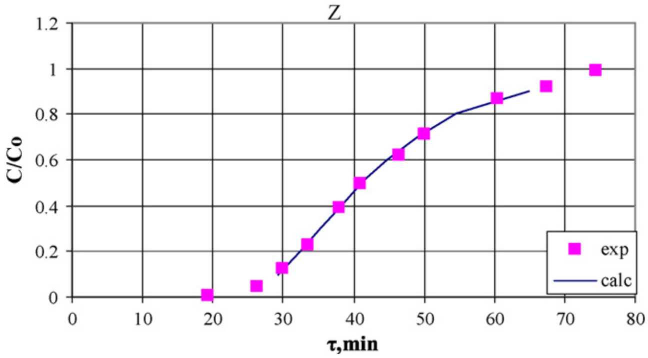

Fig. 3. Breakthrough curve for SO_2 adsorption on natural clinoptilolite.

which will lead to a decrease of the diffusion resistance. The type of the cation and its localisation in the crystal lattice define the size of the framework channels openings.

To examine the influence of the samples modification with HCl and NH_4Cl solutions on their equilibrium and kinetic relations the breakthrough adsorption curves in the region from $t_{0.1}$ to $t_{0.9}$ were described according to the equations proposed by Hashimoto and Miura [38] for a Freundlich type isotherm, a linear driving force and a constant pattern concentration front. The calculations for the natural clinoptilolite are based on earlier data for the equilibrium and kinetic parameters [39] of the system studied namely for the parameters of Freundlich equation $a = A_k \cdot C_0^n$, $A_k = 66.2$ and $\eta = 0.6$ (at concentration of sulfur dioxide a, in mg g^{-1}), Reynolds number = 18, Biot number = 25.9 and well describe the adsorption experiment on the natural material (Fig. 3).

To obtain the calculated curves of the treated samples the following corrections were made:

1. The equilibrium coefficient A_k from the Freundlich model $a = A_k \cdot C_0^n$ is corrected with the ratio of μ'_1 for the treated sample and the untreated natural clinoptilolite.
2. The Biot number is corrected with the ratio of η for the treated sample and the untreated natural clinoptilolite.[2] The Biot number ($Bi = \beta \cdot R/D$) evaluates the dominating influence of surface or intraparticle diffusion. When the experiments are conducted at a constant rate of the gaseous phase, as in the case, the verifications of the Biot number values would register only changes concerning intraparticle diffusion.
3. Both parameters A_k and Biot number are corrected.

The breakthrough curves shown in Fig. 4a–e are prepared with the corrections of the parameters presented in Table 3.

The plots in Fig. 4a–e show that due to the last correction the best fits between the calculated and the experimental results are obtained. The statistic moments method could be applied for explanation of the changes occurring in the zeolite sample during its chemical modification.

Once again it is confirmed that the decationisation resulting from the treatment of the natural clinoptilolite with NH_4Cl (Fig. 4e) or with low concentrated HCl solutions (Fig. 4a), even multiple treated (Fig. 4d) where the dealuminisation is insignificant, the adsorption capacity is nearly unchanged, while the diffusion resis-

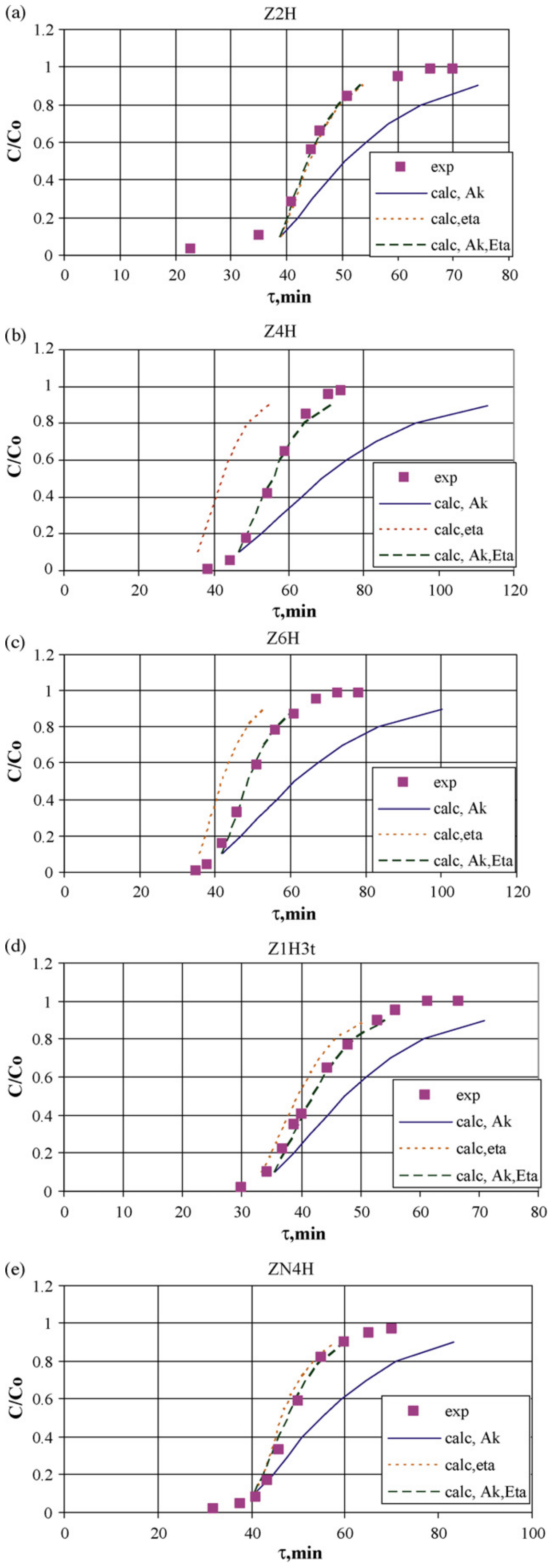

Fig. 4. Breakthrough curves for SO_2 adsorption on samples treated with various normality HCl acid and NH_4Cl: (a) 2N; (b) 4N; (c) 6N; (d) 1N three times; (e) NH_4Cl.

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[2] The reduced second central moment used in the recent investigations is valid for linear equilibrium. For nonlinear isotherm and formed steady mode of the adsorption wave-front movement η should be corrected [40]. However, as though it is not used for the calculation of diffusion coefficients but only for qualitative comparison of the diffusion resistance, it is accepted that the application of η in this study is correct. The latter conclusion will be confirmed later by the coincidence between the calculated and the experimental breakthrough curves.

Table 3
Values of the coefficients A_k and η, used in the breakthrough curves calculations.

Sample	Correction	Values of A_k	Values of *Bi*
Z2H (Fig. 4a)	Calc, A_k	65.8	25.9
	Calc, η	66.2	9.6
	Calc, A_k, η	65.8	9.6
Z4H (Fig. 4b)	Calc, A_k	86.3	25.9
	Calc, η	66.2	8.4
	Calc, A_k, η	86.3	8.4
Z6H (Fig. 4c)	Calc, A_k	77.0	25.9
	Calc, η	66.2	7.3
	Calc, A_k, η	77.0	7.3
Z1H3t (Fig. 4d)	Calc, A_k	64.6	25.9
	Calc, η	66.2	9.9
	Calc, A_k, η	64.6	9.9
ZNH_4 (Fig. 4e)	Calc, A_k	75.8	25.9
	Calc, η	66.2	8.8
	Calc, A_k, η	75.8	8.8

tance is considerably altered. In such cases the breakthrough curves can be precisely modeled through a correction only of the kinetic factor η, and not the equilibrium one A_k.

4. Conclusion

After the treatment of the zeolite with HCl acid or NH_4Cl solutions the following selective order of cation uptake is formed:

$Ca^{2+} > Na^{+} > K^{+}$

The magnesium ions content in the initial material is small, so its participation in the ion-exchange process can be excluded. Due to its large size and its location in the zeolite structure, the potassium ions poses low extent and low rate of uptake during acid modification of the samples.

During the treatment of clinoptilolite with increasing acid concentration solutions, beside decationisation, progressive uptake of aluminium ions from the solution is observed. At multiple treatment of the samples with 1N HCl significant change in the aluminium amount is detected only during the first modification. The silicate module does not alter under the impact of NH_4Cl solutions, i.e. the treatment with these solutions does not cause dealuminisation.

Due to an increase in the adsorption volume, the dealuminisation up to about 24% leads to a slight growth of the adsorption capacity $a_{0.9}$, i.e. to saturation of the adsorbent samples with SO_2. The further increase of the dealuminisation extent diminishes the adsorption capacity. The probable reasons might be changes of the role of the electrostatic and Van-der Waals interactions between the zeolite surface and the polar SO_2 molecule, as well as a destruction of the crystal lattice of the material.

The adsorption capacity increases to a higher extent until the breakthrough point $a_{0.1}$ but the tendency is the same—its decreasing after 24% dealuminisation.

The decationisation of the zeolite decreases the diffusion resistance as a result of pore openings expansion.

The treatment of the natural clinoptilolite with NH_4Cl or with low concentrated HCl solutions the adsorption capacity remains nearly unchanged, while the diffusion resistance is considerably altered.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2009.04.063.

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