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Characterization and neutralizing properties of a natural zeolite/Na_2CO_3 composite material

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Abstract

A new zeolitic active principle called NZ* has been obtained, the neutralizing properties of which are better than those of its predecessor, Neutacid N. The new product is the result of hydrothermal transformations applied to purified natural clinoptilolite. NZ* and other related products have been characterized physically and chemically using atomic emission spectroscopy with inductively coupled plasma, X-ray fluorescence analysis, X-ray diffraction, IR spectroscopy, neutralizing capacity in the presence of synthetic gastric juice and UV spectroscopy. It was demonstrated that the structure of the zeolitic raw mineral remained unchanged after hydrothermal transformation, and that NZ* is structurally stable after interaction with synthetic gastric juice. The effect of NZ* dose on the gastric enzyme pepsin was evaluated.

Keywords: Antacid; Clinoptilolite–heulandite; Natural zeolites; Pepsin

1. Introduction

Hyperacidity and its associated gastric disturbances are characterized by an abnormal increase in the hydrochloric acid concentration in the stomach and a consequent decrease in pH. Such gastric disturbances are commonly treated by means of so-called antacids, which are supposed to neutralize to some extent the excess hydrochloric acid in the gastric contents [1,2].

It has been established through pharmacological and clinical studies that natural clinoptilolite from the Tasajeras deposit (Cuba) does not cause any biological damage in humans [3,4]. This fact, plus the structural stability of natural clinoptilolite during its transit through the gastrointestinal tract as compared to synthetic zeolites [5], the use of purified natural clinoptilolite (NZ) as a gastric alcalinizant [6], as well as the use of antacids containing sodium carbonate [2], suggested the study of the combination product Na_2CO_3–clinoptilolite as an improved zeolitic antacid. We called this product NZ* [7,8].

In this work, we present a structural and chemical characterization of NZ* and some related zeolitic products through different techniques, with

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the objective of evaluating the compositional and structural stability of the natural zeolite after hydrothermal treatments and subsequent interaction with acid media. We also study the neutralizing properties of NZ* in the presence of synthetic gastric juice and compare the results with those for purified natural clinoptilolite. In particular, the pH regulation capacity of our product was evaluated taking into account that a pH of 3 or 3.5 is a currently acceptable result of antacid treatment [1]. The physical/chemical study presented in this paper constitutes a first step which has to be followed by systematic in vitro and in vivo tests which are necessary for the pharmaceutical and medical evaluation of NZ*.

2. Experimental

The zeolitic raw mineral was ground and purified via washing with distilled water by means of a fluidized bed process in order to remove the non-zeolitic mineral phases. After vacuum filtration and drying, this resulted in the product NZ, which was used as the starting material for NZC, NZ* and NZU (to be defined below). NZ is a mixture of about 70% clinoptilolite–heulandite and mordenite and 30% of other phases.

Taking into account the influence of particle size on ion exchange and adsorption mechanisms [9], we used NZ particles with diameters between 37 and 90 μm. Hydrothermal transformation (HT) was then applied with a 0.5 M Na_2CO_3 solution using a solid:liquid ratio of 1:2 for 1 h. The process took place at 100°C at atmospheric pressure in reflux conditions. After centrifugation and drying, we obtained the material called NZC [8].

NZC was then submitted to washing steps. Each step consisted of a 15 min agitation in distilled water followed by centrifugation and drying. We defined NZ* and NZU as the products resulting from one and eight washing steps, respectively [8]. Fig. 1 shows a flow chart indicating the basic steps leading to the different zeolitic materials mentioned.

Atomic emission spectroscopy with inductively coupled plasma was used to determine the Al, Ca, Na, K, Mg and Fe contents of the zeolitic samples.

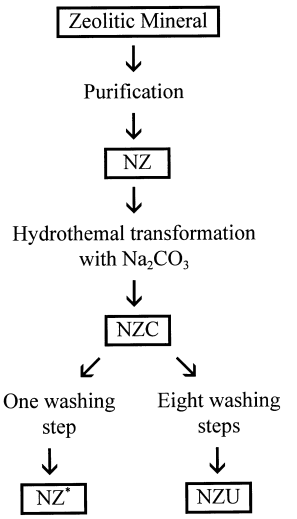

Fig. 1. Flow chart representing how the zeolitic products NZ, NZC, NZ* and NZU were prepared.

A Hilger Analytical POLYVAC E-1000 spectrometer was employed. For each analysis (which was performed three times), 200 mg of the material were digested using $HClO_4$, HF and HCl. X-ray fluorescence spectrometry was employed to determine the Si content of the zeolitic materials. A Carl Zeiss Jena VRA 30 X-ray sequential spectrometer was employed. For each sample, a quantity of 3 g was pelletized with 1 g of agglutinant.

Qualitative X-ray diffraction (XRD) analysis was used to determine whether hydrothermal transformation produced variations in the zeolite lattice parameters, the appearance of new phases, or changes in the relative diffraction intensities of the different mineral phases. A Philips PW 1218 diffractometer was employed, using Co Kα radiation ($\lambda = 1.79021$ Å). The interval $10° < 2\theta < 60°$ was swept at $2° \text{ min}^{-1}$ with a time constant of 3 s.

Infrared spectroscopy (IR) was used to evaluate possible changes in the IR vibration of the zeolitic phase modes by means of an Ati-Mattson Genesis Series Fourier-transform IR spectrometer. The samples were prepared by the KBr pressed-disk technique, with 1% inclusions of the material to be analyzed.

The neutralizing or antacid capacity was determined by acid–base titration applied to different masses of NZ and NZ* samples in the presence of

synthetic gastric juice (SGJ), which is constituted of a hydrochloric acid solution plus pepsin. For the titration, SGJ was added to each sample with 1 h agitation in order to roughly mimic the stomach conditions. The result was filtered and its neutralizing capacity was evaluated with a NaOH solution and a suitable indicator. A microburette with 0.01 ml resolution was employed, taking three measures for each point reported. The maximum difference among the titration volumes within any triad was never bigger than 0.03 ml.

pH measurements were performed on the SGJ solution before interaction with different masses of NZ and NZ* and on the filtered SGJ solution after interaction. The pH was evaluated using two different approaches: (1) by means of a commercial Radiometer PHM82 pH meter with combined glass electrode and a resolution of ± 0.05 pH units (these results will be called "experimental" pH), and (2) the expression $pH = -\log[H^+]$ was applied, where $[H^+]$ is the concentration of H^+ ions obtained from the acid–base titration described above (these results will be called "calculated" pH).

Ultraviolet spectroscopy (UV) was used to detect any possible decrease in the pepsin levels in the SGJ as a consequence of its interaction with NZ and NZ*, as well as eventual structural variations of the enzyme associated with the same cause. The spectra were collected by means of an Ultraspec III Pharmacia LKB UV spectrometer in the wavelength interval 200–400 nm.

It should be pointed out that when treating different masses of NZ* with SGJ, studies using atomic emission spectroscopy, X-ray fluorescence spectrometry, X-ray diffraction and IR spectroscopy were performed on the smallest sample (100 mg). UV spectroscopy was applied in the case of 400 and 1000 mg masses of both NZ* and NZ, respectively.

3. Results and discussion

Table 1 shows the oxide-form chemical composition of the zeolitic raw minerals, NZ, NZC, NZ*, NZU and NZ* after interaction with synthetic gastric juice (NZ*SGJ) as obtained by atomic emission spectroscopy and X-ray fluorescence spectrometry. If we compare the zeolitic raw mineral with NZ, no significant changes in composition are observed. No major changes were detected in the chemical compositions of the different zeolitic products resulting from the hydrothermal transformation and washing steps as regards SiO_2 and Al_2O_3, as expected. In particular, the interaction with SGJ does not seem to provoke dealumination in NZ*, which constitutes an important result from a pharmaceutical point of view.

The evolution of Na_2O through the different samples can be followed from Table 1: after a dramatic increase from NZ to NZC due to HT, the washing steps decrease its concentration, which has a final value of 2.6% after interaction with SGJ, relatively close to the original percentage in NZ. The variations of the rest of the oxides and, in particular, the diminution of CaO after HT, was due to the ion exchange of Ca^{+2} by $2Na^+$ in the zeolitic phase. The washing process provoked a further decrease from NZC to NZU. The diminution of Na_2O and CaO in NZU and NZ*SGJ is due to the removal of carbonates by the washing steps and by the HCl of SGJ, plus ion exchange involving H^+ from the acid solution in the latter case.

Fig. 2 shows the X-ray diffractograms of NZ, NZC, NZ*, NZU and NZ* after interaction with synthetic gastric juice, (NZ*SGJ). The XRD results indicated that clinoptilolite–heulandite and mordenite were the main phases present in our zeolitic samples, which were identified following the most intense diffraction peaks. Their relative intensities (I) and the corresponding interplanar distances (d) are shown in Table 2. The sharpness of these peaks and the negligible variation of the interplanar distances before and after the HT and washing steps suggested a high degree of crystallinity and structural stability of the zeolitic products. However, new peaks were observed after HT. The most intense of these corresponded to $Na_2CO_3.10H_2O$ and $Na_2Ca(CO_3)_2.5H_2O$. The presence of the latter can be explained by the exchange of the native zeolite Ca^{2+} ions by Na^+ ions. These two peaks diminished in intensity as washing steps were applied, finally disappearing for NZU as well as for NZ*SGJ. The relative

Table 1
Oxide-form chemical composition of the raw mineral, NZ, NZC, NZ*, NZU and NZ*SGJ, in wt.% (water content is not reported)

	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	MgO	Fe_2O_3
Raw mineral	66.2	11.7	4.5	1.9	1.3	0.6	2.3
NZ	66.5	11.3	4.3	2.0	0.6	0.5	1.1
NZC	66.8	10.8	4.0	5.4	0.5	0.5	1.0
NZ*	66.7	11.2	3.4	5.0	0.5	0.5	1.1
NZU	66.0	11.5	2.8	3.5	0.5	0.5	1.1
NZ*SGJ	66.7	12.0	1.9	2.6	0.5	0.4	1.2

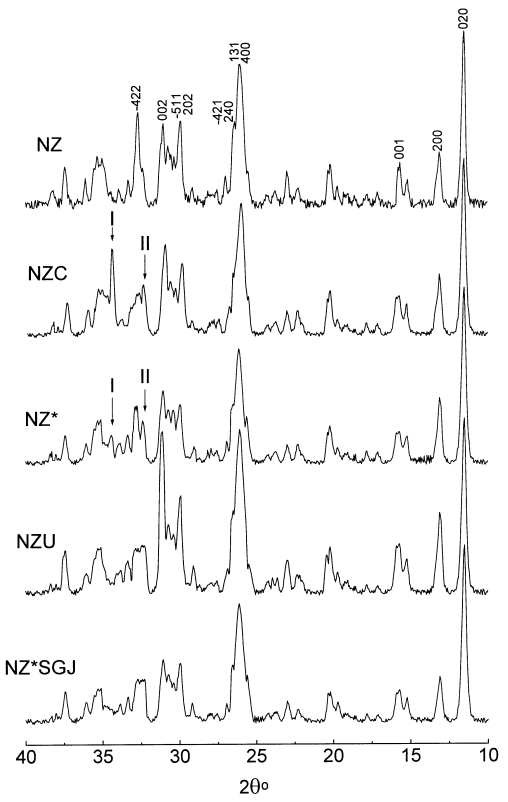

Fig. 2. X-ray diffractograms of samples NZ, NZC, NZ*, NZU and NZ*SGJ. The arrows labeled I and II indicate the peaks corresponding to $Na_2CO_3.10H_2O$ and $Na_2Ca(CO_3)_2.5H_2O$, respectively. The intensities are given in arbitrary units.

intensities of some diffraction peaks corresponding to the zeolitic phase varied due to HT, which may be interpreted as a consequence of Na^+ ion exchange. In particular, this has been demonstrated theoretically and experimentally by Petrov [10] for the case of the peaks corresponding to the (020) and (200) planes of natural clinoptilolite samples subjected to Na^+ exchange. Mir [11] studied theoretically the influence of cation exchange (including Na^+) in the X-ray patterns of NZ. She found changes in the relative intensities which were confirmed experimentally and are quite consistent with those of Petrov [10].

The X-ray diffractogram of sample NZ*SGJ demonstrates that the interaction of NZ* with SGJ does not cause structural changes in the zeolitic material with potential antacid use. It is important to note that despite the fact that we treated several masses of NZ* with a fixed amount of SGJ, we performed our XRD analysis only on the smallest amount (100 mg), which would be most affected by SGJ. Thus, we can conclude that structural transformations are not likely to take place for the rest of the masses. These results are consistent with those reported in Ref. [12], where the stability of several natural zeolites (including clinoptilolite) against an acid treatment imitating the stomach conditions was assessed through study of the sharpness and symmetry of XRD peaks.

Fig. 3 shows the IR transmittance spectra of samples NZ, NZC, NZ*, NZU and NZ*SGJ (100 mg of sample in contact with SGJ). The IR vibrational modes were assigned following Flanigen [13]. No relevant variations in the frequencies of the assigned bands were observed after HT or even after interaction with SGJ. This indicates that the zeolite structure remained unchanged after the transformation. Two new bands appeared, however, corresponding to the sodium carbonates mentioned above [14], which correspond to discrete molecular vibrations for CO_3^{2-}. The relative transmittance of these bands dimin-

Table 2
Results of the X-ray diffraction for the zeolitic products NZ, NZC, NZ*, NZU and NZ*SGJ. The interplanar distances (d) and peak relative intensities (I) are included. The following abbreviations have been used: CLI-HEU = clinoptilolite–heulandite, MOR = mordenite

Identified phases	*hkl*	NZ		NZC		NZ*		NZU		NZ*SGJ	
		d (Å)	I (%)	d (Å)	I (%)	d (Å)	I (%)	d (Å)	I (%)	d (Å)	I (%)
CLI-HEU	020	8.93	100	8.93	100	8.93	100	8.93	100	8.93	100
CLI-HEU	200	7.86	31.7	7.92	34.9	7.86	37.9	7.88	46.9	7.86	26.6
CLI-HEU	001	6.56	25.9	6.56	22.9	6.56	18.9	6.56	28.6	6.56	18
CLI-HEU	131	3.96	81.7	3.96	75.3	3.96	64.9	3.96	92.9	3.96	65.8
	400										
CLI-HEU	−421	3.90	49	3.91	36.7	3.90	34.3	3.90	46.9	3.90	31.5
MOR	240										
CLI-HEU	−511	3.47	49	3.47	41.3	3.47	34.3	3.47	56.1	3.47	34.2
MOR	202										
CLI-HEU	002	3.34	48.1	3.34	51.4	3.34	42.3	3.34	91.8	3.34	36.4
$Na_2Ca(CO_3)_2.5H_2O$		–	–	3.22	30	3.22	24.4	–	–	–	–
CLI-HEU	−422	3.18	54.8	3.18	23.9	3.18	33.6	3.18	26.8	3.18	24.3
$Na_2CO_3.10H_2O$		–	–	3.03	49.5	3.03	15.9	–	–	–	–

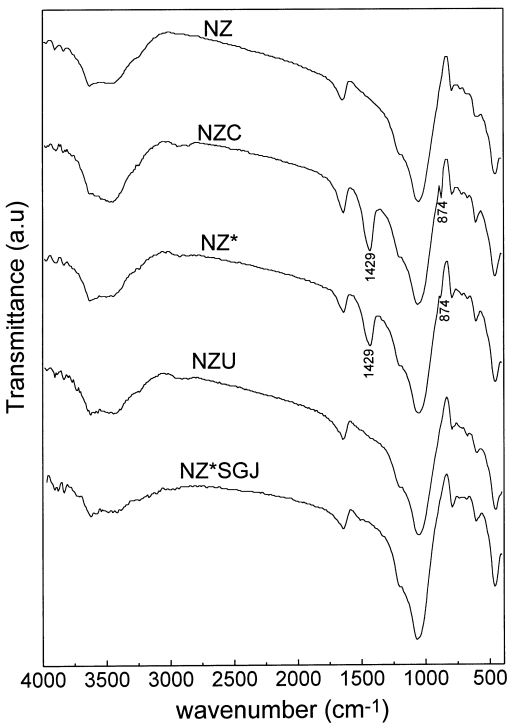

Fig. 3. IR transmittance spectra for NZ, NZC, NZ*, NZU and NZ*SGJ. The bands at 874 and 1429 cm^{-1} were assigned to sodium carbonates.

ished as washing steps were applied, and disappeared for NZU as well as for NZ*SGJ. The relative intensity of some zeolite bands changed moderately after HT, which can be associated with the ion exchange process. The changes observed in the relative transmittance of the 1205 and 456 cm^{-1} vibration bands are the same as reported by Rodríguez et al. [15] for this zeolite as a consequence of the partial exchange of Ca^{2+} by Na^{+} in NZ. These results agree well with those obtained via XRD.

Fig. 4 shows the results of the antacid capacity assays using SGJ for different zeolite masses. As expected, the neutralization capacity increases with the zeolite mass for both NZ and NZ*, but the latter gives always higher values: for a typical dose of 500 mg, for example, NZ* has more than twice the neutralization capacity of NZ. The evaluation of an antacid, however, is not only given by the neutralizing capacity of the product measured through titration, but also by its capacity to change the pH of the stomach, since this parameter influences the proteolytic role of pepsin. Piper and Fenton [16] demonstrated that, for extreme values of acidity or alkalinity, this enzyme can denature, and also found that its maximum activity takes place at pH ≈ 2, and inactivation starts at pH ≈ 5.

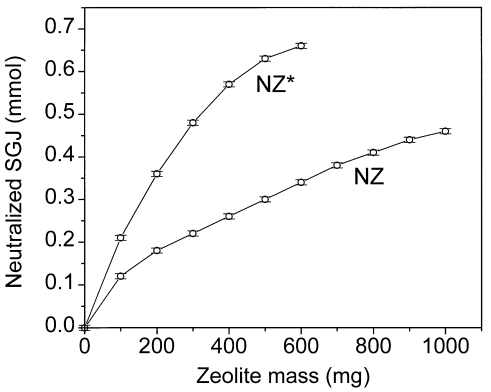

Fig. 4. Results of the neutralization capacity measurements for NZ and NZ* in the presence of synthetic gastric juice (SGJ). The vertical bars display the maximum estimated errors for the neutralization capacity values.

Moreover, for pH values between 7 and 8, pepsin inactivates irreversibly. Fordtran et al. [17] stated that the control of acidity and not of peptic activity is enough to obtain a therapeutic benefit, which means that the antacid dose must not increase the pH level above 5 in order not to inactivate pepsin. However, Piper and Fenton [16] state that a pH increase above 8 could be a result which antacid therapy should aim to achieve, supposing that it does not cause systemic effects. Taking these facts into account, we measured the pH before and after contact of NZ and NZ* with the SGJ.

The results of the pH measurements performed on the SGJ solution before the interaction with NZ and NZ* and on the filtered SGJ solution after the interaction are shown in Fig. 5(a) and (b), in which the pH versus sample mass curves are plotted. In both cases, a pH increase is observed as the zeolite mass increases, as expected from the neutralizing capacity results. However, a sizeable difference between the experimental and calculated pH values is observed, particularly for high zeolite masses. This situation can be explained as follows. While the pH meter is only sensitive to the free H^+ ions of the solution, the acid–base titration is also sensitive to the associated ions. When the expression $pH = -\log[H^+]$ is applied to the results of this titration, it is as if we consider other ions in the solution to be free H^+ ions, which makes the calculated pH lower than the experimental pH.

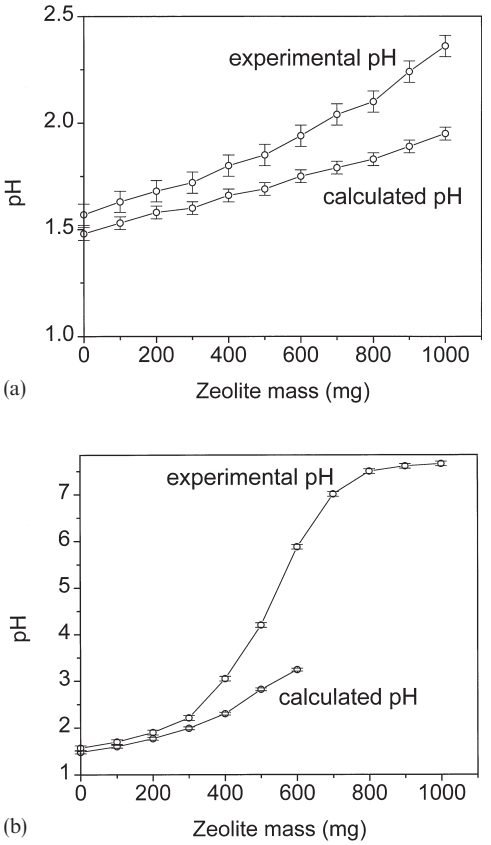

Fig. 5. Sample mass dependence of the experimental and calculated pH values for (a) NZ and (b) NZ* in the presence of synthetic gastric juice. The vertical bars display the maximum estimated errors for the pH values.

This means that, taking into account the characteristics of the system under study, the pH must be determined using a pH meter. The following example illustrates the importance of the above-mentioned differences from the point of view of evaluation of the antacid properties of our product. For 600 mg of NZ*, the experimental pH is 5.88, while the calculated value is 3.25. For such a dose, the proteolytic activity of pepsin is partially inhibited, which could be inconvenient in the light of the work of Fordtran et al. [17], as discussed above.

If we compare the experimental pH values achieved by NZ and NZ* from Fig. 5, it is clear that the latter has a much higher neutralizing capacity. For example, while 1000 mg of NZ are

required to raise the pH from 1.57 to 2.3, only 400 mg of NZ* are needed to increase the pH to a value of 3, which is within the range accepted in the literature as a reasonable objective for antacid treatments [1].

In this paper, only the neutralizing and pH-increasing capacities of NZ and NZ* have been discussed. However, it is interesting to point out that the zeolitic material with eight washing steps (i.e. NZU) also displays capacities which are up to 30% higher than NZ, even when carbonates were not detected in our XRD or IR analyses for NZU. This suggests that, besides the simple mechanism of neutralization by carbonates probably located around the zeolitic crystals, there is a contribution coming from the Na^+ ions exchanged into the zeolitic material which remain there even after several washing steps.

Fig. 6 shows the activity and stability curves of pepsin as a function of pH extracted (with a few additions) from Ref. [16], which helps in understanding the possible effects of different doses of NZ and NZ* on that enzyme. We also show in Fig. 6 the experimental pH values corresponding to three doses of NZ and NZ* which are discussed above. If the objective is to provide acidity control, but not peptic activity control, a 400 mg dose of NZ* would be sufficient. For this value, the pepsin activity would decrease to approximately 75%, while its stability remains at 100%. A 700 mg dose of the same product would decrease the pepsin activity to 3%, while the stability would be reduced to approximately 70%. It should be underlined that a NZ dose of 1000 mg (i.e. the largest dose studied in the present work) would produce an effect roughly similar to that of 400 mg of NZ*.

It is established that when zeolites with high Si contents (such as clinoptilolite) are exchanged with sodium and then treated with strong acids, substitution of native cations by H^+ takes place [18]. This suggests the following neutralizing mechanism for NZ*. After HT, we obtained a zeolitic material rich in exchanged sodium and sodium carbonate which, when added to an acid solution such as SGJ, propitiates the neutralizing action of the carbonates plus the substitution of the H^+ cations from the acid solution for the hydrolyzed Na^+ cations of the zeolitic material.

Fig. 7 shows the UV absorbance spectra recorded for SGJ before and after interaction with NZ and NZ*. A maximum at 274 nm and a minimum at 250 nm corresponding to pepsin [19] were detected for the three samples. The very small differences between the curves indicate that the zeolitic products did not capture any pepsin (which guarantees its proteolityc role), as well as the structural stability of the enzyme. This is consistent with the results shown in Fig. 6 regarding the stability curve. They are also cosistent with the

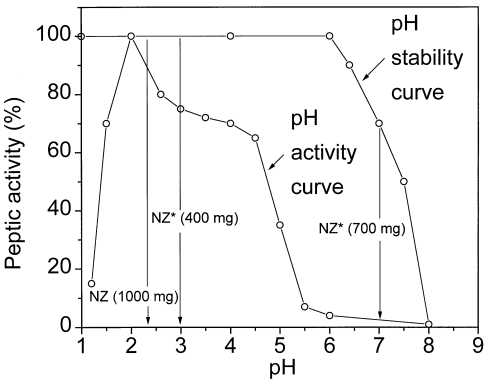

Fig. 6. Activity and stability curves of pepsin as a function of pH extracted from Ref. [16]. A few additions illustrating the effect of different doses of NZ and NZ* on pepsin are included.

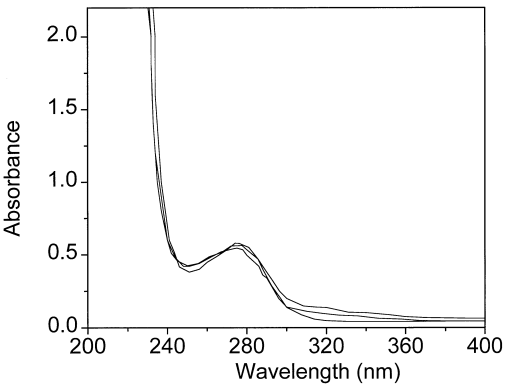

Fig. 7. UV absorbance spectra recorded for synthetic gastric juice before and after interaction with NZ and NZ*. If we choose a wavelength of 320 nm, the curves correspond, from bottom to top, to SGJ, SGJ after interaction with NZ, and SGJ after interaction with NZ*, respectively.

toxicological tests conducted in Ref. [20], in which the invariance of gastric proteolyitc activity in rats fed with NZ-supplemented food was confirmed.

4. Conclusions

Atomic emission spectromety and X-ray fluorescence indicated the compositional stability of the zeolitic materials under study. Both XRD and IR determinations demonstrated that hydrothermal transformation, washing processes and the interaction of NZ* with synthetic gastric juice did not affect the zeolitic structure. Also, we demonstrated the presence of sodium carbonate as a result of the hydrothermal treatment of NZ, which diminished as washing steps were applied. Our data suggested the occurrence of Na^+ ion exchange during hydrothermal treatment.

The neutralizing capacity measured by acid–-base titration and the pH-increasing capacity of the zeolitic product were highly improved after hydrothermal transformation. Our study indicates that, due to the complexity of the system, the pH values must be recorded using a pH meter instead of calculating them from acid–base titration. The experiments suggest that a 400 mg dose of NZ* will be able to increase the stomach pH to the value expected of an antacid treatment. Finally, UV spectroscopy demonstrated that the zeolitic active principles did not affect the concentration and stability of the enzyme pepsin in synthetic gastric juice.

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