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1 Removal of chlorinated volatile organic compounds onto natural and Cu-  
2 modified zeolite: The role of chemical surface characteristics in the adsorption  
3 mechanism

4

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1 **Abstract**

2 In this study, the effect of chemical surface characteristics of natural and Cu-modified  
3 zeolite in the adsorption of chlorinated volatile organic compounds (VOC<sub>Cl<sub>s</sub></sub>) was investigated  
4 using infrared spectroscopy. A natural zeolite mainly comprised of clinoptilolite and  
5 mordenite was used as a parent material. A succession of chemical and thermal treatments  
6 produced a Cu-modified natural zeolite (NZ-Cu) with higher adsorption properties toward the  
7 elimination of VOC<sub>Cl<sub>s</sub></sub>. The adsorption of VOC<sub>Cl<sub>s</sub></sub> onto NZ-Cu zeolite could be explained by a  
8 surface mechanism that comprises the interaction not only with Brønsted acid sites present on  
9 the original natural zeolite framework; but also with new Brønsted acid sites formed after the  
10 successive treatments.

11  
12 **Keywords:** Adsorption mechanism, Brønsted acid sites; chlorobenzene; infrared  
13 spectroscopy, natural zeolite; perchloroethylene.

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15

## 1 **1. Introduction**

2 Chlorinated volatile organic compounds (VOC<sub>Cl</sub>s) are one of the major sources of air and  
3 water pollution [1,2]. VOC<sub>Cl</sub>s play an important role in the chemical and pharmaceutical  
4 industries, where they are used as solvents and reagents. They are employed in aerosols,  
5 adhesives and in degreasers in many industrial manufacturing processes as well as in the dry  
6 cleaning industry [1,3]. About 1.5 million tons of chlorinated compounds are released into the  
7 atmosphere each year [4]. Most of these compounds are man-made and are known to be  
8 irritants, toxics, carcinogens, and flammables [5]. VOC<sub>Cl</sub>s are mainly regarded as xenobiotics,  
9 resistant to biodegradation and therefore they are very persistent in the environment [6].  
10 Among VOC<sub>Cl</sub>s, carbon tetrachloride, trichloroethane, trichloroethylene and trichlorotoluene  
11 can cause significant damage to the environment [7]. Emissions of these compounds into the  
12 atmosphere contribute to the destruction of the ozone layer, to the formation of photochemical  
13 smog and global warming. In many countries, the concern about the emissions of VOC<sub>Cl</sub>s has  
14 increased in the last years; which has led to the emergence of stronger and more restrictive  
15 environmental regulations [3,8].

16 There are some available emission control techniques for the elimination of VOC<sub>Cl</sub>s; each  
17 one has its own advantages and limitations. Among more conventional treatment processes to  
18 control the emissions of VOC<sub>Cl</sub>s; adsorption, thermal oxidation, wet scrubbing, catalytic  
19 oxidation and biofiltration are included [4,9-11]. Adsorption has been widely used as a  
20 reliable alternative process to abate VOC<sub>Cl</sub>s from industrial emissions due to flexibility, low  
21 energy consumption and cheap operating costs [3,12,13]. Microporous materials such as  
22 activated carbons, synthetic and natural zeolites have been used as adsorbents in the  
23 elimination of VOC<sub>Cl</sub>s, since their microporosity acts as a gaseous reservoir [14].

24 Activated carbons are commonly selected as adsorbents in many industrial cases due to  
25 their high adsorption capacities. However, activated carbons are relatively expensive and

1 difficult to regenerate due to their sensibility to high temperatures and the possibility to ignite  
2 [9,15]. On the other hand, synthetic and natural zeolites have been used as adsorbents in the  
3 removal of VOC<sub>Cl<sub>s</sub></sub> from waste gas streams [12,16-18], being attractive alternatives from the  
4 technical and economic point of view [14]. Zeolites have a high thermal stability [19], which  
5 makes them easy to regenerate and to reuse for further process cycles [20,21]. Unfortunately,  
6 the low adsorption capacities of natural zeolites toward VOC<sub>Cl<sub>s</sub></sub> make them uncompetitive in  
7 comparison to activated carbons. Such limitation can be overcome by chemically modifying  
8 natural zeolites in order to increase their adsorption capacities. Recent results show an  
9 increase in the removal of VOCs using modified natural zeolite with low cost transition  
10 metals such as Co, Cu, Mn, and Fe [22-25]. A surface response methodology based on a D-  
11 Optimal design of experiments has been applied to identify the transition metal-modified  
12 natural zeolite with the highest adsorption capacity for VOC<sub>Cl<sub>s</sub></sub> [26]. A succession of ion-  
13 exchange with ammonium (0.1 mol dm<sup>-3</sup>), thermal out-gassing (350°C), and ion-exchange  
14 (0.05 mol Cu<sup>2+</sup> dm<sup>-3</sup>), followed by calcination and reduction at 350°C, is claimed to produce a  
15 modified natural zeolite with optimal adsorption properties for the elimination of VOC<sub>Cl<sub>s</sub></sub>  
16 [26].

17 Unfortunately, there is a lack of information on the influence of chemical surface  
18 characteristics of natural and Cu-modified zeolite on the adsorption of VOC<sub>Cl<sub>s</sub></sub>. This work  
19 aims at some of these issues. In this study, the nature and strength of acidic surface sites of  
20 natural and Cu-modified zeolite are characterised by infrared Fourier transform spectroscopy  
21 (FTIR) using pyridine and deuterated acetonitrile as probe molecules. Two different VOC<sub>Cl<sub>s</sub></sub>  
22 (perchloroethylene and chlorobenzene) are used here in order to evaluate the effect of the  
23 chemical properties of the adsorbate on the adsorption mechanism. In addition, diffuse  
24 reflectance infrared Fourier transform spectroscopy (DRIFTS) is applied to study the  
25 adsorption of VOC<sub>Cl<sub>s</sub></sub> on natural and Cu-modified zeolites. Surface active centres are

1 identified and the nature of their interaction with  $\text{VOC}_{\text{ClS}}$  are characterised at a molecular  
2 level. Moreover, temperature-programmed desorption (TPD) experiments are conducted in  
3 order to obtain information about the adsorption energetic of the  $\text{VOC}_{\text{ClS}}$ /zeolite interactions.  
4 Finally, a surface mechanism is proposed for the adsorption of  $\text{VOC}_{\text{ClS}}$  over natural and Cu-  
5 modified zeolites.

## 6 7 8 **2. Experimental**

### 9 *2.1. Materials*

10 Natural zeolite (NZ) was supplied by the Chilean mining company “*Minera Formas*”. NZ  
11 was ground and sieved to 0.300–0.425 mm; then it was rinsed with ultra pure water, oven-  
12 dried at 125°C for 24 h, and stored in a desiccator until its further use. This zeolite is  
13 composed of clinoptilolite (53%), mordenite (40%), and quartz (7%) and has been previously  
14 characterised using standard techniques, as indicated elsewhere [27]. Table 1 summarises the  
15 main physical-chemical properties of this zeolite sample.

16 Perchloroethylene (PERC) and chlorobenzene (CLB) were supplied by MERCK  
17 (Darmstadt, Germany) with a purity > 99% and were used without further purification. The  
18 inlet concentration of the target  $\text{VOC}_{\text{Cl}}$  was fixed by vaporising the liquid phase of the  $\text{VOC}_{\text{Cl}}$   
19 in a thermally controlled saturator chamber by bubbling argon and then was diluted by mixing  
20 with another fresh stream of argon, until reaching the desired inlet concentration, as described  
21 in a previous publication [28]. Gas flow rates were controlled by mass flow controllers  
22 provided by Aalborg Instruments & Controls, Inc. (New York, NY, USA).

23 All gases used in this study were supplied by PRAXAIR Chile Ltda (Concepción, Chile).  
24 Argon 99.999% purity was used as a carrier gas, containing  $\text{O}_2$  (<1 ppm),  $\text{N}_2$  (<3 ppm),  $\text{H}_2\text{O}$   
25 (<2 ppm),  $\text{CO}_2$  (<1 ppm) and CO (<1 ppm). Oxygen with 99.8% purity, containing  $\text{H}_2\text{O}$  (<3

1 ppm), THC (<0.5 ppm) was used in the calcination treatment. Hydrogen at 5% (v/v) in argon  
2 was applied in the zeolite post-treatment.

3 Cu was used here as an active transition metal for natural zeolite modification. It was  
4 supplied in the form of metal salt by MERCK (Darmstadt, Germany) as copper nitrate  
5 ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) with a purity > 99%. Water used in chemical modification treatments was  
6 ultra-pure water ( $\geq 18.0 \text{ M}\Omega \text{ cm}$ ) and was obtained from an EASY pure® RF II system  
7 (Barnstead|Thermolyne Corp., Dubuque, IA, USA).

8

## 9 *2.2. Modification treatment of natural zeolite*

10 The natural zeolite (NZ) was chemically and thermally modified by a succession of two  
11 ion-exchange pre-treatments using ammonium salt, followed by thermal out-gassing at  
12  $350^\circ\text{C}$ ; where  $\text{Cu}^{2+}$  ions were brought into the natural modified zeolite by ion-exchange,  
13 followed by calcination in  $\text{O}_2$  flow at  $350^\circ\text{C}$  and reduction in  $\text{H}_2$  flow at  $350^\circ\text{C}$ . A more  
14 detailed description of each modification step is given below:

15 Firstly, NZ was modified by two successive ion-exchange treatments using an ammonium  
16 sulphate solution ( $0.1 \text{ mol dm}^{-3}$ ) in order to remove any unwanted cation and prepare the  
17 purely acidic form of the zeolite. A ratio of 1.0 g of NZ per  $10 \text{ cm}^3$  of solution was applied.  
18 Then, the mix was shaken for 2 h at  $90^\circ\text{C}$  and 27 rpm in a thermo-regulated bath (LSB-015S  
19 model, Korea). After that, the sample was rinsed with ultra-pure water at  $90^\circ\text{C}$  and 27 rpm for  
20 2 h. Ultra-pure water was renovated two times, each one after 1 hour of washing to eliminate  
21 the excess of salt. Subsequently, a second ion-exchange using the ammonium sulphate  
22 solution was conducted, following the same steps and experimental conditions as described  
23 before. Finally, ammonium-exchanged zeolite sample was dried at  $125^\circ\text{C}$  for 24 h.

24 Secondly, the purely acidic form of the zeolite was obtained by thermally out-gassing the  
25 ammonium-exchanged zeolite sample in a vertical tubular furnace at  $350^\circ\text{C}$ . The sample was

1 placed in a quartz U-shaped fixed-bed flow contactor (4 mm ID) and heated at a rate of 1°C  
2 min<sup>-1</sup>, under argon flow (100 cm<sup>3</sup> min<sup>-1</sup>). When the sample reached a temperature of 350°C,  
3 isothermal conditions were kept for 2 h, before quenching to room temperature. The  
4 succession of two ion-exchanges using ammonium salt followed by a thermal out-gassing at  
5 350°C were applied since, as it is reported elsewhere [27,29,30], these modification pre-  
6 treatment steps decrease the content of compensating cations with an increase in the content  
7 of Brønsted acidic sites and without a significant change in the Si/Al ratio. A lower content of  
8 compensating cations improve the diffusion of target VOCs inside the zeolite framework  
9 [27,29,30]. Moreover, experimental evidences have proved that a reduction in the amount of  
10 compensating cations united to the generation of new Brønsted acid sites after thermal out-  
11 gassing at 350°C plays a fundamental role increasing surface interactions among VOCs and  
12 Brønsted active sites [27,29,30].

13 After that, the sample under acidic form was ion-exchanged in a thermo-regulated bath  
14 (LSB-015S model, Korea) using a solution of copper nitrate (0.05 mol dm<sup>-3</sup>). Ion-exchange  
15 took place using a ratio of 1.0 g of the out-gassed sample per 10 cm<sup>3</sup> of copper nitrate  
16 solution, under constant shaking (27 rpm) at 90°C for 2 hours. Later, the Cu-exchanged  
17 zeolite sample was rinsed using ultra-pure water, applying the same washing procedure as  
18 described before and oven-dried at 125°C for 24 h. Subsequently, two sequence post-  
19 treatments were applied to the Cu-exchanged zeolite sample. Post-treatments were performed  
20 in a vertical tubular furnace. The Cu-exchanged zeolite sample was loaded into the quartz U-  
21 shaped fixed-bed flow contactor and calcined under oxygen flow (100 cm<sup>3</sup> min<sup>-1</sup>), heated at  
22 1°C min<sup>-1</sup> and isothermal conditions were kept for 4 h at 350°C. After that, the sample was  
23 cooled down to 100°C under the same oxygen flow. Then, the sample was let down to room  
24 temperature in the absence of any flow. The calcined sample was further subjected to a  
25 reduction post-treatment using H<sub>2</sub> at 5% (v/v) in argon flow (20 cm<sup>3</sup> min<sup>-1</sup>) with a heating rate



1 of  $1^{\circ}\text{C min}^{-1}$ , up to  $350^{\circ}\text{C}$ . After that, the reduced sample was cooled down to  $100^{\circ}\text{C}$  under  
2 the same  $\text{H}_2$  /argon flow. Then, the  $\text{H}_2$  /argon flow was cut and the sample was cooled to  
3 room temperature. It has been demonstrated that the incorporation of copper cations into the  
4 zeolite structure improves the adsorption capacity toward VOCs due to the increase of  
5 cationic adsorption centres and their interactions with  $\pi$ -electrons of the target VOC  
6 molecules [26,27]. Thus, the Cu-modified natural zeolite sample (NZ-Cu) was ready to  
7 contact the target  $\text{VOC}_{\text{Cl}}$ .

8

### 9 *2.3. Physical–chemical characterisation of natural and Cu-modified zeolite samples*

10 The crystallinities of natural zeolite (NZ) and Cu-modified zeolite (NZ-Cu) samples were  
11 verified using a PANalyticalX'Pert PRO diffractometer equipped with  $\text{CuK}\alpha$  radiation ( $\lambda =$   
12  $0.15418\text{ nm}$ ,  $40\text{ mA}$ ,  $45\text{ kV}$ ). Diffraction data were collected between  $2\Theta$  values of  $5^{\circ}$  and  $50^{\circ}$   
13 at intervals of  $0.1^{\circ}$  and speed of  $2^{\circ}$  per min.

14 Specific surface area and pore volume of natural and Cu-modified zeolite samples were  
15 determined by nitrogen adsorption-desorption measurements at  $-196^{\circ}\text{C}$  using the Brunauer-  
16 Emmet-Teller (BET) method and the Barret-Joyner-Halenda (BJH) method in a Micrometrics  
17 sorptometer Tri Star 3000. Before nitrogen adsorption, zeolite samples were out-gassed at  
18  $350\text{ C}$  for 2 hours.

19 Fourier transform infrared spectroscopy (FTIR) was used to identify active surface sites of  
20 natural and Cu-modified zeolite samples. Zeolite samples were ground using an agate mortar;  
21 the resulting powders were pressed ( $10^7\text{ Pa}$ ) into self-supported wafers ( $2\text{ cm}^2$  area,  $10\text{-}20$   
22  $\text{mg}$ ). Then, a wafer was placed into a home-made low temperature quartz cell equipped with  
23 KBr windows. A quartz sample holder was used to expose the wafer to the IR beam and to  
24 displace it inside a furnace located at the top of the cell for thermal treatments. The IR cell  
25 was connected to a vacuum line for evacuation and activation steps ( $P_{\text{residual}} 10^{-3} - 10^{-4}\text{ Pa}$ ). A

1 Nicolet Magna 750 IR spectrometer equipped with an MCT detector was used for the  
2 acquisition of spectra between  $4000\text{ cm}^{-1}$  and  $400\text{ cm}^{-1}$ . Natural and Cu-modified zeolite  
3 samples were activated at  $350^{\circ}\text{C}$  for 6 h under secondary vacuum. The heating rate was set to  
4  $0.5^{\circ}\text{C min}^{-1}$  in order to avoid any structure damage. Infrared spectra were recorded before (a)  
5 and after (b) activation of zeolite samples. Then, samples were cooled down to  $150^{\circ}\text{C}$  under  
6 secondary vacuum. After that, pyridine was introduced into the infrared cell system using a  
7 calibrated volume of  $1.56\text{ cm}^3$  (6-8 mbar) in order to determine Brønsted and Lewis acidities.  
8 IR spectra were recorded at  $150^{\circ}\text{C}$  during the pyridine dosing process.

9 Quantification of pyridine was also done in the desorption mode: it was introduced into the  
10 IR cell (2 Torr at equilibrium pressure) at  $200^{\circ}\text{C}$  for 30 min to ensure good diffusion inside  
11 zeolite channels. Afterwards, secondary vacuum was applied during 15 min at the same  
12 temperature in order to eliminate physisorbed pyridine over zeolites. Spectra were then  
13 recorded at different temperatures from  $200^{\circ}\text{C}$  to  $350^{\circ}\text{C}$ . IR bands at  $1545$  and  $1454\text{ cm}^{-1}$   
14 were integrated. In order to quantify Brønsted and Lewis acidic sites, molar absorption  
15 coefficients  $\epsilon_{1545\text{ cm}^{-1}} = 1.8\text{ cm}\cdot\mu\text{mol}^{-1}$  and  $\epsilon_{1454\text{ cm}^{-1}} = 1.5\text{ cm}\cdot\mu\text{mol}^{-1}$  of the bands at  $1545$  and  
16  $1454\text{ cm}^{-1}$  for Brønsted and Lewis acidic sites were used, respectively [31]. The accessible  
17 amount of OH groups was estimated by comparing the IR band areas at  $3612\text{ cm}^{-1}$  between  
18 the activated samples (without pyridine) and those having pyridine adsorbed on their surface  
19 (2 Torr at equilibrium pressure) at  $200^{\circ}\text{C}$ .

20 Finally, the accessibility of OH groups in small pores and even within the side pockets of  
21 the mordenite part of natural and Cu-modified natural zeolite samples was quantified using  
22 deuterated acetonitrile ( $\text{CD}_3\text{CN}$ ) by comparing the IR band areas at  $3612\text{ cm}^{-1}$  between the  
23 unloaded samples (without deuterated acetonitrile) and those having  $\text{CD}_3\text{CN}$  adsorbed on  
24 their surface (2 Torr at equilibrium pressure) at  $200^{\circ}\text{C}$ . Deuterated acetonitrile ( $\text{CD}_3\text{CN}$ ) is

1 preferred over acetonitrile (CH<sub>3</sub>CN) in order to avoid Fermi resonance between the vibration  
2  $\nu(\text{CN})$  and the combination  $\delta(\text{CH}_3) + \nu(\text{CC})$  frequencies [32].

#### 3 4 2.4. Adsorption experimental procedures

5 VOC<sub>Cl</sub>s adsorption experiments were conducted under dynamic conditions in a quartz U-  
6 shaped fixed-bed flow adsorber (4 mm ID) that was connected to a gas chromatograph (GC)  
7 coupled with a flame ionisation detector (FID) (Clarus 500 GC, Shelton, CT, USA), as  
8 reported elsewhere [28]. Argon was used as a carrier gas containing the target VOC<sub>Cl</sub> and  
9 circulated over the adsorber already loaded with the selected zeolite sample (NZ or NZ-Cu).  
10 The outlet concentration of VOC<sub>Cl</sub>,  $C_{\text{VOC}_{Cl_t}}$  ( $\mu\text{mol cm}^{-3}$ ), was recorded continuously by gas  
11 chromatography at the adsorber outlet as a function of time, until the zeolite sample reached  
12 the VOC<sub>Cl</sub> saturation. More detailed information about the analytical method used for VOC<sub>Cl</sub>  
13 detection and quantification can be found in a previous publication [28]. The total amount of  
14 VOC<sub>Cl</sub> dynamically adsorbed,  $q$  ( $\mu\text{mol g}^{-1}$ ), was obtained from the breakthrough curve, as  
15 follows:

$$16 \quad q = \frac{F C_{\text{VOC}_{Cl_{in}}}}{m} \int_0^{t_s} \left( 1 - \frac{C_{\text{VOC}_{Cl_t}}}{C_{\text{VOC}_{Cl_{in}}}} \right) dt \quad (1)$$

17 where  $m$  is the zeolite mass (g),  $F$  is the volumetric flow rate ( $\text{cm}^3 \text{min}^{-1}$ ),  $t_s$  is the time needed  
18 to reach the zeolite saturation with VOC<sub>Cl</sub> (min), and  $C_{\text{VOC}_{Cl_{in}}}$  and  $C_{\text{VOC}_{Cl_t}}$  are the concentration  
19 of the target VOC<sub>Cl</sub> ( $\mu\text{mol cm}^{-3}$ ) at the adsorber inlet and outlet streams as a function of time,  
20 respectively.

#### 21 22 2.5. DRIFTS study of surface interactions among zeolite samples and target VOC<sub>Cl</sub>

23 Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was applied here to  
24 allow distinguishing the various chemical interactions between surface sites on the zeolites

1 and the target  $\text{VOC}_{\text{Cl}}$ . DRIFTS *operando* experiments were performed using a commercial  
2 PIKE DiffusIR™ cell (PIKE Technologies, Fitchburg, WI, USA), containing two ZnSe  
3 windows ( $32 \times 3$  mm) and a gas flow system that was installed in a Nicolet™ iS™50  
4 spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) equipped with a DTGS  
5 detector, as described in a previous publication [28]. A powder sample of natural (or pre-  
6 treated) zeolite was loaded into a ceramic cup with a porous base. After that, the loaded cup  
7 was placed into the DiffuIR™ chamber. A mirror signal was used here as a reference. Before  
8 the measurement, the sample was post-treated inside the DiffuIR™ chamber, following the  
9 same calcination and reduction procedures at  $350^\circ\text{C}$  as in Section 2.2. Then, a spectrum of the  
10 adsorbate free sample was measured. Spectra were collected with 60 scans at a resolution of 4  
11  $\text{cm}^{-1}$  over the range of  $4000\text{--}1100 \text{ cm}^{-1}$ . In DRIFTS *operando* experiments, the adsorption of  
12 the target  $\text{VOC}_{\text{Cl}}$  (perchloroethylene and chlorobenzene) was conducted using an inlet  
13 concentration of  $7.6 \mu\text{mol dm}^{-3}$  at  $20^\circ\text{C}$ . The inlet concentration was fixed by vaporising the  
14 target  $\text{VOC}_{\text{Cl}}$  in a thermally controlled saturator chamber, as described in Section 2.1. The  
15 argon stream containing the target  $\text{VOC}_{\text{Cl}}$  was passed through the DiffuIR™ chamber until  
16 reaching the saturation and spectra were registered as a function of time. PIKE TempPro™  
17 software was used for temperature control and data collection. Results were processed with  
18 OMNIC 9.0 software.

19

## 20 2.6. Temperature-programmed desorption (TPD) of the adsorbed $\text{VOC}_{\text{Cl}}$

21  $\text{VOC}_{\text{Cl}}$  TPD experiments were conducted in a temperature-programmable flow micro-  
22 contactor loaded with 0.3 g of zeolite sample (NZ or NZ-Cu) and coupled to a GC-FID for  
23  $\text{VOC}_{\text{Cl}}$  detection. Firstly, the target  $\text{VOC}_{\text{Cl}}$  (perchloroethylene or chlorobenzene) was injected  
24 ( $50 \text{ cm}^3 \text{ min}^{-1}$ ,  $7.6 \mu\text{mol dm}^{-3}$ ) over the zeolite sample (NZ or NZ-Cu) until saturation was  
25 reached at  $20^\circ\text{C}$  and the excess of  $\text{VOC}_{\text{Cl}}$  was flushed out using argon ( $50 \text{ cm}^3 \text{ min}^{-1}$ ) at the

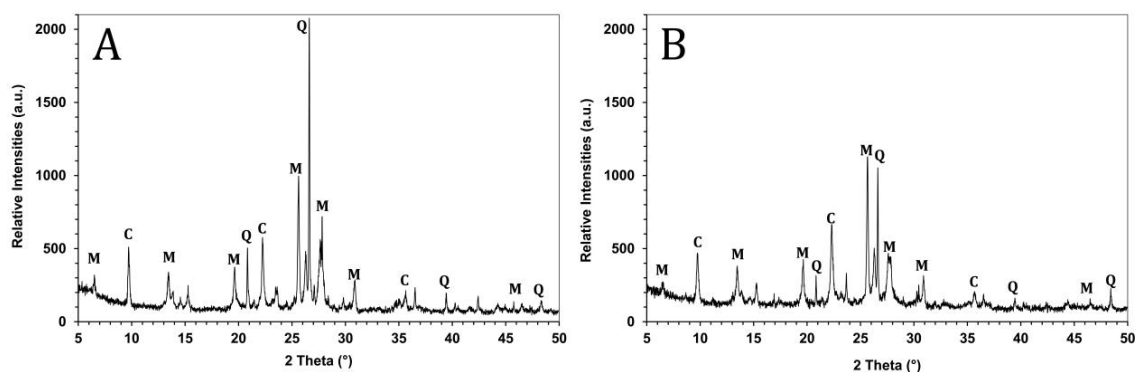
1 same temperature. The  $\text{VOC}_{\text{Cl}}$  was then progressively desorbed using a TPD procedure, as  
2 described elsewhere [28]. The saturated-sample was heated up to  $550^{\circ}\text{C}$  at a heating rate of  
3  $3^{\circ}\text{C min}^{-1}$  under an argon flow ( $100\text{ cm}^3\text{ min}^{-1}$ ). A TPD profile of the evolved  $\text{VOC}_{\text{Cl}}$  was  
4 obtained using GC-FID analysis, as described in a previous publication [28]. A concentration  
5 profile of the evolution of the desorbed  $\text{VOC}_{\text{Cl}}$  was recorded as a function of temperature. The  
6 total amount of desorbed  $\text{VOC}_{\text{Cl}}$  (perchloroethylene or chlorobenzene) per mass of zeolite  
7 was determined by integrating the area under the TPD concentration curve, using OriginPro 8  
8 SR0 v8.0725 (B725) software.

9

10

### 11 3. Results and Discussion

#### 12 3.1. Physical-chemical characterisation of natural and Cu-modified zeolite samples



13

14 **Fig. 1.** X-ray powder diffraction patterns: (A) natural zeolite, NZ, (B) Cu-modified natural  
15 zeolite, NZ-Cu. (C) Clinoptilolite, (M) Mordenite, (Q) Quartz.

16

17 XRD results, shown in Fig. 1-A and 1-B, indicate that no significant changes in the  
18 crystalline pattern of natural zeolite are observed after  $\text{Cu}^{2+}$  ions incorporation and  
19 physicochemical treatments. Characteristic peaks of clinoptilolite (C), mordenite (M) and  
20 quartz (Q) structures can be observed in the X-ray patterns, according to JCPDS 39-183,  
JCPDS 29-1257 and JCPDS 461045, respectively. However, a reduction in the intensity of

1 characteristic peaks of the natural zeolite diffraction pattern after after Cu<sup>2+</sup> ions incorporation  
 2 was observed.

3 Physical characteristics of NZ and NZ-Cu are summarised in Table 1. Results show that  
 4 specific surface area and pore volume increase after the sequences of physicochemical  
 5 treatments applied here. Such increases in the values of surface area and pore volume could  
 6 be related to unblocking porous structure of NZ. It has been reported in previous publication  
 7 that a combination of ion-exchange treatment using ammonium sulphate followed by thermal  
 8 out-gassing at 350°C reduces the amount of compensating cations in natural zeolite without  
 9 significant change on the zeolite framework [33]. The presence of different kinds of  
 10 compensating cations inside of zeolite framework has been responsible to pore clogging [33].  
 11 On the other hand, the observed increase on water adsorption capacity on NZ-Cu could be not  
 12 only related to physical adsorption of water, but also to water interaction with new Lewis acid  
 13 surface sites formed after Cu<sup>2+</sup> ions inclusion inside the zeolite framework. This could, in  
 14 turn, generate new (weak) Brønsted acid sites.

**Table 1.** Physical characterisation of natural (NZ) and Cu-modified zeolite (NZ-Cu).

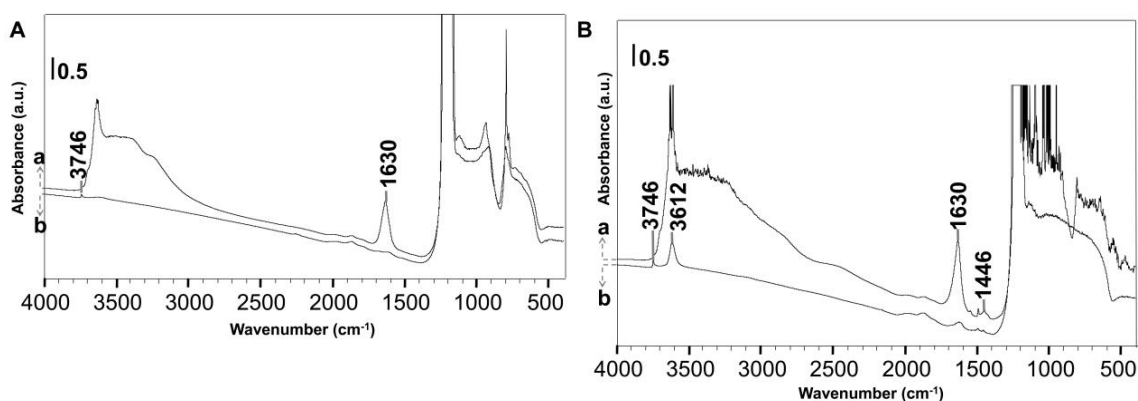
<b>Properties</b>		<b>NZ</b>	<b>NZ-Cu</b>
	<b>BET</b>	241	312
<b>Surface area <sup>a</sup> (m<sup>2</sup> g<sup>-1</sup>)</b>	<b>t-Plot Micropore</b>	224	284
	<b>t-Plot External</b>	17.8	28.8
<b>Pore volume <sup>a</sup> (cm<sup>3</sup> g<sup>-1</sup>)</b>	<b>Micropore</b>	0.07	0.11
	<b>Mesopore</b>	0.05	0.06
	<b>Total</b>	0.12	0.17
<b>Average pore diameter <sup>a</sup> (nm)</b>	<b>BET</b>	2.2	2.2
	<b>BJH</b>	10.5	8.6
	<b>D-H</b>	9.9	8.3
<b>Water adsorption capacity (%wt-dry)</b>		11.8	13.1

	<b>Si/Al</b>	5.32	5.17
	<b>Si</b>	65.39	67.67
	<b>Al</b>	12.29	13.08
	<b>Ca</b>	11.13	4.12
	<b>Fe</b>	5.27	4.72
	<b>Na</b>	2.12	0.30
	<b>K</b>	1.90	0.88
<b>Elemental analysis<sup>b</sup> (%)</b>	<b>Ti</b>	0.89	0.74
	<b>Mg</b>	0.53	0.24
	<b>Mn</b>	0.13	0.08
	<b>Sr</b>	0.12	0.08
	<b>S</b>	0.05	0.05
	<b>Zr</b>	0.05	0.04
	<b>Zn</b>	0.02	0.02
	<b>Cu</b>	ND	7.88

1 <sup>a</sup> Determined from nitrogen adsorption-desorption isotherms

2 <sup>b</sup> Determined by X-Ray Fluorescence

3  
4 Fig. 2-A and 2-B display IR spectra recorded before (a) and after (b) activation of NZ and  
5 NZ-Cu, respectively. The IR band at 1630 cm<sup>-1</sup> is assigned to the bending vibration of OH  
6 groups of surface water molecules adsorbed on zeolites [34]. This band is suppressed after the  
7 activation of the samples. The band at 1446 cm<sup>-1</sup> is only observed in the Cu-modified zeolite.  
8 This band is attributed to the bending vibration  $\delta(\text{NH})$  of the NH groups [35], indicating that  
9 this zeolite sample is partially in the NH<sub>4</sub><sup>+</sup> form before activation, as a consequence of the  
10 ion-exchange pre-treatment with ammonia. After activation, NH<sub>4</sub><sup>+</sup> are removed and NZ-Cu  
11 presents free acidic hydroxyl groups.



**Fig. 2.** Infrared spectra of zeolite samples: (A) natural zeolite, NZ, (B) Cu-modified zeolite, NZ-Cu. (a) before activation, (b) after activation.

Two IR bands are observed after the activation procedure at  $3746\text{ cm}^{-1}$  and  $3612\text{ cm}^{-1}$ . These bands are attributed to the vibration of silanol groups (Si-OH) and to the vibration of bridge hydroxyl groups (Si-OH-Al), respectively [36]. The latter band ( $3612\text{ cm}^{-1}$ ) is generated after the ion-exchange step pre-treatment of natural zeolite, creating Brønsted acidity. It is worth noting that no bands are visible between  $3660\text{ cm}^{-1}$  and  $3680\text{ cm}^{-1}$ , indicating that there is very little or no extra-framework aluminic OH phases formation during the activation of zeolite samples [32]. It is known that depending on the applied zeolite activation method (elimination of water), it can provoke partial dealumination of zeolite with the appearance of extra-framework aluminium (EFAL) species. The latter are usually detected upon pyridine adsorption, showing characteristic IR bands between  $3660$  and  $3680\text{ cm}^{-1}$  [37, 38]. In this work, experimental evidences indicate that under the carried out activation procedure under secondary vacuum a dealumination process is quite unlikely to take place.

Fig. 3-A and 3-B depict IR bands evolution during pyridine dosing at  $150^{\circ}\text{C}$  on NZ and NZ-Cu, respectively. Curves (a) and (f) indicate the smaller and the higher applied doses of pyridine, respectively. Inserted graphs represent IR difference spectra between pyridine-adsorbed and activated (pyridine-free) samples. As it can be seen, the band at  $3612\text{ cm}^{-1}$  decreases as a consequence of pyridine interaction with OH acidic groups. Nevertheless, this

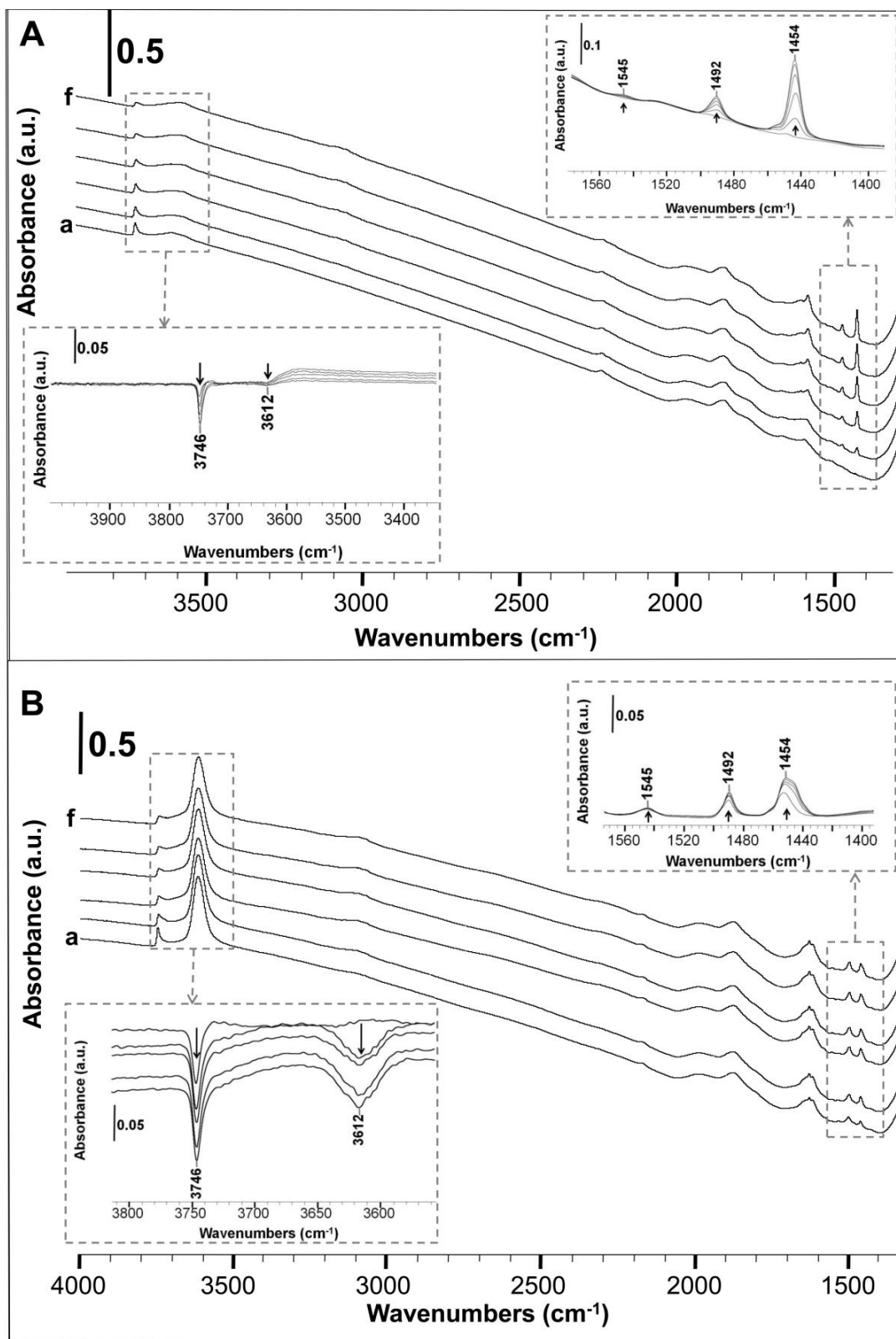


1 band does not disappear completely, even after introduction of relatively high amounts of  
2 pyridine. This could be due to some of the acidic sites not being accessible to pyridine.

3 As indicated before, NZ is composed mainly of clinoptinolite (53%) and mordenite (40%).

4 In the case of the porous framework of mordenite, it is formed by two types of elliptical  
5 channels. One of them is a 12-membered oxygen ring channel (6.7 x 7.8 Å) and the other one  
6 is an 8-membered oxygen ring channel (2.9 x 5.7 Å) often called “side pockets” [39-41] and  
7 usually not accessible to pyridine molecules. The overall amount of OH groups accessible to  
8 pyridine molecules in our samples remains low (lower than 4%) (see Table 2). It is possible  
9 that after Cu<sup>2+</sup> ions incorporation, the opening windows of the 12-membered oxygen ring  
10 channel of the mordenite part of natural zeolite are partially blocked. IR bands at 1545, 1492  
11 and 1454 cm<sup>-1</sup> increase due to pyridine interaction with accessible Brønsted (B), Lewis and  
12 Brønsted (B+L) and Lewis (L) acid sites of zeolites, respectively.

13



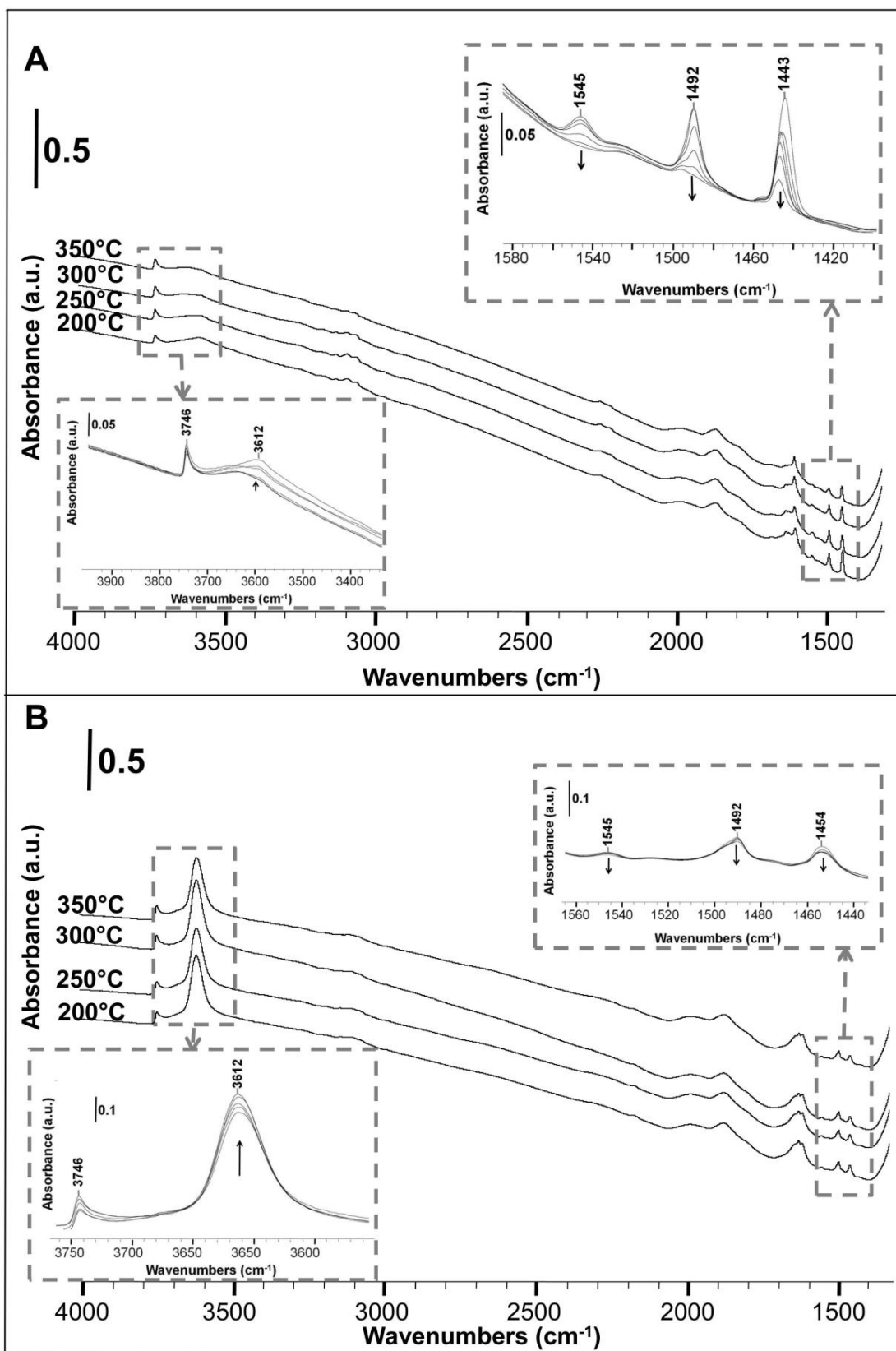
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2

1 **Fig. 3.** Evolution of infrared bands of zeolite samples during pyridine dosing process at  
2 150°C: (A) natural zeolite, NZ, (B) Cu-modified zeolite. Inserted graphs represent IR  
3 difference spectra between pyridine-adsorbed samples and unloaded samples (without  
4 pyridine). Curves (a) and (f) represent the smaller and the higher applied doses of pyridine,  
5 respectively.

6 Fig. 4-A and 4-B illustrate the IR bands evolution during pyridine desorption from natural  
7 and Cu-modified zeolite as temperature increases in the range 200 to 350°C, respectively. As  
8 it can be seen, natural zeolite presents a relatively high amount of Lewis acidic sites, probably  
9 due to the presence of  $\text{Al}^{3+}$  in the zeolite framework as a consequence of the low Si/Al molar  
10 ratio of this zeolite (Si/Al = 5.4). In the case of Cu-modified zeolite, during the ion-exchange  
11 pre-treatment step using ammonia, compensating cations balancing the zeolite framework  
12 negative charge are replaced by  $\text{NH}_4^+$  ions which will give place to bridged hydroxyl groups  
13 generation after the out-gassing procedure at 350°C, creating thus Brønsted acidity. After  
14  $\text{Cu}^{2+}$  ions incorporation into the zeolite sample, Lewis acidity is enhanced. However, it still  
15 remains lower compared to that of NZ. It is known that the temperature chosen for zeolite  
16 thermal treatments, the solution pH during the ion-exchange process, as well as the nature of  
17 the transition metal have a significant influence on the acidic character of zeolite samples  
18 [42]. The acidity presented in NZ-Cu could be explained by partial dealumination which  
19 causes zeolite dehydroxylation during the earlier thermal treatments applied to natural zeolite.  
20 The creation of several stacking faults in zeolite framework as well as the formation of copper  
21 clusters blocking the pores could explain the quite low accessibility of the OH groups of this  
22 sample. It is worth noticing that pyridine also interacts with isolated weakly acidic silanol  
23 groups (see the diminution of the IR band at  $3746\text{ cm}^{-1}$ ) as a consequence of the partial  
24 obstruction of more acidic OH groups in both samples.

25  
26



- 1 **Fig. 4.** Evolution of infrared bands during pyridine desorption from zeolite samples at
- 2 different temperatures. (A) natural zeolite, NZ, (B) Cu-modified zeolite.

**Table 2.** Lewis and Brønsted acidic site content ( $\mu\text{mol g}^{-1}$ ) of natural (NZ) and Cu-modified zeolite (NZ-Cu), detected by quantifying the amount of pyridine retained after heating the samples from 200 to 350°C.

Sample	Heating Temperature (°C)	Lewis acid sites ( $\mu\text{mol g}^{-1}$ )	Brønsted acid sites ( $\mu\text{mol g}^{-1}$ )	Total acidity ( $\mu\text{mol g}^{-1}$ )	Accessible OH groups
NZ	200	115.6	23.7	139.3	-
	250	80.5	25.4	105.9	
	300	69.6	17.9	87.5	
	350	60.3	9.9	70.2	
NZ-Cu	200	27.7	11.2	38.9	3.4%
	250	20.0	11.2	31.2	
	300	17.2	11.5	28.7	
	350	12.4	9.4	21.8	

1  
2 Results listed in Table 2 reveal the presence of acidic surface sites of different strength.  
3 The amount of pyridine that remains adsorbed after heating zeolite samples from 200 to  
4 350°C is related to the strength of Brønsted and Lewis acidic sites. Low (200–250°C), mid  
5 (300°C) and high (350°C) temperature ranges could be related to the desorption of pyridine  
6 from weak, middle and strong acidic sites, respectively. Thus, the strongest Brønsted and  
7 Lewis acidic sites are calculated as the amount of pyridine retained after heating the samples  
8 up to 350°C. On the one hand, the strength of Brønsted acidic sites is found to be enhanced  
9 after physicochemical transformation of natural zeolite (61.6% of pyridine remains adsorbed  
10 in NZ-Cu compared to 13.9% in NZ) and could be related to the sequence applied treatments  
11 of ammonium exchange, thermal out-gassing followed by post-calcination and hydrogen

1 reduction at 350°C; as well as to copper position within the zeolite framework. On the other  
 2 hand, the strength of Lewis acidic sites in natural zeolite is not significantly modified after the  
 3 applied chain of treatments conducted here (41.3% of pyridine remains adsorbed on NZ after  
 4 out-gassing at 350°C compared to 47.7% for NZ-Cu).

5 The accessibility of deuterated acetonitrile (CD<sub>3</sub>CN) to OH groups is presented in Table 3.  
 6 As it can be noticed, OH groups of natural zeolite are not accessible, even using CD<sub>3</sub>CN.  
 7 However, the amount of accessible OH groups of Cu-modified zeolite using CD<sub>3</sub>CN is higher  
 8 than those when pyridine (C<sub>5</sub>H<sub>5</sub>N) is applied (see Table 1). CD<sub>3</sub>CN is a basic probe with a  
 9 smaller molecular size than C<sub>5</sub>H<sub>5</sub>N. Nonetheless, the OH groups' accessibility is still far away  
 10 from 100%, confirming partial zeolite pore blockage.

**Table 3.** Accessible OH groups to deuterated acetonitrile (CD<sub>3</sub>CN) of natural (NZ) and Cu-modified zeolite (NZ-Cu).

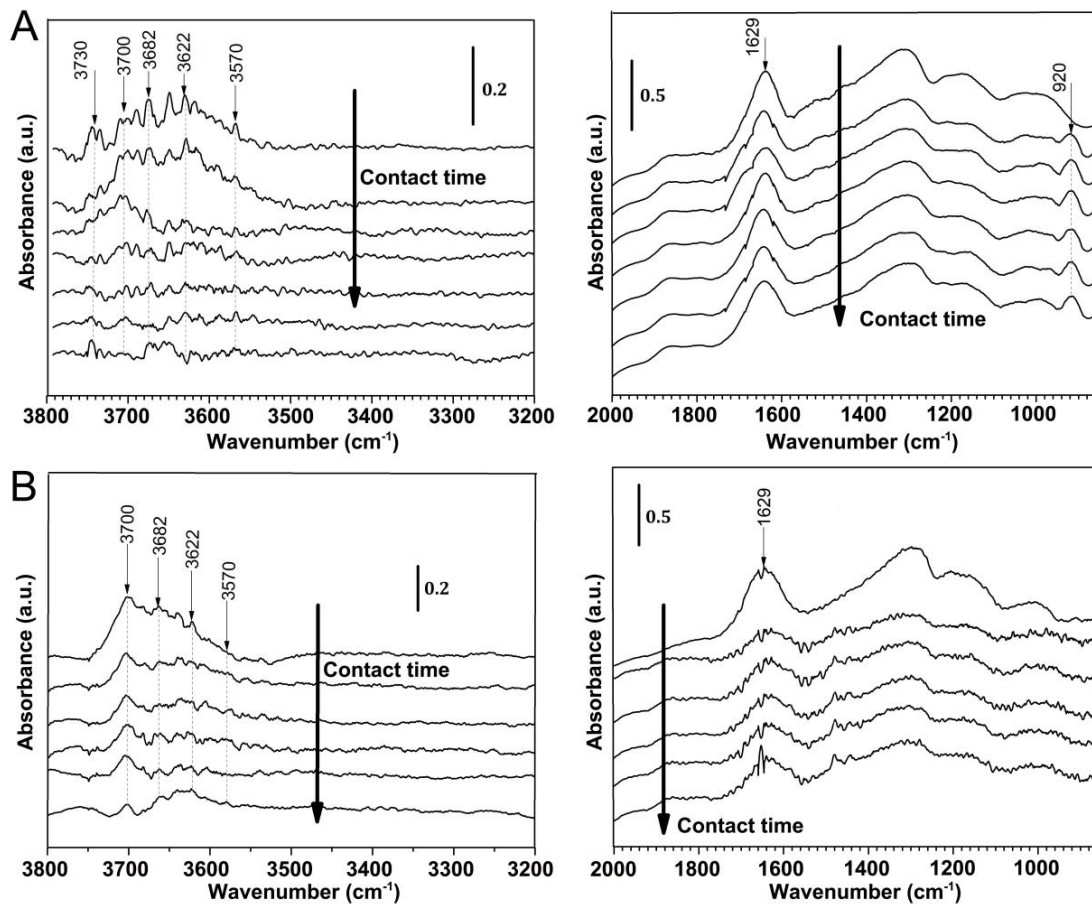
Sample	Accessible OH groups (%)
NZ	-
NZ-Cu	68.24

11

### 12 3.2. DRIFTS study of surface interactions among zeolite samples and target VOC<sub>Cl</sub>

13 DRIFTS spectra of natural (NZ) and Cu-modified zeolite (NZ-Cu) during the adsorption  
 14 of target VOC<sub>Cl</sub> are depicted in Fig. 5 and 6, respectively. Fig. 5-A and 5-B show DRIFTS  
 15 evolution during perchloroethylene and chlorobenzene adsorption onto NZ sample,  
 16 respectively; while Fig. 6-A and 6-B show DRIFTS evolution during perchloroethylene and  
 17 chlorobenzene adsorption onto NZ-Cu sample, respectively. It is worth noticing that the  
 18 quality of Figures 5 and 6 are quite much lower than that of Figures 2 to 4, since Fig. 5 and 6  
 19 were obtained using DRIFTS under flow conditions and Fig. 2 to 4 were acquired under  
 20 partial vacuum using IR transmission technique.

1

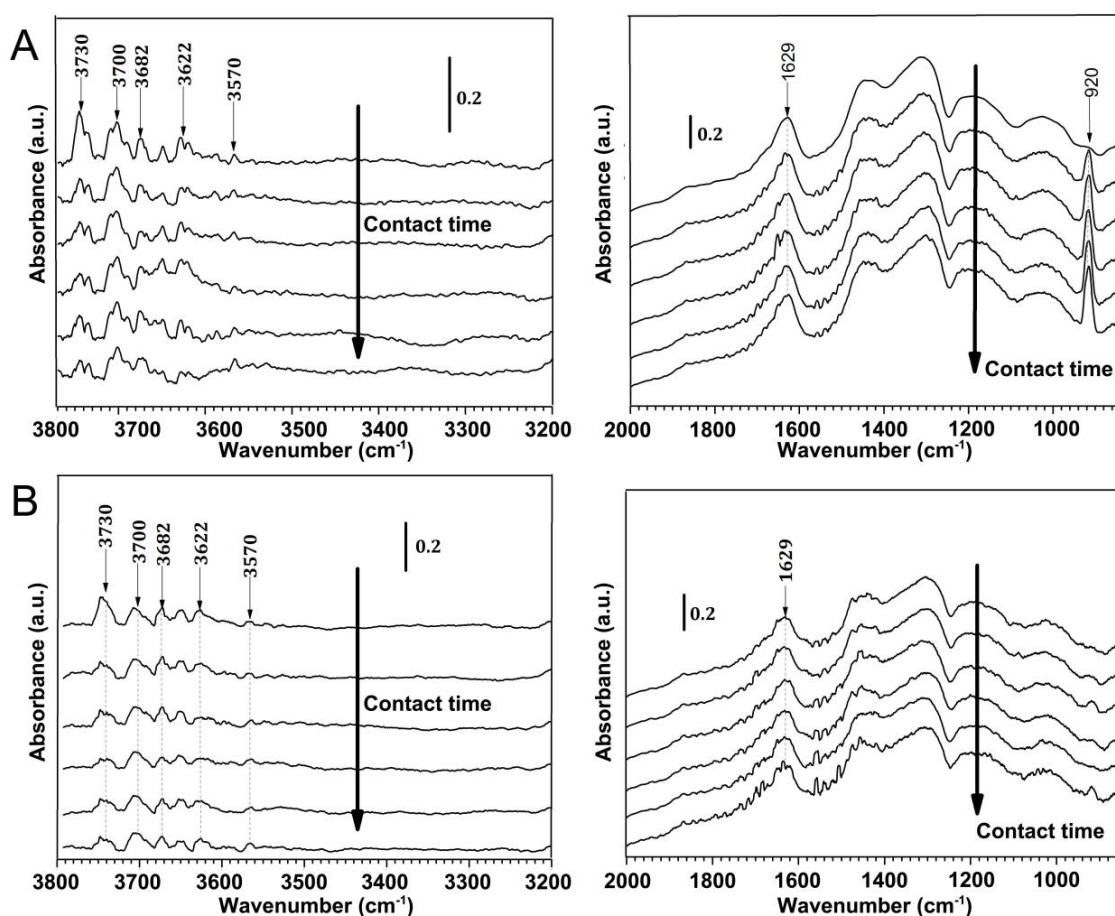


2

3 **Fig. 5.** Variation of DRIFTS spectra as a function of contact time during VOC<sub>C1</sub> adsorption  
 4 onto NZ at 20°C: (A) perchloroethylene, (B) chlorobenzene. Operating conditions: 0.03 g of  
 5 zeolite sample, 50 cm<sup>3</sup> min<sup>-1</sup>, with an inlet concentration of perchloroethylene (or  
 6 chlorobenzene) of 7.6 μmol dm<sup>-3</sup>.

7





**Fig. 6.** Variation of DRIFTS spectra as a function of contact time during  $\text{VOC}_{\text{Cl}}$  adsorption onto NZ-Cu at  $20^{\circ}\text{C}$ : (A) perchloroethylene, (B) chlorobenzene. Operating conditions: 0.03 g of zeolite sample,  $50\text{ cm}^3\text{ min}^{-1}$ , with an inlet concentration of perchloroethylene (or chlorobenzene) of  $7.6\text{ }\mu\text{mol dm}^{-3}$ .

Infrared vibration bands at  $3730\text{ cm}^{-1}$ ,  $3700\text{ cm}^{-1}$ , and  $3570\text{ cm}^{-1}$  are probably perturbed after zeolite exposure to gaseous  $\text{VOC}_{\text{Cl}}$  (perchloroethylene and chlorobenzene) due to their interaction with zeolite active sites. The presence of new Lewis acid sites after  $\text{Cu}^{2+}$  incorporation into NZ lattice, are responsible for the observed enhancement of water adsorption. Therefore, new Brønsted acid sites are induced in Cu-modified zeolites upon water adsorption. In the presence of water, introduced copper over zeolite framework may first tend to coordinate water molecules that then through a dissociative chemisorption led to

1 the observed increase in the IR signal of OH groups. In both samples, the IR bands between  
2 3730 and 3570  $\text{cm}^{-1}$  are ascribed to OH groups of adsorbed water from carrier gas coming  
3 together with VOCs. An IR band located at 1629  $\text{cm}^{-1}$  in both samples corresponds to flexion  
4 vibrations of the OH groups of residual water [36,43,44]. This band is closely related to IR  
5 bands from 3730 to 3570  $\text{cm}^{-1}$ . Vibrational IR modes in the range between 1300 and 600  $\text{cm}^{-1}$   
6 correspond to zeolite lattice structure. These IR bands are caused by the stretching and  
7 bending modes of the T-O units. Double ring vibrations are found in the IR region between  
8 650-600  $\text{cm}^{-1}$  and between 1300-700  $\text{cm}^{-1}$  related to O-T-O and T-O-T symmetric and  
9 antisymmetric stretching vibrations, respectively [45,46]. Such bands have little or no  
10 modification during the adsorption and desorption of the  $\text{VOC}_{\text{Cl}}$ .

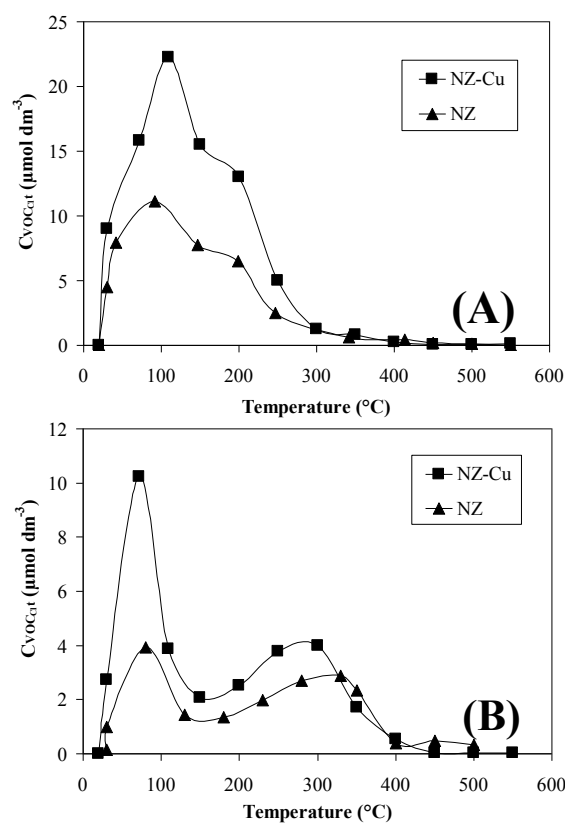
11 In the spectrum of perchloroethylene adsorption (see Fig. 5-A and Fig. 6-A), a decrease in  
12 the intensity of the IR bands from 3730 to 3570  $\text{cm}^{-1}$  is observed for both NZ and NZ-Cu.  
13 Additionally, a wide band around 1629  $\text{cm}^{-1}$  is recorded in the low wavenumbers of the  
14 spectral range (see Fig. 5-A and Fig. 6-A). This band could be related to water reappearance  
15 coming in the carrier gas. In both samples, it is also observed an IR band increasing upon  
16 contact with perchloroethylene at 920  $\text{cm}^{-1}$ . This band is assigned to perchloroethylene in gas  
17 phase after sample surface saturation. Perchloroethylene interacts, in both NZ and NZ-Cu  
18 samples, with their weakly acidic OH groups formed through water adsorption on zeolites. In  
19 the case of NZ-Cu, unlike NZ samples, the interaction of perchloroethylene with OH groups  
20 of adsorbed water is much higher because of the introduction of new Lewis acid sites ( $\text{Cu}^{2+}$ ).

21 Similar behaviours to perchloroethylene interactions are observed in the case of  
22 chlorobenzene adsorption (see Fig. 5-B and Fig. 6-B). A decrease in the intensity of the IR  
23 bands from 3730 to 3570  $\text{cm}^{-1}$  is also noticed in both zeolite samples. Analogous to  
24 perchloroethylene adsorption, in the case of chlorobenzene a band at 1629  $\text{cm}^{-1}$  is also  
25 registered at lower wavenumbers (see Fig. 5-B and Fig. 6-B). This signal is also ascribed to

1 the reappearance of residual water coming in the carrier gas. In the case of NZ-Cu, in contrast  
2 to NZ samples, chlorobenzene interacts more strongly with new OH groups formed as a  
3 consequence of water adsorption over new Lewis acid sites generated by the insertion of  
4 copper. Additionally, the stretching vibrations of the aromatic ring of chlorobenzene molecule  
5 in the gas phase at 1589 and 1500  $\text{cm}^{-1}$  (spectrum not shown here) [47,48] are recorded,  
6 indicating that both zeolite samples reach saturation by chlorobenzene.

### 7 8 *3.3. Temperature-programmed desorption (TPD) of the adsorbed $\text{VOC}_{\text{Cl}}$ onto zeolite samples*

9 Fig. 7 displays the TPD profiles of the target  $\text{VOC}_{\text{Cl}}$ s previously adsorbed on natural  
10 zeolite (NZ) and Cu-modified zeolite (NZ-Cu). Fig 7-A and Fig 7-B correspond to TPD  
11 profiles of perchloroethylene and chlorobenzene, respectively. In the case of  
12 perchloroethylene desorption from both zeolite samples, two overlapping peaks are observed.  
13 Lower temperature peaks reach a maximum around 109°C, being close to the boiling point of  
14 perchloroethylene (121°C). Such results could be related to the desorption of physisorbed  
15 perchloroethylene molecules. Second non-resolved peaks with a maximum desorption  
16 temperature around 200°C point out the presence of adsorption sites of higher strength. The  
17 evolution of perchloroethylene at 200°C from both zeolite samples could be related to  
18 perchloroethylene interaction with strong acid sites. It is well known that the required energy  
19 to release a base probe molecule from acid sites is associated to the strength of the chemical  
20 bonds (acid strength) [33]. However, different results are exhibited for chlorobenzene  
21 evolution, where TPD profiles reveal two well-defined peaks in both samples. The first peaks  
22 with a maximum at 72°C could be related to the desorption of physisorbed chlorobenzene  
23 molecules, being congruent with its boiling point (131°C). Second resolved peaks with a  
24 maximum around 300°C reflect how strongly some chlorobenzene molecules are bonded to  
25 active surface sites.



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8 **Fig. 7.** Temperature-programmed desorption profiles of adsorbed  $\text{VOC}_{\text{Cl}}$ : (A)  
9 perchloroethylene, (B) chlorobenzene. ( $\blacktriangle$ ) after adsorption onto natural zeolite at  $20^\circ\text{C}$ . ( $\blacksquare$ )  
10 after adsorption onto Cu-modified zeolite. Experimental conditions: Desorption under argon  
11 flow ( $100\text{ cm}^3\text{ min}^{-1}$ ), heating up to  $550^\circ\text{C}$  at  $3^\circ\text{C min}^{-1}$ .

**Table 4.** Comparison of perchloroethylene and chlorobenzene adsorption and desorption on natural zeolite (NZ) and Cu-modified zeolite (NZ-Cu).

$\text{VOC}_{\text{Cl}}$ s	$Q_a^a$ ( $\mu\text{mol g}^{-1}$ )		$Q_d^b$ ( $\mu\text{mol g}^{-1}$ )	
	NZ	NZ-Cu	NZ	NZ-Cu
<b>Perchloroethylene</b>	68.5	177.9	63.8	131
<b>Chlorobenzene</b>	51.8	166.5	26.8	50.3

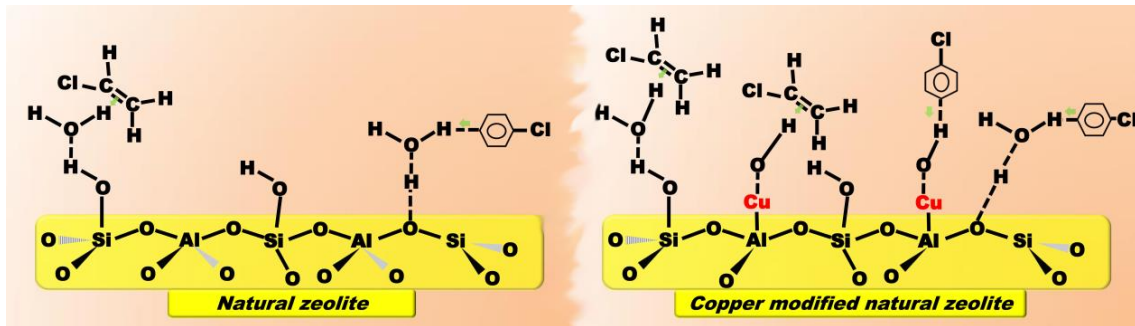
12 <sup>a</sup> Total amount of adsorbed  $\text{VOC}_{\text{Cl}}$  at  $20^\circ\text{C}$ .

1 <sup>b</sup> Total amount of desorbed  $\text{VOC}_{\text{Cl}}$  after heating the sample under Ar flow ( $100 \text{ cm}^3 \text{ min}^{-1}$ ) up  
2 to  $550 \text{ }^\circ\text{C}$  at  $3 \text{ }^\circ\text{C min}^{-1}$ .

3 In addition, the amounts of thermally desorbed perchloroethylene and chlorobenzene are  
4 lower than the adsorbed amounts (see Table 4). These results not only reflect the influence of  
5 molecular size of the target  $\text{VOC}_{\text{Cl}}$  on the adsorption capacity but also corroborate the  
6 existence of chemical surface interactions between the  $\text{VOC}_{\text{Cl}}$  and the active surface sites of  
7 zeolite samples. In particular, the highest observed adsorption capacity of NZ-Cu towards  
8 perchloroethylene could be related to a higher migration of perchloroethylene molecules  
9 through the channels of this zeolite sample, reaching more available adsorption sites in the  
10 small cages, compared to NZ zeolite. Results listed in Table 4 show that perchloroethylene  
11 and chlorobenzene are thermally desorbed from NZ-Cu at 74% and 30%, respectively;  
12 whereas from NZ they are thermally evolved at 93% and 52%, respectively. The lowest  
13 desorbed amount of chlorobenzene molecules from NZ-Cu zeolite might be a consequence of  
14 strong chemical interactions between chlorobenzene molecules and Brønsted acid sites of this  
15 zeolite framework. Such results are in agreement with those obtained by DRIFTS analyses.  
16 These results suggest that chlorobenzene and perchloroethylene are bonded to different types  
17 of OH groups of NZ-Cu surface with varying adsorption strength distributions. A higher  
18 amount of evolved perchloroethylene at mid temperature could be related to the interaction  
19 with OH groups original present on the zeolite surface; whereas upper temperature evolution  
20 of chlorobenzene could be associated to strong interactions with OH groups formed after the  
21 applied modification treatments. Therefore, TPD results evidence the different adsorption  
22 strength of the formed electron pair donor-acceptor surface complex, as described in another  
23 publication [49].

24  
25 *3.4. Mechanistic approach*

1 Perchloroethylene and chlorobenzene adsorption onto NZ and NZ-Cu could be represented  
 2 by a mechanism that incorporates the interaction not only with Brønsted (Z-OH) sites present  
 3 on the original natural zeolite framework; but also with new Brønsted acid sites, formed as a  
 4 consequence of dissociative chemisorption of water molecules over new Lewis acid sites  
 5 generated due to the insertion of copper after the successive treatments applied in this work  
 6 (see Fig. 8).



7

8 **Fig. 8.** Schematic representation of the interaction of perchloroethylene and chlorobenzene  
 9 molecules with original and new Brønsted (Z-OH) sites formed as a consequence of  
 10 dissociative chemisorption of water molecules over new Lewis acid sites.

11 Perchloroethylene and chlorobenzene molecules are able to have contact with Brønsted  
 12 acid sites (Z-OH) of NZ and NZ-Cu surfaces, forming hydrogen bonding, according to Eq.  
 13 (2):



15 The adsorption interaction of  $\text{VOC}_{\text{Cl}}$ s with active surface sites of natural and Cu-modified  
 16 zeolites is modelled using the Langmuir adsorption approach. The rate of adsorption-  
 17 desorption of  $\text{VOC}_{\text{Cl}}$  at Brønsted acid sites ( $r^{\text{Z-OH}}$ ,  $\text{m}^2 \text{m}^{-2} \text{s}^{-1}$ ) is represented by the following  
 18 expression:

$$19 r^{\text{Z-OH}} = k_{\text{ad}}^{\text{Z-OH}} S_{\text{VOC}_{\text{Cl}}} N_A \{ \text{Z-OH} \}_v C_{\text{VOC}_{\text{Cl}}} - k_{\text{des}}^{\text{Z-OH}} S_{\text{VOC}_{\text{Cl}}} N_A \{ \text{Z-OH} \cdots \text{VOC}_{\text{Cl}} \} \quad (3)$$

1 where  $k_{ad}^{Z-OH}$  ( $\text{dm}^3 \text{s}^{-1} \mu\text{mol}^{-1}$ ) and  $k_{des}^{Z-OH}$  ( $\text{s}^{-1}$ ) represent forward and reverse rate constants of  
2  $\text{VOC}_{Cl}$  surface complex formation at Brønsted acid sites, respectively.  $S_{\text{VOC}_{Cl}}$  ( $\text{m}^2$  adsorbate  
3 molecule $^{-1}$ ) is the cross-sectional area of the target  $\text{VOC}_{Cl}$  molecule, and  $N_A$  is the Avogadro  
4 constant ( $6.022 \times 10^{23}$  molecules mol of adsorbate $^{-1}$ ).  $\{Z-OH\}_v$  ( $\text{mol m}^{-2}$ ) represents the total  
5 vacant Brønsted acid sites or the total surface concentration of Brønsted acid sites.  $\{Z-$   
6  $\text{OH}\cdots\text{VOC}_{Cl}\}$  ( $\text{mol m}^{-2}$ ) is the amount of  $\text{VOC}_{Cl}$  adsorbed at Brønsted acid sites.  $C_{\text{VOC}_{Cl}}$  ( $\mu\text{mol}$   
7  $\text{dm}^{-3}$ ) is the concentration of the target  $\text{VOC}_{Cl}$ . An analogous adsorption mechanism has been  
8 suggested to represent the adsorption of VOCs onto acidic zeolites [28,50].

9 When the equilibrium is reached, the rates of adsorption and desorption are the same and  
10 the adsorption equilibrium constant is described, according to Eq. (4):

$$11 \quad K_{eq} = \frac{k_{ad}^{Z-OH}}{k_{des}^{Z-OH}} = \frac{\{Z-OH\cdots\text{VOC}_{Cl}\}}{\{Z-OH\}_v C_{\text{VOC}_{Cl}}} \quad (4)$$

12 where  $K_{eq}$  ( $\text{dm}^3 \mu\text{mol}^{-1}$ ) is the adsorption equilibrium constant of the  $\text{VOC}_{Cl}$  surface complex  
13 formation at Brønsted acid sites.

14 A site balance is used to eliminate the unknown acidic surface site concentration,  $\{Z-$   
15  $\text{OH}\}_v$ . Thus, the total concentration of Brønsted acid sites,  $Z_t$  ( $\text{mol m}^{-2}$ ), is given by Eq. (5):

$$16 \quad Z_t = \{Z-OH\}_v + \{Z-OH\cdots\text{VOC}_{Cl}\} \quad (5)$$

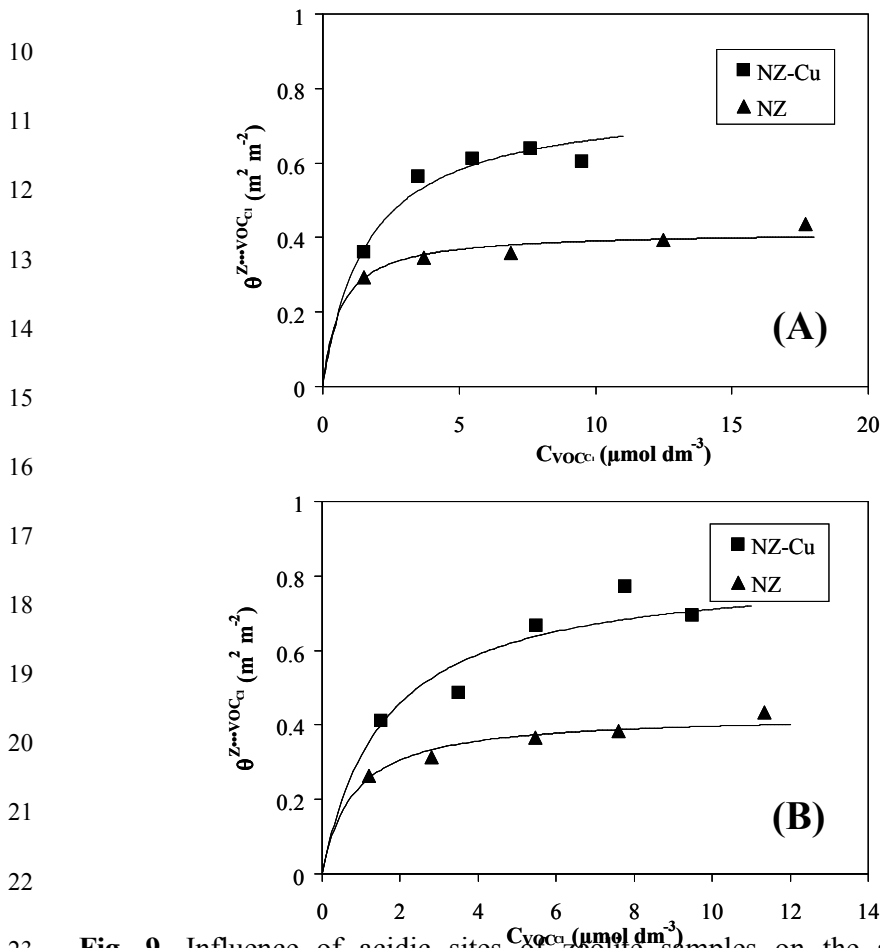
17 Replacing Eq. (5) into Eq. (3) results in Eq. (6), which is the usual form of the Langmuir  
18 equation:

$$19 \quad \theta^{Z-OH\cdots\text{VOC}_{Cl}} = \frac{K_{eq} C_{\text{VOC}_{Cl}} Z_t S_{\text{VOC}_{Cl}} N_A}{1 + K_{eq} C_{\text{VOC}_{Cl}}} \quad (6)$$

20 where  $\theta^{Z-OH\cdots\text{VOC}_{Cl}}$  ( $\text{m}^2 \text{m}^{-2}$ ) stands for the fraction of the covered OH groups of both zeolite  
21 samples (NZ or NZ-Cu) with the target  $\text{VOC}_{Cl}$  molecule (perchloroethylene or  
22 chlorobenzene) at equilibrium,  $Z_t$  ( $\text{mol m}^{-2}$ ) is the maximum adsorption capacity toward the  
23 target  $\text{VOC}_{Cl}$ , corresponding to monolayer coverage (NZ or NZ-Cu) or zeolite saturation,

1  $C_{\text{VOC}_{\text{Cl}}} (\mu\text{mol dm}^{-3})$  is the concentration of the target  $\text{VOC}_{\text{Cl}}$  (perchloroethylene or  
 2 chlorobenzene) at the equilibrium,  $S_{\text{VOC}_{\text{Cl}}} (\text{m}^2 \text{ adsorbate molecule}^{-1})$  is the cross-sectional area  
 3 of the target  $\text{VOC}_{\text{Cl}}$  molecule, and  $N_{\text{A}}$  is the Avogadro constant ( $6.022 \times 10^{23}$  molecules mol  
 4 of adsorbate $^{-1}$ ).

5 Fig. 9-A and Fig 9-B display adsorption equilibrium data obtained at 20 °C of  
 6 perchloroethylene and chlorobenzene onto zeolite samples (NZ and NZ-Cu), respectively.  
 7 Table 5 lists the equilibrium parameters of the Langmuir model, such as: the maximum  
 8 adsorption capacity,  $Z_{\text{t}}$ , and the adsorption equilibrium constant,  $K_{\text{eq}}$ , together with the  
 9 correlation factor  $R^2$ . Adsorption data are well-adjusted to the Langmuir model.



23 **Fig. 9.** Influence of acidic sites of zeolite samples on the adsorption of  $\text{VOC}_{\text{Cl}}$ : (A)  
 24 perchloroethylene, (B) chlorobenzene. ( $\blacktriangle$ ) natural zeolite, NZ; ( $\blacksquare$ ) Cu-modified zeolite, NZ-



1 Cu. Thin lines represent the fits to the Langmuir adsorption model. Experimental conditions:  
 2 0.3 g of zeolite, 50 cm<sup>3</sup> min<sup>-1</sup>, 101 kPa, 20°C.

3

**Table 5.**

Comparison of Langmuir adsorption equilibrium constants of perchloroethylene and chlorobenzene onto natural (NZ) and Cu-modified zeolite (NZ-Cu) at 20°C.

Sample	VOC <sub>Cl</sub>	Z <sub>t</sub> (μmol g <sup>-1</sup> )	Z <sub>t</sub> (m <sup>2</sup> m <sup>-2</sup> )	K <sub>eq</sub> (dm <sup>3</sup> μmol <sup>-1</sup> )	R <sup>2</sup>
NZ	Perchloroethylene	93	0.42	1.52	0.89
	Chlorobenzene	71	0.43	1.25	0.94
NZ-Cu	Perchloroethylene	222	0.77	0.61	0.96
	Chlorobenzene	179	0.82	0.63	0.87

4

5

As it can be seen in Table 5, the values of maximum adsorption capacities (Z<sub>t</sub>) of Cu-modified zeolite toward both target VOC<sub>Cl</sub>s are increased after the successive chemical and thermal treatments applied to the natural zeolite. These results agree with those previously reported for the adsorption of different kind of VOCs onto synthetic mordenite zeolites, natural and acid-treated natural mordenite [28,51-53]. The highest adsorption capacity obtained by NZ-Cu zeolite could be due to a combination of physical and chemical factors. As discussed before, the physicochemical transformation of NZ into NZ-Cu, produces a zeolite with a higher specific surface area, pore volume and with a similar strength of Lewis acidic sites but with stronger Brønsted acidic sites. The small cross-sectional area of perchloroethylene molecules (0.18 nm<sup>2</sup>) as compared to chlorobenzene molecules (0.24 nm<sup>2</sup>) might allow easier access for perchloroethylene molecules to acidic sites in the small pores of both zeolite samples. In the case of NZ, narrow pores impose higher spatial constraints,

reducing the adsorption capacity of this sample toward perchloroethylene and chlorobenzene molecules. Indeed, results suggest that NZ might inhibit the access of chlorobenzene molecules to acidic surface sites, leading to a reduction on the observed adsorption capacity of this zeolite sample. In the case of NZ-Cu zeolite the adsorption capacity is less affected. Chlorobenzene molecules could migrate inside this zeolite framework, having a dual-site interaction at acidic hydroxyl sites such as Si(OH)Al and silanol groups original present in natural zeolite and also at OH groups formed over Lewis acid sites like Cu<sup>+</sup> cations due to dissociative chemisorption of water in modified natural zeolite surface, forming adsorption complexes [49].

1

2

### 3 **4. Conclusions**

4 Results indicated that a succession of ion-exchange with ammonium salt, thermal out-  
5 gassing at 350°C, and ion-exchange using Cu<sup>2+</sup> salt (0.05 mol dm<sup>-3</sup>) followed by calcination  
6 and reduction under hydrogen at 350°C produced a Cu-modified zeolite with increased  
7 adsorption capacity for the elimination of VOC<sub>Cl</sub> compared to the natural zeolite. DRIFTS  
8 assays revealed that the modified zeolite contains mainly a single class of active site for the  
9 adsorption of VOC<sub>Cl</sub>. DRIFTS spectra indicated that the modified NZ-Cu zeolite exhibits an  
10 enhanced acidic character due to the presence of Brønsted acid sites present on the original  
11 natural zeolite framework together with new Brønsted acid sites formed after the applied  
12 modification treatments. In the presence of water, water was adsorbed on new Lewis acid  
13 sites generated after copper incorporation into the zeolite structure, leading to the formation of  
14 new Brønsted acid sites through a dissociative chemisorption. Hence, Brønsted acid sites play  
15 a fundamental role in the adsorption mechanism of VOC<sub>Cl</sub>. Assessed targets VOC<sub>Cl</sub> interacted  
16 with Brønsted acid sites, forming hydrogen bonds. A combination of chemical and thermal

1 treatment results in a powerful procedure to improve the adsorption capacity of natural  
2 zeolitic materials as potential adsorbents for the removal of  $\text{VOC}_{\text{Cl}}$  from contaminated  
3 industrial streams.

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