

## Optimization of iron load in a natural zeolite for heterogeneous catalysis

Analía V. Russo<sup>1</sup>, Ana Labourt<sup>1</sup>, Paula G. Bercoff<sup>2</sup> and Silvia E. Jacobo<sup>1\*</sup>

<sup>1</sup>LAFMACEL-INTECIN, Facultad de Ingeniería, Universidad de Buenos Aires.

Av. Paseo Colón 850 (C1063ACV), Buenos Aires, Argentina

<sup>2</sup>Fa.M.A.F., Universidad Nacional de Córdoba. IFEG-Conicet. Ciudad Universitaria.  
(5000) Córdoba, Argentina

**Abstract:-** A comparative kinetic analysis between surfactant-modified and natural clinoptilolite nanoparticles for benzene removal is presented. The structure and morphology of clinoptilolite crystals with different previous treatments were determined using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The potential of iron sorption, in different metal concentrations, was evaluated by applying Langmuir and Freundlich equations. Experimental results show that Fe (II) loading is higher on clinoptilolite when the zeolite is previously treated with NH<sub>4</sub>Cl. A cationic surfactant, cetyl trimethylammonium bromide (CTAB), was used to modify the surface of the zeolite loaded with iron. Catalytic and adsorption behavior, for an aqueous benzene solution removal was studied. The inclusion of surfactants in the zeolite structure increases benzene adsorption but reduces their catalytic capacity.

**Keywords:-** zeolites, iron nanoparticles, Fenton method, catalyst, clinoptilolite surfactants.

### I. INTRODUCTION

Organic contaminants from industrial waste streams have been recognized as an issue of much importance in recent years. Adsorption is an efficient and economically feasible process for the treatment of different classes of pollutants from water and wastewater, in particular organic compounds [1] (Apreutesei et al. 2008). Natural absorbents as natural clay minerals have high cation exchange capacities due to the isomorphous substitution of cations in their crystal structure which enables these minerals to be modified by cation surfactants such as hexadecyltrimethylammonium bromide (HDTMA-Br) for environmental remediation [2] (Ghiaci et al. 2004).

Clinoptilolite is the most abundant natural zeolite and has the chemical formula (Na, K, Ca)<sub>6</sub>Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub> · 24H<sub>2</sub>O [3]. Clinoptilolite samples from different regions show different behavior in ion-exchange processes. Some researchers have investigated modification of zeolites with Fe in order to enhance the absorption of different species (Cu, Cr, Mn, As, Pb) as iron oxides enhance the surface area of the zeolite [4,5] (Chil-Sung et al. 2009, Lv et al. 2013). They also investigated the structure of Fe species within the zeolite in order to analyze its activity. Some researchers studied the introduction of zero-valent iron (ZVI) in different zeolites [6-8] in order to improve catalysis of either organic or inorganic pollutants in water and avoid dramatic iron leaching after use. Wang et al. [6] reported lower leaching (40%) in NaY zeolite with supported ZVI nanoparticles than in the unsupported material. This result was improved in our previous work [8] where we found that in clinoptilolite loaded with ZVI, neither Fe (II) nor Fe (III) were detected in the eluted solution after the Fenton reaction. The sorption of cationic surfactants from solution onto solid surfaces has been previously studied [9,10] in order to remove different contaminants from groundwater by permeable barrier technologies. The combination of pollutant adsorption and catalytic oxidation appears to be promising, especially for the treatment of water containing highly-diluted contaminants. In these experiences iron powders are completely outside of the zeolites.

In this work, we explore the effectiveness of a composite prepared with a local clinoptilolite loaded with iron in order to obtain a heterogeneous catalyst for the Fenton process. A cationic surfactant, cetyl trimethylammonium bromide (CTAB), was used to modify the surface of the iron lodged zeolite. Catalytic and adsorption behavior, for an aqueous benzene solution removal was studied.

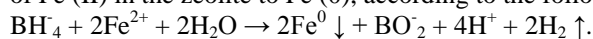
### II. EXPERIMENTAL

The tuff used in this study was clinoptilolite from Diatec SRL, La Rioja, Argentina. Samples were sieved with a Zonytest mesh N°35 and N°50, sizes 0.5 and 0.3 mm, respectively and three different treatments were performed:

a) Washed in deionized water (sample NZ),

- b) Treated in HCl 3 M (sample NZ-H) and  
 c) Treated in NH<sub>4</sub>Cl 3 M at 353 K during 8 h (sample NZ-A).

In a second stage, samples NZ, NZ-H and NZ-A were batch-loaded with iron, and they were named NZ-Fe(II), NZ-H-Fe(II) and NZ-A-Fe(II), respectively. Prior to each treatment and for characterization, the samples were dried in a furnace at 423 K for 12 h in air. Part of the samples with iron load were washed several times with deionized water and stirred with sodium borohydride for 30 min to fully reduce the adsorbed amount of Fe (II) in the zeolite to Fe (0), according to the following reaction:



The obtained reduced samples were named NZ-Fe, NZ-A-Fe and NZ-H-Fe, referring to the natural zeolite without pretreatment, the zeolite pretreated in NH<sub>4</sub>Cl and the zeolite pretreated in HCl, respectively.

The iron salts used for the zeolite modification were purchased from Anedra (FeSO<sub>4</sub>·7H<sub>2</sub>O). The following chemicals HCl, NH<sub>4</sub>OH, NaCH<sub>3</sub>COO and NH<sub>4</sub>CH<sub>3</sub>COO were reagent grade from Baker. All solutions were prepared using deionized water (Milli-Q, Millipore). Potassium borohydride (KBH<sub>4</sub>) was purchased from Sigma (USA). Pure benzene from Schuchardt was used to prepare an 11.25 mM stock solution. H<sub>2</sub>O<sub>2</sub> (30 wt%) was also obtained from Olivery Labs. A cationic surfactant CTAB with greater than 98% purity from Merck was used.

The crystallinity of the zeolite samples was studied using X-ray diffraction (XRD) with a Siemens XRD instrument, using filtered Cu K $\alpha$  radiation with accelerating voltage of 40 kV, current of 30mA and a scanning from 5° to 55° in 2 $\theta$ . The maximum experimental exchange capacity (CEC) of natural clinoptilolite NZ and the external cation capacity (EEC) were measured under static conditions with ammonium acetate and cetyl trimethylammonium bromide (CTAB), respectively [11]. The texture, morphology and composition of the prepared samples were observed using Scanning Electron Microscopy (SEM) and elemental analysis with Energy Dispersive Spectroscopy (EDS) in a Sigma Zeiss microscope with an Oxford EDS detector. In all the studied samples, iron was released from the zeolite structure with 30% phosphoric acid [12]. The quantitative determination of benzene in aqueous solution was performed in a Shimadzu Spectrometer UV-visible, through a spectrophotometer technique which consists on the benzene extraction from an aqueous solution with n-hexane.

The equilibrium adsorption isotherms (NZ-Fe(II), NZ-H-Fe(II) and NZ-A-Fe(II)) were measured at room temperature (15° ± 2 °C). They were obtained by preparing suspensions of different zeolites samples (NZ, NZ-H and NZ-A) in the following way: 10 g of zeolite were put in a vessel containing 100 cm<sup>3</sup> of metal solutions at different initial metal concentrations from 0.01M to 0.1M at pH= 4.0. Iron oxidation was prevented by using a nitrogen gas flow during the preparation of each experiment. Experiments were carried out in duplicate. According to adsorption kinetics (previous work, not shown), a mixing time of 24 h on a horizontal shaker was enough to reach the adsorption equilibrium. After the equilibration step, the concentration of the freely Fe (II) was determined by redox titration. Previous kinetic runs were performed in order to determine the adsorption rate of Fe (II) ions from aqueous solution for clinoptilolite at 15°C.

Langmuir's and Freundlich's models were applied to describe the adsorption equilibrium of the zeolites. The Langmuir equation is

$$q_{\text{eq}} = K_L S_{\text{max}} C_{\text{eq}} / (1 + K_L C_{\text{eq}}), \quad (1)$$

where  $C_{\text{eq}}$  (meq/L) and  $q_{\text{eq}}$  (meq/g) are the equilibrium Fe(II) concentration in the aqueous phase and in the solid phase, respectively. The Langmuir parameter  $S_{\text{max}}$  (meq/g) represents the maximum adsorption capacity and  $K_L$  (L/meq) is the site energy factor.

The Freundlich model is defined by the following relation

$$q_{\text{eq}} = K_F C_{\text{eq}}^N, \quad (2)$$

where  $K_F$  (meq/g)/(meq/L)<sup>N</sup> and N (dimensionless) are the Freundlich parameters.

Batch kinetic experiments were performed at room temperature (15° ± 2 °C) by preparing suspensions of different zeolites samples :

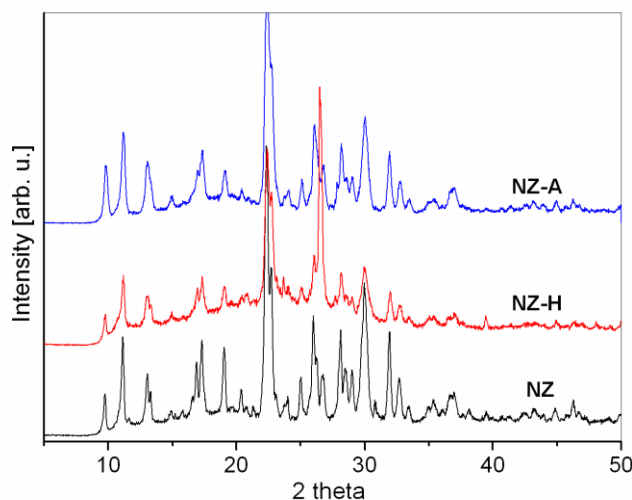
- i) Catalytic experiments for benzene degradation using zeolites without surfactant: natural zeolite (NZe), NZ-Fe, NZ-H-Fe and NZ-A-Fe and
- ii) Catalytic experiments for benzene degradation using the zeolite with surfactant: sample NZ-A-Fe imbibed in CTAB and labeled NZ-A-Fe/CTAB.

All batch experiences were performed by putting 20 g of zeolite in a vessel containing 200 cm<sup>3</sup> of an aqueous benzene solution 11.2 mM at pH= 4.0. The suspensions were stirred for ca. 10 min for obtaining a uniform mixture prior to the addition of 5 cm<sup>3</sup> of 30% hydrogen peroxide. At given time intervals, 5-mL samples of the aqueous solutions were filtered through a Millipore filter (pore size 0.45 $\mu$ m) to remove the particles. The filtrates were analyzed for benzene and for Fe.

### III. RESULTS

Figure 1 shows the diffractograms corresponding to natural clinoptilolite (NZ) and the pretreated zeolites (NZ-A and NZ-H). The diffractogram of NZ can be fitted with the corresponding to clinoptilolite (Ref. code 01-083-1260), which crystallizes in the monoclinic system, space group C2/m, where the structural parameters  $a$ ,  $b$  and  $c$  as well as the angle  $\beta$  between axes  $a$  and  $c$ , are obtained after refining the corresponding diffractograms. Table 1 shows the cell parameters after the refinements.

Crystallinity was estimated considering the eight most intense peaks in the diffractograms of the analyzed samples, corresponding to values of interplanar spacings  $d$  (Å)= 9.00; 7.94; 6.77; 5.24; 3.96; 3.90; 3.42 (Table 1). It is noticeable that basic hydrothermal treatment (NH<sub>4</sub>Cl, sample NZ-A) slightly increases the zeolite crystallinity. Crystallite size is also modified by the zeolite treatment.



**Figure 1. Diffractograms corresponding to NZ (natural zeolite), NZ-H (NZ treated with HCl) and NZ-A (NZ treated with NH<sub>4</sub>Cl).**

The chemical treatment releases a fraction of metallic cations (Na, Mg, Ca and K), shrinking the zeolite structure. The average elemental composition of clinoptilolite was found using EDS and is given in Table 2. As the Table shows, clinoptilolite is mainly composed of O, Si and Al, in addition to small amounts of Na, K, Mg and Ca. This type of clinoptilolite also contains a small amount of iron. The element Si is partially replaced by Al in zeolites, so a negative charge is introduced in the zeolite structure.

**Table 1: Cell parameters ( $a$ ,  $b$ ,  $c$ ,  $\beta$ ), crystallite size ( $D$  [nm]) and % calculated crystallinity.**

	$a$ [Å]	$b$ [Å]	$c$ [Å]	$\beta$	$D$ [nm]	Crystallinity (%)
<b>NZ</b>	17.6973	17.9639	7.3954	116.3542	27	82
<b>NZ-H</b>	17.5653	17.8110	7.3070	116.3782	18	69
<b>NZ-A</b>	17.6577	17.9099	7.3763	116.2982	24	86

If the ratio of Si/Al in the analyzed mineral is compared to that in a pure clinoptilolite which has the formula [(Na, K, Ca)<sub>6</sub>Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub> · 24H<sub>2</sub>O], a value of 4.6 is obtained. The chemical composition and the Si/Al ratio generally ranging from 4 to 5.5 are typical for clinoptilolite [13].

No variations in Si and Al resulting from the hydrothermal treatment were observed in samples NZ and NZ-A, as expected. The treatment with hydrochloric acid at a relatively mild temperature has shown that the extraction of most of the ions and aluminum from the framework was not selective and the crystalline losses were higher than 30% (Table 1) with a raise in the Si/Al ratio (Table 2).

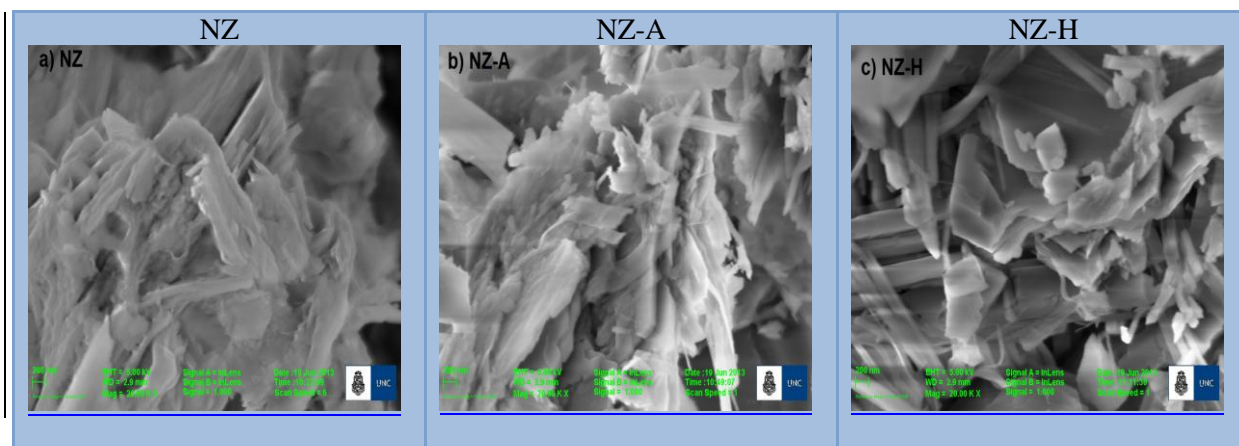
The morphology and size of clinoptilolite crystals, with different previous treatments, was determined using SEM. SEM images show that clinoptilolite (NZ) is composed of crystals with a well-defined shape, and particle sizes of several micrometers. A typical SEM image is shown in Fig. 2 for each of the studied samples, before loading with Fe.

**Table 2: Chemical composition (at%) of the natural clinoptilolite NZ and its modified forms loaded with Fe(II) solution 0.10 M, measured by EDS.**

Element	NZ	NZ-Fe(II)	NZ-A	NZ-A-Fe(II)	NZ-H	NZ-H-Fe(II)
<b>O</b>	61.41	62.02	65.12.	62.96	62.71	66.54
<b>Na</b>	3.22	2.76	0.22	1.10	0.22	0.29
<b>Mg</b>	0.52	0.65	0.35	0.51	0.0	0.0
<b>Al</b>	5.99	5.88	5.83	6.14	3.20	2.81
<b>Si</b>	27.31	26.96	27.31	27.92	33.25	29.89
<b>K</b>	0.63	0.63	0.37	0.37	0.34	0.30
<b>Ca</b>	0.61	0.53	0	0.0	0.09	0.09
<b>Fe</b>	<b>0.31</b>	<b>0.57</b>	<b>0.53</b>	<b>0.91</b>	<b>0.11</b>	<b>0.17</b>
<b>Total</b>	100.00	100.00	100.00	100.00	100.00	100.00
<b>Si/Al</b>	4.6	4.6	4.7	4.5	10.4	10.6

In all the samples, the same morphology is observed. NZ contains a low iron proportion in its structure (0.31 at %). The state of iron in natural zeolite is an important feature for the practical applications of these materials. It has been determined that iron is located as high-spin Fe (III) in the tetrahedral sites of the framework, in extraframework octahedral sites as free  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ , and as high-spin Fe(II) in octahedral coordination in extraframework sites or in another aluminosilicate associated with the zeolite [14]. Sample NZ has iron ions in two different sites (A and B). The main absorption in all the samples corresponds to Fe (III) (site A) in an octahedral site of the clinoptilolite framework while the remaining 5.5% Fe is located as Fe (II) in an extraframework octahedral site, probably as a solvated ion, within the clinoptilolite structure [8].

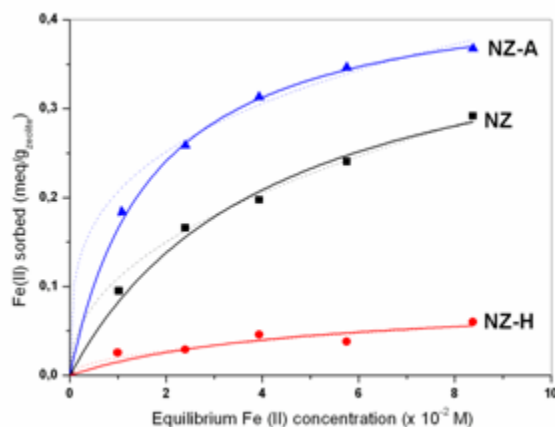
The cation exchange capacity of NZ was calculated using the data in reference [15]. According to the chemical analysis (Table 2), the total (or theoretical) exchange capacity of our material (NZ) is  $2.56 \pm 0.06$  meq/g, calculated as the sum of Mg, Ca, K and Na cations.


**Figure 2. SEM images of the studied zeolites, before loading with Fe: NZ, NZ-A and NZ-H. The bar corresponds to 200 nm.**

The maximum experimental exchange capacity (CEC) in solid phase is  $1.82 \pm 0.06$  meq/g, by conversion of the material in near homoionic Na form, a method described in detail by Inglezakis et al., (2001), while the external cation capacity (EEC) is  $0.45 \pm 0.03$  meq/g.

The iron adsorption isotherms for Fe(II) sorbed  $q_{eq}$  (meq/g) as a function of the equilibrium molar Fe(II) concentration  $C_{eq}$  are presented in Figure 3.

These results show that sample NZ-A has a higher affinity for Fe(II) adsorption than the natural material (NZ). The adsorbed amounts for the maximum explored initial concentration for Fe (II) are 0.37 meq/g in zeolite NZ-A and 0.29 meq/g in zeolite NZ. This is in agreement with EDS results (Table 2).



**Figure 3.** Adsorption isotherms of Fe(II) for the studied clinoptilolite samples. The solid and dashed lines are the Langmuir and Freundlich fits, respectively, for the observed data.

Adsorption isotherms were fitted using both Langmuir and Freundlich models for the three studied samples, in order to determine which model gives a better fit to the experimental data. Linearizing equation (1) for the Fe adsorption isotherms in the Langmuir model results in the following expression:

$$C_{eq}/q_{eq} = C_{eq}/S_{max} + 1/K_L S_{max} \quad (3)$$

This model is represented with solid lines in Figure 3.

The corresponding linear form of the Freundlich model (equation (2)) used to fit Fe sorption data is

$$\log q_{eq} = \log K_F + N \log C_{eq} \quad (4)$$

and is depicted in Figure 3 with dashed lines.

The Langmuir model effectively describes the adsorption data with regression coefficients  $R^2 > 0.95$  for the fits (Table 3).

Adsorption values of Fe(II) on the zeolites,  $K_L$  (L/meq) (Table 3) are in agreement with the proposed sequence for adsorption ability. Our experimental results agree with the reported values for the adsorption of Fe(III) by a natural zeolite [16].

The linear equations and the calculated Freundlich parameters for the three samples are presented in Table 4. In this model,  $K_F$  is the parameter related to the temperature and  $N$  is a characteristic constant for the studied adsorption systems.

**Table 3.** Characteristic parameters obtained from the experimental data according to the Langmuir equation (equation (3)).

material	$S_{max}$ (meq/g)	b (L/meq)	$R^2$
NZ	0.4276	0.430	<b>0.9920</b>
NZ-A	0.4448	0.607	<b>0.9996</b>
NZ-H	<b>0.0874</b>	<b>0.201</b>	<b>0.9249</b>

The value of  $1/N$  between 2 and 10 shows good adsorption [17]. The calculated  $N$  values (Table 4) for all the studied samples indicate that the distribution of bonding energies depends on the adsorption density [18]. This type of isotherm indicates that at lower concentrations the surface has a low affinity, which increases at higher concentrations. The Freundlich model predicts an infinite surface coverage of the sorbent by the sorbate, indicating the formation of multilayers on the surface.

**Table 4** Freundlich's adsorption equations and constants for Fe(II) adsorption.

Sample	Equation	$R^2$	$K_F$ (meq/g)/(meq/L) <sup>N</sup>	N
NZ	$y=0.4530x-0.9608$	0.9857	9.120	<b>0.45</b>
NZ-A	$y=0.2827x-0.6845$	0.9501	4.830	<b>0.28</b>
NZ-H	$y=0.4883x-1.704$	<b>0.8927</b>	<b>50.58</b>	<b>0.49</b>

Although the equilibrium data can be well fitted with both types of isotherms (Langmuir and Freundlich), Langmuir model has better regression coefficients ( $R^2$ ), as shown in Tables 3 and 4. Experimental results show that Fe(II) loading is higher on clinoptilolite when it is previously treated with  $NH_4Cl$  (NZ-A).

The performance as absorbents and the catalytic behavior of zeolites NZ, NZ-Fe, NZ-A-Fe and NZ-H-Fe was studied for 24 hrs. Table 5 shows the amount of removed benzene in mg per gram of zeolite for these experiments. In these experimental conditions, benzene absorption in the natural clinoptilolite (NZ) was around 3.2 mg Bz/ gNZ.

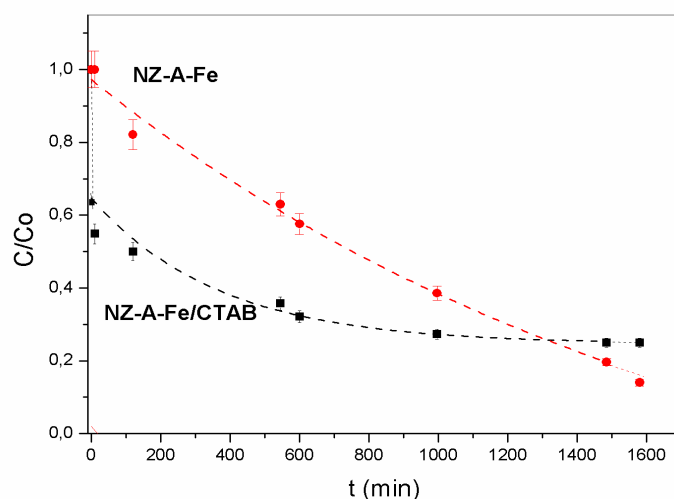
The pre-treatment with acid dramatically modifies the zeolite structure (NZ-H-Fe) and the catalytic behavior is not interesting when compared with the natural zeolite (NZ-Fe).

Experimental results show that not only Fe (II) loading is higher on clinoptilolite when it is previously treated with NH<sub>4</sub>Cl (NZ-A), but the best catalytic performance was observed (11.0 mg Bz removed /g zeolite).

**Table 5 Removed benzene (Bz) capacity after 24 hrs of natural zeolite (NZ) and of different treated zeolites after iron lodging.**

	NZ	NZ-Fe	NZ-H-Fe	NZ-A-Fe
mg Bz removed /g zeolite	3.2	8.8	4.0	11.0

The experiments with zeolites with surfactant were performed to explore the influence of the surfactant on the catalytic properties of the loaded iron zeolites. For these experiments, samples NZ-A-Fe and NZ-A-Fe/CTAB were selected. NZ-A-Fe was chosen as it shows the best catalytic properties (Table 5). Figure 6 shows two different profiles. In both samples, benzene removal is observed. In sample NZ-A-Fe, benzene removal is constant with time and it is complete after 2000 min. Although there is absorption in the zeolite (see Table 5 for NZ) the main benzene mechanism removal in this case stands by degradation through the Fenton method, where the iron loaded in the treated zeolite (NZ-A-Fe) behaves as a catalyst. The addition of CTAB (sample NZ-A-Fe/CTAB) increases the absorption mechanism of benzene (Fig.6) up to 600 min, when benzene concentration reaches a plateau ( $C/C_0 = 0.27$ ), probably because the catalytic behavior is suppressed. Leaching tests (iron release) indicate that for sample NZ-A-Fe(II), an increase of aqueous iron concentration (near 2.5 %) was observed within 1600 min, which corresponds to 12-15 ppm. After an extended period (8 days), iron concentration rose up to 60 ppm. For the reduced sample (NZ-A-Fe) a much lower iron concentration was detected in the solution after the same time (< 1 ppm).



**Figure 6. Benzene removal for NZ-A-Fe and for NZ-A-Fe/CTAB.**

#### IV. CONCLUSIONS

Preliminary treatment of clinoptilolite with ammonium chloride or with acid chloride modifies the zeolite crystallinity and its absorption properties for Fe(II). The Langmuir and the Freundlich equations were used to correctly describe the absorption isotherms of each system. Experimental results show that not only Fe(II) loading is higher on clinoptilolite when it is previously treated with NH<sub>4</sub>Cl (NZ-A), but the best catalytic performance was observed (11.0 mg Bz removed /g zeolite). Although the inclusion of surfactants in the zeolite structure increases benzene adsorption, the catalytic behavior in modified zeolites (NZ-A-Fe/CTAB) is reduced. These results support the statement that NZ-A-Fe is a convenient system for Fenton catalysis.



### ACKNOWLEDGEMENTS

The authors thank Gustavo Panizza from DIATEC S.R.L. for zeolite provision and LAMARX for giving access to the SEM facilities. This work was partially funded by UBACyT (2014-2017), Secyt-UNC and Conicet.

### REFERENCES

- [1]. Apreutesei R.E., Catrinescu C., Teodosiu C., Surfactant-Modified Natural zeolites for environmental Applications in water purification, *Env. Eng. and Management Journal*, vol 7, No2 (2008) 149-161.
- [2]. Ghiaci M., Abbaspur A., Kia R., Seyedejn-Azad F., Equilibrium isotherm studies for the sorption of benzene, toluene, and phenol onto organo-zeolites and as-synthesized MCM-41, *Separation and Purification Technology* 40 (2004) 217–229.
- [3]. Erdem E., Karapinar N., Donat R.. The removal of heavy metal cations by natural zeolites, *Journal Colloid and Interface Science* 280 (2004) 309-314.
- [4]. Chil-Sung Jeon, Baek K., Park J., Oh Y, Lee S.. Adsorption characteristics of As (V) on iron-coated zeolite. *Journal of Hazardous Materials* 163 (2009) 804-808.
- [5]. Lv G., Li Z., Jiang W., Ackley C., Fenske N., Demarco N.. Removal of Cr(VI) from water using Fe(II)-modified natural zeolite, *Chem. Engineering Research and Design* (2013). DOI: 10.1016/j.cherd.2013.08.003.
- [6]. Wang W., Zhou M., Mao Q., Yue J., Wang X., Novel NaY zeolite-supported nanoscale zero-valent iron as an efficient heterogeneous Fenton catalyst. *Catalysis Communications* 11 (2010) 937-941
- [7]. Shi L., Zhang X., Chen Z.. Removal of chromium (VI) from wastewater using bentonite-supported nanoscale zero-valent iron. *Water Research* 45 (2011) 886-892.
- [8]. Russo A. V., Toriggia L.F., Jacobo S. E.. Natural clinoptilolite zeolite loaded with iron for aromatic hydrocarbons removal from aqueous solutions. *Journal of Materials Science*, Vol. 49(2) (2014) 614-620.
- [9]. Burt T. A., Li Z., Bowman R. S.. Evaluation of granular surfactant-modified/zeolite zerovalent iron pellets as a reactive material for perchloroethylene reduction. *Journal of Environmental Engineering*, 131 (6) (2005) 934-942
- [10]. Tao X., Zhang P., Bowman R. S.. Enhanced perchloroethylene (PCE) reduction using surfactant-modified zeolite/zero-valent iron pellets; *Proceedings of the 2003 International Symposium on Water Resources and the Urban Environment* (2003) 287-291
- [11]. . Bowman R. S., Li Z., Roy S. J., Burt T. A. . Johnson T.L., Johnson R.L, Pilot test of a surfactant modified zeolite permeable barrier for groundwater remediation, In: Burns, . Smith. J.A.(Eds), *Physical and Chemical remediation of Contaminated Aquifers*, Kluwer Academic Publishers, New York, 2001. pp 161-185
- [12]. Skoog D. A., Holler F. J., *Fundamentos de Química Analítica. 4º Edición, Tomo II*, Ed. Reverté S.A. Barcelona, España (1997).
- [13]. Tsitsishvili G.V., Andronikashvili T. G., Kirov G. M., L. Filizova. *Natural Zeolites*, Ellis Horwood Limited, 1992, pp 156.
- [14]. Giannetto G. Pace, A. Montes Rendón, G. Rodríguez Fuentes. *Zeolitas: Caracterización, propiedades y aplicaciones industriales*. Ed. Innov Tecnológica UCV, Venezuela (2000) pp 331.
- [15]. Inglezakis V. J., Hadjiandreou K. J., Loizidou M. D., Grigoropoulou H. P.. Pretreatment of natural clinoptilolite in a laboratory-scale ion exchange packed bed. *Water Research* 35 (9), (2001) 2161-2166.
- [16]. Al-Anber M., Al-Anber Z.. Utilization of natural zeolite as ion-exchange and sorbent material in the removal of iron. *Desalination* 225 (1–3,1) (2008) 70-81
- [17]. Doula M.. Simultaneous removal of Cu, Mn and Zn from drinking water with the use of clinoptilolite and its Fe-modified form, *Water Research* 43 (2009) 3695-3672.
- [18]. Sheta A. S., Falath A.M., Al-Sewailem M. S., Khaled E. M., Sallam A. S.. Sorption characteristics of zinc and iron by natural zeolite and bentonite. *Microporous Materials* 61, (2003)127-136.