

MAGNETIC PROPERTIES OF AN ADSORBENT BASED ON MODIFIED NATURAL ZEOLITE

Vasile PODE^a, Eveline POPOVICI^b, Rodica PODE^{a*} and Violeta GEORGESCU^c

^a Faculty of Industrial Chemistry and Environmental Engineering, “Politehnica” University of Timisoara, P-ta Victoriei, No.2, 300006, Timisoara, Roumania

^b Faculty of Chemistry, “Al. I. Cuza” University of Iasi, Blvd. Carol I, No.11, 700506 Iasi, Roumania

^c Faculty of Physics, “Al. I. Cuza” University of Iasi, Blvd. Carol I, No.11, 700506 Iasi, Roumania

Received December 8, 2006

The objectives of this paper refer to the magnetic and structural characterization of an adsorbent with magnetic properties based on natural zeolite. The magnetic properties were induced by precipitating magnetite followed by adsorption on zeolite particles (with mean diameters less than 63 μm). The magnetic characteristics of the samples prepared in various conditions were measured by an induction method (50 Hz magnetic field) at room temperature by using a Howling-type device with the aim to determine the optimum of magnetic behaviour. The device was provided with a computerized acquisition data system. The results showed the major influence of ammonia excess and ammonia addition time on magnetic properties of the modified natural zeolite. The results of analyses carried out by XRD demonstrated the presence of magnetite in the samples of modified zeolite. Data obtained by XRD were consistent with the magnetic measurements.

INTRODUCTION

The increase of soil pollution led to new materials and technologies for pollution abatement. Soil pollution by heavy metals put the blame on extraction and processing of non-ferrous ores, aluminium, chemical fertilisers and cement, and also to coal-fired power stations. An alternative to abate pollution of soil by heavy metal ions is the use of natural zeolites.

Zeolites belong to the natural aluminosilicates family and they are characterised by rigid cage-like structures and by the presence of internal cavities and channels which can be occupied by molecules such as water with no change of crystal dimensions. The negative charge excess within the zeolitic network is compensated by cations, which have great mobility in the zeolite open-channels and are available for the ion exchange with other cations. Based on adsorption and ion exchange properties, zeolites were used in water treatment for drinking purpose and advanced wastewater

treatment.¹⁻⁵ Ion exchange properties also recommend zeolites for abating pollution of soil by heavy metal. However, the use of zeolites for sticky textures face problems related to zeolite-polluted environment phase separation after pollution abatement treatment. These problems determined initiation of research with the aim of synthesising new materials based on magnetite supported zeolites, which have besides adsorption capacity also magnetic properties that ease phase separation.⁶⁻⁸

Studies carried out on quite high granulated zeolite samples have shown that magnetization occurred only at the surface of particles.⁶ Without knowing of magnetization depth, to determine the optimal conditions, it was required to synthesise homogeneous samples of ferromagnetic zeolite starting with very fine ground natural zeolite.

The present paper aimed at establishing a relationship between synthesis conditions and magnetic characteristics of the adsorbent based on magnetite supported zeolite. In addition, a

* Corresponding author: rodicapode@yahoo.com

structural characterization of synthesised adsorbent was made.

RESULTS AND DISCUSSION

Magnetic characterization

The working conditions for adsorbent synthesis are shown in Table 1, for representative samples.

Magnetic measurements were carried out with the aim of checking the efficiency of synthesis and found out correlations between synthesis conditions and magnetic characteristics of the adsorbent.

The magnetization processes of the samples were investigated by recording both total

magnetization (M) and differential susceptibility ($\chi = dM/dH$) plots. As an example, the recorded plots for the sample #1 are shown as follows: the unfolded magnetization curve (Figure 1) and the corresponding differential susceptibility curve (Figure 2) as functions of time. These plots were analysed by eliminating time between the two channels in each figure. The resulting curves for the sample #1 are the following: the hysteresis cycle (shown in Figure 3.a) and the differential susceptibility curve (Figure 3.b). The unit of grid lines on X-axis in these figures was equivalent to 11.462 kA/m. The scale on Y-axis was identical for all samples to ensure the comparison of the magnetic characteristics.

Table 1

Parameters of synthesizing zeolite adsorbent samples

Sample #	Fe ₃ O ₄ : zeolite mass ratio	Concentration of ferrous-ferric solutions (% wt.)	NH ₃ Excess (% wt.)	Duration of NH ₃ addition (hours)
1	1:5	3	100	2
2	1:5	5	100	2
3	1:7	5	100	2
4	1:5	5	50	2
5	1:5	5	100	1

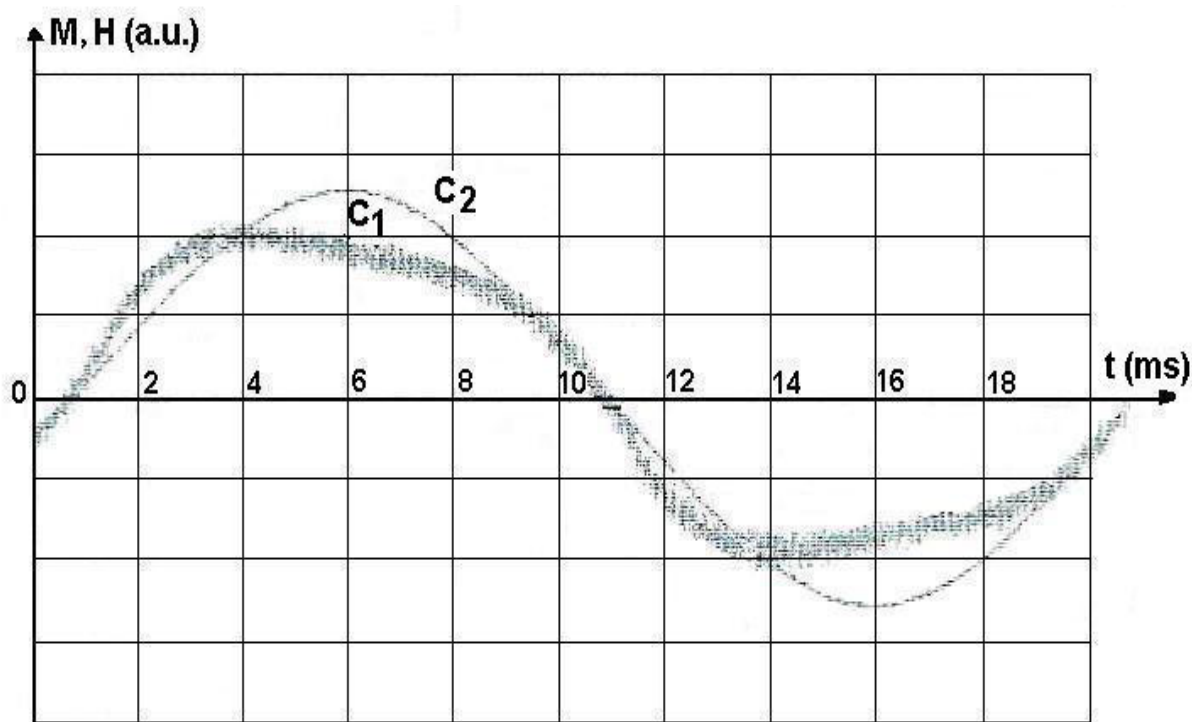


Fig. 1 – Oscilloscopic plots for total magnetization (C1) and applied magnetic field (C2) as functions of time for the sample #1. C1 - the output voltage of Y1-channel (proportional to the total magnetization M of the sample #1), C2 - the output voltage on Y2-channel (proportional to the applied field H) as a function of the time (t).

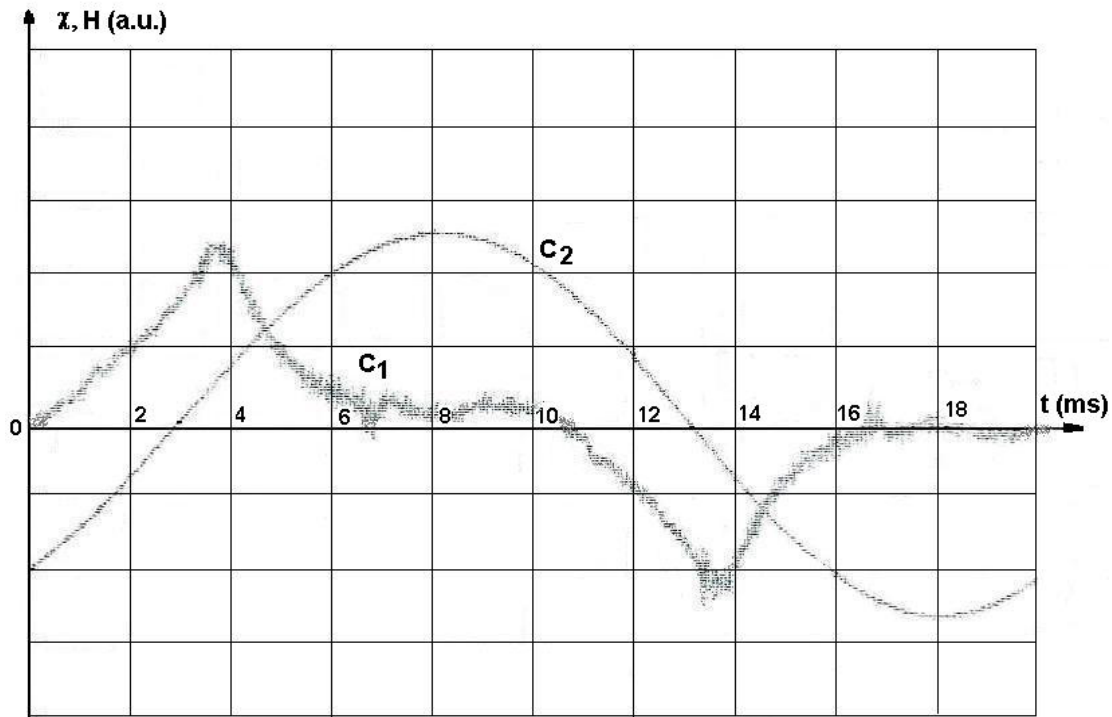


Fig. 2 – Oscilloscopic plots for differential susceptibility (C1) and applied magnetic field (C2) as functions of time, in the case of sample #1. C1 - the output voltage of Y1-channel, C2 - the output voltage on Y2-channel (i.e., applied field H vs. t).

The experiments carried out on our samples showed that total magnetic moment (total magnetization) and differential susceptibility plots (or magnetic hysteresis curves) had the same basic shape for all samples. The small differences between the shape of magnetization cycle in figures 3a and 4a could be attributed in our case principally to the anisotropy of the samples. This anisotropy could be explained by a various distribution of zeolite particles in the pellets (20 mm in diameter) used for magnetic measurements (see the experimental section). Therefore, we can suppose that the magnetization processes could be considered similar in all samples, taking into account that in our case magnetic measurements indicate a statistical mean result for each sample. It is possible that super-paramagnetic behaviour could be present in some nanoparticles in our samples. However, now, we are not able to correlate the dimension of magnetic particles included in zeolite channels or on the zeolite particle surface with magnetic measurements results obtained by this method. Therefore, the magnetic processes were identical in all samples. The samples behaved as a relatively soft magnetic material with a coercive field of about $5 \text{ kA}\cdot\text{m}^{-1}$ ($\sim 63 \text{ Oe}$). The initial magnetic permeability of the cycle was about 75% of the maximum permeability.

It is known that the shape of hysteresis loops depends on the main magnetization processes occurring within samples, i.e., wall displacements and magnetisation rotation. The absence of Barkhausen noise and shape of the curves in Figures 1-3 suggested that magnetisation occurred mainly by rotation processes without a considerable fraction of wall displacements. This might be due to the fact that the magnetic material adsorbed in the channels of zeolite sample could not magnetise by wall displacements.

With the aim to compare the total quantity of magnetite adsorbed in various samples, the induced signal recorded on the Y1 channel (as in Figure 1) would be labelled ΔU . This signal is proportional to both magnetization and volume of magnetic material included in each sample as specify formula (2) from experimental section. It is known that in ferromagnets, the conventional concept of magnetization density (as magnetic moment per unit volume) can be interpreted as an intrinsic or uniform volume property. The electronic states responsible for magnetism in transition metal oxides are well-defined states, little affected by their environment once their valence is established⁹, therefore, the magnetic moment per unit volume is an intrinsic property. The samples studied in this work were measured in

the same installation, with the same geometry and identical mass of samples. Therefore, one can conclude that ΔU corresponded to the quantity of magnetic material included in zeolite channels, because the magnetic moment of the unit volume of magnetic material was the same for all samples. The adsorption in the zeolite channels depended on the area of the zeolite granules, i.e., on the numbers of channels distributed on this surface. The adsorption area for a sample was considered the same for the samples studied here (most granules had a medium diameter less than 63 μm). Therefore, the differences between magnetic properties of various samples could be attributed to the influence of chemical preparation conditions on the magnetite adsorption processes.

The values of ΔU (corresponding to the quantity of magnetic material included in zeolitic channels) and of the χ (differential susceptibility in the plane of the sample) for the studied samples are shown in Table 2.

The variation of synthesis parameters results in a variation of the quantity of magnetite included in the samples, expressed in arbitrary units by ΔU . Thus, these values were used to set up the

relationship between synthesis conditions and magnetic characteristics.

Table 2

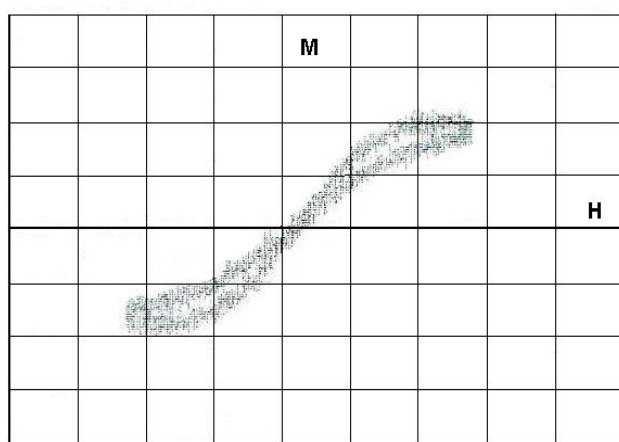
Magnetic properties of zeolite adsorbent samples

Sample #	ΔU (mV)	χ (arb. units)
1	38.43	484
2	26.00	340
3	22.40	316
4	7.60	80
5	4.00	38

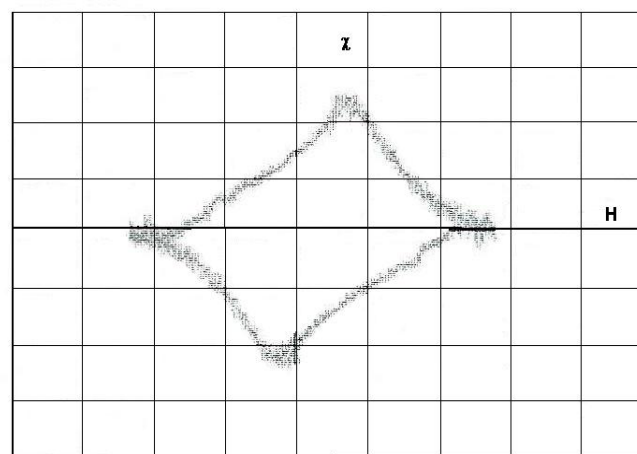
ΔU – A signal proportional to total magnetization and quantity of magnetic material included in samples;

χ - Differential magnetic susceptibility.

The influence of the initial concentration of ferrous/ferric solutions could be deduced by comparing samples 1 and 2. The total magnetisation and differential susceptibility of those samples are comparatively shown in Figures 3 and 4. When the concentration of ferrous/ferric solutions increased from 3 to 5% for samples #1 and #2, ΔU decreased by 1.5 times, pointing up the favourable initial concentration of 3%.



a



b

Fig. 3 – Magnetization cycle (a) and differential susceptibility (b) plot for the sample #1. A unit of grid on X-axis corresponds to 11.462 kA/m. The scale on Y-axis was marked in arbitrary units (identical for all samples).

For samples #2 and #3 synthesised at different magnetite/zeolite mass ratio (Table 1), ΔU corresponding to quantity of magnetite within each sample (Table 2) decreased from 26.00 (sample #2) to 22.00 (sample #3). That is the reason for recommending a magnetite/zeolite ratio higher than 1/5.

For samples #3 and #4 synthesised under conditions of 100% and 50%, respectively

ammonia excess as, ΔU decreased by 3.4 times (from 26.00 – sample #2 to 7.60 – sample #4, Table 2). High excess of ammonia might be justified by increase of temperature (90⁰ C), when synthesis occurred, thus, ammonia losses were significant.

Also, high differences of ΔU were recorded for samples #2 and #5 (Table 1), synthesised under conditions of different duration for ammonia

addition. For this situation, ΔU decreased by 6.5 times (from 26.00 – sample #2 to 4.00 – sample

#5), pointing out the importance of this parameter for the magnetization process.

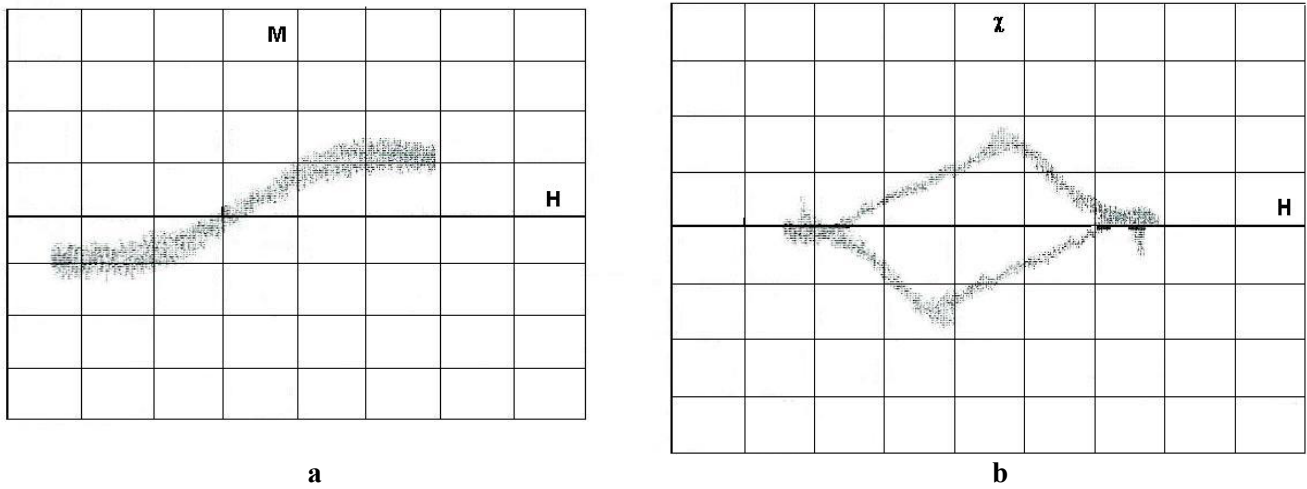


Fig. 4 – Magnetization cycle (a) and differential susceptibility (b) plot for sample #2.
A unit of grid lines on X-axis corresponds to 11.462 kA/m.

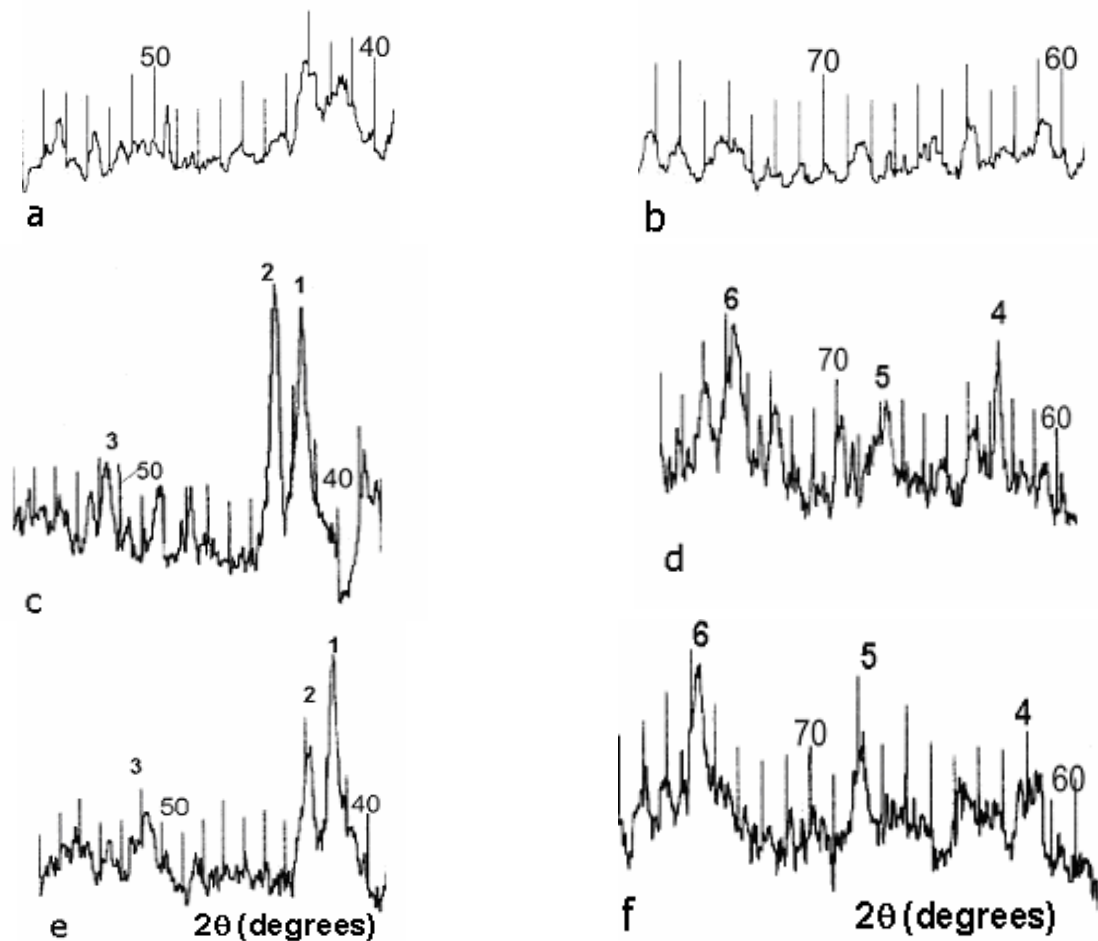


Fig. 5 – The XRD patterns Diffractograms of the samples: (a, b) zeolite substrate, (c, d) sample labelled 1 in table 1 and (e, f) sample 2, for two different angular regions (a, c, e) – for $2\theta = (39-56)$ degrees and (b, d, f) for $2\theta = (59-78)$ degrees. The magnetite structures lines were indexed as follows: 1 - (422), 2 - (333,511), 3 - (440), 4 - (620), 5 - (533), 6 - (622). The intensity (in arbitrary units) is the same for all spectra.

Structural characterization

Powder diffraction patterns for the samples were measured and compared to a reference sample (labelled sample 0) made of untreated zeolite. The result showed that angular regions $2\theta = (39-56)$ degrees and $2\theta = (59-78)$ degrees are favourable for comparison because sample 0 displayed less intense diffraction peaks in those regions.

Figure 5 shows examples of diffraction patterns recorded for sample 0 (a, b), sample 1 (c, d) and sample 2 (e, f). The presence of a magnetic phase, Fe_3O_4 (magnetite), was identified for samples 1 and 2. The diffraction patterns were indexed based on calculated interplanar spacings as follows: 1 – (422), 2 – (333,511), 3 – (440), 4 – (620), 5 – (533), 6 – (622). For all diffraction patterns in Figure 5, the intensity was represented at the same scale. Characteristic diffraction patterns of other iron oxides, such as FeO , $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ were not detected.¹⁰ However, the diffraction patterns of magnetite are slightly shifted from the standard ones, which point to the existence of some slightly changed lattice parameters for the treated zeolite in accordance with the proposed method in this work. This change of the oxide layer lattice parameter might be explained both by the influence of zeolite mass on material deposited onto the surface and within

pores of zeolite lattice, and the influence of chemical growth of the adsorbed layer. Data obtained by XRD and magnetic measurements were in good agreement. Samples 1-5 showed the existence of magnetite, Fe_3O_4 ; diffraction patterns were more intense as ΔU (in Table 2) went higher.

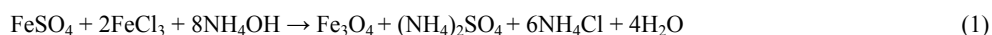
EXPERIMENTAL

Synthesis of zeolite-based adsorbent with magnetic properties

The starting material for this study was natural zeolite from Mirsid-Romania, with particles size of about 63 μm . The clinoptilolite content of the natural zeolite was about 65 wt% and assessed by X-Ray Diffraction. Besides clinoptilolite, the natural zeolite contained: illite, micas, feldspar, limonite and α quarts. The chemical composition of the volcanic tuff (wt%) determined in accordance with the standardisation method¹¹ was as follows: SiO_2 62.2; Al_2O_3 11.65; Fe_2O_3 1.30; CaO 3.74; MgO 0.67; K_2O 3.30; Na_2O 0.72; TiO_2 0.28; I.L. (ignition loss) 9.14³.

To improve ion exchange properties, the zeolite was chemically activated. The activation was carried out by treating zeolite with 2M NaCl solution at 1:5 solid-liquid ratio, intense stirring and room temperature for two hours. After activation, the zeolite was washed with distilled water and dried at 105 °C for 10 hours.

To get zeolite-based adsorbent with magnetic properties various concentration ferrous-ferric solutions at the required stoichiometric ratio for magnetite precipitation (reaction 1) were warmed up to 75 °C.



Then the solution was added the activated zeolite at a pre-set Fe_3O_4 /zeolite mass ratio corresponding to full precipitation of magnetite, which was carried out by slowly adding a 25% NH_3 solution under intense stirring. The temperature during precipitation process was kept between 85-90° C. Finally, the samples of adsorbent were filtered, washed and dried.

Magnetic characterization

To assess magnetic characteristics, zeolite particles were shaped as pellets (20 mm diameter) contained in a non-magnetic frame. Each sample contained the same quantity of modified adsorbent.

The magnetic characteristics were measured by *a.c.* induction in a Howling type device at room temperature. Two identical pick-up coils with inverted windings were mounted in series, one contained the magnetic sample and the other one was reference. Both coils had the same diameter of 22 mm. The alternating longitudinal magnetic field was parallel to the plane of sample. The plots of total magnetization (M) versus time (t), the derivative of magnetization (dM/dt) versus time and the variation of the applied magnetic field (H) as a function of time were recorded by using a computer assisted oscilloscope.

The output response in induction method devices¹² is most directly related to the magnetic moment (total magnetization)

of the sample, M . The total moment M is related to the volume magnetic susceptibility χ , sample volume V , and external magnetizing field H by

$$M = \chi HV \quad (2)$$

In SI, the units for the total magnetization are (Tesla*meter³) and χ is dimensionless.

The curves (dM/dt) versus t were recorded by digital scope interfaced to computer. They are determined by the differential susceptibility of the sample (χ) and by the rate of change of field with time:

$$\frac{dM}{dt} = \left(\frac{dM}{dH} \right) \left(\frac{dH}{dt} \right) = \chi \cdot \frac{dH}{dt} \quad (3)$$

Therefore, there is a similar shape of (dM/dt) versus (t) curves and differential susceptibility $\chi(t)$ curves.

The maximum available field, H , was 57.312 kA/m and the measurements were performed using a sinusoidal-field excitation at a frequency of 50 Hz. The magnetic field was applied in the plane of the sample. The differential susceptibility curve (and magnetization curve) were digitised (2048 sampling points), stored on disk and then analysed.

Structural characterization

The XRD investigations on the zeolite samples were carried out by using Co K α radiation with a DRON-3 installation.

Acknowledgements: This work was supported by Ministry of Education and Research of Romania, through CNCSIS Grant 208/2005.

REFERENCES

1. R. Pode, G. Burtica, V. Pode, A. Iovi and E. Popovici, *Stud. Surf. Sci. Catal.*, **1999**, 125, 769-776.
2. R. Pode, T. Todinca, A. Iovi, R. Radovet and G. Burtica, *Stud. Surf. Sci. Catal.*, **2002**, 142 b, 1655-1662.
3. E. Popovici, G. Burtica, R. Pode, I. Bedeleian and I. Calb, "Natural Microporous Materials in Environmental Technology", P. Misaelides (Ed.), Kluwer Academic Publisher, Series E, 1999, vol.362, p. 345-352.
4. R. Pode, G. Burtica, S. Herman and A. Iovi, "International Symposium on Multi-Phase Flow and Transport Phenomena", D.M. Maron (Ed.), Begell House inc., New York, 2000, p. 421-427.
5. R. Radovet, T. Todinca, R. Pode, A. Iovi and G. Burtica, *Rev. Roum. Chim.*, **2003**, 48, 171-176.
6. I. B. Serova, V. A. Nikashina, B. A. Rudenko and S. S. Meshalkin, "International Symposium and Exhibition on Natural Zeolites Proceedings", Sophia Zeolite Meeting '95, G. Kirov (editor), Pensoft Publishers, Sofia – Moscow, 1997, p. 115-121.
7. S. P. Zhdanov, M. A. Subaieva and N. P. Adreeva, *Bull. Russ. Acad. Sci.*, **1988**, 10, 2208-2214.
8. V. Pode, V. Georgescu, V. Dalea, R. Pode and E. Popovici, *Stud. Surf. Sci. Catal.*, **2001**, 135, CD.
9. R. C. O'Handley, "Modern Magnetic Materials. Principles and Applications", Willey-Interscience Publication, John Willey & Sons, Inc, 2000, p.123-131
10. ICDD-JCPDS cards: 11-614, 15-615, 16-895, 13-534, 19-615, 19-629
11. H. Minato, "International Symposium and Exhibition on Natural Zeolites Proceedings, Sophia Zeolite Meeting '95", G. Kirov (Ed.), Pensoft Publishers, Sofia – Moscow, p. 282-290.
12. ABBESS Technical Notes: ABBESS Instruments and Systems, INC. www.abbess.com/manuals/tech-note01.html.

