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PRELIMINARY INVESTIGATIONS ON CLINOPTILOLITE USAGE AS SELECTIVE ADSORBENT FOR WASTEWATER ANALYSIS

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ABSTRACT. This work presents some preliminary studies regarding natural zeolite, namely clinoptilolite (from volcanic zeolitic tuff) as selective adsorbent. This material was used to separate organic isomers of industrial interest (dichlorobenzenes, dinitrobenzenes, chloronitrobenzenes). The quality of the separations achieved were sufficiently encouraging as to promote further investigations of its potential as selective adsorbent both for bulk liquid separations and in analytical applications. These preliminary results showed that good chromatographic resolutions were obtained - $R_{S,o,p\text{-}DCB}$=3.53; $R_{S,o,p\text{-}DNB}$=3.09 and $R_{S,o,p\text{-}CNB}$=4.25 and seem to be very promising in order to use this natural zeolite as selective adsorbent in different applications.

Keywords: *natural zeolite, clinoptilolite, selective adsorbent, dichlorobenzenes, dinitrobenzenes, chloronitrobenzene*

INTRODUCTION

Zeolites are a group of hydrated aluminosilicates of the alkali or alkaline earth metals (sodium, potassium, magnesium, calcium), with a three-dimensional crystalline framework. Zeolite structure has a special characteristic, the alumino-silicate framework, which is formed from $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra, where each of the oxygen atoms belong to two neighboring tetrahedral (bonding oxygens), with the exception of those situated in the exterior of the crystal. While each $[SiO_4]^{4-}$ tetrahedra is charged neutral, each $[AlO_4]^{5-}$ tetrahedra contain an extra negative charge. This excess charge is compensated by cations, such as Na^+, K^+, Ca^{2+}, Mg^{2+}, which will be placed in the framework gaps, coordinated by a defined number of water molecules. Silica and alumina tetrahedras are bonded in rings, therefore the zeolite structure will contain channel and pores with diameters between 3 and 10 Å. These channels (gaps) are filled with cations and water molecules with a higher or lower mobility, depending on the intensity of the bonds which are linked to the residual valence of the alumina tetrahedra.

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The main consequence of this structure type is represented by the reversibility of hydration and cation exchange processes that preserve the original network. These channels also allow easy movement (after removal of the zeolitic water) of different molecules depending on their size. Molecules with a diameter smaller that the channel diameter will be retained inside the zeolite framework, while higher molecules will remain in the exterior. Due to this type of selectivity towards the components of a mixture (molecule size, channel diameter), zeolites are also called molecular sieves. The existence of a negative charge in the alumina tetraedra, allows also the uses of zeolites as acid-basic catalysts. In hydrated conditions, on the surface of the zeolite Brönsted centers are formed due to the water adsorption on Al^{3+} site, while upon dehydration the same site became a Lewis center [1].

Natural zeolites are important aluminosilicates in sorption processes [2,3] because of their low cost and selectivity. In environmental applications, natural zeolites have been studied extensively to remove harmful substances from wastewater by adsorption and ion exchange processes [4,5].

The sedimentary zeolitic rocks from Romania are represented by volcanic tuffs of Neogene age. The main zeolite present in these rocks is clinoptilolite.

Clinoptilolite is a natural occurring zeolite, a hydrated aluminosillicate member of the heulandite group. Heulandite group zeolites, including mineral clinoptilolite and heulandite and their synthetic analogues, have the same framework topology (structure code HEU) characterized by infinite three-dimensional frameworks of aluminium, silicon and oxygen. The distinction between the clinoptilolite and the heulandite is based on the Si/Al ratio, i.e., clinoptilolite if Si/Al > 4 and heulandite if Si/Al < 4 [6]. The chemistry of these two species varies almost continuously between [7]:

$$(Na, K, Ca_{0,5})_{10}(Al_{10}Si_{26}O_{72})\cdot 24H_2O \quad \text{(heulandite, Si:Al=2,6)}$$

$$(Na, K, Ca_{0,5})_{5,4}(Al_{5,4}Si_{30,6}O_{72})\cdot 20H_2O \quad \text{(clinoptilolite, Si:Al=5,7)}$$

Clinoptilolite was used as adsorbent in many applications, namely: as solid-phase material for removal of some radionuclides from low-level radioactive liquid waste [8], as a novel drug carrier for the flavonoid aglycone constituents [9] and antibiotics [10], as adsorbent for low concentration of lindane and aldrin removal from wastewater [11], as cation exchanger [12], as catalyst in the estherification of glycerol with oleic acid [13] etc.

The aim of this paper was to investigate the potential of a natural zeolite, clinoptilolite (from volcanic zeolitic tuff) as selective adsorbent. A variety of aromatic isomeric structures found in wastewaters, such as dichlorobenzenes, dinitrobenzenes and chloronitrobenzene were chosen for this study.

RESULTS AND DISCUSSION

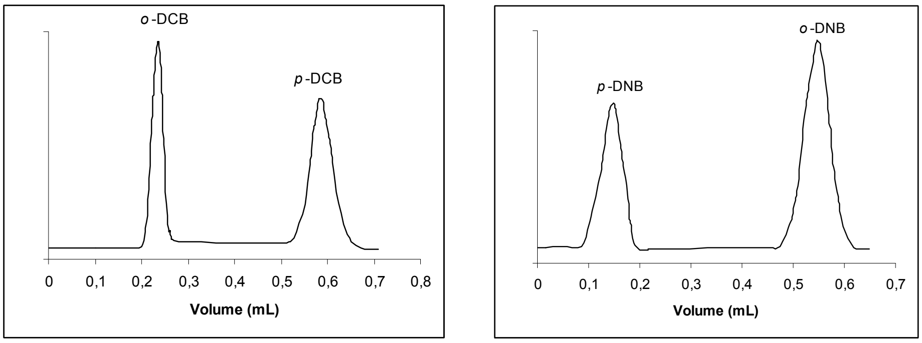
Prior chemical and mineralogical investigations realised on the zeolitic volcanic tuff samples collected from the same area, showed that: tuff samples contain high quantity of secondary and hydrated material (zeolite and probably smectitic clay minerals) as indicated by the high values of loss of ignition (L.O.I.) determined by bulk chemical analyses; tuff samples have a vitric and vitric crystal texture and are zeolitized and they consist of 60-70% of volcanic glass, 10-25% of crystals and lithic fragments in subordinate amounts (2-3%); the zeolites are present mainly as tabular clinoptilolite; the zeolite content reached values between 70% and 80% from the crystallized fractions of the tuff (semi-quantitative estimation from the X-ray diffraction patterns); FTIR spectra indicates presence of specific zeolite peaks; specific surface area (BET) is around 35 m^2/g [1,14].

Chromatographic separation

Dichlorobenzenes (DCBs), dinitrobenzenes (DNBs) and chloronitrobenzene (CNBs) are important organic intermediates which are extensively used in the production of dyes, pesticides, pharmaceuticals and rubber chemicals. In the viewpoint of clean technology, the recovery of valuable chemicals from the wastewaters is superior to the treatment of wastewater using degradation techniques. Based on high toxicity and stability of DCBs, DNBs and CNBs, they are resistant to biodegradation. The application of polymeric adsorbents in the recovery of DCBs, DNBs and CNBs from the wastewaters is limited because the recovered chemicals mainly consist of a mixture of isomers, and further purification by distillation or/and crystallization is necessary to obtain pure compounds. Therefore, the exploration and utilization of selective adsorbents is highly desirable to directly recover chemicals in high purity from wastewaters.

The optimum separation of *o- and p-DCB* was performed using heptane mixed with 0.1% ethanol as mobile phase (Figure 1a). The retention volumes were $V_{R,o\text{-DCB}}$ = 0.24 mL and $V_{R,p\text{-DCB}}$ = 0.59 mL. These results showed that the 1,4 isomer was more strongly adsorbed on stationary phase than 1,2 isomer. The order of elution was preliminary determined using standard solution of each isomer.

The *o- and p-DNB* were best separated by elution with heptane mixed with 1% ethanol (Figure 1b). In this case the retention parameters were: $V_{R,p\text{-DNB}}$ = 0.15 mL and $V_{R,o\text{-DNB}}$ = 0.57 mL. Introduction of the nitro-groups constituted an increase in polarity and it necessitated an increase in mobile phase polarity. The *o*-DNB was most preferred isomer, clinoptilolite having reverse order of elution, compared to DCBs and CNBs.



a b

Figure 1. Separation of: a) DCBs using 0.1% ethanol in heptane as eluent and b) DNBs using 1% ethanol in heptane as eluent.

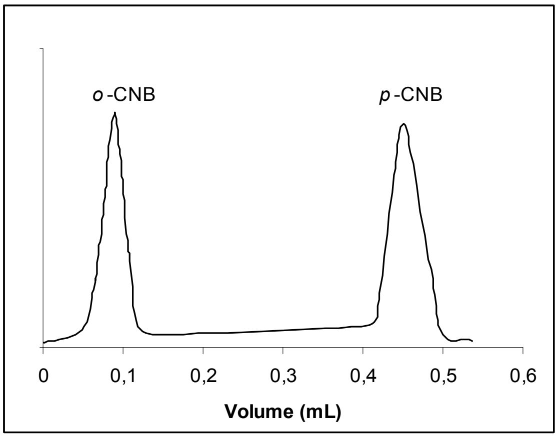


Figure 2. Separation of CNB isomers using heptane as eluent.

The following retention volumes were obtained for the o- and p-CNB using heptane as mobile phase: $V_{R,o\text{-}CNB}$ = 0.09 mL and $V_{R,p\text{-}CNB}$ = 0.48 mL. Elution order was the same as with DCBs compounds, *p*-isomer being the most strongly bounded (Figure 3).

From these preliminary experimental data it could be observed that good chromatographic resolutions were obtained: $R_{S,o,p\text{-}DCB}$=3.53; $R_{S,o,p\text{-}DNB}$=3.09 and $R_{S,o,p\text{-}CNB}$=4.25. These results seem to be very promising in order to use this adsorbent as stationary phase in liquid chromatography.

In order to completely establish the potential of natural zeolite as stationary phase in liquid chromatography further investigation such as: studies of the retention mechanism and the reproducibility of the retention parameters and comparison with other stationary phases are required.

CONCLUSIONS

The separations of DCBs, DNBs and CNBs previously observed on synthetic zeolites are confirmed here [15]. The purpose of the work reported here was to make a broadly based study of natural zeolite to assess its potential to perform bulk separations of important organic molecules. Liquid chromatography was chosen as a convenient approach, and also raised the possibility that the clinoptilolite could find use as stationary phases for this analytical technique.

The results will need further study if a detailed understanding of all the factors involved in the separations is to be attained. The zeolitic tuff presented mainly as tabular clinoptilolite, is a natural zeolite with a great potential for use as stationary phase in liquid chromatography. Moreover, the quality of the separations achieved were sufficiently encouraging as to promote further investigations of its potential as solid phases both for bulk liquid separations and in analytical applications.

In order to completely establish the potential of natural zeolite as stationary phase in liquid chromatography further investigation such as: studies of the retention mechanism and the reproducibility of the retention parameters and comparison with other stationary phases are required.

EXPERIMENTAL SECTION

The chromatographic separations were performed on a 20 cm glass column with internal diameter of 5 mm filled with clinoptilolite, laboratory made. The zeolitic volcanic tuff representative sample was collected from Măcicaş (M) quarry (Cluj County, Romania). In order to use this material as a stationary phase, the zeolitic volcanic tuff sample was subjected to a physical treatment (crushing, grinding, size separation) in order to obtain clinoptilolite samples with a grain diameter smaller than 0.2 mm.

Chromatographic analyses were optimised by using a series of mobile phases (heptane 100%, heptane mixed with 0.1% and 1% ethanol). The isomers used were from the purest materials available and injected first as individual standard, and then were injected simultaneously, as mixtures, onto the columns as 25 μL stock solution, using an automatic pipette. Standard stock solutions containing 0.1 mg/mL of *o*- and *p*-DCB, *o*- and *p*-DNB and *o*- and *p*-CNB were prepared in absolute ethanol. The compound separations were monitoring using TLC and UV detection at 254nm. For this purpose, equal fractions of the effluent were collected and then, spots from 0.03mL to 0.03mL were applied on the chromatographic plate and were examined under UV light. The intensity of the spots colour was examined and the spots area was determined using ImageJ software.

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