

ACTIVATED NATURAL ZEOLITES FOR PETROLEUM HYDROCARBONS ADSORPTION

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ABSTRACT. This study was carried out with the aim of increasing and determining the activated zeolites' adsorption capacity by testing their efficiency on petroleum hydrocarbons. Natural zeolite samples were sequentially studied after thermal and chemical activations. The results indicated that after the activations, the zeolite samples gained an increasing adsorption capacity of petroleum hydrocarbons. Furthermore, the zeolites with small particulate sizes (<10 µm) have a higher adsorption capacity than the zeolites with a granulometry of 1-3 mm. The metal content ranged between 4200-7400 mg/kg Na, 15090-22990 mg/kg Ca, 2670-3950 mg/kg Mg, 19470-19670 mg/kg K, 6140-7210 mg/kg Fe and 149-178 mg/kg Mn. Mineralogical analyzes (X-ray diffraction - XRD and scanning electron microscopy - SEM) were applied for the characterization of the zeolites. According to the XRD results, the zeolites are characterized by a 64 % crystallization level. The main mineral which was determined was Clinoptilolite-Ca. The SEM micrographs indicate the morphology of zeolite surfaces.

Keywords: zeolites, thermal treatment, chemical activation, adsorption capacity

INTRODUCTION

Petroleum hydrocarbons are a valuable fuel source, as well as a raw material for a wide range of industrial applications all over the world. On the

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other hand, they are a major environmental polluter, being classified as priority pollutants [1]. Oil and oil products spillages generate considerable damages, thus, more focus is being given to the development of advanced solutions to eliminate these pollutants. Besides the environmental impact of petroleum hydrocarbons, these pollutants cause a major risk to both humans and other forms of life [2, 3, 4, 5]. Ahmed and Fakhrudin [6] provided an overview on the impact of petroleum hydrocarbons on soil, water, and human health, as well as on the use of microorganisms for their degradation.

Different techniques and solutions are being used for the isolation, treatment, removal and control of petroleum-polluted environments. The decontamination technique using zeolites as adsorbents proved to be beneficial to the economy and to the environment [7, 8].

Zeolites are crystalline aluminosilicates composed of three-dimensional structures of AlO_4 and SiO_4 tetrahedra bound together by oxygen ions. Molecular sieves are a term that is often used to describe them. They are expressed chemically by the analytical formula: $\text{M}_2/n\text{OAl}_2\text{O}_3 \cdot y\text{SiO}_2 \cdot w\text{H}_2\text{O}$, where y is 2-200; n is the cation valence and w is the water contained in the voids [9].

Due to their structure, both synthetic and natural zeolites have been used in many industrial processes such as adsorption (gas separation), catalysis (petroleum refining, petrochemical production), separation (detergents, soaps). Many studies focus on synthetic zeolites used as mineral sorbents of diesel fuels and used engine oil [10], as sorbents of benzene, toluene, p-xylene (BTX) [11], as desulfurization sorbents of hydrocarbon fuels, containing benzothiophene and dibenzothiophene [12].

Among the natural zeolites, clinoptilolite has been widely used due to its abundance and ion exchange properties. In a study conducted by Favvas et al [13], clinoptilolite from the area of Drista River (North Greece) was used as a dehydration agent of diesel fuels and their findings indicated an increase in the physicochemical properties of the analyzed fuels. Natural clinoptilolite's potential as a Fenton catalyst in the removal of aromatic hydrocarbons was investigated by Rusoo et al [14]. Al-Jamal et al [15] studied the potential of Jordanian raw zeolitic tuff in adsorbing the oil from oil-contaminated water, by the use of de-alumination and micro-emulsification treatments. Zeolites originated from Romania have been used by different studies in environmental protection and medicine, such as biomonitoring of air pollution, waste water treatment, removal of Fe and Mn from diverse solutions, behavior of zeolites in simulated gastric fluid [16, 17, 18, 19].

In the present study, the determination of the adsorption capacity of a natural zeolite (clinoptilolite) was studied by using two activation methods: (i) thermal activation, and (ii) chemical activation, in order to increase the petroleum hydrocarbons adsorption capacity.

The zeolites were activated with surfactants with the aim of increasing the petroleum hydrocarbons adsorption capacity. After the activation with surfactants, the surface of material is changed from hydrophilic to hydrophobic.

The findings will contribute to the understanding of the potential use of natural zeolites in improving petroleum hydrocarbons spill cleanup.

RESULTS AND DISCUSSION

Zeolite characterization

The physico-chemical and mineralogical characteristics of the zeolites (not activated, thermally activated, and thermally and chemically activated) under this study are indicated as it follows.

X-ray diffraction (XRD) analysis

The XRD patterns of the thermally activated (at 500°C) zeolites are presented in figure 1.

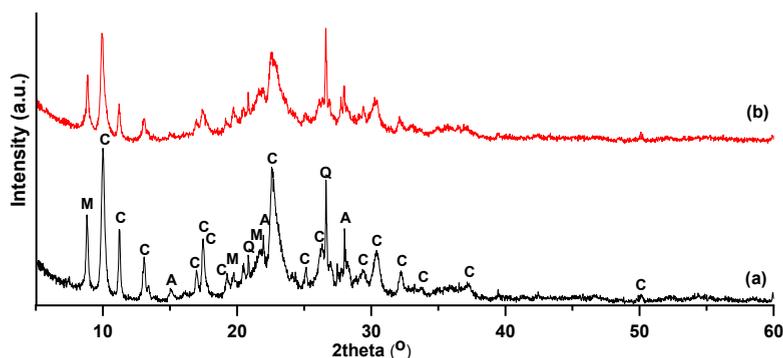


Figure 1. XRD patterns of thermally activated zeolites with particle sizes of (a) <10 μm and (b) 1-3 mm. Note: A- albite, C- clinoptilolite, Q- quartz, M- muscovite

According to the XRD analysis, the investigated zeolites contain clinoptilolite (00-070-1859) as the major crystalline phase, accompanied by muscovite (00-006-0263), quartz (00-005-0490) and albite (00-020-0548). The non-crystalline components were not quantified by the XRD analysis, but the presence of amorphous volcanic glass in zeolites is indicated by the broad diffraction hump at $2\theta = 20\text{-}25^\circ$. A slight decrease in the degree of crystallinity was remarked for higher particle size (54.6%) comparing with lower particle size (63.6%).

Scanning electron microscopy (SEM) results

SEM was applied for Az1 and Az2 zeolites, with particles dimensions < 10 μm and 1-3 mm, not activated and thermally activated at 500 $^{\circ}\text{C}$.

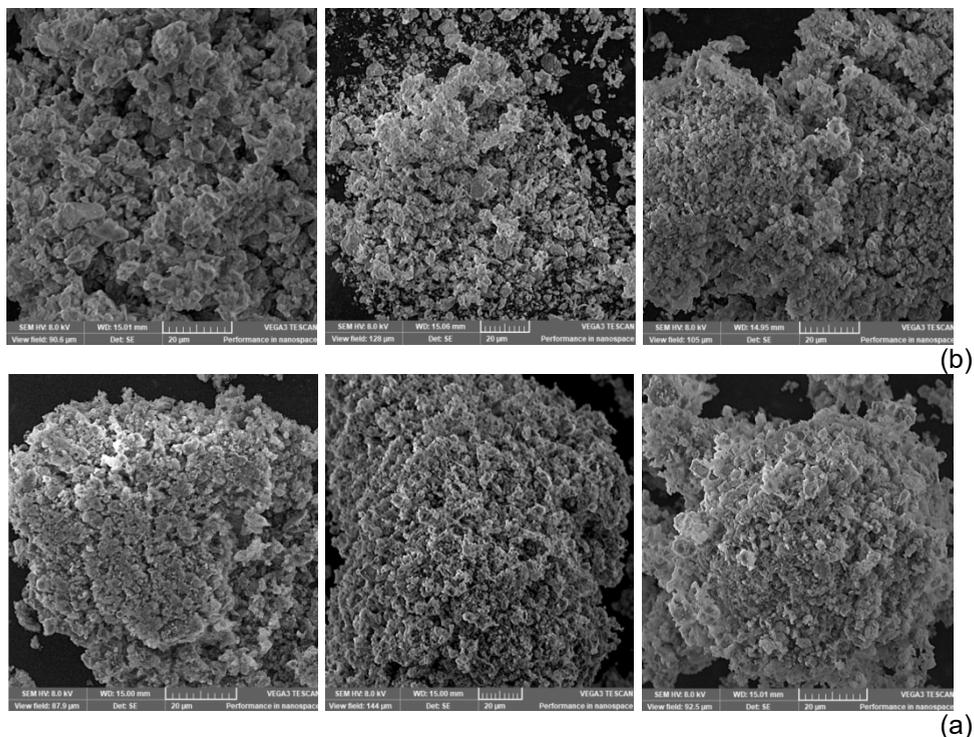


Figure 2. SEM micrographs indicating the occurrence of zeolites thermally activated a) Az1 (particle sizes < 10 μm) and b) Az2 (particle sizes 1-3 mm)

The Energy-Dispersive X-ray Spectroscopy (EDX) analysis indicate that the zeolites samples are characterized by concentrations of 43.0-61.7 % silicon and 7.10-37.4 % oxygen.

Metals and oxides content

The metals (Al, Ca, Fe, K, Mg, Mn, Na) and major oxides (Al_2O_3 , CaO, Fe_2O_3 , K_2O , MgO, MnO, Na_2O) contents in the zeolites only thermally activated were determined in a previous study [20]. The results indicate variations of the Al content between 59000-68000 mg/kg, Na, Ca, Mg and K ranging between 4200-7400 mg/kg, 15090-22990 mg/kg, 2670-3950 mg/kg and 19470-19670 mg/kg [20]. Fe and Mn vary between 6140-7210 mg/kg and 149-178 mg/kg. Generally, the metal content is higher in the zeolite with lower particle sizes [20].

In the current study, the results of the metals content in chemically activated zeolites are showed in Table 1.

Table 1. The metal content (mg/kg) in the chemically activated zeolites (Az3-Az8)

Sample	Al	Ca	Fe	K	Mg	Mn	Na
Az3 10	62524	15468	5210	18418	3470	147	4919
Az4 1-3	67886	20983	4204	17736	4207	229	3677
Az5 10	64747	16507	5698	19166	3521	157	4904
Az6 1-3	68875	20873	4607	17636	6298	157	3552
Az7 10	60386	15404	5391	18802	3408	144	4745
Az8 1-3	69882	20362	4594	18413	4669	133	3397
Mean	65717	18266	4951	18362	4262	161	4199
Min	60386	15404	4204	17636	3408	133	3397
Max	69882	20983	5698	19166	6298	229	4919

The Al concentrations vary between 60386 to 69882 mg/kg, with higher values obtained in the zeolites with the particle sizes of 1-3 mm and particularly in Az8. The Ca, Mg and Mn amounts are slightly higher in the not activated samples with particle size of 1-3 mm with values between 15404-20983 mg/kg, 3408-6298 mg/kg and 133-229 mg/kg. For the Fe, K and Na, the highest values were found in the samples that were not activated with particle size < 10 μm . The amounts vary between 4204-5698 mg/kg Fe, 17636-19166 mg/kg K and 3397-4919 mg/kg Na.

No significant variations are observed between the samples activated with different surfactant concentrations.

The major oxides results obtained for the chemically zeolites are indicated in Table 2.

Table 2. The major oxides content (%) obtained in the chemically activated zeolites (Az3-Az8)

Sample	Al ₂ O ₃	SiO ₂	CaO	Fe ₂ O ₃	K ₂ O	MgO	MnO	Na ₂ O
Az3	11.8	67.3	2.17	0.74	2.22	0.58	0.02	0.66
Az4	12.8	68.1	2.94	0.60	2.14	0.70	0.03	0.50
Az5	12.2	67.0	2.31	0.81	2.31	0.59	0.02	0.66
Az6	13.0	66.4	2.92	0.66	2.13	1.05	0.02	0.48
Az7	11.4	65.7	2.16	0.77	2.27	0.57	0.02	0.64
Az8	13.2	68.2	2.85	0.66	2.22	0.78	0.02	0.46
Mean	12.4	67.1	2.56	0.71	2.21	0.71	0.02	0.57
Min	11.4	65.0	2.16	0.60	2.13	0.57	0.02	0.46
Max	13.2	68.2	2.94	0.81	2.31	1.05	0.03	0.66

The Al₂O₃ content varies between 11.4-13.2 %, SiO₂ 65.0-68.2 %, while Na₂O, CaO, MgO and K₂O range between 0.46-0.66 %, 2.16-2.94 %, 0.57-1.05 % and 2.13-2.31. The content of Fe₂O₃ varies between 0.60-0.81%, whereas no significant differences are noticed in the MnO results.

Metals in the thermally activated zeolites were indicated in a previous study [20].

Petroleum hydrocarbon adsorption

In order to increase the petroleum hydrocarbon adsorption, the surface of the zeolites is modified with surfactants. This activation changes the character of the surface from hydrophilic to hydrophobic, increasing the organic pollution affinity of the zeolite which acts like a sorbent [21, 22]. The activated zeolite samples chemically activated with surfactant (methyl dodecylbenzene sulfonate) solutions were tested to study the petroleum hydrocarbon adsorption capacity. The highest petroleum hydrocarbon adsorption capacity is observed at samples activated with the most concentrated surfactant solution (2.0 mmol/L). Results vary between 101-253 mg/g adsorbed hydrocarbons by zeolites (Figure 3).

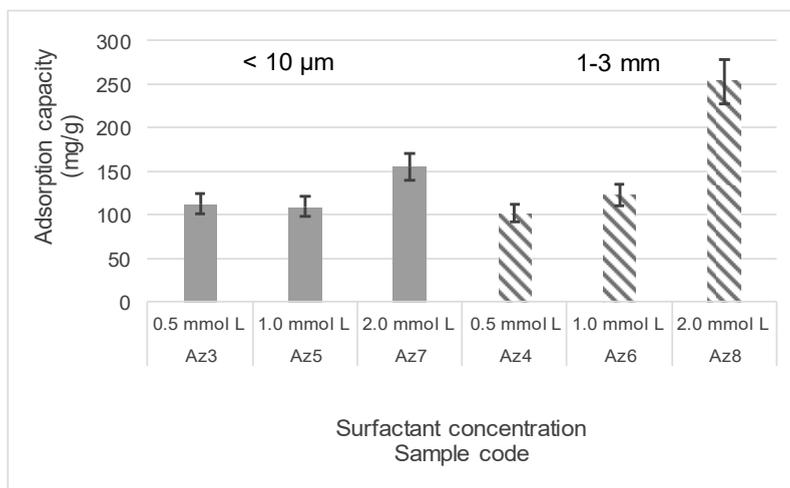


Figure 3. Adsorption capacity (mg/g) in the activated zeolites samples with two granulometries (<10 μm and 1-3 mm) with three different surfactant concentration levels (0.5 mmol/L, 1.0 mmol/L, 2.0 mmol/L)

Samples with the highest granulometry and activated with the 2.0 mmol/L surfactant solution are characterized by the highest petroleum hydrocarbon adsorption capacity. The increasing trend of the zeolite samples is the following $\text{Az6} < \text{Az4} < \text{Az3} < \text{Az7} < \text{Az5} < \text{Az8}$.

According to the results, an increase of the adsorption capacity was noticed. The zeolite treated with a high concentration of surfactant solution was the most effective (2.0 mmol/L).

The results obtained by Torabian et al [23] also revealed that the zeolite's adsorption capacity is enhanced by the increase of surfactant loading.

Simpson et al. [24] examined the sorption of volatile petroleum hydrocarbons using surfactant modified zeolite and their results showed an increase in the sorption coefficient. The zeolites' affinity for hydrocarbons can be enhanced by transforming their surface from hydrophilic to hydrophobic, under the surfactants' action [25].

CONCLUSIONS

Based on the X-ray diffraction and scanning electron microscopy results, thermally activated zeolites contain clinoptilolite, quartz, muscovite and albite. The SEM micrographs indicate the occurrence of thermally activated zeolites and silicon and oxygen concentrations.

The Al, Ca, Mg and Mn concentrations were slightly higher in the zeolite samples with granulometry of 1-3 mm compared to the samples with lower granulometry ($< 10 \mu\text{m}$), while the Fe, Na and K amounts were higher in the samples with lower particle sizes. According to the study's results, activated zeolites with 2.0 mmol/L methyl dodecylbenzene sulfonate solution were characterized by the highest petroleum hydrocarbon adsorption capacity. Likewise, the granulometry of samples play an important role in the increasing adsorption capacity.

EXPERIMENTAL SECTION

Sampling, mechanical and thermal treatments

The studied zeolite materials (clinoptilolite tuffs) were provided from the Rupea deposits (Brasov County, central Romania). Clinoptilolite-type minerals represent the predominant zeolite resources in these deposits and generally in the country [26, 27]. After the collection, the samples were crushed and grounded and powdered at two different particle sizes ($< 10 \mu\text{m}$ and 1-3 mm). Afterwards, the zeolites were dried at a temperature of $105 \text{ }^\circ\text{C}$, using a thermostatic oven INE 200 (Mettler, Germany) for at least 5 h. Then, they were thermally activated at $500 \text{ }^\circ\text{C}$ for a period of at least 2 h, using an electrical oven model LT9 muffle furnace (Nabertherm, Lilienthal, Germany). Samples were left for cooling in a desiccator, transfused and kept in clean polyethylene bags until the chemical activation.

Chemical activation

The chemical activation consists of treating the zeolites with surfactant (methyl dodecylbenzene sulfonate) solutions. Three different surfactant solutions (0.5 mmol/L, 1.0 mmol/L and 2.0 mmol/L) were prepared. The samples were

immersed (1:10, v:v) and homogenized for 24 h using a magnetic stirrer. Before the separation of the resulted phases, they were left to settle for 45 minutes. The solid phase was washed a coupled of times with distilled water in order to remove the surfactant. The activated zeolites were then dried at 45 °C for 24 h.

After the activation procedures, eight types of materials were obtained as indicated in Table 3.

Table 3. Characteristics for the obtained zeolite materials after three different activations

Sample	Particle sizes	Temperature (°C)	Concentration of methyl dodecylbenzene sulfonate solution (mmol/L)
Az1	< 10 µm	500	-
Az2	1-3 mm	500	-
Az3	< 10 µm	500	0.5
Az4	1-3 mm	500	0.5
Az5	< 10 µm	500	1.0
Az6	1-3 mm	500	1.0
Az7	< 10 µm	500	2.0
Az8	1-3 mm	500	2.0

Characterization techniques

Scanning electron microscopy (SEM)

The SEM was applied with a scanning electron microscope at 8 kV, using a Tescan VEGA 3 SBU – EasyProbe model (NanoSystems MC, Czech). The field dimension was 146 µm and the focalization distance at 20 µm.

X-ray diffraction determination

The X-ray diffraction patterns were recorded at room temperature using a D8 Advance (Bruker, Germany) diffractometer operating at 40 kV and 40 mA with CuK α radiation ($\lambda=1.54060$ Å).

Metals and major oxides determinations

The metal content (Al, Ca, Fe, K, Mg, Mn, Na) was determined in the activated zeolites (Az3-Az8) after digesting a quantity of 1.0 ± 0.001 g with 28 ml of aqua regia using a closed digestion system DK6 VELP (Velp Scientifica, Usmate Velate, Italy). The solutions were left for at least 12 h at room temperature before the extraction. The extraction took 240 minutes at 120 °C. After the procedure was ended, the samples were filtered through 0.45 µm acetate cellulose filters and brought at a volume of 100 mL with ultrapure water (obtained with a Merck system, Millipore, Merck). The samples were measured using an inductively coupled plasma optical emission spectrometer (ICP-OES), model Optima 5300 DV (Perkin Elmer, Canada).

The obtained concentrations were used for the calculation of the proposed major oxides using conversion factors [19].

The quality assurance was accomplished by measuring soda feldspar BCS-CRM, no. 375/1 (Bureau of Analysed Samples Ltd). For the SiO₂ determination, gravimetric method was applied [19].

Petroleum hydrocarbon adsorption

In order to determine the efficiency of the adsorption capacity, a simulation was carried out on contaminated ex-sites with petroleum hydrocarbons (diesel). Commercial diesel was used in the experiments, that consists of a mixture of hydrocarbons having different carbon number in the range between C10-C22, which are mainly aliphatic and aromatic in nature [28]. Three chemical parameters were used to characterize the diesel: sulphur, sulfated ash content and the acid number.

Sulfur was determined by ICP-OES, as previously described, the sulfated ash content was determined gravimetrically and the acid number by titration with HCl against bromocresol green. The results indicated that the used diesel in the adsorption method was characterized by 3.0 mg/kg S, 0.02 % for the sulfated ash content and the acid number with values below 0.01 mgKOH/g.

The adsorption capacity was gravimetrically determined. The zeolites were weighted and added as a uniform thin layer on the contaminated site. The samples were left for adsorption for 8 h. Afterwards, the contaminated zeolites were carefully and quickly removed and weighed.

After the adsorption of petroleum hydrocarbons, the resulted zeolites-petroleum hydrocarbons mixtures could be used as fuel resources in cogeneration stations. Zeolites could be regenerated, but this implies a serious use of chemicals and/or energy in order to eliminate the amount of petroleum hydrocarbons and to purify the zeolite.

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