New materials based on natural zeolites used for petroleum products sorption and waste recovery

Maria-Alexandra Hoaghia[1], Ioan Aschilean[2], Eniko Kovacs[1,3], Cecilia Roman[1], Marin Senila[1]

[1]*INCDO-INOE 2000, subsidiary Research Institute for Analytical Instrumentation, 67 Donath Street, 400293, Cluj-Napoca, Romania*
[2]Zeolites Production S.A., Rupea, Brasov, Romania
[3]*University of Agricultural Sciences and Veterinary Medicine, Calea Manastur, 3-5, 400372, Cluj-Napoca, Romania*

Introduction

Zeolites are natural microporous resources, minerals included in the **aluminosilicate** groups with the origin in volcanic activities (Bandura et al., 2017). Due to their specific and **crystalline structure** (cages and channels), zeolites are considered **very efficient adsorbents** of different pollutants, such as heavy metals, nitrogen compounds, petroleum products and different other toxic compounds (Li et al., 2017). Certain materials can be activated in order to increase the efficiency of the adsorption capacity, by applying different techniques and activation methods. The most useful activation techniques are chemical, mechanical and thermal techniques (Maicaneanu et al., 2018).

The **aim of the study** was **to determine** and **to increase** the **sorption capacity** of petroleum products by using natural zeolitic materials from Rupea, to determine the **chemical content** (metals and oxides) and the **heat of combustion level** of the obtained zeolitic material which adsorbed petroleum products (Diesel oil).

Objectives

- **Characterization of the zeolitic material (chemical composition – metals, oxides content and cations exchange capacity - CEC);**
- **Increasing the sorption efficiency of petroleum products (Diesel oil);**
- **Determination of the sorption capacity of petroleum products by using natural zeolites resources (Rupea zeolites deposits, Brasov County).**

Materials and methods

- The **metal content** (Al, Ca, Fe, Na, Mg, Mn, K), the **oxide content** (K_2O, MnO, CaO, MgO, Fe_2O_3, Al_2O_3, Na_2O and Si_2O) and **CEC** were determined with atomic emission inductively coupled plasma (Spectro Analytical Instruments Germany), gravimetric and extraction methodologies.
- For the **increase of the sorption capacity**, a thermal technique is used: the zeolite is calcinated at 500 °C for at least 4 h and left for cooling in controlled humidity and temperature conditions (Fig. 1 and 2).
- In order to determine the **sorption capacity** of petroleum product, zeolites with two different granulations (10 µm and 1-3 mm) were **washed** with **distilled water** until the supernatant becomes clear. Furthermore, the material is **dried at 105 °C** for **2 to 4 h** and kept in controlled conditions (humidity ~ 65 % and temperature ~ 20 °C) until proceeding the chemical analysis. The zeolitic material is **weighed** and then **saturated** with Diesel oil and left for a coupled of h. Both phases were **separated** and the zeolite material with the adsorbed petroleum product **weighted** again.
- The **heat of combustion value** for the zeolitic material which adsorbed the Diesel oil was measured by using a 6200 calorimeter system (PARR Instrument Company, USA))

Fig. 1 The zeolitic material before adsorption

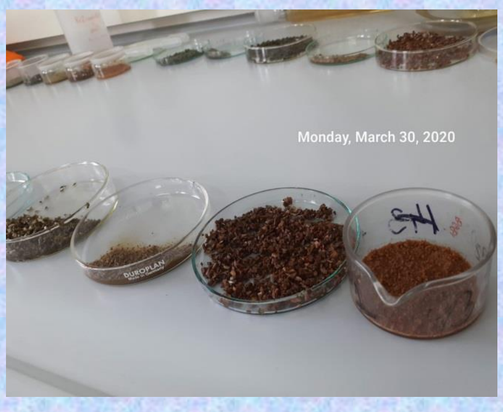

Fig. 2 The zeolitic material adsorbing the Diesel oil

Results and discussions

The results regarding the **metals** and **oxides contents** are indicated in **Tables 1** and **2**, for both particle sizes (10 µm and 1-3 mm) and two types of zeolitic materials (inactivated and thermic activated at 500 °C).

CEC results range between 2.0 and 1.7 meq/g for the inactivated zeolitic materials and 1.2 meq/g and 1.0 meq/g for the zeolitic material activated at 500 °C.

Sorption capacity results range between 1.55 – 1.68 g/g for the zeolitic material (with the granulometry lower than 10 µm) and 0.20 – 0.30 g/g for the zeolitic material (with the granulometry between 1-10 mm).

The heat of combustion value (25 kJ/g) characterizes the zeolitic material which adsorbed the Diesel oil with a relatively high combustion capacity.

Table 1. The metal content (Al, Ca, Fe, Na, Mg, Mn, K) determined in the zeolitic material before and after thermal activation (TA)

Element (%)	Zeolite material			
	Before TA 10 µg/L	Before TA 1-3 mm	After TA 10 µg/L	After TA 1-3 mm
Al	6.35	6.10	6.50	6.05
Ca	1.45	2.00	1.60	2.10
Fe	0.70	0.67	0.75	0.70
Na	0.81	0.60	0.80	0.65
Mg	0.25	0.38	0.31	0.40
Mn	0.04	0.06	0.05	0.06
K	2.00	2.25	2.10	2.30

Table 2. The oxides content (K_2O, MnO, CaO, MgO, Fe_2O_3, Al_2O_3, Na_2O and Si_2O) determined in the zeolitic material before and after thermal activation (TA)

Element (%)	Zeolite material			
	Before TA 10 µg/L	Before TA 1-3 mm	After TA 10 µg/L	After TA 1-3 mm
K_2O	2.40	2.42	2.45	2.41
MnO	0.02	0.03	0.02	0.02
CaO	2.10	2.95	2.15	3.00
MgO	0.50	0.58	0.52	0.60
Fe_2O_2	1.48	1.10	1.50	1.12
Al_2O_3	7.45	7.90	7.50	7.95
Na_2O	1.06	0.90	1.05	0.87
Si_2O	67	66	68	69

Conclusions

The studied zeolitic materials (particle sizes of 10 µm and 1-3 mm) originated from Rupea, Brasov County deposits were thermally activated with the purpose of increasing the sorption capacity. Results indicated a higher sorption capacity for the zeolitic material with particle sizes of < 10 µm compared to the zeolitic material with higher particle size (1-3 mm).

After the sorption of the Diesel oil, the zeolitic material was analyzed for the heat of combustion level and the obtained results present relatively high values ⇨ the wastes resulted after adsorbing the petroleum products can be reused in heating processes.

References (selection)

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Acknowledgments

This work was supported by the Ministry of Research and Innovation through Program 1 - Development of the National Research and Development System, Subprogram 1.2 - Institutional Performance- Projects for Financing Excellence in RDI, Contract No. 19PFE/2018 and by the Competitiveness Operational Programme of the Ministry of European Funds through the Contract No. 7/01.09.2016, MY SMIS 105654