MINERALOGIA, *51, 1-7 (2020)*
DOI: 10.2478/mipo-2020-0001
www.Mineralogia.pl

MINERALOGICAL SOCIETY OF POLAND
POLSKIE TOWARZYSTWO MINERALOGICZNE

Original paper

Sorption of oil products on the synthetic zeolite granules

Magdalena Król[1], Piotr Rożek[1]*

[1]AGH University of Science and Technology, Faculty of Materials Science and Ceramics
Al. Mickiewicza 30, 30-059 Krakow, Poland
** Corresponding author*
e-mail: prozek@agh.edu.pl

Received: *October 2, 2019*
Received in revised form: *March 15, 2020*
Accepted: *July 6, 2020*
Available online: *October 15, 2020*

Abstract. In this work, lightweight granules of zeolite Na-P1 based on expanded glass aggregates were synthesized for the application in oil products' sorption. The sorption of gasoline, diesel and silicone oil tests were also conducted for raw expanded glass, zeolite A, clinoptilolite and mineral sorbent available at a fuel station. All sorbents were also characterized in terms of the phase composition (X-ray diffraction) and structure (infrared spectroscopy). The zeolite Na-P1 granules achieved the highest values of sorption capacities (1.8, 2.1 and 2.6 g/g, respectively), which makes them promising materials for oils' removal.

Key-words: sorbent, adsorption, oil pollution, zeolite Na-P1, expanded glass

1. Introduction

Oil products refer to such materials as edible oils, crude oil and its derivatives (e.g. diesel, gasoline) (Zadaka-Amir et al. 2013), as well as liquid polymers (silicone oil). Among them, petroleum substances are a common source of environmental pollution, for example in the form of spills on roads and pavements. The removal of such substances can be carried out by adsorption, with the use of mineral and organic sorbents (Bandura et al. 2017). This method is considered as easy, safe, effective and inexpensive. The sorption capacities of mineral sorbents towards petroleum derivatives are between 0.2 and 0.5 g/g (Bandura et al. 2017). Mineral sorbents are resistant to acids, bases and fire. Studies regarding the sorption of oils describe the use of the following mineral sorbents: sepiolite

(Zadaka-Amir et al. 2013), vermiculite (Zhao et al. 2011), and diatomite (Pijarowski, Tic 2014), as well as zeolites (Bandura et al. 2015a; Muir, Bajda 2016).

Zeolites are commonly used as sorbents, not only of oil products but also in the removal of heavy metals' ions (Mozgawa et al. 2009). Zeolites are hydrated tectosilicates, built of a network of [AlO_4] and [SiO_4] tetrahedra, linked together by common oxygen atoms (Auerbach et al. 2003). Zeolites possess open spaces (channels and chambers of strictly defined sizes) filled with cations and water molecules. The porous framework of these minerals gives them the ability to selectively adsorb particles and ions, so they can be applied for ion-exchange, catalysis and adsorption (Król, Mozgawa 2019). For oils' sorption, zeolites are used such as clinoptilolite (Bandura et al. 2015a; Muir, Bajda 2016), zeolite X (Bandura et al. 2015a; Sakthivel et al. 2013), and zeolite Na-P1 (Bandura et al. 2015a; Muir, Bajda 2016). After sorption, they can be utilized for the production of lightweight fired aggregates (Franus et al. 2017; Król et al. 2016b).

The aim of this study was to determine the usefulness of synthetic zeolite Na-P1 granules based on expanded glass aggregate in the sorption of three substances: silicone oil, and dieseland gasoline (the latter both petroleum products). Their sorption capacity was compared to the capacities of other sorbents, such as clinoptilolite and zeolite A. To the best of our knowledge, this is one of the first investigations concerning the use of zeolite granules based on expanded glass aggregates as oil adsorbents.

2. Materials and methods

Expanded glass aggregates (*Poraver*®) with the grain size of 0.1-2.0 mm were utilized as a support for the synthesis of zeolite Na-P1 granules. The chemical composition of expanded glass, determined with the use of X-ray fluorescence spectrometry (*Axios mAX* 4 kW, *PANalytical*, Rh source, wavelength dispersive), is presented in Table 1. The results show that this material is composed mainly of silicon and sodium oxides, which is a typical composition for a conventional glass, because expanded glass is prepared from post-consumer recycled glass. Sodium hydroxide pellets (*POCH*) were used for the preparation of the synthesis medium (i.e. 3 M NaOH aqueous solution).

TABLE 1

Expanded glass aggregates' chemical composition (in wt.%)

SiO_2	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**K_2O**	**Na_2O**	**others**
64.2	4.7	0.3	6.9	1.9	0.7	20.3	1.0

Synthetic zeolite Na-P1 granules were prepared according to the procedure described previously by (Król, Mikuła 2017): expanded glass aggregates were mixed with NaOH solution (in a ratio of 1 g per 10 cm^3), and then placed in closed containers at 90°C for 24 h. The final product was filtrated and washed with distilled water. The microstructure of granules was observed via scanning electron microscope (*FEI Nova NanoSEM 200*).

The sorption capacities of oil products were established not only for zeolite Na-P1 granules (denoted as ZPG), but also, for comparison, for the following materials: expanded glass aggregates (EGA), sorbent available at a fuel station (SOR), natural clinoptilolite (CLI), and commercial zeolite A (CZA). Their phase compositions were determined using a diffractometer (*Empyrean PANalytical*) with CuKα radiation, and the FT-IR spectra were registered with a *Bruker VERTEX 70v* vacuum spectrometer using the KBr (*Merck*) pellets method.

Sorption capacity can be easily determined by weighing the sorbent before and after sorption, and using the equation:

$$SC = (M - M_0)/M_0$$

where: SC – sorption capacity (g/g); M – weight of the sorbent after sorption; M_0 – weight of the sorbent before sorption (Bandura et al. 2017). In this study, the sorption of silicon oil (*Polsil*), diesel and gasoline (*PKN Orlen*) was investigated according to a method equivalent to the standard Westinghouse method (Cheeseman et al. 2012): (1) weighing a sorbent (M_0) and placing it in a stainless steel cone sieve; (2) immersing the sieve with the sorbent in a container with a substance to be adsorbed for 20 min; (3) taking the sieve from the container and leaving to drain for another 20 min; and (4) drying the excess of the sorbate from the sieve with a tissue paper and weighing the sorbent (M). For the results, an average of three tests was taken.

3. Results and discussion

The obtained granules (ZPG), with a bulk density of 170 kg/m^3, can be included in the group of lightweight materials. The images of their microstructure are shown in Figure 1. The porous amorphous phase is a support for Na-P1 zeolite crystallites. These crystallites have a diamond-like morphology, and the size of each granule is of few microns. They are densely distributed on the surface of a support (i.e. expanded glass). The presence of zeolite gives the material sorption properties, while the high open porosity of the support should promote the diffusion of adsorbed molecules.

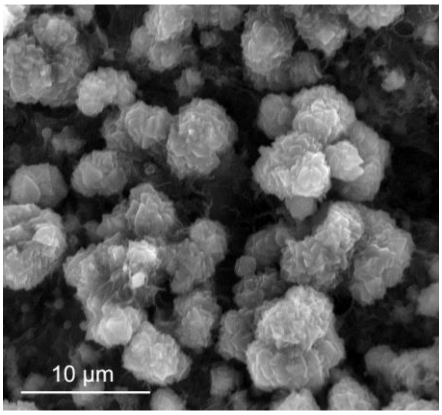

Fig. 1. Microstructure of ZPG observed in scanning electron microscope with crystallites of zeolite Na-P1.

The diffraction patterns of sorbents are presented in Figure 2. EGA is completely amorphous, which is typical for glass material. ZPG, as supposed, is characterized by the presence of peaks related to zeolite Na-P1, with some minor phases of carbonates, formed in the reaction of NaOH with atmospheric carbon dioxide. SOR, taken from a fuel station, turned out to be clinoptilolite with sand (quartz). CLI is almost pure clinoptilolite, while only weak peaks from quartz were registered. In the case of CZA, peaks related to zeolite A can be observed.

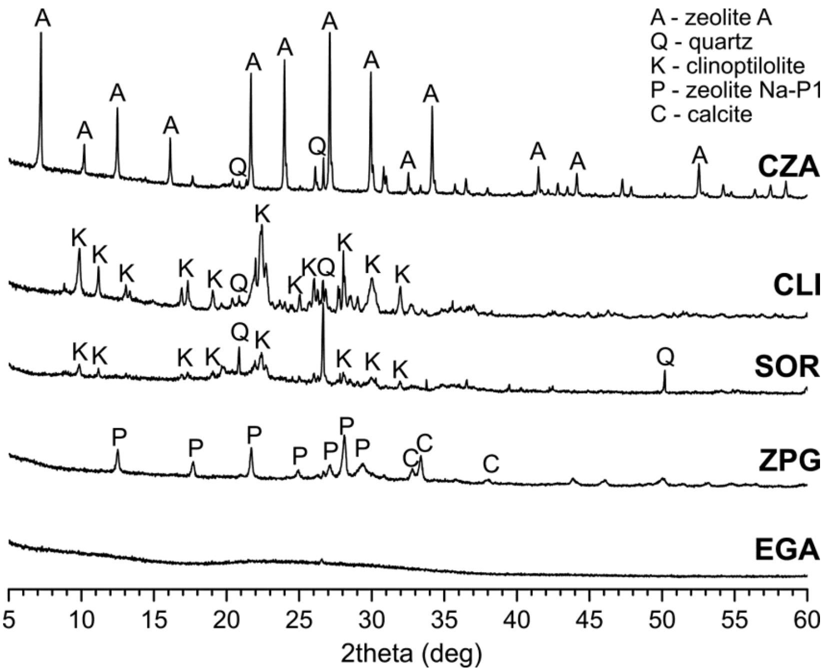

Fig. 2. X-ray diffraction patterns of materials used for sorption tests (A – zeolite A, Q – quartz, K – clinoptilolite, P – zeolite Na-P, C – calcite).

Figure 3 presents infrared spectra of the sorbents. In general, bands at 3623–3422 cm^{-1} can be assigned to the stretching vibrations in OH groups and absorbed water; at 2956–2855 cm^{-1} to the vibrations of C–H bonds; at 1656–1636 cm^{-1} to the bending vibrations of H–O–H; at 1492–1472 cm^{-1} and 876 cm^{-1} to the vibrations of CO_3 groups; at 1068–997 cm^{-1} to the stretching vibrations of Si–O–(Si,Al); at 800–600 cm^{-1} to the stretching vibrations of Si–O–Si; and bands at 600–400 cm^{-1} to the bending vibrations of Si–O–(Si,Al) (Rożek et al. 2018). In the case of ZPG, vibrations of zeolite structural units can be identified in a pseudolattice region: the bands at 743, 667 and 604 cm^{-1} indicate the presence of zeolite Na-P1 (Król et al. 2014). Also, a relatively intense band at 1492 cm^{-1} confirms the presence of carbonates. Therefore, using NaOH solution for the zeolite granules' preparation makes them vulnerable to carbonates' formation as a result of the reaction of sodium hydroxide with atmospheric carbon dioxide (carbonation). The amorphous character of EGA is confirmed by a relatively high full width at half maximum

(FWHM) of the main band (at 1038 cm^{-1}). The presence of quartz in SOR and CLI is confirmed by the band at around 796 cm^{-1}, and in the case of the SOR bands at 2956–2855 cm^{-1} they are related to the vibrations of C–H bonds that indicate organic impurity, probably with soil. In the case of CZA, the band at 553 cm^{-1} is related to the presence of zeolite A, namely with double four-membered rings' vibrations (Król et al. 2016a).

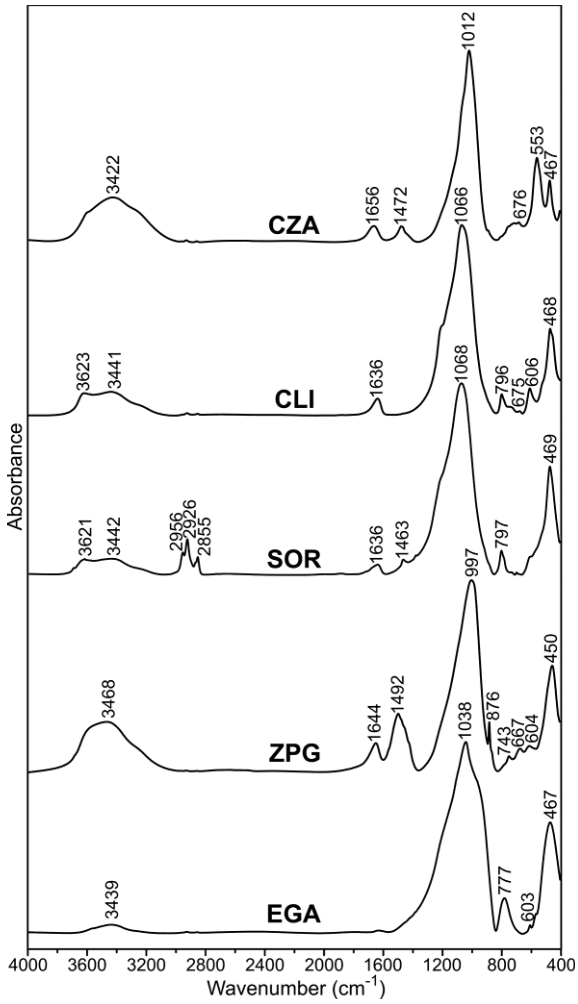

Fig. 3. FT-IR spectra of materials used for sorption tests.

The gasoline, diesel and silicon oil sorption capacities of the tested sorbents are presented in Figure 4. ZPG is definitely the best sorbent, achieving 1.8, 2.1 and 2.6 g/g, respectively. It can be seen that such high values are the result of zeolite Na-P1 presence – raw expanded glass aggregates showed much lower sorption capacities. The values of other sorbents are much lower – for expanded glass aggregates they do not exceed 0.6, 0.7 and 1.1 g/g, respectively. SOR and CLI achieved similar values, while CZA seemed to be the worst sorbent of oil products (0.2, 0.2 and 0.3 g/g, respectively), which is probably the effect of its microporous structure. Zeolite Na-P1 is regarded as a mesoporous mineral. The SC values achieved by clinoptilolite are similar to the ones described for this zeolite in the work of (Muir, Bajda 2016).

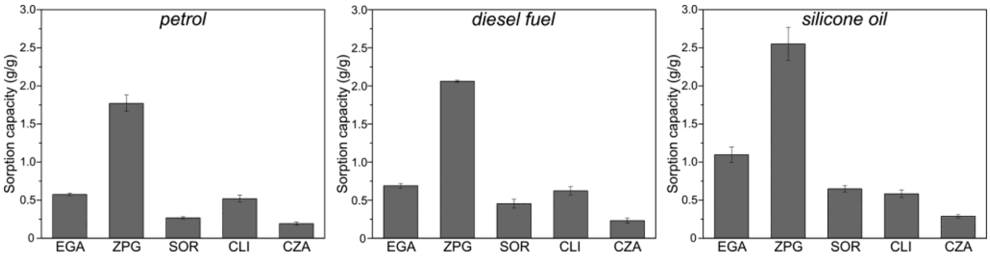

Fig. 4. Sorption capacities of materials used for the sorption of gasoline, diesel and silicone oil.

The obtained granules (ZPG) are a promising material for oil products' sorption. The achieved sorption capacity values are higher (1.8–2.1 g/g) than in the case of the zeolite Na-P1 sorption capacities towards petroleum substances described elsewhere: 0.86–0.91 (Bandura et al. 2015a), 0.89–1.18 (Muir, Bajda 2016), and 1.24–1.40 g/g (Bandura et al. 2015b). The obtained values are also higher than the values of other mineral sorbents summarized in the review of (Bandura et al. 2017), with the only exceptions being organo-clays, that is, DDDMA-bentonite and DDDMA-monmorillonite (where DDDMA refers to dodecyldimethylammonium bromide) (Carmody et al. 2007).

4. Conclusions

Expanded glass in the form of granules is a promising material for the synthesis of zeolites. As a result of the alkaline treatment of expanded glass at 90°C zeolite Na-P1 was obtained, and its crystals were observed in the whole microstructure of granules. This granulate was successfully utilized for petroleum substances (dieseland gasoline) and silicone oil sorption. Its sorption capacity was definitely higher than the values obtained by other tested mineral sorbents: clinoptilolite, zeolite A, and sorbent available at a fuel station, as well as raw expanded glass aggregates.

Acknowledgements. This work was financially supported by the National Science Centre in Poland under Grant No. 2016/21/D/ST8/01692.

5. References

Auerbach, S. M., Carrado, K. A., & Dutta, P. K. (2003). *Handbook of Zeolite Science and Technology*. CRC Press.

Bandura, L., Franus, M., Józefaciuk, G., & Franus, W. (2015a). Synthetic zeolites from fly ash as effective mineral sorbents for land-based petroleum spills cleanup. *Fuel*, *147*, 100-107. DOI: 10.1016/j.fuel.2015.01.067.

Bandura, L., Franus, M., Panek, R., Woszuk, A., & Franus, W. (2015b). Characterization of zeolites and their use as adsorbents of petroleum substances. *Przemysl Chemiczny*, *94*(3), 323-327. DOI: 10.15199/62.2015.3.11.

Bandura, L., Woszuk, A., Kołodyńska, D., & Franus, W. (2017). Application of mineral sorbents for removal of petroleum substances: A review. *Minerals, 7*(3), 1–-5. DOI: 10.3390/min7030037.

Carmody, O., Frost, R., Xi, Y., & Kokot, S. (2007). Adsorption of hydrocarbons on organo-clays-Implications for oil spill remediation. *Journal of Colloid and Interface Science*, *305*(1), 17-24. DOI: 10.1016/j.jcis.2006.09.032.

Cheeseman, C. R., Tyrer, M., Greaves, R. I. W., Lupo, R. A., & Madan, S. (2012). *U.S. Patent Application No 13/264,468*.

Franus, W., Jozefaciuk, G., Bandura, L., & Franus, M. (2017). Use of spent zeolite sorbents for the preparation of lightweight aggregates differing in microstructure. *Minerals*, *7*(2). DOI: 10.3390/min7020025.

Król, M., & Mikuła, A. (2017). Synthesis of the zeolite granulate for potential sorption application. *Microporous and Mesoporous Materials*, *243*, 201-205. DOI: 10.1016/j.micromeso.2017.02.028.

Król, M., Minkiewicz, J., & Mozgawa, W. (2016a). IR spectroscopy studies of zeolites in geopolymeric materials derived from kaolinite. *Journal of Molecular Structure*, *1126*, 200-206. DOI: 10.1016/j.molstruc.2016.02.027.

Król, M., & Mozgawa, W. (2019). Zeolite layer on metakaolin-based support. *Microporous and Mesoporous Materials*, *282*(November 2018), 109-113. DOI: 10.1016/j.micromeso.2019.03.028.

Król, M., Mozgawa, W., Morawska, J., & Pichór, W. (2014). Spectroscopic investigation of hydrothermally synthesized zeolites from expanded perlite. *Microporous and Mesoporous Materials*, *196*, 216-222. DOI: 10.1016/j.micromeso.2014.05.017.

Król, M., Wons, W., Brylska, E., Wróbel, B., & Mozgawa, W. (2016b). Wypalane kruszywo lekkie z dodatkiem zeolitów po sorpcji substancji ropopochodnych. *Materiały Ceramiczne*, *68*(3), 259-266.

Mozgawa, W., Król, M., & Pichór, W. (2009). Use of clinoptilolite for the immobilization of heavy metal ions and preparation of autoclaved building composites. *Journal of Hazardous Materials*, *168*(2-3), 1482-1489. DOI: 10.1016/j.jhazmat.2009.03.037.

Muir, B., & Bajda, T. (2016). Organically modified zeolites in petroleum compounds spill cleanup - Production, efficiency, utilization. *Fuel Processing Technology*, *149*, 153-162. DOI: 10.1016/j.fuproc.2016.04.010.

Pijarowski, P. M., & Tic, W. J. (2014). Research on using Mineral Sorbents for A Sorption Process in the Environment Contaminated with Petroleum Substances. *Civil And Environmental Engineering Reports*, *12*(1), 83-93. DOI: 10.2478/ceer-2014-0008.

Rożek, P., Król, M., & Mozgawa, W. (2018). Spectroscopic studies of fly ash-based geopolymers. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *198*, 283-289. DOI: 10.1016/j.saa.2018.03.034.

Sakthivel, T., Reid, D. L., Goldstein, I., Hench, L., & Seal, S. (2013). Hydrophobic high surface area zeolites derived from fly ash for oil spill remediation. *Environmental Science and Technology*, *47*(11), 5843-5850. DOI: 10.1021/es3048174.

Zadaka-Amir, D., Bleiman, N., & Mishael, Y. G. (2013). Sepiolite as an effective natural porous adsorbent for surface oil-spill. *Microporous and Mesoporous Materials*, *169*, 153-159. DOI: 10.1016/j.micromeso.2012.11.002.

Zhao, M. Q., Huang, J. Q., Zhang, Q., Luo, W. L., & Wei, F. (2011). Improvement of oil adsorption performance by a sponge-like natural vermiculite-carbon nanotube hybrid. *Applied Clay Science*, *53*(1), 1-7. DOI: 10.1016/j.clay.2011.04.003.