

JUSTYNA KWAŚNY, WOJCIECH BALCERZAK, PIOTR REZKA\*

## APPLICATION OF ZEOLITES FOR THE ADSORPTIVE BIOGAS DESULFURIZATION

---

## ZASTOSOWANIE ZEOLITÓW DO ADSORPCYJNEGO ODSIARCZANIA BIOGAZU

### Abstract

The article presents the issue of adsorptive removal of hydrogen sulphide from biogas using zeolite. Based on literature data, comparing performance of the biogas desulphurisation process for various mineral adsorbents, eg. activated carbon, zeolites and metal oxides, was carried out. The efficiency of biogas desulphurisation by adsorption on zeolites is significantly lower than for the activated carbons. Therefore, this article presents opportunities for improving efficiency desulphurization by modifying the structure of adsorbents.

Keywords: zeolites, biogas desulphurisation, activated carbon, biogas, adsorbents

### Streszczenie

W artykule omówiono zagadnienie adsorpcyjnego usuwania siarkowodoru z biogazu za pomocą zeolitów. Na podstawie danych literaturowych dokonano porównania wydajności procesu odsiarczania biogazu dla różnych mineralnych adsorbentów, np. węgla aktywnego, zeolitów i tlenków metali. Efektywność odsiarczania biogazu w wyniku adsorpcji na zeolitach jest zdecydowanie niższa niż dla węgla aktywnych. Dlatego też w niniejszym artykule przedstawiono możliwości zwiększenia skuteczności odsiarczania poprzez modyfikację struktury adsorbentów.

Słowa kluczowe: zeolity, biogazu odsiarczanie, węgiel aktywny, biogaz, adsorbenty

DOI: 10.4467/2353737XCT.15.358.4823

---

\* MSc. Justyna Kwaśny, DSc. PhD. Assoc. Prof. Wojciech Balcerzak, MSc. Piotr Rezka, Institute of Water Supply and Environmental Protection, Faculty of Environmental Engineering, Cracow University of Technology.

## 1. Introduction

Demand for energy increases with the development of civilization. The depletion of traditional energy resources, mainly fossil fuels, such as coal, oil and natural gas takes place. It is well known that the use of conventional energy sources promotes environmental pollution, mainly by greenhouse gases. These issues make renewable energy sources increasingly important. Renewable energy sources are a group of non-fossil sources that arise spontaneously in recurring natural processes of nature. They don't have a negative impact on the environment [1].

Biogas is produced from processing of biomass under anaerobic conditions. Biomass is one of the main renewable energy sources. Chemically, biogas consists mainly of methane and carbon dioxide, but its chemical composition depends largely on the type of the raw materials from which it is derived [1]. Hernández et al. [2] demonstrated that the landfill biogas from Pianezza MSW contains, among others, methane, carbon dioxide, water vapour, but also a substantial amount of hydrogen sulphide, mercaptans, aromatic hydrocarbons, halogenorganic and organofluorine compounds and siloxanes. While biogas, which was obtained from the sludge from wastewater treatment plants is free from halogenorganic or organofluorine compounds [3]. The most desirable component of biogas is methane, while the other gaseous substances are considered to be impurities. This is due to the fact that they do not improve the energy potential of biogas, and in addition, are corrosive. In order to increase the possibility of biogas application, its purification or treatment to natural gas quality is carried out. The essence of this process is to remove all gaseous impurities by appropriate techniques, such as adsorption.

Removal of hydrogen sulphide from biogas is called desulfurization [4, 5]. There are several methods for biogas desulphurisation, which can be divided into biological oxidation and catalytic oxidation, wet method, adsorption techniques, and a method using bog iron ore [6]. As hydrogen sulphide adsorbents coal, mineral, and mineral-carbon adsorbents are used. Zeolites are classified as mineral adsorbents.

## 2. Synthesis and modifying the structure of zeolites

Zeolites are crystalline aluminosilicates of alkali metals or alkaline earth metals. They are characterised by a regular and homogeneous structure of the pores (diameter of 2–10 Å), which are filled with water. This water is called zeolitic water, which evaporates when zeolite is heated. There are two groups of zeolites – natural and synthetic, that have a structure similar to natural. Chemically, aluminosilicates are a crystalline lattice consisting of  $\text{SiO}_4$  tetrahedra and  $\text{AlO}_4^-$  (aluminate oxyanions), which are interconnected vertices. The negative charge derived from  $\text{AlO}_4^-$  ions is compensated by cations of sodium, potassium, magnesium, calcium, strontium and barium. Type of cation depends on the type of zeolite. Among the synthetic zeolites, the A, X and Y zeolite types are mainly singled out, but some of them have counterparts in nature. The chemical composition of zeolites can be expressed by the formula  $\text{Me}_n\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x \text{SiO}_2 \cdot y \text{H}_2\text{O}$  where Me is an alkali metal cation, n is its valence and x, y are integer numbers [7].

Synthetic zeolites are prepared by two hydrothermal methods [8, 9]. The first method is based on the crystallization of the alkali aluminosilicate hydrogel of suitable composition. As the raw material sodium aluminate (aluminosilicate support material), and sodium silicate, amorphous silica and water glass as raw materials silicon carrier are used. The second method consists of recrystallization of natural aluminosilicate. In this case, the most commonly used raw materials are minerals of the kaolinite group.

The structure and chemical properties of zeolites meant that they are widely used also in the areas of environmentally-friendly methods [10]. The zeolites are used as pollutants adsorbents, detergent components and catalysts. For example, they are used to remove radionuclides from the wastewater of the nuclear industry, also to remove ammonia from the wastewater and to remove heavy metal ions (As, Pb, Cu, Zn, Cr, Cd, Ni and others) from water and wastewater [11–28]. Zeolites are also used in catalytic oxidation processes of sulphur compounds – gases from flue gas cleaning [13].

The zeolites are used as adsorbents of which structure is modified to increase their adsorption capacity, increase their capacity ion exchange, increase capacity and to obtain the more selective material (inside the zeolite crystals only those molecules whose critical diameter is no greater than the diameter of the windows can be adsorbed). The modification can be carried out by chemical and thermal treatment. Chemical modification of zeolite surface consists in the substitution of the cations  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$  by macromolecular compounds or d-block metal cations. Introduction of metals into the zeolite structure can be done by ion exchange, necking pores or prior adsorption of polar molecules [16, 17, 29, 30].

### 3. Desulfurization of biogas using zeolites

Studies on zeolites [2, 29, 31] shows that zeolites have low efficacy of adsorption of hydrogen sulphide as compared to other adsorbents. Sisani et al. [31] compared the concentration of hydrogen sulphide adsorbed on several commercial adsorbents, such as activated carbons (RGM1, RBAA1 Ultra DS and RB1), ATZ zeolite, aluminium oxide Galipur S and sepiolite. The results of what the authors have obtained are shown in Fig. 1. The highest efficiency of adsorption at 30°C was obtained using the activated carbons ( $C_{\text{ads}}$  amounted to 27.15 mg/g), whereas in the case of zeolite and sepiolite, the concentration of the adsorbed  $\text{H}_2\text{S}$  does not exceed 0.1 mg/g.

Hernández and co-workers [2] compared the efficiency of biogas desulphurisation process using copper and chromium salts-impregnated activated carbon (RGM-3), zeolite 13X, molecular sieves Sylobead 522 and Sylobead 534 and two metal oxides, which commercial names are ST and Sulfcatch ECN. Desulphurisation efficiency, which the authors obtained, is shown on Figure 2. In this case, the highest efficiency was obtained for the adsorption of activated carbon, but in the presence of steam, efficiency is significantly decreased. Zeolite 13X has proven to be far more effective than metal oxide Sulfcatch ECN and studied molecular sieves.

Micoli et al. [32] conducted biogas desulphurisation and as adsorbents, they used modified by ion exchange (Ex) and impregnated (Im) with copper and zinc ions zeolite and also impregnated with solutions of KOH, NaOH and  $\text{Na}_2\text{CO}_3$  activated carbons (AC). The results are shown in Fig. 3.

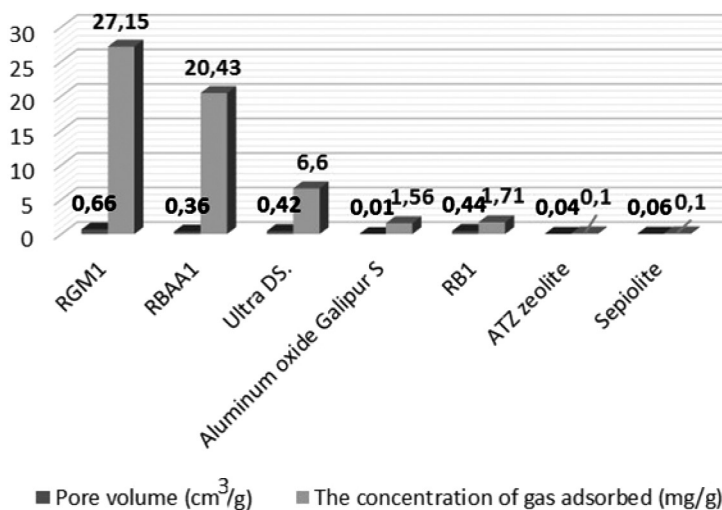


Fig. 1. Comparison of properties of some hydrogen sulphide adsorbents [31]

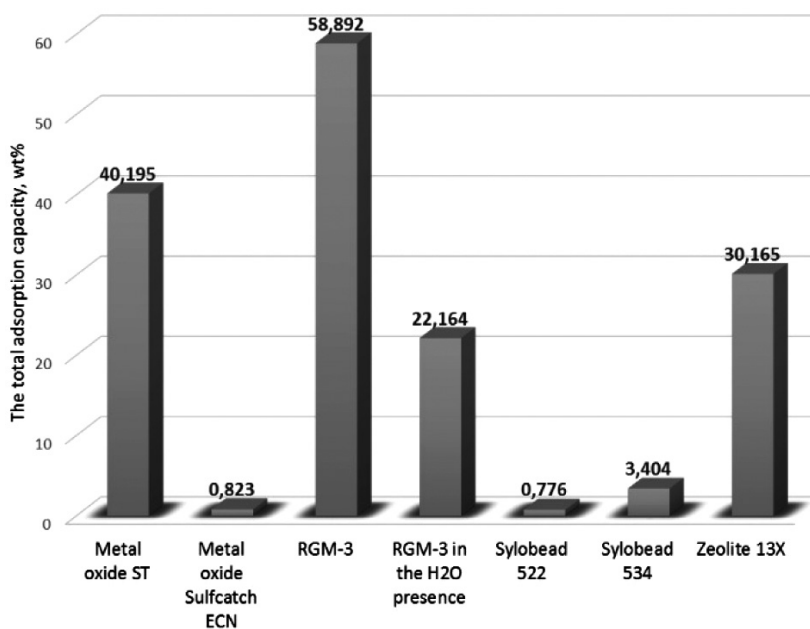


Fig. 2. The effectiveness of biogas desulphurisation for a variety of commercial adsorbents [2]

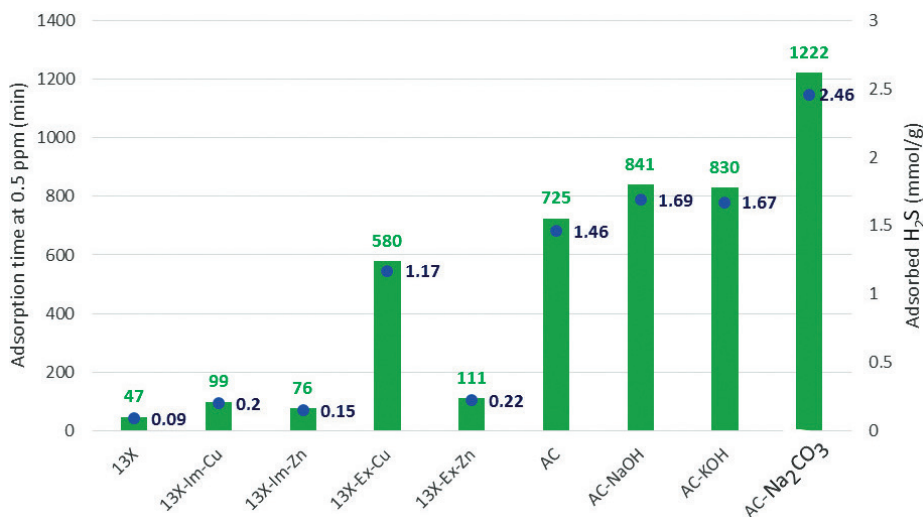


Fig. 3. The operating time (the H<sub>2</sub>S concentration of 0.5 ppm), and the adsorption efficiency of the tested adsorbents – activated carbon and zeolite [32]

In the case of zeolites, all modified and impregnated samples achieved better results (two times longer operating time of the adsorbent – 300 min.) than the parent zeolite sample. The most effective was the one that was modified by ion exchange with copper ions zeolite, whose operation time was significantly longer than the others and was over 600 minutes at the H<sub>2</sub>S concentration of 0.5 ppm. However, much better results were obtained with activated carbons. The best was impregnated by Na<sub>2</sub>CO<sub>3</sub> solution activated carbon whose work time was longer than the others and was more than 1,400 min. and additionally, absorbed greater amounts of H<sub>2</sub>S. Micoli and colleagues studies [32] confirmed the better efficacy of carbonaceous adsorbents with respect to the zeolites. The authors also confirmed the thesis that modifying of zeolites increases the desulphurisation efficiency.

#### 4. Conclusion

Zeolites have been used as adsorbents because of their chemical structure and properties. They are characterised by the selectivity of adsorption associated with particle size and with their polarity. These adsorbents are capable of selective adsorption of polar molecules, such as water and hydrogen sulphide. Unfortunately, in the case of hydrogen sulphide, the adsorption efficiency is not satisfactory. Frequently, the effectiveness of adsorption on zeolites is much lower than on activated carbon. In order to increase the efficiency of adsorption on zeolites, the modification of their structure is carried out. This modifications cause a change in pore size. Depending on the used modifier ions, enlargement or reduction of the pore diameter occurs. In the first case, the molecule of larger size, e.g. n-paraffin hydrocarbons, are adsorbed. In the second case, only small polar molecules (such as water, hydrogen sulphide) are adsorbed. In order to increase the efficiency of biogas desulphurisation using zeolites, modification of their structure in the direction of reducing the pore diameter must be carried out.

## References

- [1] Kwaśny J., Banach M., Kowalski Z., *Przegląd technologii produkcji biogazu różnego pochodzenia*, Czasopismo Techniczne 2-Ch/2012, 83-102.
- [2] Hernández S.P., Scarpa F., Fino D., Conti R., *Biogas purification for MCFC application*, International Journal of Hydrogen Energy 36, 2011, 8112-8118.
- [3] *Biogas renewable energy*, www.biogas-renewable-energy.info/ (available: 30.03.2015).
- [4] Peu P. et al., *Prediction of hydrogen sulphide production during anaerobic digestion of organic substrates*, Bioresource Technology 121, 2012, 419-424.
- [5] Gutiérrez Ortiz F.J., Aguilera P.G., Ollero P., *Biogas desulfurization by adsorption on thermally treated sewage-sludge*, Separation and Purification Technology 123, 2014, 200-213.
- [6] Pokorna D., Zabranska J., *Sulfur-oxidizing bacteria in environmental technology*, Biotechnology Advances, 2015, in press <http://dx.doi.org/10.1016/j.biotechadv.2015.02.007>.
- [7] Figueiredo H., Quintelas C., *Tailored zeolites for the removal of metal oxyanions: Overcoming intrinsic limitations of zeolites*, Journal of Hazardous Materials 274, 2014, 287-299.
- [8] Jon H. et al., *Hydrothermal conversion of FAU into \*BEA zeolites*, Microporous and Mesoporous Materials 96, 2006, 72-78.
- [9] Kong Ch., Tsuru T., *Zeolite nanocrystals prepared from zeolite microparticles by a centrifugation-assisted grinding method*, Chemical Engineering and Processing 49, 2010, 809-814.
- [10] Rhodes C.J., *Zeolite mediated reactions: Mechanistic aspects and environmental applications*, Progress in Reaction Kinetics and Mechanism 33, 1, 2008, 1-79.
- [11] Colella C., *Natural zeolites in environmentally friendly processes and applications*, Studies in Surface Science and Catalysis 125, 1999, 641-655.
- [12] Colella C., *Recent advances in natural zeolite applications based on external surface interaction with cations and molecules*, Studies in Surface Science and Catalysis 170, 2007, 2063-2073.
- [13] Colella C., *Natural zeolites in environmentally friendly processes and applications*, [in:] Kiricsi I., Nagy J.B., Pál-Borbély G., Karge H.G., *Porous Materials in Environmentally Friendly Processes*, Studies in Surface Science and Catalysis 125, 1999, 641-650.
- [14] Anielak A. M., Wojnicz M., Piaskowski K., *Ocena skuteczności zastosowania zeolitów w oczyszczaniu ścieków komunalnych*, Gaz, Woda i Technika Sanitarna 7-8, 2009, 27-31.
- [15] Anielak A. M., Schmidt R., *Removal of As (III) and Cr (III) on modified clinoptylolite*, Polish Journal of Environmental Studies 24, 2, 2015, 477-482.
- [16] Schmidt R., Anielak A. M., *Usuwanie Cu(II) i Ni(II) na modyfikowanym klinoptylolicie*, Przemysł Chemiczny 90, 4, 2011, 1-4.
- [17] Anielak A. M., Schmidt R., *Sorption of lead and cadmium cations on natural and manganese-modified zeolite*, Polish Journal of Environmental Studies 20, 1, 2011, 15-19.
- [18] Anielak A. M., Smarzyńska M., *Oczyszczanie ścieków zeolitami naturalnymi w systemie SBR na oczyszczalni w Krokowej*, Gaz, Woda i Technika Sanitarna 5, 2007, 30-35.
- [19] Díaz E., Ordóñez S., Vega A., Coca J., *Inverse GC investigation of the adsorption of thiophenic compounds on zeolites*, Chromatographia 64, 3-4, 2006, 207-213.

- [20] Liao J.-J., Bao W.-R., Chang L.-P., *An approach to study the desulfurization mechanism and the competitive behavior from aromatics: A case study on CeY zeolite*, Fuel Processing Technology, 140, 2015, 104-112.
- [21] Ozekmekci M., Salkic G., Fellah M.F., *Use of zeolites for the removal of H<sub>2</sub>S: A mini-review*, Fuel Processing Technology 2015 in press.
- [22] Nagarjuna R., Challagulla S., Alla N., Ganesan R., Roy S., *Synthesis and characterization of reduced-graphene oxide/TiO<sub>2</sub>/Zeolite-4A: A bifunctional nanocomposite for abatement of methylene blue*, Materials and Design 86, 2015, 621-626.
- [23] Chalupka K.A., Maniukiewicz W., Mierczynski P., Maniecki T., Rynkowski J., Dzwigaj S., *The catalytic activity of Fe-containing SiBEA zeolites in Fischer–Tropsch synthesis*, Catalysis Today 257, 2015, 117-121.
- [24] Śrębowata A., Tarach K., Girman V., Góra-Marek K., *Catalytic removal of trichloroethylene from water over palladium loaded microporous and hierarchical zeolites*, Applied Catalysis B: Environmental 181, 2016, 550-560.
- [25] Behin J., Kazemian H., Rohani S., *Sonochemical synthesis of zeolite NaP from clinoptilolite*, Ultrasonics Sonochemistry 28, 2016, 400-408.
- [26] Simon V., Thuret A., Candy L., Bassil S., Duthen S., Raynaud C., Masseron A., *Recovery of hydroxycinnamic acids from renewable resources by adsorption on zeolites*, Chemical Engineering Journal 280, 2015, 748-754.
- [27] Pandey P.K., Sharma S.K., Sambhi S.S., *Removal of lead(II) from waste water on zeolite-NaX*, Journal of Environmental Chemical Engineering 3, 2015, 2604-2610.
- [28] Zhao J., Wang G., Qin L., Li H., Chen Y., Liu B., *Synthesis and catalytic cracking performance of mesoporous zeolite Y*, Catalysis Communications 73, 2016, 98-102.
- [29] Xu X., Yang W., Liu J., Lin L., *Synthesis and perfection evaluation of NaA zeolite membrane*, Separation and Purification Technology 25, 2001, 475-485.
- [30] Kim J.-H., Kang S.W., Nah I.W., Oh I.-H., *Synthesis and characterization of Fe-modified zeolite for spin conversion of hydrogen at cryogenic temperature*, International Journal of Hydrogen Energy 40, 2015, 15529-15533.
- [31] Sisani E. et al., *Adsorptive removal of H<sub>2</sub>S in biogas conditions for high temperature fuel cell systems*, International Journal of Hydrogen Energy 39, 2014, 21753-21766.
- [32] Micoli L., Bagnasco G., Turco M., *H<sub>2</sub>S removal from biogas for fuelling MFCs: New adsorbing materials*, International Journal of Hydrogen Energy 39, 2014, 1783-1787.