

## Application of micro- and nanostructural multifunctional halloysite-based sorbents from DUNINO deposit in selected biotechnological processes

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### ABSTRACT

**Purpose:** The aim of this paper was to present some research data from real industrial tests of halloysite-based sorbents in simultaneous removal of various groups of gaseous hazardous substances produced in selected industrial-scale biotechnological processes. Special attention was paid on effectiveness of original, newly developed micro- and nanostructural, universal “Dunino” halloysite-based sorbents in simultaneous removal of odors, ammonia, hydrogen sulphide, silanes, siloxanes and VOCs.

**Design/methodology/approach:** Numerous studies including SEM, analytical method of continuous flame-ion detection (FID), identification of outlet gas stream composition with spectrophotometric methods, olfactometry tests and practical verification in real industrial-scale biotechnological processes were made to examine sorption properties of the halloysite-based filters.

**Findings:** Newly invented nanostructural multifunctional halloysite-based sorbents show high capabilities in respect to simultaneous removal of unwanted substances from biotechnological processes penetrating into natural environment, e.g. odors, ammonia, hydrogen sulphide, silanes, siloxanes, VOCs.

**Research limitations/implications:** Experimental studies described in this work should contribute to improvement of halloysite-based sorbents composition and optimal selection of their work parameters.

**Practical implications:** Enhanced research results in the discussed problem area will make appropriate, rational composition of filtration bed possible – sorbent mixture (halloysite with other sorbents admixtures, natural or synthetic), disintegration degree (granulated form, powder, dust), activation method (physical, chemical) and optimal conditions for interphase contact between sorbent of a given size distribution and purified gas stream to reach the possibly maximal efficiency in unwanted components removal.

**Originality/value:** Newly invented nanostructural halloysite-based sorbents demonstrate higher sorption capabilities in relation to known conventional solutions, moreover simultaneous sorption of many hazardous species is possible.

**Keywords:** Halloysite; Micro- and nanostructural sorbent; Odors; Ammonia; Hydrogen sulphide

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## PROPERTIES

### 1. Introduction

Quantitative and qualitative reduction of unwanted substances penetrating into natural environment, e.g. odors, ammonia, hydrogen sulphide, silanes, siloxanes, VOCs becomes in the present day a serious technical challenge. In more and more commonly applied biotechnological processes of various scales, like e.g. biogas plants, composting plants, biological wastewater treatment plants, etc. one can observe high variability within the reacting systems. Characteristic feature of biotechnological processes is uncontrolled side-synthesis of large amount of unwanted, hazardous substances [1-16]. Such biotechnologies must be thus closely integrated with modern technical solutions, making significant decrease of potentially adverse effects on the environment possible. One of more popular methods for reduction of concentration of gaseous impurities from biotechnological processes are sorption methods [17,18]. However, an essential drawback of commonly used methods is their selectivity. In result complex cleaning systems, of strictly and precisely determined work parameters of many devices in series must be designed and constructed. One of technical variants representing both demanded here low selectivity and high general efficiency for purification of waste gases can be application of appropriate filter construction filled with specific sorbents. Material inside the filter should provide high efficiency and universality at the same time, resulting in compact size of the device. Working as the multifunction system, it should demonstrate not only sorption, but also catalytic properties. It may be at the same time also optionally used as a convenient substrate for microorganism cultures. In this work authors presented new, original material with a complex micro- and nanostructure, based on specific aluminosilicate, halloysite, mineral from “Dunino” (Poland)

deposit. The discussed sorbent was then subject of preliminary physicochemical processing resulting in final specific material of chemical affinity to a broad range of substances, usually of diverse intrinsic properties. Depending on individual requirements of a given final application it can be a subject of further, addressed modifications. Activation of halloysite resulted in rise of its specific surface area, porosity (at very broad pore size distribution) and amount of active sites. Such technological approach should originally be part of environmental-friendly, green technologies, thus spent sorbent from the filter should also not cause later any hazard for biosphere. One of the authors' assumption was elaboration of efficient technology for gas stream purification in ambient temperature and pressure, what significantly simplifies technological and constructional conditions of the process and can be also decisive economical criterion in selection of purification method.

Neutralization of organic wastes in such processes like composting or methane fermentation is connected with side-generation of various odor substances. Concentration of odor substances in gases produced during composting usually exceeds 180,000 ou/m<sup>3</sup> [19]. From within many odor substances into the most unpleasant one can include ammonia and hydrogen sulphide, as well as numerous VOCs. Ammonia emission during composting of organic fractions of municipal wastes varies from 18 to 150g NH<sub>3</sub>/Mg wastes [20]. Non regulated in legislative and technical aspects unequivocal status of air quality in Poland and EU, lack of standards and methodology of smell grade assessment are mainly responsible for low efficacy of administrative decisions ordering to do the source reduction of odors emission. One of the consequences is lack of the “EU odour directive”, being the subject of legislative works for many years. However, discomfort and community protests are especially manifested locally

during construction of new biotechnological plants or municipal wastes processing plants (composting plants, wastewater treatment plants, food industry establishments, etc.). Removal of odor substances from the air can be nowadays done using such techniques like: burning, adsorption on active coal, absorption with the use of reactive oxidizing solution and biological methods [21]. Considering this, authors decided to verify experimentally the properties of newly elaborated micro- and nanostructural halloysite-based sorbent beds for simultaneous removal of various odors from the postprocessed air.

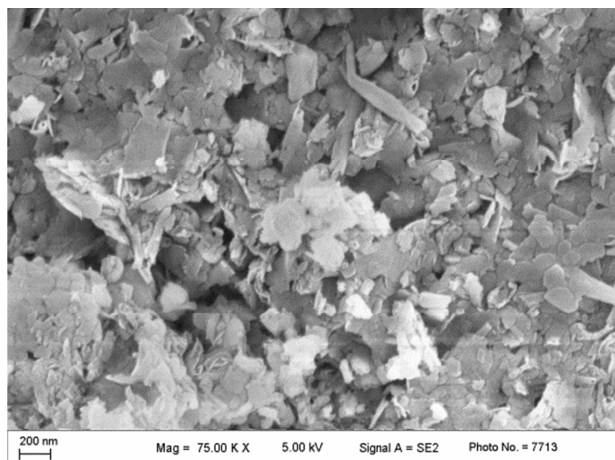


Fig. 1. Nanoplates and nanotubes identified in structure of halloysite from “Dunino” deposit (SEM)

Extensive research done so far around the world led to the development of solutions that reduce significantly the risk of the environment contamination, but none of them is able to eliminate them completely. A number of research [4-18] allowed to assess the influence of the physicochemical factors on the sorption run and efficiency. Because of their broad, universal sorption capabilities clay, silica mineral sorbents and zeolites are the subject of high interest. One representative of such type minerals classified into layered aluminosilicates from kaolinite subgroup is halloysite, being in the present day object of intensive basic and applicative research [22, 23], e.g. as a matrix for enzyme immobilization [24], catalyst [25], matrix for porous materials synthesis [26] or high-efficiency sealing systems production [27]. Halloysite may be used for many purposes, especially in the environment protection, e.g. for the manufacturing of sorbents, coagulants for municipal and industrial wastewater treatment, remediation of postindustrial ecologically degraded areas, landfills, catalysts and fillers for nanocomposites [27-31].

Authors attention was directed on unique natural nanostructures of halloysite-nanotubes and nanoplates

(Fig. 1). Similar observations concerning the halloysite structures are presented in the available literature [32]. Halloysite originated from “Dunino” deposit was used for the study. The open pit mine is located in Lower Silesia (this is one of some currently exploited deposits of this mineral in the world). “Dunino” deposit contains at least 10 million tons of a homogeneous raw material. Halloysite extracted from this deposit is a product of basalt weathering. Microscopic view of the material used for the research is presented in Fig. 1.

As a mineral, halloysite belongs to the kaolinite subgroup which is represented by the same chemical formula  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ , where  $n$  is the number of water molecules that occupy the interlayer spaces of the clay aggregates. The value of  $n$  is zero for kaolinite and up to 4 for halloysite. Halloysite mineral contains a layer of water in its interlayer space which results in increase in layer thickness up to 1.01 nm [33, 34]. The interlayer water molecules of halloysite can easily and irreversibly be removed by a slight increase in the temperature, which, in turn, results in formation of the 0.7 nm halloysite characterized by the interlayer distance ranging from 0.718 nm up to 0.75 nm (Fig. 2). However, after a dehydration process the halloysite platelets stay separated. Structural unit of halloysite consists of two sheets: Si-tetrahedra and Al-octahedra. The octahedral external surface is built up from the hydroxyl groups with outstanding hydrogen and has positive surface charge when the oxygen surface of the tetrahedral sheet has negative charge. Halloysite from “Dunino” deposit is also characterized by a great number of substitutions (e.g. Fe, Ti, Mg for Al and Al, Fe, Ti for Si). These substitutions create a big number of active sites with unbalanced charge playing a very important role for the sorption capacity. Another advantage of halloysite is its ability to absorb large amounts of ion particles and heavy metals, e.g. Pb(II), Zn(II), Cd(II) and As(V) [35-38].

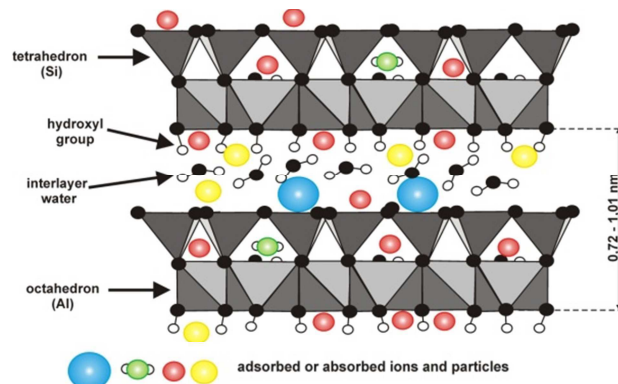


Fig. 2. Structure of halloysite

The surface charge can be radically changed by cation substitution. In opposition to kaolinite, single halloysite plates are not touched together; there is usually a bigger distance between the layers than the one in kaolinite which stems from the presence of either water or different cations. In kaolinite the layers are held together by strong hydrogen bonds between the oxygen from the tetrahedral layer and hydrogen from the octahedral hydroxyl group. Halloysite from "Dunino" deposit, in opposition to kaolinite, is characterized by the great number of Al atoms substitutions in octahedral layer for divalent atoms (usually Mg or Fe), trivalent Fe or four-valent Ti. Furthermore, Si in the tetrahedral sheet is often replaced by Al and Fe [39, 40]. This substitution changes the local microstructure creating new possibilities for different bonds on both sides of a single layer, which is not possible with, for example, montmorillonite [40].

Halloysite has Si-tetrahedral sheet on one side and a Al-octahedral sheet on the other. The oxygen atoms of halloysite tetrahedra form a regular 6-fold hexagonal structure. This structure remains intact even after dehydration which suggests that either the "hole" water remains within the structure or that the rotation is blocked by physical forces [39, 40]. The hexagonal shape of the hole can remain intact also due to the activity of Fe-cations substituted for Al in the octahedra. This causes cation activity which can be incorporated to the cavity or has better conditions to close near the sheet surface and form an inner-sphere complex.

When using halloysite, this sheet forms the surface of the basic unit. Each Al atom is connected to three external hydroxyl groups and to one inner hydroxyl group that can be found on the tetrahedral sheet. These groups are very active in forming different bonds within wide pH area. This original structure of halloysite can be modified by means of thermal and chemical treatment increasing its specific surface area, pore size distribution and the number of active sites within it. Considering wide possibilities of modification and adaptation of halloysite composition and structure responsible for sorption ability in case of mixture with a given impurity composition, the halloysite-based filtration-sorption systems can be used, among others, in purification of strongly diverse in respect to chemical composition gaseous products from biotechnological processes. Because of limited theoretical knowledge making full explanation and rational prediction of sorption phenomena possible, in such complex process environments data necessary for proper design of such filters can be obtained nearly exclusively on the basis of laboratory or industrial experiments.

Presented specific properties and experimentally verified sorption efficiency of halloysite-based sorbent in

various process systems [39-42], point on broad potential possibilities and applicability area, especially resulting from high-effective, simultaneous removal of many hazardous and toxic compounds from gaseous mixtures of complex chemical composition and strongly diversified concentration ranges of individual components [42].

Important and decisive proecological aspect of the proposed technology is also fact, that halloysite, as a natural mineral present in biosphere, is inert to ecosystem. Contrary to active coal it is non-flammable (self-ignition resistant). Mechanical parameters of the bed are stable under the influence of humidity and water, what is important in case of humid gases processing or hazard of flooding the bed in emergency situation. The key economical factor can be also its relatively low, competitive market price.

## 2. Materials and research methodology

In biotechnological processes, like e.g. methane fermentation or composting, large complexity within the reacting system is usually observed. It covers, among others, phenomena observed in multiphase solid-liquid or solid-liquid-gas systems, numerous parallel or consecutive reactions, catalyzing or inhibiting effect of products or not totally converted substrates. Equally important is also variation in time of chemical and phase composition of process environment in case of batch processes. In such processes one usually observes synthesis, besides main product(s), also large amount of unwanted compounds, usually in trace concentrations. These form, however, essential fraction, responsible for chemical purity of the product, as well as serious hazard for the natural environment. Purification of gaseous products from biochemical processes based on sorption should be possibly inexpensive, easy handling, while sorbent alone should characterize by large unit yield (sorption capacity), as well as efficiency of simultaneous removal of both identified and unidentified impurities. Halloysite-based sorbents characterize by developed, and at the same time relatively easily accessible sorption active specific surface (raw halloysite 65-80m<sup>2</sup>/g, appropriately physicochemically activated halloysite even up to 450-500 m<sup>2</sup>/g). Specific structure (micro-, mezo- and macropores), after activation reaching even up to 85% in volume, provides also simultaneously small flow resistance of purified gas, what is advantageous for constructional and exploitational filter parameter. Halloysite and manufactured on its basis sorbents can find them useful in target technological applications, both directly (in raw form, of different disintegration degree of original mineral), and in dried,

roasted or chemically activated forms. Halloysite-based sorbent, depending on process needs and a given technology requirements, can be contacted with purified gas as water suspension, dust, powder or in granulated form. Presence of interlayer water creates additional possibility of sorption mechanism occurrence for some compounds with the use of hydrogen bonds.

Experiments were done with initially raw halloysite exposed to multistage chemical and thermal processing (INTERMARK's internal technical procedure). Prepared this way material forming the bed was placed inside an original filter construction. Experiments were carried out with the use of filter device especially designed for long-term tests of filtration-sorption processes in real conditions of biotechnological plant work since these were located in industrial scale objects.

Preliminary verification of halloysite-based sorbent properties for reduction of concentration of unwanted gaseous products covered experimental tests in three different applications oriented for simultaneous sorption of:

- siloxanes and hydrogen sulphide ( $\text{H}_2\text{S}$ ) from the biogas production system integrated with system of municipal wastewater treatment plant *Aquanet* in Poznań,
- hydrogen sulphide ( $\text{H}_2\text{S}$ ), ammonia ( $\text{NH}_3$ ) and volatile organic compounds (VOCs) from bioreactor for waste protein hydrolysis in Olkusz,
- odors emitted from four composting plants located in southern Poland.

The research stand was equipped with 4 internal filtration sections with the possibility of direct sampling of both purified gas (within flow range of  $2\text{-}20\text{ m}^3/(\text{m}^2\text{h})$ , and bed's material itself without the necessity of breaking the continuous work mode of the installation. Experimental plant makes identification of: current efficiency/selectivity of sorption, current composition of the bed, optimal fraction of the sorbent, necessary total height of layer and process time corresponding to full saturation of the bed working under given process conditions (the breakthrough point), as well as the purposefulness of diversification the bed into filtrating sections possible. For the used measurement method and equipment, considering local conditions during the instrument readings the measurement uncertainties are:  $\text{H}_2\text{S}$  concentration: 8.2%,  $\text{NH}_3$  concentration: 8.7%, VOCs concentration: 5.0%.

In the first test series framework in a given time intervals analytical measurements (chromatographic methods) of concentrations were done in respect to the following silica compounds: hexamethyldisiloxane, octamethylthreesiloxane, decamethyltetrasiloxane, hexamethylcyclothreesiloxane, octamethylcyclo tetra-siloxane, decamethylcyclopentasiloxane, tetramethylsilane, three-methylsilanol, as well as total concentration of all silica

compounds and hydrogen sulphide in the gas phase.

Experiments in the second test series framework focused on determination of possibility of simultaneous removal of: hydrogen sulphide, ammonia and volatile organic compounds (VOCs) in outlet gases from hydrolysis bioreactor (working volume  $2\text{ m}^3$ ) were done also with application of the bed composed of micro- and nanostructural multifunctional "Dunino" halloysite-based sorbent. Concentration of  $\text{H}_2\text{S}$  in the outlet gas stream was determined with spectrophotometric method-object sampling and samples analyses were done according to research procedure PB-956/02/2012, 2 ed. from 01.02.2013. Identification of  $\text{NH}_3$  concentration in the outlet gases from bioreactor was also based on spectrophotometric method-sampling followed by analysis were done according to research procedure PB-95/02/2012 2 ed. from 01.02.2013. Total concentration of VOCs was determined with automatic analyzer using the method of continuous flame-ion detection (FID).

Odors concentrations (third test series framework) were tested in real conditions provided by four composting places in Poland with the use of olfactometer TO 7 according to PN\_EN 13725 norm restrictions.

### 3. Results and discussion

In case of first measurement series biogas purification ran with the use of sorbent presented in Fig. 3. Silica compounds (siloxanes) content in a raw biogas produced in a plant integrated with technological system of municipal wastewater treatment plant, as well as the effects of their concentrations reduction as a result of halloysite-based sorbent use through 25 days are presented in Figs. 4,5 as well as in Table 1. On the basis of analysis one can confirm dominating (ca. 90% in average) fraction of decamethylcyclopentasiloxane and octamethylcyclo tetrasiloxane (ca. 8% in average) compounds in a gas mixture from biogas plant. Concentration of other silica compounds was  $<0,1\text{ mg}/\text{Nm}^3$ . Methane content in a raw biogas was 64.5 - 68.1%, while hydrogen sulfide 39 - 342 ppm. Concentration of silica compounds at the filter outlet did not exceed  $5.5\text{ mg}/\text{Nm}^3$ . This value is acceptable by requirements concerning quality of biogas for internal ignition engines. The research demonstrated also the halloysite-based sorbent ability for simultaneous reduction of hydrogen sulfide concentration (to  $<40$  ppm level). None disadvantageous effect of  $\text{H}_2\text{S}$  co-presence in purified biogas on silica compounds sorption was observed.

Harmful influence of siloxanes on the work of internal combustion engine fed with biogas can be demonstrated by cylinder head in engine fed with crude and purified biogases (Fig. 5 and Fig. 6 respectively).

Spark plug is completely clogged, the valves covered by deposit and thus damaged. After siloxanes burning fine-grained silica is produced, which as deposit covers sparking plugs, valves, piston and internal surface of cylinder head, as well as elements of turbocompressor making their overheating leading to mechanical defects (Fig. 6). Silica also easily penetrates into lubricating oil making strong acceleration in bearings, pistons and cylinders surface consumption. These phenomena shorten times between the engines overhauls and lubricating oil renewal, as well as generate significant rise in exploitation costs, thus overall costs of electrical energy generation. It was observed, that lowering of silica components content can extend the lubricating oil durability even 3-time, whereas inspection times even several times.

During the tests oxygen content represented 0-0.3%. During experiments filtration device was provided with small amount of air to make continuous autoregeneration of the bed possible.

In case of second measurement series gas product from bioreactor for waste protein hydrolysis, containing the following odor compounds: hydrogen sulphide, ammonia and numerous group of volatile organic compounds (VOCs) (without the possibility of their individual analytical identification) was processed. Experimental tests were done in two technological variants of the given gas mixture purification-alternatively using a cascade system of three washers and single filter with "Dunino" halloysite-based sorbent. Comparison of the results is presented in Table 1.

The filtration-sorption system of micro- and nanostructural "Dunino" halloysite-based sorbents demonstrated clearly higher efficiency in purification of gas mixtures after biotechnological processes of hydrolysis from all analyzed unwanted compounds than classical system composed of three washers arranged in series.

It should be emphasized, that concentrations of  $\text{NH}_3$ ,  $\text{H}_2\text{S}$  and volatile organic compounds (VOCs) in biogas after "Dunino" halloysite-based sorbent fulfill the requirements of Regulation of Minister of Labour and Social Policy from 29 11 2002 (Dz. U. No 217, item 1833). Contrary, in case of currently used cascade system of three washers the norm is not fulfilled anyway.

In case of third measurement the postprocessed air from four composting plants located in southern Poland was flittered. The industrial filter capacity (Fig. 7) was  $4000 \text{ m}^3/\text{h}$ .

Crucial problem in compost plants is odour emission. Postprocessed air contaminated with odors entered the filter directly, without any preprocessing-promptly from the windrows packed into plastic sleeves (see Fig. 7). The halloysite adsorber, because of its high specific surface area and porosity, provides very good conditions for the growth of microorganisms population typically observed in

classical biofilters. This way such filter after a short time after its installation (lag-time for bacteria population) simultaneously offers the double role: as a mineral filter and as an inorganic biofilter. It results in the higher sorption capacity towards various gas impurities and longevity significantly longer than for typical organic biofilters.



Fig. 3. The halloysite-based sorbent after sorption process



Fig. 4. Gas engine cylinder head after 1500h exploitation without any filter, with deposit caused by siloxanes



Fig. 5. Biogas engine cylinder head after 1500 h exploitation with micro- and nanostructural multifunctional halloysite-based sorbents from "Dunino" deposit



Fig. 6. Deposit on the turbocharger of a biogas engine formed by siloxanes



Fig. 7. Halloysite-based postprocessed air filter working in industrial-scale compost plant

Table 1.

Comparison of process effectiveness for the filtration-sorption system composed of micro- and nanostructural “Dunino” halloysite-based sorbents in respect to  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ , VOCs, siloxanes and odors removal.

Impurity type	Inlet concentration, [ $\text{mg}/\text{m}^3$ ]	Outlet concentration (after sorbent), [ $\text{mg}/\text{m}^3$ ]	Reduction, [%] (varied during the tests)
Ammonia ( $\text{NH}_3$ )	370-575	<1	>99
Hydrogen sulphide ( $\text{H}_2\text{S}$ )	164	<0.8	>99
Volatile organic compounds (VOCs)	3.4-4.2	0.8-1.1	70-81
All Si compounds	9.9-50.3	0.1-5.5	78-99
Odours-compost plants			
	Odors-inlet concentration [OUe]	Odors-outlet concentration [OUe]	Reduction [%]
Composting plant A	212470	1512	99.29
		1579	99.26
		1722	99.19
Composting plant B	327680	1579	99.52
		1798	99.45
		1878	99.43
Composting plant C	210000	450	99.79
Composting plant D	305000	800	99.74

Table 1 presents comparison of process effectiveness for the filtration-sorption system composed of micro- and nanostructured “Dunino” halloysite-based sorbents in respect to  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ , VOCs, silanes and odors removal. The results from research were collected together under study in municipal wastewater treatment plant, bioreactor for waste protein hydrolysis and four composting plants.

#### 4. Conclusions

Micro- and nanostructural “Dunino” halloysite-based sorbent was used for simultaneous removal of selected impurities present in gaseous products from various, typical

biotechnological processes. During research done with biogas producing plant high efficiency of siloxanes sorption (78-99%) was observed, with simultaneous reduction of  $\text{H}_2\text{S}$  concentration to <40 ppm level. In case of purification of gas formed during waste protein hydrolysis simultaneous sorption efficiency of halloysite-based sorbent was:  $\text{NH}_3$  95-99%,  $\text{H}_2\text{S}$  >99%, volatile organic compounds (VOCs) 70-81%, appropriately. In case of odours removal from composting places 99.2-99.8% effectiveness was experimentally confirmed. Proposed technical solution is waste-free because after reaching saturation state the spent halloysite-based sorbent can find itself useful in agriculture or gardening as a valuable fertilizer component. Significant reduction of odours

concentrations in composting plants under study, reaching even 99%, makes successful implementation of halloysite-based sorbents in many commercial applications possible.

Based on the research results one can conclude, that micro- and nanostructural filtration beds composed of "Dunino" halloysite-based sorbent can work independently in different technological systems used for purification of outlet gases from various bioreactors systems, in various biotechnological processes. It can be also used as an optional supplement of already existing technical constructions facing the significant problem of inhomogeneity of chemical composition of hazardous gaseous wastes.

The comprehensive "Dunino" halloysite-based sorbent made effective, simultaneous reduction of concentrations of various impurities in outlet gases, what is its unique merit. Next essential merit is a possibility of secondary utilization of the saturated, spent sorbent bed from the filter as a mineral fertilizer component or soil substitute. This way total elimination of burdensome in exploitation cascade system of three washers and their replacement with one, more effective, compact and multifunctional halloysite-based filter is possible. Important economic factor is also prospect of eliminating the problems with utilisation of spent sorbent regarded as a troublesome solid waste. During the preliminary research tests on the bed it turned out, that this bed was not fully saturated yet (clear breakthrough point was not observed) retaining, at least partly, some sorption potential simultaneously with still high efficiency of reductions of gaseous impurities concentrations. Further research is thus necessary, especially oriented for identification of maximal permissible exploitation parameter values and corresponding bed capacities, as well as for later optimisation of its working conditions (height-including single bed's height, working time-saturation, possibility and profitability of eventual regeneration, modification of composition and fractions within the bed, linear velocity of purified gas flow, flow hydrodynamics, critical velocity for fluidisation, flow resistances-pressure drop within the bed, etc.).

Also theoretical, at last partly, interpretation of the observed phenomena and establishing their mechanism(s), kinetic aspects and explanation of physicochemical conditions of simultaneous sorption of many components (e.g. competition, inhibition effects), sorbent yields and their eventual regeneration abilities will be possible.

Halloysite-based sorbents can be regenerated many times, however regeneration method depends mainly on the adsorbed impurity types. In case of siloxanes simple thermal regeneration is satisfactory enough since these compounds can be emitted into atmosphere, are not harmful for the environment and are subject of natural decomposition in biosphere. In case of hydrogen sulphide regeneration with oxygen is possible, both during bed's

work and during its work breaks. Other impurities found in biogas and postprocessed air require application of individual procedures dependent on their chemical composition and individual physicochemical properties.

Enhanced research results in the discussed problem area will make appropriate, rational composition of optimal combination and proportions of filtration bed possible-sorbent mixture (halloysite with other sorbent admixtures, natural or synthetic), disintegration degree (granulated form, powder, dust), activation method (physical, chemical) and optimal conditions for interphase contact between sorbent of a given size distribution and purified gas stream to reach the possibly maximal efficiency in unwanted components removal.

It should be also mentioned about other authors research on application of micro- and nanostructural, multifunctional "Dunino" halloysite-based sorbents in biofiltration processes. Halloysite, as a material inert for biosphere, creates environment for microorganisms, in appropriate and strictly defined conditions like: humidity, temperature and pH. Bacteria present in filtration material (biofilm) are responsible for degradation of dissolved impurities during their metabolic processes, removing thus these compounds from the purified gas stream. In case of research on the filters working in composting plants presence of numerous microorganisms (bacteria, fungi, etc.) within halloysite-based sorbent structure, derived from proper inoculation, was confirmed.

It is phenomenon requiring further research. The most important fact is that, contrary to typical biofilters, the halloysite-based filters were not subject of any water humidifying nor fed with any nutrients. This observation, however, confirms that halloysite is a very advantageous medium for bacteria metabolism environment, thus this type filters combine both adsorption filters and biofilters properties.

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## Additional information

Selected issues related to this paper are planned to be presented at the 22<sup>nd</sup> Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME'2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS'2015 celebrating the 10<sup>th</sup> anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering.

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