

Application of halloysite sorbent for ammonia and odors removal from dry toilet facilities

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Abstract

Halloysite sorbent was added to liquid urine (dose 10 g/dm³) and solid faeces (unmodified structure, dose 50 g/kg) being a subject of anaerobic fermentation in a hermetic system for 20 days. Identification of surface morphology and elementary chemical composition in microregions of the spent sorbent were done using scanning electron microscope Zeiss Supra 35 equipped with EDS detectors. Both grain surface and mixed internal and external part of the grain after its shredding were analysed. It can be concluded, that shredding of the halloysite sorbent before application is recommended, preventing its pores clogging thus blocking accessibility to deeper fraction of active sorption surface. Technological concepts of possibilities of halloysite sorbent application in dry toilets are presented and discussed.

Ammonia emission, odors emission, halloysite, sorption, ammonia and odors removal

Introduction

Common application of dry toilets is strongly connected with elaboration of new, efficient and inexpensive methods of their safe and environmentally friendly exploitation. To be an attractive technological approach in the present market, practically no harmful effects should be observed. One of potential crucial factors significantly influencing the future development of dry toilets is undoubtedly ammonia [1-16] and odors [17-23] emission connected with biological processes of liquid urine and faeces decay. These processes occur spontaneously during both human metabolic products collection, fermentation and sterilization (liquid urine). Because of dry toilet idea and practical requirements (safe and convenient handling), simultaneous ammonia and odors removal methodology should be equally effective both in application to liquid urea and to solid faeces.

Many gaseous ammonia removal methods are reported in literature [24-31] like absorption in aqueous solutions, catalytic oxidation to N₂ or NO, advanced aqueous phase oxidation with chemical oxidizers (ozone, peroxone), electrochemical oxidation or hypochlorination. Methods of excretion nitrogen reduction, convenient in animal breeding by proper diet manipulation, seem to be not suitable for human population directly. These methods require also complex biological processing like urease inhibitors, reduction of manure pH, etc. or application of expensive catalysts working in high temperatures (500°C).

Considering dry toilets construction some special requirements should be met, like compact size, not troublesome handling and possibly low costs. Adsorption on acidic solids (zeolite clays, graphite oxides, etc.) seems to be attractive for direct application [32-39]. Such multifunction sorbents should make reduction of NH₃ formation by effective lowering of free NH₄⁺ ions in liquid environment through sorption/ion exchange, as well as by equally effective sorption of already formed gaseous NH₃.

One of the promising naturally occurring minerals seems to be halloysite with its unique surface properties [40-47]. It is a two-layer mineral belonging to kaolinite subgroup (Al₂Si₂O₅(OH)₄·nH₂O), demonstrating affinity to the monovalent cations, playing important role in inner-sphere and interlayer cation-water structure complexes, as well as having water layer of 7–10.1 Å interlayer distance (Fig. 1). Halloysite unit is composed of two sheets: Si-tetrahedral (oxygen surface negatively charged) and Al-octahedral (external surface with hydroxyl groups with hydrogen outstanding demonstrating positive charge). Surface charge of halloysite can be strongly modified by cation substitution, especially of Al atoms in octahedral layer for divalent atoms (e.g. Mg, Fe), trivalent Fe or four-valent Ti, while Si in the tetrahedral structure can be replaced by Al. In result important changes in local microstructure are observed, with the unique possibility of new specific bonds formation, in various places of halloysite structure, together with cavity trapping mechanism(s).

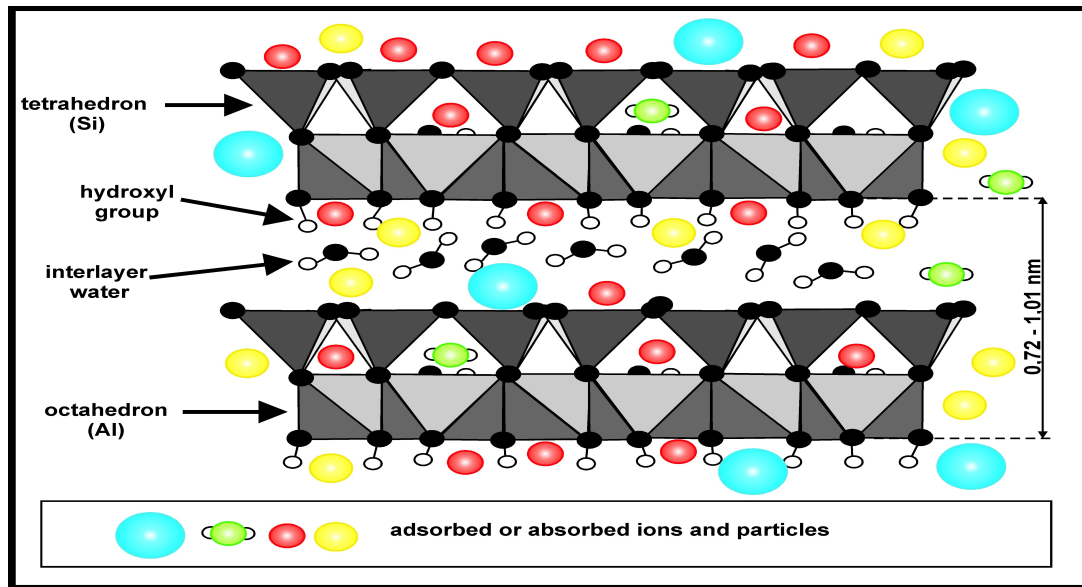


Fig. 1. The model of spatial structure of halloysite as urine composites sorbent

Purposefully modified halloysite can be promising variant in ammonia emission lowering technology. Its low costs (thus no necessity of regeneration) can be deciding economical factor, while universal application, wide sorption/binding properties (of not only ammonia but also other co-present odor substances), easy handling and working in a room temperature are design factors influencing its potential use in a dry toilets technology.

Materials and methods

Both liquid (urine) and solid-liquid (faeces) systems were contacted with halloysite sorbent. Fresh sorbent, directly from mineral deposit, was dried in the oven in temperature 60°C through 4 h and shredded in mechanical schredder. Mechanical sieving provided fraction 0 – 1 mm which was directly used in the tests (code: halloysite HT1a). Specific surface area of halloysite HT1a was 70 m²/g.

Human urine collected from toilet facilities modeling the dry toilets idea was used for the tests. It was then fermented hermetically closed in presence of dispersed halloysite sorbent (dose 10 g/dm³) and inoculum (collected from working methane fermentation plant) through 20 days in temperature 38°C for attaining the equilibrium. Periodical shaking was applied every day. Resulting sludge was separated with gravitational settling method and dried in temperature 28°C. Dry mass was a subject of elementary analysis.

Tested solid faeces (10% of dry mass) were diluted with demineralized water. To 100 g of faeces the 100 g of inoculum was added, following with demineralized water addition up to 1 dm³. Halloysite was added (dose 50 g/kg) and the mixture was fermented hermetically closed in temperature 38°C also through 20 days for attaining the equilibrium. After filtration the solid residue was a subject of elementary analysis.

Analysis of surface morphology and local chemical composition (in microregions) of the samples were done using scanning electron microscope Zeiss Supra 35, equipped with EDS detectors. Samples before the tests and after fermentation process were subjects of analysis in respect to chemical compounds presence and concentration in surface of grain (sample no. 1 and 2, Table 1) and within mixed internal and external parts of the grain after its shredding (sample no. 3, Table 1).

Analysis and discussion

The research of qualitative character was oriented for identification and/or confirmation of surface occurrence of individual elements within the halloysite sorbent structure.

In case of halloysite sorbent grains contacted with urine during 20 days of its fermentation in a closed system X-ray EDS analysis (Fig. 2–3) of their external surface regions demonstrated clearly higher concentration of nitrogen compounds compared to the bulk grain. The tests shown that mean surface concentrations from 2 test series are 1.65 and 1.41 mass %, respectively (Table 1). However, analysis after shredding of 10 g of sorbent dried after the sorption process, representing internal structure properties of the grains, demonstrated that mean concentration of nitrogen in a sample was negligible (Table 1). It results that sorption of nitrogen compounds runs mainly on the external surface of sorbent grains (clogging effect – see Fig. 4–5).

Quantitative analysis (based on elements proportions in Table 1) provided, that mass fraction of the pure halloysite sorbent represented ca. 2-3 mass % only. It thus suggests, that about 35-50-time larger amount of adsorbate can be subject of sorption on the halloysite, clearly demonstrating its very good sorption capabilities.

Active sorption on the halloysite surface, being result of its structure and active groups presence, can, however, make quick clogging of the pores (sterical effects), making thus any contact/communication with internally developed surface impossible. It will result in process rate inhibition or even stopping. This tendency can isolate the grain interior, where developed active surface can be even higher. Thus the idea is to provide larger available sorption surface just at the process beginning. The internal surface will be thus accessible independently, resulting in higher sorption efficiency. This can be achieved after modifying original grain composition of halloysite sorbent using, for example, some form of mechanical shredding.

Smaller, more homogeneous in size grains can be more effectively distributed in the liquid or semi-liquid systems, reducing thus possibility of unwanted concentration gradients occurrence considerably.

At this research stage it is very difficult to conclude whether agglomeration of sorbents/products took place – during drying or during earlier anaerobic fermentation.

Table 1. Chemical composition of samples surface/homogenized interior after fermentation process and drying

Element	EDS surface analysis of chemical composition [mass %] of:			
	pure halloysite sorbent HT1a (before the tests)	sample no. 1	sample no. 2	sample no. 3 (after mechanical grain shredding)
Oxygen	54.17	47.47	50.45	52.84
Calcium	---	29.88	27.82	---
Phosphorus	---	16.14	14.43	---
Carbon	---	2.38	3.42	---
Sodium	---	0.53	0.19	0.38
Sulfur	---	0.47	0.55	---
Magnesium	---	0.07	0.34	---
Aluminium	21.84	0.20	---	19.05
Silicon	19.90	0.24	0.15	18.18
Potassium	---	0.31	--	0.23
Iron	3.28	0.59	0.76	8.48
Nitrogen	---	1.65	1.41	---
Chlorine	---	---	0.21	---
Titanium	0.78	---	---	0.80
other	0.03	0.07	0.07	0.04

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Σ	100.00 %	100.00 %	100.00 %	100.00 %
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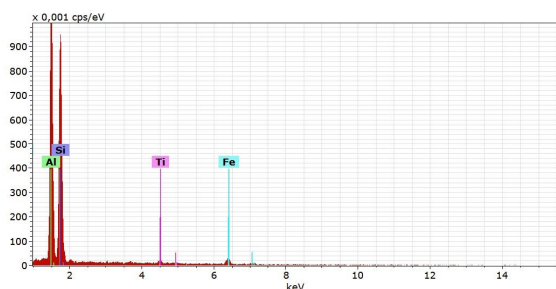


Fig. 2. Energy dispersive X-ray analysis (EDS) of the surface morphology of pure halloysite sorbent type HT1a

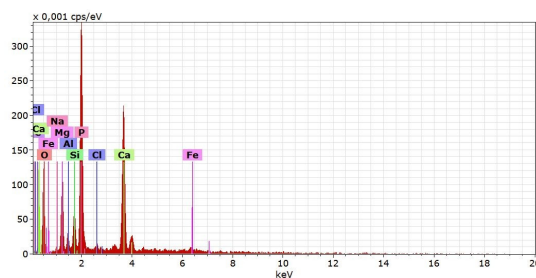


Fig. 3. Energy dispersive X-ray analysis (EDS) of the samples surface morphology after 20 days of contact with human urine (after fermentation process).

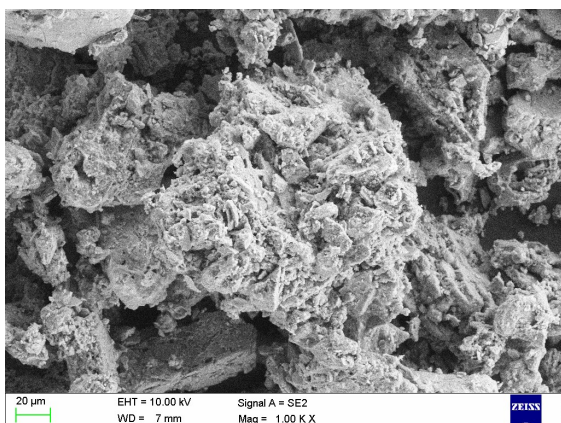


Fig. 4. Morphology of fresh halloysite sorbent type HT1a – the research object (SEM)

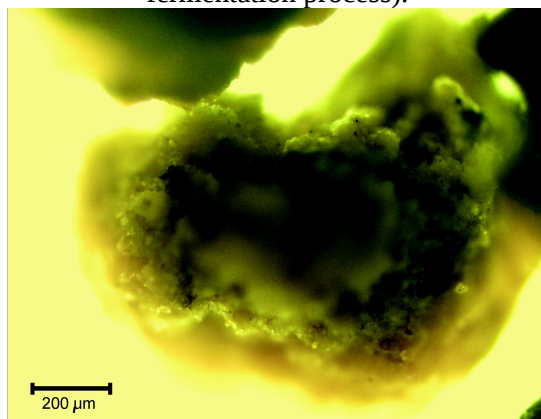


Fig. 5. Halloysite sorbent after 20 days of contact with human urine (fermentation process). Biological optical microscope OLYMPUS CH-30, magnification 10×

Future research will cover sorbent size distribution optimization, various modes of its surface activation in respect to enhancement of nitrogen (ammonia) and organic compounds (odors) sorption. Technological concept turned out to be advantageous, clearly demonstrating high potential possibilities of the method. Moreover, considering relatively low production costs of HT1a sorbent and possibility of its common application, the method is attractive since it is based on direct, simple application of various naturally occurring aluminosilicates. Manufacturing/improving of natural carriers of organic or inorganic substances can be substitute of industrially produced mineral fertilizers.

Essential advantage of halloysite application in agriculture is that it does not contribute to soil degradation. Contrary, being inert towards natural environment it facilitates water retention in the soil structure, slow, delayed water evaporation, provides its controlled dosing (soil humidity adjustment) – natural function of the forests.

Based on elementary analysis the following elements are present on the surface: O, Ca, P, C, Al, Si, K, Na, Fe, N. Some organic compounds can be also formed. Based on the analysis it can be concluded, that compounds of complex structure, including organic ones, identified on the surface (indirectly by elementary analysis) require further identification with appropriate analytical methods. It concerns especially complex organic odor substances (VOCs) which are usually present in trace concentrations. Simultaneous co-sorption of ammonia and odors is thus reported, what is a great advantage of the halloysite sorbent in such technological applications.

Conclusions

Halloysite powders (*Dunino* mine, Poland) were successfully applied for ammonia and odors emission lowering in model dry toilets.

Halloysite sorbent presence in appropriate construction of the dry toilet facility makes binding of ammonia/ammonium ions as early as during making use of the toilet possible. Halloysite, because of its good sorption properties, absorbs urine which penetrating into the halloysite specific interlayer space is protected against relatively fast evaporation. Products of eventual internal evaporation must relatively slow diffuse towards external parts of the sorbent, thus efficient sorption on surface via diffusion path is possible. Moreover, residence time of volatile components is long enough (slow diffusion), advantageous for requirements of surface sorption kinetics.

Application of separated urine in agriculture requires some fermentation/sterilization processes. During fermentation ammonia releases, what is regarded both with atmosphere contamination and decrease of fertilizer properties (lower content of valuable nitrogen). Application of cheap halloysite sorbent can inhibit this tendency, thus its application is strongly advantageous and recommended. It can be used as “ammonium ions reservoir” in agriculture.

Presented research methodology can reflect real process in countries with hot climate (e.g. sun drying of wet halloysite with nutrients applied on the agricultural areas).

Sorption of nitrogen was confirmed by X-ray EDS analysis what is a proof of various nitrogen compounds presence on the halloysite. Presence of other elements, in various chemical components, can be regarded advantageous since these can be micronutrients required by the soil. The research results can be regarded as the first qualitative trials, confirming purposefulness of next research ideas and verification of the technological conception. Future research will involve, among others, optimization of sorbents properties and dozes towards higher selectivity for different elements (e.g. N, P, K) sorption.

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