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Halloysite as main nanostructural filler in multifunctional mixed matrix membranes – review of applications and new possibilities

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ABSTRACT

Innovative, composite mixed matrix membrane (MMM) structures with specific naturally occurring halloysite nanotubes (HNTs) provide new possibilities in gaseous and liquid mixtures separation. Halloysite filler, introduced into the polymer phase, can find itself useful both as natural clay mineral with adsorption/catalytic properties, as well as the convenient support for other, targeted and highly specialised nanoparticles. Numerous laboratory studies indicate that hydrophilicity of the resulting membrane is advantageously improved, providing higher pure water flux than obtained in the one-phase membrane. Optimised structures of the halloysite-based nano-fillers can find them useful in various technological applications, for example, separation of dyes or/and oils from post-processed wastewaters, the concentration of salts in solutions, inhibition of bacterial population growth, as well as separation of gaseous mixtures components. The research done so far and reported in the literature in respect to MMMs with halloysite, applied as a natural mineral and with targeted functionalisations, was systematized and presented. Particular attention was paid to the natural, unique halloysite nanoplates (HNPs), which potential use in technological applications is still not fully discovered and exploited.

Keywords: Halloysite nanotube (HNT); Halloysite nanoplate (HNP); Mixed matrix membrane (MMM); Gaseous components separation; Wastewater purification; Antibacterial activity

1. Introduction

A relatively new idea in modern membrane technology is the mixed matrix membrane (MMM) technique [1–9]. Such an alternative approach enhances the separation process possibilities and performance limits of a pure raw membrane polymer. In MMM application the polymer is only one of the components – a continuous phase where various solid fillers are purposefully dispersed. These are connected with the polymer matrix by covalent, hydrogen bonds or by van der Waals forces. The fillers can be porous or nonporous particles, usually zeolites, layered silicates, some forms of carbon, molecular sieves, metal-organic frameworks, etc. The solid phase – with its own intrinsic chemical properties (especially surface chemistry – functional groups and unique morphology) – is dispersed within the flexible polymer phase resulting in some nanocomposite material, with conveniently improved separation characteristics, together with advantageous mechanical properties, acceptable chemical durability, heat stability and corrosion resistance. According to the Maxwell model, even a relatively small fraction of the inorganic species dispersed within the continuous polymer phase can significantly improve the separation abilities of such defined systems [10]. Also, new

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possibilities appeared in the tailoring of the nanocomposite properties for some dedicated applications by, for example, polymer/filler proportion adjustment or/and some additional pretreatment. The new mechanisms resulting from foreign solid-phase presence involve molecular sieving, diffusion, selective adsorption within the internal pore system of the filler, complex chemical surface interactions between organic (polymer) and inorganic (filler) fractions, etc. All these phenomena affect the resulting final permeability and selectivity of such defined systems in a complex manner [1–10].

Some difficulties during the manufacture of mixed matrix membranes must be also overcome, especially concerning proper dispersion of the filler (minimization of the filler concentration gradients – prevention of its possible agglomeration or aggregation). These difficulties result from specific intrinsic properties of the solid phase. Equally important is also the interaction between the polymer and filler structures (wettability), warranting the degree of interface defects within the polymer – filler contact surface.

The main challenge in the modification of mixed matrix membranes is based on matching such polymer matrix and filler(s) to obtain high performance at possibly low producing costs. This may be gained only based on thorough knowledge and laboratory experience, especially in the identification and control of the dominant mass transport mechanisms (Fig. 1).

Equally important is the ecological aspect of both material groups used. Thus preference is focused on biodegradable polymers. Also environmentally friendly fillers, naturally occurring in the biosphere, are strongly recommended. However, at the present day, carbon nanotubes are non-economical and reported to be a danger for health. One alternative, inexpensive and simultaneously multifunctional filler can be halloysite, which application in mixed matrix membranes will be discussed in this review.

2. Halloysite filler

Halloysite, as layered aluminosilicate, is one of the fillers used in mixed matrix membranes. Its specific properties may be fully exploited in the original, promising area of MMMs.

Halloysite is representative of the kaolinite mineral subgroup characterized by a general chemical formula of $Al_2Si_2O_5(OH)_4 \cdot nH_2O$ (where n represents the number of H_2O molecules found within the interlayer spaces of the natural clay aggregates; $n = 0$ for kaolinite, whereas in case of halloysite n can even reach 4). Water content within the interlayer space of mineral halloysite broadens this layer's thickness up to 10.1 Å [11]. However, this water load may be irreversibly removed when the temperature is raised (dehydration), narrowing the interlayer distance down to 7.2–7.5 Å (Fig. 2).

During dehydration, simultaneous separation of the halloysite platelets is observed. In the halloysite, an elementary unit structure two complementary sheets can be distinguished: Si-tetrahedra and Al-octahedra. The octahedral external surface shows a positive charge, whereas the surface of the tetrahedral sheet – negative charge. Halloysite clay mineral from the polish natural deposit "Dunino" demonstrates another specific intrinsic property – the possibility of multi-variant substitutions (e.g., Fe, Ti, Mg for Al, whereas Al, Fe, Ti for Si). The resulting substitutions are responsible for the establishment of numerous active sites, with unbalanced surface charge, modifying the original mineral's surface charge and providing thus convenient conditions for different bond types on the available clay surface. Moreover, the same surface interactions induce complex sorption and sometimes even catalysis phenomena. Other property of halloysite, important in practice, is its potential of sorption of large amounts of ions and heavy metals like Pb(II), Zn(II), Cd(II) or As(V) [12–14].

Contrary to kaolinite, in halloysite, one observes some clear distance among the layers where water molecules or different cations can be fixed. In kaolinite, these neighboring layers interact together via hydrogen bonds between oxygen from the tetrahedral layer and hydrogen from the octahedral hydroxyl group. Moreover, in halloysite from "Dunino" clay mine in Poland numerous substitutions of Al atoms from the octahedral layer with divalent (e.g., Mg or Fe), trivalent (e.g., Fe) or four-valent (e.g., Ti) atoms were confirmed analytically. Similarly, Si from the tetrahedral sheet is frequently replaced with Al and Fe [11,15].

Oxygen atoms in tetrahedral sheets form some regular 6-fold hexagonal structure, remaining stable even after being

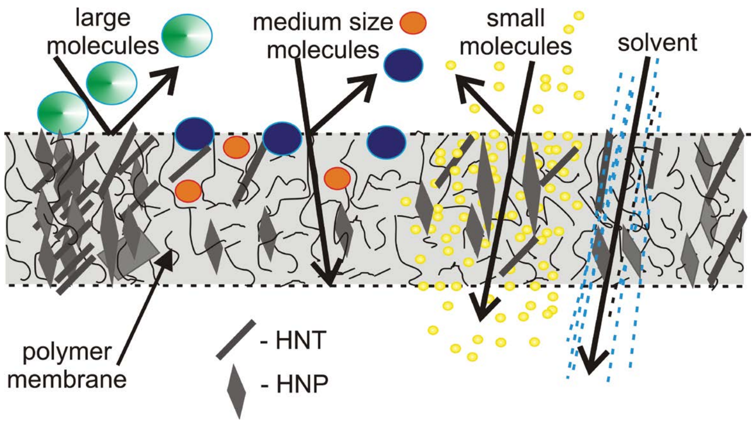

Fig. 1. Scheme of the mixed matrix membrane (MMM) with embedded halloysite nanotubes (HNTs) and halloysite nanoplates (HNPs).

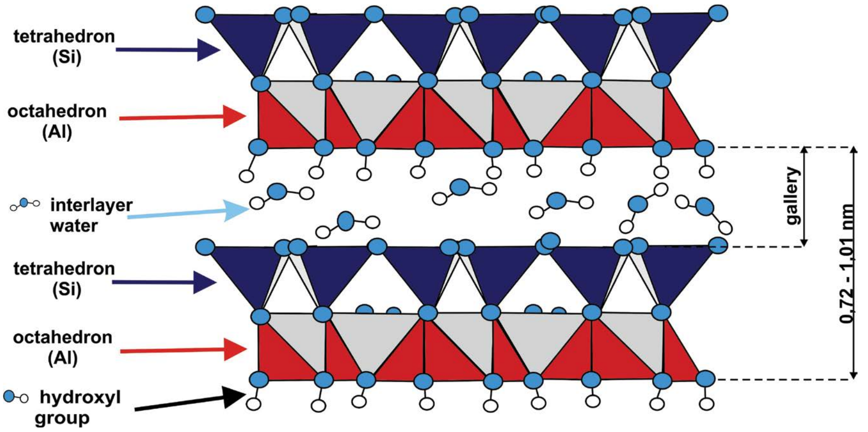

Fig. 2. Scheme of a single halloysite nanoplate (HNP) structure.

mentioned above dehydration. This observation proves that either the "hole" – trapped water molecules remain within the hexagonal structure or that the potential rotation is hindered by the action of some internal forces [15].

In halloysite, each Al atom is bound to three external hydroxyl groups and to one inner hydroxyl group located on the tetrahedral sheet. These groups are reported to be very active, especially in the creation of different bonds within the broad pH range. For potential applications, it is important, that the original surface chemistry and structure of natural halloysite may be also optionally altered by adequate thermal or/and chemical processing, modifying, for example, aluminosilicate morphology, its specific surface area, pore structure, volume and pore size distribution, as well as active sites distribution. This provides the opportunity for the rational design of the complex separation processes based on four possible mass flux routes through the mixed matrix membrane structure, namely: via diffusion through polymer matrix (like in classical homogeneous polymer membranes), via passageways in the specific halloysite interlayer structure, via complex stochastic 3-D structure formed by natural halloysite nanotubes and nanoplates (increasing voids within MMM) and via imperfections in the halloysite-polymer adhering surfaces (microvoids, etc.) (Figs. 3 and 4).

Both specific physicochemical properties of natural halloysite and experimentally confirmed the usability of halloysite-based sorbents in diverse practical applications [15–17] suggest a broad spectrum of its applicability, especially where high-effective, simultaneous removal of hazardous components from various complex (sometimes even of practically unknown composition) mixtures of strongly diversified concentration ranges is demanded, like, for example, in biotechnological processes [18–20].

For many different polymer nanocomposites, especially including mixed matrix membranes, some unique properties of natural halloysite, like tubular nanostructure (of HNTs), aspect ratio, appropriate mechanical resistance for the tensions, tensile strength, flexural strength, adequate toughness, thermal stability, flame retardance and biocompatibility [21] can be fully employed. In some cases, these may even be further improved by appropriate modifications. Technically verified, successful applications of halloysite in the separation of liquid and gaseous mixtures components are presented below.

3. Halloysite-based mixed matrix membranes for wastewater purification

Analyzing the literature reports [22–28] (Table 1) it results, that halloysite clay filler incorporated into the polymer's continuous phase provides new, advantageous properties to the separation system. In particular, ultrafiltration and forward osmosis membranes were investigated, composed of polyether sulfone (PES) [22,27], polyamide (PA) [23], polysulfone (PSF) [24,25], polyvinylidene fluoride (PVDF) [26] and cellulose acetate (CA) [28]. As the filler hydrophilic raw halloysite nanotubes (HNTs) were applied, however, more often their developed surface was adopted as the advantageous support for different active species modifying its original structure (e.g., HNTs grafted with 2-methacryloxyethyl phosphorylcholone [22], grafted with Dextran [27], with TiO_2 nanoparticles incorporated onto the HNTs surface [24] or functionalized with L-DOPA [28]).

In general, higher hydrophilicity of the membrane surface responsible for higher water permeability was observed. Moreover, better anti-fouling properties, reduction of concentration polarization effects and minimization of reverse solute flux were commonly noticed during the described tests. The resulting anti-fouling properties were attributed to the hydrophilic character of nanoparticles (many hydroxyl groups on the HNTs surface, growth in porosity, as well as in mean pore size of membrane system), efficiently resisting the hydrophobic impurities. The presence of halloysite clay filler was also responsible for improved mechanical parameters and separation abilities of MMM systems, especially in the terms of pore size distribution and a number of pores on the membrane surface.

The available experimental data suggest, that a relatively small concentration of the halloysite clay filler (0.05–0.5 mass % of HNTs [23,25], 0.05 mass % of TiO_2/HNTs [24], 3 mass % of TiO_2-HNTs/PVDF [26], 3 mass % of LPDHNTs [28]) is satisfactory enough and sometimes even optimal for the improvement of original separation properties of the pure polymer membrane. Such experimentally identified concentration ranges provide optimal

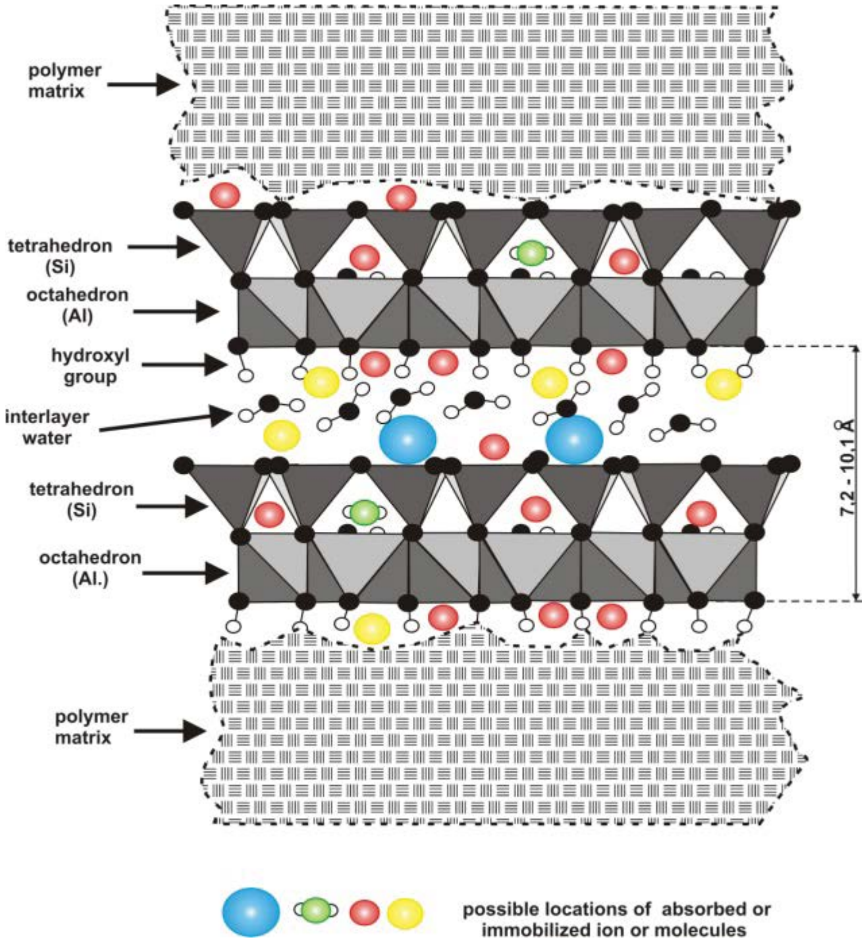

Fig. 3. Detailed scheme of the mixed matrix membrane – polymer matrix with incorporated halloysite structure (with marked potential allowable locations of sorbed and immobilized species).

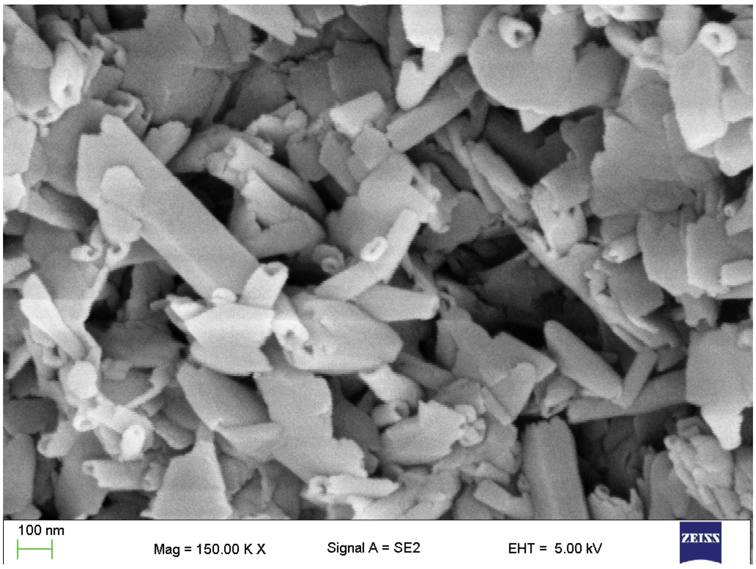

Fig. 4. Scanning electron microscopy (SEM) image of raw halloysite with visible halloysite nanotubes (HNTs) and halloysite nanoplates (HNPs) – stochastic 3-D structure responsible for specific surface area development.

Table 1
Halloysite-based mixed matrix membranes for wastewater purification

No.	Composition of mixed matrix membrane, clay filler pretreatment	Observed advantages	Reference
1	Polyether sulfone (PES) ultrafiltration membrane. Halloysite nanotubes grafted with 2-methacryloxyethyl phosphorylcholine (HNTs-MPC). Reverse atom transfer radical polymerization (RATRP method). Phase inversion method.	Higher anti-fouling ability and stability in long-term ultrafiltration. Higher hydrophilicity – providing higher water flux. Significantly lowered surface sorption of bovine serum albumin (BSA).	Wang et al. [22]
2	Polyamide forward osmosis membrane involving HNTs. Interfacial polymerization.	High water permeability. Low reverse solute flux (0.05% HNTs). Higher fouling resistance.	Ghanbari et al. [23]
3	Polysulfone (PSF) Udel P-3500 forward osmosis membrane. TiO_2 nanoparticles/halloysite nanotubes (HNTs) nanocomposites. One-step solvothermal method.	Optimal combination of specific tubular structure of HNTs and anti-fouling properties of TiO_2. The 0.05% (w/v) TiO_2/HNTs was optimal in respect to its high water permeability at low reverse solute flux. Distinctly improved anti-fouling properties. Fully reversible fouling – tests with bovine serum albumin (BSA). Complete recovery of pure water flux after water cleaning procedure.	Ghanbari et al. [24]
4	Polysulfone (PSF) forward osmosis (FO) membrane. Hydrophilic halloysite nanotubes (HNTs). Interfacial polymerization on the top surface.	Minimization of concentration polarization phenomenon. The 0.5 mass % of HNTs showed the best results in respect to the pure water permeability, with low reverse solute flux.	Ghanbari et al. [25]
5	Polyvinylidene fluoride (PVDF) membrane. Titanium dioxide – HNTs. TiO_2 incorporated onto the HNTs surface homogeneously using sol–gel method.	Addition of TiO_2-HNTs increased the MMM hydrophilicity significantly. Pure water flux in respect to 3% TiO_2-HNTs/PVDF was higher by 264.8% (compared with pure PVDF polymer membrane) and by 35.6% (compared with 3% TiO_2/PVDF mixed matrix membrane). Anti-fouling properties. Rejection of bovine serum albumin (BSA) slightly lowered. Application of HNTs as the support for titanium dioxide improved its dispersion within the polymer matrix.	Zeng et al. [26]
6	Polyether sulfone (PES) ultrafiltration membrane. HNTs grafted with Dextran.	Higher hydrophilicity of the membrane surface. Better anti-fouling characteristic. Better morphology, mean pore size and separation abilities of the membrane system.	Yu et al. [27]
7	Cellulose acetate (CA) ultrafiltration membrane. Phase inversion method. L-DOPA functionalized (coated) HNTs (LPDHNTs).	Excellent anti-fouling properties. Addition of 3.0 mass % of filler into the LPDHNTs/CA membrane system was responsible for pure water flow increase from 11.4 $dm^3/m^2/h$ up to 92.9 $dm^3/m^2/h$ (rejection ratio ca. 91.2% – only slightly lower compared to pure CA membranes). Better mechanical properties. Introduction of LPDHNTs filler into CA solution was responsible for larger pore size and number of pores on the MMM surface, as well as higher hydrophilicity.	Mu et al. [28]

spatial dispersion of HNTs filler within the polymer matrix, minimizing disadvantageous agglomeration/aggregation tendencies. Further improvement of their functionality and stability can be achieved, however, in a different way – by more complex nano-constructions like functionalisation of the halloysite filler now used as the support for different active species. This very promising trend is represented by, for example, HNTs-MPC [22], TiO_2/HNTs [24], HNTs-Dextran [27] or LPDHNTs [28]. Individual substrates for such nano-constructions can be appropriately selected considering their unique chemical nature, interactions and potential functionality and dosed, providing thus optimal combination for the required, tailored target application.

It may be assumed, that specific effects will be dependent on some key factors – HNTs dose, preprocessing schemes sequence both in respect to HNTs and to the polymer matrix, as well as the technology of MMM manufacturing. However, in all reported cases advantageous effects of halloysite clay filler presence are confirmed experimentally. A small dose of this cheap, natural filler is responsible for the improvement of MMM structure and resulting separation abilities. This also influences the process economy and thus naturally points to some new engineering challenges in this area.

Generally, three main application domains of halloysite-based mixed matrix membranes in wastewater purification can be generally distinguished. These include oil(s)-water mixtures separation, reactive dye(s)-water mixtures separation and biological systems where antibacterial properties of MMMs can be fully employed.

3.1. Oil–water mixtures separation

From the accessible articles [29–31] (Table 2) it results, that application of HNTs (1–3 mass % of HNTs) provides demanded oleophobic properties of the resulting MMM. It may be thus effectively used in oil/water suspensions separation. An interesting method of such MMM manufacturing is the controlled poly(diallyldimethylammonium chloride) PDDA-HNTs multi-layer deposition on a stainless steel mesh support [30] flexibly altering the original mesh roughness by hierarchical coating (superoleophobic mesh

Table 2
Halloysite-based mixed matrix membranes for oil–water mixtures separation

No.	Composition of mixed matrix membrane, clay filler pretreatment	Observed advantages	Reference
1	Polyacrylonitrile (PAN) nanofibrous membranes. 1–3 mass % of HNTs. Electrospun technique applied.	Membrane reinforcement. Higher thermal stability. Higher filtration yield. Tensile strength and elongation at break. Good oil/water separation properties.	Makaremi et al. [29]
2	Durable underwater superoleophobic mesh prepared by layer-by-layer assembly of poly(diallyldimethylammonium chloride) (PDDA)/HNTs on a stainless steel construction (mesh).	Hierarchical template. Roughness of PDDA/HNTs Can be flexibly adjusted by various number of coating layer depositions. Ten deposition cycles of PDDA/HNTs layers on the parent mesh structure (of ca. 54 μm size) formed superoleophobic mesh representing oil–water separation performance with effectiveness more than 97% in respect to many oil/water suspensions. Possibility for water to pass through while completely repelling the oil component. Stability of the separation system after 20 processing cycles. Ca. 97% separation efficiency in case of hexane/water and chloroform/water mixtures. Construction resistant to strong alkaline or salt solutions and mechanical abrasion.	Hou et al. [30]
3	Poly(vinylidene fluoride) (PVDF) ultrafiltration membrane. HNTs modified by surface covalent functionalization with 3-aminopropyltriethoxysilane (APTES).	Four oil–water emulsions were successfully (90% rejection ratio) separated. APTES-HNTs/PVDF MMM characterized by higher water permeation (flux) together with smaller contact angle, with surface roughness devaluation. Better results than in case of PVDF membrane and in case of simpler HNTs/PVDF system. After 3 repeating fouling/washing cycles the flux recovery ratio (FRR) was still able to attain 82.9%.	Zeng et al. [31]

completely repelling the oil fraction). A different approach is based on lowering the contact angle and altering surface roughness using HNTs modified chemically by surface covalent functionalisation with 3-aminopropyltriethoxysilane (APTES-HNTs) [31]. Experimental results proved, that APTES-HNTs/PVDF [31] mixed matrix membrane demonstrated better separation abilities than PVDF membrane alone or less complex HNTs/PVDF nanocomposite.

Other advantageous effects were, however, also observed like membrane structure reinforcement and its better thermal stability. Improvement of other parameters, like tensile strength and elongation at break was also reported.

3.2. Reactive dye-water mixtures separation

Some approaches for the reactive dye-water mixtures separation, especially in respect to technologically troublesome reactive textile industry wastewaters, are presented in the literature [32–37] (Table 3). In particular the polyvinylidene fluoride (PVDF) [33,34], polyacrylonitrile [32], polyether sulfone (PES) [35,36] and polyetherimide (PEI) with polyvinylpyrrolidone (PVP) K29–32 [37] polymer membranes were examined. These experimental attempts can be roughly divided into two different schemes. The first approach is based on the application of well-ordered HNTs coating (organized arrays), providing better separation abilities compared to the disordered HNTs layer [32]. This way superiority of organized HNTs nanoarchitecture in molecular separation was confirmed experimentally. The second approach covers classical chemical modification/functionalisation of HNTs like DA-HNTs [33], APTES grafted HNTs [34], poly(NASS)-HNTs [35], styrene grafted HNTs with sulfonation establishing highly crosslinked HNTs-SO_3H structure [36] or oxidative polymerization PHNTs [37]. For example, higher hydrophilicity of such MMM was experimentally verified and explained by the effect of APTES-HNTs presence, with abundant hydrophilic hydroxyl and amino functional groups. As a result, higher pure water flux was attainable. The higher separation efficiency of the MMM tested was explained by electrostatic interactions between membrane surface and reactive dye molecules (e.g., Direct Red 28) or/and heavy metal ions, as well as intrinsic adsorption properties of APTES-HNTs.

Better anti-pollution and reuse possibilities were explained in the terms of decrease of mixed matrix membrane's surface roughness as the effect of such prepared clay filler addition.

The specific surface provided by HNTs was mainly responsible for better dispersion of the filler, its more homogeneous spatial distribution and aggregation/agglomeration prevention, but also hydrophilicity. Simultaneously other advantages were also observed, like improvement of MMM microstructure advantageously influencing the

Table 3
Halloysite-based mixed matrix membranes for reactive dye-water mixtures separation

No.	Composition of mixed matrix membrane, clay filler pretreatment	Observed advantages	Reference
1	Polyacrylonitrile porous membrane. Highly oriented layer of halloysite. Facile evaporation-induced technique. Nanoarchitecture-controlled membrane establishing, formation of well-ordered nanotubes coating.	Superiority of organized arrays of HNTs in molecular separation. Dye rejection (97.7% in case of Reactive Black 5). High salt permeation during concentration (86.5% for aqueous NaCl solution). Superiority of such defined nanostructure in respect to the classical polyacrylonitrile membrane or membrane coated with disordered HNTs layer.	Qin et al. [32]
2	Polyvinylidene fluoride (PVDF) membrane. Halloysite nanotubes (HNTs) functionalized by reaction with dopamine (DA).	Application in dyes removal from textile industry wastewaters. DA-HNTs nanoparticles demonstrated not only appropriate dispersion within the continuous membrane polymer phase (PVDF), but also advantageously improved the membrane microstructure responsible for the permeability/selectivity balance. MMM is more hydrophilic, achieving pure water flux of 42.2 $dm^3/m^2/h$, higher by 80.3% in relation to pure PVDF membrane structure. Higher rejection ratios for the dyes after incorporation of DA-HNTs: 86.5% in case of Direct Red 28, 85% for Direct Yellow 4, as well as 93.7% for Direct Blue 14. Excellent anti-fouling abilities, even after several regeneration cycles.	Zeng et al. [33]

(continued)

Table 3 Continued

No.	Composition of mixed matrix membrane, clay filler pretreatment	Observed advantages	Reference
3	Polyvinylidene fluoride (PVDF) nanofiltration membrane. HNTs functionalized using 3-aminopropyltriethoxysilane (APTES grafted HNTs).	Improvement of dyes and heavy metal ions removal. Higher hydrophilicity. Higher pure water flux. Dye rejection ratio for the investigated 3% APTES-HNTs@ PVDF mixed matrix membrane reached 94.9%. Better separation of heavy metal ions. Better membrane sorption capacity. Better anti-pollution and reuse possibilities.	Zeng et al. [34]
4	Polyether sulfone (PES) membrane. HNTs-poly(sodium 4-styrenesulfonate) (HNTs-poly(NASS)) filler composed of sodium 4-styrenesulfonate grafted onto the HNTs surface by means of surface initiated atom transfer radical polymerization (SI-ATRP). Phase inversion method.	Increase in hydrophilicity (in respect to the original pure PES membrane). Lowering of water–soluble dyes rejection. Enlarged permeation in saline solution processing. Negatively charged nanofiltration (NF) membrane.	Zhu et al. [35]
5	Polyether sulfone (PES) nanofiltration membrane. Phase inversion method. Styrene grafted onto the HNTs surface using distillation–precipitation polymerization, together with sulfonation of HNTs using concentrated sulfuric acid responsible for establishment of highly crosslinked HNTs-SO_3H structure.	Dye wastewater purification or desalting. Higher water flux (2 mass % of HNTs-SO_3H resulted in 73 $dm^3/m^2/h$ flux at 0.4 MPa). Higher rejection for Reactive Black 5 (more than 90%) or Reactive Red 49 (80%–90%) dyes. Rejection sequence: $Na_2SO_4 > MgSO_4 > MgCl_2 > NaCl$. Advantageous properties of negatively charged nanofiltration membrane system.	Wang et al. [36]
6	PEI (polyetherimide) membrane with polyvinylpyrrolidone (PVP) K29-32 (invariable additive). Nanocomposite hollow fiber (HF) membrane. Dry-wet spin technique. Natural halloysite nanotubes functionalized by means of facile self-polymerization of *m*-aminophenol under moderate acidic environment (oxidative polymerization method) (PHNTs).	Reactive dyes removal. Filler was regarded as hydrophilic additive. Water permeation reached 104.9 $dm^3/m^2/h$. 2% dose of such prepared filler demonstrated 97% removal efficiency (rejection) for Reactive Red 102 and 94% for Reactive Black 5.	Hebbar et al. [37]

permeability/selectivity balance, more efficient separation of heavy metal ions and higher membrane adsorption capacity, as well as its anti-fouling morphology.

3.3. Antibacterial activity

Incorporation of halloysite clay filler, especially its unique nanotube structures into the polymer membrane (e.g., PES, PVDF) structure can also improve the complex antibacterial (bio)processes on the MMM surface. Relatively numerous, successful tests presented in literature [38–44] (Table 4) include *Salmonella* [38] and *Enterobacter aerogenes* [38], as well as both Gram-negative (*Escherichia coli*) [39,40,41,42,43,44] and Gram-positive (*Staphylococcus aureus*) [39,40,43] bacteria. High bacterial rejection indicators were reported from within the 92.6%–99.9% range.

The strong antibacterial effect of halloysite-based MMM is manifested by a broader inhibition zone self-formed in the membrane vicinity and bacteriostasis. Other mechanisms may be also employed, like filtration-based separation of bacteria or/and inhibition of their growth rate. Purposeful incorporation of some types of the commonly known and validated specific antibacterial components like Cu^{2+} nanoparticles [39], Ag^+ nanoparticles

Table 4
Antibacterial activity of the halloysite-based mixed matrix membranes

No.	Composition of mixed matrix membrane, clay filler pretreatment	Observed advantages	Reference
1	Polyvinylidene fluoride (PVDF) polymer. Silver lactate (SL)-halloysite nanotubes (HNTs) clay filler. HNTs modified by N-β-(aminoethyl)-γ-aminopropyltrimethoxy silane (AEAPTMS) oriented for SL immobilization on HNTs.	Antibacterial properties by filtration-based removal of microorganisms (antibacterial separator). 99.0%–99.8% bacterial rejection. LRV above 3. Relatively broad inhibition zones in respect to agar. Higher permeation flux and flux declination. Uniform distribution and immobilization of SL on HNTs nanostructural support. SL/HNTs dispersion within the polymer. Significant inhibition of *Salmonella* and *Enterobacter aerogenes* bacteria growth (incubation period 24 h). Strong antibacterial effect. Inhibition zone self-formed in membrane vicinity.	Moslehyani et al. [38]
2	Polyether sulfone (PES) membrane. Halloysite nanotubes loaded with Cu^{2+} as antibacterial component (Cu^{2+}-HNTs/PES). The filler was obtained using chemical modification of HNTs by means of silane (coupling agent) and copper dichloride (complexation of Cu^{2+} ions).	Higher pure water flux. Hydrophilicity growth (3% of Cu^{2+}-HNTs provided its 64% raise). Mechanical resistance improved. Owing to HNTs support copper ions were distributed within the MMMs structure more homogeneously. Cu^{2+}-HNTs/PES ultrafiltration MMM system demonstrated required antibacterial abilities in respect to Gram-negative (*Escherichia coli*) and Gram-positive (*Staphylococcus aureus*) bacteria. The original PES polymer microstructure not modified (except, however, the external surface where roughness was reduced).	Chen et al. [39]
3	Polyether sulfone (PES) membrane. HNTs modified chemically with chitosan, followed by mixing with silver nitrate for silver ions complexing and adding sodium tetrahydroborate as reductor for silver nanoparticles formation – resulting HNTs-chitosan-Ag nanofiller (HNTs-CS@Ag).	Convenient change in filler hydrophilicity. Pure water flux of 375.6 $dm^3/m^2/h$–233% higher in respect to classical PES membrane. Good anti-fouling characteristic. Antibacterial activity (*Escherichia coli* 94%, *Staphylococcus aureus* 92.6% removal).	Chen et al. [40]
4	Polyether sulfone (PES) ultrafiltration membrane. *N*-halamine grafted HNTs.	Antibacterial agents against *Escherichia coli*. 1 mass % of *N*-halamine/HNTs produced pure water flux of 248.3 $dm^3/m^2/h$.	Duan et al. [41]
5	Polyether sulfone (PES) polymer membrane. HNTs filler on which lysozyme was immobilized by covalent binding reaction.	For 3 mass % of HNTs-Ly pure water flux reached 400 $dm^3/m^2/h$. Rejection for PEG 20000 was 69%, PVA 30000–70000 was 99.6%. Antibacterial activity (Gram-negative *Escherichia coli*) bacteriostasis rate parameter reached 63%.	Zhao et al. [42]
6	Polyether sulfone (PES) UF membrane. Complex filler – grafted HNTs surface with poly(4-vinylpyridine) (P4VP) by means of *in situ* polymerization, followed by silver ions immobilization on P4VP using complex reaction and their final reduction to silver nanoparticles.	Antibacterial activities. Antibacterial rates against *Escherichia coli* and *Staphylococcus aureus* – 99.9% and 99.8%.	Zhang et al. [43]

(continued)

Table 4 Continued

No.	Composition of mixed matrix membrane, clay filler pretreatment	Observed advantages	Reference
7	Polyether sulfone (PES) UF membrane. Poly(4-vinylpyridine) (P4VP) grafted onto HNTs using reverse atom transfer radical polymerization, followed by copper nanoparticles loading by complexation/reduction.	Bacteriostasis rate in respect to *Escherichia coli* – 94.5%.	Duan et al. [44]

[38,40] was reported, but also different active agents like silver lactate (SL) [38], *N*-halamine [41] and lysozyme [42] were investigated. Especially poly(4-vinylpyridine) (P4VP) [43,44] was first grafted on HNTs, being then more convenient support for active silver and copper nanoparticles deposition. It should be mentioned, that halloysite, because of its complex structure and chemical composition, demonstrates some antibacterial effects itself, thus acts not only as of the pure inert support. Also another property of MMM with halloysite – roughness modification – may be at least partly responsible for stabilization and adhesion of the surface bacterial biofilm. In the accessible literature studies, the observed effects are partly related to the improved, more homogeneous distribution and better exposition of bioactive copper Cu^{2+}/silver Ag^{+} nanoparticles when the developed HNTs surface (sometimes improved with chitosan) is used as their convenient support. On the other hand, the remaining MMM properties were improved, like separation abilities and mechanical characteristics.

Different possible and experimentally tested approaches for HNTs mixed matrix membrane-assisted separation were also reported by Yu et al. [45]. Authors described natural HNTs, HNTs/AgNPs (silver nanoparticles), HNTs/Cu(II), HNTs/Cs/AgNPs, HNTs/CuNPs (copper nanoparticles), HNTs/rGO/AgNPs (reduced graphene oxide), HNTs/MPC (2-methacryloxyethyl phosphorylcholine), HNTs/Dextran, HNTs/*N*-halamine, HNTs/lysozyme, HNTs/PSS (poly(sodium-4-styrenesulfonate)), HNTs/PIL (poly(ionic liquid)), sulfonated HNTs and HNTs/TiO_2. As the main mixed matrix matrices PES (polyether sulfone), PA (polyamide), , PVDF (polyvinylidene fluoride) and PAN (polyacrylonitrile) were applied. Also, different membrane processes and operating modes were considered, including UF (ultrafiltration), NF (nanofiltration), FO (forward osmosis), RO (reverse osmosis), MR (membrane reactor) and nanofibers. The HNTs-based filler structures in MMMs were generally responsible, among others, for hydrophilic modification, antimicrobial properties, anti-fouling characteristics, ion-exchange, photocatalytic action, as well as composite structural reinforcement.

4. Halloysite-based mixed matrix membranes for gaseous mixtures separation

Mixed matrix membranes with halloysite can be also applied in the separation of gaseous mixtures components. Literature provides examples [46–48] (Table 5) of the effective CO_2/CH_4 [46,47,48], CO_2/N_2 [47] and O_2/N_2 [47] separation. Tests covered the following membrane polymers: 6FDA-durene polyimide [46], polysulfone (for asymmetric membrane) [47], as well as commercial polyetherimide Ultem 1000 [48].

Some modifications of raw HNTs structure were tested, resulting in its improved applicability. In particular, some chemical pretreatment procedures were investigated experimentally based on silylation and Ag^{+} ion exchanging in various sequences (S-Ag-HNTs [48]: Ag^{+} ion exchanging followed by silylation of HNTs and Ag-S-HNTs: silylation followed by Ag^{+} ion exchanging of HNTs). Analytical data confirmed, that such pretreatments resulted in the formation of a less crystalline structure of the mixed matrix membrane. This change influenced process performance advantageously. General enlargement in relative permeabilities of CO_2 and CH_4 was reported. Moreover, an increase in Ag^{+} ions concentration in the Ag-S-HNTs composite structure provided a better effect in respect to CO_2 selectivity and permeability.

The clay filler dose and dedicated pretreatment scheme should be chosen carefully. Some correlation between silane concentration and HNTs agglomeration was reported, providing poor separation with higher permeability [49]. Silylation made, however, that the halloysite particles are separated and appropriately dispersed. It is also responsible for a less crystalline structure of the resulting MMM. As a result higher CO_2 and CH_4 relative permeabilities were reported. Based on experimental test results Hashemifard et al. [50] distinguished five morphologies expected for large pore size particles used as the fillers. These are: ideal, void, rigidified, pore blocking and agglomeration combined with pore-blocking [50]. The selectivity-permeability morphological diagram was demonstrated, with halloysite nanotubes (HNTs) representing large pore size filler. It confirmed, that the filler pore structure, its size distribution, as well as general structure of the membrane (dense symmetric, asymmetric, etc.) mainly determine the intrinsic mixed matrix membrane separation properties.

Other reported in literature chemical modifications of raw halloysite nanotubes covered alkali etching, (3-aminopropyl)triethoxysilane grafting, *in situ* polymerization of aniline, as well as application of N-β-(aminoethyl)-γ-aminopropyltrimethoxy silane (AEAPTMS) and silver nitrate. Some auxiliary physical pretreatment schemes were also presented. These were oriented to better spatial dispersion of solid phase, as well as for the improvement of the filler–polymer affinity. These activities included ultrasonic sonication, wetting and priming of the HNTs clay filler. Surface etching was especially responsible for appearing of

Table 5
Halloysite-based mixed matrix membranes for gaseous mixtures separation

No.	Composition of mixed matrix membrane, clay filler pretreatment	Observed advantages	Reference
1	6FDA-durene polyimide membrane. Raw HNTs were chemically modified using alkali etching or (3-aminopropyl)triethoxysilane grafting.	Significant improvement of specific surface area and CO_2 sorption yield. Application of surface etching resulted in formation of surface defect holes, producing rougher HNT surface. Introduction of surface etching improved the interfacial affinity between polymer matrix and dispersed phase (before surface etching the void was 0.06%, whereas after this procedure – 0.02%). Solid filler dispersion demonstrated higher level, especially pronounced after grafting. Optimal MMM structure (10 mass % of etched HNTs) improved CO_2 permeability (807.7 Barrer) together with CO_2 selectivity (for CO_2/CH_4 it is 27.8) based on the Robeson upper bound limit.	Ge et al. [46]
2	Polysulfone asymmetric membrane. HNTs modified by *in situ* polymerization of aniline.	Higher dose of polyaniline *in situ* modified halloysite nanotubes within the polymer matrix (0.5 – 2.5 mass %) – higher permeances: CO_2 from 17.4 to 68.4 GPU, CH_4 from 0.8 to 4.8 GPU, O_2 from 3.9 to 18.8 GPU, N_2 from 0.7 to 3.1 GPU. Abilities for CO_2/CH_4, CO_2/N_2 and O_2/N_2 separation.	Murali et al. [47]
3	Commercial polyetherimide Ultem 1000 used as membrane polymer. HNTs modified by means of N-β-(aminoethyl)-γ-aminopropyltrimethoxy silane (AEAPTMS) and silver nitrate. Ultrasonic sonication of the filler. Filler wetting and priming.	S-Ag-HNTs (first Ag^+ ion exchanging followed by silylation of HNTs) and Ag-S-HNTs (first silylation followed by Ag^+ ion exchanging of HNTs) pretreatment schemes produced less MMMs crystalline structure, resulting in enhancement in both CO_2 and CH_4 relative permeabilities. General enhancement in CO_2 relative permeability was observed. Higher Ag^+ ions concentration in the Ag-S-HNTs produced advantageous, more pronounced effect in CO_2 permeability and selectivity.	Ismail et al. [48]

surface defect holes, defining thus rougher HNTs surface. This pretreatment scheme, however, enhanced the interfacial affinity between the continuous polymer phase and dispersed halloysite nanotubes. Simultaneously distinct improvement of specific surface and adsorption capacity in respect to CO_2 was observed. Also grafting pretreatment caused convenient, higher dispersion of HNTs clay filler within the polymer membrane structure.

5. Halloysite nanoplates – new research trends

Halloysite naturally occurs in three forms:

- halloysite nanotubes (HNTs),
- halloysite nanoplates (HNPs),
- spherical halloysite (the form, however, relatively rare in the biosphere).

Considering this, various variants of the halloysite-based mixed matrix membrane nanostructures are possible to be potentially established using these three fundamental halloysite forms.

One can also employ their nanostructural properties for simultaneous three-level (nano-, micro-, meso-) separation channels, namely:

- <1 nm (Å size range), employing the interactions within the separate sheet, especially between Si- tetrahedra and Al-octahedra layers,
- 1 – 50 nm size range, employing the structure of tightly packed sheets,
- 50 nm – 5 µm size range, employing the stochastic, porous structure of neighboring multi-particle aggregates dispersed within the continuous polymer phase.

Moreover, all these possibilities can be combined and further improved through chemical functionalisation of the halloysite support, as well as design and preparation of the appropriate membrane structure (including polymer matrix properties and dispersion homogeneity of halloysite phase) – what makes establishing a new, highly specific nanostructural composite tailored for various dedicated target applications possible.

However, relatively small attention is still focused on halloysite nanoplates (HNPs), which specific properties can be also employed in the concepts of nanostructural constructions, especially in the enhancement of contact surface between HNPs and polymer matrix, which can be crucial and adjustable key-parameter for additional separation abilities. Moreover, the unique structure of halloysite nanotubes (HNTs) interlaced with halloysite nanoplates (HNPs), the specific intrinsic interlayer structure of halloysite and its adjustable (7.2–10.1 Å) space (Figs. 5–7), as well as the advantageous presence of impurities provide new potential technological possibilities and routes in mixed matrix membrane applications.

Future research work may focus, among others, on specific properties of the Polish "Dunino" halloysite, where the specific natural structure of the aluminosilicate (nanotubes naturally coexisting with nanoplates), as well as on numerous natural additives incorporated within its structure, which – together – can be responsible for its specific, advantageous chemical surface properties.

Exemplary authors' own energy-dispersive X-ray spectroscopy analysis of the raw dry halloysite powder from the "Dunino" deposit is presented in Fig. 8. The test covered average qualitative and quantitative analysis within the selected representative 25 μm^2 area of the grain. The data confirmed, that besides fundamental, classical halloysite components – SiO_2 and Al_2O_3 – also Fe (2.91 mass %) and Ti (2.03 mass %), incorporated within the halloysite nanotubes and nanoplates, are present. Such structure with natural specific, complex surface chemistry can play a key role in the separation of various impurities based on precisely designed, specific nanostructures, which – together with continuous membrane phase – may provide one with the new separation and processability limits. No literature reports

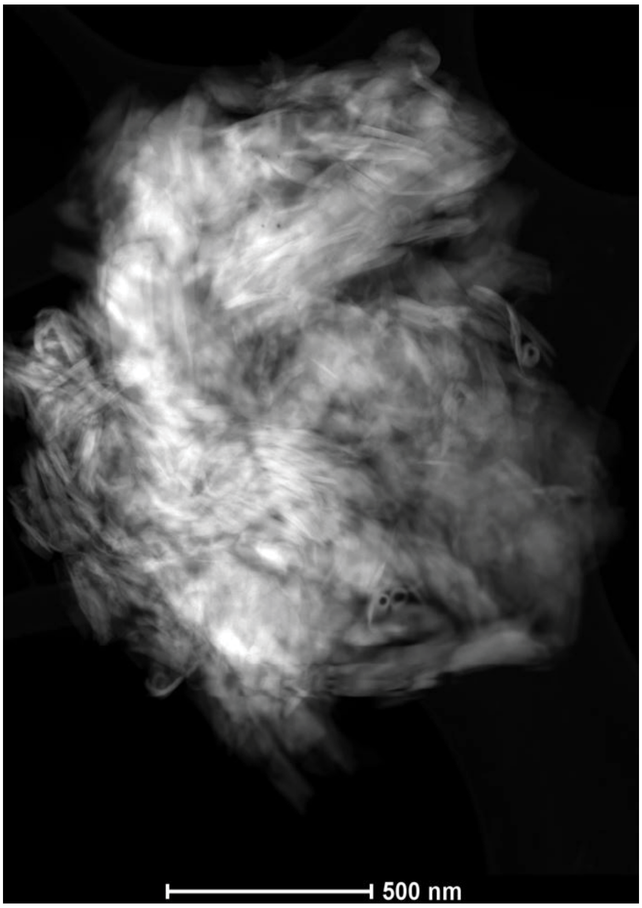

Fig. 6. Transmission electron microscopy (TEM) image of a single halloysite grain structure composed of loosely bound halloysite nanotubes (HNTs) integrated with halloysite nanoplates (HNPs) providing significantly developed specific surface area.

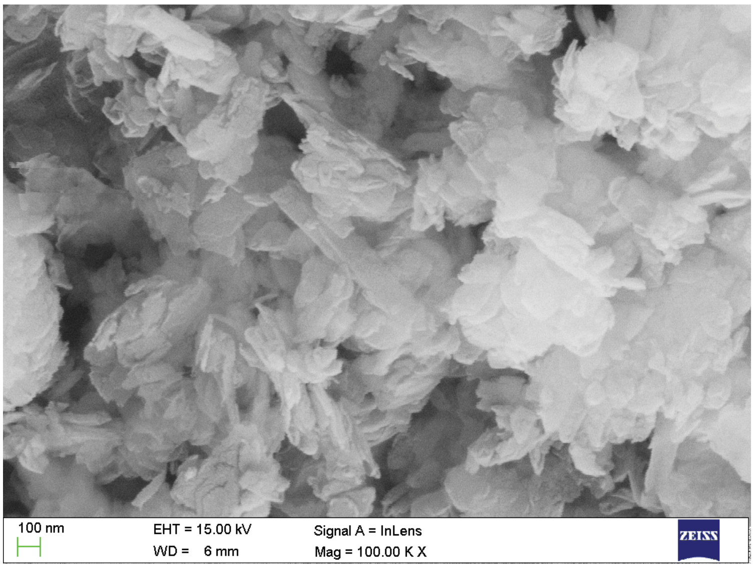

Fig. 5. Scanning electron microscopy (SEM) image of raw halloysite from Polish open-pit halloysite mine "Dunino" – tight structure with halloysite nanotubes (HNTs) and halloysite nanoplates (HNPs).

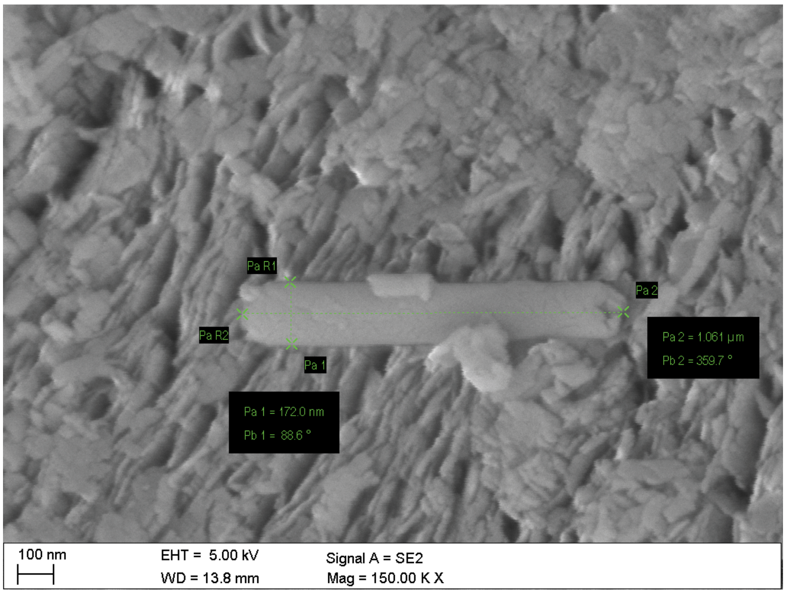

Fig. 7. Scanning electron microscopy (SEM) image of layered structure of halloysite nanoplates (HNPs) and visible halloysite nanotube (HNT) on the top of halloysite nanoplates, responsible for highly developed contact surface within the mixed matrix membrane structure.

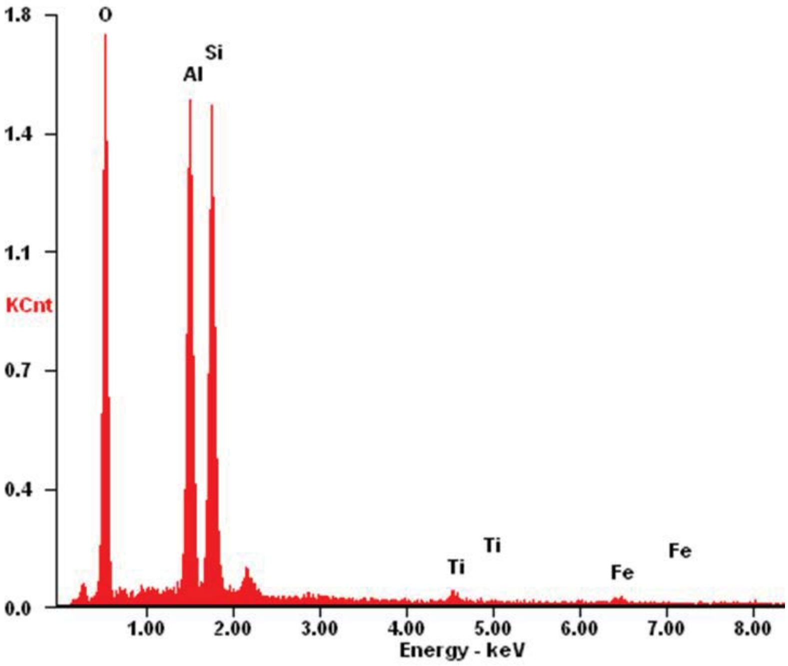

Fig. 8. Exemplary energy-dispersive X-ray spectroscopy (EDS) analysis of the raw dry halloysite powder sample from "Dunino" deposit in Poland – besides Al, Si and O also natural impurities (Ti, Fe) are visible.

concerning the halloysite nanoplates (HNPs) were found in relation to the MMM concept, thus it may indicate some new, original research trend in the future.

Moreover, systematic work must be also done on optimisation of the MMM structure for selected target applications, for example, by substitution, grafting, addition, decoration of these complex systems with some new functional nanoparticles, etc.

The technological conditions for the production of MMM membranes, which determine the spatial structure of the membrane, decisively influencing the exposure of halloysite particles to purified stream and the aforementioned interactions at the polymer-halloysite interface, directly responsible for the resulting complex separation mechanisms, are also gaining importance. Exemplary structures of the polymer-halloysite MMM membranes manufactured

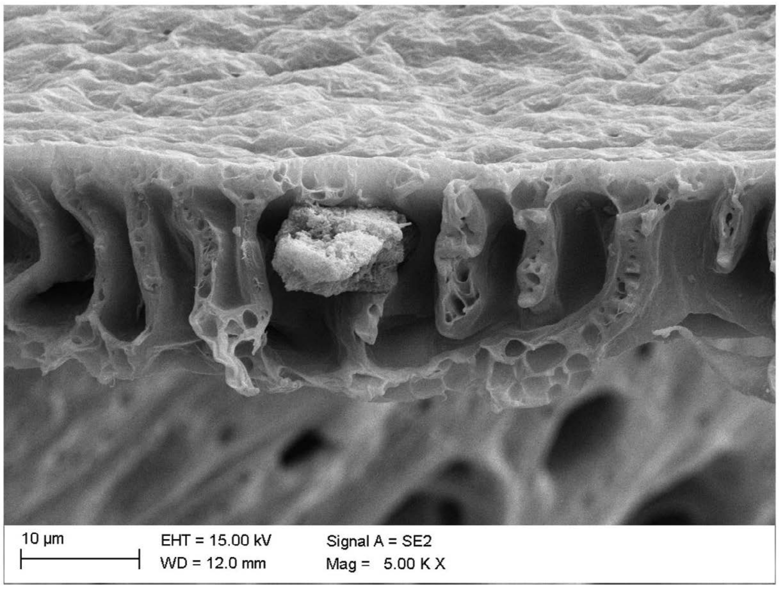

Fig. 9. SEM image of mixed matrix membrane with halloysite filler – visible sub-surface vertical channels and a significant variation in the size of the porous system cells.

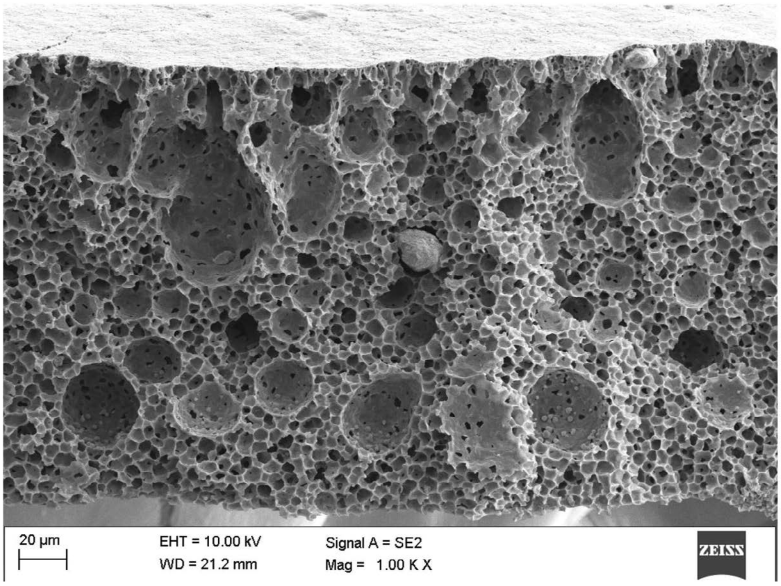

Fig. 10. SEM image of mixed matrix membrane with halloysite filler – visible multi-hierarchical pore structure.

in the laboratory by the authors and pointing to this technical problem are shown in Figs. 9 and 10.

6. Conclusions

Literature reports concerning technological applications of mixed matrix membranes with halloysite nanotubes used as the filler or as advanced filler's support were presented. Attention was focused on the broad range of applications, as well as on the methods of pretreatment and chemical functionalisation purposefully used to obtain specific, possibly tailored separation properties required in a given purification technology.

In general, the HNTs used as the convenient support in various forms of nano-constructions are generally responsible for higher hydrophilicity, which results in higher pure water flux and generally better process yield – parameters necessary in process intensification. By appropriate decoration, polymerization and grafting some new, promising functional nanocomposite structures can be established, with highly specialized targets and precisely tailored selectivity, for example for reactive dyes separation or bacteria growth inhibition.

Equally important is also a selection of appropriate membrane polymer – in this field, some new, especially biodegradable (environmentally friendly) polymers, with specific manufacturing technologies must be tested focusing on identification of the possibly best filler – membrane polymer combination.

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Abbreviations

AEAPTMS — N-β-(aminoethyl)-γ-aminopropyltrimethoxy silane
AgNPs — Silver nanoparticles
APTES — 3-aminopropyltriethoxysilane
BSA — Bovine serum albumin
CA — Cellulose acetate
CuNPs — Copper nanoparticles
CS — Chitosan
DA — Dopamine
FO — Forward osmosis
FRR — Flux recovery ratio
GPU — Permeance unit [1 GPU = 10^{-6} (cm^3(STP)/cm^2 s cm Hg)]
HNP — Halloysite nanoplate
HNT — Halloysite nanotube
LPD — L-DOPA
LPDHNT — L-DOPA/HNTs
LRV — Log reduction value
Ly — Lysozyme
MMM — Mixed matrix membrane
MPC — 2-methacryloyloxyethyl phosphorylcholine
MR — Membrane reactor
NASS — Sodium 4-styrenesulfonate
NF — Nanofiltration
P4VP — Poly(4-vinylpyridine)
PA — Polyamide
PAN — Polyacrylonitrile
PDDA — Poly(diallyldimethylammonium chloride)
PES — Polyether sulfone
PIL — Poly(ionic liquid)
PSF — Polysulfone
PSS — Poly(sodium-4-styrenesulfonate)
PVDF — Polyvinylidene fluoride
RATRP — Reverse atom transfer radical polymerization
RO — Reverse osmosis
rGO — Reduced graphene oxide
SI-ATRP — Surface initiated atom transfer radical polymerization
SL — Silver lactate
UF — Ultrafiltration

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