Ministry of Education

National University of Science and Technology* Politehnica *Bucharest

Doctoral School Chemical Engineering and Biotechnologies

Abstract Thesis

Decision No. 8 from 08 March 2024

Methods of eliminating the bad smell generated by industrial production activities */* Metode de eliminare a disconfortului olfactiv generat de activitățile de producție industriale.

PhD Student: **Dumitru PAȘCU**

Supervisor:

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March 2024

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CONTENT

Chapter 1

Introduction

Odour can be defined as the "perception of smell" or in scientific terms as "a sensation resulting from the reception of stimulus by the olfactory sensory system". Whether pleasant or unpleasant, odour is induced by inhaling air-borne volatile organics or inorganics [1,2].

One of the most important global environmental problems is the air pollution. The danger is caused by the release of various volatile and toxic substances which change the air composition and quality. The latter may have negative impacts not only on the public health but also on the planet's climate [2]. The environmental experts divide all the factors that affect the air into anthropogenic and natural [3]. The greatest damage to environment comes from the former—the factors that are associated with human activity [4]. The major contributors to the air pollution are industrial productions, transport, and landfills [5]

The atmosphere surrounding a plant has great capacity for dispersing odorous effluents. Favorable influences are stack height, gas velocity and gas temperature. Adverse influences are aerodynamic, terrain and meteorologic [6].

Odors and fumes are the natural by-product of many chemical manufacturing processes. Up until a few years ago, odors were considered something inevitably present around many chemical plants (Figure 1) [5,6]. But recently several methods have been developed for controlling or eliminating industrial odors [4-6]. Most odors emanating from chemical plants are not physically dangerous. But they have proved to be psychologically dangerous. The fact that they do not cause organic disease is a difficult point to prove — particularly when the surrounding community, submerged in a disagreeable odor, has been aroused by uninformed rumors and misleading information [7,8].

Exposure to chemical carcinogens imbued with foul odor in various manufacturing industries remains a serious occupational health concern [9]. Workers are exposed to these carcinogens via inhalation [10]. The toxic fumes that were produced throughout the process doesn't just affect the people inside; instead, the concern extends towards the vicinity putting the locals, flora and fauna at risk [11]. Odors and fumes are the natural by-product of many chemical manufacturing processes [12]. Up until a few years ago, odors were considered something inevitably present around many chemical plants [13]. Most odors emanating from chemical plants are not physically dangerous [15]. But they have proved to be psychologically

dangerous [16]. The fact that they do not cause organic disease, is a difficult point to prove particularly when the surrounding community, submerged in a disagreeable odor, has been aroused by uninformed rumors and misleading information [7, 8].

The highest release of hydrogen sulfide into the atmospheric air is observed in places where wastewater from pressure pipelines is poured into gravity sections, differential wells, and drainage points with a high temperature and a low pH value (high acidity), as well as wastewater with a high content of organic substances (Table 1)[11], which is due to the violation of a phase equilibrium between the gases dissolved in the waste liquid and the gaseous medium in these areas. Large cities are more likely to face the problem of emissions of foul-smelling substances into the atmospheric air near sewer networks. To study the gas removal from the atmospheric air near the sewer networks, the main urban sewer collector in the city of Perm is considered. The route under consideration includes pressure and non-pressure sections with a total length of 10575 m. Gas exchange in the sewer collector, i.e. network ventilation, is of a practical interest [7-10].

Tanning is the chemical process that converts animal hides and skin into leather and related products. The transformation of hides into leather is usually done by means of tanning agents and the process generates highly turbid, colored and foul-smelling wastewater.

Table 1. Effects of H_2S [2,8]

Concentration H_2S (ppm)	Symptoms and signs
0.0004–0.02	Odour threshold
20–30	'Rotten eggs' smell
70–200	Irritation of respiratory tract and conjunctiva
100–150	Olfactory paralysis
250–500	Pulmonary oedema
400–700	Headache, dizziness, ataxia, unconsciousness
>500	Respiratory paralysis, death (no warning)

*ppm=parts per million.

The major components of the effluent include sulfide, chromium, volatile organic compounds, large quantities of solid waste, suspended solids like animal hair and trimmings. For every kilogram of hides processed, 30 liters of effluent is generated, and the total quantity of effluent discharged by Indian industries is about 50,000 m3 /day. The various components present in the effluent affect human beings, agriculture and livestock besides causing severe ailments to the tannery workers such as eye diseases, skin Tannery waste material also varies

considerably in volume and concentration due to continuous operation and intermittent discharge [4-7,12].

Thiols are a fundamental and important functional group in organic chemistry, and the literature contains ample reports of organic and bioorganic chemistry on this group. Commonly used thiols like ethanethiol and benzyl mercaptan have a foul smell making them difficult and unpleasant to use in the laboratory without fume hoods. The problem becomes even worse in industry where these malodorous reagents are used on a large scale. Odorless substitutes are therefore always required. While experimental assessment of human olfactory thresholds has been reported for four alkanethiols including 1-dodecanethiol,2 there have been no serious attempts to pursue this research [1,2].

In the production of antibiotics, gases are discharged into the atmosphere which possess peculiar unpleasant odors. In view of the fact that factories producing antibiotics are located mainly in the dwelling areas of large towns, the problem of protecting the air from gaseous discharges is an extremely urgent one. Decreasing the loss of finished product and of organic solvents in these manufactures is primarily a technological problem the solutionof which is economically acceptable and is connected exclusively with improvements in technology and equipment. At the same time, the waste gases from fermentation, because of their specific unpleasant odor and complex composition, require the development of special methods of purification and monitoring. Questions of the standardization and elimination of smells are among the most difficult that exist. Difficulties of standardization are connected with the fact that the perception of smells by man is a very individual characteristic and the laws of the mutual influence of smells has been little studied. The intensity of the perception of smells depends to a considerable extent on the concentration of the substances causing the smells. However, where the concentration of such a substance is considerably higher than the threshold level, even when 99% of it has been removed, practically no effect in decreasing the intensity of the smell is observed. The threshold values are usually very low concentrations, and therefore the purification of the air requires almost 100% elimination of the odoriferous substances. This can be illustrated with the case of ethyl mercaptan. [7-9]. It is difficult to eliminate its smell when this requires the removal of 99.99% of ethyl mercaptan when its original concentration is 3 mg/m^3 [1,2, 13]. The discharges from fermentation factories include several tens of organic substances of different classes (hydrocarbons, ketones, aldehydes, alcohols, esters, volatile C2-C6 fatty acids, oxo acids, organic bases, and, in some cases, phenols) with a total concentration of i-I00 mg/m 3 [13-15].

The transportation and treatment of the urban wastewater involves the formation and emission into the environment of fetid substances: sulfur and nitrogen compounds, volatile fatty acids, aldehydes and ketones. Fetidly smelling odors of a sewage system are formed as a result of the anaerobic biological decomposition of organic substances (proteins, carbohydrates), the presence in the wastewater of sulfate-reducing microorganisms that receive energy through the organic substance oxidation [16-18].

A method and apparatus for deodorizing waste gases containing foul-smelling constituents that are chemically decomposable on being washed with aqueous. acid formed by dissolving an acid-forming gas, such as chlorine or sulfur, in water and wherein the waste gas is washed with the aqueous acid containing a suspension of one or more alkaline earth metal carbonates, such as magnesium carbonate or calcium carbonate. In a vessel, the carbonate suspension may be sprayed downward at the top, and the waste gases directed upwardly at the bottom. Both the suspension and the gases pass through loose layers of limestone intermediate the top and bottom of the vessel [19-21].

Conclusions

Industrial production leads along with the goods needed by society and residues, a large part of which are emitted into the atmosphere.

A large part of the materials emitted into the atmosphere are toxic, but fortunately they also have an unpleasant smell.

Thus, the elimination of foul-smelling substances from the atmosphere also contributes to improving air quality.

In this PhD thesis, a series of techniques and methods are presented for removing foul-smelling substances or generating substances of this type: hydrogen sulfide, mercaptans, and phenols.

Among the techniques for separating foul-smelling substances are addressed: liquid membranes, polymer and composite membranes.
This chapter was created based on the article

Paşcu, D., Nechifor, A.C., Grosu, V.-A., Oprea, O.C., Tanczos, S.-K., Man, G.T., Dumitru, F., Grosu, A.R., Nechifor, G. Hydrogen Sulphide Sequestration with Metallic Ions in Acidic Media Based on chitosan/sEPDM/ Polypropylene Composites Hollow Fiber Membranes

Capitolul 3

Experimental part

3.1. PhD thesis scope and objectives

The doctoral thesis "Methods of eliminating the bad smell generated by industrial production" aims to correct the bad smell generated by industrial activities through membrane methods and techniques.

The specific objectives

- Identification of foul-smelling substances and those that can generate compounds with an unpleasant smell

- Preparation of polymer and composite membranes

- Obtaining liquid membranes

- Morphological, structural and process performance characterization of the membranes

- Removal of hydrogen sulfide and thiols from liquid and gaseous effluents

- Recuperative separation of hydrogen sulfide

Chapter 4.

Unpleasant smell compounds separation

4.1. Hydrogen sulfide sequestration with metallic ions in acidic media with the chitosan/sEPDM/polypropylene composites hollow fiber membranes system

Abstract:

Unpleasant smell released by hydrogen sulphide from different gaseous mixture is generally associated with its toxicity from where, the interest of the membrane area's researchers to find the ways to capture and sequestrate it. This paper presents the preparation and characterization of composite membranes based on chitosan (Chi), sulfonated ethylene-propylene-diene terpolymer (sEPDM) and polypropylene (PPy) that are designed for hydrogen sulfide sequestration. The membranes have been obtained by posting a deep coating polypropylene hollow fiber membrane in a 10g/l sEPDM-Chi (w/w) toluene dispersion followed by a controlled evaporation. They have been morphologically and structurally characterized by scanning electron microscopy (SEM), Fourier Transform InfraRed spectroscopy (FTIR), energy-dispersive spectroscopy analysis (EDAX), thermal analysis (TG, DSC), thermal analysis coupled with chromatography and infrared analysis but also from the point of view of their performance in the process of hydrogen sulfide sequestration in acidic media solution which metallic ions content (Cu^{2+}, Cd^{2+}, Pb^{2+}, and/or Zn^{2+}). Pertraction operational parameters are the pH, pM, the flow of the matrix gases and its composition. The results of pertraction from synthetic gases mixture (nitrogen, methane, carbon dioxide) prove an efficient removal of the hydrogen sulphide through especially prepared composite membranes and its appropriate fixing as sulfides. Hydrogen sulfide sequestration and its recupertive separation as suplhides from acidic media reach up to 96% and it is decreasing in the following order: CuS>PbS>CdS>ZnS. Efficiency of the hydrogen sulfide removement from gaseous mixtures decreases as follows: nitrogen>methane>carbon dioxide. The presented recuperative separation method it might at the same time be a method of valorization for Cu-Zn or Pb-Cd wate types as generated by the industries of electronics and/or electrotechnics.

Keywords: hydrogen sulfide sequestration; composite membranes; chitosan; sEPDM; polypropylene, hollow fiber membrane; hydrogen sulfide sequestration; electrotechnics waste.

4.1.1. Introduction

Within this chapter we have studied both, the recuperative separation of the hydrogen sulfide from the gaseous mixtures whom it contaminates and also of the metallic cations from the waste of electronic and electrotechnical industries under the form of long-lasting acidic solutions.

For the sequestration of hydrogen sulfide from sources phase (RP) of the poor gas, we are studying the pertraction via the composite membranes based on chitosan (Chi), sulfonated

ethylene-propylene-diene terpolymer (sEPDM), and polypropylene hollow fiber (PPy) into acidic receiving phases (RP) with metallic ions content (Cu^{2+}, Cd^{2+}, Pb^{2+}, and/or Zn^{2+}).

Pertraction operational parameters are the pH, pM, the flow of the matrix gases and its composition.

4.1.2. Materials and methods

4.1.2.1. Reagents and materials

4.1.2.1.1. Reagents

The materials used in the present work were of analytical purity. They were purchased from Merck (Merck KGaA, Darmstadt, Germany) – sodium sulfide (Na_2S) [78,0452 g/mol (anhydrous)], hydrogen sulfide, sodium hydroxide, nitric acid, and hydrochloric acid.

$Cu(NO_3)_2 \cdot 3 H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Pb(NO_3)_2$, $Zn(NO_3)_2$, NaCl, chitosan, and glacial acetic acid (analytical grade, Sigma-Aldrich Chemie GmbH, Steinheim, Germany) were used in the studies. NaOH pellets, H_2SO_4 (96%), HCl (35%), (62%), ultrapure and NH_4OH 25% (analytical grade) were purchased from Merck KGaA Darmstadt, Germany.

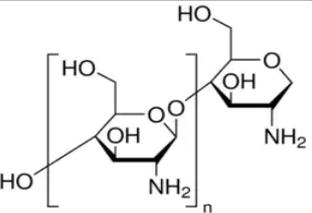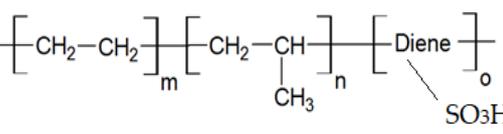Ultrapure waters were used for preparing the feeding solutions for every case.

The purified water, characterized by 18.2 µS/cm conductivity, was obtained with a RO Millipore system (MilliQ^R Direct 8 RO Water Purification System, Merck).

The tubular dialysis membranes were from Visking (Medicell Membranes Ltd., London, UK). *MQuant®* sulfide test (Merck Millipore), Sulfide Test photometric, *Spectroquant®* (*Merck* KGaA, Darmstadt, Germany).

4.1.2.1.2. Materials

The polymers used to get the composite membranes are chitosan (Chi) (Sigma-Aldrich Chemie GmbH, Steinheim, Germany) and sulfonated ethylene-propylene-diene terpolymer (sEPDM), which were recently used in our research group for ionic and molecular separations [1]. Their main characteristics are highlighted by the Table 1.

Table 1. The characteristics of the used polymers

Polymers	Name and Symbol	Molar mass (g/mol)	Solubility in water (g/L)	pKa
	Chitosan (Chi)	1526.5	soluble in acid media (0.5 M HCl: 50 mg/mL)	6.2 to 7.0
	sulfonated ethylene-propylene-diene terpolymer (sEPDM)	–	soluble in toluene	1.9 to 2.2

The hollow polypropylene fibers used as membranes' support (PPM) were provided by GOST Ltd., Perugia, Italy) and their characteristics have been presented into detalis within the our prior works. [2].

4.1.2.2. Procedures

4.1.2.2.1. Preparing the composite membranes (Chi/sEPDM/PPy)

One dispertion of 10g/L mixture of chitosan (Chi) polimer and sulfonated ethylene-propylene-diene terpolymer (sEPDM) (1:1;w/w) in toluene has been prepared by the dispersion of 5g chitosan powder into one liter of toluenic solution of sulfonated ethylene-propylene-diene terpolymer (5g/L).

Hollow polypropylene fibers membrane (PPy) are assembled (Figure 2) as to fit its mounting into a pertraction module that ensure a masic transfer surface of $1.0 m^2$. Fiber's assembly (Figure 2a) are wheighted with an analytical balance, than introduced into a tank of 2 liters volumes containing 1 liter of dispersion, exposed to a low vacuum (100mmHg) for 30 minute (Figure 2b); finally it is introduced two hours into a vacuum oven at 60°C for drying purpose. The membrane's assembly coverd by the composite membrane it is introduced into an excitatory system in order to get the room's ambiental temperature than it is wheighted by analytical balance to evaluate the quantity of the polimers as placed on the fibres. If during the wheighting, the mass wheighted is not constant, the fiber's assembly will pe exposed again into the the vacuum oven for a time of 10 minutes and this step is repeated and repeated again till

the constant mass is reached and regsitered. Two sealing elements are attached to ends of the fiber's assembly by fixing them to each end with an acrylic polimer (Figure 2c). In the same time the composite chitosan (Chi) membrane, the sulfonated ethylene-propylene-diene terpolymer (Chi/sEPDM) and sulfonated ethylene-propylene-diene terpolymer (sEPDM) are going to be prepared (Figure 2) as necessary to straightly characterize the control samples.
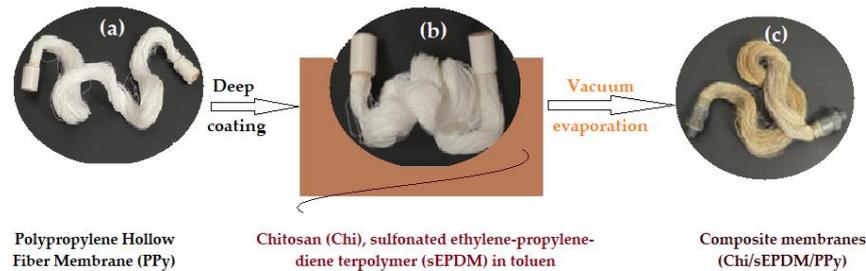

Figure 1. Schematic presentation of getting the composite membrane (Chi/sEPDM/Ppy)

Figure 2. Schematic presentation of obtaining the polymer membrane (sEPDM) or of the composite membrane (Chi/sEPDM)

The beam of composite membrane is mounted into a pertraction module; in this way a membrane contactor is obtained in similar way to a tubular preheater, like to all similarities deeply described into our previous works [2-5]. This module is placed into the working installation (Figure 3).

4.1.2.2.2. Hydrogen sulpfide's pertraction with composite membranes

The solutions (Cu^{2+}, Zn^{2+} , or/and Cd^{2+}) can be prepared from the available reagents without any restrictions, but the aqueous solutions containing Pb2+ require precautions therefore the corresponding nitrates are to be used.

The separation tests are performed with $5 \cdot 10^{-7}$-10^{-3}mol/L solutions of Cu(NO$_3$)$_2$, Cd(NO$_3$)$_2$, Zn(NO$_3$)$_2$, Pb(NO$_3$)$_2$ obtained in ultrapure water [6].

The experiment of pertraction of the hydrogen sulfide sequestration from gaseous mixture is performed in installations with tubular configuration module as presented in the Figure no 3. This installation has its central element as the pertraction module (1) into which the composite membranes are fastened. 5 liters of receiving solution with specified composition (pH and the extent of metallic ions concentration) is handled by the pump (3) through the outside part of the membrane fibers with a variable flow of 100-500mL/min; the source phase of gaseous mixture with a content of 20-120ppm hydrogen sulfide is handled by 2-20 L/min inflow, trough the inner part of the capillary fibers. Residual gas is passed via gas-liquid separators (4, 5) and at the evacuation point it pushed away via a sodium hydroxide hatch. The gaseous phases composition at the source it is obtained by dosing of the matrix gas (nitrogen, methane, carbon dioxide) into a reducing system based on reducers and flowmeters. The system allows the flow adjustments for the stream in which the appropriate quantity of hydrogen sulfide it is injected. A glass capillary serpentine of 10 meters length plus a detention tank are to be used to homogenize the gaseous mixture. Operational parameters (pH, pM, the flow and the composition of gaseous mixture) are specified for each experiment and one type of experiment has already been three–five times repeated (from case to case) in order to assess the maximum accuracy.

The determination of the gas composition is done in one point located after the homogenization serpentine and just before the sodium hydroxide capturing hatch, using a specific sensor. Validation of the results is also performed with a clear analyze of the sulfide ions concentration in sodium hydroxide capturing hatch [7].

The pertraction efficiency (*PE%*) for the species of interest (hydrogen sulfide) using the concentration of the solutions [8] was calculated as follows (1):

$$PE(\%) = \frac{(c_0 - c_f)}{c_0} \cdot 100 \qquad\qquad (1)$$

where: c_f – final concentration of the solute (hydrogen sulfide), c_o – initial concentration of solute (hydrogen sulfide).
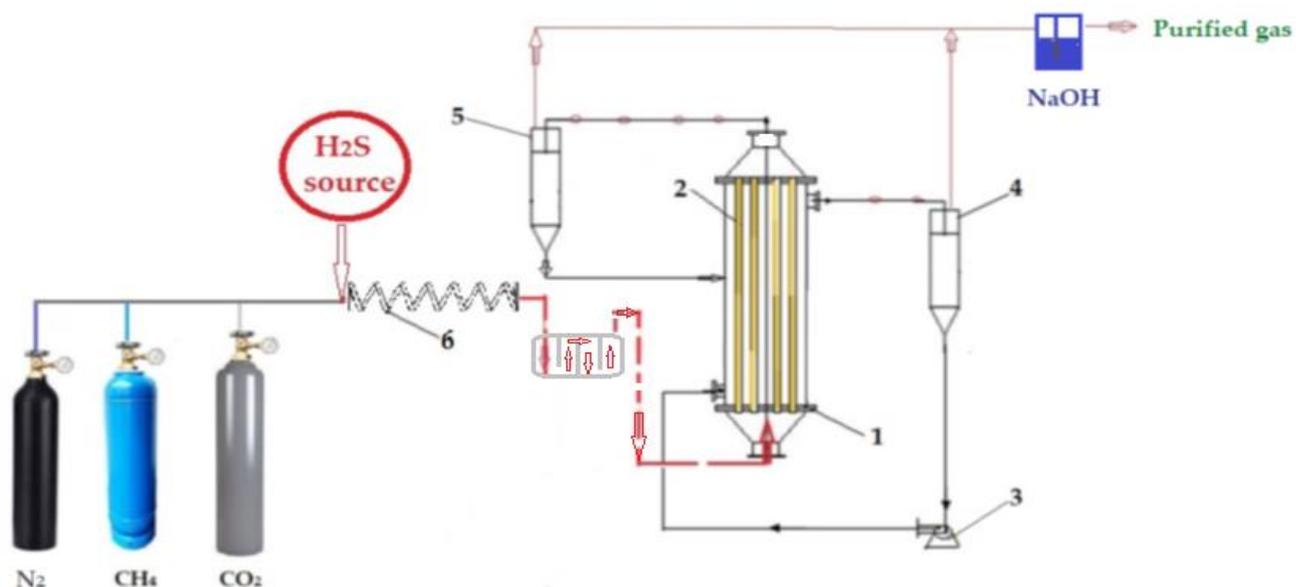
Figure 3. The schematic presentation of the hydrogen sulfide sequestration from gaseous mixture in lab installation: 1- membrane contactor; 2-composite hollow fiber membranes; 3-poump for acidic solution of metallic ions solutions; 4 and 5-gas-liquid separator; 6-homogenization.

The measurements have been independently validated using a gas detector Oldham (MX 21 Plus Multigas France) equipped with electrochemical sensors or H_2S Model 3000RS Analyzer (MultiLab LLC, Bucharest, Romania) [9].

The parallel determination of the free metallic ions in the receiving phase are made with the atomic absorption spectrometry.

4.1.3. Results and discussion

The recuperative separation covered by this study aims to the purification of the common gases such us nitrogen, methane and carbon dioxide from the polluted hydrogen sulfide through its sequestration as valorization sulfides. The recuperative separation is performed on acidic solution from waste generated by electronics and electrotechnics industries with a low extent of metallic ions (Cu^{2+}, Cd^{2+}, Pb^{2+} , and/or Zn^{2+}), according to the chemical equations underlined by (2)-(5).

$$Cu^{2+} + S^{2-} \rightleftharpoons CuS_{(s)} \tag{2}$$

$$Zn^{2+} + S^{2-} \rightleftharpoons ZnS_{(s)} \tag{3}$$

$$Pb^{2+} + S^{2-} \rightleftharpoons PbS_{(s)} \tag{4}$$

$$Cd^{2+} + S^{2-} \rightleftharpoons CdS_{(s)} \tag{5}$$

The composite membranes used to separate the hydrogen sulfides is prepared by immersing the tubular fiber of polypropylene into a dispersion of chitosan in a toluene sEPDM solution followed by controlled evaporation. They have been morphologically and structurally characterized by different methods such us: scanning electron microscopy (SEM), Fourier Transform InfraRed spectroscopy (FTIR), energy-dispersive spectroscopy analysis energy-dispersive spectroscopy analysis (EDAX), thermal analysis (TG, DSC), thermal analysis coupled with chromatography and infrared analysis.

The results of pertraction process are assessed by managing variations in operational parameters pH, pM (for the receiving phase) and the flow of the matrix gas and its composition (for the source phase).

4.1.3.1. Morphological and structural membrane and membrane materials characteristics
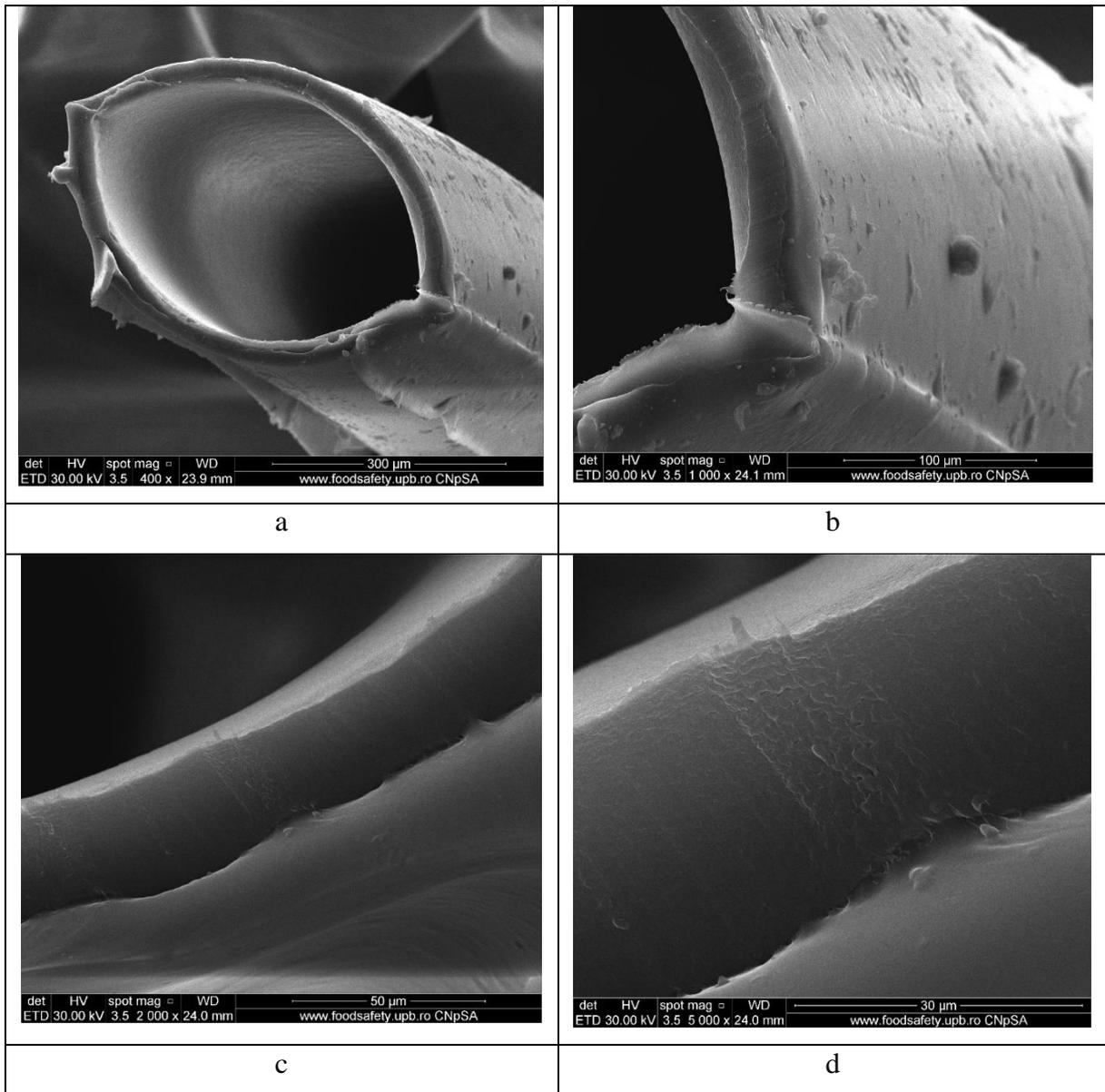
4.1.3.1.1. Scanning electron microscopy (SEM)

The composite membrane samples based on chitosan (Chi), sulfonated ethylene-propylene-diene terpolymer (sEPDM), and polypropylene hollow fiber (PPy) with a length of 3 cm, have been fractured in liquid nitrogen and metallized with a superficial layer of gold, to be able to examine the surface and the section of the membranes (scanning electron microscopy, SEM) and the elemental distribution on the surface (energy-dispersive spectroscopy analysis, EDAX), analyses available on a Hitachi S4500 system.

The composite menbrane's morphology (Chi/sEPDM/PPy) is pictured in figure 4. In this way, the image of the membrane's profile examinate from the right side at low magnitude-400x as presented in Figure 4a let to distinguish on the external and inner diameters of the fiber located at around 300μm.

In 4b figure: for -100X magnitude we have captured the uniformity of the superficial chitosan and sulfonated ethylene-propylene-diene terpolymer deposited agglomeration which consists

now in a consistent and active layer. The thickness of around 30µm of the polypropylene fiber wall can be measures in the figures 4 c and d performed at magnitudes of 2000x and 5000X respectively. Looking into the polypropylene fiber from the right side 4a figures, the features of the pores in terms of size and their distribution have been highlighted (for an use of 10000x magnitude-Figure 4e and 40000x -Figure 4f) all of them confirming the results presented within the prior works [10-12].
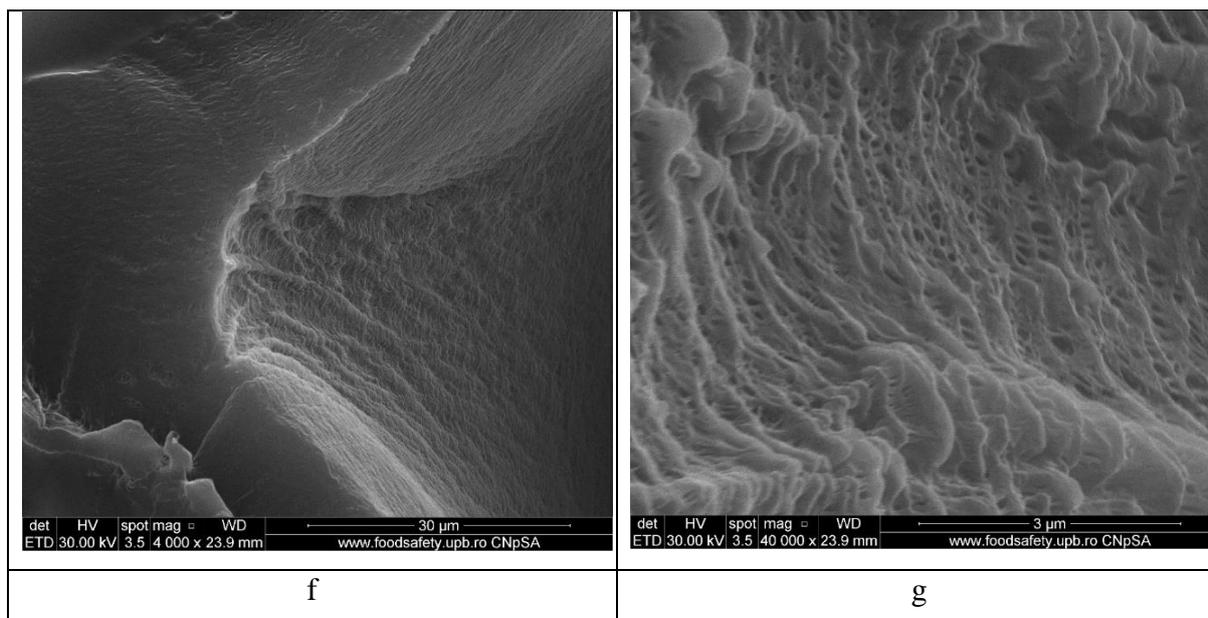

a

b

c

d

Figure 4. Scanning electron microscopy (SEM) images for the chitosan/sulfonated ethylene-propylene-diene terpolymer composite membranes (Chi/sEPDM/PPy): (b), (d) and (f).

In the figure no 5 the focus is spotted on chitosan and sulfonated ethylene-propylene-diene terpolymer membrane layer. In this way, the active layer as presented in the left side of the 5a image of 1000x magnitude, it might be scanned to the left therefor the image is obtained from a more ample and larger perspective (Figure 5b-magnitude of 10000x) highlighting the Chi/sEPDM composed surface. Accurately analyzing the layer of chitosan and sulfonated ethylene-propylene-diene terpolymer at 40000X magnitude (Figures 5c), we can observe the polymeric Chi/sEPDM plaques that have an infrastructure formed by a continue phase of sulfide polymer while the dispersion (spherical nanoparticles) is built by chitosan (Figure 5e magnitude 50000x).

The data provided by scanning electronic microscopy (SEM) (Figures 5) has been additionally concluded using an energy dispersive spectroscopy analysis (EDAX) as we can see in the diagram no 6 for the top surface membrane materials: sulfonated ethylene-propylene-diene terpolymer (sEPDM) (Figure 6a) and chitosan (Chi)–sulfonated ethylene-propylene–diene terpolymer (Chi–sEPDM) (Figure 6 b). However, in the EDAX spectres distinctly appear only the atoms of carbon ©, oxygen (O) and sulphur (S) whereas the atoms of nitrogen could not be underlined due to the working technique. The active structure of the layer has also been analysed by an infrared spectroscopy plus the microscopy techniques.
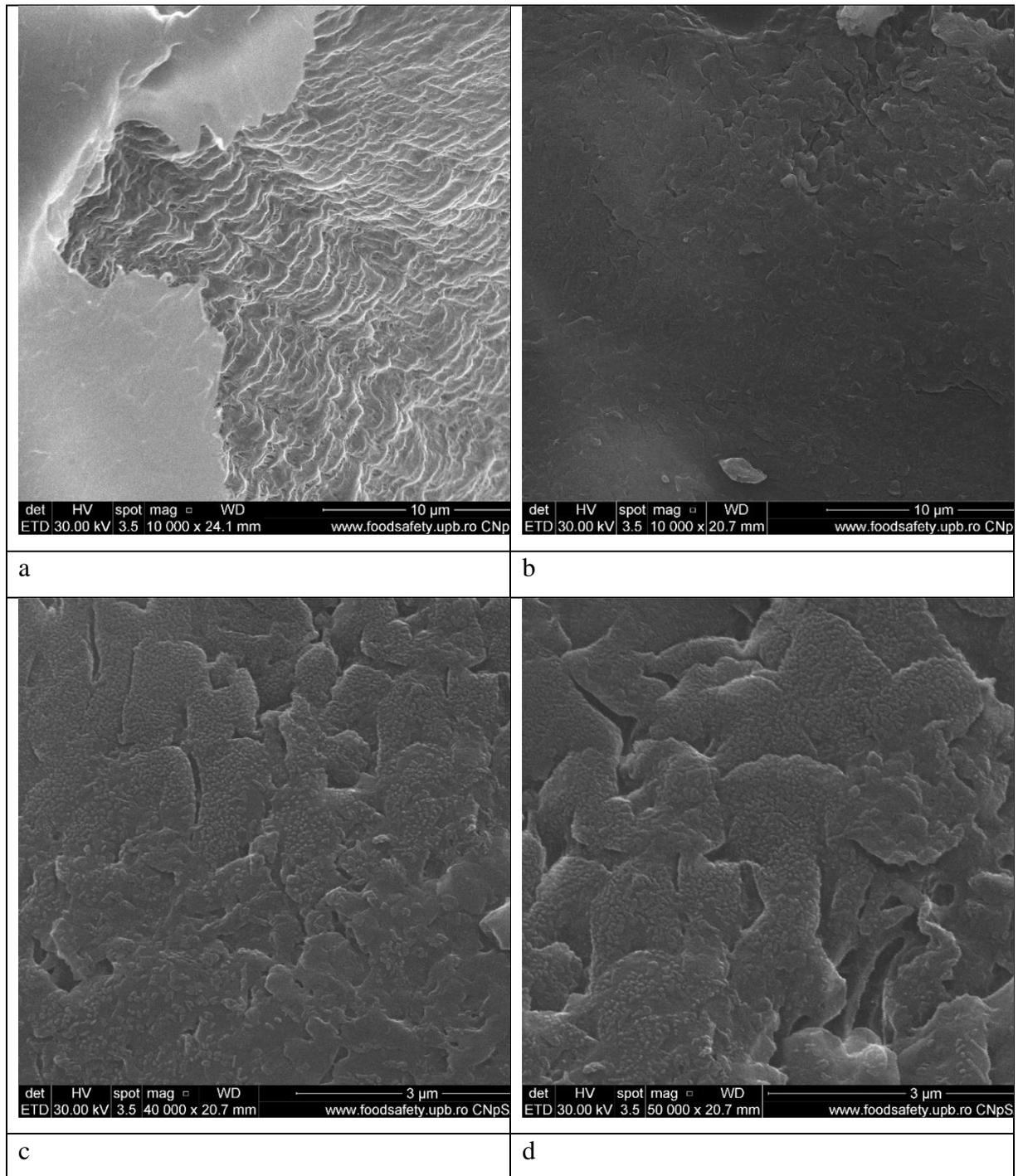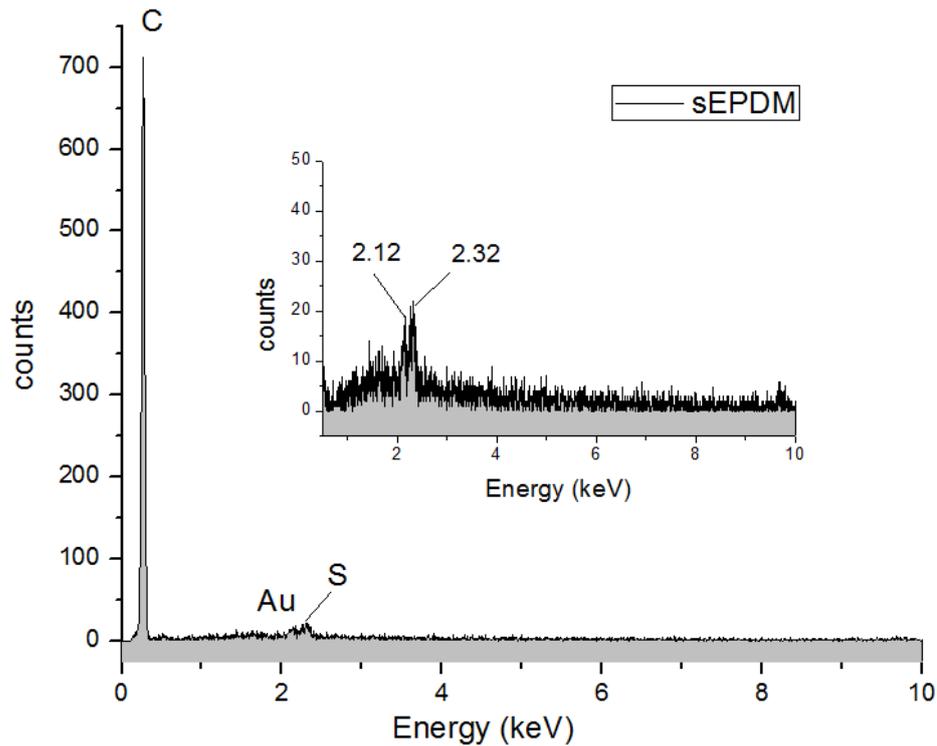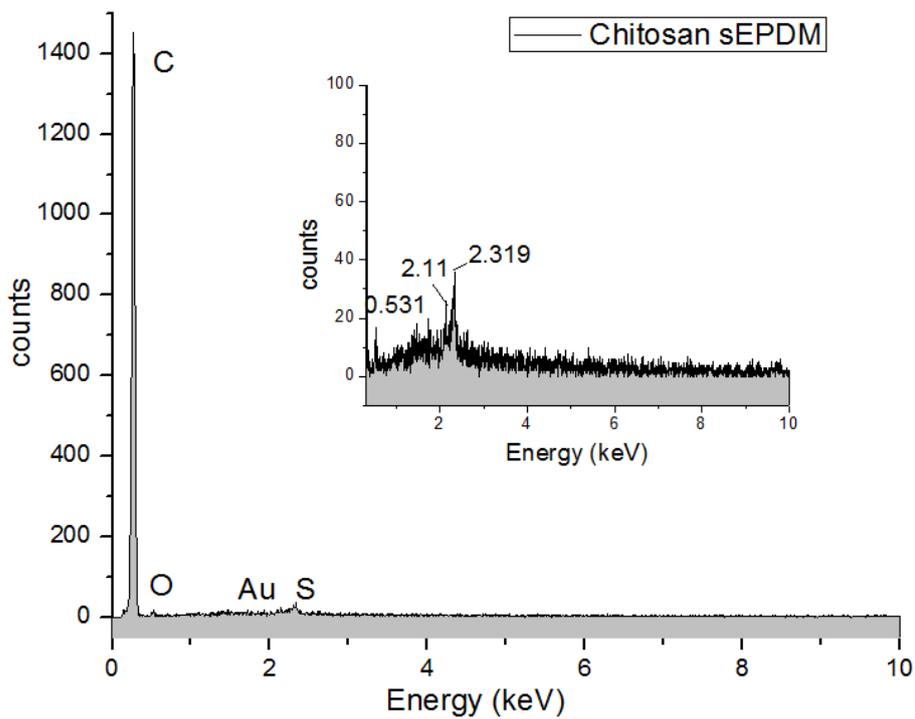
Figure 5. Top surface scanning electron microscopy (SEM) images for the chitosan/sulfonated ethylene-propylene-diene terpolymer composite membranes (Chi/sEPDM/PPy): (b), (d) and (f).

(a)

(b)

Figure 6. Energy-dispersive spectroscopy analysis (EDAX) diagram for the membrane materials: sulfonated ethylene-propylene-diene terpolymer (sEPDM) (a); chitosan/sulfonated ethylene-propylene–diene terpolymer membrane (Chi/sEPDM) (b).

4.1.3.1.2. Fourier Transform InfraRed spectroscopy (FTIR) membrane characteristics

The data obtained by using (EDAX) elemental analisys have imposed a further study in the infrared area both spectral (FTIR) and also IRM (interfferecne and reflective microscopy). This study'results have completed the structural information of the membranes and their surface composition versus the sample membranes as they have been prepared (Figure 2).

The FTIR specres for the sample membranes have been built: sulfonated ethylene-propylene-diene terpolymer membranes (sEPDM) and chitosan/sulfonated ethylene-propylene–diene terpolymer composite membranes (Chi/sEPDM) (Figure 7).
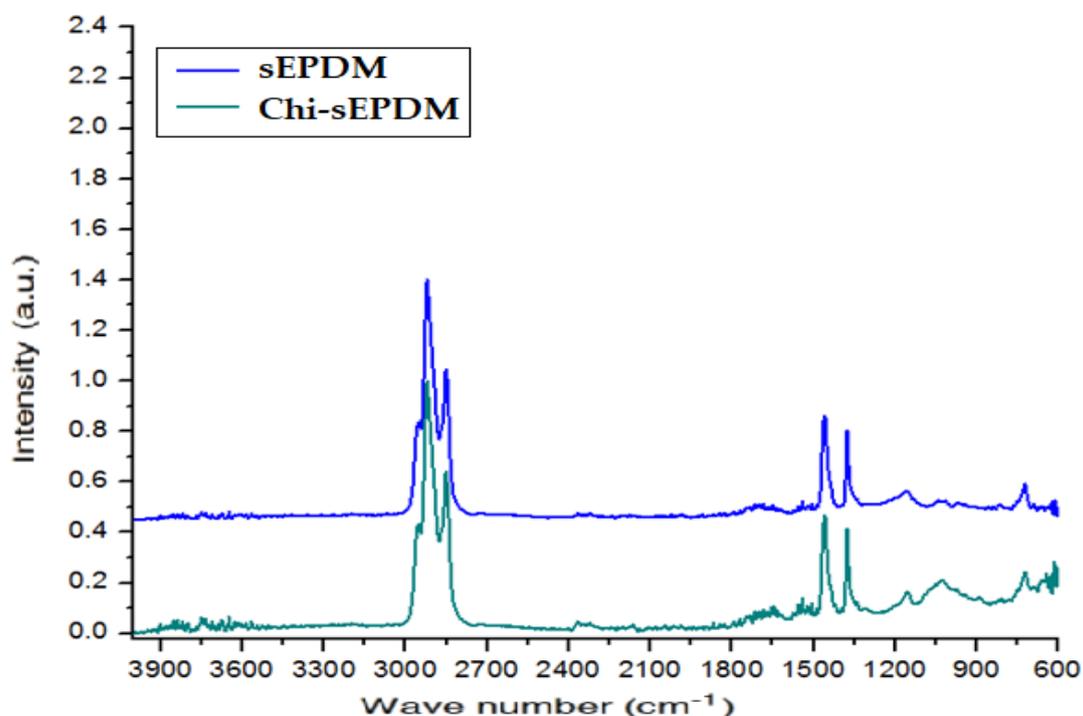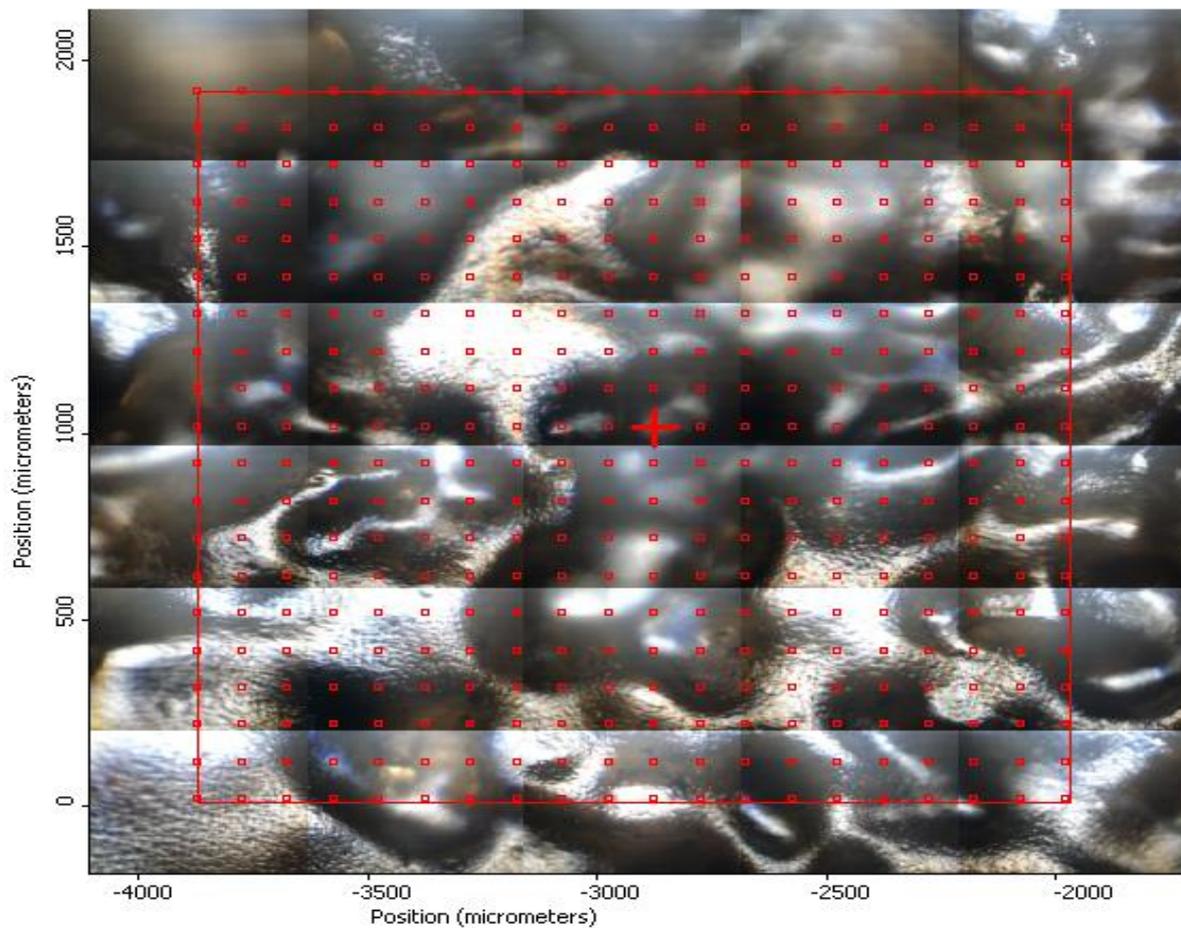

Figure 7. Fourier Transform InfraRed spectra for membrane and membrane's materials: sulfonated ethylene-propylene-diene terpolymer (sEPDM) and chitosan/sulfonated ethylene-propylene-diene terpolymer composite membrane (Chi/sEPDM).

All the obtained spectres as from figure 7 are not presenting specific bands appropriate to analyze data by infrared reflective microscopy (IRM) so that to focus on the superficial layer of chitosan/sulfonated ethylene-propylene-diene terpolymer of the composite membrane, we have selected an individual band's number from every specific interval on the domain of 3345 cm^{-1}, 1385 cm^{-1} , 1050 cm^{-1}, si 728 cm^{-1}.

HD-IR charts as get for the composite membrane area (figure 8a) prove an outstanding spectral uniformity (Figures 8b-e), materialized in a formal assembly specter as pictured in 8f figure. These results shows that the examined superficial layer is almost entirely build by sulfonated ethylene-propylene-diene terpolymer which integrally covers the composite membrane including the chitosan nanoparticles presented within the figures 5c and 5d. Superior layer of ethylene-propylene-diene terpolymer that cloth the composite membrane it might be in the favor of the pertraction process taking into consideration that its absence may generate the chitosan particles implosion.

This phenomenon is already pointed out, registered, and further studied in order to get a testing membrane of chitosan/sulfonated ethylene-propylene-diene terpolymer whom the chitosan aggregates may accumulate water during the pertraction process (if exposed to an osmotic pressure) therefore generating the membrane's degradation (Figure 8).
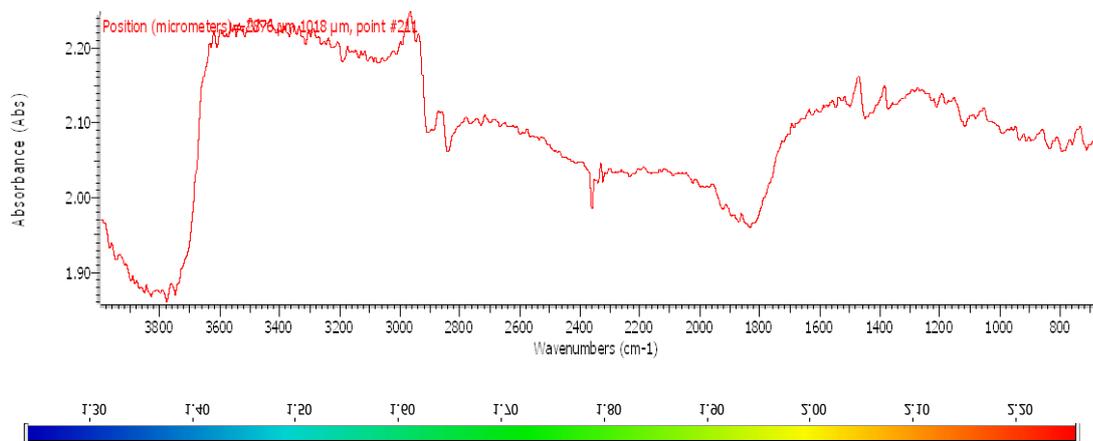
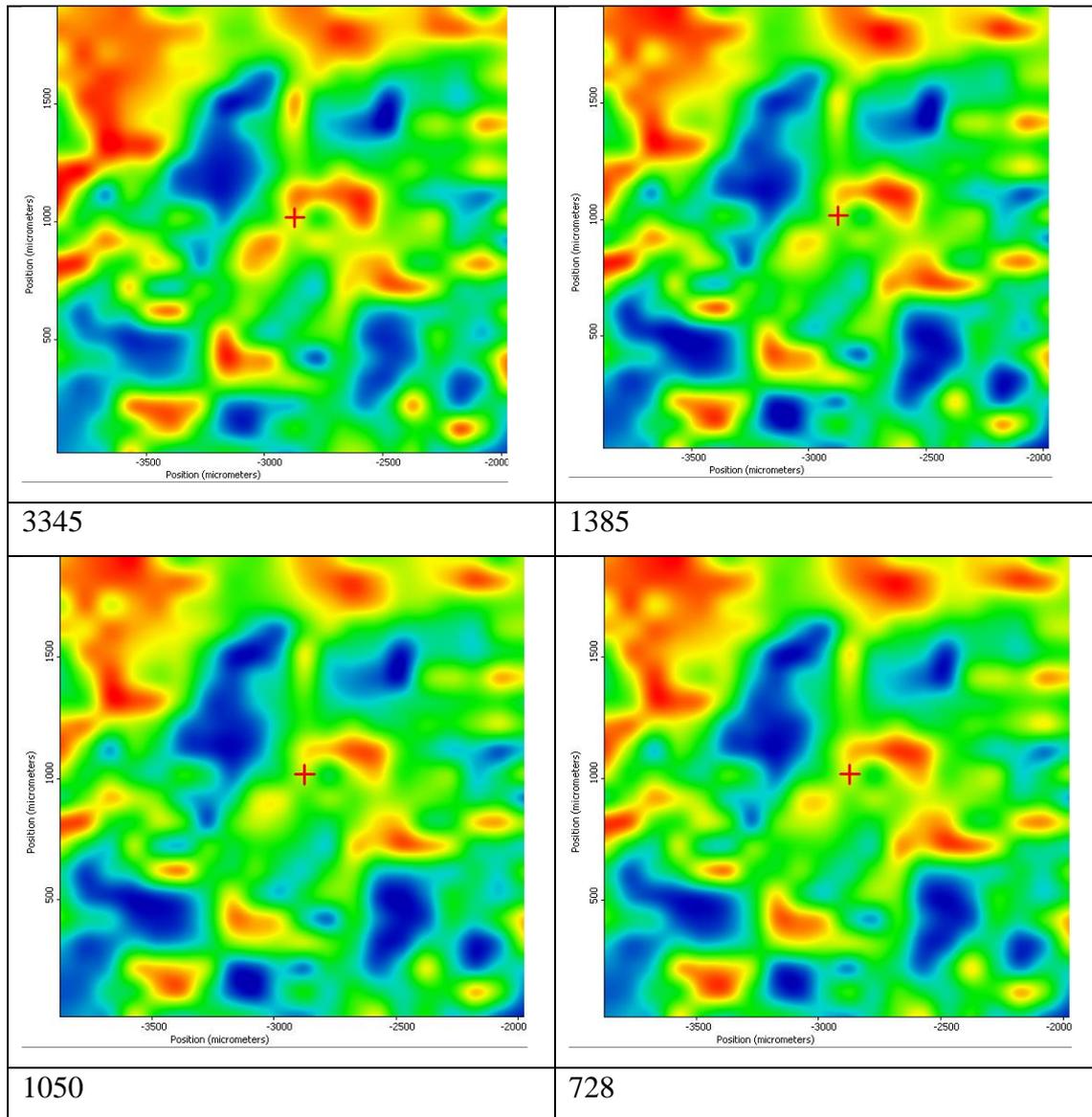

a

Figure 8. Video-images (a), the 2HD-IR obtained maps at the specific wave number (b-e); and infrared associated spectrum and colour scales (f) for the chitosan–sulfonated ethylene-propylene/diene terpolymer composite membrane (Chi/sEPDM).
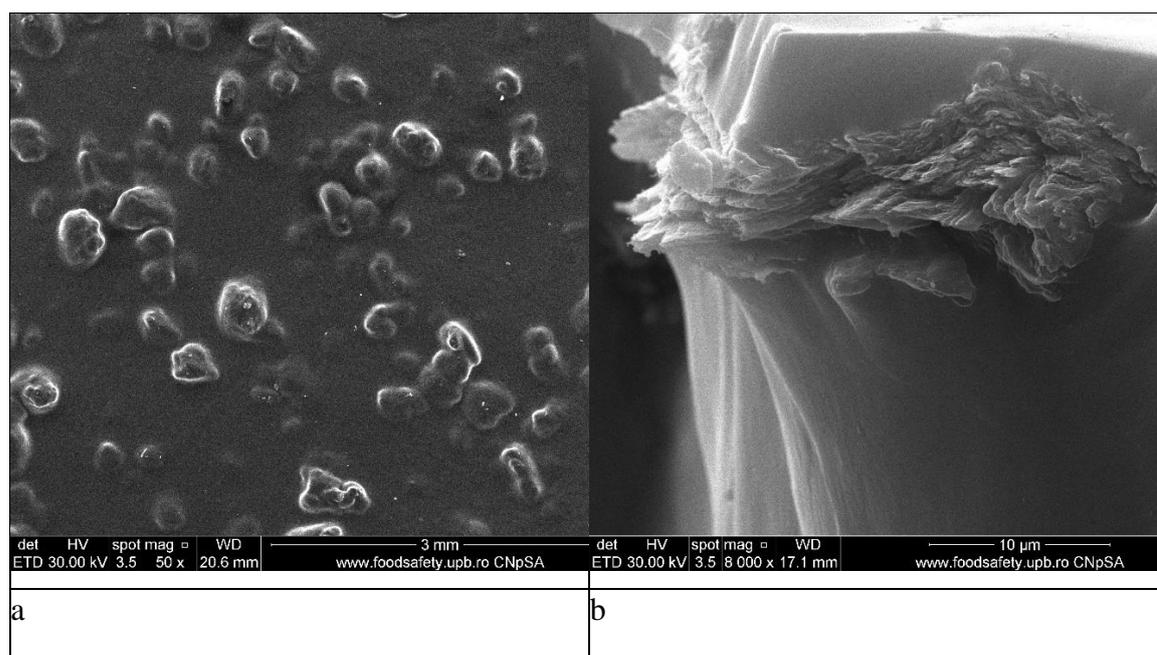
Figure 9. Scanning electron microscopy (SEM) images for the chitosan/sulfonated ethylene-propylene-diene terpolymer test composite membranes (Chi/sEPDM): top surface (a) and cross-section (b).

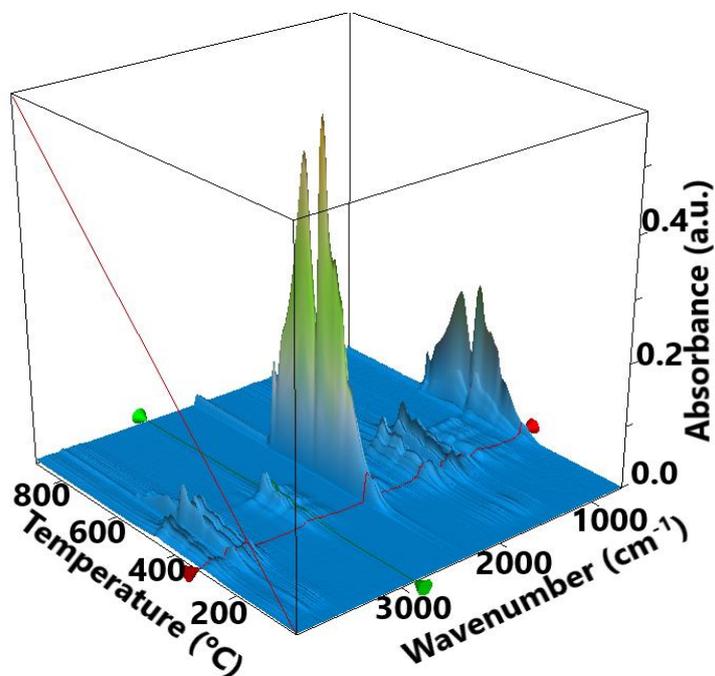*4.1.3.1.3. Thermal characteristics of the prepared test membranes*

The complex thermal analysis has been conducted to monitories the membrane's thermically behavior as to utilize it into the processes at temperature areas higher than the ambiental one (targeted interval until 200°C); the same complex analysis has been conducted to validate the composition of the composite chitosan/sulfonated ethylene-propylene-diene terpolymer membrane (targeted interval above 200°C). The membrane's composition is done via a gas chromatography analysis plus an infrared spectrometry on exhausted burnt gases (until 800 °C).

The chitosan/sulfonated ethylene-propylene-diene terpolymer membrane's probe loses 4.54% till the temperature reach a 220 °C value (Figure 10a), especially the water molecules and some slight trace of SO_2 as indicated by FTIR specters (Figure 10b and c). The main degradation processes came into the place between 220-475 °C when on the DSC profile some exothermic processes are there recorded thus indicating several reactions of oxidation. The most important part of gaseous products CO, H_2O, hydrocarbons fractions and SO_2 are removed within this interval. The mass loss is 69.49%. From the above of 475°C, the carbonic residual mass burns and the main identified product of degradation (FTIR usage) is CO_2.

Figure 11 presents the released gases as identified as trasses, during the increase of temperature of examinate sample to specific band's numbers: : sulfur dioxide (SO_2) to 1367 cm^{-1} (Figure 11a), carbon dioxide (CO_2) to 2355 cm^{-1} (Figure 12b), hydrocarbons to 2964 cm^{-1} (Figure 12c) and water (H_2O) to 3566 cm^{-1} (Figure 12a).
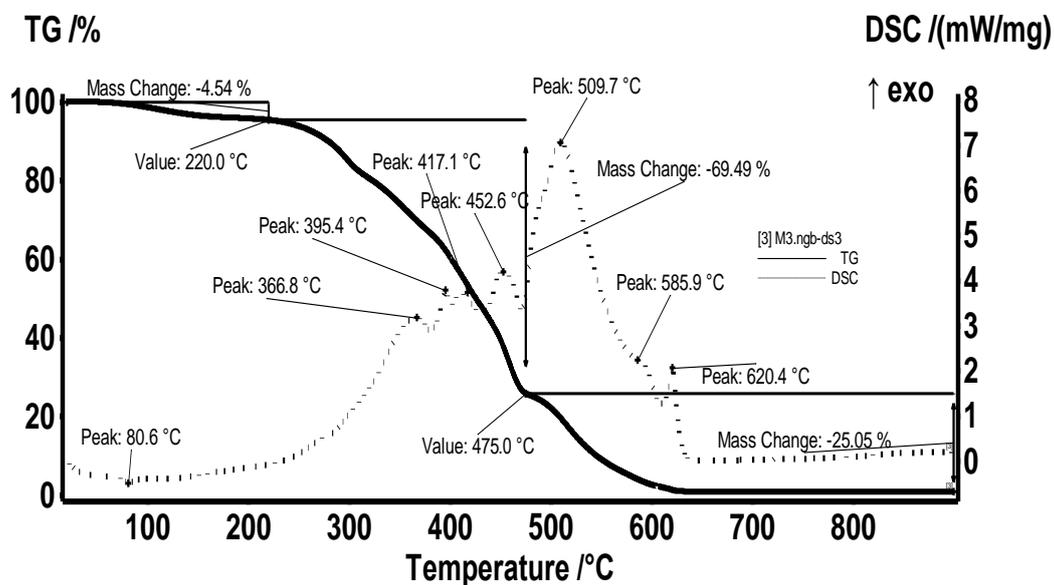
a

b
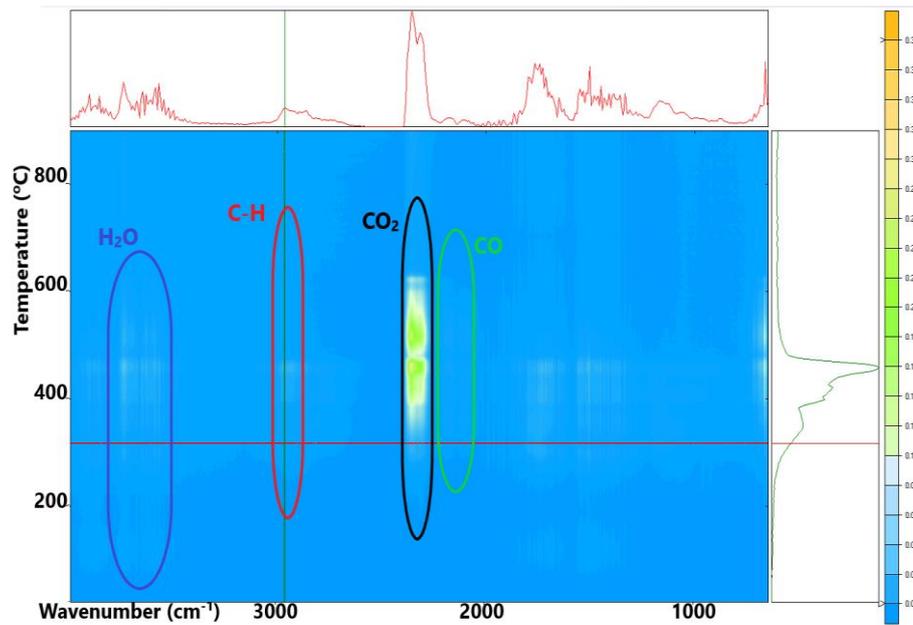
c

Figure 10. Thermal characteristics of the sulfonated ethylene-propylene-diene terpolymer (sEPDM) membrane (M1): (a) thermal diagram; (b) 3D complex analysis; (c) 2D complex analysis.

(a)

(b)

(c)   (d)

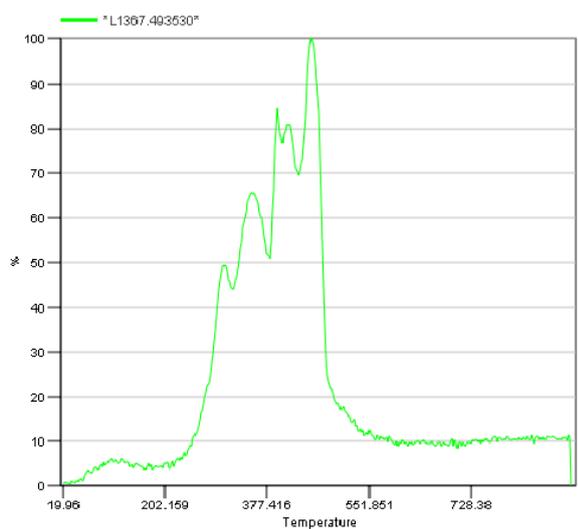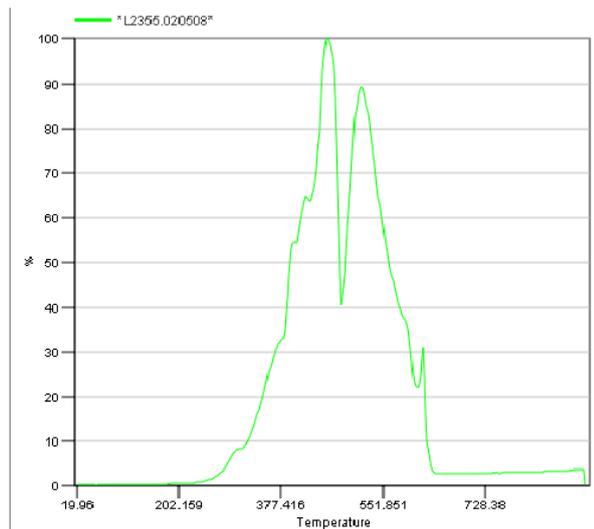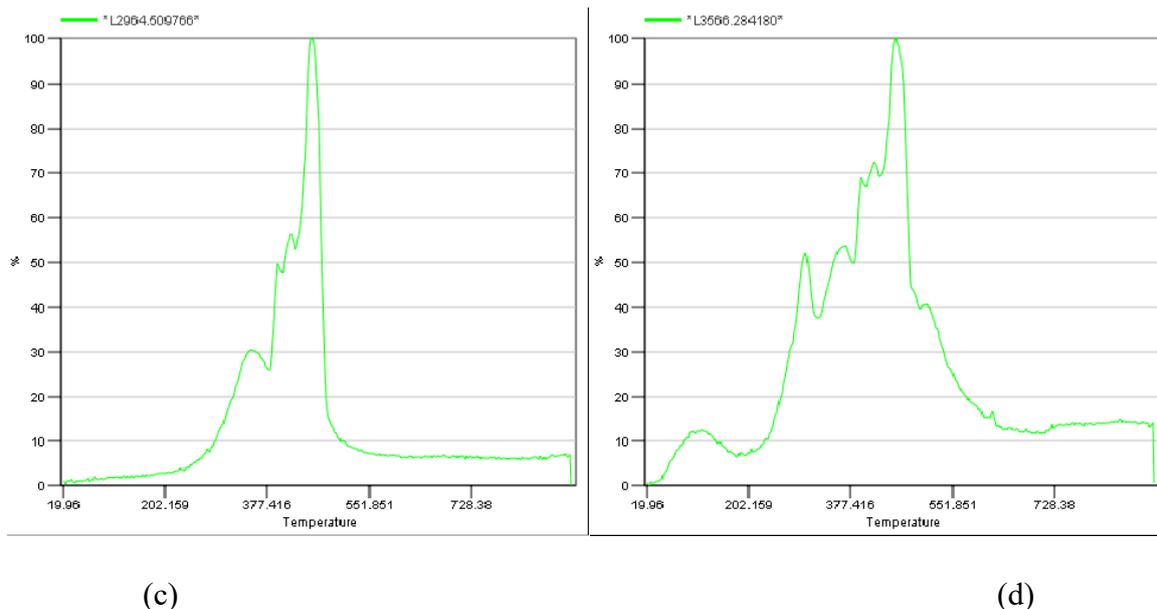**Figure 11.** Trace for evolving (a) SO_2 (1367 cm^{-1}); (b) CO_2 (2355 cm^{-1}); (c) hydrocarbons (2964 cm^{-1});   and   (d) H_2O (3566 cm^{-1}) vs temperature.

4.1.3.2. The pertraction performance for the hydrogen sulfur separation with prepared composite membranes (Chi/sEPDM/PPy)

Removal of hydrogen sulphide from different gaseous mixtures (air, biogas, natural gas) is known via classical consecrated methods [12] such us th absortion on iron sponge, iron oxide pellets, activated carbon, water scrubbing, NaOH scrubbing, biological removal on a filter bed etc. but also some modern elaborated methods: chemical oxidation, photo-oxidation, electrochemical oxidation, extraction and pertraction [13].

In the following steps we are presenting the results of the experiments for a concentrated 20 to 120 ppm hydrogen sulfide sequestration from synthetic gaseous mixtures (nitrogen, methane and carbon dioxide) that reasonable simulates the situations encountered in air pollution (farms, holiday resorts, landfill deposits), for the neutral methane but also for biosynthesis gases that contain such the compounds in different concentrations [14].

The study's objective is to remove the polluting hydrogen sulfides from synthetic gaseous source phases by its sequestration in metallic-ions acidic solutions (Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}) so that the metallic cations are recovered under sulfide forms during the sequestration of hydrogen sulfide. The chosen metallic ions are common parts of electronic and electrotechnical wastes as founded into acidic solution during their degradation [15,16].

27

The sequestration process of hydrogen sulphide is performed by pertraction with chitosan/sulfonated ethylene-propylene-diene terpolymer/polypropylene hollow fiber composite membranes (Chi/sEPDM/PPy) aiming at the following process'parameters: the concentration and the flow of the source gaseous phase, pH-ul (acidity) and si pM-ul (metallic-ions'concentration) of the ionic recepting watery phase. Following the obtained results, a mechanism for pertration of hydrogen sulphide from gasesous phases is than proposed using acidic watery solutions with metallic-ions content.

4.1.3.2.1. The influence of pM of the receiving phase on hydrogen sulfide pertraction through composite membranes (Chi/sEPDM/PPy) from syntetic gas mixture

- ✓ As to track the influence the mettalic ions of receiving phase' on the hydrogen sulphide during the pertraction process in the mix of synthetic gaseous source, we take the help of one installtion as presented in the figure 4 with the following parameters of the membraning phases:
- ✓ chitosan/sulfonated ethylene-propylene-diene terpolymer/polypropylene hollow fiber composite membranes (Chi/sEPDM/PPy), into one module with active area of $1m^{2;}$
- ✓ Sourcing phase with 20 ppm hydrogen sulphide concentration into nitrogen, methane or carbon dioxide;
- ✓ Source phase flow: 10 L/min.
- ✓ Receivng phase of 5l acidic solution (*pH* 0.5 as done with cu nitric acid).
- ✓ Recirculating flow of the receiving phase 200 mL/min.
- ✓ Metallic ions concentration of $5 \cdot 10^{-7}$-10^{-3}mol/L (*pM*=3-7), realised with metallic ion's nitrates;
- ✓ Time spent for pertration experiments of the hydrogen sulphide: 5 hours;

The results as obtained are presented within the fugure 12 and indicates an increase of pertration of the hydrogen sulphide in the same time with the incrse of metallic ions in the receiving phase.

The matrix of the gaseous mixture with hydrogen sulphide influences the extraction efficiecncy: is significantelly higher for the nitrogen and methane and lower for carbon dioxide along the whole concentrations interval and for all four cations.

Te pertraction effciency based on the compostition in the receiving phase depends by the nature of the metallic ion nature in the receiving solution respectivelly decreasing in the following order: : $Cu^{2+}>Pb^{2+}>Cd^{2+}>Zn^{2+}$.
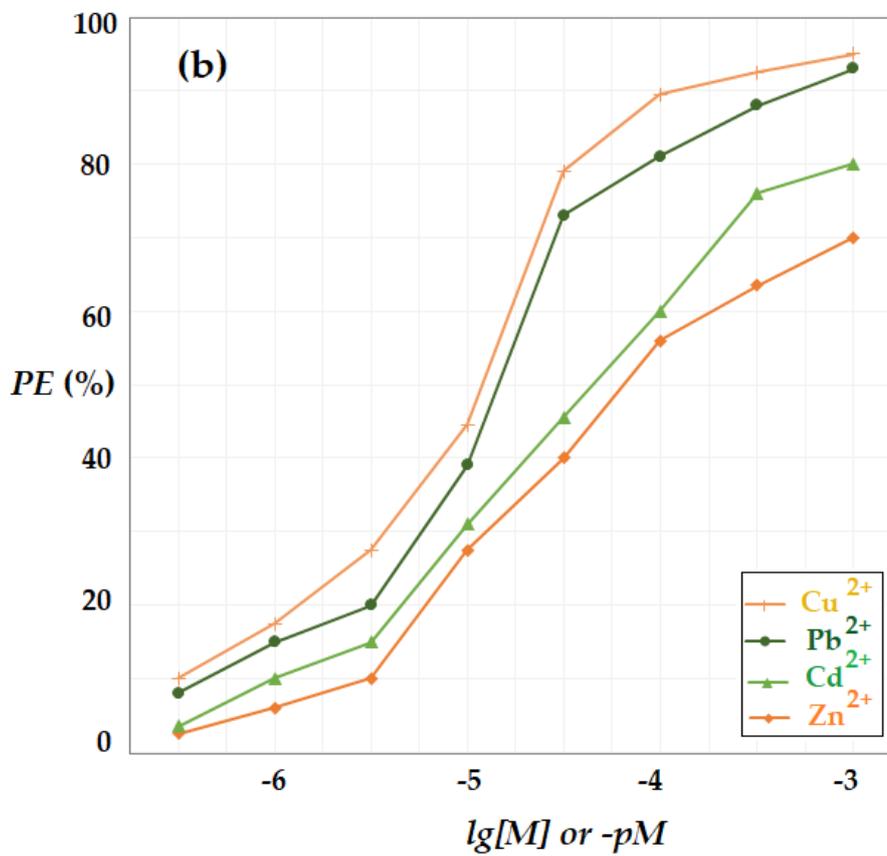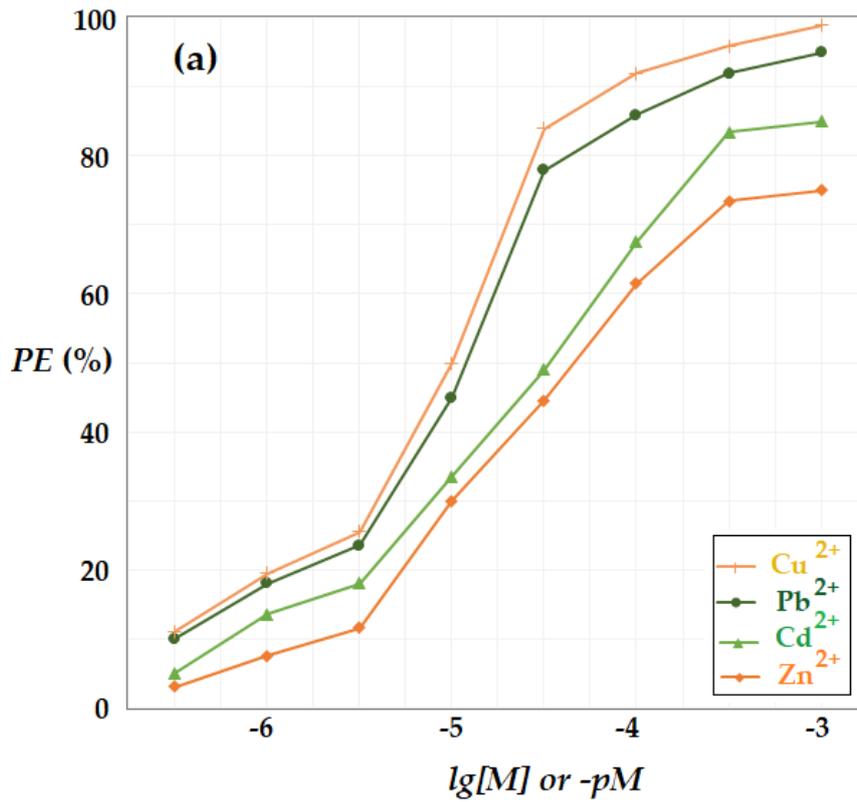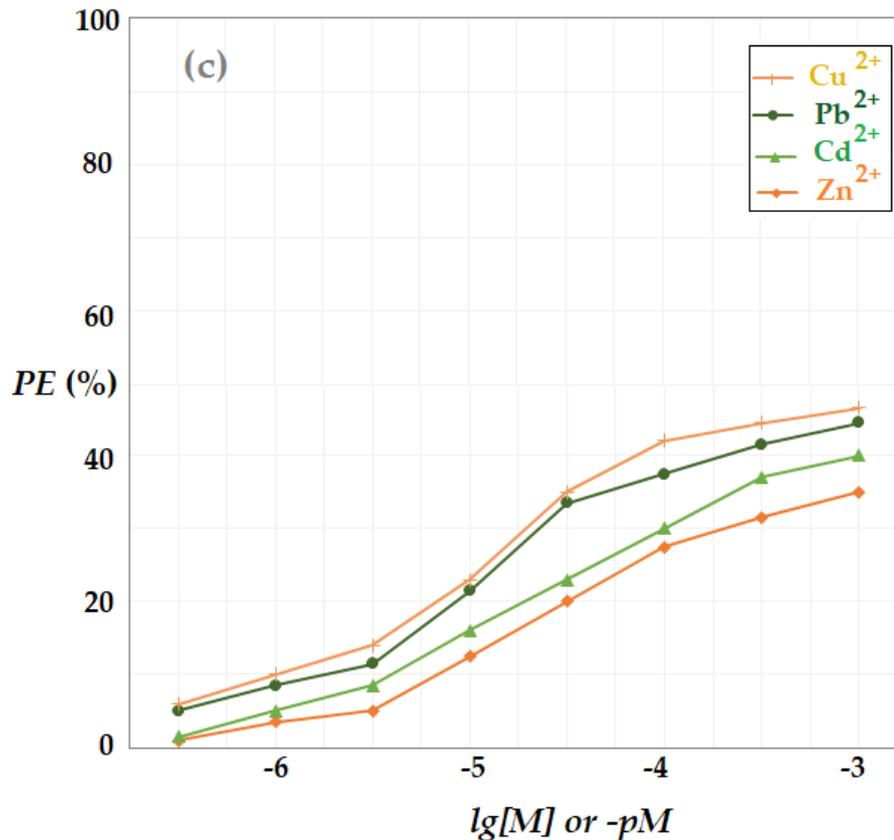
Figure 12. Hydrogen sulfide pertraction efficiency (PE%) vs. pM for 20ppm H$_2$S in gas mixture: nitrogen (a); methane (b), and dioxid de charbon (c)

The extraction efficiency when the matrix is carbon dioxide will be reduced almost at half in all the working systems we studied indicating a competition at the level of gases solubility into the composite membrane. Tehrefore the proposed system of hydrogen sulphide sequestration requests a special attention when in the gaseous mix appar any chemichal species that interract with any components of the composite chitosan/sulfonated ethylene-propylene-diene terpolymer/polypropylene hollow fiber membrane.

From the point of view of the metallic ion from the solution, it is preferred a value close to 10^{-3} mol/L. This value assumes that all the chem solutions that arrive following the electronic/electrotechnics waste processing activity may be taken/considered without any pH modification conditioned by their content of cations of the above 10^{-4}mol/L.

4.1.3.2.2. The influence of pH of the receiving phase on hydrogen sulfide pertraction through composite membranes (Chi/sEPDM/PPy) from syntetic gas mixture

For the sequestration of hydrogen sulphide in acidic solutions with content of all the ions of copper, zinc, lead into the composite membranes, the studied interval for pertraction

efficiency has been delimited between 0.5 si 2.0 form 0.5 to 0.5 units. Any exceedings of this inteval has not been conssidered for the present study as it is known the posibility that other ions to enter as part into ractions to precipitate the cations (for example hydroxyl and carbonates ions). Operational parameters of the installation are set as follows:

Source's phase'concentration: 20ppm

- ✓ Source's phase flow: 2L/min
- ✓ Metallic ion's concentration from the receiving phase: 10^{-3}mol/L
- ✓ Recirculation flow of the receiving phase: 300mL/min
- ✓ Membrane's surface: $1.0m^2$
- ✓ The time spent for hydrogen sulphideé experiment: 5 hours.

The results as registered (figure no 13) show a slightly increase of pertraction efficiency during the pH increase, for all the studied cations. In respect of concluding on recuperative separation of the metallic ions in the same time with the sequestration of hydrogen sulphide, the increase of pH it is not recommended because it means either the source's system dillution (acidic solution from electronics and electrotechnical's industries) or a signifcant consumption of neutralizing reactive.

Also in the case of gasesous mixture with content of carbon dioxide, an incrase of pH to the value of 5 it cand generate a consumption of metallic ions ready to precipitate as hydroxids or hydroxi-cabonates.
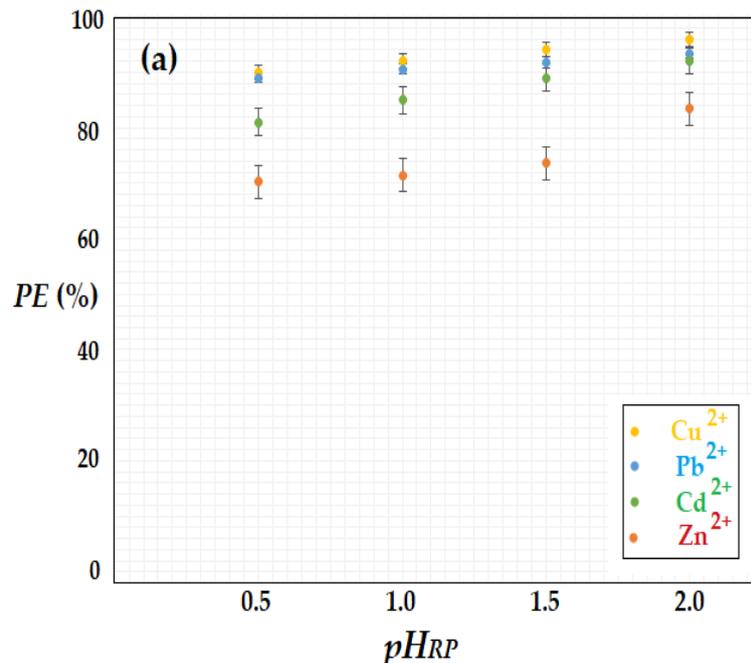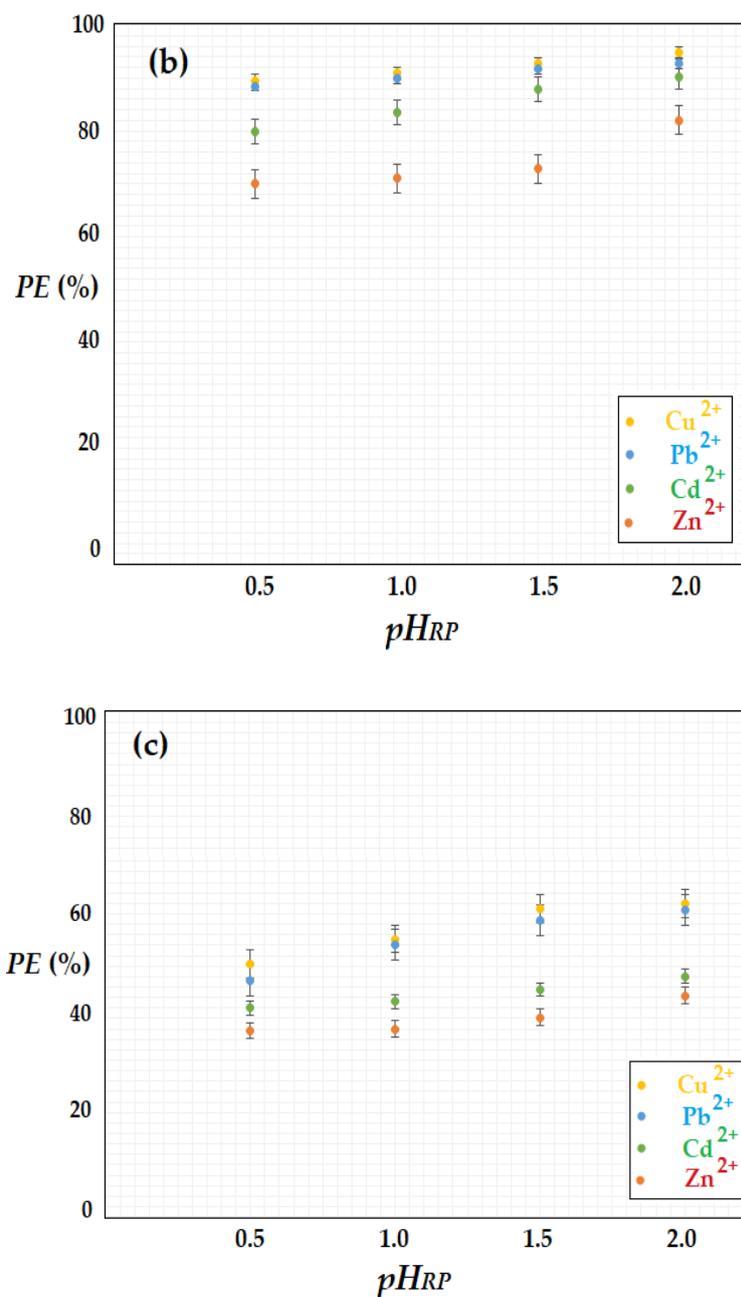
Figure 13. Hydrogen sulfide pertraction efficiency (PE%) vs. pH for 20ppm H$_2$S in gas mixture: nitrogen (a); methane (b), and carbon dioxide (c)

The increased value of separaton for gaseous mixtures of whom the matrix is an inert gas (nitrogen, methane) recommends the usage of receiving phases with content of metallic ions, pH test and the concentration obtained by the valorsation through the acidic attack on electrotechnical wastes.

4.1.3.2.3. The influence of the hydrogen sulfide concentration on pertraction through composite membranes (Chi/sEPDM/PPy) from syntetic gas mixture

The targeted gasesous systems to apply on the results of this study are those as poor in gase emissions with content of hydrogen sulphide (populated enclosures in the area of moffets, farms, municipal waste landfilled deposits, waste treatement water station). In the experiments of sequestration of the hydrogen sulphides as sulphides from different gaseous mixtures an interval between 20 and 120 ppm has been chosen.

During the experiments, the installation from figure no 3 has operationally been managed as follow:

- ✓ Source phase's flow: 4L/min
- ✓ Metallic ions concentration from receiving phase 10^{-3}mol/L la pH 1.0
- ✓ Recirculation flow of the receiving phase: 500mL/min
- ✓ The time spent for the pertraction of hydrogen sulphide: 5 hours.
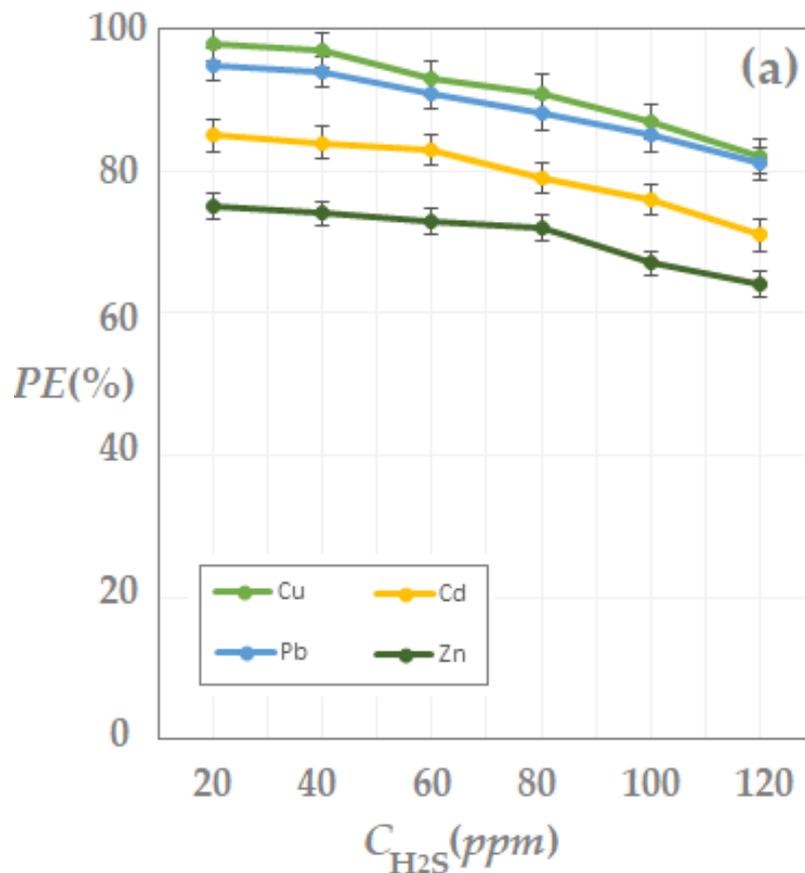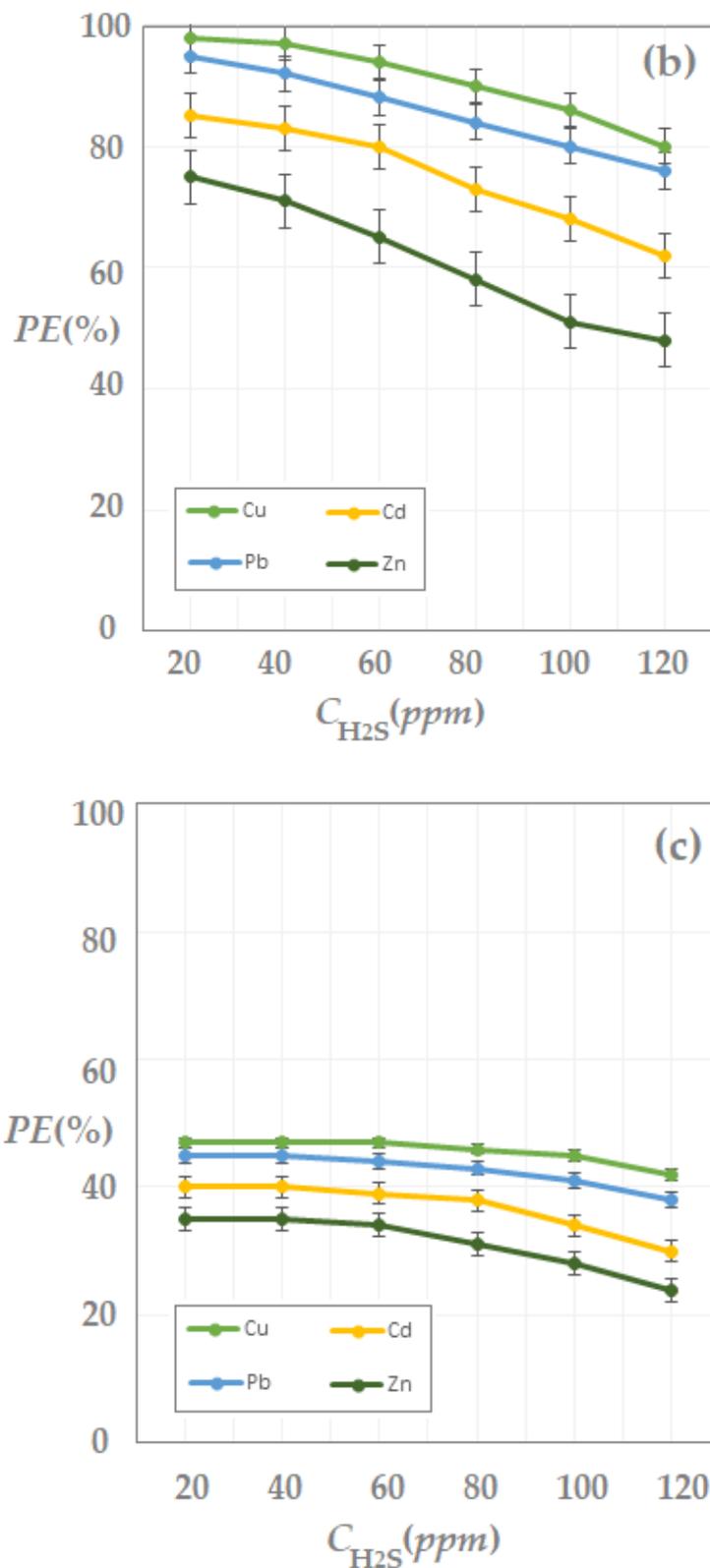
Figure 14. Hydrogen sulfide pertraction efficiency (PE%) vs. hydrogen sulfide concentration in gas mixture: nitrogen (a); methane (b), and carbon dioxide (c)

In figure 14 the experimental results are underlined and shows an worsening of pertraction efficiency at the same time with the increase of hydrogen sulphide 's concentration

when fed. In the operational conditions proves the pertraction efficiency as mentained almost constant during the feeding in 20-60 ppm intelval. Ater this limit, the decrease of pertraction efficiency is significant with over 30% at the concentration of 120 ppm H_2S. From practical point of view, the efficiency of the separation can be mentained if work in two or three pertraction steps are to be done but this requests an increase of membrane s therefore a rise in invenstment.

4.1.3.2.4. The influence of the gas mixture flow on hydrogen sulfide pertraction through composite membranes (Chi/sEPDM/PPy)

The flow of the mix of source gases represents an important parameter of the hydrogen sulphide suequestration as sulphides in the acidic media. The interval in flow of the mixed surce gase as chosen for the experiment has been into spotted for the possibility to improve the quality of resonable biogas quantity (the domestic installation faremed to 2-20m³ biogas/day, of air into enclosures (kitchens, badrooms, offices from the farms) or hospitality hotelier spaces delimited bt moffets.

The operational parameters for the pertraction installation of hydrogen sulphide in different gasesous mixtures:

- ✓ The concentration of hydrogen sulphide in the sourcing gasesous phase 40ppm;
- ✓ The flow of the source gasesous phase: 2-20L/min;
- ✓ The metallic ions concentration into receiving phase 10^{-3}mol/L si pH-ul 1.0;
- ✓ Recurculation flow of the receiving phase: 500mL/min
- ✓ Membrane's surface: $1.0m^2$
- ✓ The time spent for the pertraction of hydrogen sulphide: 5 hours.
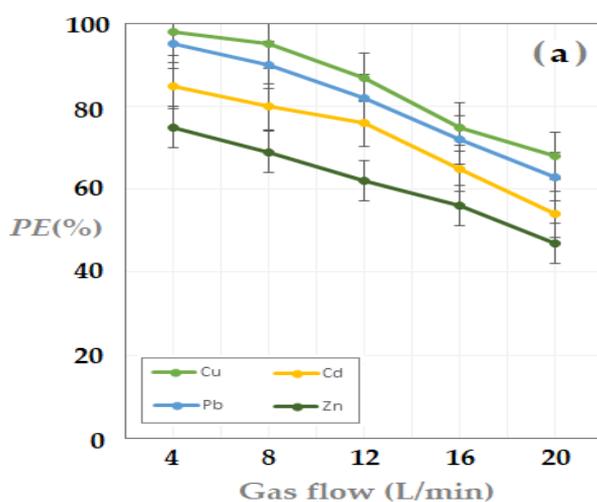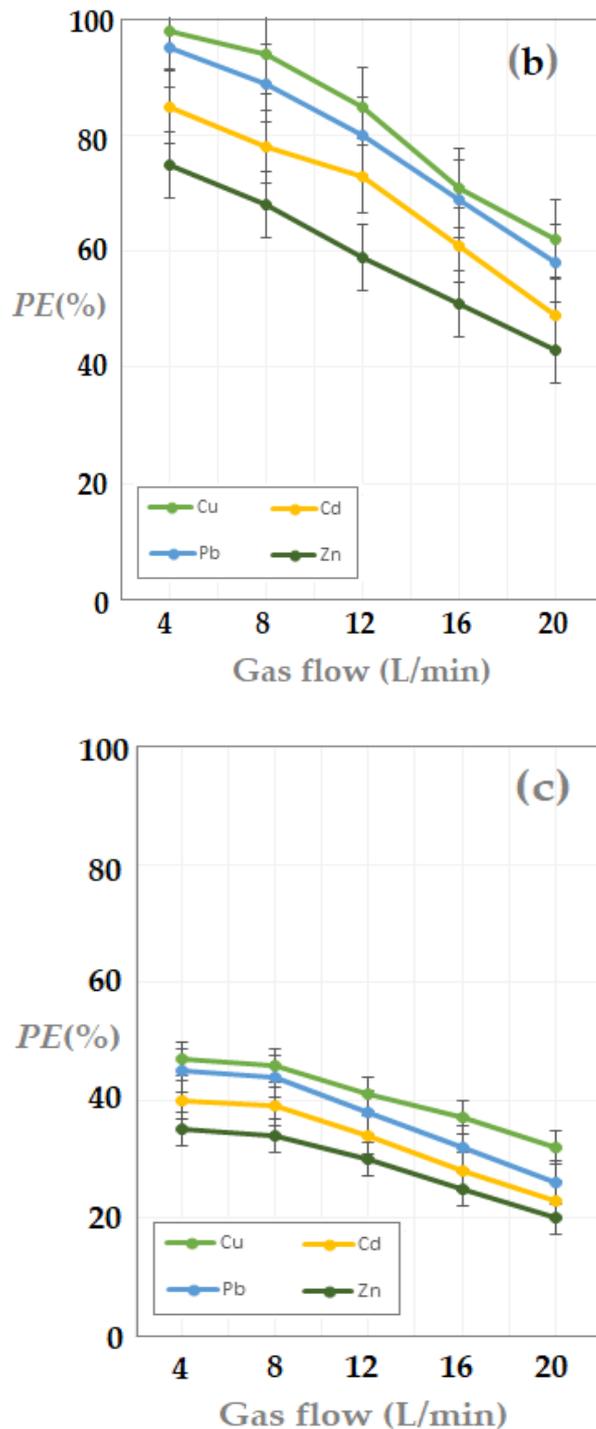
Figure 15. Hydrogen sulfide pertraction efficiency (PE%) vs. gas flow mixture: nitrogen (a); methane (b), and carbon dioxide (c)

For all the studied cases, the pertraction's efficiency of the hydrogene sulphide from gaseous mixture (nitrogen, methane, carbon dioxide - Figure 15) decreases as we increase the feeding flow. At an increase of 10 times in the feeding flow the pertraction efficiency decreases with around 40%. The results proves that in order to keep the efficiency of the installation,

either in incearse of the membrane surface or to operate under some more pertraction stages it have to be performed.

4.1.3.2.5. The proposed mechanism of the hydrogen sulfide squestation through pertraction with mettalic ions in acidic media by composite membranes (Chi/sEPDM/PPy) from syntetic gas mixtures

The sequestration of hydrogen sulphide as sulphides into acidic media of pertraction with chitosan/sulfonated ethylene-propylene-diene terpolymer/polypropylene hollow fiber composite membranes (Chi/sEPDM/PPy) has been also imposed by the necessity os valorisation for all acidic solutions with metallic ions (Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}) from the studies industrial wastes.

The main aspects of the technical proposed solution rising issues during the experiments:

- ✓ The reticular chitosan (selective membrane material) that impregnates the polypropylene hollow fiber support membrane.
- ✓ The optimization of the concentrations for the metallic and sulfide ions in order to provide metallic sulfide's precipitation and their fixing into the receiving phase.

For the first challenging point that into our previous studies has been partially solved by using poly ether ether ketone sulfonate [17,18], we call for a resistant polymer with strong acidic sulfonated groups of ethylene-propylene-diene terpolymer (sEPDM) that has demonstrated been in the benefit of the experiments as shown in figure 5 and 6.

For the second above mentioned aspect it has been conducted the experimental study as presented throughout the actual paper and whose technical considerations are briefly summarized by the pages [18,20].

For the heavy soluble sulfide type MS in saturation solution in the presence of the solid phase, we may write the heterogeneous equilibrium (6):

$$MS_{(s)} \rightleftharpoons MS_{(aq)} \rightleftharpoons M^{2+}_{(aq)} + S^{2-}_{(aq)} \tag{6}$$

The anion S^{2-} with its basic character is formed depend of the pH into the chemichal species HS^- şi H_2S as results of the equilibium (70 si (8):

$$S^{2-} + H_3O^+ \rightleftharpoons HS^- + HOH \tag{7}$$

with the constant (7'):

$$K_{a_2} = \frac{[S^{2-}][H_3O^+]}{[HS^-]} = 10^{-13} \qquad (7')$$

$$HS^- + H_3O^+ \rightleftharpoons H_2S + HOH \qquad (8)$$

with the contant (8'):
$$K_{a_1} = \frac{[HS^-][H_3O^+]}{[H_2S]} \qquad (8')$$

In these apparent solubility conditions S through relations (9 or 9'):

$$S = [M^{2+}] = [S^{2-}] + [HS^-] + [H_2S] \qquad (9)$$

or (11')

$$S = [S^{2-}](1 + \frac{[H_3O^+]}{K_{a_2}} + \frac{[H_3O^+]^2}{K_{a_1} \cdot K_{a_2}}) \qquad (9')$$

Using the solubility expression of $K_s = [M^{2-}][S^{2-}]$ (10 or 10') is generated:

$$S = \sqrt{K_s} \cdot \sqrt{1 + \frac{[H_3O^+]}{K_{a_2}} + \frac{[H_3O^+]^2}{K_{a_1} \cdot K_{a_2}}} \qquad (10)$$

or:

$$S^2 = K_s(1 + 10^{pK_{a_2}-pH} + 10^{pK_{a_1}+pK_{a_2}+2pH}) \qquad (10')$$

that practically can be used to argue the influence of both the metallic ion and also the pH on pertraction efficiency during the well defined normal working conditions.

In Figure 16 are depicted the characteristical diagrams that explain the formation of conssidered metallic ions sulphides.

In this way, when pH decreases, sulphide stability respects the order: $Cu^{2+} > Pb^{2+} > Cd^{2+} >>, Zn^{2+}$. Actually, at an acidic pH, copper sulfide precipitates first followed by the cadmium one than zinc sulfide.

In the case of a multicomponent solution, in the proposed membrane system we can recover separately the metallic ion sulfides in the same time with the sequestration of hydrogen sulfide.

The most likely mechanism of hydrogen sulphide sequestration as sulphide in acidic media by pertraction with chitosan/sulfonated ethylene-propylene-diene terpolymer/polypropylene hollow fiber composite membranes (Chi/sEPDM/PPy) using acidic solutions with metallic ions (Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}) is summarized in figure no 17.
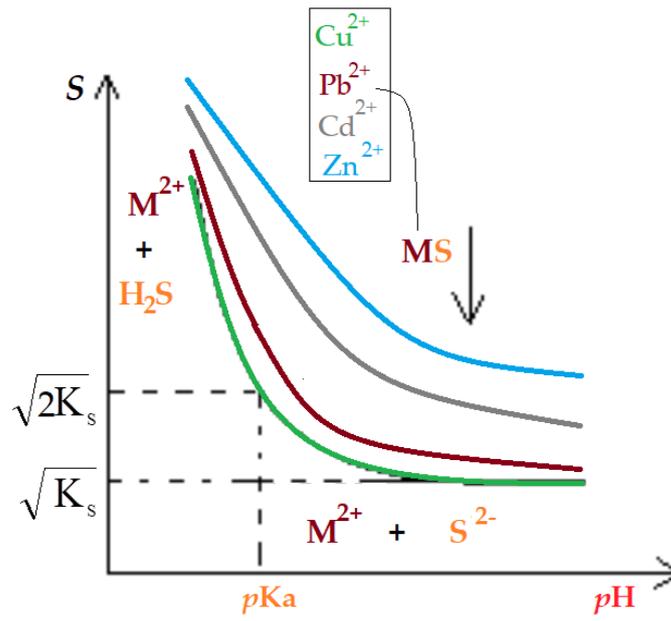
(a)
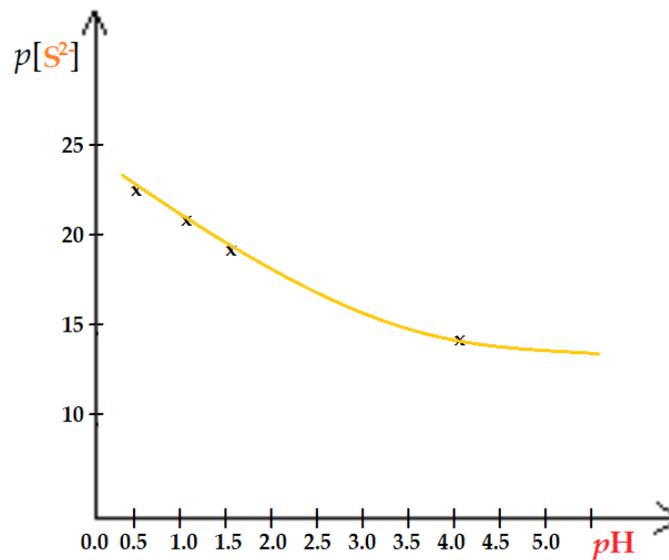
(b)

Figure 16. Diagrams of the: sulfide metals solubility (S) vs. pH (a) and pS^{2-} vs. pH (on the interest interval).

Hydrogen sulphide sequestration by pertraction with chitosan/sulfonated ethylene-propylene-diene terpolymer/polypropylene hollow fiber composite membranes (Chi/sEPDM/PPy) takes place in different stages:

- Gase's diffusion from the source phases via polypropylene hollow fiber membrane support;

- Concentration of hydrogen sulfide into the selective chitosan lay of the composite membrane following a solubility-extraction mechanism in the solid phase and the diffusion to the interface with acidic receiving solution that posts metallic ions content.

- hydrogen sulfide's solubility into the receiving phases;

-retainment of hydrogen sulfide by precipitation as sulfide in the receiving phase;
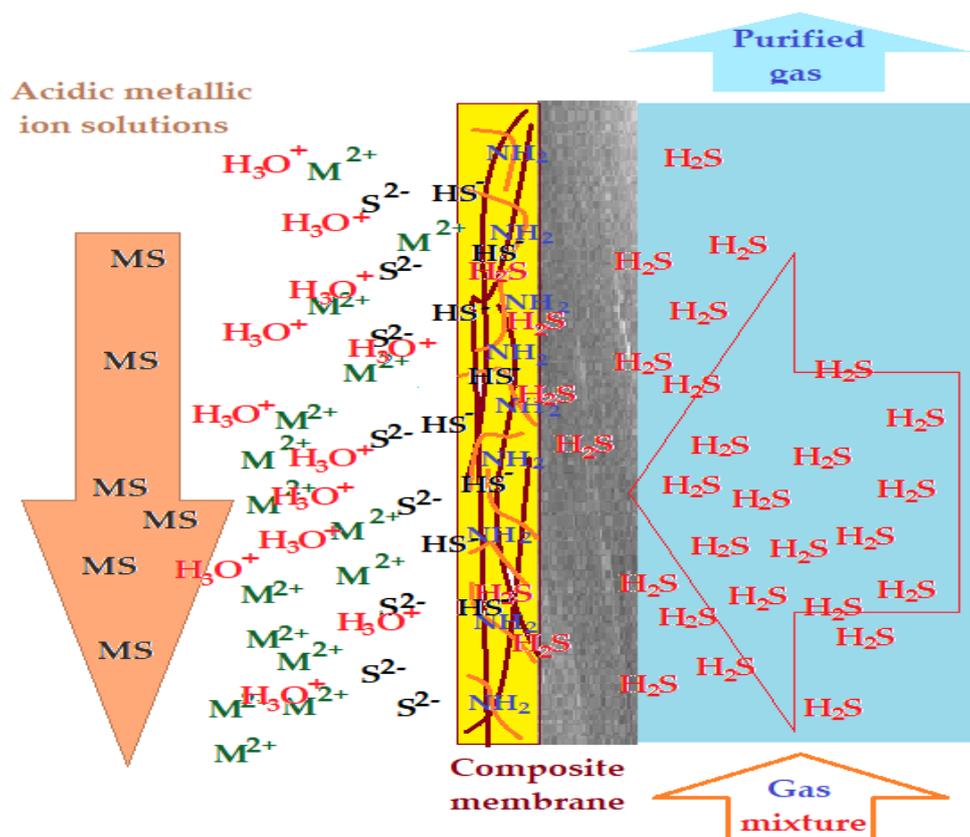

Figure 17. Schematic mechanism of of the hydrogen sulfide squestation through pertraction with mettalic ions in acidic media by composite membranes (Chi/sEPDM/PPy) from syntetic gas mixtures

The stages as above described justify both the better results of hydrogen sulphide's pertraction from nitrogen and methane mixtures and the decreasing in hydrogen sulphide

extraction efficiency in the carbon dioxide based mixture that cames into competition with hydrogen sulphide from the solubility-extraction stage in chitosan active layer. The process selectivity if given by the fact that under significant acidic conditions the sulfides of the conssidered metalls are only formed and not corbances or their hidroxhides. The solubility products of the bathing conssidered ions are entirelly in consent with the results of the experiments as separatelly conducted on each of the ions.

4.1.4. Conclusions

This chapter presents the preparation and characterization of composite membranes based on chitosan (Chi), sulfonated ethylene-propylene-diene terpolymer (sEPDM), and polypropylene (PPy) designed for hydrogen sulfide sequestration. The composite membranes have been obtained by deep coating and controlled evaporation on the polypropylene hollow fiber membranes Chi-sEPDM (1:1) in toluene dispersion. The composite membranes were morphologically and structurally characterized by scanning electron microscopy (SEM), Fourier Transform InfraRed spectroscopy (FTIR), energy-dispersive spectroscopy analysis (EDAX), thermal analysis (TG, DSC), thermal analysis coupled with chromatography and infrared analysis. They have also been characterized from the point of view of performance obtained in for sequestration of the hydrogen sulfide pertraction in acidic media solution which contain metallic ions (Cu^{2+}, Cd^{2+}, Pb^{2+}, and/or Zn^{2+}).

The operational parameters of the pertraction are pH, pM, flow of the matrix gas and its composition. The pertraction results of synthetic gaseous mixture (nitrogen, methane, carbon dioxide) is indicating an efficient removal of hydrogen sulfide through composite membranes as prepared and its restrain as sulfides. The sequestration and recuperative separation as sulfides in acidic media reach up 96% for hydrogen sulfides decreasing in the following order: CuS>PbS>CdS>ZnS. The effectiveness removal of the hydrogen sulfide from gaseous mixtures decreases following the order nitrogen > methane >carbon dioxide. The recuperative separation methods as realized it may consist further in a recuperative way to recover the acidic solution Cu-Zn or Pb-Cd from waste of the electronic and electrotechnical industries.

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Part C.

General conclusions, Originality, and Perspectives of the research

C1. General conclusions

The PhD thesis "Methods of eliminating the bad smell generated by industrial production" aims to correct the bad smell generated by industrial activities through membrane methods and techniques.

The specific objectives

- Identification of foul-smelling substances and those that can generate compounds with an unpleasant smell

- Preparation of polymer and composite membranes

- Obtaining liquid membranes

- Morphological, structural and process performance characterization of the membranes

- Removal of hydrogen sulfide and thiols from liquid and gaseous effluents

- Recuperative separation of hydrogen sulfide

Chapter 2 conclusions

Industrial production leads along with the goods needed by society and residues, a large part of which are emitted into the atmosphere.

A large part of the materials emitted into the atmosphere are toxic, but fortunately they also have an unpleasant smell.

Thus, the elimination of foul-smelling substances from the atmosphere also contributes to improving air quality.

In this PhD thesis, a series of techniques and methods are presented for removing foul-smelling substances or generating substances of this type: hydrogen sulfide, mercaptans, phenols and amino acids.

Among the techniques for separating foul-smelling substances are addressed: liquid membranes, polymer and composite membranes.

Chapter 4.1. conclusions

This chapter presents the preparation and characterization of composite membranes based on chitosan (Chi), sulfonated ethylene-propylene-diene terpolymer (sEPDM), and polypropylene (PPy) designed for hydrogen sulfide sequestration. The composite membranes have been obtained by deep coating and controlled evaporation on the polypropylene hollow fiber membranes Chi-sEPDM (1:1) in toluene dispersion. The composite membranes were morphologically and structurally characterized by scanning electron microscopy (SEM), Fourier Transform InfraRed spectroscopy (FTIR), energy-dispersive spectroscopy analysis (EDAX), thermal analysis (TG, DSC), thermal analysis coupled with chromatography and infrared analysis. They have also been characterized from the point of view of performance obtained in for sequestration of the hydrogen sulfide pertraction in acidic media solution which contain metallic ions (Cu^{2+}, Cd^{2+}, Pb^{2+}, and/or Zn^{2+}).

The operational parameters of the pertraction are pH, pM, flow of the matrix gas and its composition. The pertraction results of synthetic gaseous mixture (nitrogen, methane, carbon dioxide) is indicating an efficient removal of hydrogen sulfide through composite membranes as prepared and its restrain as sulfides. The sequestration and recuperative separation as sulfides in acidic media reach up 96% for hydrogen sulfides decreasing in the following order: CuS>PbS>CdS>ZnS. The effectiveness removal of the hydrogen sulfide from gaseous mixtures decreases following the order nitrogen > methane >carbon dioxide. The recuperative separation methods as realized it may consist further in a recuperative way to recover the acidic solution Cu-Zn or Pb-Cd from waste of the electronic and electrotechnical industries.

Chapter 4.2. conclusions

The bad smell of air in the metropolitan areas is generated by multiple sources of the industrial economic agents, including those dealing with the storage, treatment and recycling of various wastes. The special situation of Bucharest metropolitan area caught attention through numerous deviations from air quality, including unbearable odor.

This chapter presents aspects regarding the possibility of correcting the air odor using cellulose acetate membranes impregnated with silver in polypropylene fibers. The cellulose acetate used is itself a waste from the film industry (contains silver nanoparticles).

The impregnated membranes obtained were morphologically and structurally characterized (SEM, HF SEM, EDAX, FTIR, TG, ATD) but also in terms of performance in the

process of retaining hydrogen sulfide and ethanethiol (as foul-smelling gas-generating target substances).

The membrane process must be used to remove the target substances at the source (synthetic solutions were used) because after dispersion in the air the removal is difficult and both technically and economically inefficient.

The solution chosen for the design of the membrane module is based on impregnated fiber bundles having a mass transfer surface of 1 m^2/bundle and 100 m^2/m^3 when scaled up (100 bundles per pertraction unit).

The obtained results show that the target substances can be removed with an efficiency of over 95% from synthetic solutions of 50 ppm H_2S or 25 ppm C_2H_5SH.

The flow of chemical species through membranes depends on the amount of cellulose acetate impregnated in the polypropylene fibers, the flow regime of the source phase and the concentration of electrolytes (NaCl).

Chapter 4.3. conclusions

Starting from the obtained results for the separation and transport of the chemical species in a permeation module with dispersion of aqueous phases, in the form of droplets, in this paper we studied the effect of interposing spheres in free rotation between the droplets and the membrane phase. These spheres determine the contact of aqueous phases in the form of a film with the membrane phase of the organic solvent. The study was performed in a membrane system in which the variable pH source phase consists of phenolic derivatives of technical-economic and environmental interest ((PD), 4–nitrophenol (NP), 2,4–dichlorophenol (DCP) and 2,4–dinitrophenol (DNP)), membrane of *n*–alkyl alcohols (*n*–octanol and *n*–decanol) and the receiving phase of high pH aqueous solution.

The transport of 4-nitrophenol is determined both by the difference in pH between the aqueous phases, the nature of the membrane solvent and the nature of the spherical material. Thus, the transport in which the module has glass spheres (Gl) is superior to that using copper spheres (Cu), but especially those made of steel (St). In all the studied cases the module with spheres (Ms) has superior transport results to the module with drops (Md).

The extraction efficiency (EE) and the transport of 2,4–dichlorophenol (DCP) and 2,4–dinitrophenol (DNP), studied in the module with glass spheres, show that the two phenolic derivatives can be separated by adjusting the pH of the source phase. At a source phase with

strong acid character (pH = 2) the two derivatives are extracted with good results (EE>90%), while at pH in the range [4, 6] they can be separated, DCP having doubled separation efficiency compared to DNP. At a pH = 8 of the source phase, the extraction efficiency halves for both phenolic compounds.

The influence of the material of the spheres in the extraction module suggests possibilities to control the performance of the membrane process by chemically modifying the surface of the spheres, especially those made of glass.

C2. Originality

Within the thesis "**Methods of eliminating the bad smell generated by industrial production activities**" the following elements of originality can be noted:
- Elimination of the foul smell of liquid or gaseous effluents with innovative membrane systems.
- Preparation of liquid membranes based on nanodispersions or with elements for generating extended surfaces.
- Obtaining hollow fiber type composite membranes with polymeric or liquid active layer.
- Separation of hydrogen sulfide and mercaptans from liquid or gaseous effluents.
- Sequestration of hydrogen sulfide with metal cations in an acidic environment.
- Transport and separation of phenols with liquid and composite membranes.
- The use of the magnetic field in the transport processes through membranes.

C3. Perspectives of the research

The results obtained during the research activities for the doctoral thesis **"Methods of eliminating the bad smell generated by industrial production activities"** allow the development of the following research directions:
- Diversification of the methods of obtaining liquid and composite membranes using nanodispersions.
- The use of composite membranes containing magnetic particles to amplify the transport through the membranes.

- Diversification of the types of membranes used in correcting the bad smell from various premises and domestic spaces.

- Increasing the number of foul-smelling substances in the membrane separation and transport study.

The thesis fulfilled all its proposed objectives, and the obtained data were validated in 8 ISI articles, seven of which in Q1 journals (Membranes and Nanomaterials).

Dumitru Pascu

Publications list realized on the doctoral research period of the author

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