UNIVERSITY POLITEHNICA OF BUCHAREST
FACULTY OF MATERIALS SCIENCE AND ENGINEERING

DOCTORAL THESIS
SUMMARY

CONTRIBUTIONS TO FABRICATION OF NANOPARTICLE MEMBRANES FOR LIQUID PURIFICATION

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INTRODUCTION

Threats associated with global water scarcity are becoming more and more current news, as the continuous increase in agricultural production, the expansion of urban borders, the production of large water-consuming industrial facilities and the increased sensitivity to environmental needs, lead to increased demand for water. Water supply constraints are further exacerbated by increasingly intense and frequent drought events, such as the recent four-year (2012-2016) drought in California, which has led to economic losses of tens of billions dollars only in the agricultural sector, or the drought in the Middle East, which continues from 1998 to the present, being considered by NASA scientists as the worst in the region, in the last 900 years. In response to these concerns, water supply managers in large areas around the world are constantly looking for creative solutions to address these shortcomings.

A key development in water supply markets is the differentiation of drinking water from non-potable water. Drinking water must meet stringent public health requirements to ensure that water-related diseases and harmful levels of pollutants are not transmitted to humans. In contrast, agricultural irrigation, landscape irrigation, toilet washing and, in some cases, water released into the environment, do not necessarily have to meet such strict treatment requirements. This differentiation has allowed water managers to implement wastewater recycling and reuse, where water is treated to the minimum standards necessary to meet the standards set out in environmental legislation.

Alternatively, wastewater treated and discharged into rivers has been mixed with natural water for decades, then withdrawn downstream, treated and used for municipal supply. Instead, the repotabilization of water in wastewater treatment plants and injected directly into a water supply system, had an unforeseen impact on the population nicknamed the process "toilet to tap", being evaluated by "yuck factor ”, in translation a feeling of disgust generated by this idea.

The European Commission estimates an unmet global demand of 3,000 cubic kilometers of water by 2030. Global wastewater production accounts for about half of this volume. Keep in mind that not all wastewater streams are recoverable, but most are.

Thus, a proliferation of wastewater recycling in the coming decades could support a significant reduction in the problem of water scarcity. As consumers begin to accept technological solutions that can reliably clean water, until it becomes potable, the reuse of drinking water will become more widespread.

However, many municipalities and industry decision-makers are now at a point where they are ready to submit projects. Due to the growth of wastewater treatment markets, the recycling and reuse of wastewater is also in favor of regulators. Local and national governments are working to implement more recycling-friendly policies. Thus, the global markets for wastewater recycling and reuse are at a time with strong market growth and revenue generation potential [1].

Global interest in wastewater recycling technologies has grown steadily since the early 1990s and is gaining more and more due to the increasing need for water supply. This growing need affects many global regions and leads to increased environmental regulation in both developing and developed countries. Many countries, cities and local governments are trying to recycle wastewater as a potential source of water for various uses, especially non-potable uses, such as landscaping, toilet water and industrial processes [1]. Analysts and statisticians around the world are trying to provide insight into an industry that is poised to see significant developments over the next decade.

In this context, the general objective of the research thesis was to obtain functionalized materials that can be used in the field of wastewater treatment. The paper has two main research directions:

I) obtaining new adsorbent materials made on cellulosic matrix, functionalized with metal oxides and having a morphological structure that allows an adsorption capacity of pollutants from wastewater, as high as possible;
II) development of testing methods for the new adsorbent material obtained with industrial wastewater, in order to obtain the highest possible treatment efficiency and obtaining values of the measured parameters, compatible with the environmental regulations in force.

The following objectives were pursued in the first direction:
a) obtaining a new adsorbent material, having a high porosity, consisting of a cellulosic matrix embedded with micro and nanoparticles of metal oxides;
b) characterization of the obtained material, from the point of view of the morphological and morphochemical structure;

The following objectives were pursued in the second direction:
a) establishing the optimal parameters for testing the material obtained in order to maximize the efficiency of industrial wastewater treatment;
b) the morphostructural and morphochemical characterization of the adsorbent material, after utilisation, and the qualitative and quantitative evaluation of the pollutants retention capacity in the structure of the obtained material;
c) characterizing from a qualitative and quantitative point of view the water samples obtained after testing and evaluating their quality, by measuring the general and specific parameters, as well as framing their value within the limits allowed by environmental regulations, regarding the quality of water that can be discharged into sewerage network.

The thesis includes 160 pages, and the support of theoretical and experimental data is achieved through 91 figures and graphs of which 78 own, 19 tables of which 13 own and 119 bibliographic references. The thesis is structured in two parts, the first comprising the critical study of data from the literature, and the second part, comprising the experimental part and personal contributions. The two parts are organized into five chapters.

The ***first chapter*** of this paper **"Trends in the development of environmental remediation technologies"** presents the current state and trends in the development of environmental technologies. This chapter contains numerous studies, current data and forecasts for the coming years on research and development of environmental remediation technologies [4, 5]. Studies include data on increasing water demand with increasing population [7], increasing the volume of wastewater due to the development of industries and global population growth, industrial wastewater treatment technologies, water treatment technologies for reuse, for both drinking and non-drinking purposes, hazardous waste management and environmental remediation technologies in general. The chapter consists of 6 subchapters in which are presented in more detail, reports on nanoporous and microporous materials [12, 13], microfiltration membranes [14, 16], reverse osmosis [17], mining chemicals [18] and water treatment with chemicals [19]. It also presents general aspects related to trends in the *clean-tech* sector. Summaries of several reports are presented, which include statistical data on clean / green technologies, their importance in developing a sustainable economy, sectors where clean technologies have development prospects, extrapolation of these data and their transformation into market forecasts. Issues related to investments made by world leaders in the clean-tech sector and issues related to the design, construction, operation and maintenance of industrial wastewater management systems are discussed [23, 25].

In the ***second chapter*** **"Wastewater treatment processes"** are presented, from a theoretical point of view, wastewater treatment processes. Both conventional and unconventional processes currently used or researched for development are discussed. The types of processes and processes used to treat wastewater are mainly presented in terms of the advantages and disadvantages of each technology. It also presents aspects related to the processing techniques in the leather industry, the chemicals used and the main pollutants present in the wastewater resulting from this industry [100 - 107]. The reason for approaching this industrial sector is due to the fact that the experimental part of the test is performed with wastewater from the leather processing industry. Aspects of the chemical species of chromium [109], one of the main pollutants present in wastewater from the leather industry, are also presented.

In the ***third chapter*** "**Research on the preparation and morphostructural and morphochemical characterization of a nanostructured adsorbent material with cellulose matrix"** are presented the experimental research on the preparation and characterization of the new material. The first part of the chapter presents the equipment (GC / MS, SEM / EDX, FTIR), materials and working methods. Theoretically, the general and specific parameters are presented (alkalinity / basicity / hydrogen ion concentration, biochemical oxygen demand - BOD5, chemical oxygen demand COD-Cr, total suspended solids, ammonium nitrogen, chlorides , sulphates) and the inclusion of their values in the provisions of the environmental legislation in force (NTPA 002 - Wastewater discharge in the sewerage networks of the localities and directly in the treatment plants).

3.1. EQUIPMENT, MATERIALS AND METHODS USED

3.1.1. A VEGA II LMU scanning electron microscope (SEM) equipped with an X-ray dispersion microanalysis unit (EDX) was used to investigate the adsorbent material obtained. The Bruker AXS EDX unit uses a QUANTAX 4000 X-ray radiation detector and an Xflash silicone drift spectrometer. A Philips XL30 ESEM scanning electron microscope (SEM) equipped with an X-ray dispersion microanalysis unit (EDAX) was used to investigate the adsorbent material resulting from the tests.

3.1.2. The IR spectra were made on a Jasco Fourier Transform Infrared Spectrometer (FT - IR) 6300 with infrared total reflectance.

3.1.3. GC-MS analyzes were performed with a GC Thermo Scientific Trace 1310 gas chromatograph coupled with a TSQ 9000 tripluquadrupol (MS / MS) mass spectrometer and equipped with a TriPlus RSH autosampler.

3.1.4. The pH was determined in accordance with the SR ISO 10523/2012 standard.

3.1.5. Determinations of biochemical oxygen demand in water were performed according to SR EN 1899 -1/2003.

3.1.6. Determinations of chemical oxygen demand in water were performed according to the standard SR ISO 6060: 1996 "Determination of chemical oxygen demand COD-Cr (in closed and open system)".

3.1.7. The determination of the total suspended matter was performed according to the standard SR EN 872:2005 „Water quality. Determination of the content of suspended matter".

3.1.8. Quantitative determinations of ammonium nitrogen were performed with Merck kit 1.4752.0001.

3.1.9. Quantitative determination of chlorides was performed according to the standard SR ISO 9297/2001 „Water quality. Determination of chloride content".

3.1.10. Quantitative determination of sulphates was performed with Merck Kit 1.4791.0001.

3.1.11. General method of testing the efficiency of the adsorbent material

To test the efficiency of the material, a batch of water from the technological flow of leather processing (leather and footwear industry) was used. All tests were performed at a temperature of 20-24 °C and humidity of 52%.

Water from the leather processing industry was chosen because the market of the leather industry, globally grows in proportion to the urbanization of countries and population growth, making feasible the development of technologies for wastewater treatment specific to this industry, now and in the near future.

In order to have a more comprehensive picture of the behavior of the adsorbed material on the contaminants existing in the technological water, a series of experimental works were performed in which a general working pattern was observed but whose parameters were modified at each test, in order to obtaining the most conclusive results. The main parameter whose value oscillated between its extreme values was the trigger pH, defined as the pH value at which the adsorbent material used has the best reactivity with the pollutants in the tested water. The value of this parameter was deliberately varied from the value 2 to the value 10 in order to establish its optimal value, which led to the variation of the other parameters that influence the treatment process and therefore the final results are obtained. Thus, ten case studies were performed on testing the adsorption efficiency of the new material, of contaminants in technological water from the leather industry [111, 112].

The general working template is presented in the following diagram:

Step 1
- Addition of adsorbent material in technological wastewater
- Adjusting the pH of the solution in order to destructuring the material

Step 2
60 min
- Addition of hydrogen peroxide to the solution

Step 3
30 min
- Adjusting the pH of the solution to 7

Step 4
2-4 h
- Coarse filtration
- Characterization of the filtrate / solid residue

Step 5
15 min
- Carbonation of the aqueous solution
- Alkalization of the solution

Step 6
15 min
- Addition of iron chloride

Step 7
15 min
- Addition of phosphoric acid
- Adjusting the pH to 7.5

Step 8
2-4 h
- Solution filtration

Step 9
10 min
- Clarification by the addition of aluminum chloride

Step 10
1 h
- Final filtering
- Characterization of the resulting water

Test protocol

Step 1: To 1 L of wastewater was added 0.25 (*) g of composite material. The formed solution was adjusted to different pHs, to conclude what is the optimal pH of destructuring the material. Thus, the acidification was performed with the addition of 98% H_2SO_4, and the alkalinization was performed with the addition of 2.2% CaO.

<u>Note:</u> * - 0.5 g of composite material was used for test 1;

Step 2: After stabilizing the desired pH, 30% H_2O_2 was added in a 5:1 ratio (**) acid / base with which the pH was adjusted : H_2O_2. The reaction is perfected for 60 min.

Note: ** - for test 1 an H_2SO_4: H_2O_2 ratio of 5:2 was used.

Step 3: Add CaO and NaOH 5:2 until the pH is adjusted to 7.5. The mixture is matured for 30 min.

Step 4: The mixture is filtered in the gravitational field, using several filter papers with medium porosity. The ease of filtration depends on the size of the particles in the mixture. After completion of this phase, the solid residue is collected, dried at 60 °C and characterized by SEM / EDX investigations.

Step 5: The aqueous phase resulting from the filtration is carbonated with H_2CO_3, then the pH is adjusted with CaO and NaOH in a ratio of 5:2, to 7.9-8 (if applicable). The mixture matures for 15 minutes.

Step 6: Add $FeCl_3$ to the mixture and mature for 15 minutes.

Step 7: The mixture is phosphorylated with H_2PO_4, then the pH is adjusted with CaO and NaOH in a ratio of 5:2, to 7.5. The reaction is perfected for 15 min.

Step 8: The mixture is filtered in the gravitational field, using several low porosity filter papers. The ease of filtration depends on the size of the particles in the mixture.

Step 9: After filtration, $AlCl_3$ is added to the solution for clarification and the reaction is perfected for 10 min.

Step 10: The mixture is filtered in the gravitational field, using several low porosity filter papers.

3.2. RESEARCH ON OBTAINING A NANOSTRUCTURED ADSORBENT MATERIAL WITH CELLULOSE MATRIX

The second part of the chapter includes the working method for the preparation of the material matrix, the preparation of the oxide mixture, its incorporation into the material and the preparation of the material for testing. Figure 3.1 shows the working protocol for preparing the material.

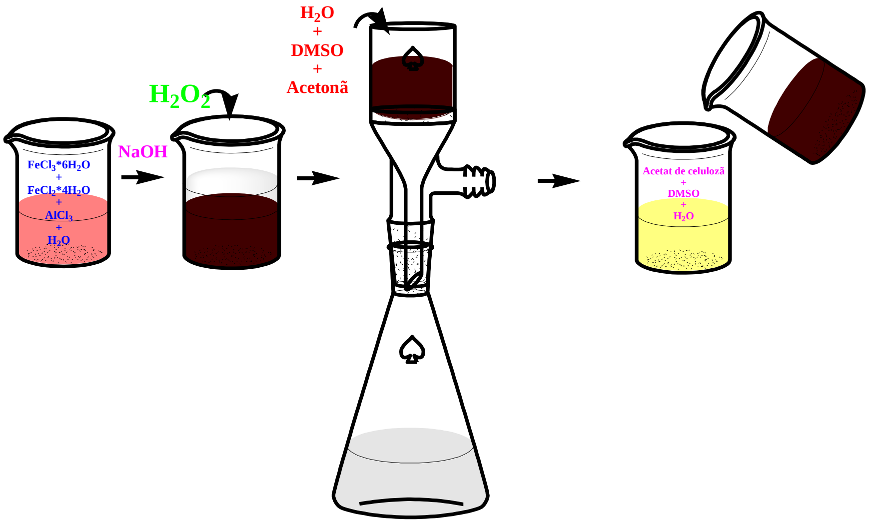


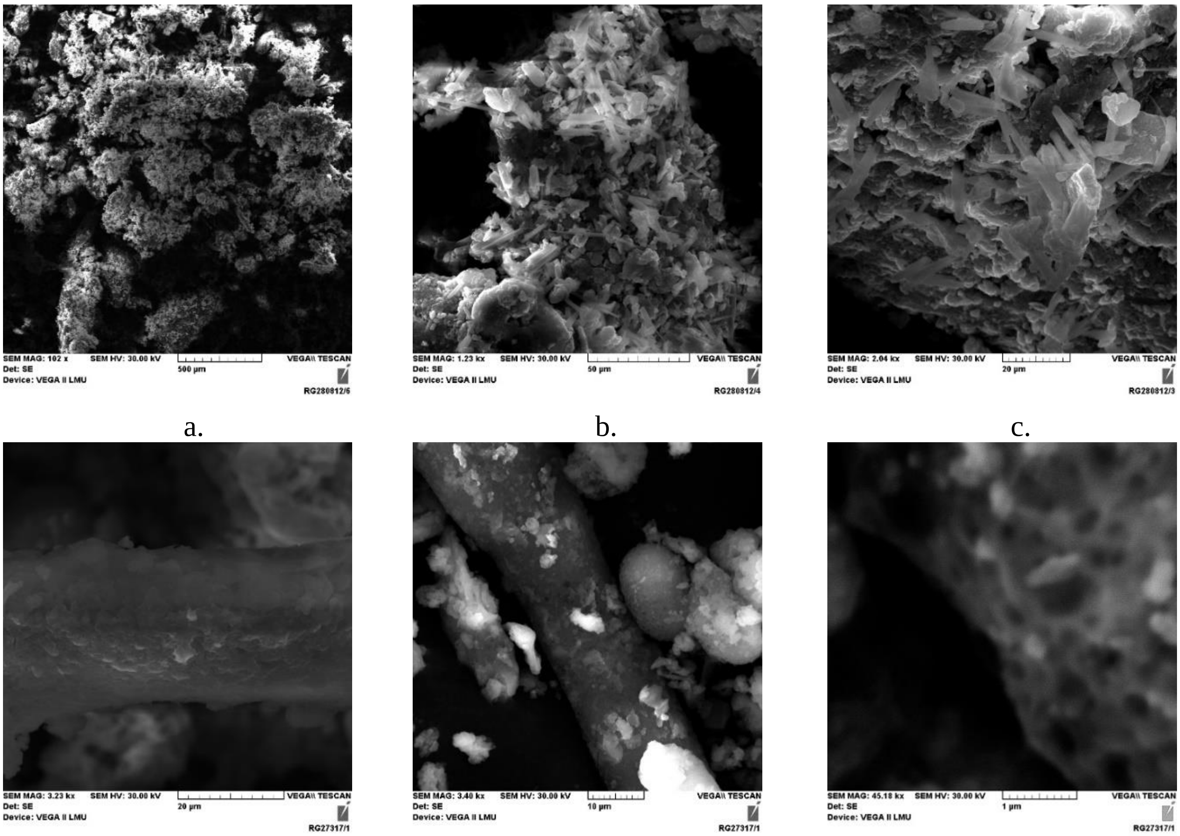
Fig. 3.1 Scheme for the preparation of the adsorbent material

3.3. RESEARCH ON THE MORPHOSTRUCTURAL AND MORPHOCHEMICAL CHARACTERIZATION OF NANOSTRUCTURED ADSORBENT MATERIAL WITH CELLULOSE MATRIX

The last part of the chapter includes the researches regarding the morphostructural and morphochemical characterization of the nanostructured adsorbent material with cellulose matrix obtained.

Through ***SEM investigations*** (Fig. 3.5) it was observed that the material is in the form of cellulose microfibers on the surface of which is observed the oxide mixture dispersed in randomly distributed agglomeration domains. The thickness of the microfibers is about 10 µm, and the observed agglomeration domains, at magnifications of 100 x up to 4 kx, vary between 1 and 30 µm. At magnifications of 12 kx to 45 kx, nanometer-sized agglomeration subdomains are observed.

The random arrangement of the particles that enter the structure of the agglomeration domains allows the formation of micro and nanometric voids, giving the material a high porosity, therefore a high specific surface area.



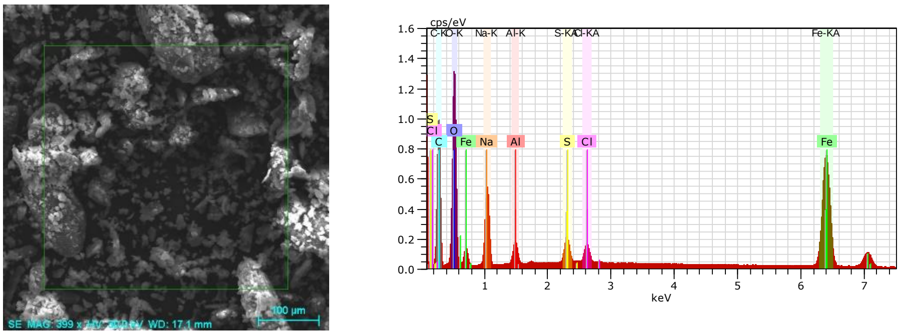
a. b. c.

d. e. f.

Fig. 3.5 SEM investigations of the material obtained at different magnifications (a) 102 x (b) 1.23 kx (c) 2.04 kx (d) 3.23 kx (e) 3.40 kx (f) 45.18 kx

From the qualitative-quantitative ***EDX microanalysis*** was observed the chemical nature of the substrates of the synthesized material, the way of their distribution on the material surface (Fig. 3.8) and the concentration of the chemical elements present in the substrate.

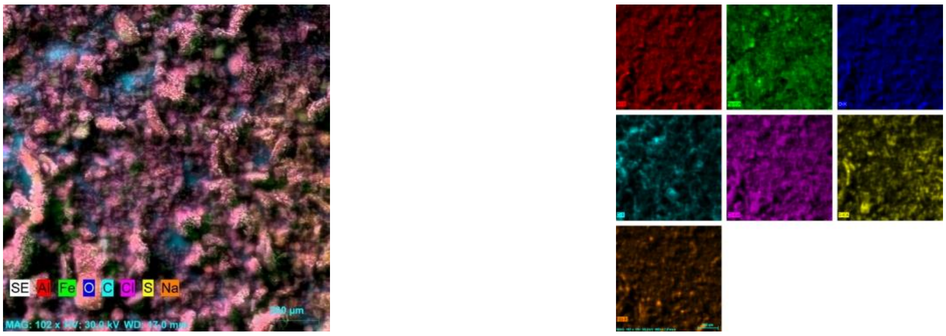
The composite material prepared is composed mainly of Al, Fe, Na, S and O; Their mass concentrations are shown in Fig. 3.7. The concentration of the elements resulting from magnifications of 100 x and 400 x shows insignificant variations, which leads to the conclusion that the types of oxides are mixed and dispersed mainly uniformly, without having control of the distribution.



Element	wt.%
C	**11.61**
O	**52.82**
Na	**14.61**
Al	**2.40**
S	**1.54**
Cl	**1.15**
Fe	**16.04**
	100.00

a. b. c.

Fig. 3.6 X-ray emission spectrum emitted by the sample (b) corresponding to the magnification SEM image 399 x (a). (c) Type of chemical elements and their mass concentration in the material



a. b.

Fig. 3.8. General distribution of the elements on the analyzed area (a). Individual distribution of elements on the analyzed area (b)

From the FTIR investigations were highlighted the functional groups O = H from the absorption region located between 4000 and 3000 cm^{-1}. This region of spectral absorption is difficult to separate, noting that the absorption maxima in the range 4000 and 3000 cm^{-1} are very wide, obtained by superimposing several distinct particular absorption maxima. The maxima in this region can also be attributed to functional forms of the type = C = NOH as well as to the traces of free OH groups remaining after dehydration of the investigated material. The peak with the maximum at 3420 cm^{-1} (Fig. 3.11) was attributed to the O = H streaching connection. The peaks located in the absorption region 2900 - 3200 cm^{-1} were assigned to the C - H bonds (asymmetric and symmetrical stretching), with a maximum at 2923 cm^{-1}. In the region 2100 - 2240 cm^{-1} a wide absorption band is observed, presenting some absorption maxima of low intensity, these can be attributed to the type C = C - Cl connections. At 1567 cm^{-1}, specific absorptions of carboxylate bonds are observed (asymmetric and symmetrical stretching of the functional groups C = O, respectively). These experimental records demonstrate the successful functionalization of the oxide mixture. Moreover, the experimental evidence demonstrates that the final material obtained has an active, distinct chemical functionality that preserves that of its structural elements. Peaks with maxima at 1409 cm^{-1} and 1438 cm^{-1} were attributed to the C = C and C - C streaching bonds. The sharp peak with a maximum at 1022 cm^{-1} was attributed to the C - O streaching bond. The absorption maximum 1182 cm^{-1} can be attributed to both the alcoholic and ester C - O bonds. The peaks in the region 600 - 800 cm^{-1}, with a maximum at 661.5 cm^{-1} are attributed to the C - Cl connections.

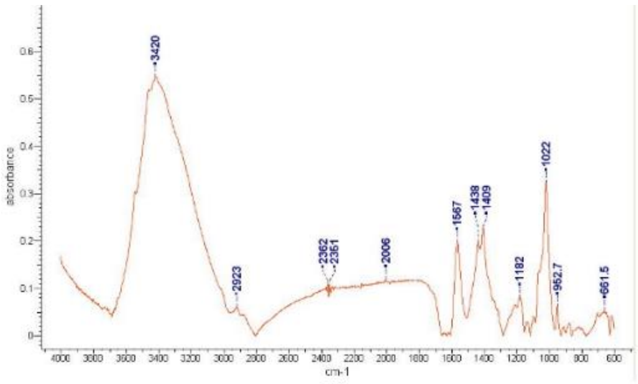


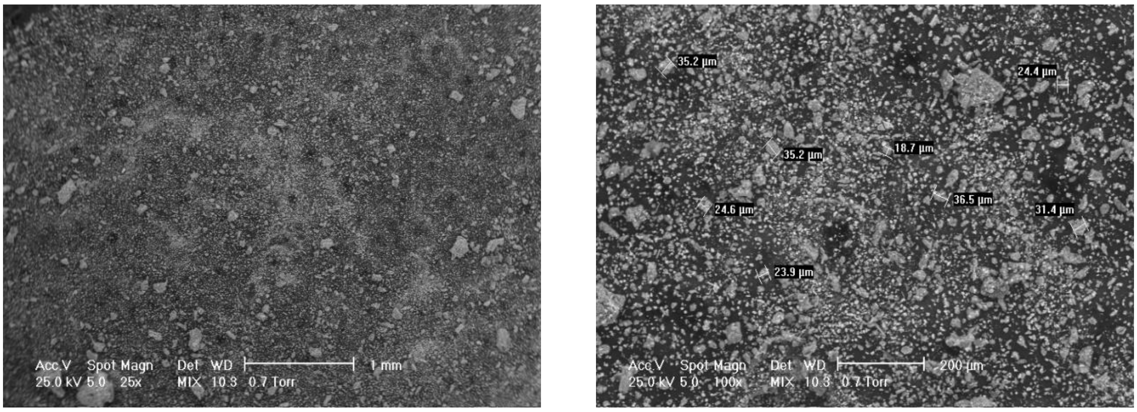
Fig. 3.11. FTIR spectrum of the obtained adsorbent material - the seated material

The ***fourth chapter*** **"Research on testing the efficiency of nanostructured adsorbent material with cellulose matrix"** presents experimental research on optimizing the methods of testing the adsorbent material obtained with industrial wastewater, in order to obtain the highest possible treatment efficiency. The morphostructural and morphochemical characterization of the adsorbent material resulting as solid waste after testing and the qualitative and quantitative evaluation of the pollutant retention capacity in the structure of this material is presented. It is also presented the qualitative and quantitative characterization of water samples obtained after testing, assessing their quality by measuring general and specific parameters and framing the values obtained in the provisions of environmental legislation in force [117 - 119].

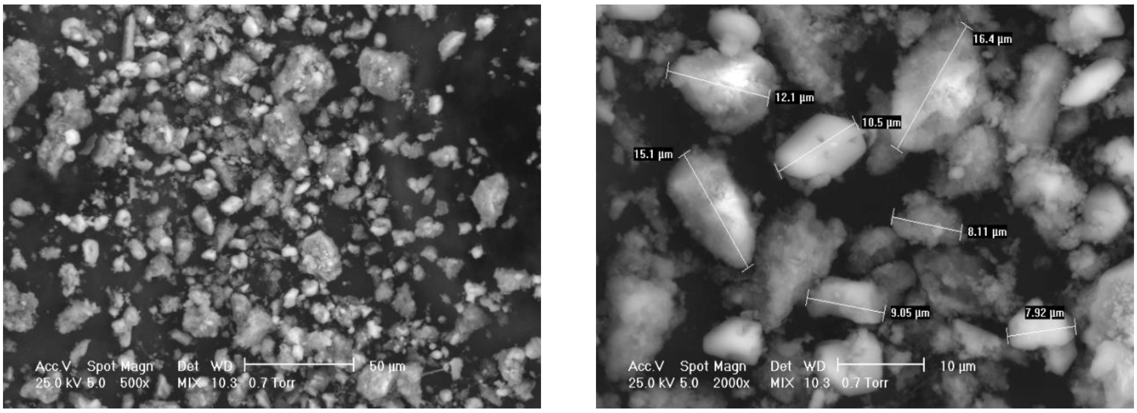
To test the efficiency of the material, a batch of wastewater from the technological flow of leather processing (leather and footwear industry) was used. The water has a cloudy appearance, dark gray color and an unpleasant odor of sulfur. Prior to testing, water was investigated on the following parameters: organic substances extractable with organic solvents investigated by GC / MS, alkalinity - basicity, biochemical oxygen demand - BOD5, chemical oxygen demand - COD- Cr, total suspended solids , ammonium nitrogen, chlorides, sulfates.

4.8.2. Characterization of the solid residue corresponding to the sample 7

- SEM: The particle size (Fig. 4.35) at magnifications of 100x is between 18.7 and 36.5 µm, and at an magnification of 2000x an average particle size of between 7.92 and 16.4 µm is observed.



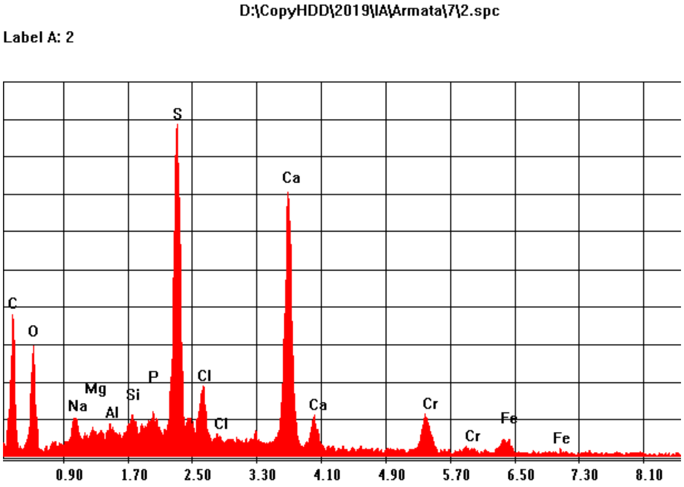
a. b.



c. d.

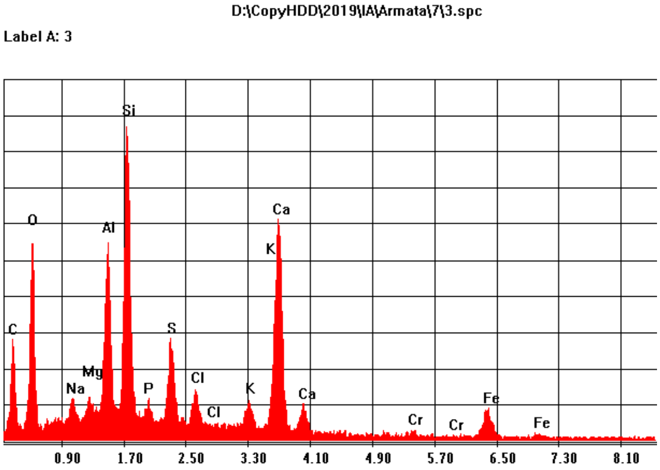
Fig. 4.35 Morphological structure of the resulting solid residue, corresponding to case study 7 at different magnifications (a) 25 x (b) 100 x (c) 500 x (d) 2 kx

- EDX



Element	Wt %	
C	0.94	
O	50.02	
Na	4.92	
Mg	2.15	
Al	1.58	
Si	1.47	
P	1.96	
S	13.97	
Cl	3.53	
Ca	13.91	
Cr	3.44	Total
Fe	2.11	100

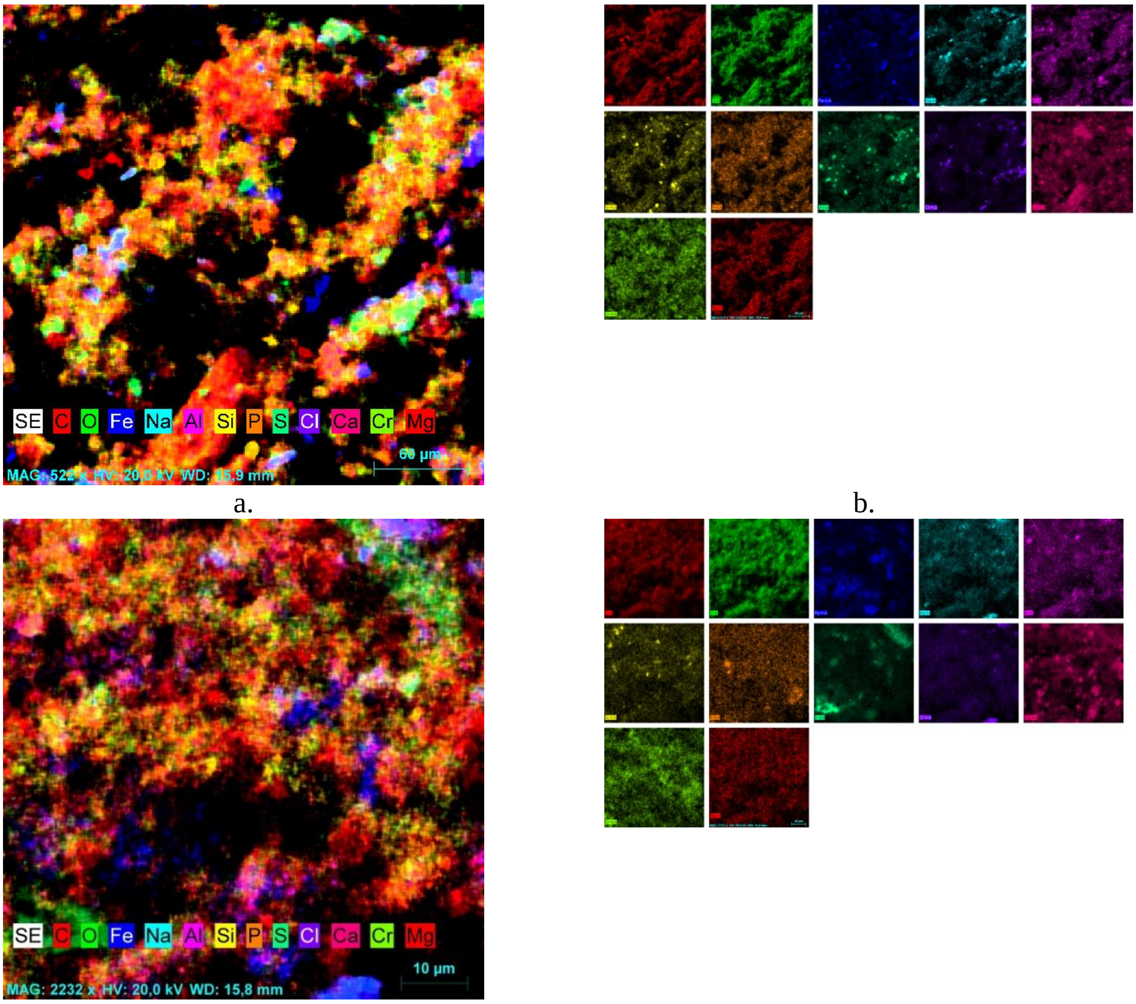
c. d.



Element	Wt %	
C	0.44	
O	56.83	
Na	3.61	
Mg	2.46	
Al	7.6	
Si	9.63	
P	1.36	
S	3.29	
Cl	1.56	
K	1.19	
Ca	8.92	
Cr	0.37	Total
Fe	2.74	100

e. f.

Fig. 4.36 X-ray emission spectra emitted by sample 7 at different magnifications (c) 500 x (e) 2 kx and the concentration of the chemical elements present in the samples corresponding to the spectra (d) 500 x (f) 2 k



a. b.

c. d.

Fig. 4.37 General distribution of chemicals on the analyzed surfaces at different magnifications (a) 522 x (c) 2232 x. Individual distribution of elements on the analyzed areas corresponding to the magnifications (b) 522 x (d) 2232 x

4.8.3. Characterization of the resulting water corresponding to the case study 7

- <u>Organic substances extractable with organic solvents investigated by GC / MS</u>

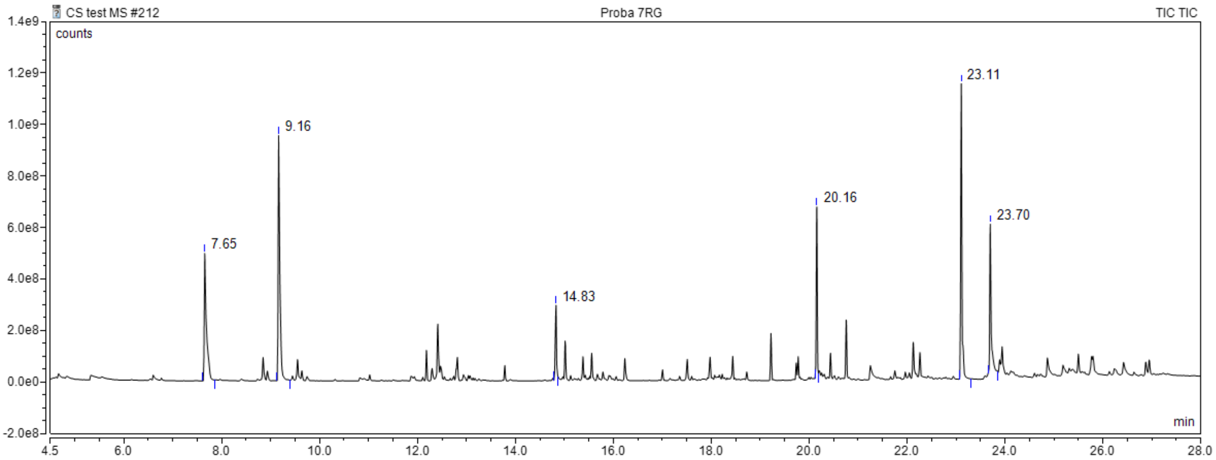


Fig. 4.38 Chromatogram of sample 7 corresponding to case study 7

Table 4.8 The values of the quality parameters of sample 7 corresponding to the case study 7

Parameters	Maximum allowed value	Standard	Sample 7
pH	6.5-8.5 unit. pH	SR ISO 10523/2012	7.5
Total suspended solids	350 mg/L	SR EN 872/2005	20
Biochemical oxygen demand at 5 days (BOD5)	300 mg/L	SR EN 1899 -1/2003	200
Chemical oxygen demand - potassium chromate method (COD-Cr)	500 mg/L	SR ISO 6060:1996	394
Ammonium nitrogen	30 mg/L	Kit Merck 1.4752.0001	<0.149*
Chlorides	500 mg/L	SR ISO 9297/2001	2439
Sulfates	600 mg/L	SM 4500-SO4 E, EPA 427C	2340

The ***fifth chapter*** **"Results, conclusions and personal contributions"** summarizes the results obtained in the 10 case studies, the interpretation and comparative evaluation of the values obtained, the general conclusions of all theoretical and experimental studies performed for this paper and personal contributions.

5.1. COMPARATIVE ANALYSIS OF RESULTS

The adsorbent material resulting from the first stage of filtration together with the pollutants adsorbed from the tested water, was investigated by SEM / EDX in order to conclude its adsorption capacity, qualitative and quantitative.

SEM investigations have shown that the material is in the form of inhomogeneous agglomeration domains. The particle size at 100x magnifications is on average between 20 and 100 µm. Samples P9 and P10 are highlighted, which at a magnification of 100x have a much smaller particle size between 10 and 30 µm. At a magnification of 2000x the presence of subdomains is observed, with an average particle size between 5 and 20 µm. This magnification also shows that samples P9 and P10 have a much smaller particle size, between 1 and 5 µm. Also, the presence of particles of submicron dimensions is observed (Fig. 4.38 and 4.43). An average particle size can be seen in Fig. 5.1. The particle size found in the solid residual material is equivalent to the size of the sedimentable flakes in the first filtration step.

The notion of trigger pH defines the pH value at which the adsorbent material used has the best reactivity with the tested water pollutants. The value of this parameter was deliberately varied from the value 2 to the value 10 in order to establish, following the comparison of the final results obtained, the optimal value.

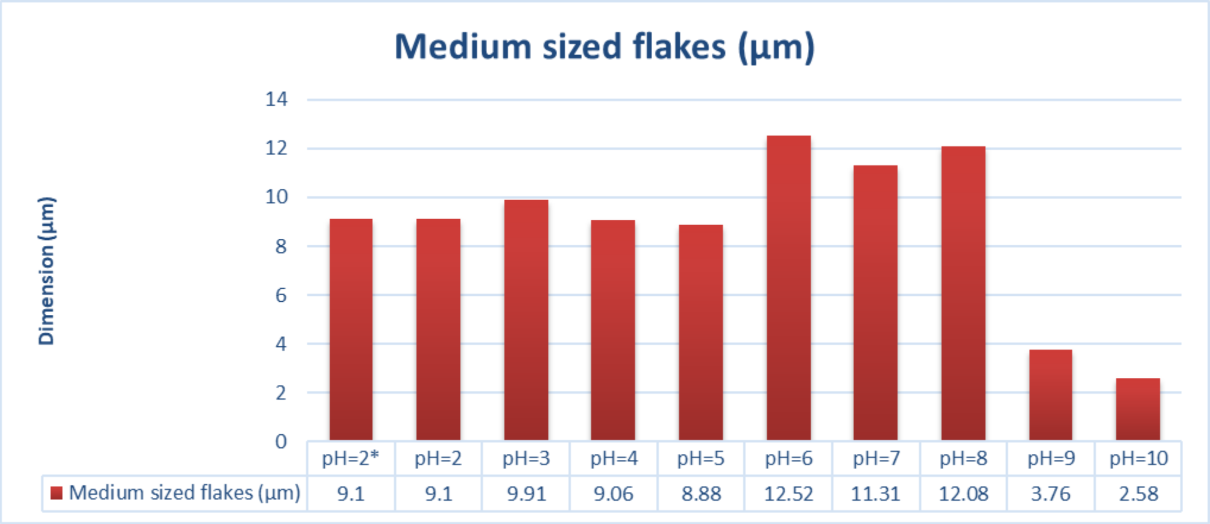


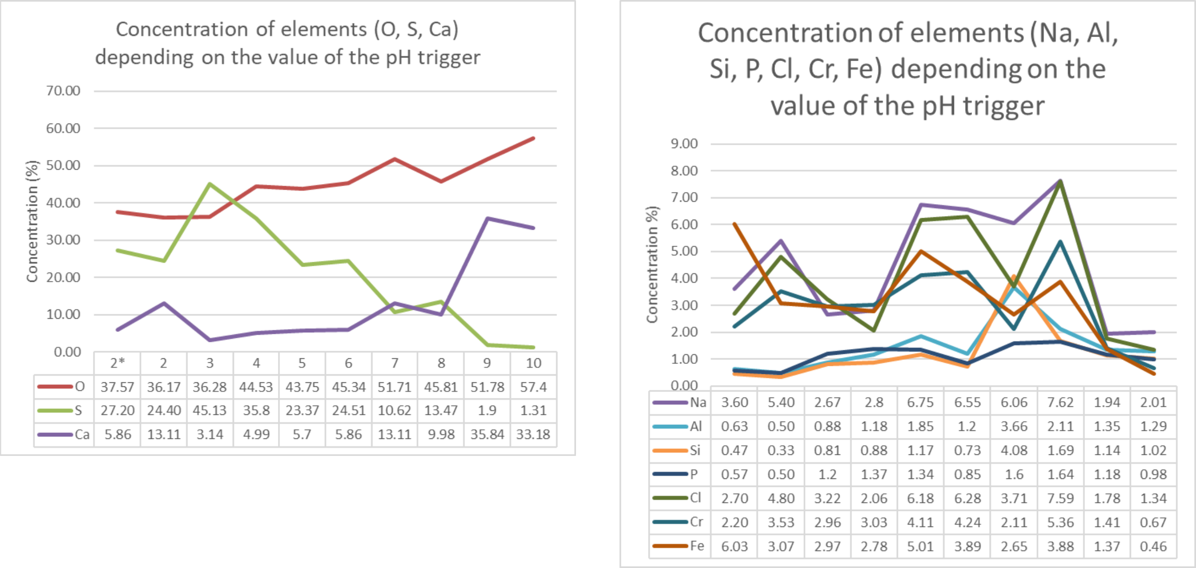
Fig. 5.1 Average particle size in the residue

The purpose of EDX investigations is to observe the chemical nature of the solid residue substrates and to determine the concentration of the chemical elements present in the substrate.

The residue is composed mainly of C, O, Na, Al, Si, P, S, Mg, Cl, Ca, Cr, Fe (Table 5.1). Oxygen is the element that is found in the highest concentration in all samples, with an approximate value between 36.28% and 57.4%, showing a growth trend directly proportional to the increase of trigger pH value. The high concentration of oxygen leads to the idea of the existence of several types of oxides in the structure of the residue, such as oxides of Al, Fe, Ca, Mg, Cr.

Sulfur is the element with the second highest concentration in the structure of the solid residue. The S concentration is between 45.13% in P3, decreasing proportionally with the increase of the trigger pH value, up to 1.3% in P10. The high concentration found in the samples with the low trigger pH value can be attributed to the use of H_2SO_4 for acidification.

Calcium is the third most abundant element present in the solid residue, its variation being inversely proportional to that of sulfur. Calcium is found in concentrations of 3.14% in P3, increasing to 35.84% in P9. The increased concentration found in samples with a high trigger pH value can be attributed to the use of CaO for water alkalinization (Fig. 5.2.a). Elements such as Al, Fe, S, O, Na are also found in the structure of the adsorbent material used in treatment. Additionally, Ca and Na were used in the first stage of preparation. Elements such as Cr, Cl, Si, Mg come entirely from the composition of wastewater, also variable concentrations of other elements may come from wastewater (Fig. 5.2.b).



	2*	2	3	4	5	6	7	8	9	10
O	37.57	36.17	36.28	44.53	43.75	45.34	51.71	45.81	51.78	57.4
S	27.20	24.40	45.13	35.8	23.37	24.51	10.62	13.47	1.9	1.31
Ca	5.86	13.11	3.14	4.99	5.7	5.86	13.11	9.98	35.84	33.18

Na	3.60	5.40	2.67	2.8	6.75	6.55	6.06	7.62	1.94	2.01
Al	0.63	0.50	0.88	1.18	1.85	1.2	3.66	2.11	1.35	1.29
Si	0.47	0.33	0.81	0.88	1.17	0.73	4.08	1.69	1.14	1.02
P	0.57	0.50	1.2	1.37	1.34	0.85	1.6	1.64	1.18	0.98
Cl	2.70	4.80	3.22	2.06	6.18	6.28	3.71	7.59	1.78	1.34
Cr	2.20	3.53	2.96	3.03	4.11	4.24	2.11	5.36	1.41	0.67
Fe	6.03	3.07	2.97	2.78	5.01	3.89	2.65	3.88	1.37	0.46

a. b.

Fig. 5.2 Comparative analysis of the concentration of elements in solid residues (a) for elements O, S, (b) for elements Na, Al, Si, P, Cl, Cr, Fe

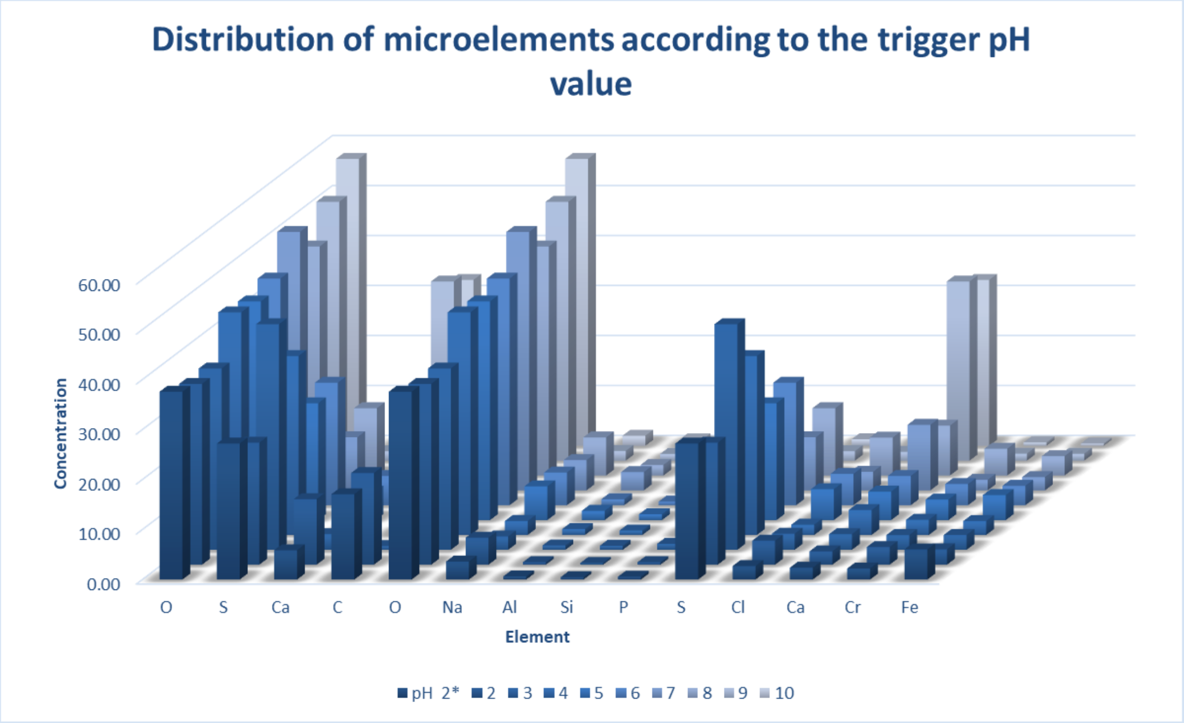


Fig. 5.3 Comparative analysis of the distribution of elements in the destructured material

- ***GC-MS***

For GC / MS investigations, 2 samples of 5 mL were taken from each water sample resulting after the treatment. Each 5 mL of sample was extracted with 2 mL DCM (dichloromethane). The samples were stirred for 2 minutes in a separatory funnel. The phases are separated, to be processed as follows:

The organic phase is dried over anhydrous sodium sulfate and filtered through a 0.45 micron Sartorius filter. For GC / MS analysis we use 5 µL of organic phase in 1 mL DCM. To avoid cross-contamination and to observe good laboratory practices, a blank DCM sample is injected before each analysis.

The remaining aqueous phase is brought to dryness by centrifugation. The samples are eluted with 500 µL ACN and then derivatized with 100 µL BSTFA at 60 °C for 30 min. Add 1 mL DCM and analyze by GC / MS. A solution of DCM, ACN and BSTFA is used as the blank sample, the percentages corresponding to the quantities used to prepare the samples.

Because some of the organic compounds present in the water samples cannot be extracted entirely with an organic solvent, or some of them have an affinity for the aqueous medium, as well as the possibility of incompatible compounds to be analyzed as such in GC / MS, it was decided to analyze both the organic extract and the aqueous phase brought to dryness and silanized.

25 compounds were identified as follows: Phenol [RT 7.65], 2-Ethyl-1-hexanol [RT 8.37], P-cresol [RT 9.16], m-Di-t-butylbenzene [RT 11,85], Pentadecan [RT 12,19], p-Chloro-m-cresol [RT 12,42], Indole [RT 12,44], 2,6,11-Trimethyldodecan [RT 12,81], 2-Indolone [RT 14,83], 2,4-Di-t-butylphenol [RT 15,22], 2,2-dihydroxybiphenyl [RT 15,38], Hexadecan [RT 15,56], heptacosan [RT 16 , 24], Indole, 5-ol [RT 17,51], Octadecan [RT 18,44], 1,2 benzenedecarboxylic acid, bis (2-methyl propyl) ester [RT 19,22], Dibutyphthalate [RT 20, 15], Eicosan [RT 20,44], 2,5-Di-t-butyl-1,4-benzoquinone [RT 20,76], Hexadecanamide [RT 22,13], Docosan [RT 22,27], acid 3-Chloro-heptadecyl propanoic [RT 23,11], 9-Octadecenamide [RT 23,7], Octacosan [RT 23,94], 2-Palmitoglycerol [RT 24,863].

In Fig. 5.4. the chromatograms of the organic extracts of the 10 samples (P1… P10) and of the initial samples (P0) are presented comparatively.

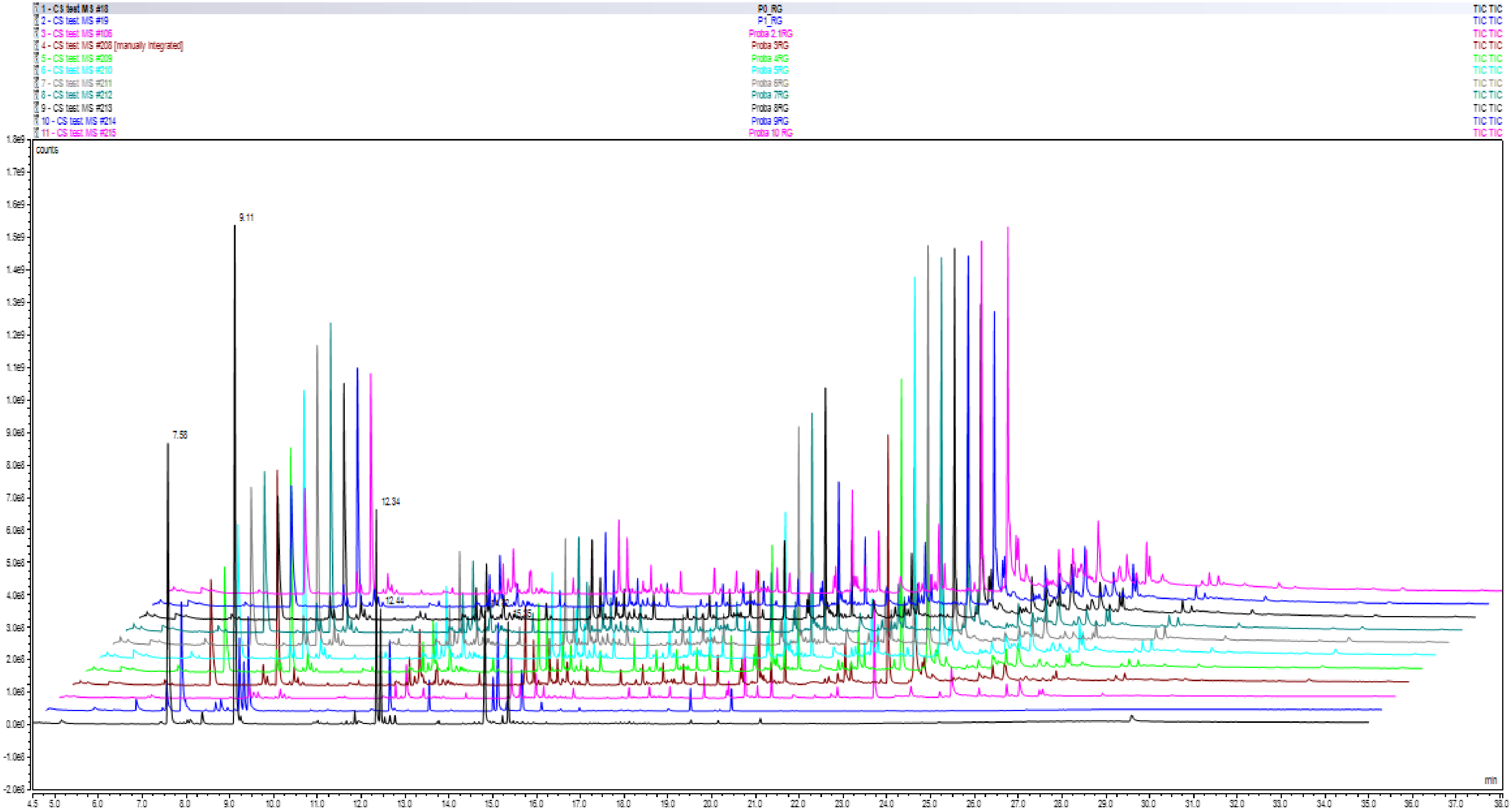


Fig. 5.4 Comparative analysis of chromatograms obtained by GC / MS analysis of water

From the evaluation of the quantitative analyzes resulting from the GC-MS investigations, a considerable decrease of the concentration of the identified organic compounds in water can be observed (Fig. 5.4), comparing the control sample (P0) with the treated water samples. Sample 1 and sample 2 were prepared at the same trigger pH = 2, the difference being given by the ratio, on the one hand of the ratio H2SO4: H2O2 of 5: 2 in P1 and 5: 1 in P2 and on the other hand of the amount of material used for testing 0.5 g in P1 and 0.25 g in P2. From Table 6.13 it can be seen that the values of the concentrations of organic compounds in P2 are much lower than those in P1, which is why it was decided to use a ratio of 5:1 H2SO4:H2O2 and a quantity of 0 for subsequent tests. 25 g adsorbent material.

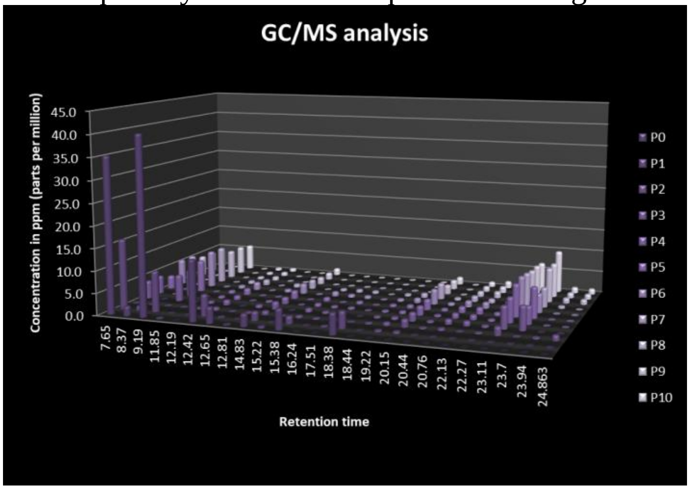


Fig. 5.6 Comparative analysis of the concentration of compounds extracted with organic solvent from water samples (P0 - P10)

In Fig 5.7. the concentrations of the organic compounds identified in the samples prepared at the same H2SO4:H2O2 ratio of 5:1 are evaluated comparatively, the differences being given by the trigger pH of each sample. It can be seen that samples prepared at a neutral or slightly acidic trigger pH (P7 - pH 7 and P6 - pH 6) have a higher concentration of organic compounds present in the treated water. Improved results are observed, as the trigger pH value is farer from neutral (both acidic and basic), with the observation that those prepared in an acidic environment have slightly lower concentrations of organic compounds compared to those prepared in the basic environment. The concentrations of organic compounds have values between 8.3 ppm and 0 (absence of compounds), being evaluated samples P2 - P10.

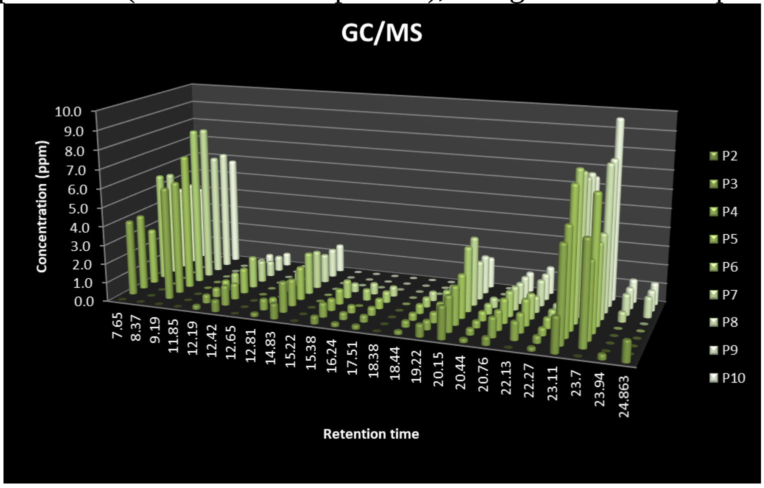


Fig. 5.7 Comparative analysis of the concentration of compounds extracted with organic solvent from water samples (P2 - P10)

- The concentration of ***hydrogen ions*** (pH) expresses the intensity of acidity or alkalinity. According to NTPA 002, the pH value must be between 6.5 - 8.5 units. pH. From Fig. 5.8. it is observed that the pH of the treated water samples is within the acceptance range of NTPA 002, the values being between 7 and 8.1. It can be stated that the pH of the samples has a neutral character with slight alkaline tendencies.

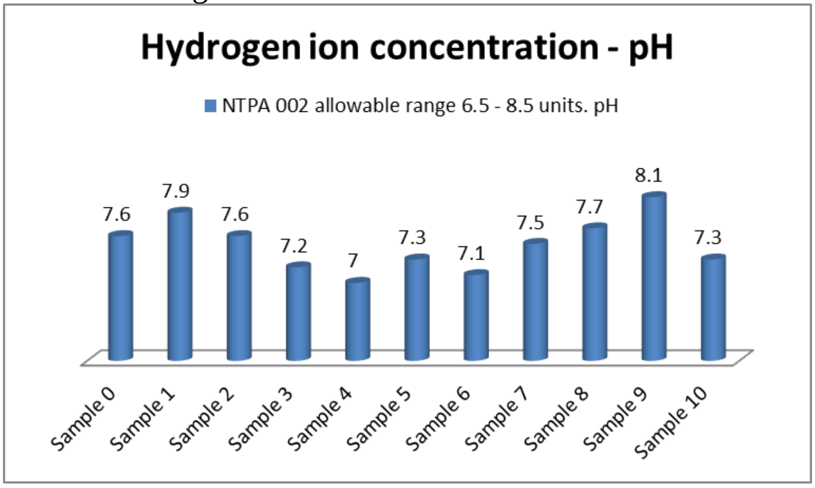


Fig. 5.8 Comparative analysis of pH value in water samples

- ***Biochemical oxygen demand at 5 days*** (BOD5) represents the amount of oxygen that is consumed for the oxidative degradation by microorganisms of the organic substances contained, at a temperature of 20 °C, for 5 days. According to NTPA 002, the maximum allowed BOD5 value is 300 mg / L.

In Fig. 5.9. the values obtained after performing the analysis of the samples are compared. The BOD5 value of sample 0 exceeds the maximum permissible value by 205%. There is a decrease in the value of BOD5 between 61.8% to 91.7% of the value of the initial / untreated sample.

It is also found that only sample 8 has a BOD5 value that does not fall within the acceptance range of NTPA 002. It exceeds the maximum permissible value by 16.3%. Taking into account the fact that the BOD5 determinations were performed accredited, with a measurement uncertainty of 19.4% we can conclude that the CBO5 value of sample 8 falls within the range allowed by NTPA 002.

Comparatively evaluating sample 1 and sample 2 which were prepared at the same trigger pH, the difference being given by the ratio H_2SO_4:H_2O_2, a much better result is observed in sample 2 (ratio 5:1). Although both values are within the range allowed by NTPA 002, the treatment of P2 had an efficiency of 14.3% better than in the case of P1.

Comparatively evaluating the BOD5 values, there is a tendency to improve the results obtained, as the pH of the trigger used in the preparation deviates from the neutrality value. The best results were obtained in samples P10 (pH trigger=10), followed by P2 (pH trigger=2)

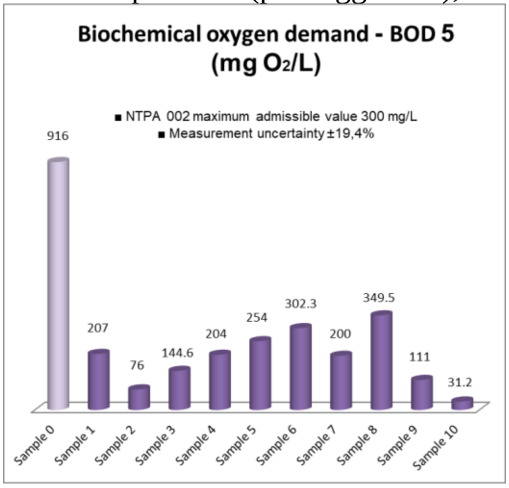


Fig. 5.9 Comparative analysis of the value of biochemical oxygen consumption at 5 days in water samples

- ***Chemical oxygen demand (potassium dichromate method)*** (COD-Cr) is the mass concentration of oxygen equivalent to the amount of potassium dichromate consumed for the oxidation in acid medium of dissolved and suspended organic matter present in water. According to NTPA 002, the maximum permitted limit of COD-Cr is 500 mg / L.

In Fig. 5.10. the values obtained after performing the analysis of the samples are compared. The COD-Cr value of sample 0 exceeds the maximum permissible value by 327.6%. There is a decrease in the value of COD-Cr between 70.8% to 91.9% of the value of the initial / untreated sample. COD-Cr determinations were performed in an accredited regime, with a measurement uncertainty of 7.0%. It is thus found that three of the samples exceed the maximum allowed limit by 45% - P1, 24.8% - P5, 15% - P8. However, compared to the initial sample P0, the 3 samples show a decrease in COD-Cr value of 63.7% - P1, 70.8% - P5 and 73.1% - P8.

Comparatively evaluating sample 1 and sample 2 which were prepared at the same trigger pH, the difference being given by the ratio H_2SO_4:H_2O_2, a much better result is observed in sample 2 (ratio 5:1). The treatment of P2 had an efficiency of 23.2% better than in the case of P1, mentioning that the COD-Cr value of P1 does not fall within the range allowed by NTPA 002. Evaluating comparatively the BOD_5 values, there is a tendency to improve the results obtained, as the pH trigger used in the preparation it's getting further from the neutrality value. The best results were obtained in samples P10 (pH trigger = 10), followed by P2 (pH trigger = 2).

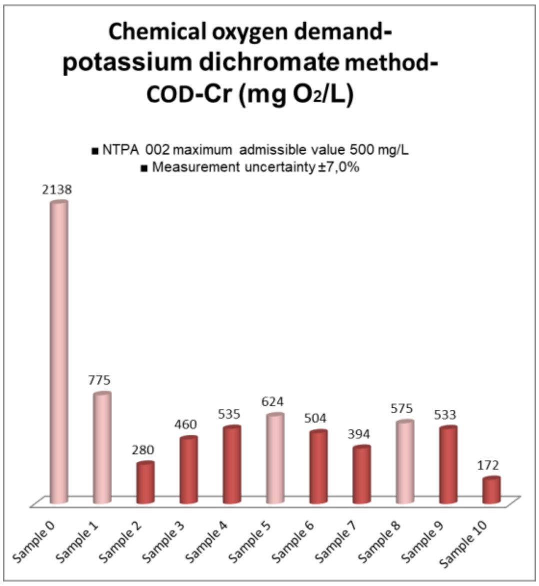


Fig. 5.10 Comparative analysis of chemical oxygen consumption - potassium dichromate (CCO-Cr) method in water samples

- ***Total suspended materials*** are water-insoluble substances that can be separated by filtration, centrifugation or sedimentation (<2 mm). According to NTPA 002, the maximum allowable limit of TSM is 350 mg / L.

In Figs. 5.11. the values obtained after performing the analysis of the samples are compared. It is noted that all samples, including the initial sample, fall within the range allowed by NTPA 002. However, compared to P0, there is a decrease in the TSM value between 57.2% to 88.6% of the value of the initial sample / untreated. Sample 6 shows the lowest treatment efficiency from the point of view of TSM, the value obtained being, however, well below the maximum allowed limit. The other samples have very low TSM values.

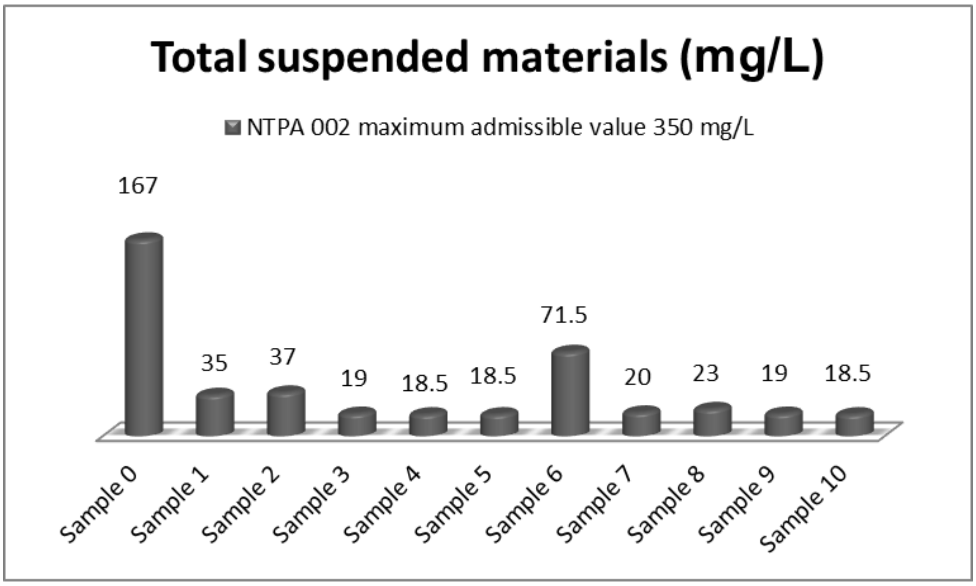
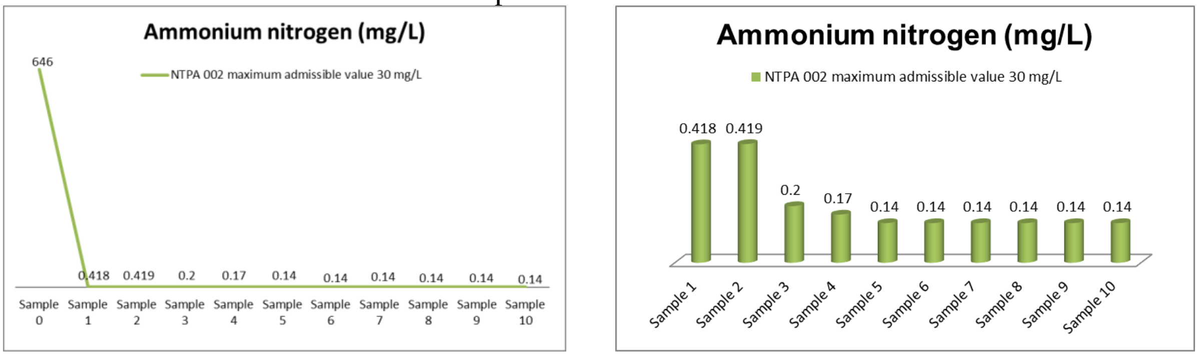


Fig. 5.11 Comparative analysis of total suspended matter in water samples

- ***Ammonium nitrogen*** (NH_4^+) is the nitrogen content of NH_4^+ ions in water. In Fig. 5.12.a and 5.12.b are presented comparatively the values obtained after performing the analyzes of the samples. The ammonium nitrogen concentration of sample 0 exceeds the maximum permissible value by 2053%. A decrease in ammonia nitrogen concentration of more than 99.9% is observed in all samples.



a. b.

Fig. 5.12 Comparative analysis of ammoniacal nitrogen concentration in water samples (a) P0 -P10 (b) P1 - P10

- ***Chlorides*** are a measure of the concentration of Cl^- ions. Quantitative determination is performed by titration with silver nitrate and is based on the chemical reaction between chlorine ions and silver ions. According to NTPA 002, the maximum permissible limit of chlorides is 500 mg / L.

In Fig. 5.13. the values obtained after performing the analysis of the samples are compared. It is observed that the initial sample P0 exceeds the maximum permissible limit by 20%. It is also noted that only the values obtained for samples P1 and P2 fall within the range allowed by NTPA 002 shows a decrease in the amount of chlorides of 31.7% - P1 and 25.0% - P2, from the value of the initial sample / untreated.

The chloride concentrations for samples P3 to P10 show an increase of 239 to 308% compared to the initial sample. This may be due to the fact that aqueous $FeCl_3$ solution was used to treat the samples. $FeCl_3$ in aqueous solution dissociates into Fe_3^+ and Cl^- ions. A slight excess used at the last stage of treatment could lead to inadequate / insufficient removal from the water.

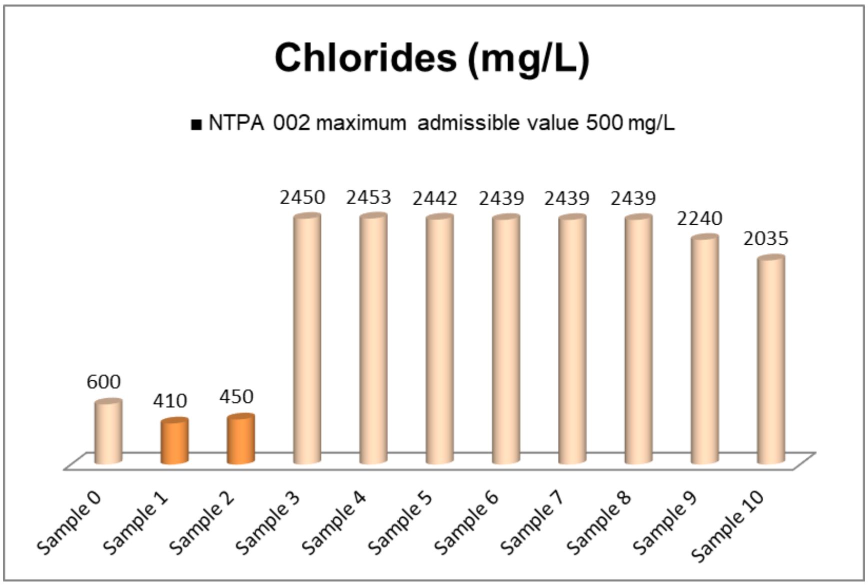


Fig. 5.13 Analiza comparativă a concentrației clorurilor în probele de apă

- ***Sulphates*** represent the concentration of SO_4^{2-} ions. According to NTPA 002, the maximum permitted limit for sulphates is 600 mg / L.

In Fig. 5.14. the values obtained after performing the analysis of the samples are compared. It is observed that the initial P0 sample exceeds the maximum permissible limit by 502%. It is noted that the values obtained for samples P2, P7, P8, P9 and P10 show a decrease in the amount of sulfates of 5.2% - P2 to 81.7% - P9 of the value of the initial / untreated sample. None of the samples is low enough to be included in the range allowed by NTPA 002. The lowest value of the sulphate concentration was obtained at P9, which exceeds the maximum permissible value by 10%. Samples P1, P3, P4, P5 and P6 show an increase in sulfate concentration of 5.7% - P4 to 26.7% - P3, compared to the value of sulfate concentration of P0. With the exception of P2, all other samples showing an increase in sulphates are samples which have been treated at a more acidic trigger pH than the initial water pH. The presence of the SO_4^{2-} ion is due to the use of H_2SO_4 to regulate the pH of the water in different treatment stages.

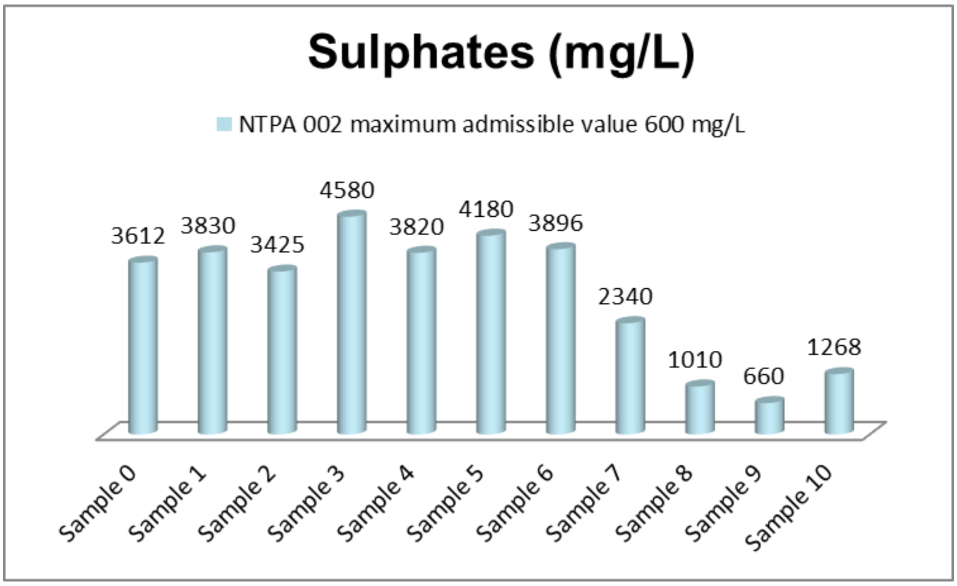


Fig. 5.14 Comparative analysis of sulphate concentration in water samples

5.2. GENERAL CONCLUSIONS

The aim of this thesis was to obtain new types of adsorbent materials doped with metal oxides of micro and nanometric dimensions, with role and applicability in the field of wastewater treatment and to demonstrate their efficiency through testing on industrial wastewater.

In this sense, the paper was approached through two main research directions:

- *RESEARCHES REGARDING THE PREPARATION AND MORPHOSTRUCTURAL AND MORPHOCHEMICAL CHARACTERIZATION OF A NANOSTRUCTURED ADSORBENT MATERIAL WITH CELLULOSE MATRIX*

Within this theme, the following objectives were pursued:

a) obtaining a new adsorbent material, having a high porosity, consisting of a cellulosic matrix embedded with micro and nanoparticles of metal oxides;

b) characterization of the obtained material, from the point of view of the morphological and morphochemical structure;

The research carried out in the first direction led to the following conclusions:

- the prepared material is in the form of cellulosic microfibers on the surface of which the oxide mixture dispersed in inhomogeneous agglomeration domains is observed;
- the size of the microfibers is on average about 10 µm, and the agglomeration domains and subdomains present on their surface have dimensions between 1 and 30 µm, respectively submicronic dimensions;
- the material has a high porosity due to the random agglomeration domains that favor the creation of gaps of micro and nanometric dimensions;
- the high porosity of the adsorbent material leads to the conclusion that the material has a high specific surface area, therefore a high reaction surface area;
- the adsorbent material consists mainly of Al and Fe oxides fixed on the cellulosic fibers;
- there were insignificant variations in the concentration of the elements on the investigated surfaces;
- it can be concluded from the EDX investigations that the oxide mixture was predominantly uniformly dispersed, without, however, having control of the distribution;

- *RESEARCH ON TESTING THE EFFICIENCY OF NANOSTRUCTURED ADSORBENT MATERIAL WITH CELLULOSE MATRIX*

Within this theme, the following objectives were pursued:

a) establishing the optimal parameters for testing the material obtained in order to maximize the efficiency of industrial wastewater treatment;

b) the morphostructural and morphochemical characterization of the adsorbent material, after utilisation and the qualitative and quantitative evaluation of the pollutants retention capacity in the structure of the obtained material;

c) characterizing from a qualitative and quantitative point of view the water samples obtained after testing and evaluating their quality, by measuring the general and specific parameters, as well as framing their value within the limits allowed by environmental regulations, regarding the quality of water that can be discharged into sewerage network.

The research carried out in the second direction led to the following conclusions:

- the general test method, optimized by changing some parameters in the test chain, is appropriate for the characterization of sorbent materials used in water purification;
- an H_2SO_4: H_2O_2 ratio used in the second phase of the test is optimal at 5: 1, conclusion evaluated based on the values of the measured water quality parameters;
- the consumption rate of the prepared adsorbent material is 0.25 g of material per liter of tested wastewater, quantified, of approximately 250 g/tonne of wastewater;
- the evaluation of the water quality parameters resulting from the treatment was made according to the pH of the destructuring of the material, which varied from the value 2 to 10.

- the residual material resulting from the filtration contains the adsorbent material together with the pollutants in the water, which react with it, making possible the sedimentation and separation;
- the dimensions of the sedimented flakes were investigated and we concluded that depending on the trigger pH used in the test, the particle sizes ranged from 100 to 20 µm, in the case of easily sedimentable particles and from 10 µm to submicronic dimensions, in the case of fine particles, difficult to sediment;
- the high oxygen weight concentration identified in the composition of the solid residue and quantified by EDX analyzes, leads to the idea of the existence of several types of oxides, such as oxides of Al, Fe, Ca, Mg, Cr;
- the composition of the residue varies depending on the pH of the trigger at which the tests were performed;
- there is an increase in the concentration of sulfur the more acidic the pH of the trigger used, and an increase in the concentration of calcium, the more basic the pH of the trigger used, in the resulting solid residue;
- part of the concentration of the elements Al, Fe, S, O comes from the adsorbent material used in the test;
- 25 organic substances present in the wastewater were identified;
- the identified compounds were monitored in all samples of treated water, finding a reduction in their concentration from 35-40 ppm in the original sample to about 2-3 ppm, even the complete removal in the case of some samples. The organic compounds present in the wastewater, in smaller amounts of about 10 ppm, were removed to concentrations below 1 ppm;
- the pH of the treated water samples is within the acceptance range of NTPA 002, the values being between 7 and 8.1;
- the BOD5 values of all treated water samples are lower than the maximum value allowed by NTPA 002- Wastewater discharge in the sewerage networks of the localities and directly in the treatment plants;
- there is a tendency to improve the BOD5 results obtained, as the pH of the trigger used in the preparation it's getting further from the neutrality value. The best results were obtained in samples P10 (pH trigger = 10), followed by P2 (pH trigger = 2);
- seven of the tested water samples have a COD-Cr value lower than the maximum value allowed by NTPA 002- Wastewater discharge in the sewerage networks of the localities and directly in the treatment plants;
- the three samples which have a COD-Cr value higher than the maximum value allowed by the legislation, however, show a decrease of the COD-Cr value from 63.7 to 73.1% of the COD-Cr value of the untreated water;
- there is a tendency to improve the COD-Cr results obtained, as the pH of the trigger used in the preparation it's getting further from the neutrality value. The best results were obtained in samples P10 (pH trigger = 10), followed by P2 (pH trigger = 2);
- all samples have an TSM value lower than the maximum value allowed by NTPA 002.
- the samples show a decrease of the TSM value from 57.2% to 88.6% of the value of the initial / untreated sample.
- all samples have a much lower ammonum nitrogen concentration than the maximum allowed by law;
- the samples show a decrease in ammonium nitrogen concentration of more than 99.9% compared to the initial, untreated sample;
- samples P1 and P2 have a chloride concentration lower than the maximum permitted value of NTPA 002;
- the chloride concentrations for samples P3 to P10 show an increase of 239 to 308% compared to the initial sample. This may be due to the fact that aqueous $FeCl_3$ solution was used to treat the samples. $FeCl_3$ in aqueous solution dissociates into Fe_3^+ and Cl^- ions. A slight

excess used at the last stage of treatment could lead to inadequate / insufficient removal from the water.

- the sulphate concentrations obtained for samples P2, P7, P8, P9 and P10 show a decrease in the amount of sulphates of 5,2% - P2 to 81,7% - P9 from the value of the initial / untreated sample, the values obtained not being sufficient for be classified below the maximum value allowed by NTPA 002;
- samples P3 to P7 have a higher sulphate concentration than in the original, untreated sample. All these samples were treated at a more acidic trigger pH than the initial water pH. The presence of the SO_4^{2-} ion is due to the use of H_2SO_4 to regulate the pH of the water in different treatment steps.

5.3. ORIGINAL CONTRIBUTIONS

Below are a series of elements of originality found in the paper:

1) a new adsorbent material was prepared consisting of a cellulosic matrix, functionalized with metal oxides of Fe^{2+} and Fe^{3+} (Fe_2O_3, Fe_3O_4), and of Al^{3+} (Al_2O_3) which has applicability in the field of wastewater treatment;
2) it was prepared an adsorbent material with high porosity and a high specific surface area, therefore a high reaction surface, characteristic of important competitiveness for the field of adsorbent materials;
3) the optimal consumption norm of the adsorbent material of 0.25 g / L wastewater (250 g / ton of wastewater) was determined, which classifies the material in the category of highly adsorbent, superior to most similar materials on the market;
4) an optimized test method has been developed for the evaluation of the treated water parameters and the establishment of compliance with the environmental legislation regarding the discharge of wastewater in treatment plants or in the sewerage network corresponding to the localities;
5) the adsorbent material together with some of the contaminants adsorbed from the wastewater, resulting as solid waste, was investigated and characterized morphostructurally and morphochemically showing that the material has a very good adsorption for compounds with Cr, Mg, P, Cl and S, organic compounds such as alkylhexanol, phenol, p-cresol and p-chlorocresol, indole, indolol, indolone, benzenes and alkylbenzenes, alkanes, dihydroxybiphenyl;
6) the adsorbent performances of the new material in wastewater treatment were determined, in terms of pH, CBO5, CCO-Cr, MTS and ammonium nitrogen values, the results being very good, in accordance with NTPA 002 regulations;
7) the adsorbent performance of the new material in wastewater treatment was determined, in terms of chloride concentration values, where the classification in the values allowed by NTPA 002 was only partially achieved, in the case of sulphates where, although the decrease in concentration compared to the initial sample up to 81.7%, a concentration in the values allowed by NTPA 002 could not be reached;
8) the optimal trigger pH for the new material was highlighted as having the value in the range 2 ÷ 3, but also the fact that the adsorbent performance has a tendency to improve when the trigger pH used in the preparation it's getting further from the neutrality value;
9) the adsorbent material obtained and the proposed test method can be implemented and used in the technological flows of wastewater treatment;
10) the research results were published in three ISI - listed journals (Materiale Plastice and the UPB Scientific Bulletin) and one international conference (APMAS - International Advances in Applied Physics & Materials Science Congress & Exhibition).

5.4. PERSPECTIVES FOR FURTHER DEVELOPMENT

The field of industrial wastewater treatment using composite, adsorbent, nanostructured or intelligent materials shows an upward trend in development. This is due both to the continuous development of industries and the increase in requirements under environmental legislation. The field attracts both researchers who have the opportunity to integrate new technologies applicable to the field, and investors who observe a continuous and profitable development of this field.

In the context of the paper, both the material developed, the test methods and the field of applicability present prospects for improvement.

The nanostructured adsorbent material functionalized with metal oxides, can be improved with a series of other nanoparticles that have adsorbent characteristics for a much wider range of pollutants present in industrial waters. Also, wastewater from other technological flows can be tested, and the results can be quantified for the specific pollutants present in these waters.

In the context of applicability in other fields, considering the results obtained in the studies performed in the paper as well as in the studies performed separately, the material has potential for development and use in the field of chemical decontamination of toxic substances of military interest.

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