THE pH INFLUENCE IN THE PROCESS OF INDUSTRIAL WASTEWATER TREATMENT

Raluca Elena GINGHINĂ[1], Dionezie BOJIN[2], Florin MICULESCU[2], Petrișor ZAMORA IORDACHE[1], Tudor Viorel ȚIGĂNESCU[3], Iulian ANTONIAC[2]

The study proposes a treatment process for the wastewater resulting from the technological processing of the skin (leather industry) using a new developed adsorbent material embedded with metal oxide nanoparticles. The paper focused on the influence of the pH in this process and the optimal value of the pH for triggering the mechanism of interaction between material and pollutants. The measured parameters in the water samples resulting after treatment include the chemical oxygen demand, biochemical oxygen demand, total suspended solids, ammonium nitrogen, chlorides, sulphates, organic compounds extractable in organic solvents and the solid residue adsorbed by the material.

Keywords: pH trigger, wastewater, composite material

1. Introduction

Most human activities that use water produce wastewater. As global water demand increases, the amount of wastewater produced and the global pollution load are steadily increasing worldwide. Over 80% of the world's wastewater and over 95%, in some least developed countries, is released into the environment without treatment [1]. The water treatment market remains a fragmented but highly competitive industrial sector. This is due to the number of competing technologies, both advanced and traditional, as well as the many components that may be needed to create any other system. The discharge without discernment in the water bodies, of the untreated effluents from the industries, represents a serious threat to the environment and to the health of the people. With the rapid growth of industrialization in developing countries, governments have adequately regulated wastewater management. The enterprises that have as object of activity

[1] Sci. Res. 3th grade, Scientific Research Center for CBRN Defense and Ecology, Bucharest, e-mail: ginghinaraluca@gmail.com
[2] Prof., University POLITEHNICA of Bucharest, e-mail: d.bojin@gmail.com
[2] Prof., University POLITEHNICA of Bucharest, e-mail: florin.miculescu@gmail.com
[3] Prof., Military Equipment and Technologies Research Agency, Clinceni, e-mail: tiganescu.viorel.t@gmail.com
[1] Sci. Res. 3th grade, Scientific Research Center for CBRN Defense and Ecology, Bucharest, e-mail: iordachezamora1978@gmail.com
[2] Prof., University POLITEHNICA of Bucharest, e-mail: antoniac.iulian@gmail.com

the management of the industrial wastewater, assist the industries - big consumers of water, such as the cement, the agricultural processing, the mining, the leather, the textiles and the electricity for the treatment of the effluents before the discharge [2].

The present paper proposes a treatment process for the wastewater resulting from the technological processing of the skin (leather and footwear industry) using an adsorbent material embedded with metal oxide nanoparticles, presented in a previews study. The paper focuses on the influence of the pH in this process and the optimal value of the pH for triggering the mechanism of interaction between material and pollutants.

2. Experimental part

2.1. Characterization of the wastewater used for tests

The skin tanning stage uses chemicals to transform the raw material into the finished product, which is why the leather industry is a major producer of high toxicity and environmentally hazardous pollutants. Studies show that one metric ton of raw material is transformed into only 200 kg of usable products, which contains 3 kg of chromium. In the resulting amount of waste, there are approximately 250 kg of untanned solid waste, 200 kg of tanned wastes, containing 3 kg of chromium and 50,000 kg of wastewater effluents, containing 5 kg of chromium. In other words, one metric ton of raw material is converted into 20% finished product, and solid and liquid waste represent more than 60%. [3,4].

The pre-tanning process results the pH variation and increased the chemical oxygen demand (COD), total solids dissolved, concentration of chlorides and sulphates in the wastewater. The conventional process of coating with sodium sulphate and calcium oxide is responsible for 84% of the biochemical oxygen demand (BOD), 75% of the COD and 92% of the suspended solids from a tanner. The use of Na sulphate also affects the efficiency of the water treatment plants. The absorption of only 50-70% of the Cr during the chromium tanning leads to both, material losses and the creation of ecological imbalances. The post-tanning process also leads to changes of total solids dissolved, COD and heavy metal quantity [5].

A batch of water from the technological processing of the skin (leather and footwear industry) was used for testing. The water presents as a dark grey colour, turbid and with a strong sulphur odour. The batch was investigated for the following parameters: extractable organic substances with organic solvents investigated by GC/MS, biochemical oxygen demand in water - BOD_5, chemical oxygen demand COD-Cr, total suspended materials - TSM, ammonium nitrogen, chlorides, sulphates.

The initial batch of wastewater showed a composition with high concentration of organic compounds from phenol, benzene, phthalates, alkanes classes, a value of 916 mg/L BOD_5 (3 times higher than the maximum admissible concentration of 300 mg/L), 2138 mg/L COD-Cr (4 times higher than the maximum admissible concentration of 500 mg/L), 646 mg/L ammonium nitrogen (21 times higher than the maximum admissible concentration of 30 mg/L), 600 mg chlorides (500 mg the maximum admissible concentration), 3612 mg/L (6 times higher than the maximum admissible concentration) and 167 mg/L TSM.

2.2. Wastewater treatment procedure

The proposed method consists of testing the efficiency of removal of pollutants from the water batch, using a new adsorbent material based on a cellulose matrix embedded with metal oxide nanoparticles. The purpose of the tests is to establish the pH trigger, defined as the optimal value of the pH for triggering the mechanism of interaction between material and pollutants. For this, were performed ten tests, where the pH trigger varied between values 2 to 10. All the tests were performed on the same batch of wastewater resulted from the technological processing of the skin (sample 0), in the same conditions and using same steps. In first step, where the adsorbent material was added into the wastewater, the pH trigger was set from 2 to 10, differently for each case study, in order to establish the optimal one. Each value generates changes in the following steps of the treatment process, and finally different values for the evaluating parameters. The parameters measured for the initial batch are presented comparative with the results from the case studies in Results and discussions chapter.

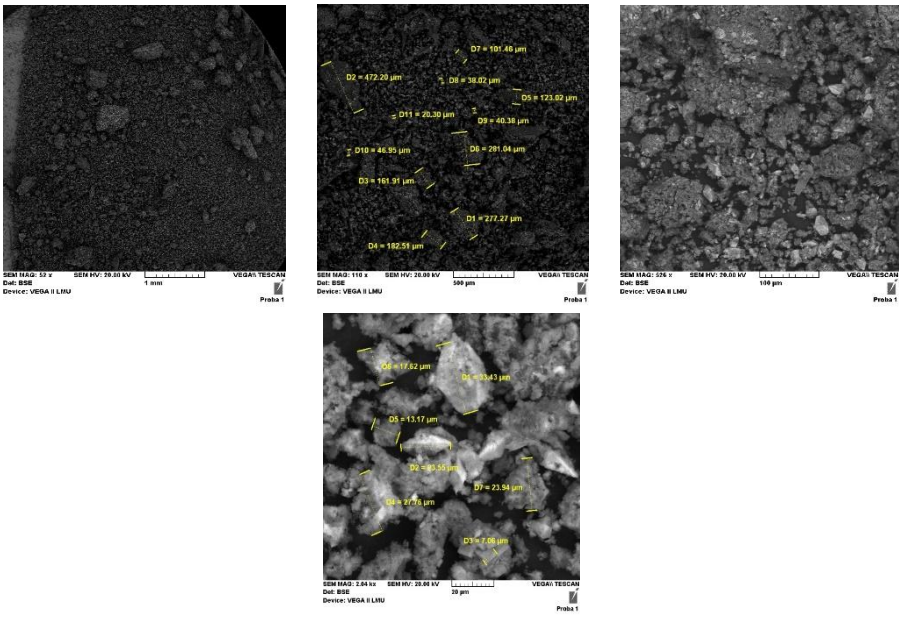
Into a batch of 1 L of wastewater were added 0.25 g of adsorbent material embedded with metal oxide nanoparticles. To reach the pH of 2 to 7, H_2SO_4 98% was used, and for the pH of 8 to 10, CaO 2.2%. After establishing the pH trigger value, H_2O_2 30% was added with a mass ration of 5:2, considering the amount of H_2SO_4 or CaO added in the previews step [6]. With a solution of CaO and NaOH in a mass ration 5:2, the water pH was adjusted to neutral and was slowly stirred for 30 minutes. The mixture was gravitationally filtered and the solid resulted was investigated by SEM/EDS. The water phase was treated with H_2CO_3 and $FeCl_3$, adjusted to a neutral pH and filtered again [7]. $AlCl_3$ was added for clarifying the water, and then filtered in the gravitational field on several filter papers with fine porosity [8,9]. The water resulted was characterised for the same parameters as the original batch.

3. Results and discussions

3.1. SEM investigations

The solid phase resulted after first filtration step was analyzed. The investigations were carried out on a Tescan Vega II LMU SEM equipped with a Bruker Quantax EDS microanalysis system containing the XFlash energy dispersive X-ray detector that works according to the principle of the silicon drift detector and on a Philips XL30 ESEM equipped with an X-ray scattering microanalysis unit (EDAX).

Both morphological and microanalysis studies were performed at an acceleration voltage of 20 keV. Scans were performed on 4 micro-surfaces at 25x/50x, 100x, 500x and 2kx magnifications. In the present paper are presented the three from ten samples investigated by SEM/EDS, choosing one from each pH domain as following: Sample 2 for the acidic domain, Sample 7 for the neutral and Sample 10 for the basic one. The analysis of the solid resulted from the Sample 2 (pH trigger = 2) (Figs. 1-4), Sample 7 (pH trigger = 7) (Figs. 5-8), and Sample 10 (pH trigger = 10) (Figs. 9-12) are presented.



a. b. c. d.

Fig. 1. The morphological structure of the solid residue at different magnifications (sample 2)

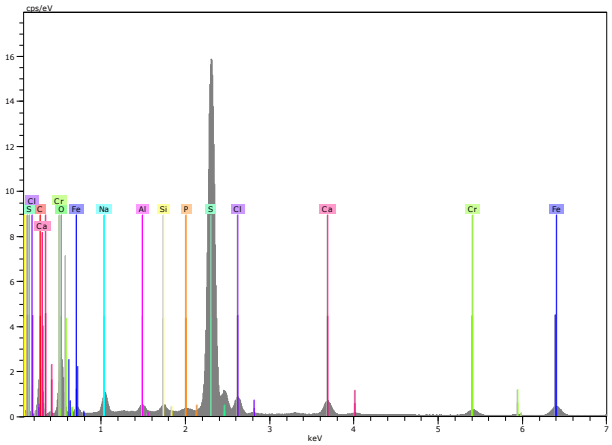
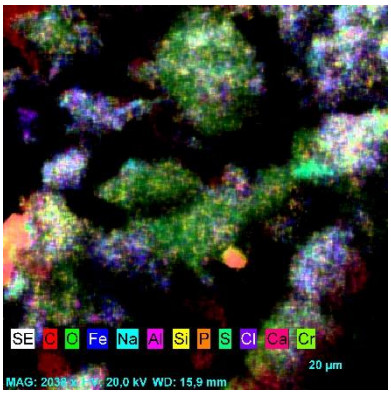


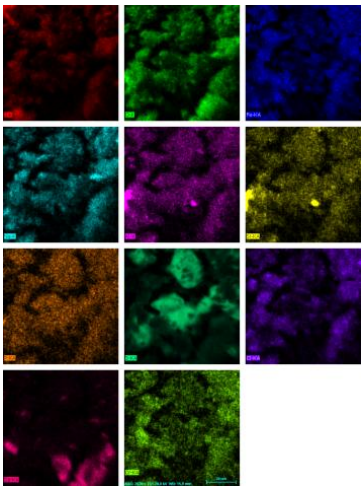
Fig. 2. X-ray emission spectrum of the sample 2

Element	Wt.%
C	17.30
O	39.80
Na	3.70
Mg	0.10
Al	0.60
Si	0.40
P	0.50
S	24.30
Cl	2.80
Ca	2.20
Cr	2.40
Fe	5.90
Total	100

Fig. 3. The chemical elements and their concentration in the sample 2

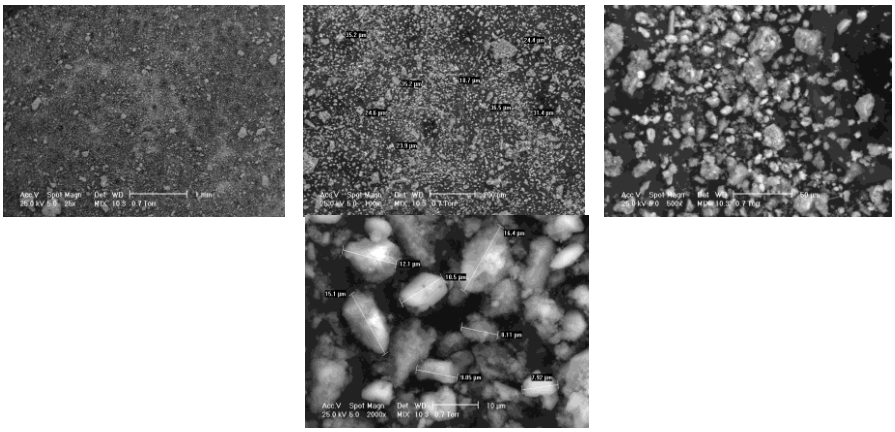


a.



b.

Fig. 4. Distribution of chemical elements on the analyzed surfaces (sample 2)



a. b. c. d.

Fig. 5. The morphological structure of the solid residue at different magnifications (sample 7)

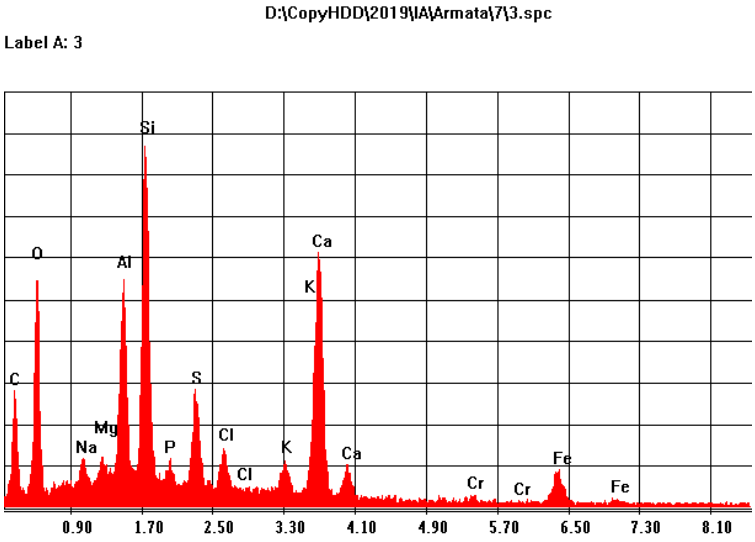
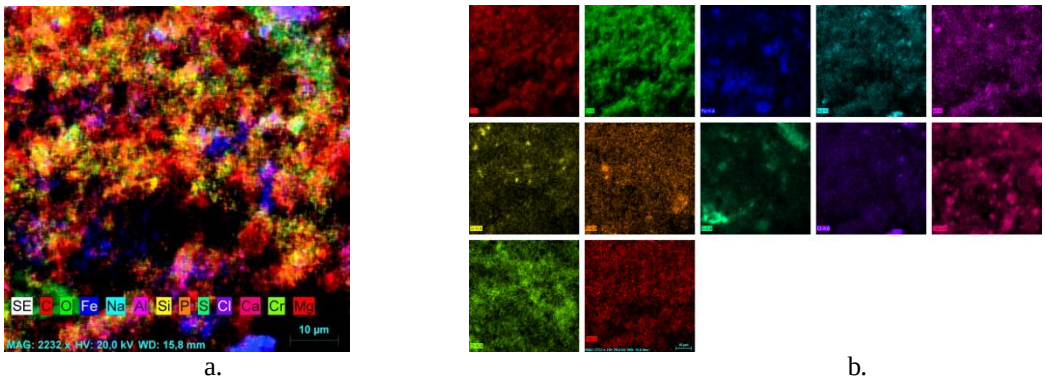


Fig. 6. X-ray emission spectrum of the sample 7

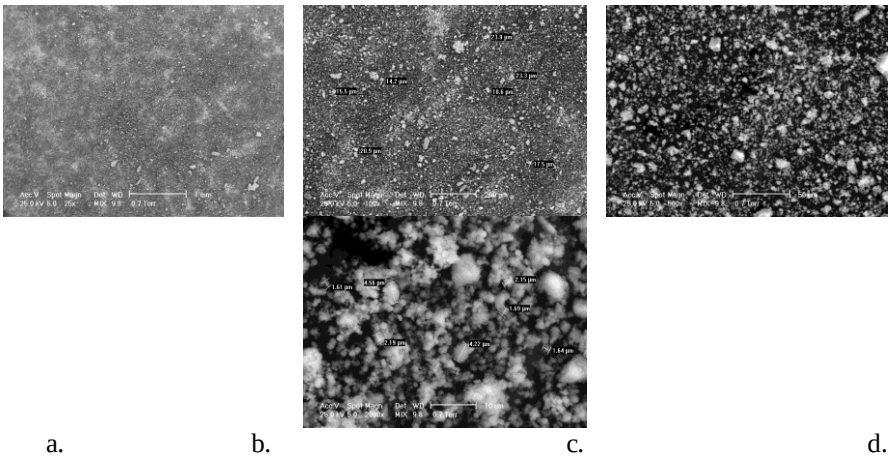
Element	Wt %
C	0.44
O	56.83
Na	3.61
Mg	2.46
Al	7.6
Si	9.63
P	1.36
S	3.29
Cl	1.56
K	1.19
Ca	8.92
Cr	0.37
Fe	2.74
Total	100

Fig. 7. The chemical elements and their concentration in the sample 7



a. b.

Fig. 8. Distribution of chemical elements on the analyzed surfaces (sample 7)



a. b. c. d.

Fig. 9. The morphological structure of the solid residue at different magnifications (sample 10)

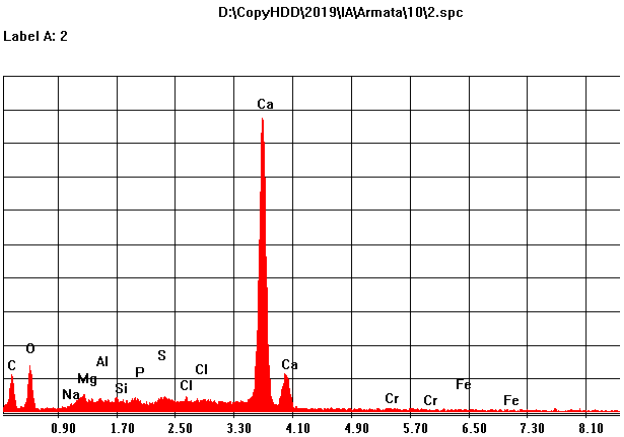
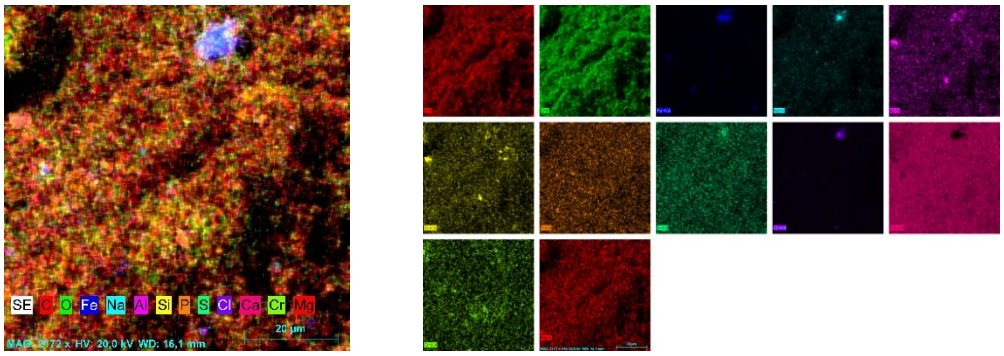


Fig. 10. X-ray emission spectrum of the sample 10

Element	Wt %
C	0.28
O	57.03
Na	1.7
Mg	2.84
Al	1.4
Si	0.96
P	1.06
S	1.26
Cl	1.21
Ca	31.55
Cr	0.36
Fe	0.35
Total	100

Fig. 11. The chemical elements and their concentration in the sample 10

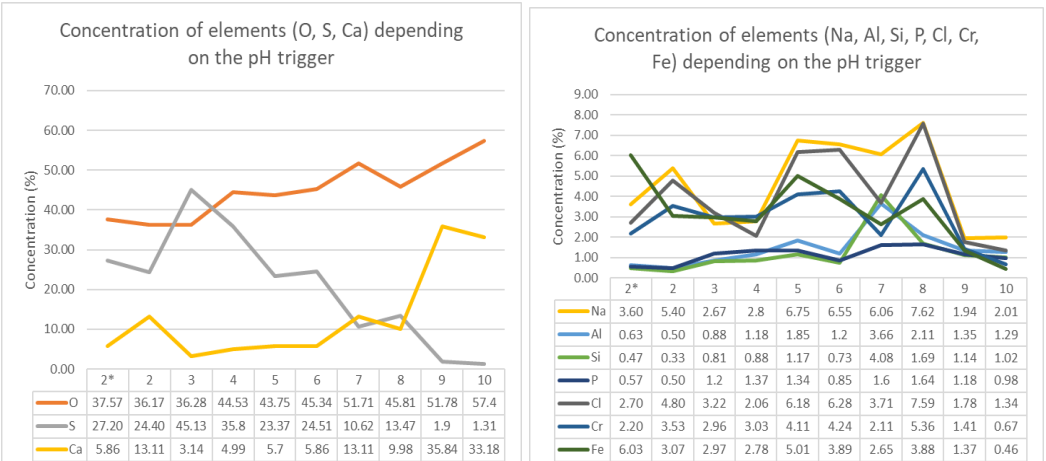


a. b.

Fig. 12. Distribution of chemical elements on the analyzed surfaces (sample 10)

The EDS data showed a chemical composition of O, Na, Al, Si, P, S, Mg, Cl, Ca, Cr, Fe. Fig. 13 shows in diagrams the concentration of the elements in all 10 samples.

Al, Fe, S, O, Na are elements present also in the structure of the adsorbent material used in the treatment. Cr, Cl, Si, Mg come entirely from the composition of the wastewater, also, variable concentrations of the other elements may come from the wastewater. The percentage of the oxygen increases with the pH. This may lead to a partial conclusion that the amount of oxides eliminated from the wastewater increased with the pH, considering that the chemical introduced in the process of treatment doesn't have a high variation.



	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

	2*	2	3	4	5	6	7	8	9	10
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

Fig. 13. The concentration of the elements from the solid resulted after first filtration
2* - First test was carried out on pH trigger = 2, but the quantity of the adsorbent material was higher.

3.2. GC-MS investigations

GC-MS investigations were performed on a GC Thermo Scientific Trace 1310 gas chromatograph coupled with TSQ 9000 triplequadrupol mass spectrometer (MS/MS) using a TR5MS capillary column (5% phenyl 95% dimethylpolysiloxane). The injection mode used was splitless, with 250°C the injector temperature and helium as carrier gas (1.5 mL / min). The temperature program starts from 40°C up to 300°C, with a rate of 10°C / minute. Electron impact ionization (EI) mode (mass range between 40 and 650 amu) was used. The compounds were identified based on the interpretation of MS / EI fragmentation.

GC-MS analysis showed the presence of 25 organic compounds extractable from wastewater by dichloromethane, being seen in concentrations between 8.3 ppm and 0 ppm. Compounds as phenol, indole, cresols showed good results in the treated samples compared with the original batch. The batches prepared at neutral pH trigger showed a higher concentration of organic compound, but improved results were seen in the samples where the pH is farther from the value of 7 (both acid and basic pH).

3.3. COD-Cr and BOD_5 investigations

COD investigations were performed using $K_2Cr_2O_7$ method at 100°C, in accordance with SR ISO 6060:1996 and the BOD_5 in accordance with SR EN 1899 - 1/2003.

Fig. 14 shows the variation of the COD-Cr and BOD_5 with the value of the pH trigger. The diagrams show in some samples a decree of about 91.7% for BOD_5 considering a measurement uncertainty of 19,4% and of 91,9% for COD-Cr considering a measurement uncertainty of 7%. In most of the cases the COD-Cr and BOD_5 are below the maximum admissible concentration of 500 mg/L for COD-Cr and 300 mg/L for BOD_5.

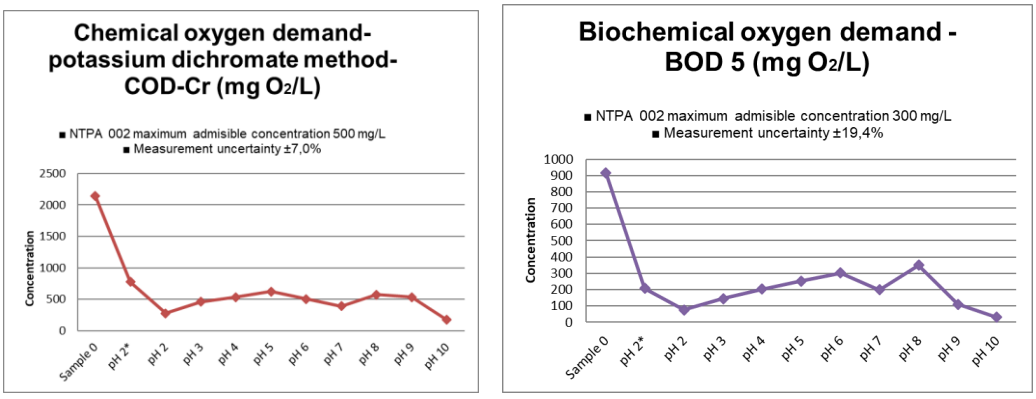


Fig. 14. COD-Cr and BOD_5 variation with the pH trigger compared with the original batch (Sample 0)

3.4. Sulfates and chlorides investigations

Sulfates determinations were performed using Kit Merck 1.4791.0001 and the chlorides were measured with $AgNO_3$ titration method using chromate as indicator, in accordance with SR ISO 9297/2001.

The concentration of sulphates and chlorides present in the treated water samples showed in some cases a slightly decrease, but not enough to reach a value under the maximum admissible value. The results conclude that their presence might belong to the treatment process.

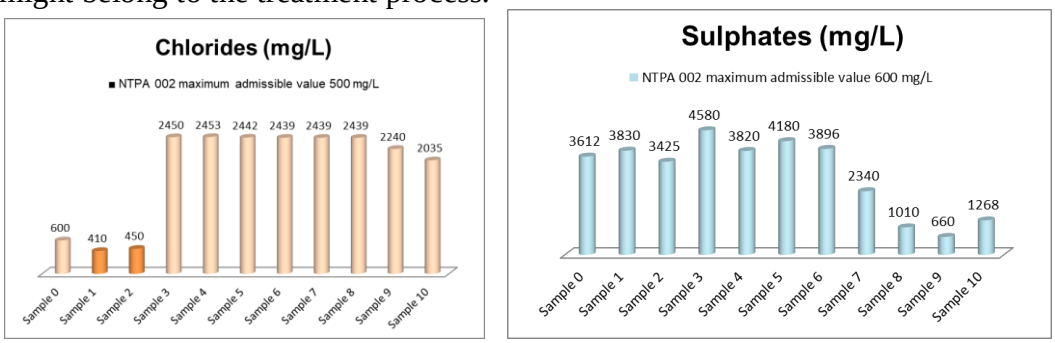


Fig. 15. The concentration of sulphates and chlorides present in the treated water samples

3.5. TSM and ammonium nitrogen investigations

TSM were measured in acordance with SR EN 872:2005 and ammonium nitrogen was measured using kit Merck 1.4752.0001. The TSM value obtains in treated water sample showed a decrease of a maximum of 88.6% compared with the original water. All the samples presented TSM values lower that the maximum admissible value of 350 mg/L. Ammonium nitrogen presents a decrease of 99.9% compared with original batch.

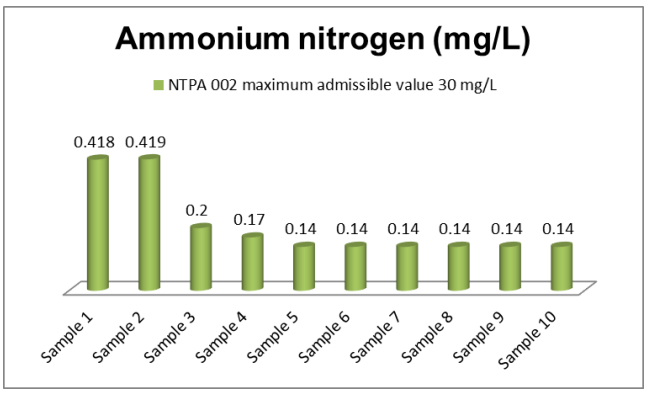


Fig. 16. Ammonium nitrogen variation in water samples

4. Conclusions

The values of the parameters COD-Cr and BOD_5, TSM and ammonium nitrogen fall largely or entirely within the values allowed by the environmental legislation. In the case of chlorides, where the framing is made only partially and in the case of sulphates where, although the decrease of the concentration compared to the initial sample was up to 81.7%, a concentration under the values allowed by NTPA 002 could not be reached.

From the present results it is observed that a pH trigger value farther from the neutral value gives a better result in all the measured parameters. At the same time, the acidic values showed better results than the basic ones. The treatment method allows further improvement and development.

R E F E R E N C E S

[1] https://www.watertechonline.com/tech-market-unesco-report/;
[2] http://www.infodev.org/sites/default/files/innovations_for_scaling_green_sectors_-_infodev_-_climate_ technology_program_-_2017_-_web.pdf;
[3]. International Trade Centre, http://www.intracen.org/itc/sectors/leather;
[4] *S. Hüffer, T. Taeger* Sustainable leather manufacturing: a topic with growing importance. J. Am. Leather Chem. Assoc. **99**(10), 424–428, 2004;
[5] *N.M. Sivaram, D. Barik*, Toxic waste from leather industries, Energy from Toxic Organic Waste for Heat and Power Generation, Pages 55-67, 2019;
[6] *I. Gulkaya, G. Surucu, F. Dilek*, Importance of H_2O_2/Fe^{2+} ratio in Fenton's treatment of a carpet dyeing wastewater. Journal of Hazardous Materials, **136** (3), 763–769, 2006.
[7] *Q. Dong, W. Parker, M. Dagnew*, Impact of $FeCl_3$ dosing on AnMBR treatment of municipal wastewater. Water Research, **80**, 281–293, 2015;
[8] *R.E. Ginghina, D. Bojin, T.V. Tigănescu, N. Petrea, D.E. Mosteanu*, Research on the Efficiency of Testing a New Adsorbent Material with Cellulose Structure for the Depollution of Waste Water, Mater. Plast. **57(1)**, p. 306 – 315, 2020.
[9] *L. Zhang, J. Mao, Q. Zhao, S. He, J. Ma*, Effect of $AlCl_3$ concentration on nanoparticle removal by coagulation. Journal of Environmental Sciences, **38**, 103–109, 2015.