Biodegradability and Adaptability Studies of Geothermal Wastewater in a Biological Treatment Plant

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The purpose of this study was to identify the optimal conditions for the operation of biological treatment plant by carrying out biodegradability tests for geothermal wastewaters with high salt content. The biodegradation tests for geothermal wastewaters were carried out in a discontinuous flow bioreactor. The phases of the biodegradation process were: adaptation of the biological sludge, control of the biological treatment process, experiments in the laboratory bioreactors (BATCH). The results of the biodegradability tests revealed that geothermal waters with high salt content influence the treatment process. The dilution of these waters with domestic water up to chlorine concentrations below 800 mg L^{-1}, makes the purification process to have a good biodegradation yields for CCO-Cr (about 75%) and CBO-5 (about 72%). If these geothermal wastewaters are not diluted to concentrations lower than 800 mg L^{-1}, the biological sludge after 6 days is mineralized, which makes the use of biological treatment plant to be impossible.

Keywords: geothermal waters, biodegradation, wastewater, mineral salts

The need for tests for biodegradability arose from the large-scale use of synthetic surfactants, or surface-active agents, soon after the Second World War. Bioremediation is an attractive alternative that has been used to eliminate or minimize the effects of pollutants, employing microorganisms with potential for biodegradation and being able to transform contaminants into less toxic substances or mineralizing them [1, 2]. For the success of bioremediation technologies, the occurrence of microorganisms with the appropriate metabolic abilities is the most important requisite on pollutants-bioremediation [3-5]. Bioreactors have played an important role in the detoxification of hazardous pollutants and have been successfully applied in ex-situ bioremediation strategies [6]. Bioreactors are basically tanks in which living organisms carry out biological reactions [7-9]. These types systems display as main advantage a larger control of environmental and physico-chemical conditions affecting rates and extents of microbial growth and oil transformation such as oxygen supply, optimal pH, temperature and specific quantity nutrient providing an increase on biodegradation [7]. On the other hand, in environments where the ex-situ bioremediation can hardly be used, bioreactors can be also efficiently applied to provide the biostimulation of autochthonous microorganisms growing in the presence of oil for subsequent reintroduction in the affected environment as strategy of bioremediation of polluted [10].

The use of geothermal water plays an important role for enviromental and for the economy due to its therapeutic properties and the possibility of its use in heating the population [11 – 14]. The existence of important thermal water deposits in the north-west part of Romania facilitates the use of this energy form on the local area, for different purposes, ensuring the saving of a quantity of conventional fuels [15 -17].

The geothermal waters from Calimanesti county is procured from 3 springs, from a depth of about 3000 meters. The temperature of these geothermal waters ranges between 90 and 97°C. The physico–chemical and geothermal properties of geothermal waters create a series of problems for urban wastewater treatment plants.

The technical problems faced by the urban wastewater treatment plant are due to the high content of mineral salts (chlorides, sodium, etc.) of these geothermal waters [18-25].

In this study, the biodegradation tests have been carried out for geothermal wastewaters with high salt content, in order to identify optimal solutions for the operation of the treatment plants that contain this geothermal water.

Experimental part
Materials and methods
Reagents

Reagents used were of recognized analytical quality (Merck, Fluka, etc.) which were used as such. Distilled water was used for quality 2 according to ISO 3696. Determination of quality indicators was done according to standards water in force specific to each indicator analyzed.

Aparatus and methods

Experimental studies on the physico-chemical characterization of the studied samples were performed by electrochemical methods using a Multiparameter Orion Star A 215 and a Oxygenometer HANNA (for pH, CBO5, and Dissolved oxygen concentration); by volumetric methods using calibrated biurettes (for chlorides and CCO-Cr); by gravimetric methods using a analytical balance Precision XB 220 (for filterable residue and suspensions). All methods used were standardized methods and are in accordance with current legislation.

Biodegradability experiments were carried out in two laboratory bioreactors. The microscopic analysis of inoculation sludge was performed with a NID-3479 laboratory microscope.

Results and discussions

The experimental studies for biodegradation of geothermal wastewater were conducted in discontinuous laboratory bioreactors.

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For the adaptation studies of sludge was used biological sludge, which was harvested from the recirculation system of the Râmnicu Valcea City wastewater treatment plant. The microscopic analysis of the biological inoculation sludge revealed a well-structured biocoenosis with a diversified microfauna, represented by free ciliate (Aspidisca, Euphlotes) and fixed (Vorticella and Opercularia), which indicates a good purification. The active sludge also represented good characteristics for sedimentation around 100cm^3 / g (table 1).

Control of the biological treatment process in laboratory bioreactors, was carried out by checking the influent/effluent at every new feed and by determining the following indicators: pH, organic load expressed by CCO-Cr and CBO-5, inorganic load expressed by chlorides, sodium and filterable residue.

For biomass from bioreactors, where biodegradation experiments were performed, were determined periodically pH, concentration of biological sludge, sludge index, dissolved O2 concentration, and also daily was monitored at microscope the biocenos of the active sludge.

Because the geothermal wastewater, used to feed laboratory bioreactors, contains large amounts of mineral salts, for the experiments was used dilute geothermal wastewater in a favorable ratio for the development of the bacterial population in good conditions.

In parallel were used two laboratory bioreactors for biodegradability studies. The feed water from the first bioreactor contain geothermal wastewater and domestic water, and feed water for the second bioreactor was composed of the domestic water with contain of geotermal wastewater, from the biological treatment plant and domestic water.

For the initial tests, for first laboratory bioreactor was used geothermal wastewater and domestic water in the ratio of 1:3 for 3 days and 1:2 for another 3 days. For the second bioreactor was used domestic water with geothermal water content, undiluted. At the beginning of its adaptation, the biological sludge from both bioreactors had good sedimentation properties (IVN = 114.3 cm^3/ g for the first bioreactor and IVN = 92.1 cm^3/ g for the second bioreactor) (table 1).

Initially, the first bioreactor was fed with geothermal wastewater and domestic water in a ratio of 1:3 for 3 days, then fed with geothermal wastewater and domestic water in a ratio of 1:2 for another 3 days. After 6 days adaptation of the sludge with geothermal wastewater diluted with domestic water, it was observed that the sludge was mineralized. The volume indice of the sludge were 34.7 cm^3/ g for the first bioreactor (table 1).

The second laboratory bioreactor was fed for 6 days with domestic water containing geothermal water from the municipal wastewater treatment plant without dilution. After the 6 days adaptation of the sludge with domestic water containing geothermal water it was observed that the sludge was mineralized. The volume indice of the sludge were 45.0 cm^3/g (table 1).

Thus, for the two types of geothermal water studied, after about 6 days of adaptation of the sludge to the studied waters, it was observed that the sludge was mineralized. The volume index of the sludge has reached values less than 50 cm^3/g (table 2).

In table 2 the optimum values for the sludge volume index (Mohlman Index) are displayed.

For the subsequent tests, in the first bioreactor was used, geothermal wastewater and domestic water in the ratio of 1:10, and for the second bioreactor, was used domestic water with geothermal water content in the ratio of 1: 2.5. Adaptation of the sludge was performed for 7 days, during which time the influent and the effluent of the bioreactors were analyzed.

QUALITY INDICATORS		U.M.	DETERMINED VALUES			
Date of sampling			06.04. 2017	9.04. 2017	10.04. 2017	11.04. 2017
Name of samples			295RV	301RV	305RV	317RV
First laboratory bioreactor, the initial test	pH	unit. pH	6.4	5.4	5.7	5.6
	Sludge concentration	g/L	3.9	8.0	8.9	8.6
	Dissolved oxygen concentration	mg/L	6.4	7.0	6.9	6.9
	Volume index (IVN) or Mohlman index	cm^3/g	114.3	56.9	38.8	34.7
Name of samples			296RV	302RV	306RV	318RV
Second laboratory bioreactor, the initial test	pH	unit. pH	6.6	6.51	6.69	6.77
	Sludge concentration	g/L	6.4	7.6	8.4	8.5
	Dissolved oxygen concentration	mg/L	5.4	5.5	5.6	5.8
	Volume index (I$_{VN}$) or Mohlman index	cm^3/g	92.1	47.3	45.0	45.0

Table 1
QUALITY INDICATORS ANALYZED FOR BIOLOGICAL SLUDGE SAMPLES FROM THE TWO LABORATORY BIOREACTORS USED FOR THE INITIAL TESTS

The quality of the sludge	Sludge volume index values or "Mohlman Index", I$_{VN}$ (cm^3 / g)
sludge with low sedimentation properties ("swollen" sludge)	≥ 120
good sludge	≤ 80
sludge very good	>50
sludge mineralized	≤50

Table 2
THE OPTIMUM VALUES FOR THE SLUDGE VOLUME INDEX (*MOHLMAN INDEX*)

On the 7th day, after the two bioreactors were fed with the samples studied, water samples were taken from them at 5 min, 1, 3, 6 and 24 h and were characterized physico-chemical (table 3). On the eighth day, water samples were taken again at the same time as the 7th day.

For both bioreactors the organic load expressed by CCO-Cr and CBO5 was followed. Values for CCO-Cr were between 19.2 mgO$_2$/L and 76.8 mgO$_2$/L for the first bioreactor and between 19.2 and 67.2 mgO$_2$/L for the second bioreactor. And for CBO5 the values were between 6.0 and 21.5 mgO$_2$/L for the first bioreactor and between 6.0 and 17.5 mgO$_2$/L for the second bioreactor (table 3).

Also, for both bioreactors the inorganic loading expressed by filtration residue, chlorides and sodium was also followed. Filtrable residue values ranged between 964.0 and 1285.0 mg/L for the first bioreactor and between 700.0 and 865.00 mg/L for the second bioreactor. For chlorides the values were between 453.8 and 467.9 mg/L for the first bioreactor and between 290.7 and 304.9 mg/L for the second bioreactor. And for sodium, its values ranged between 133.6 and 202.5 mg/L for the first bioreactor and between 87.7 and 64.7 mg/L for the second bioreactor (table 3).

At the same time with the analysis of the effluents of the bioreactors, the analysis of the biological sludge samples was carried out by monitoring the pH, the biological sludge concentration, the volume index of the sludge and the dissolved oxygen concentration. Biological sludge from the two laboratory bioreactors had good sedimentation properties at the start of the biodegradability test (volume index of sludge around 75 cm^3/g). After 24 h it was observed that the sludge had sedimentation properties as good as the beginning with a volume index of sludge of about 55 cm^3/ g for both laboratory bioreactors.

So we can say that at 1:10 dilutions for geothermal waste water and 1:2.5 dilutions for domestic water with geothermal water content, the biological sludge was not mineralized and had the sedimentation properties as good as the beginning of the tests.

The biodegradation yields obtained for the two bioreactors are shown in the table 4. The biodegradability yields for the first bioreactor were between 75% for CCO-Cr and 3% for chlorides, and for the second bioreactor were between 66.7% for CCO-Cr and 4.7% for chlorides.

Table 3

THE PHYSICO-CHEMICAL CHARACTERIZED FOR WATER SAMPLES THAT WERE TAKEN FOR BOTH BIOREACTORS AT 5 min, 1h, 3h, 6 AND 24 h IN 7TH DAY AND 8TH DAY. THE BIODEGRADATION YIELDS, FOR QUALITY INDICATORS DETERMINED INITIAL TESTS

QUALITY INDICATORS		U.M.	DETERMINED VALUES					
Date of sampling 25.05.2017, time interval			5 minutes	1 hours	3 hours	6 hours	24 hours	Biodegradation yield
Name of samples			460RV	461RV	462RV	463RV	464RV	
First laboratory bioreactor, BATCH I	pH	unit. pH	6.5	6.9	6.5	6.9	6.9	
	CCO-Cr	mg/ L	76.8	48.0	28.8	28.8	19.2	75.0%
	CBO5	mg/ L	21.5	14.4	8.9	8.6	6.0	72.3%
	Filterable residue	mg/ L	1285.0	1220.0	1175.0	1108.0	964.0	25.0%
	Sodium	mg/ L	202.5	133.6	133.6	133.6	133.6	34.0%
	Chlorides	mg/ L	467.9	467.9	467.9	460.9	453.8	3%
Name of samples			465RV	466RV	467RV	468RV	469RV	Biodegradation yield
Second laboratory bioreactor, BATCH I	pH	unit. pH	6.8	7.1	6.7	7.2	7.0	
	CCO-Cr	mg/ L	48.0	38.4	38.4	28.8	19.2	60,0%
	CBO5	mg/ L	13.0	11.2	11.2	8.6	6.0	54,1%
	Filterable residue	mg/ L	865.0	840.0	820.0	784.0	700.0	19,1 %
	Sodium	mg/ L	87.7	87.7	87.7	87.7	64.7	26,2 %
	Chlorides	mg/ L	304.9	304.9	304.9	297.8	290.7	4,7%
Date of sampling 26.05.2017, time interval			5 minutes	1 hours	3 hours	6 hours	24 hours	Biodegradation yield
Name of samples			470RV	471RV	472RV	473RV	474RV	
First laboratory bioreactor, BATCH II	pH	unit. pH	7.0	7.3	7.4	7.3	7.4	
	CCO-Cr	mg/ L	67.2	48.0	19.2	38.4	19.2	71.4%
	CBO5	mg/ L	17.5	13.4	6.0	11.2	6.0	66.0%
	Filterable residue	mg/ L	1224.0	1136.0	1028.0	1108.0	1028.0	16.0%
	Sodium	mg/ L	218.8	218.8	172.9	209.6	172.9	21.0%
	Chlorides	mg/ L	623.9	609.8	588.5	595.6	588.5	5.7%
Name of samples			475RV	476RV	477RV	478RV	479RV	Biodegradation yield
Second laboratory bioreactor, BATCH II	pH	unit. pH	7.2	7.4	7.5	7.2	7.5	
	CCO-Cr	mg/ L	48.0	48.0	19.2	19.2	16.0	66.7%
	CBO5	mg/ L	12.0	13.4	5.6	5.8	4.8	60.0%
	Filterable residue	mg/ L	744.0	744.0	740.0	688.0	656.0	12.60%
	Sodium	mg/ L	167.7	163.7	163.7	154.5	145.3	13.40%
	Chlorides	mg/ L	404.2	404.2	382.9	382.9	382.9	5.30%

Table 4

THE BIODEGRADATION YIELDS OBTAINED FOR THE TWO BIOREACTORS AFTER THE TWO DAYS OF BIODEGRADATION TESTS (BATCH I AND BATCH II)

Biodegradability test for the first bioreactor			
Quality indicator	Biodegradation yield after 24 hours	Quality indicator	Biodegradation yield after 24 hours
BATCH I (Date of sampling 25.05.2017)		BATCH II (Date of sampling 26.05.2017)	
CCO-Cr	75.0 %;	CCO-Cr	71.4 %
CBO-5	72.3 %	CBO-5	66.0 %
Sodium	34.0 %;	Sodium	21.0 %
Filtrable residue	25.0 %	Filtrable residue	16.0 %
Chloride	3.0 %	Chloride	5.7 %
Biodegradability test for the second bioreactor			
BATCH I (Date of sampling 25.05.2017)		BATCH II (Date of sampling 26.05.2017)	
CCO-Cr	60.00 %;	CCO-Cr	66.70 %
CBO-5	54.1 %	CBO-5	60.00 %
Sodium	26.2 %;	Sodium	13.40 %
Filtrable residue	19.10 %	Filtrable residue	12.60 %
Chloride	4.70 %	Chloride	5.30 %

Table 5

THE LIMIT VALUES ALLOWED BY H.G. 352/2005, ANNEX NO. 3 TABLE NO. 1- (NTPA 001) FOR WASTEWATER

QUALITY INDICATORS	U.M.	H.G. 352/2005 Annex no. 3 Table no. 1- (NTPA 001) Limit values allowed
pH	unit. pH	6.5 – 8.5
CCO-Cr	mg/ L	125
CBO5	mg/ L	25
Filterable residue	mg/ L	2000
Sodium	mg/ L	-
Chlorides	mg/ L	500

From the physico-chemical characterization of the effluents of the laboratory bioreactors (BATCH I and II), it is observed that all the quality indicators analyzed fall within the limits imposed by H.G. 352/2005 (NTPA 001) NTPA001 / 2002 (table 5).

Conclusions

In this study biodegradability tests of geothermal wastewater and domestic water with geothermal water content were carried out. These biodegradability tests were performed to see the biodegradation yields of the samples analyzed and to find the conditions in which the biological treatment plant containing these waters can function without the sludge being mineralized.

From the experimental studies carried out with discontinuous flow laboratory bioreactors, it was observed that the best biodegradation yields (for CCO-Cr about 75% and CBO-5 about 72%) were obtained for 1:10 ratio for geothermal wastewater and domestic water and respectively for the ratio of 1:2.5 for domestic water with geothermal water content and domestic water. It is also noted that the removal rate for chlorides was very low (comprised between 5.7 and 3%), for filterable residue was between 25 and 12.6 %, and for sodium was included between 34 and 13.4%.

The biodegradation yields are influenced by high chlorine concentrations that have a biological sludge mineralization effect. For good sewage treatment, the chlorine concentration should be less than 800 mg/L.

The data obtained from the experimental studies are important for obtaining the necessary technical data for a good function of wastewater treatment plant, which contain domestic water with geothermal water content.

Reference

1.CERQUEIRA, V.S., HOLLENBACH, E.B., MABONI, F., CAMARGO, F.A.O., PERALBA, M.C.R., BENTO, F.M., World J. Microbiol. Biotechnol, 28, 2012, p. 1203-1222.
2.PUIU, D., GALAON, T., CRUCERU, L.V., NICULESCU, M., MIHALACHE, M., PASCU, L.F., POPESCU, M., Rev. Chim.(Bucharest), **68**, no. 8, 2017, p.1740-1743.
3.AL-WASIFY, R.S., HAMED, S.R., Int. J. Bacteriol. 2014, p. 1-8.
4.WOINAROSCHI, A., SINGUREANU, C., Rev. Chim.(Bucharest), **68**, no. 12, 2017, p.2812-2816
5.BUMBAC, C., MANEA, E. E., TIRON, O., BADESCU, V.R., Rev. Chim. (Bucharest), **69**, no. 1, 2018, p.10-13.
6.KUYUKINA, M.S., IVSHINA, I.B., SEREBRENNIKOVA, M.K., KRIVORUTCHKO, A.B., PODOROZHKO, E.A., IVANOV, R.V., LOZINSKY, V.I., Int. Biodeterior. Biodegrad. 63, 2009, p. 427-432.
7.CHIKERE, C.B., CHIKERE, B.O., OKPOKWASILI, G.C., Biotech. 2, 2012, p. 53-66.
8.STEFANESCU, M., NECHIFOR, G., BUMBAC, C., IONESCU, I, TIRON, O., Rev. Chim.(Bucharest), **69**, no. 1, 2018, p.31-33
9.MARIN, N.M., TIRON, O., PASCU, L.F., COSTACHE, M., LAZAR, M. N., BADEA, I. A., Rev. Chim.(Bucharest), **69**, no. 1, 2018, p.38-44
10.MALIJI, D., OLAMA, Z., HOLAIL, H.,. Int. J. Curr. Microbiol. Appl. Sci. 2, 2013, 1-18.
11.ROMOCEA, T., GHERGHELES, C., PANTEAREV. E., Rev. Chim. (Bucharest) **63**, no. 6, 2012, p. 636-640
12.SONG, F.M., KIRK, D.W., GRAYDON, J.W., CORMACK, D.E., Journal of Corrosion Science and Engineering, 3, 2002, p. 24
13.POPA, L., RADULESCU, M., DINU, A., VELCIU, L., BRANZOI, I.,V., Rev. Chim. (Bucharest), **59**, no. 2, 2008, p. 140
14.PATZAY, G., Electrochimica Acta, 43, nr.1-2, 1998, p.137
15.RICHTER, S., HILBERT, L.R., THORARINSDOTTIR, R.I., Corrosion Science, 48, nr. 7, 2006, p.1770
16.VASILESCU, M., VASILESCU, I., Rev. Chim. (Bucharest), **60**, no. 10, 2009, p. 23
17.AFIF, A., IGNATIADIS, I., Proceedings of the World Geothermal Congress, Florence, Italy, 1995, vol 4, p. 2491

18.HALLDOR, A., HREFNA, K., Geothermics, 21, 1992, p. 869
19.POPA, L., RADULESCU, M., DINU, A., VELCIU, L., BRANZOI, I.,V., Rev. Chim. (Bucharest), **59**, no. 2, 2008, p. 140
20.VASILESCU, M., VASILESCU, I., Rev. Chim. (Bucharest), **60**, no. 10, 2009, p. 23
21.SONG, F.M., KIRK, D.W., GRAYDON, J.W., CORMACK, D.E., Journal of Corrosion Science and Engineering, 3, 2002, p. 24
22.RICHTER, S., HILBERT, L.R., THORARINSDOTTIR, R.I., Corrosion Science, 48, nr. 7, 2006, p.1770

23.ADRIAN, L., MANZ, W., SZEWZYK, U., GÖRISCH ,H., Applied and Environmental Microbiology, 64, 1998, p. 496–503
24.ZHANG, H., LU Y., SHIA ,Y., WANG, T., XING, Y., DAWSON, R. W., Environmental Science & Policy, 8, 2005, p. 153-160
25. IORDACHE, M., PAVEL, V. L., MYUNGHEE, L., IORDACHE,? I., Environmental Engineering and Management Journal, 8, no. 2, 2009, p. 201-206