ORIGINAL PAPER

ANALYSIS OF WASTE WATER FROM ECOLOGICAL CAR WASH – A CASE STUDY

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Abstract. *Wastewaters resulted from different stages of washing process from ecological car wash were investigated for its physicochemical parameters and several heavy metals contents. For this purpose 75 samples were collected and analyzed by conductometric, potentiometric techniques and by Flame Atomic Absorption Spectrometry during of November 2010. The results showed that the amount of zinc, copper, cadmium and lead elements in wastewater samples were higher than the Maximum Admitted Level (MAL) values for investigated heavy metals, according to the Order 161/2006, after washing different cars in one week (from Monday to Friday at 14,00). The increase of Pb, Cu, Cd, and Zn concentrations is visible (average weekly collections) and these were higher especially on rainy days when cars came with a load more visible than in the days with good weather. In according with the Order 161/2006, regarding pH tolerance limit, the mean pH values for all collected samples were between 6.00 and 9.00. The temperature ranged between 14.10 - 17.10°C with an average value of 14.91±1.61°C. The highest values for conductivity, turbidity and TDS was found for samples Sp2, Sp5, Sp8, Sp11 and Sp14, before entrance in the first separator.*

Keywords: *heavy metal, FAAS, wastewater, ecological car wash, quality indicator*

1. INTRODUCTION

Anthropogenic activities carried out in civilized societies in order to increase people's comfort, affect the environment more than ever, as well as quality of life.

According to statistics of the Driving Licenses and Vehicle Registration Department, in Romania, it is estimated that until 2012 the auto park will increase with about 60%. The increase of the registered vehicles number will lead to rethinking of the strategies to reduce the pollution in order to protect the environment, through the application of drastic measures [1]. Romania will have to review the environmental legislation, especially the laws relating the polluted emissions from effluents, in accordance with European legislation, as well as

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with the last provisions provided in the Copenhagen Agreement. In this respect, a possible first step will be the moving of classic car washes in the peripheral area of the cities, to reduce the harmful effect of the wastewater resulted after cars were washed with water and detergents. Therefore, the ecological washes without water, called *Waterless Car Wash,* will be such a serious alternative which must take into consideration.

This alternative is called the *Green Alternative* because the *Waterless Car Wash* is 100% ecological, is a new concept to wash, clean, polish and protect by a single operation any surface without using water, detergents or other washing classical and not discharge pollutants into the sewage system as well [1, 2]. Moreover, the used products are non-toxic, biodegradable and environmentally safe. The procedure involves the spraying with an organic solution on the dirty surface and instant dissolving of the dirt by emulsification, and then the obtained emulsion will be removed by wiping with a microfiber towels. Waterless wash solution not scratches (creates a slippery film and contains organic compounds extracted from a Brazilian palm) and not affect the clean surface. This solution protects the car against both of UV radiations and of acid rain for a long time, and gives to the car the shine due to a special ingredient [3-6]. This ingredient is a nontoxic, nonflammable, organic, organic and completely biodegradable, which contains special ingredients, wetting agents, lubricants, special polymers, organic soap, carnauba, surfactants, anti-UV and anti-acid rain agents, in a unique formula in the world. The allocated time for ecological washing for a car by medium size is about 15-20 minutes and the amount of consumed solution is only 100 -150 mL.

Used initially by the U.S. armed forces, this concept was further developed and improved, now being launched and implemented in over 40 countries. Waterless washing or dry cleaning has caused a revolution in the cleaning market in the United States of America, Australia and soon in Europe. In Romania, this waterless car wash project was launched, for the first time, by the *American Freedom International Company* in April 2010.

Until to the appearance of this company, car washes from Romania were divided into two categories [1]: classic, which, surely, will disappeared or will need to move out of cities and to adjust to the new requirements, and obvious the environmental ones, which using biodegradable cleaning products, non-toxic, but using water and steam, in small quantities.

This article aims to analyze the wastewaters resulted from ecological car wash, which are localized in Dambovita County, on the road DN7 Bucharest-Pitesti (Fig. 1). In this area the traffic is intense, and the level of noise pollution and car noxious is quite high due to location.

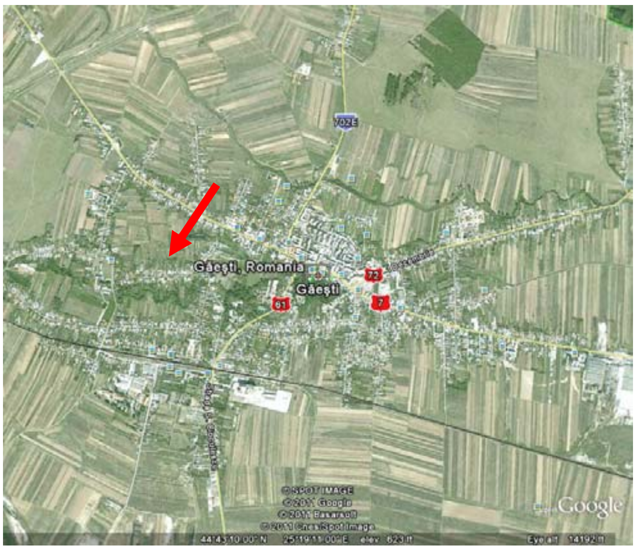

Fig. 1. The location of ecological car washes on the road DN7 Bucharest-Pitesti.

The several heavy metal emissions and other physicochemical parameters, regardless of scale or category, was investigated by the collection of samples from well-established points, considering the treatment process of wastewaters resulted from car washing and climatic conditions, before being discharged into the sewage.

2. EXPERIMENTAL

Samples were collected manually into polyethylene bottles. Prior to use, all bottles were cleaned with 10% HNO_3, rinsed with distilled water to be analyzed. The wastewater samples were collected in November, 2010, three samples per day, from Monday to Friday, for five weeks, a mean of 15 samples per week, in totally 75 samples, at the entrance and exit of the washing process.

2.1. PHYSICOCHEMICAL INDICATORS

The pH was performed with a pH meter Consort P501. Determination of wastewater parameters (electrical conductivity, salinity and total dissolved solid) was achieved by using a portable HACH CO150 Conductivity - conductometric cell with platinum electrodes. Conductivity /TDS meter was calibrated with 0.001M KCl to give a value of 14.7µS/m at 25ºC. Turbidity was performed with a Turb-550 apparatus, in accordance with SR EN ISO 7027:2001. The samples were thoroughly rinsed with distilled water after each measurement. Levels of turbidity and total suspended solid of the wastewater samples were determined using standard procedures.

2.2. *CHEMICALS AND STANDARD MATERIALS*

All chemicals used in this study were analytical grade reagents. Chemicals include nitric acid (65% Aldrich), hydrochloric acid (37% Fluka) in part 1:3 (aqua regia). Distilled deionised water had a rezistivity better than 17.5MΩcm.

In order to perform the metal calibration curve, certified reference materials (CRMs) were used for Zn, Cu, Cd and Pb with a certificate of analysis and NIST traceability (e.g. zinc standard solution (Merck) traceable to SRM from NIST $Zn(NO_3)_2$ in HNO_3 0.5 mol/L; copper standard solution (Merck) traceable to SRM from NIST $Cu(NO_3)_2$ in HNO_3 0.5 mol/L; cadmium ctandard colution (Merck) traceable to SRM from NIST $Cd(NO_3)_3$ in HNO_3 0.5 mol/L and lead standard solution (Merck) traceable to SRM from NIST $Pb(NO_3)_2$ in HNO_3 0.5 mol/L). The standard solutions were prepared in aqueous solution containing 2% of HNO_3.

2.3. MICROWAVE ASSISTED DIGESTION

Samples are digested in aqua regia using a Berghof MWS-2 microwave assisted digestion apparatus. The Teflon digestion vessels used in this procedure are reusable and the clean-up step is relatively easy and less time consuming. The samples (15 mL) are introduced into the digestion vessels and then 2.5 mL nitric acid and 7.5 mL hydrochloric acid are added. Before the vessels are closed we wait 20 min. The program of digestion was chosen. After digestion time (40 min) the vessels was cooled at room temperature (about 30 min.). The clear solution volume is made up to 25 mL for each sample.

2.4. FLAME ATOMIC ABSORPTION SPECTROMETRY

The Flame Atomic Absorption Spectrometry (FAAS) technique is one of the most commonly used analytical method for determining the concentrations of heavy metals in polluted samples. This technique was sensitive, fast, accurate, and less expensive offering a good sensibility [7]. The possibility of atomic absorption spectrometry utilization in view of determination of pollution agents becomes more and more important in the protection of environment and health, taking into account the cumulative effects of some metallic ions.

The elemental content of samples was determined by Flame Atomic Absorption Spectrometer, equipped with an AVANTA GBC flame and hollow cathode lamps (HCL). The technique of flame atomic absorption spectroscopy (FAAS) requires a liquid sample to be aspirated, aerosolized, and mixed with gas flow into a nebulizing/mixing chamber to form small droplets before entering the flame. The mixture is ignited in a flame whose temperature ranges from 2100 to 2800^{o}C. This technique is based on the fact that ground state metals absorb light at specific wavelengths. Metal ions in a solution are converted to atomic state by means of a flame. Light of the appropriate wavelength is supplied and the amount of light absorbed can be measured against a standard curve [8-11]. Determination of elemental concentrations in samples was performed using the method of calibration curve according to the absorber concentration. Several solutions of different known concentrations have been prepared and the elemental concentration in unknown sample was determined by extrapolation from the calibration curve. The measured levels for water were compared with the admitted levels according to the Romanian legislation (MAPPM Ord. 161/2006).

The relative standard deviations was in the range of 1- 8% (N = 5), with recoveries greater than 95%.

3. RESULTS AND DISCUSSION

The technological automatic wash process is conducted for the purposes of avoiding any wastage or misuse of cleaning solutions, maintenance and disinfection. The solutions used for automatic washing installation shall be those recommended by the manufacturer of equipment (biodegradable) and are dosed automatically. It is known that if the automatic car wash process, through the tunnel, water quantity, category I, is higher than hand washing and significantly higher compared with steam procedure (Fig. 2). Wastewater (Sp2, Sp5, Sp8, Sp11, and Sp14) was collected by collecting channels where it is a first separation of sludge and heavy residue. After this first separation the wastewaters were collected in three separator basins, each of them approximately 10 m^3. In the first separator was made a decantation of heavy solids. In the second separator, which has a special design, was made a deceleration of the solid fractions and waste oils. In the third separator was achieved the last decantation and cleaning, in particular the easy fractions, which could escape from the second separator. After this treatment the wastewater (Sp3, Sp6, Sp9, Sp12, and Sp15) was discharged into the sewage of the city. Sludge and heavy suspensions were deposited on land owned of the company (not dangerous). Hazardous liquid fractions, such as oil, was collected and transferred to an employee for destruction.

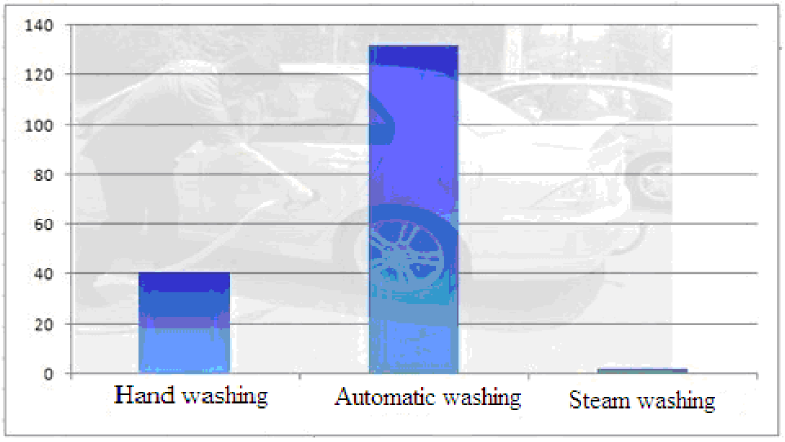

Fig. 2. Water consumption per car, L/hour.

The Sp1, Sp4, Sp7, Sp10 and Sp13 samples represent the water, category I (Ord. 161/2006), used in ecological washing process. Each numbered sample (Table 1) represents the mean values obtained for the analyzed period. The levels of the physicochemical parameters are presented in Table 1 and Figs. 3-6. From the results of this study the levels of pH varied between 6.75±1.02 to 7.90±1.56 for points Sp1, Sp4, Sp7, Sp10 and Sp13; 8.24±1.32 to 8.99±2.03 and 7.28±1.43 to 8.27±0.54 for points Sp2, Sp5, Sp8, Sp11, Sp14 and Sp3, Sp6, Sp9, Sp12, and Sp15, in the wastewater respectively. Generally point Sp2, Sp5, Sp8, Sp11, and Sp14 shows the highest concentration followed by Sp3, Sp6, Sp9, Sp12, and Sp15, while point Sp1, Sp4, Sp7, Sp10 and Sp13 shows the least concentration (Fig. 5). In according with the Order 161/2006, regarding pH tolerance limit, the mean pH values for all collected samples were between 6.00 and 9.00. The temperature ranged between 14.10 - 17.10°C with an average value of 14.91±1.61°C. The highest values for conductivity, turbidity and TDS was found for samples Sp2, Sp5, Sp8, Sp11 and Sp14, before entrance in the first separator (Table 1 and Figs 3, 4 and 6).

Table 1. Physicochemical parameters investigated for wastewater samples.

No	*Samples*	*Physico-chemical indicators*				
		pH	*Turbidity*	*Conductivity*	*Salinity*	*TDS*
1.	Sp1	7.86	0.00	351	0.2	167
2.	Sp2	8.25	37.31	1757	0.4	1365
3.	Sp3	7.28	30.81	928	0.3	902
4.	Sp4	6.75	0,00	365	0.2	176
5.	Sp5	8.62	58.0	1912	0.4	1442
6.	Sp6	7.99	55.0	1003	0.3	839
7.	Sp7	7.90	7.0	345	0.2	164
8.	Sp8	8.24	100	1654	0.4	1320
9.	Sp9	8.07	49.15	989	0.3	736
10.	Sp10	7.81	0.00	362	0.2	168
11.	Sp11	8.99	113.0	1816	0.4	1392
12.	Sp12	7.89	43.77	861	0.3	881
13.	Sp13	7.75	0.00	351	0.2	161
14.	Sp14	8.52	152	1825	0.4	1402
15.	Sp15	7.68	36.75	812	0.3	711

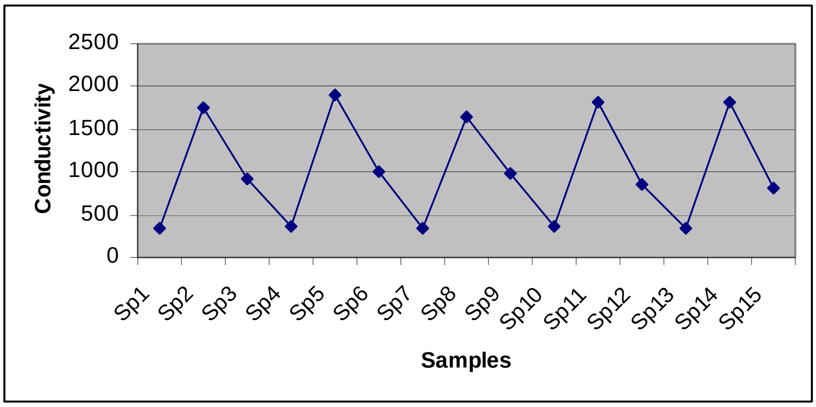

Fig. 3. Conductivity variation of samples.

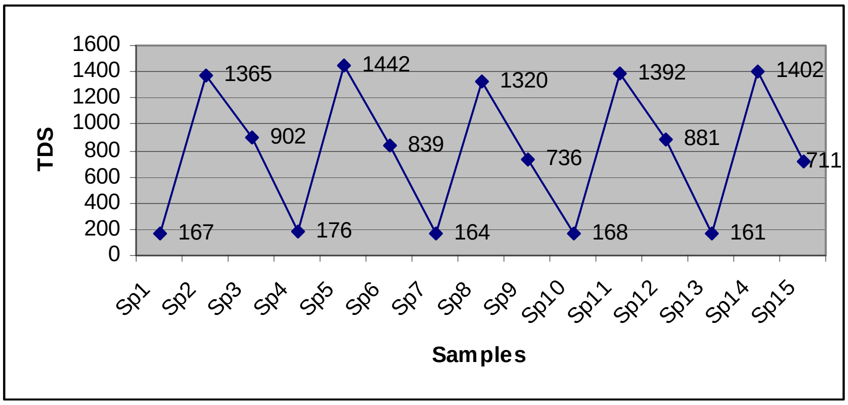

Fig. 4. TDS variation with salinity.

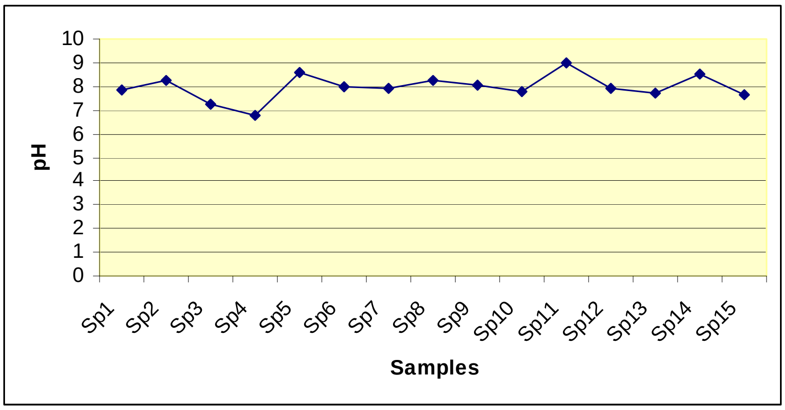

Fig. 5. pH variation of collected samples.

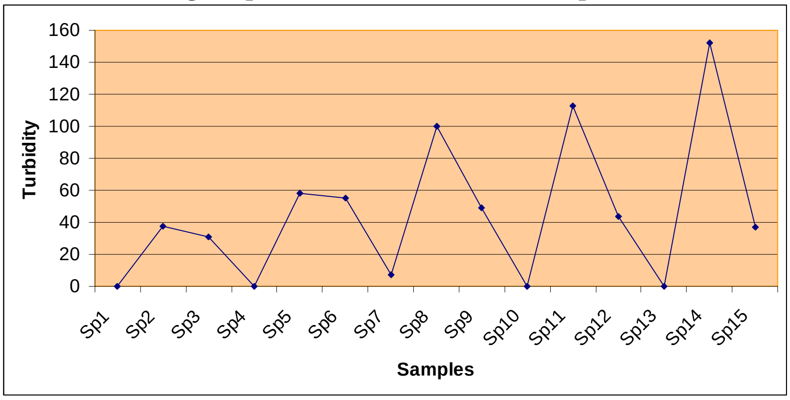

Fig. 6. Turbidity variation of analyzed samples.

The obtained experimental results (Table 1) were correlated with the determined heavy metal concentrations in samples. By comparing these results with the Maximum Admitted Level (MAL) for heavy metals, according to the Order 161/2006, it can observe an increase of heavy metal concentrations in collected samples (Table 2), after washing different cars in one week (from Monday to Friday at 14,00). The increase of Pb, Cu, Cd, and Zn concentrations (Table 2) is visible (average weekly collections) and these were higher especially on rainy days when cars came with a load more visible than in the days with good weather. This has been observed at Sp2, Sp5, Sp8, Sp11, and Sp14 samples digestion, which due to the sediment loads (dust, lint, etc.) required a double time for digestion, acidification of samples with sulfuric acid as required (1 mL / sample) for the dissolution of impurities from samples.

The highest load of heavy metals had results from the first wash water, before entering in the first separator. Lead was one of the most measured metals since it is a criterion of water pollutant, ubiquitous and was present at high concentrations environment.

Table 2. Heavy metals concentrations for the collected samples.

No	*Samples*	*Heavy metals concentration [µg/ L]*			
		Pb	*Cd*	*Zn*	*Cu*
1.	**Sp1**	1.008±0.3	0.346±0.1	121.982±4.4	22.453±1.1
2.	**Sp2**	18.342±2.2	2.789±1.02	567.892±7.5	53.892±2.3
3.	**Sp3**	17.456±2.4	2.354±0.4	533.943±7.2	51.098±1.9
4.	**Sp4**	1.023±0.2	0.256±0.1	110.903±4.2	21.907±1.6
5.	**Sp5**	27.934±1.5	3.217±0.5	592.341±7.9	56.821±2.4
6.	**Sp6**	25.657±1.3	2.781±0.2	556.324±6.5	53.091±2.2
7.	**Sp7**	1.987±0.3	0.451±0.1	114.257±3.9	24.982±1.7
8.	**Sp8**	19.982±1.4	3.129±0.6	576.291±6.7	53.981±2.6
9.	**Sp9**	18.092±1.1	2.832±0.3	562.903±5.3	50.023±2.1
10.	**Sp10**	1.015±0.1	0.378±0.1	112.267±3.2	22.083±1.3
11.	**Sp11**	22.034±1.3	3.009±0.6	582.340±6.4	56.782±2.7
12.	**Sp12**	19.823±1.1	2.671±0.3	564.239±4.9	55.782±2.5
13.	**Sp13**	0.902±0.1	0.472±0.1	110.982±3.5	20.891±1.2
14.	**Sp14**	26.782±1.7	2.905±0.5	583.023±7.1	53.902±2.3
15.	**Sp15**	25.432±1.3	2.767±0.4	579.056±5,2	52.451±2.2

Table 3. Maximum Admitted Level (MAL) for heavy metals, according to the Order 161/2006.

No	*Heavy metal*	*Unit.*	*Quality class*				
			I	*II*	*III*	*IV*	*V*
1	Total Chromium (Cr^{3+} + Cr^{6+})	µg/L	25	50	100	250	>250
2	Copper (Cu^{2+})	µg/L	20	30	**50**	**100**	>100
3	Zinc (Zn^{2+})	µg/L	100	200	**500**	**1000**	>1000
4	Arsenic (As^{2+})	µg/L	10	20	50	100	>100
5	Selenium (Se^{4+})	µg/L	1	2	5	10	>10
6	Cobalt (Co^{3+})	µg/L	10	20	50	100	>100
7	Lead (Pb^{2+})	µg/L	5	10	**25**	50	>50
8	Cadmium (Cd^{2+}, Cd^{6+})	µg/L	0,5	1	**2**	**5**	>5
9	Total Iron (Fe^{2+} + Fe^{3+})	mg/L	0,3	0,5	1	2	>2
10	Total Manganese (Mn^{2+} + Mn^{7+})	mg/L	0,05	0,1	0,3	1	>1
11	Nickel (Ni^{2+})	µg/L	10	25	50	100	>100

The experimental data show high level of lead in collected samples (except the water category I), compared with the maximum values allowed by Romanian legislation. Therefore, the amount of lead in analyzed samples exceeds the accepted MAL (Table 3). For all the above-mentioned elements, the maximum levels in samples correspond to the category III or IV (table 3) for Sp2, Sp5, Sp8, Sp11, and Sp14 and Sp3, Sp6, Sp9, Sp12 and Sp15 (Table 2).

4. CONCLUSIONS

In all analyzed samples the presence of heavy metals like Cd, Zn, Cu and Pb was detected. The higher concentration of Cu and Zn of analyzed wastewaters samples can be explained by the fact that during on the analyzed period, being an autumn rainy month, the amount of dirt on cars was very high. The lead level exceed in wastewaters samples can be a consequence to the traffic pollution, considering the fact that this researched source lies nearby principal road DN7. The presence of heavy metals in wastewaters which were discharged into the sewage of the city is a major problem because all the heavy metals analyzed form, with ligands present in the detergents, some stable combination hardly biodegradable. Thus, government agencies from Romania recommend to all ecological car wash to reduce the heavy metals problems by converting as much waste as possible into a solid product instead of washing the waste away into the wastewater. Generally, solid waste is fairly easy to control, requires less energy and is cheaper than wastewater treatment.

REFERENCES

[1] Radulescu, C., *Emisii Poluante. Metode pentru reducerea acestora*, Ed. Bibliotheca, Targoviste, 2008.
[2] Browner R.F., Boorn A.W., *Anal Chem*., **56**, 875A, 1984.
[3] Crites, R.W., *Environ. Sci. Technol*., **18**, 141, 1984.
[4] Lundin, M., Molander, S., Morrsion, G.M., *Wat. Sci. Tech*., **39**, 235, 1999.
[5] Fu, T., Zheng, X., Chen, J., *China Water & Wastewater*, **23**(18), 5, 2007.
[6] Xiaoyan, S., Bo, X., Jianfen, L., *Water Saving Irrigation*, **2,** 28, 2007.
[7] Radulescu C.**,** Stihi, C., Gh. V. Cimpoca, I.V. Popescu, Busuioc, G., Gheboianu, A.I., *Scientific Study & Research*, **12**(2), 155, 2011.
[8] Dulama I.D., Popescu, I.V., Cimpoca Gh.V., Radulescu C**.**, Gheboianu, A.I., *Journal of Science and Arts,* **13**(2), 341, 2010.
[9] Popescu, I.V., Frontasyeva, M., Stihi, C., Cimpoca, Gh. V., Radulescu, C., Gheboianu, A., Oros, C., Vlaicu, Gh., Bancuta, I., Dulama, I.D., *Journal of Science and Arts,* **11**(2), 268, 2009.
[10] Radulescu, C., Stihi, C., Popescu, I.V., Busuioc, G., Gheboianu, A.I., Cimpoca, Gh. V., Dulama, I.D., Diaconescu, M., *Ovidius University Annals of Chemistry*, **21**(1), 9, 2010.
[11] Ene A., Popescu, I.V., Stihi, C., Gheboianu, A., Radulescu, C., Tigau, N., Gosav, S., *Journal of Science and Arts,* **12**(1), 113, 2010.