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Cu (II), Zn (II) AND Pb(II) ANALYSIS IN WHITE WINE SAMPLES USING FAAS

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Abstract: This work presents some results regarding Cu, Zn, and Pb content in white wine samples (Romanian DOC and local producer in Diosig, Bihor County. Flame Atomic Absorption Spectroscopy (FAAS) was performed for the study. The results reveal that the dry wines have the highest content of Cu (II) and the sweet wines have the highest content of Zn (II). Pb (II) content for all the studied wines is below the limit of detection. Exceeding of the concentration (over MAC-legal maximum admissible concentration) was observed only for the copper ion content in white wines purchased from the local producer. Probably the exciding of Cu(II) concentration is due to exogenous sources as the treatments of the grapes with CuSO₄.
Key words: FAAS, Cu, Zn, Pb, white wine

INTRODUCTION

On the market consumers are the driving force. Consumer confidence in the food industry has fallen sharply due to food scandals. For this reason, it is very important to improve the food quality and to strict monitor the food safety. [1]

Heavy metals have a toxic effect on all living organisms. People, both through their diet and their activities, are exposed to the action of heavy metals. Lead, manganese, zinc and copper are metals that cannot be removed or destroyed from the matrices so they contamination persist and cause health risks by their bioaccumulation in the animal and plant organisms. [2,3,4]

The main way of exposure to heavy metals is the consumption of polluted food. As a percentage, the consumption of polluted food exceeds the exposure pathway represented by skin contact and inhalation. In the food industry, one of the main raw materials is cultivated plants, which have the potential to accumulate heavy metals from the soil or from applied treatments, which pose risks to the health of the population. [5]

The content of metals in wines, as in other food, must not exceed a certain quantity, in order not to have negative effects on the body. There is an optimal range of concentrations for each essential element [5]. If the concentration of these elements exceeds the maximum concentration allowed, toxicity occurs, these metals being considered as contaminants. The permitted content of heavy metals in wine or other food is limited by legislation being specified as the maximum admissible concentrations. [6]

Today there is a great interest in identifying the presence of the heavy metals in food and the various sources that lead to the presence of heavy metals, aiming at reducing the content of these metals through the use of various treatments permitted by the legislation in force. An essential role is played by analytical methods, which must meet certain conditions regarding precision, reproducibility, analysis time and application costs.

Factors that can contribute to the presence of metals in wine can be endogenous and exogenous nature. Endogenous ones are related to the characteristics of the soil and the grape variety. Those of exogenous nature are due to treatments applied to grapes, certain oenological practices and materials, atmospheric pollution and natural conditions. [6]

MATERIALS AND METHODS

Samples. Four types of DOC Romanian white wine (dry, semi-dry, semi-sweet and sweet) purchased from the supermarket and two samples of dry and

semi-dry white wine purchased from a local producer from Diosig, Bihor county area.

Method. Determination of the copper, zinc and lead metal ions in the analyzed white wine samples was performed by flame atomic absorption spectrometry (FAAS) using a VARIAN SpectrAA 110 spectrometer. The flame absorption technique was used.

The standard solutions of Cu (II), Zn (II) and Pb (II) were prepared in a solution that replicates the wine matrix. The solution which replicates the wine matrix is prepared as follows: in a 250 mL flask 1.0 g of fructose was dissolved in 11 ml ethanol and 100 ml double distilled water; then 22 ml of ultrapure concentrated nitric acid was

added. After the homogenization were added 4 g of di-ammonium phosphate and 0.9 g of magnesium nitrate, the solution was well stirred and then brought to the volume with double distilled water.

The standard solutions were: 1 mg/L Cu (II); 5 mg/L Zn(II), 0,2 mg/L Pb (II). From the standard solutions were prepared the solutions for the calibration. The blank was a solution which replicates the wine matrix.

In the tables 1, 2 and 3 are specified the etalon solutions preparation and concentrations and the results for the absorbance measured to obtain the calibration curves and in figure 1, 2 and 3 the registered calibration curves.

ml standard Cu II solution (1 mg/L Cu (II)) diluted to 25 ml	Cu (II) ppb	Absorbance
0	0	0,001
3	0,12	0,022
6	0,24	0,040
9	0,36	0,057
12	0,48	0,075

Table 1. *Data for the Cu (II) calibration curve*
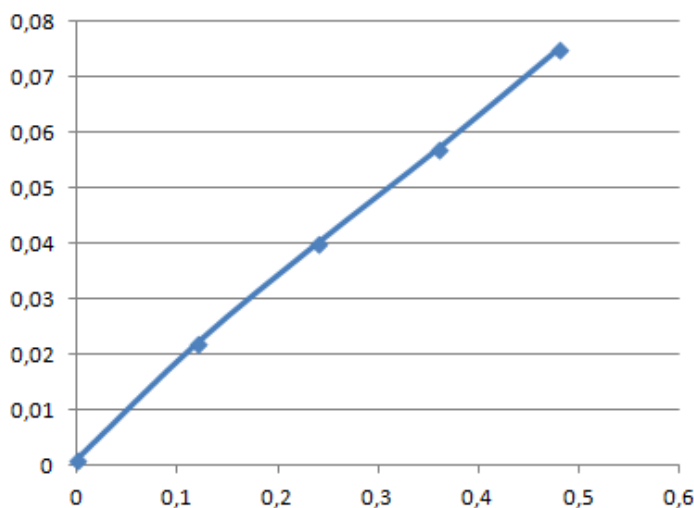
Figure 1. *Calibration curve for Cu (II)*

ml standard Zn II solution (1 mg/L Zn (II)) diluted to 25 ml	Zn (II) ppb	Absorbance
0	0	0,001
3	0,6	0,028
6	1,2	0,050
9	1,8	0,069
12	2,4	0,090

Table 2. *Data for the Zn (II) calibration curve*
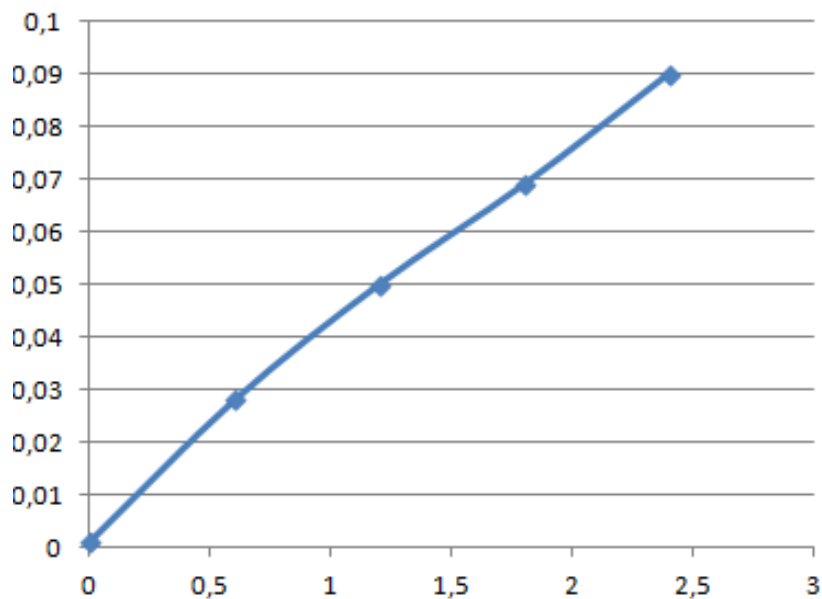
Figure 2. *Calibration curve for Zn (II)*

ml standard Pb II solution (1 mg/L Pb (II))diluted to 25 ml	Pb (II) ppb	Absorbance
Calibration curve for	Calibration curve for	Calibration curve for
0	0	0,001
3	0,024	0,014
6	0,048	0,030
9	0,072	0,048
12	0,096	0,068

Table 3. *Data for the Pb (II)*
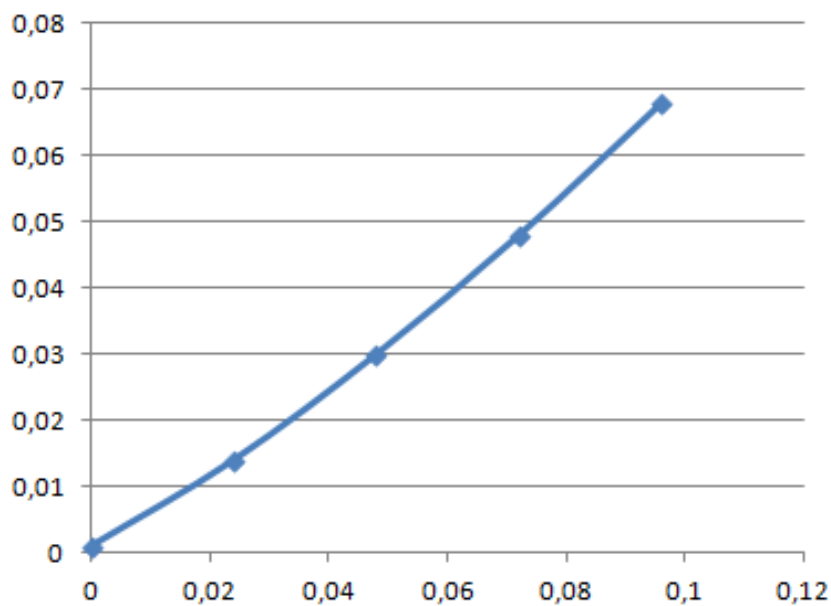
Figure 3. Calibration curve for Pb (II)

After measuring the absorbance and drawing the calibration curves, the samples of wine which were previously diluted with solution which replicates the wine matrix (10 ml wine in 250 ml flask) were analysed. For the heavy metals content in the wine samples calculus shall be taken the dilution applied to wine samples (10/25 = 0,4).

For each determined metal ion before the analysis, the lamp was changed.

RESULTS AND DISCUTIONS

The absorption measured for the heavy metals in the studied white wines samples are presented in table 4. The results for the heavy metals in the studied white wines samples are presented in table 5.

White wine sample		Absorbtion		
		Cu (II)	Zn(II)	Pb (II)
Dry	DOC	0,030	0,018	
	Local producer	0,045	0,021	
Demy-dry	DOC	0,024	0,025	**BDL**
	Local producer	0,041	0,030	
Demy-sweet	DOC	0,018	0,038	
Sweet	DOC	0,012	0,043	

Tabelul 4. Results for heavy metal determination in the white wine sampled
BDL-below detection limit

White wine sample		Concentrations mg/L						Conclusion
		Cu (II)		Zn(II)		Pb (II)		
		Determinate/ MAC		Determinate/ MAC		Determinate/ MAC		
Dry	DOC	0,45		1,65				
	local producer	1,25		1,80				Cu(II)> MAC
Demy-dry	DOC	0,25		2,00				Cu (II)>MAC
	local producer	1,20		2,25				
Demy-sweet	DOC	0,2	**1**	3,00	**5**	**BLD**	**0,2**	
Dulce	DOC	0,1		3,5				

Table 5. The results obtained for the heavy metals from the white wine samples
DOC- wine of controlled origin, MAC-maximum admissible concentration [7], BDL-below the detection limit

From the obtained data it can be observed that
- dry wines have the highest content of Cu (II) and the sweet wines have the highest content of Zn (II), but below the maximum concentration allowed by the law
- Pb (II) content for all the studied wines is below the limit of detection.
- DOC wines do not have metal ion content higher than the maximum permitted concentration for all investigated metals
- White wines purchased from the local producer (in the Diosig area, Bihor County) have slightly exceeded the copper ion content.

CONCLUSIONS

A day-to-day subject for modern enology is the presence of contaminating metals in wines, especially heavy metals, which have a great interest in monitoring their concentration in wine, but also in identifying the various sources (endogen or exogenous) that lead to their presence in wine because if the concentration of these elements exceeds the maximum concentration admitted by the law, toxicity occurs,

these metals being considered as contaminants.

Because an essential role is played by analytical methods used for the heavy metals determination, which must meet certain conditions regarding precision, reproducibility, analysis time and application costs, flame atomic absorption spectrometry (FAAS) can be a trustfully method for the wine samples.

The analysis performed on the white wine samples (dry, semi-dry, semi-sweet and sweet) from Romanian DOC and local producer (Diosig area, Bihor County) reveal that dry wines have the highest content of Cu (II) and the sweet wines have the highest content of Zn (II). Pb (II) content for all the studied wines is below the limit of detection.

Exceeding of the concentration (over MAC) was observed only for the copper ion content in white wines purchased from the local producer (Diosig area, Bihor County).

Probably the registered exciding of Cu(II) content is due to exogenous sources as the treatments of the grapes with $CuSO_4$.

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DISSOLVED OXYGEN CONTENT AND CHLORIDE ION IN SURFACE WATER

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Abstract
Water is a renewable, vulnerable and limited natural source, a life-indispensable substance for society, a raw material for productive activities, a source of energy and a transport path, a determining factor in maintaining an ecological balance. Sweet surface waters are the majority of liquid fresh water. The flowing waters are characterized by a series of physical and chemical indicators, including dissolved oxygen and chloride ion. The annual evolution of these parameters was determined for the Crisul Repede River for over two years

Key words: surface water, physicochemical properties, quality parameters

1.INTRODUCTION

The rivers contain water with a similar composition of spring water. The composition is influenced by the bed of mineral rocks, tributaries and waste water discharged into rivers and has the following characteristics: poorly mineralized, contain Ca and HCO_3^- ions; hardness in the range $2 \div 8$ °d; and pH in the range of 6.6 to 8.6. The river water has a low mineralization degree and is a soft water, it has a temperature of 0-30 degrees depending on the season. The flowing waters are characterized by a series of physical and chemical indicators, including dissolved oxygen and chloride ion. The following are the standard methods for determining these parameters.

For the determination of dissolved oxygen indicators, ie chloride ion in the flowing surface waters, the volumetric method is used. The paper presents the values of these indicators, monthly and annual average values, resulting from daily measurements made from surface water, respectively from Crisul Repede river, Oradea station.

2.MATERIALS AND METHODS
2.1.Determination of Dissolved Oxygen by Iodometric Method

The procedure is used to determine the dissolved oxygen content of water after the Winkler process. In the presence of oxidising substances or reducing substances, it is necessary to make changes to the method for their removal.

The principle of the method. Reaction of the dissolved oxygen in the sample to the freshly precipitated manganese (II) hydroxide. Acidification and oxidation of iodine by the manganese compound formed at the upper valence, with the release of an equivalent quantity of iodine. Determination of the amount of iodine released is done by titration with sodium sodium thiosulphate presently as starch.

Materials. Pipettes and bottles quoted, winkler bottles used to make solutions, shall be Class A, with specified tolerance and calibration certificates issued by the manufacturer.

The reagents used are the following: sulfuric acid, starch, potassium iodate, azide iodide, alkaline solution: manganese sulphate solution, sodium thiosulfate, sodium hypochlorite, iodine, solution, potassium iodide, phenolphthalein.

Method. The sample to be analyzed is harvested directly in Winklers. Apply the water sample by adding 1 ml of manganese sulphate solution and 2 ml of alkaline iodine solution to the vial using a pipette. Put the stopper, then shake the vial. Allow the precipitate to settle for 5 minutes, then stir again to achieve good homogenization. The bottle thus prepared can be kept for 24 hours or shielded from light. Remove the stopper, remove a volume of about 30 ml of the solution and introduce 1.5 ml of H_2SO_4. Put

the stopper and shake, until inverted, to completely dissolve the precipitate.

The sample thus treated is transfected into a 300 ml Erlenmeyer. Titrate with sodium thiosulphate solution until yellowish, add a few drops of starch solution and continue titration until discoloration. As the flushing water is used, the sample is discarded, followed by titration if the color returns. Note the volume of thiosulphate consumed.

If the presence of oxidizing or interfering reducing organic substances is suspected, take 50 ml of the sample to be analyzed and neutralize in the presence of two drops of phenolphthalein solution. Add 0.5 ml of sulfuric acid solution, some potassium iodide crystals and a few drops of starch indicator solution

If the solution stains in blue, oxidizing substances are present.

If the solution remains colorless, add 0.2 ml of iodine solution and shake. Leave it for 30 seconds. If there is no blue stain, it means we have reducing substances.

In the presence of oxidising or reducing substances, the determination of dissolved oxygen will change accordingly to each interference.

2.2 Determination of Chloride Ion

The procedure establishes how to determine the chloride content of water. Determination of chlorine content is done according to the standardized method SR ISO 9297: 2001 - Water quality. Titration with AgNO$_3$ using chromate as indicator (Mohr Method).

Materials. Pipettes and bottles used to prepare solutions shall be of Class A with the specified tolerance and calibration certificates issued by the manufacturer. 200 ml Erlenmeyer flasks without metrology mark, pH paper

The reagents used are: silver nitrate, sodium chloride, potassium chromate, sodium hydroxide, solution, nitric acid.

The principle of the method. Reaction of chloride ions with silver ions to form insoluble silver chloride, which is a quantitative precipitate. Add a small excess of silver ions and brown-red silver chromate formation with chromate ions used as an indicator.

This reaction is used to indicate the turn. During titration, the pH is kept between 5 and 9.5 to allow precipitation.

Method. Into an Erlenmeyer flask, introduce 100 ml of the sample to be analyzed, filtered. If the pH of the sample is not between 5 and 9, adjust with either nitric acid solution or sodium hydroxide solution as appropriate. Add 1 ml of potassium chromate solution and continuously stir by titration with the AgNO$_3$ solution until the yellow-brick color appears.

After addition of a drop of standard sodium chloride reference solution, this coloring must disappear. Titrate the solution with sodium chloride solution as a control solution for the following titrations.

3.RESULTS AND DISSCUSIONS

The two chemical parameters of the water, the dissolved oxygen content, respectively the chloride ion, were determined with the above methods by daily measurements.

Monthly average values were also calculated.

The dissolved oxygen content (mg / l) is calculated as follows:

$$\text{Dissolved oxigen (OD)} = \frac{200 \cdot V \cdot f}{V_1 - V_2},$$

in which:

V - the amount of sodium thiosulphate used in the titration, in ml,

f - factor of sodium thiosulphate solution,

V1 - capacity of the bottle used for the determination of oxygen in ml,

V2 - the amounts of manganese sulphate and alkaline iodide added, in ml.

Figure 1 shows the evolution of the dissolved oxygen concentration (mg / l), monthly average values on the parcels of 2016 and 2017, respectively.

The ion chloride concentration, mg / l, is calculated as follows:

$$c_{Cl^-} = \frac{(V_s - V_b)}{V_a} \cdot c \cdot f$$

in which:

C$_{Cl}$-chloride ion concentration, mg/l

Va - sample analyzed volume , ml;

Vb - the volume of silver nitrate solution used to titrate the control sample, ml;

Vs - volume of the silver nitrate solution used for the titration of the sample, ml;

c - the actual concentration of the silver nitrate solution expressed in moles of $AgNO_3$ per liter

f - conversion factor; f = 35453 mg / mol

Figure 2 shows the evolution of chloride ion concentration (mg / l), monthly average values during 2016 and 2017 respectively.

Concentration of dissolved oxigen, mg/l

	1	2	3	4	5	6	7	8	9	10	11	12
2016 OD	13.1	12.0	11.5	11.4	9.6	8.8	8.4	6.4	8.5	9.5	11.1	13.0
2017 OD	14.1	13.2	12.1	9.6	10.6	8.8	8.2	7.7	8.1	10.5	11.6	12.4
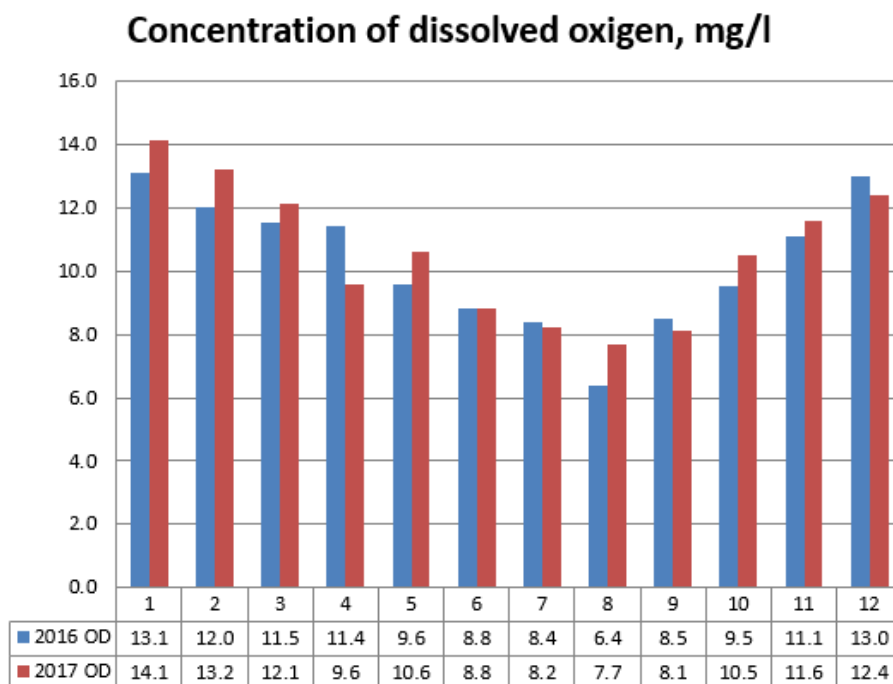
Figure 1. *Monthly average values of dissolved oxygen concentration (mg / l) in 2016 compared to 2017.*

Chloride concentration, mg/l

	1	2	3	4	5	6	7	8	9	10	11	12
2016 Cl	5.6	7.1	7	5.8	5.5	7.1	7.4	6.6	7.9	5.1	5	6.7
2017 Cl	5	5.9	6.8	5.3	5	5	5.5	6.1	6.4	5	5.5	5

Figure 2. *Monthly average concentrations of ion chloride (mg / l) in 2016 compared to 2017.*

4.CONCLUSIONS

The chemical content of surface water is very important, depending on the possibility of water recovery and the chemical treatments to be applied depending on their use. Annual mean concentrations of dissolved oxygen were 10 mg/l in 2016 and 11 mg/l respectively in 2017 compared to the 18 mg/l limit. Chloride concentration was 7 mg/l in 2016 and 6 mg/l in 2017 respectively, well below the admissible limit of 250 mg/l. It is noted that the monthly and annual average values of the two measured parameters did not exceed the admissible limits.

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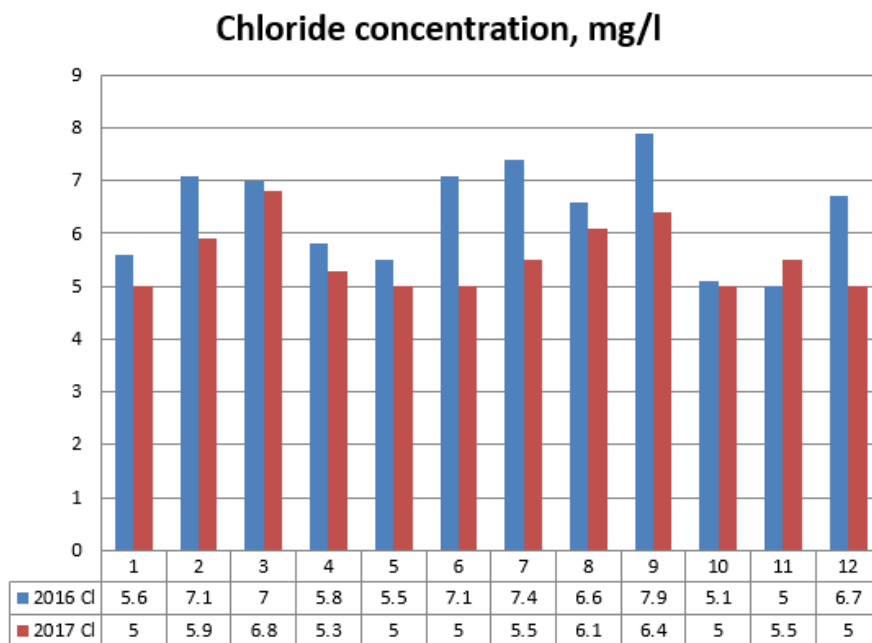4. Creţ P, Ionescu Gh.C., Badea G.E., Reliability Levels In Water Transport And Distribution Networks Due Mainly To Corrosion, Revista de tehnologii neconvenţionale, Nonconventional Technologies Review (ISSN 2359 – 8646),CNCSIS B+, vol. XXI, nr.4, pg.53-57, dec 2017,
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THE CHEMICAL PROPERTIES OF SURFACE WASTEWATER

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Abstract

Suspended solid matter, that are separable by means of a decanter, must be fully understood in order to properly design the capacity of said decanter and sludge fermentation basins. Dissolved organic matter constitutes organic impurity and the biological treatment step from water purification plants is structured based on the values that it presents.
Keywords: wastewater, chemical properties.

INTRODUCTION

For the right treatment of the surface water, the chemical properties of water must be well known[1-12].

In general, a clean water without impurities contains a quantity of oxygen the corresponds to its saturation level; oversaturation is rarely encountered, usually when the water is in a state of excessive turbulence, when there is an abundance of underwater vegetation that feed on carbon dioxide and in turn release oxygen.; undersaturation is generated when the water is impure.

The oxygen quantity that is missing from a body of water in order for the water to be classified as saturated is called *oxygen deficiency*.

In order to establish the degree of filth of surface water, it is imperative that its oxygen content must be known.

In wastewater, dissolved oxygen (**O_2**) is found in relatively small quantities (1 – 2 mg/l), but only when the wastewater is fresh and straight out of the biological treatment step. Surface water, in their degree of pollution, contain variable quantities of oxygen. At saturation and at different temperatures, the oxygen quantities that are found within clean water are showcased in table 1.

Table 1.The oxygen quantities within water, at saturation in regard to water temperature.

Temperature [°C]	0	5	10	12	14	16	18
O_2 in water [mg/l]	14,23	12,80	11,33	10,83	10,37	9,95	9,64

Temperature [°C]	20	22	24	26	28	30
O_2 in water [mg/l]	9,17	8,83	8,53	8,22	7,92	7,63

If a given body of water contains the quantities of oxygen[6] that are presented in table 1, then that water is considered saturated; exceeding these values, the water becomes oversaturated, and at lower values, the water is undersaturated.

Biochemical Oxygen Consumption (**BOC**) of wastewater and rivers represents the value of consumed oxygen within the biochemical decomposing process, within an aerobic medium, of total solid organic matter, at a standard temperature of 20°C, during a period of respectively 5 days; in this case, the respective value is denoted with BOC_5 – biochemical oxygen consumption over 5 days.

The biochemical oxygen consumption represents the impurity degree of surface wastewater; the larger its value is, the more polluted the water is.

The chemical decomposition of wastewater, respectively the biochemical oxygen consumption is produced in two phases:

• *primary phase* (*of carbon*)**,** in which oxygen is consumed within the oxidation of organic substances, that has an immediate start and has, in the case of household wastewater, a half-life of about 20 days, at a temperature of 20°C. Following the decomposing of organic matter - that have carbon, nitrogen and phosphorous in their composition - carbon dioxide is formed (CO_2), that remains in gaseous form within the liquid or is ejected;

- *secondary phase (of nitrogen),* in which oxygen is primarily consumed in order to transform ammonia in nitrites (NO_2^-) and then in nitrates (NO_3^-); it begins in about 10 days and can last 100 days or more; This transformation constitutes the "nutrification process of organic matter".

All these transformations are realized in conformity with the law established by Wilhelmy, even before the year 1900: the speed of oxygen consumption by a transforming matter – noted with K_1 – is, in any given moment, proportional with the quantity of transforming matter, not yet entered within the reaction and is expressed with the following differential equation:

$$\frac{dx}{dt} = K_1(a - x), \qquad (1)$$

in which:

a is the quantity of transforming matter at the beginning of the process;

x – the quantity of matter transformed during the t timeframe;

K_1 – oxygen consumption speed (constant), that depends on the nature of the reaction with the given conditions in which it takes place.

Following laboratory experimentation, Streeter and Phelps, later Theriault as well, have proven that Wilhelmy's law is applicable to organic matter as well (transforming matter) in wastewater that is oxidized in the primary phase.

Integrating Wilhelmy's equation from timeframe 0 to timeframe t, we get the following result:

$$K_1 = \frac{1}{t}\ln\frac{a}{a - x}. \qquad (2)$$

If the quantity of organic matter is measured (transforming matter) through the oxygen that is consumed within the primary phase (primary oxygen) then the following notes are made:

L_t – primary oxygen consumption that is necessary for the water after timeframe t has elapsed, up to 20 days;

X_t – primary oxygen consumption, during timeframe t;

L – total primary oxygen consumption (over the course of 20 days),

$L = L_t + X_t$,

replacing these parameters within Wilhelmy's equation, we get the following:

$$K_1 = \frac{1}{t}\ln\frac{L}{L_t}. \qquad (3)$$

Transforming the natural logarithm in a decimal one and noting

$$k_1 = 0{,}4343 \cdot K_1, \qquad (4)$$

we obtain:

$$k_1 = \frac{1}{t}\lg\frac{1}{L - X_t} = \frac{1}{t}\lg\frac{L}{L_t}. \qquad (5)$$

Two more equations result out of this equation, that are very important for calculating the transformation process of organic matter within natural waters and wastewater:

$$\begin{cases} X_t = L(1 - 10^{-k_1 \cdot t}); \\ L_t = L \cdot 10^{-k_1 \cdot t}. \end{cases} \qquad (6)$$

The speed of oxygen consumption, k_1, is determined within the laboratory; for city wastewater it varies between $0{,}1 – 0{,}3$ (days^{-1}), the limits being however far larger for industrial wastewater.

For the biochemical oxygen consumption over 5 days of urban wastewater, some average values have been outlined within table 1.1; for industrial wastewater, the BOC_5 values are sometimes larger, capable of reaching even 50.000 mgf/dm^3. We can therefore attest that between the biochemical oxygen consumption over 5 days and the one over 20 days (primary consumption, *L*) the following relation:

$$CBO_5 = 0{,}684 \cdot CBO_{20}. \qquad (7)$$

The chemical oxygen consumption (COC) measures the carbon content from al categories of organic matter, by establishing the consumed oxygen of potassium bicarbonate within an acidic solution [8].

Total nitrogen is composed of free ammonia, organic nitrogen, nitrites and nitrates. Organic nitrogen and free ammonia are taken as indicators of organic substances containing nitrogen, that are present within wastewater and albuminoidal ammonia as indicator of organic nitrogen, that can decompose. Free ammonia is the result of bacterial decomposition of organic substances. The quantities of free ammonia larger than 0,2 mg/l indicate the existence of impurity within an analyzed body of water.

Fresh wastewater has a high concentration of organic nitrogen and a low concentration of free ammonia, and less than fresh waters contain these substances and inverse proportions, respectively a higher concentration of ammonia and a low concentration of nitrogen.

Nitrates represent the most stable form of organic nitrogen matter and generally their presence dictates a stable water in

according to the transformation process within. In fresh wastewater, nitrites and nitrates are in lower concentrations (under 1/1 mil.) [7].

Sulfurs are the result of organic or inorganic substances decomposing and come from, most of the time, from industrial wastewater.

Chlorides can come from different sources (such as urine); that is why, quantities of 8 – 15 g sodium chloride, the amount a person outputs a day, cannot constitute impurity indicators.

Volatile acids indicate the anaerobic fermentation progress of organic substances. From these acids, by means of fermentation, is where carbon dioxide and methane emerge. In the case of a good fermentation, for household wastewater, volatile acids, expressed as acetic acid, must be about 500 mg/l (over 300 mg/l and under 2.000 mg/l).

Oils and fats, of vegetable of mineral origin, in large quantities, form a layer on the water's surface, that can prevent aeration, can damage and clog biological filters, can deny anaerobic processes in fermentation tanks etc.

Gases that are most commonly encountered within the purification of water are sulfuric hydrogen, carbon dioxide and methane. Sulfuric hydrogen indicates wastewater that has been kept in an anaerobic medium for a prolonged period of time. Methane and carbon dioxide are indicators of anaerobic fermentation. When mixed with air, at a ratio of 1:5 – 1:15, methane becomes explosive.

Ion hydrogen concentration (pH) is an indicator of the purification's progress; the activity of microorganisms is dependent on it, as well as the chemical precipitations. The pH must be at about 7.

Oxidoreduction potential (Redox potential, rH) provides information about the power of oxidation, or reduction of water and sludge within the Redox scale; the rH notation expresses the logarithmical inverse of the oxygen pressure. The measuring scale of the Redox potential has the extreme values of 0 and 42. Values under 15 are characteristic of the anaerobic oxidation stage (fermentation) and values over 25 represent the aerobic oxidation stage.

Putrescibility is a characteristic of wastewater that indicates the possibility that a quantity of water can decompose faster or slower. *Stability* the opposite of putrescibility.

Relative stability is expressed in percentages and represents the ratio of available oxygen found within the analyzed sample (in dissolved form or in nitrite and nitrate form) and the oxygen requirement in order to satisfy the requirements of the primary phase of oxygen consumption. In deterministic terms, relative stability is seldom used, because some colloidal substances that are dissolved in the water can precipitate the color (given by methylene blue) and furthermore the values of relative stability are uncertain due the fact that they vary from case to case, based on the properties of the wastewater.

RESULTS AND DISCUSSIONS

The total of solid matter represents the sum between the suspended solid matter and the dissolved solid matter.

Table 2 comparatively showcases the values regarding suspended solid matter, in the case of a German city [10] and for a neighborhood from within the city of Bucharest[6].

Table 2. The properties of solid substances found within wastewater

Substances		Solid substances [mg/l]/[g/loc and day]			CBO_5
		Mineral	Organic	Total	[mg/l]/ [g/person, day]
Suspended solid matter:					
– separable through decanter	A	130/20	270/40	400/60	130/19
	B	20/10	30/10	50/20	55/20
– cannot be separated through decanter	A	70/10	130/20	200/30	80/12
	B	40/15	40/15	80/30	40/15
Dissolved solid matter	A	330/50	330/50	660/100	150/23
	B	280/100	90/35	370/135	80/30
Total	**A**	**530/80**	**730/110**	**1260/190**	**360/54**
	B	**340/125**	**160/60**	**500/185**	**175/65**

A – German city, split sewage system, wastewater, especially household wastewater, specific consumption of water supply of 350-400 l/person and day.
B – industrial area in Bucharest, unitary sewage system, specific consumption of water supply of 350-400 l/person and day.

The specific consumption of water supply for each person greatly influences the composition of wastewater; the larger the consumption, the more diluted the end wastewater shall be and vice versa, because the quantities of matter, be it organic or mineral, that is ejected alongside wastewater are usually under the same form of measurement.

Taking into account that during rainfall the wastewater and rain water are generally equally polluted in the same fashion as wastewater is during the dry seasons, it is recommended that the values outlined in Table 2, section A to be enlarged by 15 - 20 % in order to factor in the suspensions brought forth by rainwater washing over streets, yards or that are concentrated within the sewer system.

sense that mineral substances quantitively outweigh the organic substances in the case of Bucharest, even though we are generally told by specialty literature that the usual ratio between the two is generally reversed in most noted cases. The reverse of the values is due to the influence of industry, which emanates vast quantities of mineral substances and further demonstrates the influence of industrial wastewater over a city's overall wastewater

Depending on their quantity and quality, subterranean water that infiltrate within the sewage system have an influence over the characteristics of wastewater.

The necessary analysis for designing water purification plants, in order to establishing the characteristics of wastewater, outline enough details of the afore mentioned aspects; but the general development of the settlement must also be taken in account, as future modifications to its infrastructure can significantly influence the characteristics of wastewater.

CONCLUSIONS

After studying the two cases, we can conclude that, in general, the values are comparable, with one small caveat in the

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THE SEPARATION OF CAROTENOIDS FROM PARSLEY LEAVES BY TLC

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Abstract:

Carotenoids are plant pigments spread in plant tissues and animals. These pigments print yellow, red or blue color, tissues that were. In herbal the carotenoids were in leaves, fruits, stems, roots, seeds, petals and in pollen.

The amounts of carotenoids in dried leaves is between 250-650 mg/g. Carotenoids pigments are synthesized only of vegetable. Carotenoids have practical applications in medicine and cosmetics and their use as food additives, dyes and antioxidants.

Key words: carotenoids, leucina, tirozina, luteina, zeaxantina, β-criptoxantina ,TLC, Silica gel (SilG, Merk).

INTRODUCTION

Carotenoids along with flavonoids and isoflavones are biological substances, called phytochemicals („phyto" means „from herbals") which give the flavor, aroma and resistance to the disease having an important role in photosynthesis and photoprotection .

Food consumption rich in β – criptoxantina, carotenoid a color orange – red significantly decreases risk of lung cancer, according to a study published in 2003 in „Cancer Epidemiology, Biomarkers and Prevention"magazine[1] .

Analysis of carotenoids from plants was inserted by Tswett (1906), subsequent findings, identification and elucidation structure have been developed by Karrer, Zechmeister, Talerand, Goodwiszi [2-5].

Curent methods for operation and analysis carotenoids includes new methods separation as TLC and HPLC to replace or complementary with classical technique (locked column chromatography) [6-8].

There is limited on composition carotenoids from the parsley leaves separated by open column chromatography. Purpose of this study is characterizing the type of carotenoids from parsley leaves using methods of separation (TLC, HPLC) to identify major components.

EXPERIMENTAL

Solvents used in chromatographic separation are of analytical purity (methyl acetate, hexane, chloroform, acetonitrile) or distilled (acetone, ethyl ether, ethanol) and as buffer substances use : TEA and antioxidants (butylated hidroxytoluene – BHT).

The parsley leaves were dried at room temperature in airflow about 3 – 4 days, have shelled and after which the maceration. Seeds macerated dry in oven about 2 hours, then are crushed in mortar to reach as a powder. The powder to be extracted with chloroform : ethanol : petroleum ether (3 : 2 : 1 v/v/v) for 5 hours at dark to prevent degradation and oxidation of carotenoids. Crude extract filtered, evaporate to drying in Rotovapor and re – suspended in ethyl ether.

Saponification was done in ether being added to 20 % KOH in ethanol until the final concentration of 10% V/V KOH. Mixture was stirred with a magnetic stirrer for 8 hours, carotenoids being extracts for 3 – 4 times successively with ethyl ether a solution with neutral pH.

Soap is removed, extract all the carotenoids was evaporated with Rotovapor, brought to a certain volume and used for chromatographic separation.

The total concentration of carotenoids of total extract (TE) is calculated by comparing absorbance A ($\alpha_{max} = 450$ nm) with a specific absorbing ($\alpha = 400$ nm).

$$X = (A \times Y \times 1000) : (2500 \times 100) = A \times Y / 250 \quad (1)$$

Where:

X – weight carotenoids of sample (mg)

Y – sample volume (ml)

To characterize the composition in carotenoids of parsley leaves has made a preliminary separation total extract (TE) on a column of alumina (Al_2O_3 with 5% water).

Small volumes were taken of total extract and were placed on the column and eluted with 3 solvent systems:

- 100% petroleum ether (fraction 1)
- petroleum ether : ethyl ether (1 : 1 v/v) (fraction 2)
- ethanol in ethyl ether 5% v/v (fraction 3)
-

Total extract and fractions 1 – 3 released from the alumina column were separated on silica gel plates (SilG, Merk) and chromatograms were analysed in Shimadzu CS – 5000 with beam with dual wavelength. For total extract used a separation of two stages:

- with 20% v/v acetone in petroleum ether
- with 100% petroleum ether

For fractions 1 – 3 developing systems was:

- 5% v/v acetone in petroleum ether (fraction 1)
- 10% v/v acetone in petroleum ether (fraction 2)
- 15% v/v acetone in petroleum ether (fraction 3)

RESULTS AND DISCUSSIONS

Total extract has undergone quantitative analysis. Peakurile obtained of densitograma TLC (figure 1) recorded at 450 nm have been identified and compared with total extract, with separation standard (S) same conditions.

Major carotenoids identified were: leucine, tyrosine, peporezine, luteine and β – criptoxantine.
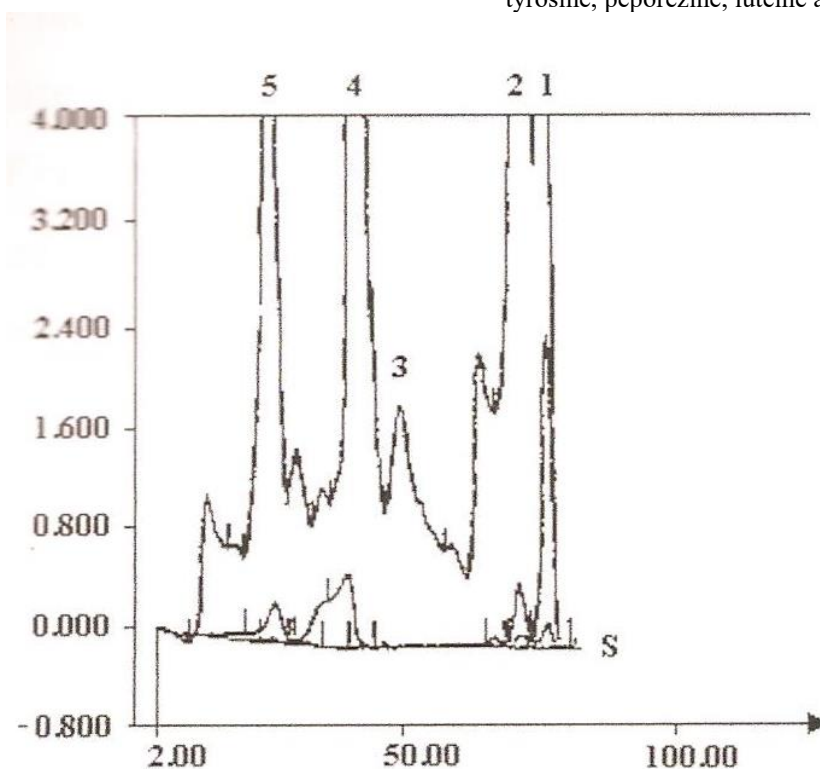

Figure 1. TLC chromatogram the total extract: 1-leucine; 2-tyrosine; 3-peporezina;

4-β- criptoxantine; 5-luteine.

So we learned only percentage composition the main carotenoids in extract and not in their absolute: 26,46% leucine; 21,30% tyrosine; 19,75% luteine and 12,58% β-criptoxantine.

Fractions 1 – 3 collected from alumina columns were analysed by TLC.

Fraction 1 contains 2 main peakuri results of TLC separation representing non – polar carotenoids (leucine and tyrosine ; fig.2.A).

Fraction 2 results of TLC contain leucine (II.1), tyrosine (II.4) and β – criptoxantine (II.5). (fig. 2.B). Fraction 3 results by TLC were rich in polar carotenoids: β – criptoxantine (III.1), luteine (III.2) and peporezine (III.3). (fig.2C).
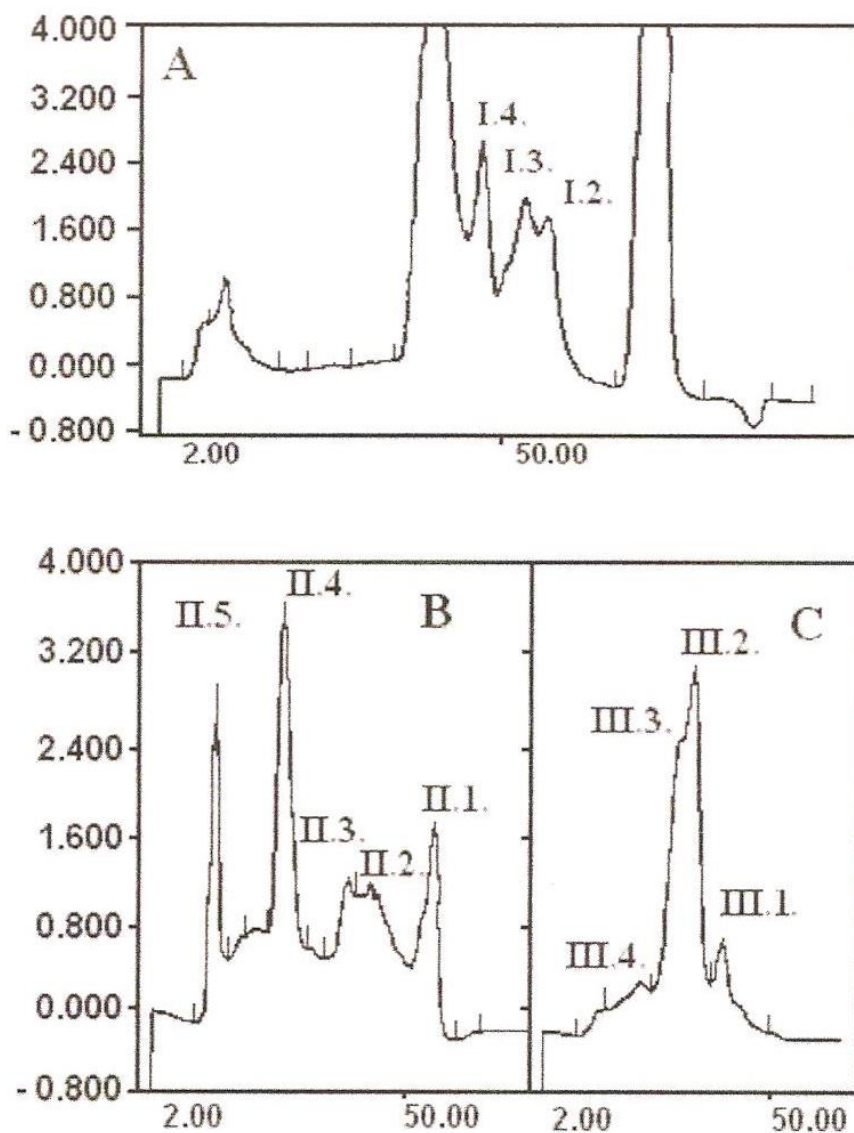

Figure 2. TLC chromatogram registered for fractions 1 – 3 separated by alumina column.

CONCLUSIONS

Total amount of carotenoids from parsley leaves assessed by spectrometry in the VIS the total extract was 80 mlg^{-1} dry mass. By chromatographic analysis (TLC) have highlighted the main carotenoids present in parsley leaves: leucine, tyrosine, peporezine, luteine and β – criptoxantine in total extract distributed differently between fractions diluted of alumina column. TLC proved a rapid and useful method for separation of carotenoids from parsley leaves.

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ANTICORROSION PROTECTIVE COATINGS BY ADSORBED NATURAL EXTRACT INHIBITOR FOR MILD STEEL CORROSION IN NEUTRAL SOLUTIONS

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Abstract: *In order to prevent mild steel corrosion during immersion in different aggressive media, recent research studies now focus on the development of non-toxic, inexpensive and environmentally friendly corrosion inhibitors as alternatives to different synthetic compounds, inhibitors derived from natural extracts, readily available from a wide range of renewable sources.*

As the extraction process is a simpler and low-cost procedure, this paper attempts to assess the inhibitive effect of natural plants selective extracts obtained from indigenous flora. Thus, the alcoholic extract from Juglans Regia buds (JRB) can be valorised after the expiration date by using it as a natural green inhibitor.

The inhibitor effects of this vegetal extract tested at different concentrations has been determined by various electrochemical techniques in 1N NaCl solution using a thermostated three electrode electrochemical cell. The next step was to determine the kinetic parameters and hence the corrosion rate. The inhibition efficiency was found to increase with increasing extract concentration, up to a limiting value.

The addition of the JRB extract in the corrosive solution decreases the charge capacitance facilitating the formation of an adsorbed layer over the steel surface. The cumulated results suggest that this natural extract may serve as effective inhibitor for the corrosion of mild steel in aggressive neutral solutions.

Keywords: protective coatings, natural inhibitor, mild steel, neutral solutions, NaCl

INTRODUCTION

The use of inhibitors is one of the most practical methods of corrosion prevention. Most inhibitors act by adsorbing on the surface of metals [1-4], corrosion being prevented by the protective film formed.

The protection efficiency of organic corrosion inhibitors depends on the type of adsorption process, determined by various factors: nature and superficial charge of metals; the adsorption type of the inhibitors; the chemical structure of the inhibitors; the nature of the corrosion environment [5-8].

As alternatives to different synthetic compounds, often toxic and dangerous for living organisms and also for the environment, numerous research studies now focus on the development of non-toxic, inexpensive and environmentally friendly corrosion inhibitors, in order to prevent mild steel corrosion during immersion in different aggressive media.

However, as the environmental legislation becomes more restrictive, there is a new approach: using low environmental impact inhibitors derived from natural extracts, readily available from a wide range of renewable sources [9-14].

This present paper assess the inhibitive effect of natural plants selective extracts obtained from indigenous flora based on a simpler and low-cost procedure for the extraction process. Thus, the alcoholic extract from *Juglans Regia* buds (JRB), recognized as a homeopathic drug, can be valorized after the expiration date by using it as a green inhibitor.

The inhibitor effects of this natural vegetal extract tested at different concentrations has been determined by various electrochemical techniques (potentiodynamic polarization, electrochemical impedance spectroscopy) in 1N NaCl solution using a thermostated three electrode electrochemical cell. The next step was to determine the kinetic parameters and hence the corrosion rate in order to establish the JRB optimum concentration for maximum inhibition efficiency.

EXPERIMENTAL METHODS

The working electrodes used in these experiments were made of mild steel sheets having a surface area of 1 cm^2. Their surface was mechanically cleaned by polishing them, then degreased, rinsed with double distilled water and dried. The experiments were carried out in a conventional three electrodes double wall glass electrochemical cell where the working electrode, the saturated silver/silver chloride reference electrode (Ag/AgCl), and a platinum counter electrode (active area of 1.13 cm^2) were placed directly into the solution.

All solutions were prepared from analytical reagent grade (Merck) and double distilled water. The investigated corrosion inhibitor (*Juglans Regia buds* JRB, crude extract) is a natural plant extract in ethyl alcohol (75% vol.). For tested solutions of plant extracts, the appropriate amount was added to the neutral electrolyte solution to obtain the final concentrations of 0.05, 0.15, 0.25 and
.

0.5% (% vol.). Experimental determinations were performed at a constant temperature of $25 \pm 0.1°$ C.

The polarization curves were recorded using a Voltalab 40 Radiometer Analytical potentiostat/galvanostat connected to a computer equipped with VoltaMaster 4.0 software for data acquisition and processing. The scan rate, at which the polarization curves were recorded, from cathodic potentials towards anodic direction, was 20 mV/min. Potentiodynamic polarization and electrochemical impedance spectroscopy measurements were carried out at $25\pm 0.1°$ C, in aerated solutions, in the absence and in the presence of JRB. Studies were carried out in 1N NaCl, the concentration of JRB was 0.05, 0.15, 0.25 and 0.5% (% vol.) using a thermostatated cell. Electrochemical impedance spectroscopy (EIS) measurements were performed with the amplitude of 10 mV using the same equipment, with the frequency range swept between 100 kHz and 50 mHz.

RESULTS AND DISCUSSIONS

The first step was the determination of the JRB optimum concentration in 1N NaCl solution, by comparing the inhibition efficiency values calculated from the polarization resistance Rp obtained by plotting the Nyquist curves.

By representing the electrochemical impedance spectroscopy experimental data as Nyquist plots, as can be seen from Figure 1, the capacity loops as depressed semicircles; moreover, from calculated data presented in Table 1, the addition of the JRB at the corrosive solution decreases the charge capacitance and simultaneously increases the function of the charge/discharge of the interface, facilitating the formation of an adsorbed layer over the steel surface
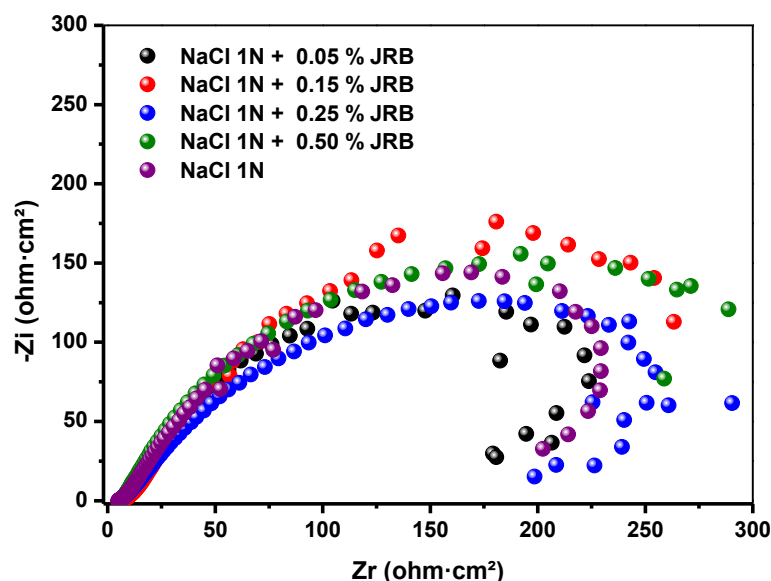
Figure 1. Nyquist plots obtained for different concentrations of JRB in NaCl 1N solution

Table 1. Electrochemical parameters calculated by circular regression from Nyquist plots obtained for different concentrations of JRB in NaCl 1N solution

Tested solutions	Rs, $\Omega \cdot cm^2$	Rp, $\Omega \cdot cm^2$	Cdl, $\mu F \cdot cm^{-2}$	IE, %
NaCl 1N	8.22	383	13140	–
NaCl 1N + 0.05% JRB	7.72	421	4237	9.92
NaCl 1N + 0.15% JRB	8.84	647	4921	68.93
NaCl 1N + 0.25% JRB	7.37	430	2958	12.27
NaCl 1N + 0.50% JRB	6.99	467	851	21.93

Since the 0.15% JRB extract solution exhibits the highest inhibition efficiency value, according to the results from Table 1, the following investigations were performed using this specific inhibitor concentration.

Prior to the beginning of potentiodynamic polarization experiments, the open circuit potential (OCP) values have been continuously monitored for 10 minutes until stable values were obtained. Then the corrosion potential Ecor values were determined by extrapolating the Tafel lines plotted in potentiodynamic conditions.

Modifying the OCP and Ecor values in presence of the investigated natural extract provides information about the nature and type of the inhibitor (anodic, cathodic or mixed). As can be observed from Figure 2, the presence of JRB extract leads to shifting in open circuit potential towards slightly more electropositive values, for all investigated concentrations, compared to the blank 1N NaCl solution.

As can be noticed from the polarization curves in Figure 3, both partial corrosion reactions of mild steel in 1N NaCl medium are influenced by the presence of the JRB extract, the highest inhibition efficiency values being obtained at the concentration of 0.15% JRB, compared to the blank solution.
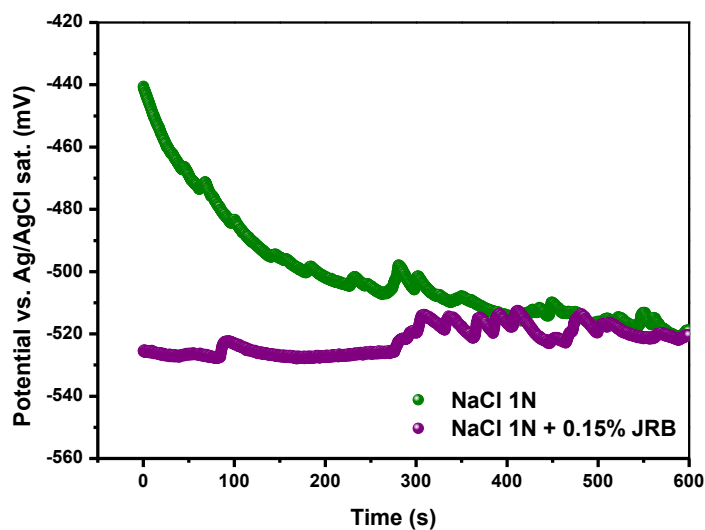
Figure 2. Open circuit potential dependence versus time for JRB optimum concentration (0.15%) compared to NaCl 1N blank solution
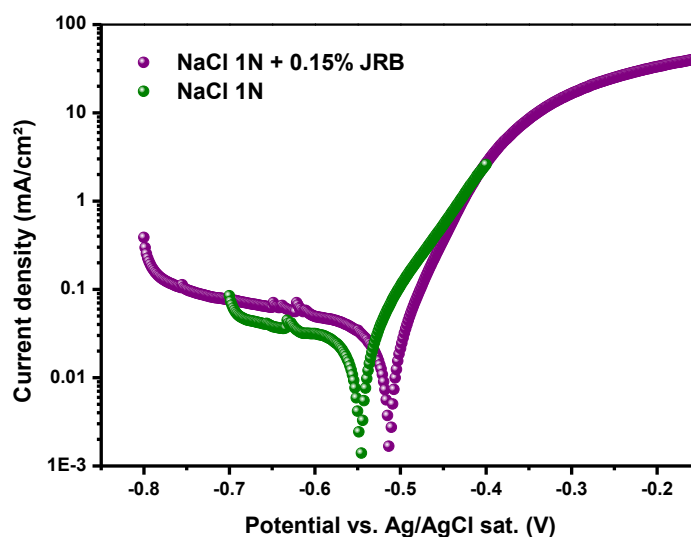

Figure 3. Tafel polarization curves for JRB optimum concentration (0.15%) compared to NaCl 1N blank solution

Table 2. Electrochemical parameters obtained by Tafel lines extrapolation for mild steel in NaCl 1N solutions, in absence and presence of tested inhibitor JRB of 0.15% concentration

Tested solutions	E_{corr}, mV	R_p, ohm·cm^2	i_{corr}, mA/cm^2	b_a, mV/dec	$-b_c$, mV/dec	p, mm/year
NaCl 1N	−552	744	25.93	73	659	303
NaCl 1N + 0.15% JRB	−518	847	20.57	50	185	241

However, this natural compound inhibits to a greater extent the cathodic reaction than the anodic reaction, as confirmed by the modified cathodic Tafel slopes (Table 2).

Thus, adding the JRB extract in small concentrations reduces the rate of hydrogen evolution reaction, and implicitly the corrosion rate of mild steel.

CONCLUSIONS

The potentiodynamic polarisation curves and the OCP evolution in time have indicated that the *Juglans Regia* buds natural extract (JRB) presents a mixed-type inhibitor mechanism. The inhibition effectiveness was found to increase with increasing extract concentration, up to a limiting value of 0.15% JRB extract.

The effect of JRB appears to decrease the overall corrosion current densities and shifted the corrosion potential toward more positive values.

The cumulated results suggest that this natural extract may serve as effective inhibitor for the mild steel corrosion in different aggressive neutral media.

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INSTRUCTIONS FOR AUTHORS (TIMES 14 PT BOLD, CAPITAL LETTERS, CENTRED)

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First name SURNAME¹, First name SURNAME² (10 pt bold)
¹Affiliations and addresses (10 pt)Affiliations and addresses (10 pt)

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Abstract: *Abstract of 50-120 words (10 pt italic). It contains concise information about: objectives of the work, the results obtained, conclusions*
Key words: *List 2-6 keywords. (l0 pt, italic).*

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The paper has to be written in English. Each paper should be concise including text, figures and tables. Authors are kindly requested to submit a paper a hard copy or in electronic format in Microsoft Word file form. Acceptable versions are MS-Word 2003, 2007, 2010. The suggested structure of the main text: Introduction; Methods, techniques, materials, Study area; Results and Discussions; Conclusions; References. (10pt)
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[1] Abbott, M. B., Petersen, M. M., and Skovgaard, O. (1978). On the numerical modelling of short waves in shallow water, Jnl Hydraulic Res; Vol 16 (3), pp. 23-44.
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