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CONTENT


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POSITIVE IMPACT OF EUROPEAN DIRECTIVES ON THE IMPLEMENTATION OF BIOFUELS IN CROATIA

PROFESSIONAL PAPER

Jona Šurić[1✉], *Nikola Bilandžija*[1], *Anamarija Peter*[1], *Marsela Miliša Gregurić*[2], *Neven Voća*[1]

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ABSTRACT:
The first Directive on the promotion of renewable fuels was adopted in 2003 - Directive 2003/30/ EC of the European Parliament and of the Council of 8 May 2003 on the promotion of biofuels or other renewable fuels for transport. In 2009, a new (so called RED Directive, 2009/28/ EC) was adopted, which creates a legal framework to promote the use of energy from renewable sources. First generation biofuels require an increased share of arable land on which crops are grown for biofuel production. The Directive RED II limits the share of conventional biofuels to 7% and requires a minimum share of advanced biofuels from lignocellulosic feedstocks and waste in final energy consumption in the transport sector of at least 0.2% in 2022, 1% in 2025 and 3.5% in 2030.

KEYWORDS: biofuels, renewable energy sources, Renewable Energy Directive

INTRODUCTION

The main driving force for the development and implementation of renewable energy projects comes from the Directive related to renewable energy sources and the reduction of greenhouse gas emissions. According to the plan European Commission, the Energy Union is based on the existing energy policy, which has three main objectives: Security of energy supply, reduction of dependence on oil imports and environmental protection (Russo et al., 2012).

To prepare for advanced biofuels and minimise the impact of direct and indirect land use, it is appropriate to limit the number of biofuels and liquid biofuels produced from grains and other starch- and sugar-rich crops and oilseeds that directly compete with food production. Advanced biofuels, particularly second-generation biofuels and biogas produced from lignocellulosic biomass and waste, can reduce greenhouse gas emissions and spur decarbonization of the transport sector, as well as improve energy diversification in the transport sector and reduce dependence on energy imports (Krička et al., 2006; Knothe, 2010; Lari et al., 2019).

Liquid biofuels used to achieve the Union's goals should meet sustainability criteria and save as many greenhouse gas emissions as possible. Setting transparent standards for biofuel production is essential for achieving the Union's single energy policy. It is essential that the previously agreed criteria for sustainability and greenhouse gas emission savings, which ensure that liquid biofuels qualify for support, are met. Only if it is guaranteed that the agricultural raw materials do not come from biodiversity areas, protected areas or protected areas for the conservation of rare and endangered species will it be favorable to the production of biofuels. It is assumed that future biofuel production will be based on feedstocks that are not used for food production. The lack of available agricultural land for food production, the situation on the food market and the prices of food for humans and animals will lead to alternative sources of raw materials for biofuel production (Tomić et al., 2008; Knothe, 2010, Naik et al, 2010).

On the basis of all these facts, the article aims to determine the obligations arising from the Directive RED II, which the Republic of Croatia assumed upon accession to European Union. First of all, it is necessary to limit the amount of cereals and other crops used for food purposes for the production of biofuels and to determine the limits for the production of biofuels from these raw materials. Only then can such biofuels be considered as part of the objectives set out in the Directive without limiting the overall possibility of using such biofuels and bioliquids.

EUROPEAN UNION DIRECTIVES ON THE USE AND PROMOTION OF BIOFUELS

Biofuels were used to start the first cars, and the first internal combustion engines were powered by various fuels made from biological raw materials. At the first World's Fair in 1900, Rudolf Diesel demonstrated an engine that ran on peanut oil. With the transition to fossil fuels, global energy consumption has grown steadily. The production of fossil fuels (oil, coal, gas) produces most of the energy, about 87%, forming carbon dioxide. It is one of the main causes of the greenhouse effect, rising temperatures and climate change. To meet the growing demand for energy sources, new ones are constantly being sought. Energy dependence and instability of energy supply are a result of accelerated consumption of fossil fuels due to population growth and industrialization. Until 1973, non-renewable natural forms of energy (oil and coal) were consumed uncontrollably and without regard for future generations. This year is important in history as the year when people began to understand the importance of energy and the role of energy in human life. After 1973, it was realized that energy consumption should be better planned and used more rationally used. In that year, the world learned that major problems in energy supply will arise unless new forms of energy are provided. Projections show that the world's total petroleum resources will be depleted in 100-150 years, depending on the world market's demand for fuels produced from crude oil. Significant efforts are being made to develop renewable energy production (Rezić et al., 2014; Kolundžić, 2015). Pollution is to be prevented with alternative fuels, among others. Transport is responsible for up to 25% of carbon dioxide emissions, as fossil fuels are used in this sector (Mujčinović, Vukošić, 2017). For this reason, transport has become an essential segment in the struggle to reduce greenhouse gasses (Jegathese, Farid, 2014).

The importance of implementing biofuels in transport is highlighted in the EU documents White Paper at Renewable Energy Sources (1997) and Green Paper: Towards a European strategy for the security of energy supply (2000) (Kurevija, 2007). In 2003, the European Commission adopted the first Directive to promote the use of biofuels and other renewable fuels for transport. This directive provided the framework for biofuel market development policy and set indicative targets for biofuels (Jones et al., 2007). With the adoption of the above mentioned Directive, the European Union officially started to focus on renewable energy in transport fuels. Within the same Directive, three main objectives were set: reducing CO_2 emissions, improving security of supply and supporting rural economies (Mirabela, 2011).

The purpose of the Directive is to promote biofuels to partially replace mineral fuels in the transport of Member States with specific national targets to be achieved by 2010 (National Renewable Energy Action Plan, 2011-2020). Indeed, Directive 2003/30/ EC requires Member States to set a national target to ensure a minimum share of biofuels in total transport fuels placed on the market. The reference values were 2% share of biofuels in transport in 2005 and 5.75% in 2010. The 2% target set in the Directive was not reached in 2005 and the EU average for 2005 was 1.4% (Jones et al., 2007). Due to various problems such as limited national potential for production of raw materials, loss of state subsidies or high production costs, more than half of the countries in the Union failed to meet the target set for 2005 (Kurevija, 2007). Similarly, the Directive was subject to objections from green associations because the primary raw materials for biofuel production was still food products. It became a competition for food production and increased food prices. Mainly for this reason, Directive 2003/30/ EC on the promotion of the production and use of biofuels for transport is replaced by another Directive in 2009 (National Renewable Energy Action Plan, 2011-2020, Đurišić-Mladenović et al., 2016).

The Renewable Energy Directive - RED I (Directive 2009/28/ EC) was prescribed in 2009 by the European Commission (Directive 2009/28/ EC), which establishes a general policy for the promotion and production of energy from renewable sources in the Union. The main task of the Directive was to reduce greenhouse gas emissions and dependence on energy imports, to develop renewable energy sources and to increase energy efficiency. The Directive regulates the production and use of all forms of energy from renewable sources and biofuels. In addition to energy use, the Directive defines binding targets for the Member States to achieve by 2020 (Directive 2009/28/ EC). For this reason, it is known as "20-20-20", which means reducing greenhouse gas emissions by 20%, increasing the share of energy from renewable sources in total consumption to 20% and increasing energy efficiency to 20%. The same Directive requires that a percentage of 10% share of biofuels in transport be achieved by 2020. The achievement of this target is still based on biofuels obtained from the same raw materials as those used for food production. For this reason, restrictions are introduced on the maximum quantities of first-generation biofuels produced. The Directive refines the definition of biofuels, which are now liquid or gaseous fuels derived from biomass as the biodegradable fraction of products, waste and residues of biological origin from agriculture (including plant and animal matter), forestry and related production activities, including fisheries and aquaculture, and biodegradable industrial and municipal waste.

In addition, the Directive regulates the calculation of the share of renewable fuels in transport fuels, the analysis of greenhouse gas savings, the criteria for the sustainability of biofuel production and other requirements to be implemented in national regulations. The Directive introduced some sustainability criteria, including standards for the protection of high biodiversity value land from high carbon stock land. Nevertheless, it did not cover the issue of indirect land use change. Indeed, the growing demand for biofuels should not lead to the destruction of high biodiversity land through the application of this directive.

The European Union adopted Directive 2015/1513/EU amending Directive 98/70/ EC on the quality of petrol and diesel fuels and amending Directive 2009/28/ EC on the promotion of the use of energy from renewable sources. The Directive is essential because for the first time it formally limits the consumption of first generation biofuels and increases the share of advanced biofuels produced from raw materials not used for food production. Directive 2015/1513/EU is called "ILUC", which is derived from the English acronym: "Indirect Land Use Change". ILUC is a factor referred to as indirect land use change. It indicates the extent to which the use of arable land for biofuel production leads to the need to develop new arable land at the expense of the use of non-agricultural land in other parts of the world.
Deforestation is cited as the most significant negative trend in the expansion of agricultural production for biofuel production. Indirect changes in land use occur when the cultivation of raw materials for biofuels and biomass replaces traditional agricultural production of food for humans and animals. This additional demand increases land pressure and can lead to expansion of agricultural land into carbon-rich areas such as forests, wetlands and peatlands, causing further greenhouse gas emissions.

The ILUC Directive for the first time set a limit of 7% for the share of conventional biofuels for 2020. It obliged member states to introduce an indicative target for advanced biofuels for 2020, which should be 0.5% (it can be lower for objective reasons, but only according to the Member State's assessment). In addition, double scoring was introduced for all biofuels produced from non-food raw materials, including category 1 and 2 cooking oil and slaughterhouse waste.

EU Directive 2015/1513/EU confirmed that large-scale indirect change in land use related to greenhouse gas emissions could offset some or all greenhouse gas emissions savings from biomass fuels. The risks arising from indirect land use change are proportional to their impacts. Depending on the type of raw material, the level of additional demand for raw materials due to biofuels and how high carbon land is protected will depend on the risks of indirect change. The amount of greenhouse gas emissions caused by indirect land use change cannot be accurately determined. The greatest opportunities for indirect land use for biofuel production from raw materials have been identified. Significant expansion of the production area has been observed on land with high carbon stocks. For these reasons, it is appropriate to limit biofuels from biomass-based crops for food and feed production. In addition, a further restriction in the form of requests from Member States to set a specific and progressively decreasing limit value for biofuels, bioliquids and fuels produced from biomass used for food and feed crops where a significant expansion of the production area on land with high carbon stocks is observed is appropriate. Biofuels produced from low-risk biomass with indirect land-use change should be exempted from the specific and decreasing limit value. Directive 2015/1513/EU proposes to provide a long-term perspective for investment in sustainable biofuels with low risk of indirect land use change, with the primary objective of decarbonising the transport sector. Decarbonisation involves feedstocks that cause indirect land use change when used for biofuel production.

In 2017 and 2018, the Directive was created, amended and supplemented at RED II EU Directive 2018/2001/EU. It promotes renewable sources and provides guidelines for its implementation in the period from 2021 to 2030. The binding target of the European Union is to reduce greenhouse gas emissions by at least 40% below 1990 levels by 2030. For this reason, a binding Union target of at least 32% energy from renewable sources has been set. All members should identify their contribution to achieving this target through integrated national energy and climate plans. The national targets for 2020 should represent a minimum contribution from the Member States to the new framework by 2030. If a country fails to meet its share, it should take additional measures to achieve a baseline share. If it still fails, a Member State can make up the market shortfall through organized trading of energy shares from renewable sources (Directive 2018/2001/EU).

The Union's overall binding target for 2030 is for Member States to ensure that the share of renewable energy in the Union's total gross final energy consumption is at least 32% in 2030, although Member States may set their own more ambitious national targets. This is because the European Parliament went further and concluded, under the influence of the Paris Agreement, that it would be desirable to propose much more ambitious targets for renewable energy sources. Member States should define their contribution to this target in the context of their integrated national energy and climate plans. The target set at Union level would give Member States more leeway to achieve their greenhouse gas reduction targets in the most cost-effective way and according to their specific circumstances and respective renewable energy production capacity. In addition, it was proposed on European Commission to reduce the share of biofuels produced from feedstocks from 7% in 2020 to 3.8%. Such an offer was not accepted and these Member States should limit the share of conventional biofuels to 7% and maintain it until 2030.

The agreed rules also serve to create a stimulating environment for accelerating public and private investment in innovation and modernisation in all key sectors. Member states are to set out their contribution to achieving the target in their integrated national energy and climate plans. Each Member State will set out a detailed plan for achieving the targets in the integrated national energy and climate plans. The plan will be prepared by each Member State on the basis of the guidance set out in the Energy Union Management Regulation. The national targets set for 2020 should represent the minimum contributions of Member States in the new framework by 2030.

The share of biofuels, bioliquids and biomass fuels produced from crops used for the production of food and feed that have a high risk of indirect land use change and have been identified as having a significant expansion of production area on high carbon stock land shall not exceed the consumption of those fuels in 2019, unless they are certified as biofuels with a low risk of indirect land use change. From 31 December 2023 until 31 December 2030 at the latest, this limit will be gradually reduced to 0%. In this way, the EU limits the production and use of HIGH ILUC biofuels (currently only palm oil) to 0% by 2030. Biofuels used to meet the Union's targets set out in RED II and those benefiting from the scheme must meet sustainability and greenhouse gas emission reduction criteria. Harmonization of those criteria for biofuels and bioliquids is key to achieving the Union's energy policy objectives. The setting of limits at Union level should not prevent Member States from providing for lower limits for the quantities of biofuels and other bioliquids produced from cereals and other starch-, sugar- and oilseed-rich crops calculated without restriction at national level in accordance with the objectives of RED II.

Unlimited opportunities for the use of such biofuels and other bioliquids. The promotion of feedstocks that have a low impact on indirect land use change when used for biofuels is necessary because of their contribution to the decarbonisation of the economy.

LEGISLATION IN THE REPUBLIC OF CROATIA

The flexibility of Member States, including the Republic of Croatia, in achieving the targets based on the Directive RED II depends on whether the State distinguishes between different fuel suppliers and energy carriers when determining the way to achieve the required targets. The State is free to choose the most appropriate way to promote renewable energy sources for transport and to distinguish between different types of conventional biofuels and to set different limit values for each generation of biofuels. Indeed, the State may set lower limits for first generation biofuels or higher limits for second generation biofuels produced from lignocellulosic biomass or waste. As Member States have to transpose the provisions of the Directive RED II into national law, some national legislative acts and national plans have to be adopted.

The Act on Biofuels for Transport (Official Gazette, 65/09) aims to achieve sustainable development in transport by reducing the negative impact on the environment, improving the security of fuel supply in an environmentally friendly way and meeting consumer demand for fuel. The Republic of Croatia, as a member of the Union, should fulfill its international obligation in the form of reducing greenhouse gas emissions by promoting the use of biofuels in transport as a substitute for diesel or motor gasoline (Stupin, 2015). The use of biofuels and advanced biofuels and electricity from renewable energy sources in transport realizes the interests of the Republic of Croatia in the field of energy, which are determined by the Energy Development Strategy of the Republic of Croatia (Official Gazette, 130/09). Laws and various regulations govern the implementation of energy activities, especially with the intention of achieving the national target for energy use from renewable energy sources in all modes of transport in 2020, which is 10% of total energy consumption for transport within the Republic of Croatia.

World demand for agricultural products is growing, and part of this increase in demand is likely to be met by increasing the amount of land in agricultural use. Reconstruction of land that is severely degraded and therefore cannot be used for agricultural purposes is one way to increase agricultural land. The sustainability program should encourage the use of such restored land.

The promotion of biofuels and fuels derived from biomass will contribute to the growth of demand for agricultural products in the Republic of Croatia.

Biofuels may be placed on the market as pure biofuels or as biofuels blended with diesel or petrol only if they meet the prescribed technical requirements for fuel quality established under the conformity assessment procedure. They must also be labeled in accordance with the fuel quality requirements. To ensure that the target is met, an obligation has been introduced for distributors who place diesel or motor gasoline on the market for powering motor vehicles to market biofuels in a certain percentage. Obligated parties that adjust biofuels to the needs of the Republic of Croatia are obliged to report to the relevant ministries on the placing of biofuels on the market. Suppose in the previous calendar year A distributor of biofuels did not place the prescribed amount of biofuels on the market. In that case, it is obliged to pay a special environmental levy for not placing biofuels on the market according to the polluter pays principle.

Each Member State shall adopt a National Renewable Energy Action Plan setting national targets for the share of energy from renewable sources for 2020, taking into account cooperation between local, regional and federal authorities, planned statistical transfers or joint projects, national strategies for the development of existing biomass sources for different uses and compliance measures. Member States should draw up national renewable energy action plans containing information on sectoral targets, taking into account that biomass is used in different ways. It is therefore important to mobilize new biomass sources.

National Renewable Energy Action Plan for the promotion of biofuel production and use in the Republic of Croatia was prepared in accordance with the Act on Biofuels for Transport (Official Gazette 65/09). The National Renewable Energy Action Plan is a document adopted for ten years (for the period from 2011 to 2020). It is in accordance with Directive 2009/28/ EC and the Energy Development Strategy, Sustainable Development Strategy, Agriculture Strategy and National Forestry Strategy and policy, which establishes a policy to promote the increase of production and use of biofuels in transport in the Republic of Croatia.

The labeling of a blend of biofuels with fossil fuels is obligatory in the Republic of Croatia as it is at the level European Union. Namely, blends of ethanol and gasoline are marked with the E sign and number, i.e. "E" numbers describing the percentage of ethanol fuel in the blend by volume. For example, E85 is a blend of 85% anhydrous ethanol and 15% gasoline. The most common designations are E5, E10, E85 and E95. The standards used in European Union are EN 15736 and EN 228, which prescribe ethanol characteristics and blend quality. Ethanol is not the only fuel that can be blended with fossil fuels. Biodiesel can be blended or mixed with fossil diesel in a smaller amount of 1.5-5% or in a larger amount of 5-30%. Such blends have a B symbol and number. The B stands for biodiesel and the number is a percentage. There are B5, B7, B20 and B100 on the market. The European standard for biodiesel is EN 14214 This standard specifies the requirements and test methods for fatty acid methyl ester (FAME) for diesel engines. Diesel fuel B7 is provided with up to 7% FAME (Đurišić-Mladenović i sur., 2016). The European standard EN 590 defines test methods and properties of diesel fuel.

CONCLUSION

Increased use of energy from renewable sources plays a key role in promoting energy security, sustainable energy at affordable prices and technological development. It also offers environmental, social and health benefits, as well as significant employment opportunities, particularly in rural and remote areas. It opens up the possibility of regional development in areas of low population or in areas of partial deindustrialisation. The European Union believes that renewable energy sources should partially replace fossil fuels, so it aims to expand and promote the use of biofuels and improve their production. By setting national targets, the Republic of Croatia will determine the contribution of the renewable energy sector, including biofuels. The recommendations of the European Union are certainly the transition to the second generation of biofuels with low greenhouse gas emissions.

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CORROSION INHIBITION OF PEKTIN C ON ST-34 IN HYDROCHLORIC ACID

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT:
Construction materials in the form of any products are subject to unintentional or harmful changes, occurrences and processes that reduce their usability. The destruction of construction materials is aimed to be slowed down or prevented by measures and procedures of a special technological discipline - material protection, which is usually called surface protection, since harmful occurrences and processes mostly begin on the surface of the product. In addition to the many protective methods that are used, corrosion inhibitors have a special place due to their specificity and widespread use. Based on the performed tests and their analysis, it was determined that the inhibition efficiency obtained by electrochemical measurements is in good correlation with the results obtained by the FTIR method. Impedance measurements of steel St 37-4 Pectin C in the tested media show corrosion resistance. Pectin C in 3.5% HCl at a concentration of 2.0 g / l increases the value of the charge transfer resistance and the increases of the size of the absolute impedance in the Bode diagram, which further confirms the improved resistance to corrosion of steel.

KEYWORDS: Corrosion, Pectin C, EIS, FTIR

INTRODUCTION

Corrosion is a natural process that shortens the life of structures, causes losses in production, endangers human health and affects environmental disasters. In order to reduce, various protective measures are applied. Due to the prevalence and specificity of application, corrosion inhibitors have a special place. With the development of techniques and technology, environmentally friendly inhibitors are gaining importance.

Table 1. Development of corrosion inhibitors and main parameters of their choice [2]

Time period	Required property	Type of the inhibitor
Before 1960	Efficacy	Chromates, phosphates, nitrates, borates, silicates, zinc inhibitors
1960-1980	Economy	Polyphosphates, gluconates, molybdates, vitamins
Since 1980	Ecological acceptability	Tannins, natural polymers, vitamins

Adding inhibitors to aggressive environments in small concentrations, it can greatly reduce the corrosion rate. The use of inhibitors has established itself today and has wide application. When choosing the type of inhibitor bear in mind the metal to be protected, the environment in which the metal is located, the conditions, toxicity and economy of the inhibitor [1]. Table 1. provides an overview of the development of inhibitors that have been used and which inhibitors should be used, and the main parameters of their selection:

Research by Mohammad M. Faresa et all has proven that the use of a promising green eco-friendly pectin is a natural polymer on the surface of an aluminum metal in an acidic medium. The highest inhibitory efficacy obtained at 10 ° C using pectin at a concentration = 8.0 g / L was 91%, while at 40 ° C it dropped markedly to 31%. As the pectin concentration increased, higher activation energy, enthalpy of activation, and entropy of activation were obtained. In the presence of 2.0 M HCl, the aluminum sheet showed longitudinal parallel grooves along with a huge amount of irregular deep voids distributed along the sheet, while in the presence of inhibitors and acid medium the number of deep voids decreased [3].

Adsorbed inhibitors in acidic solution act by stopping the cathodic hydrogen excretion reaction or the anodic dissolution of the metal or even both reactions. This effect occurs as a consequence of the influence on the electrical bilayer, reduction of metal reactivity, partial precipitation of inhibitors and formation of a physical barrier. The decrease in the reactivity of the metal occurs as a result of the adsorption of the inhibitor on the active sites of the electrode, and not on the entire surface, reducing the area of the cathodic or anodic reaction or both.[6]

EXPERIMENTAL

The material used for the test is St 37-4, and the chemical composition is shown in Table 2.

The condition for conducting and the accuracy of the analysis depends on the surface preparation of the tested steels. The preparation of steel was performed by mechanical and chemical processes.

To perform the experimental part, in addition to the mentioned steel, the eco inhibitor Pectin C in an acidic medium of 3.5% HCl was used.

Table 2. Chemical composition St 37–4

Sample	Fe	C	Si	Mn	P max	S max	Cr	Ni
St 37-4	99,39 – 99,63%	≤0,17	≤0,04	≥0,35	0,04	0,04	-	-

Pectin is a polysaccharide, made up of galactouronic acid units. Pectins differ from each other in the length of the polymer chain, complexity, as well as the structure of the monosaccharide unit. One third of the dry cell wall is represented by pectins, and the highest concentrations of pectin are found in the middle lamella of the cell wall with a gradual decrease through the primary wall, towards the plasma membrane. Most commercial pectins are obtained from lemon peel or soup pomace. Apple puree contains 10-15% dry matter-based pectin, and citrus korar 20-30%. [4]

According to the chemical structure shown in Figure 1, pectin has a large amount of associated D-galctrouronic acid residues. D-galactouronic acid is a cyclic monosaccharide with one carboxylic acid on the side and four hydroclic groups. A small proportion of the carboxyl groups in the D-galactouron residues are esterified and on the side arcs the residue can deprotonate and form anions.

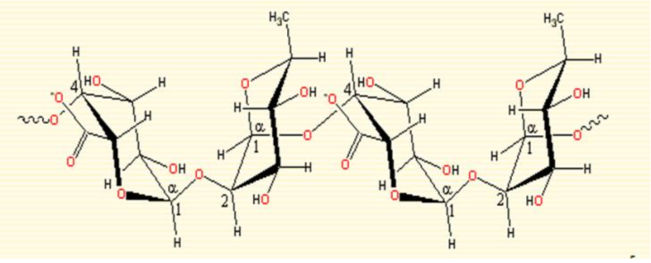

Figure 1. Chemical structure of Pectin C

Electrochemical methods were used to determine the corrosion behavior of St37-4 steel in 3.5% HCl without and in the presence of inhibitors. Electrochemical measurements were performed on Potentiostat / Galvanostat Model 263A in a corrosion cell (Figure 24) model K47 with a saturated calomel electrode as a reference electrode, graphite electrodes as counter-electrodes and steel (DIN 2391 St 37.4 and X5 CrNi 18-10) as the working electrode. [2]; [8]

Alternating current methods are non-destructive methods, because there is no disturbance of the system, so the methods of electrochemical impedance spectroscopy (EIS) are preferred when testing at the phase boundary. The method is based on the response of a circuit to alternating voltage or current as a function of frequency.

In addition to the electrochemical method, the FT-IR spectroscopic technique (Fourier Transform Infrared Spectroscopy Technique) was used. FTIR spectrum of Mimosa tannin and Pectin C was measured on Nicolet iS10 FTIR Spectrophotometer-Thermo Fisher Scientific.

RESULTS AND DISCUSSION

The aim of the measurement is to determine the mechanism of dissolution of St 37.4 steel in 3.5% HCl without and in the presence of tested inhibitors. The pictures show Bode's diagrams (Figure 2 – 3). The points on the diagrams represent the experimentally obtained test results while the lines represent the simulated curves corresponding to the constructed models of the electrical circuit shown in the figure.

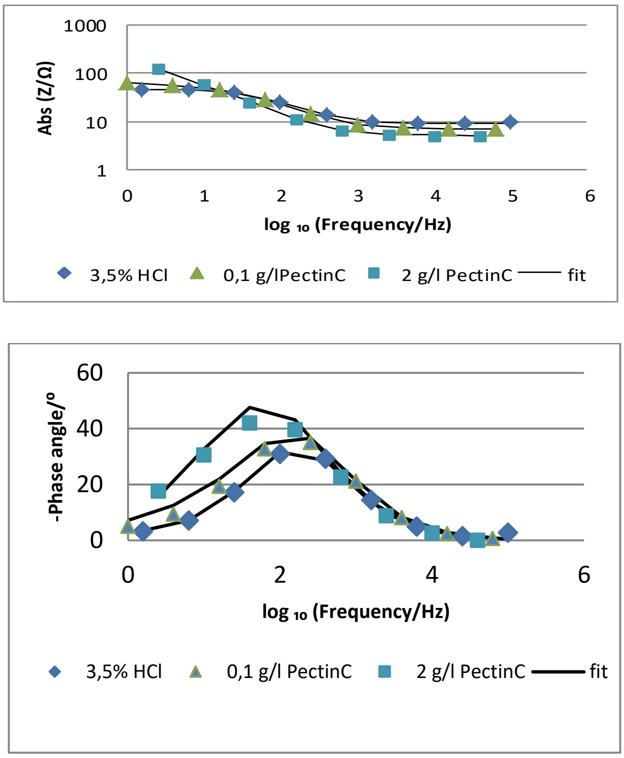

Figure 2. Bode curves St 37.4 steel in 3.5% HCl with and without PectinC inhibitor

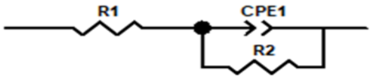

Figure 3. Equivalent electrical circuit for modeling experimental impedance measurement results

The resistance and capacitance values shown in Table 3. obtained by adjusting the experimental results and the equivalent circuit parameters show that PectinC caused an increase in the R2 value, which is also noticeable with the increase in the magnitude of the absolute impedance in the Bode diagram, ie. PectinC improves the corrosion resistance of steel St 37-4.

Table 3. Electrochemical impedance parameters of corrosion St 37.4 steel in 3.5% HCl with and without the presence of Pectin C inhibitors

	R_1 (Ω)	CPE			R_2 (Ω)
		Q	n	C (μF)	
without inhibitor	8,645	0,0002136	0,8096	64,67	38,64
0,1 g/l	6,856	0,00032234	0,77275	102,0	52,73
2 g/l	5,055	0,00041232	0,81371	191,1	79,84

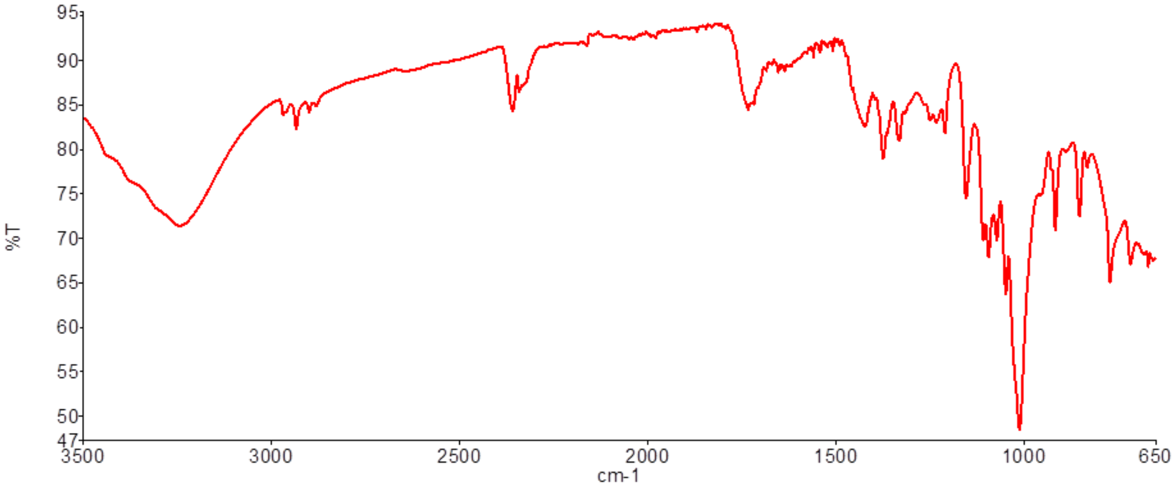

Figure 4. FTIR spectrum of pectin C

The presence of carboxyl and hydroxyl groups in the pectin molecule, as well as the glycosidic bonds, makes the FTIR spectrum of pectin relatively complex, especially in the region below 1500 cm-1. The stretching vibration of the O – H bond was recorded at 3244 cm – 1 as a broad band of medium intensity. Several bands of low intensity in the range of 2970-2900 cm-1 correspond to the vibrations of the C-H bonds. The band of lower intensity at about 1733 cm-1 corresponds to the stretching vibration C = O and indicates the presence of an acetyl group in the pectin. The band of strong intensity at 1011 cm-1 corresponds to C-O-C symmetrical vibrations.

Table 4. presents the results of the analysis of adsorption bonds and intensities of functional groups of commercial Pectin from apples.

Table 4. Overview of adsorption bonds and intensities of functional groups of commercial Pectin from apples determined by FTIR technique [10]

Adsorption binding	Functional groups	Intensity
3438,0	O-H stretching	Strong bond
2923,9	C-H stretching symmetrically, asymmetrically	Sharp
1750,3	C=O esterified	Strong
1636,1	COO^- asymmetric stretching	Strong
1446,4	COO^- asymmetric stretching	Weak
1381,7	C-H bending	Weak
1300-1000	C-O elongation	Weak

CONCLUSION

The concentration range used for the assay was 0.1 to 2 g / l of eco inhibitor. Inhibitors have been found to reduce the rate of corrosion. Impedance measurements of steel St 37-4 Pectin C in the tested media show corrosion resistance. Pectin C in 3.5% HCl at a concentration of 2.0 g / l increases the value of the charge transfer resistance and increases the size of the absolute impedance in the Bodeo diagram, which further confirms the improved resistance to corrosion of steel.

FTIR results of PectinC indicate the presence of functional groups -OH and -COOH which contain oxygen atoms with solitary pairs that act as adsorption centers in order to reduce corrosion, ie. represent places where the formation of chelates is possible.

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INVESTIGATION OF THE INFLUENCE OF MGO AND CAO CONTENT ON THE QUALITY OF TECHNICAL CERAMICS

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT:
In this paper, the influence of MgO and CaO content on the quality of technical ceramics (which originally represents the Al_2O_3 - SiO_2 - CaO - MgO system) has been investigated. Therefore, quality tests were performed on samples where the contents of CaO and MgO were taken as variable values. Based on the obtained test results and their analysis, certain characteristics of ceramics are defined with the different percentages of individual oxides content in 98.2 - 99% Al_2O_3.

KEYWORDS: MgO, CaO, Technical ceramics

INTRODUCTION

Ceramic materials are inorganic non-metallic materials. They consist of metallic and non-metallic elements, interconnected by ionic and / or covalent bonds. In Anglo-Saxon languages, the term "ceramics" includes glass, enamel, glass - ceramics and inorganic binders (lime, cement). Ceramic materials are formed at room temperature, from dry mass. The final properties are achieved after firing at high temperatures (sintering).[1] In ceramic technology, the molding process occurs before the heat process, while during heat treatment the ceramic shrinks (volume changes). Only after sintering, ceramics get their real characteristics, ceramic material is formed.[2] Research in the field of materials for the last 15 years has been strongly focused on the development of technical ceramics. By studying the composition, structure and technology of shaping, they want to improve some unfavorable properties of classical ceramics; fragility, unpredictability of behavior in complex load conditions, susceptibility to cracking, resistance to heat stroke and heat shocks. At the same time, the field of application expands, from the working conditions where technical ceramics were primarily used; resistance to various aggressive media and high temperatures, high hardness requirements, to additionally mechanically or tribologically loaded parts.

Despite large investments in research, a number of serious problems remain that prevent the even wider application of ceramics for typical structural parts. The principles of construction with ceramics are significantly different from those of metallic materials, and the behavior under the action of impact and variable mechanical load has not yet been fully explained - such as how to consume excess energy without breaking. Furthermore, due to the significant influence of the quality of the raw material and technological parameters of shaping on the final properties of ceramic products, there is a large variation in the value of properties from nominal and generally different quality of similar parts.

THEORY

The production of technical ceramics takes place in several steps. It is these steps in the production process that affect the underlying properties. In addition to the molding and sintering processes, the selection of powder for production also plays an important role in the structure or properties of ceramics. In Figure 1, the factors that influence the microstructure of ceramic materials can be seen.

In the whole complex production process, a certain powder, shaping and sintering process together influence the creation of a crucial microstructure and thus the desired properties of the product.[13]

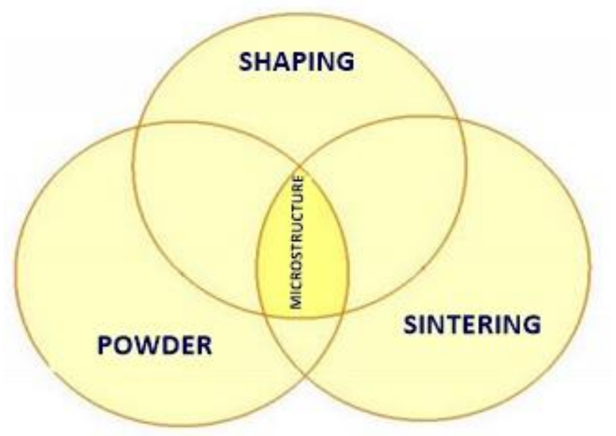

Figure 1. Effects on the microstructure of ceramic materials

EXPERIMENTAL

The aim of the experimental part of this paper was to examine the influence of MgO and CaO content on the quality of technical ceramics, which originally represents the Al_2O_3 - SiO_2 - CaO - MgO system. Therefore, quality tests were performed on samples where the contents of CaO and MgO were taken as variable values. Based on the obtained test results and their analysis, certain characteristics of ceramics are defined when we have different percentages of individual oxides content in 98.2 - 99% Al_2O_3.

The experimental part is divided into three phases, as follows:

- Preparation of powders (ceramic materials) for making samples,
- Sample production (powder pressing, machining and sintering),
- Quality control of prepared samples.

MATERIALS AND METHODS

Aluminum oxide ceramics on which the test was performed was made in the company Almatis from Germany, and the preparation of powders (ceramic materials) for the experiment was done in the Factory of car spark plugs and industrial ceramics Enker d.d. from Tešanj. Determination of the chemical composition of the starting material of aluminum oxide was performed by the manufacturer of raw materials (Almatis, Germany) and the results of chemical analysis of prepared powders (ceramic materials) were obtained in the laboratories of the quality management department of the spark plugs factory Enker d.d.

Chemical composition of prepared powders (ceramic materials):

• SiO_2	0.0093%
• CaO	0.0270%
• Na_2O	0.06%
• Fe_2O_3	0.0225%
• B_2O_3	0.0129%
• Al_2O_3	99.86%

Powder (ceramic material) is prepared by weighing the components in a mill, where it is ground for 24 hours. When the grinding operation is completed, the ceramic material is transferred to a mixer, where additives are added and mixing is performed. Finally, from the mixer, the ceramic material - "*schliker*" is pumped to the dryer where it is dried and powder is formed. After cooling, the powder goes to further technological processing. For conducting experimental tests, three powders of different composition were prepared, as follows:

- Powder 1 (P1): 98.5% Al_2O_3; 0.417% CaO; 0.40% MgO; 0.40% SiO_2
- Powder 2 (P2): 99.1% Al_2O_3; 0.21% CaO; 0.20% MgO; 0.40% SiO_2
- Powder 3 (P3): 98.2% Al_2O_3; 0.62% CaO; 0.60% MgO; 0.40% SiO_2

Two cassettes / sagers (118 PCS) of ceramic parts of the car spark plug, ie insulators, were prepared from each powder. Since MgO and CaO show their influence in the Al_2O_3 - SiO2 - CaO - MgO system at different sintering temperatures, the samples were sintered at two temperatures, 1550°C and 1600°C.

PRODUCTION OF SAMPLES

After the powders are prepared, the next operation in the technological process of production of samples, ie insulators for the production of car spark plugs, is pressing, then molding.

The most efficient method of mass production is isostatic pressing and shaping of ceramic molding by profile grinding. The grinding unit is located within the press itself and is interconnected by a conveyor belt. Isostatic pressing means even pressure on the ceramic material from all sides.

This significantly reduces the problems of unevenness due to pressing and allows even compaction of larger volumes of ceramic material, including shapes with a large ratio of length to diameter. Raw ceramic insulators are stacked in refractory packaging (cassettes - sagers) and then sent for sintering operation.

Sintering, ie densification of the molding, is basically the removal of pores between particles (followed by shrinkage) of the ceramic material.

Figure 2. Ceramic part of the car spark plug (before and after sintering)

SAMPLE ANALYSIS

Determination of density

Determination of the density of the tested samples was done in the factory of spark plugs and industrial ceramics Enker d.d. on apparatus from which the density of ceramic samples is read directly after sintering. 10 samples were analyzed from each sager cassette.

Thermo test

The thermal test is performed by immersing the top of the tested sample (insulator) in molten tin to a depth of 7 mm. At a temperature of 625°C, for a period of 20 s, the ceramic part immersed in molten tin must not show cracks. Since up to 625°C there was no cracking of the insulator from any of the three prepared materials, the test was performed until the cracking of the samples occurred. The temperature was increased by 25°C.

Hardness

The hardness of ceramics is determined by the Vickers method, on the device of the control sector in the factory of spark plugs and industrial ceramics Enker d.d Tešanj. The basic principle, as with all common measures of hardness, is to observe a material's ability to resist plastic deformation from a standard source. The basic condition for successful analysis and correct results is that the sample is representative and well prepared. The techniques involved in preparing the sample are as follows: cutting the sample, watering the sample with polymeric material, grinding, polishing, corrosion.

Porosity

The porosity of the prepared materials is determined using an optical microscope, on the same samples on which the hardness of the prepared materials was determined. Closed porosity is determined by microscopic analysis, and the results are read directly on the device. Closed porosity represents pores that are not interconnected. Closed porosity ceramics in different percentage values, depending on the conditions, are most often used in the refractory industry and thermal insulation.

RESULTS AND DISCUSSION

Test results of density of prepared materials

The results of measuring the density of the prepared samples are given in Tables 1, 2 and 3.

Table 1. Values of density of material samples P1

Material	Sample number	γ (g/cm^3) (Ts = 1550°C)	γ (g/cm^3) (Ts = 1600°C)
P1	1	3.770	3.855
	2	3.771	3.853
	3	3.780	3.857
	4	3.776	3.850
	5	3.778	3.852
	6	3.790	3.857
	7	3.776	3.855
	8	3.781	3.851
	9	3.760	3.852
	10	3.766	3.854

Table 2. Values of density of material samples P2

Material	Sample number	γ (g/cm^3) (Ts = 1550°C)	γ (g/cm^3) (Ts = 1600°C)
P2	1	3.669	3.850
	2	3.691	3.853
	3	3.675	3.859
	4	3.688	3.850
	5	3.671	3.852
	6	3.645	3.857
	7	3.776	3.855
	8	3.662	3.856
	9	3.669	3.852
	10	3.661	3.855

Table 3. Values of density of material samples P3

Material	Sample number	γ (g/cm^3) (Ts = 1550°C)	γ (g/cm^3) (Ts = 1600°C)
P3	1	3.752	3.854
	2	3.770	3.853
	3	3.774	3.854
	4	3.688	3.859
	5	3.725	3.852
	6	3.645	3.853
	7	3.726	3.855
	8	3.595	3.856
	9	3.669	3.856
	10	3.668	3.855

The results show that the sintering temperature T = 1550°C is not sufficient to achieve quality, ie density corresponding to the density of the material with 98.2 - 99% Al_2O_3. The sintering temperature T = 1600°C is sufficient to achieve a certain quality of the material. For materials above 98.5% Al_2O_3, the minimum density is 3.82 g/cm^3.

Results of thermal shock of prepared materials

Tables 4, 5 and 6 give the results of thermal shock of prepared ceramic materials.

Table 4. Results of thermal shock for material P1

Material	Ts = 1550 (°C)	Test temperature (°C)			Ts = 1600 (°C)	Test temperature (°C)		
	Sample number	750	850	900	Sample number	750	850	900
P1	1	✓	-	-	1	✓	✓	✓
	2	✓	-	-	2	✓	✓	✓
	3	✓	-	-	3	✓	✓	✓
	4	✓	-	-	4	✓	✓	✓
	5	✓	-	-	5	✓	✓	✓
	6	✓	-	-	6	✓	✓	✓
	7	✓	-	-	7	✓	✓	✓
	8	✓	-	-	8	✓	✓	✓
	9	✓	-	-	9	✓	✓	✓
	10	✓	-	-	10	✓	✓	✓

Table 5. Results of thermal shock for material P2

Material	Ts = 1550 (°C)	Test temperature (°C)			Ts = 1600 (°C)	Test temperature (°C)		
	Sample number	750	850	900	Sample number	750	850	900
P2	1	✓	✓	-	1	✓	✓	✓
	2	✓	✓	-	2	✓	✓	✓
	3	✓	✓	-	3	✓	✓	✓
	4	✓	✓	-	4	✓	✓	✓
	5	✓	✓	-	5	✓	✓	✓
	6	✓	✓	-	6	✓	✓	✓
	7	✓	✓	-	7	✓	✓	✓
	8	✓	✓	-	8	✓	✓	✓
	9	✓	✓	-	9	✓	✓	✓
	10	✓	✓	-	10	✓	✓	✓

Table 6. Results of thermal shock for material P3

Material	Ts = 1550 (°C)	Test temperature (°C)			Ts = 1600 (°C)	Test temperature (°C)		
	Sample number	750	850	900	Sample number	750	850	900
P3	1	✓	-	-	1	✓	✓	-
	2	✓	-	-	2	✓	✓	-
	3	✓	-	-	3	✓	✓	-
	4	✓	-	-	4	✓	✓	-
	5	✓	-	-	5	✓	✓	-
	6	✓	-	-	6	✓	✓	-
	7	✓	-	-	7	✓	✓	-
	8	✓	-	-	8	✓	✓	-
	9	✓	-	-	9	✓	✓	-
	10	✓	-	-	10	✓	✓	-

The results show that the samples that were sintered at T_S = 1550°C, resistant to thermal shock up to 750°C, while the samples that were sintered at T_S = 1600°C, except for material P3, at a temperature of 900°C have shown cracks, which shows that this ratio of oxides in the material has the lowest resistance to thermal shock.

Hardness test results of prepared ceramic materials

Tables 7, 8 and 9 give the results of hardness measurements (HV 5) for prepared ceramic materials.

Table 7. Display of hardness (HV 5) results for material P1

Material	Ts = 1550°C		Ts = 1600°C	
	Sample number	Hardness HV 5	Sample number	Hardness HV 5
P1	1	1303	1	1524
	2	1283	2	1648
	3	1314	3	1486
	4	1346	4	1552
	5	1303	5	1524
	6	1283	6	1486
	7	1304	7	1684
	8	1245	8	1369
	9	1303	9	1346
	10	1225	10	1314

Table 8. Display of hardness (HV 5) results for material P2

Material	Ts = 1550°C		Ts = 1600°C	
	Sample number	Hardness HV 5	Sample number	Hardness HV 5
P2	1	1379	1	1449
	2	1225	2	1369
	3	1303	3	1346
	4	1225	4	1283
	5	1225	5	1245
	6	1021	6	1303
	7	1060	7	1606
	8	1379	8	1369
	9	1303	9	1552
	10	1283	10	1225

Table 9. Display of hardness (HV 5) results for material P3

Material	Ts = 1550°C		Ts = 1600°C	
	Sample number	Hardness HV 5	Sample number	Hardness HV 5
P3	1	1225	1	1606
	2	1303	2	1552
	3	1346	3	1684
	4	1060	4	1552
	5	1103	5	1314
	6	1379	6	1369
	7	1303	7	1486
	8	1245	8	1524
	9	1225	9	1606
	10	1162	10	1314

Porosity test results of prepared ceramic materials

The percentage of closed porosity was determined by microscopic analysis of the examined samples, which is shown in the report. For the material sample (1), sintering temperature T = 1600°C, a closed porosity of 1.36% was determined, the microscopic view is shown in the figure 3. On samples sintered at temperature T = 1550°C, the measured closed porosity was 16.2%.

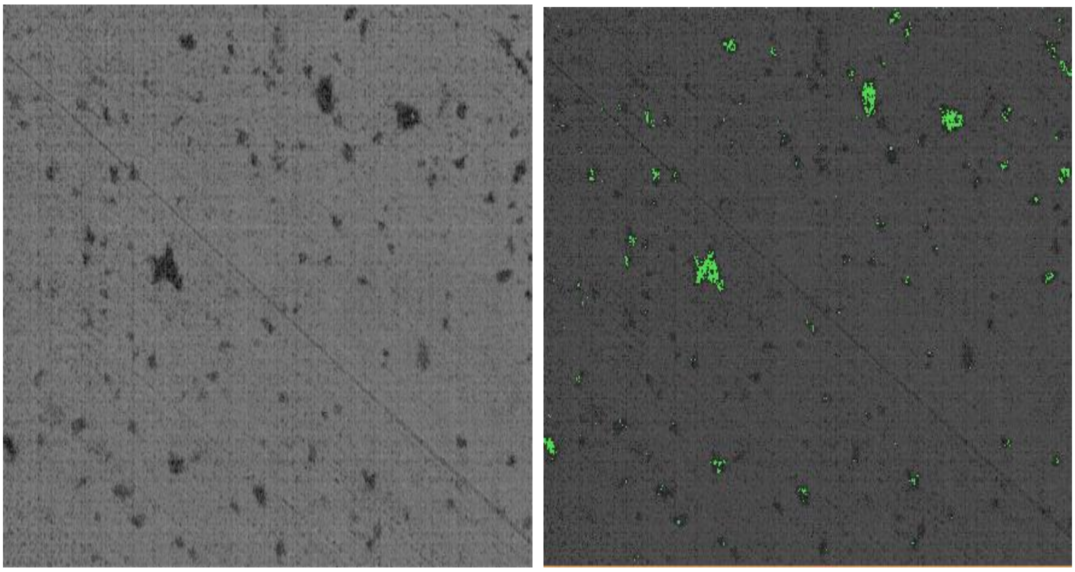

Figure 3. Original (a) and microscopically processed (b) image of the material sample surface (P1)

Figure 4 shows the number of grains in areas of certain sizes for the analyzed sample.

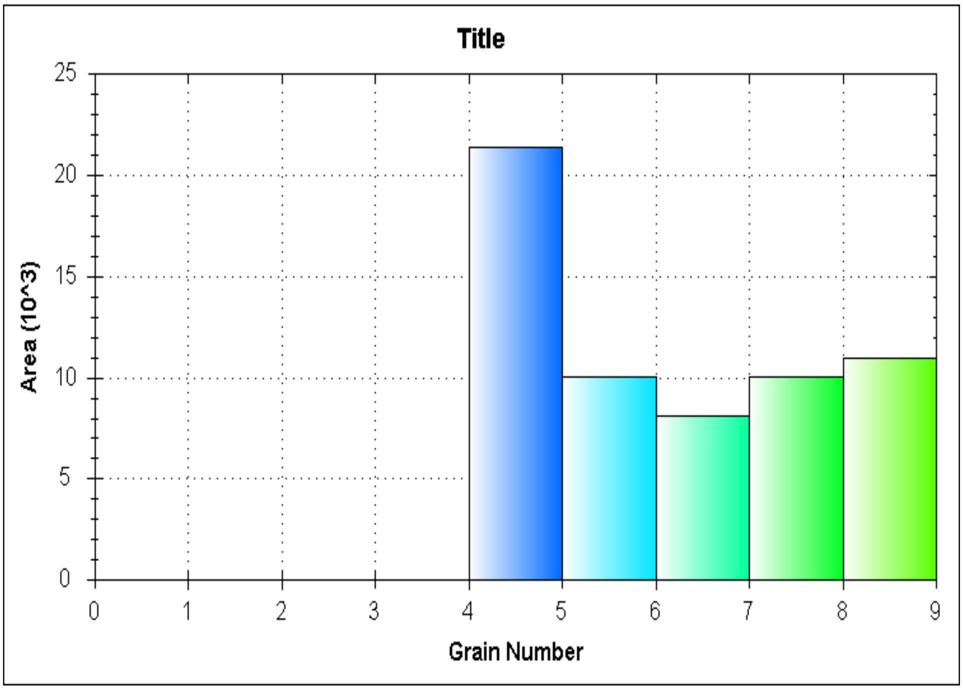

Figure 4. Grain size distribution for material P1, Ts = 1600°C

For material (P2), sintering temperature T = 1600° C, the percentage of closed porosity is 12%, the microscopic view is shown in Figure 5. On samples sintered at a temperature T = 1550°C, the closed porosity is 24%.

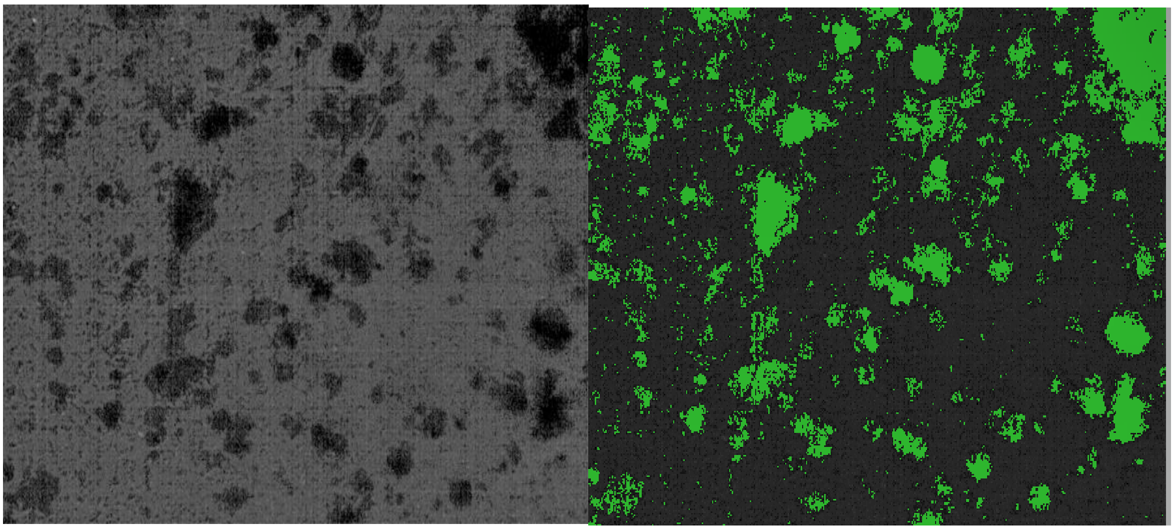

Figure 5. Original (a) and microscopically processed (b) image of the material sample surface (2)

Figure 6 shows the number of grains in areas of certain sizes for the analyzed sample.

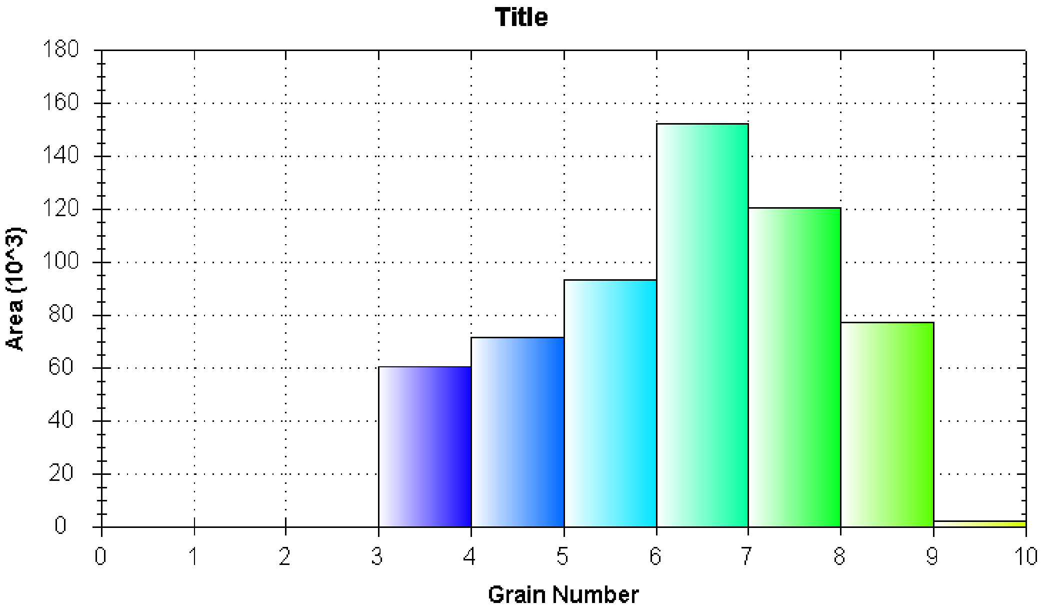

Figure 6. Grain size distribution for material P2, Ts = 1600°C

For material (P3), sintering temperature T = 1600°C, the percentage of closed porosity is 6.5%, the microscopic view is shown in the figure 7. On samples sintered at temperature T = 1550°C, the closed porosity is 18%.

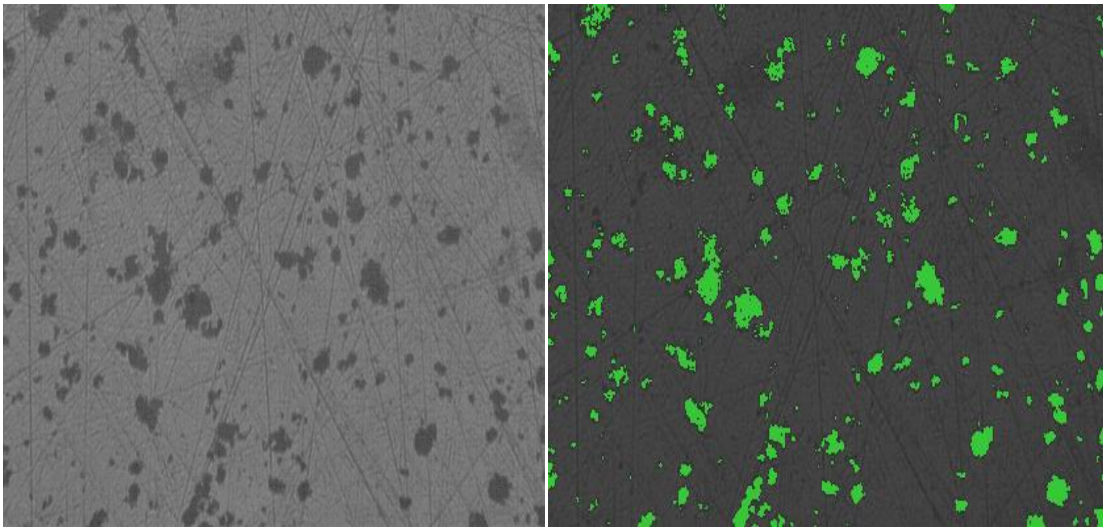

Figure 7. Original (a) and microscopically processed (b) image of the surface of the material sample P3

Figure 8. shows the number of grains in areas of certain sizes for the analyzed sample (P3).

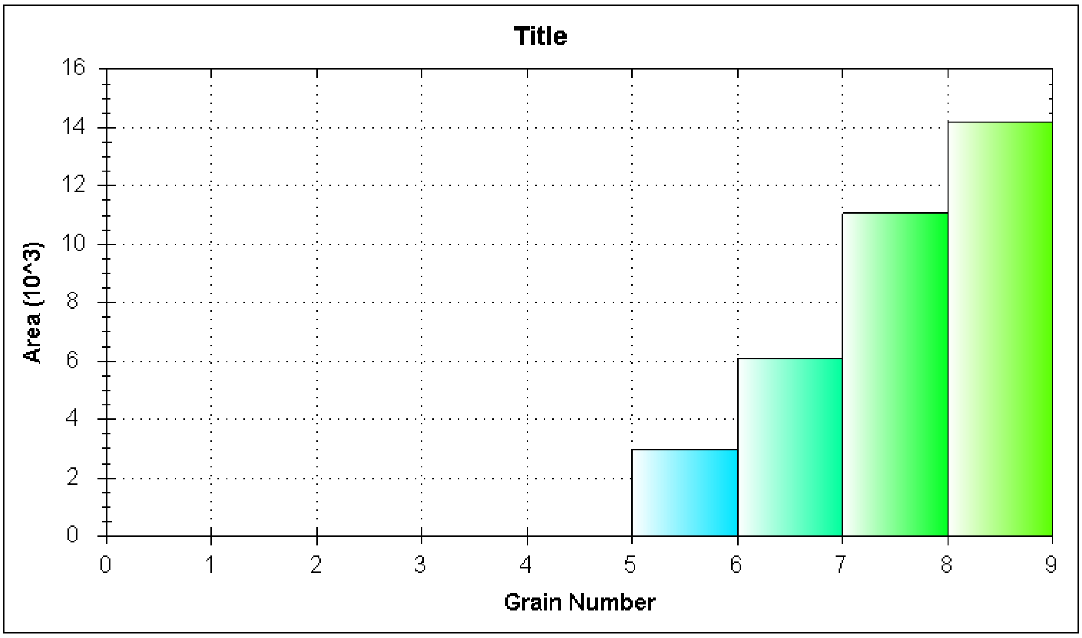

Figure 8. Grain size distribution for material (P3), Ts = 1600°C

CONCLUSION

The choice of raw material has a great impact on the end result. Each raw material has certain characteristics that in different processes of preparation, sintering, processing can show specificity in behavior.

It is necessary to know the action of raw materials, to know in which direction to go when developing new materials, or when determining the purpose of a particular finished material.

The analyzed materials, regardless of the changes in composition, which are not large, showed certain similarities but also certain differences in behavior. This means that when choosing materials for the production of ceramic segments, each of them can be a good choice, depending on the customer's requirements.

If the customer's desire is high resistance to abrasion, followed by withstanding elevated temperatures, according to these results we see that we can use the material P1 (because it met the requirement for hardness and thermal shock).

However, for applications where high resistance to thermal shocks (≥ 400 °C) is required, the choice will be a material with a higher percentage of porosity.

To achieve the prescribed values of specific weights and that for materials with ≥ 98% is a minimum of 3.82 g /cm^3, from the obtained results it can be seen that the temperature of 1550 °C is insufficient. A temperature of 1600 °C is sufficient to achieve specific weights, even when there is a change in the content of magnesium and calcium oxide. The most important ratio in the material is the oxide ratio (SiO_2:MgO, SiO_2:CaO) as well as the content of the basic oxide (Al_2O_3).

For materials above 98% Al_2O_3, it is best to determine empirically the ratio of SiO_2:MgO:CaO oxides, which will give the best results when tested for the intended purpose.

When determining resistance to thermal shock, for material P1 samples with sintering temperature of 1550 °C are resistant up to 750 °C, while samples with sintering temperature of 1600 °C, except for material P3, all passed the test. Considering these results, we can conclude that ceramic materials with ratios as in materials P1 and P2 at a sintering temperature of 1600 °C have higher resistance to thermal shock and such materials can be recommended for future research of this type.

Satisfactory values for hardness were shown by samples of materials P1 and P3, because they had an average value of hardness HV5 ≥ 1500 on testing.

Materials with higher specific gravity have lower porosity. The production of materials with a higher percentage of porosity (open and closed) is on the rise, because these materials are characterized by better resistance to thermal shocks, and some to the influence of aggressive media. This is one of the better ways to know the influence of certain oxides, such as CaO and MgO, on the formation of a material with a higher percentage of porosity, if the need for that material arises.

For 98.5 to 99% Al_2O_3 material, the minimum sintering temperature is 1600 °C. For materials up to 95% Al_2O_3 by changing the content of the tested oxides (CaO, MgO, SiO_2) it is possible to lower the sintering temperature below 1550 °C.

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CHEMICAL COMPOSITION AND ANTIOXIDANT AND ANTIMICROBIAL ACTIVITY OF *HELICHRYSUM ITALICUM* (ROTH) G. DON. ESSENTIAL OIL FROM BOSNIA AND HERZEGOVINA

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT:
In this study, the chemical profiles, antioxidant and antibacterial activity of *Helivhrysum italicum* essential oils from three plantation fields in Herzegovina were analysed. GC/MS analysis showed that all samples were rich in sesquiterpenes (45.19%-50.07%) and monoterpenes (21.15%-23.21%), followed by oxygenated monoterpenes (9.92%-14.03%). Diketones in the essential oil were detected in quantities ranging 5.72% to 6.67%. The main components in essential oils were γ-curcumene, α-pinene, β-selinene and neril-acetate. All tested essential oils exhibited relatively weak DPPH$^\cdot$-scavenging capacity. The antimicrobial activity of the essential oil was assayed by using the disk diffusion method. *E. coli* was most resistant against all three tested *H. italicum* essential oils, while moderate inhibitory activity against *S. aureus* and *C. albicans* was detected. The *L. monocytogenes* was the most sensitive where all three tested samples showed inhibitory activity.

KEYWORDS: *Helichrysum italicum*, essential oils, chemical profile, antioxidant activity, antibacterial activity

INTRODUCTION

Genus *Helichrysum* is a medicinal aromatic plant that belongs to the family *Asteraceae* and includes over 600 species distributed mainly in the Mediterranean area, at sea level up to 1700 m and growing preferably on sandy or loamy soils [1]. *Helichrysum italicum* (Roth.) G. Don. subsp. *italicum* is one of the most common species

The essential oil that is found mainly in the green parts of the plants is widely used in folk medicine as a source of choleretic, diuretic and expectorant material [2,3]. Also, it is known that the essential oil and extracts of *H. italicum* show antioxidant, antibacterial, anti-inflammatory, antialergic and antiviral properties [4-6].

The application of essential oil of immortelle depends on chemical composition of essential oil, which is affected by the plant genotype, the geographic origin and climatic conditions [7]. Three different chemotypes for the essential oils of *H. italicum* ssp. *Italicum* are reported: (I) a genotype rich in nerol and its esters; (II) a genotype with a dominance of α- and β-selinene; (III) a genotype with high amounts of γ-curcumene [8]. It was found that main components of *H. italic* essential oils from the Mediterranean part of Croatia are α-pinene, neryl acetate, α-cedrene, nerol, α-curcumene, γ-curcumene and geranyl acetate [9].

H. italicum has only recently been cultivated in Bosnia and Herzegovina (B&H) as a crop for industrial processing and for production of essential oil [10]. Previous *H. italicum* essential oil studies from the area of Bosnia and Herzegovina showed the differences in the chemical composition depend on the growing stage and the part of plants [11,12]. It was shown that the essential oils collected from wild growing *H. italicum* in B&H contained mainly monoterpenes and sesquiterpenes, followed by diketones, non-terpene esters and non-terpene ketones, which indicated that the essential oils from B&H are similar to those from Croatia and southeast Italy in their chemical composition [12].

The aim of this study was to determine the chemical composition and antioxidant and antimicrobial activity of *H. italicum* essential oils cultivated at three different locations in Bosnia and Herzegovina.

MATERIALS AND METHODS

PLANT MATERIAL

H. italicum plants were collected in June 2019 from three plantation fields in Herzegovina region at three locations in municipalities Stolac (Sample 1), Grude (Sample 2) and Posusje (Sample 3). Samples of collected plant material were identified and stored at Faculty of Pharmacy, University of Tuzla. The dried aerial parts of the plants, cut into small pieces, were water-distilled in semi-industrial distillation equipment. The essential oil was stored in a sealed vial at 4°C until the analysis.

STANDARDS AND REAGENTS

The reagents and chemicals used for the analysis were analytically pure. 2,2-diphenyl-1-picrylhydrazyl (DPPH), $FeSO_4x7H_2O$, $FeCl_3 \times 6H_2O$, HCl and methanol were obtained from Sigma-Aldrich (Germany) and 2,4,6-Tris (2-pyridyl)-s-triazine (TPTZ) was obtained from Himedia (India). FRAP reagent was prepared using the acetate buffer + TPTZ reagent + $FeCl_3$ x $6H_2O$ in a ratio of 10: 1: 1.

MICROBIAL STRAINS

The antimicrobial activity of essential oils was evaluated using the laboratory control strains: *Staphylococcus aureus* ATCC 25923, *Listeria monocytogenes* ATCC 19118, *Escherichia coli* ATCC 25922 and *Candida albicans.* Positive controls were Kanamycin for *S. aureus* and *L. monocytogenes* and Chloramphenicol for *E. coli.* Nystatin was positive control for *C. albicans.*

ANALYSIS

GC-MS method

The gas chromatograph-mass spectrometer GC-MS analysis was performed on a Shimadzu GC/MS QP 2010 Ultra GC with GC FID 2010 Plus-flame ionization detector. Operating conditions were as follows: column HP-5MS (30 m, internal diameter 0.32 mm, coating thickness 0.25 μm). Helium was carrier gas with a flow rate of 3 mL/min. Injector temperature was 250°C, injection volume 1 μL in split mode (1:50). The percentage share of individual components in each sample was calculated over the surface of the GC peak, and the percentages of components were calculated as mean values from duplicate samples of essential oil.

Antioxidant activity by DPPH

Samples were dissolved in 100 ml of methanol. A series of dilutions of different concentrations were made by adding different volumes of the essential oil stock solution and filling with methanol to 2 ml. Then, 500 μl of DPPH reagent solution was added to the solution. The mixture was incubated for 30 min in the dark at room temperature. The absorbance is measured against the blank (methanol) at 517 nm. The results are expressed as the IC_{50} value (mg/ml) or the concentration of extract that caused the 50% neutralization of DPPH radicals. Vitamin C was used as the comparator of the results of antioxidant activity.

Antimicrobial activity of the essential oils

The antibacterial activity of the essential oils was tested using the agar diffusion method according to the American Clinical Laboratory Standards Institute (CLSI) [13]. Mueller-Hinton agar (15 ml), sterilized in a flask and cooled up to 45–50 °C, was distributed to the sterilized Petri dishes. The sterile swab was used to transfer the bacterial suspension and inoculate the bacteria on the surface of Mueller-Hinton agar. The wells with a diameter of 10 mm were cut with the sterile stainless steel borer down to the plastic into Mueller-Hinton agar plates and then filled with a volume of 20, 50, and 100 μl of the extracts samples. The Petri dishes were incubated at 37 °C for 24 h. All experiments were performed in triplicate for each tested sample of essential oils and each microbial strain and the results were recorded as the mean. Data were analysed unidirectional using ANOVA analysis. The antimicrobial activity was measured on the basis of the diameter of the growth inhibition as follows: (<10 mm) – no antimicrobial activity; (10-15 mm) – weak antimicrobial activity; (16-20 mm) – moderate antimicrobial activity; (>20 mm) – strong antimicrobial activity [14]. Kanamycin, chloramphenicol, and nystatin (10.0 mg/mL) were used as references.

Statistical analysis

All the analyses were performed in triplicate. Statistical differences between samples were tested using ANOVA.

RESULTS AND DISCUSSION

THE CHEMICAL COMPOSITION

The chemical composition of the tested *H. italicum* essential oils characterized by GC/MS is presented in Table 1. A total of 45 compounds with a percentage share above 0.10% were identified, representing 92.65-93.52 % of the whole oil composition of the essential oils.

Table 1. The identified components and the percentage share in the sample. Components with a proportion less than 0.10% are not shown

Number	Component	RI	Sample 1 (%)	Sample 2 (%)	Sample 3 (%)
1	3- hexanone	914			0.11
2	α-pinene	937	17.83	15.96	17.98
3	Fenchen	941	0.33	0.26	0.38
4	Camphene	953	0.11	0.10	0.14
5	β-pinene	981	0.39	0.46	<0.10%
6	α-terpinene	1021	0.15	0.23	0.17
7	β-mircene	1024	<0.10%	0.11	<0.10%
8	Hexenil-acetat	1027	<0.10%	0.11	<0.10%
9	p-cimene	1029	0.13	0.12	0.19
10	Limonene	1035	2.23	3.26	3.17
11	1.8-cineole	1038	0.31	0.29	0.34
12	Izobutil angelat	1048	0.17	0.38	0.28
13	γ-terpinene	1061	0.38	0.47	0.47
14	α-terpinolene	1090	0.15	0.18	0.17
15	2-nanonene	1091	0.56	1.17	1.04
16	Methyl-butyrate	1097	0.18	0.21	0.16
17	Mt 170, Dione 2.4 dim	1155	0.60	1.23	0.85
18	Terpinene 4-ol	1172	0.18	0.26	0.28
19	3.4 octadion	1185	0.25	0.40	0.33
20	α-terpineole	1194	0.22	0.31	0.32
21	Nerol	1225	0.57	0.50	1.18
22	3.5-heptadione	1283	<0.10%	0.10	0.10
23	Neryl-acetate	1357	7.91	7.55	10.68
24	α-ylangene	1368	0.31	0.33	0.28
25	α-copaene	1375	2.49	2.71	2.19
26	Italicenes	1406	3.62	3.63	2.71
27	Bergamoten cis-α	1417	1.17	1.04	0.80
28	β-caryophillen	1427	5.44	5.06	4.96
29	Bergamoten trans-α	1436	1.07	0.96	0.79
30	Mt 210, italdione	1447	2.85	2.85	2.39
31	Neryl-propionate	1452	1.31	1.23	1.74
32	α-humulente	1461	0.19	0.40	0.22
33	γ-seline	1473	0.37	0.44	0.29
34	γ-curcumen	1480	17.72	20.62	14.39
35	Ar-curcumen	1485	3.89	2.92	3.57
36	β-seline	1488	9.92	8.51	10.24
37	α-seline	1497	5.13	4.10	5.73
38	Mt 224, dione	1512	1.66	1.50	1.34
39	γ-cardinene	1519	<0.10%	0.35	0.36
40	δ-cadinene	1526	1.16	1.24	1.13
41	Mt 238, dione	1533	0.66	0.55	0.68
42	Cariophilene-oxide	1581	0.52	0.44	0.50
43	Guaiol	1593	0.18	0.33	0.18
44	Naphtalene-methanol	1622	0.23	0.65	0.29
45	α-eudesmol	1637	0.11	<0.10%	0.13
TOTAL			**92.65**	**93.52**	**93.25**

Figure 1 shows distribution of terpene fractions and diketones in the tested essential oils samples. All three samples of essential oils were rich in sesquiterpenes (50.07% Sample 1, 49.27% Sample 2, and 45.19% Sample 3, respectively), while their oxygenated derivatives were presented in fewer quantities (from 0.81 up to 0.83%). Monoterpenes were the second most represented components with shares in the total composition of essential oil of 21.77% for Sample 1, 21.15% for Sample 2, and 23.21% for Sample 3. Oxygenated monoterpenes were also detected in percentages of 9.92% for Sample 1, 9.76% for Sample 2 and 14.03% for Sample 3. The proportion of diketones in the essential oil was 6.09% in Sample 1, 6.67% in Sample 2, and 5.72% in Sample 3. Comparing the composition of the tested essential oils with the results of studies conducted on samples of wild immortelle collected in Herzegovina, similar concentration of hydrocarbon monoterpenes and a lower concentration of sesquiterpenes were found, while the content of oxygenated monoterpenes and sesquiterpenes were also very low [11].

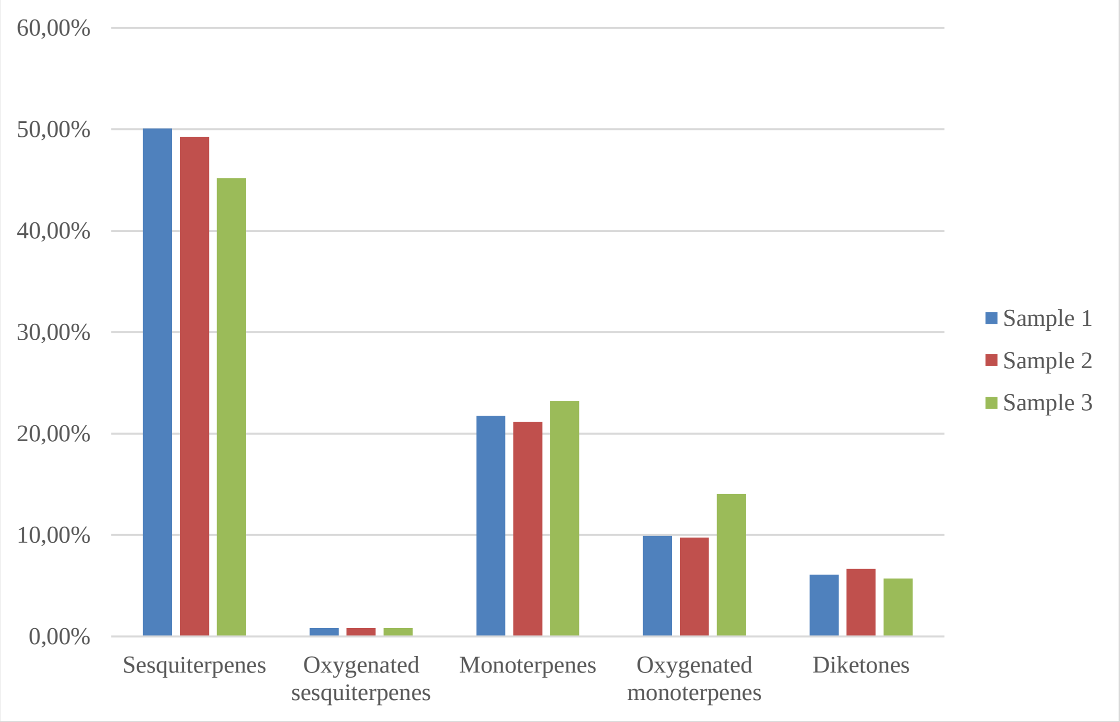

Figure 1. Distribution of terpene fractions and diketones in the tested essential oils

Regarding the results of GC-MS analysis of three *H. italicum* samples from Stolac, Grude and Posušje, it can be noticed that there were differences in the ratios of the most common active components within the tested oil, as well as differences between the analyzed samples. Also, the results showed that none of the samples stood out with the dominant content of active components.

Although all three oils have α-pinene (15.96-17.98%) and γ-curcumen (14.39-20.62%) as the most abundant components, Sample 1 contains equal proportions of these two components, Sample 2 contains more γ-curcumin and Sample 3 contains more α-pinene. The characteristic of essential oils from B&H and Croatia is α-pinene as the main component. Another important characteristic of the tested essential oils is the presence of 4,6,9-trimethyldec-8-ene-3,5-dione (2.39 to 2.85%) in the composition, which makes it different from other chemotypes. This component is also found in the main composition of wild immortelle from Herzegovina [11-12]. Also, the γ-selinen component was identified as a characteristic component that was not detected in other essential oils described in the literature. The content of this component in the analyzed essential oils is still slightly lower (0.29 to 0.37%) than the content determined in wild immortelle from Herzegovina (3.1%) [11]. According to the proportions of individual components in essential oils, the analyzed essential oils can be characterized as chemotype α-pinene, neryl acetate, γ-curcumen and β-seline. This chemical composition is very similar to the classification of *H. italicum* essential oils according to geographical origin proposed recently [6]. Here the authors classify essential oils obtained from *H. italicum* along the Adriatic coast as essential oils where the main components are γ-curcumen (15–29%) or α-pinene (25–30%) as well as neryl acetate (4–14%). It can be concluded that the tested essential oils were chemically similar to the essential oils from Dalmatia.

ANTIOXIDANT ACTIVITY

The antioxidant activity of *H. italicum* extracts was determined using the DPPH method. The obtained results were compared with the activity of the natural antioxidant vitamin C (ascorbic acid). The highest antioxidant potential was registered by the Sample 2 essential oil, which an IC_{50} value of 5.76 mg/ml, while Samples 1 and 3 showed a slightly lower antioxidant capacity, with IC_{50} values of 6.48 and 8.74 mg/ml, respectively. Vitamin C is one of the strongest antioxidants and was used as a reference sample (IC_{50} 0.005 mg/ml) and it was used to compare the antioxidant activity of the tested samples of *H. italicum* essential oils. All tested essential oils exhibited relatively weak DPPH scavenging capacity. The DPPH values of the tested essential oils are similar to the DPPH values obtained for *H. italicum* from Montenegro [15].

ANTIMICROBIAL ACTIVITY

E. coli is a common pathogenic bacterium present in urinary tract infections and *S. aureus* is the cause of pneumonia and several infections in the intestines or urinary tract. Statistically significant results were determined by t-test at a statistically significant difference of $p < 0.05$. The effect of different volumes of three samples of essential oils on four microbial strains was analysed.

Table 2. Antimicrobial effects of *H. italicum*

Microbial strain	Volume applyed (µl)	Inhibition [mm]		
		1	2	3
E. coli	50	-	-	-
	100			
L. monocytogenes	20	10 (+)	10 (+)	12 (+)
	50	15 (+)	20 (++)	15 (+)
	100	Not tested		
S. aureus	50	-	-	-
	100	-	15 (+)	12 (+)
C. albicans	50	-	-	11 (+)
	100	-	17 (++)	11 (+)

None of the tested samples of *H. italicum* essential oils showed antimicrobial activity on *E. coli* and the zone of inhibition of all tested samples was <3 mm. Sample 1 showed activity on the strain *L. monocytogenes*, but did not show activity on strains *E. coli*, *S. aureus* and *C. albicans* with any tested volume, while Samples 2 and 3 showed activity on the microbial strain *L. monocytogenes* and *S. aureus,* as well as *C. albicans* when tested with 100 µl of essential oil.

Table 3. Analysis of antibacterial activity by t-test

Microbial strain	1-2	1-3	2-3
L. monocytogenes	0.000008	1.000000	0.000008
S. aureus	-	-	0.000562
C. albicans	-	-	0.000003

The results of the t-test show that the antimicrobial activity of essential oils on the tested strain of *L. monocytogenes* differed statistically significantly between samples 1-2 ($p = 0.000008$), as well as between samples 2-3 ($p = 0.000008$). Also, for *S. aureus* and *C. albicans*, a statistically significant difference in activity was found between Samples 2 and 3, while Sample 1 showed no antimicrobial activity on these two strains.

All studies indicated that *H. italicum* oils from the Mediterranean region have significant biological potential, but also significantly differ from the area and ecological conditions.

CONCLUSION

GC/MS results showed that the tested *H. italicum* essential oils collected from three plantation fields in Herzegovina region were rich in sesquiterpenes and monoterpenes and the rest consisted of diketones, oxygenated- terpenes and -sesquiterpenes. The main components detected were γ-curcumene, α-pinene, β-selinene and neril-acetate. The tested oils showed similarities in chemical composition with essential oils from Croatia.

Antibacterial activity of the essential oils were tested against microorganisms *E. coli*, *L. monocytogenes*, *S. aureus* and *C. albicans*. The *E. coli* was the most resistant and none of the tested essential oils showed inhibitory activity, while the *L. monocytogenes* strain was the most sensitive where all three tested samples showed inhibitory activity. *S. aureus* and *C. albicans* showed moderate sensitivity.

The tested essential oils contained flavoring substances, such as neryl acetate, pinenes, limonene, curcumenes and could be applied in food industry and as perfume supplement. Since the biological activity is correlated with the chemical composition, further research is needed on other biological activities.

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A STUDY OF THE EFFECT OF ORGANIC AND CONVENTIONAL CULTIVATION ON THE POTATO YIELD

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT:
Potato is one of the most expanded vegetable crops, and it is one of the most important agri-food products in the world and our country, too. Because of its high reproductive potential and ability to achieve high yield, the potato has taken a very high position among vegetable crops. The goal of this study was to show differences in the rates of crop performance, comparing six potato varieties organically and conventionally cultivated. The potato varieties are Adora, Jaerla, Agria, Desiree, Kennebec and Triplo. Depending on the regime of cultivation, more specifically on the treatments unique to the cultivated regime, different varieties have achieved different yields, and with a precise weighing mass, values for each variety have been determined. Different measurements have been carried out on the visually smallest tubers, visually biggest tubers, and total potato yield for each variety.

KEYWORDS: potato, yield, organic growing, conventional growing

INTRODUCTION

The potato (lat. *Solanum tuberosum*) is the most widespread tuberous crop in the world and the fourth largest vegetable crop in terms of fresh products, after rice, wheat and corn [1]. The potato belongs to the nightshade family, *Solanaceae*. It is an annual, dicotyledonous plant in terms of its vegetative and flowering habits, but can be considered perennial in terms of its ability to be reproduced by tubers [2]. The potato has a significant capacity for adaptation. Potato production systems show differences in different countries and regions within the same country, depending on climatic and soil conditions and socio-economic structure [3]. Potato is an intensive crop that requires a large investment of labour, which is of special interest for economically underdeveloped areas because by focusing on this production, significant surpluses of living human labour can be absorbed. Nothing less important is the large consumption of material necessary for the production of potatoes, and especially large amounts of mineral and organic fertilizers and seed planting material [4]. To achieve a high yield of potatoes, a large amount of nutrients is needed [5-7]. The presence of nitrogen up to 180 kg / ha has a positive effect on potato yield, but also market-sized tubers [8]. However, the use of nitrogen in large quantities is not acceptable from an agronomic, ecological or economic point of view [9]. Potato is a plant that removes large amounts of minerals from the soil and therefore has significantly higher requirements in terms of fertilization (compared to other field crops). The highest yield is achieved by a combination of organic and mineral fertilizers. The most important organic fertilizers are manure, slurry and green manure, which provide higher yields and improve the structure and physic-chemical properties of the soil and enhance microbiological activity in the soil. Manure fertilization is performed in autumn before autumn-winter tillage in the amount of 30 to 35 t/ha. Mineral nutrients are crucial for the growth and development of potato plants [10]. Although tuber growth is influenced by many elements, mineral fertilization is based on the intake of three basic macro elements: N, P and K. Each variety, but also the technological purpose of potatoes (early to late harvest), has special requirements in terms of fertilization [11].

MATERIALS AND METHODS

The experiment was conducted at the fields of “Milo Selo” farm in Lukavac, in 2018.

Using the farm's resources, production was organized in two separate regimes, as follows:
- Organic (plot 1) and
- Conventional (plot 2).

Two separate cultivation regimes are marked with the numbers "1" – organic cultivation and "2" - conventional cultivation. The experimental part of this work was performed on the mentioned plots, and the subject of cultivation was six different varieties of potatoes. The cultivated varieties of potatoes are Adora, Jaerla, Agria, Desiree, Kennebec and Triplo.The plots on which potatoes were grown had similar exposures, soil structure and fertility as well as soil pH. The subjects of monitoring were two rows, both of them ten meters long, for each variety in both cultivation regimes.

Seed potatoes

Seed potatoes were bought in March and April of 2018. Tubers of the varieties Desiree, Agria, Adora, Triplo and Kennebec were cut in two in the period from 13th to 15thof March and left in a dark place at a temperature of 15 °C for germination until planting, and tubers of the variety Jaerla were cut the same day as they were planted.

Organic and mineral fertilizers

The following organic fertilizers were used on plot 1: stallatico (pelleted organic fertilizer), amixol (L-amino acids of plant origin in liquid form), slavol (liquid microbiological fertilizer), and diamond-grow (liquid fertilizer from Ascoum seaweed species).

The following synthetic fertilizers were used on plot 2: N: P: K - 15:15:15 (complex mineral fertilizer) and KAN (nitrogen mineral fertilizer). Mature sheep manure (pre-sowing soil preparation) was applied to both plots.

Organic and mineral fertilizers for plant protection

The following organic agents were used on plot 1: ozoneem (organic liquid insecticide - contains active substances from tropical neem tree seeds), kraken (biological insecticide containing Bacillus thuringiensis). The following synthetic agents were used on plot 2: cadillac (preventive contact fungicide from the Dithiocarbamate group), calypso (systemic insecticide), mospilan (systemic insecticide).

Soil and plants treatments during cultivation

On plot 1, the application of mature sheep manure in the amount of approximately 20 t was performed in March 2018, after which tillage and milling of the plot were performed as pre-sowing preparations. Planting of potatoes in mechanically open rows was done at the beginning of the second decade of April 2018, when the application of pelleted fertilizer in the amount of 115 kg was also done. The weather conditions at the time of planting were extremely favourable, and the air temperature measured at the time of planting was 18 ºC. Potatoes were planted manually, with a distance of 40 cm in a row to a depth of 5 cm. The plot has an area of 0.2 ha.

On plot 2, the application of mature sheep manure in the amount of approximately 24 t was performed in March 2018, after which tillage and milling of the plot were performed as pre-sowing preparations. The potatoes were planted at the same time as on plot 1 under the same weather conditions, and the mineral fertilizer N: P: K - 15:15:15 was applied in the amount of 225 kg. Potatoes were planted manually, with a distance of 40 cm in a row to a depth of 5 cm. The plot has an area of 0.25 ha.

During cultivation, we applied organic means and fertilizers for protection and fertilization on plot 1, while on plot 2 we applied synthetic means and fertilizers for protection and fertilization, according to the manufacturer's instructions.

Tuber weight measurement

Measurement of the mass of extracted tubers was performed with a digital scale CAS XE 1 500, and the total yield for each variety was measured with a digital scale Straus - 350 kg. Ten visually smallest tubers and ten visually largest tubers were measured for each variety in both cultivation regimes, and the total yield height for each variety was measured. We entered the results in the table, after which the yield height was compared, depending on the type of cultivation regime.

RESULTS AND DISCUSSION

Table 1 shows the average values of weights (g) of the visually smallest tubers of all cultivars obtained by measuring ten samples for each variety in organic (1) and conventional (2) cultivation.

Table 1. Average values of masses (g) of visually smallest tubers

Variety	Tubers' mass (g) 1	Tubers' mass (g) 2
Adora	2.24	2.84
Jaerla	2.21	9.85
Agria	4.31	3.06
Desiree	2.25	2.76
Kennebec	2.82	2.75
Triplo	3.95	2.98

Statistical data processing was performed using ANOVA Test and the processing results are shown in the following tables:

Table 2. Statistical data processing

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3.477633333	1	3.477633	0.772984	0.399929	4.964603
Within Groups	44.98973333	10	4.498973			
Total	48.46736667	11				

Table 3. Statistical data processing

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	17.71836667	5	3.543673	0.691471	0.648743	4.387374
Within Groups	30.749	6	5.124833			
Total	48.46736667	11				

Since p>>0.05 there is no statistically significant difference between the observed parameters, from that there is no relationship between the masses of the visually smallest potato tubers.

The average weight of the smallest samples of tubers for the Adora variety in the organic regime was 2.24 g, while the average weight of the smallest samples of tubers for the same variety in the conventional regime was 2.84 g. The Adora variety cultivated in the conventional regime had an average of 26.78% higher mass of visually smallest tubers compared to the organic regime.

The average weight of the smallest samples of tubers for the Jaerla variety in the organic regime was 2.21 g, while the average weight of the smallest samples of tubers for the same variety in the conventional regime was 9.85 g. The Jaerla variety cultivated in the conventional regime had an average of 345.7% higher mass of visually smallest tubers compared to the organic regime.

The average weight of the smallest samples of tubers for the Agria variety in the organic regime was 4.31 g, while the average weight of the smallest samples of tubers for the same variety in the conventional regime was 3.06 g. The Agria variety cultivated in the conventional regime had an average of 29%less mass of visually smallest tubers compared to the organic regime.

The average weight of the smallest tuber samples for the Desiree variety in the organic regime was 2.25 g, while the average weight of the smallest tuber samples for the same variety in the conventional regime was 2.76 g. The Desiree variety cultivated in the conventional regime had an average of 22.66% higher mass of visually smallest tubers compared to the organic regime.

The average weight of the smallest tuber samples for the Kennebec variety in the organic regime was 2.82 g, while the average weight of the smallest tuber samples for the same variety in the conventional regime was 2.75 g. The Kennebec variety cultivated in the conventional regime had an average of 2.48% less mass of visually smallest tubers compared to the organic regime.

The average weight of the smallest samples of tubers for the variety Triplo in the organic regime was 3.95 g, while the average weight of the smallest samples of tubers for the same variety in the conventional regime was 2.98 g. The variety Triplo cultivated in the conventional regime had an average of 24.55% less mass of visually smallest tubers compared to the organic regime.

Table 4 shows the average values of the masses (g) of the visually largest tubers of all cultivars obtained by measuring ten samples for each cultivar in organic (1) and conventional (2) cultivation.

Table 4. Average values of masses (g) of visually largest tubers

Variety	Tubers' mass (g) 1	Tubers' mass (g) 2
Adora	298.77	329.14
Jaerla	316.00	320.75
Agria	404.86	397.49
Desiree	336.50	449.67
Kennebec	225.15	454.40
Triplo	560.48	398.58

Statistical data processing was performed using ANOVA Test and the processing results are shown in the following tables:

Table 5. Statistical data processing

Source of Variation	***SS***	***df***	***MS***	***F***	***P-value***	***F crit***
Between Groups	461,1685	5	8043,837	1,042693	0,470836	4,387374
Within Groups	11,28125	6	7714,486			
Total	86506,10589	11				

Table 6. Statistical data processing

Source of Variation	***SS***	***df***	***MS***	***F***	***P-value***	***F crit***
Between Groups	3614,699408	1	3614,699	0,436076	0,523941	4,964603
Within Groups	82891,40648	10	8289,141			
Total	86506,10589	11				

Since p>>0.05 in both cases there is no statistically significant difference between the observed parameters, from that there is no relationship between the masses of the visually largest potato tubers.

The average weight of the largest samples of tubers for the Adora variety in the organic regime was 298.77 g, while the average weight of the largest samples of tubers for the same variety in the conventional regime was 329.14 g. The Adora variety cultivated in the conventional regime had an average of 10.16% higher mass of visually largest tubers compared to the organic regime.

The average weight of the largest samples of tubers for the Jaerla variety in the organic regime was 316 g, while the average weight of the largest samples of tubers for the same variety in the conventional regime was 320.75 g. The Jaerla variety cultivated in the conventional regime had an average of 1.5% higher mass of visually largest tubers compared to the organic regime.

The average weight of the largest samples of tubers for Agria variety in the organic regime was 404.86 g, while the average weight of the largest tuber samples for the same variety in the conventional regime was 397.49 g. The Agria variety cultivated in the conventional regime had an average of 1.82% less mass of visually largest tubers compared to the organic regime.

The average weight of the largest samples of tubers for the variety Desiree in the organic regime was 336.5 g, while the average weight of the largest samples of tubers for the same variety in the conventional regime was 449.67 g. The variety Desiree cultivated in the conventional regime had an average of 33.63% higher mass of visually largest tubers compared to the organic regime.

The average weight of the largest samples of tubers for the Kennebec variety in the organic regime was 225.15 g, while the average weight of the largest samples of tubers for the same variety in the conventional regime was 454.4 g. The Kennebec variety cultivated in the conventional regime had an average of 101.82% higher mass of visually largest tubers compared to the organic regime.

The average weight of the largest samples of tubers for the variety Triplo in the organic regime was 560.48 g, while the average weight of the largest samples of tubers for the same variety in the conventional regime was 398.58 g. 28.88% less mass of visually largest tubers compared to the organic regime.

Table 7 shows the total yields of extracted tubers for all cultivated varieties in organic (1) and conventional (2) cultivation regime.

Table 7. Total yield of extracted tubers (kg)

Variety	Total yield (kg) 1	Total yield (kg) 2
Adora	15.15	32.6
Jaerla	31.4	29
Agria	15.14	32
Desiree	24.5	28.7
Kennebec	11.23	27.3
Triplo	18.2	24

Based on the measurement results, it was concluded that all varieties except the Jaerla variety achieved higher yields in the conventional cultivation regime compared to theorganic cultivation regime.

The Adora variety grown in the conventional regime had a 115.18% higher yield compared to the yield in the organic cultivation regime. The cultivar Agria cultivated in the conventional regime had a 111.36% higher yield compared to the yield in the organic cultivation regime.

The variety Desiree grown in the conventional regime had a 17.14% higher yield compared to the yield in the organic cultivation regime. The variety Triplo cultivated in the conventional regime had a 31.86% higher yield compared to the yield in the organic cultivation regime. The Kennebec variety grown in the conventional regime had a 143.09% higher yield compared to the yield in the organic cultivation regime. The Jaerla variety cultivated in the conventional regime had a 7.64% lower yield compared to the yield in the organic cultivation regime.

In a study conducted by Hamouz et al. (2005), the yield of six different potato varieties in the conventional regime was 60.173% higher than in the organic regime in the amount of 37 t / ha, while in the organic regime it was 23.1 t/ha [12]. Jarvan et al. in a study in 2007 state that the yield of Laura potatoes in the conventional regime was 188.728% higher than in the organic cultivation regime and amounted to 29.97 t / ha, while in the organic regime (organic I) it was 10.38 t/ha [13].

To sum up, in this experiment, the Jaerla variety proved to be the most favourable for cultivation in the organic cultivation regime, while the Kennebec variety found the largest difference in yield in two different cultivation regimes, 143.09% in favour of the conventional regime.

CONCLUSION

The use of synthetic fertilizers and pesticides in potato cultivation, in addition to harmful effects in relation to organic cultivation, has its advantages which can be seen in the results of this experiment, the yield depending on agro ecological conditions, agrotechnics and potato varieties. The yield of the same varieties cultivated in different regimes and measured in this experiment, varied greatly depending on the treatments. So, it can be concluded that the Kennebec variety had the largest percentage difference in the amount of yield in favour of conventional cultivation. All cultivated varieties except Jaerla achieved higher yields in conventional cultivation. The only exception is the Jaerla variety, which achieved a higher yield in organic cultivation, 7.64% higher than the conventional one.

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PLUM PITS AS NATURAL SORBENT FOR REMOVAL OF LEAD IONS

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT:
Water quality is deteriorating over the years, and the main source of water pollution is industrial, agricultural and municipal wastewater. Heavy metals, organic compounds and microorganisms, present even in traces, can be very dangerous to human health, aquatic organisms and the environment. Therefore, in this study was investigate the possibility of modified and unmodified plum pits as biosorbents for Pb (II) ions removal from aqueous solution. Experimental data have shown that these bisorbents show a certain potential for application in the metal removal process. The feasibility was tested for an unmodified and modified biosorbent based on plum pits in the range of concentrations 150-200 mg/l (unmodified sample) and 100-200 mg/l (modified sample) at a contact time of 30 and 60 minutes . Adsorption parameters were determined using the Freundlich isotherm. The results showed that unmodified biosorbent based on plum pits with increasing concentration from 150 mg/L to 200 mg/L leads to a large increase in the percentage of removal of Pb (II) ions, with no significant effect on contact time. In contrast to the unmodified sample, the modified biosorbent based on plum pits % of removed Pb (II) ions significantly increases the contact time at the initial Pb (II) concentration of 100 mg/L, while at the initial concentration of 150 mg/L and longer mixing, the removal efficiency increases and amounts to 86.032 %. The calculated values of the parameters used in the Freundlich isotherm indicated the existence of high-energy sorption centers in the unmodified bisorbent based on plum pits, while the calculated values of the parameters used in the Freundlich isotherm for the modified biosorbent based on plum pits showed moderate mode adsorption.

KEYWORDS: adsorption, plum pits, modified and unmodified biosorbent, lead

INTRODUCTION

The most prized substance found in nature and an irreplaceable resource that is limited in the world is precisely water. Due to the growing population and global development, the amount of water pollution is also increasing, which is becoming an increasing problem in today's world. [1] The food industry generates large amounts of organic waste of plant origin (seeds, fruit pulp, shells, etc.). In order to minimize this type of waste, it is possible to single out many valuable components that can be further used such as pectin, fiber, antioxidants and the like. However, very often the lignocellulosic part of solid waste remains unused in large quantities. Such waste can be used for the purpose of obtaining bioethanol, as livestock, and recently such waste has been tested as an adsorbent for the removal of heavy metals from wastewater. [2] ,[3]

Heavy toxic metals such as Pb, Cu, Zn, Cd, Ni enter the water through wastewater from the metal industry and the Cd-Ni battery industry, phosphate fertilizers, mining, pigment industry, stabilizers, galvanic alloy industry, etc. they are collected in the food chain and due to the tendency of bioaccumulation they need to be removed from wastewater. [4] Pb (II) ions are able to penetrate the cell membrane and accumulate in the cell, thus causing its damage. [5] Therefore, poisoning can also be caused by quantities of lead below the maximum permitted concentrations, if the exposure to the source of poisoning is long-lasting, which is why its removal is very important.

There are many procedures and techniques of varying degrees of efficiency that are used to control and reduce water pollution caused by various pollutants, including heavy metals. However, these procedures often have various disadvantages in terms of high operating and maintenance costs, low pollutant removal efficiencies, generation of toxic waste sludge and by-products, complicated procedures and applications. On the other hand, sorption processes have proven to be a good alternative for natural and wastewater treatment given the practicality and simplicity of the process, economy and high efficiency [6]. Therefore, natural sorbents that are readily available and abundant are increasingly being used. Based on literature data, among the readily available types of biomass, there are strong natural biosorbents such as plant parts, especially those that contain cellulose: e.g. tree bark, rice peel, wheat peel, banana peel, orange peel, tea leaves, corn cob, hazelnut peel, walnuts, seaweed, microorganisms (bacteria, fungi, yeasts), activated sludge, etc. [7],[8].

The ability to remove heavy metals from water by biosorption by lignocellulosic biomaterials is enabled by the relatively porous structure and the presence of different functional groups on their surface. The advantage of lignocellulosic materials, which includes the selected biosorbent based on plum pits for wastewater treatment, is reflected in the fact that cellulose has good chemical stability and mechanical strength due to its crystal structure. [9]. In addition, in BiH this type of waste material is present in large quantities and is economically available.

The aim of this study was to investigate the sorption capacity of removing Pb (II) ions from water using a unmodified and modified biosorbent on base plum pits, that was chemically modified with sodium hydroxide. And as the efficiency of the adsorption process is affected by the pH value, contact time, initial concentration of heavy metal and mixing rates, these parameters were examined.

MATERIAL AND METHODS

In this paper, the sorption capacity of samples of unmodified and modified biosorbent based on plum pits with 1% NaOH against Pb (II) ions at a pH higher than a certain pH point of zero charge was investigated. Also, the influence contact time and mixing rate on the sorption capacity of the selected bisorbent on the removal of Pb (II) ions from water was investigated**.**

MATERIAL

The plum pits classified as waste material were used as bisorbents. The plum pits are first washed in distilled water, then dried first in air and then in an oven to remove as much moisture as possible. The lignocellulosic part was separated from the core of the pits, and it was used in further work. Manual grinding was performed, followed by sieving through a sieve (- 0.6 mm +0.3). The samples were then dried in an oven at 60˚C to constant weight and then stored in hermetically sealed containers.

METHODS

pH point of zero charge of the modified and unmodified bisorbent based on plum pits was first determined by contacting 0.2 grams of the biosorbent with 50 ml of 0.1 M KNO_3 solution. pH values were previously precisely adjusted from 3 to 10 with 0.01 M HNO_3 and 0.01 M NaOH. (pH meter of the Mettler Toledo 220 brand). After 24 h, all samples were filtered and their pH value was measured. The pH value that did not change after 24 h corresponds to the pH point of zero charge.

For the preparation of the unmodified sample, lead solutions with a concentration of 150 mg/l and 200 mg/l (two of each concentration) were used, which were mixed with 0.2 g of the prepared sample of biosorbent. The two samples were mixed for 30 minutes, while the remaining two were 60 minutes. The Rotamix SHP-10 magnetic mixer was used for mixing. After the contact time, the separation of the biosorbent was performed by filtration, and then the concentration of lead was determined from the filtrate with the atomic absorption spectrophotometer.

The preparation of the modified sample consisted of the preparation of 3 g of the unmodified sample treated with 1 M NaOH relative to 1:15 and then stirred on a magnetic stirrer for 6 h at room temperature. The sample was then washed with distilled water to constant pH and dried at 50°C to constant weight. Four solutions of lead concentration 100 mg/l and 150 mg/l were prepared and contacted with 0.2 g of modified biosorbent. The two samples were mixed for 30 minutes, while the remaining two were 60 minutes. The separation of the biosorbent was performed by filtration, and then the concentration of lead was determined from the filtrate with the help of an atomic adsorption spectrophotometer. The adsorbed amount of lead ions on the bisorbent (bisorption capacity), qe (mg/g) was calculated according to the equation:

$$qe = \frac{(C_i - C_f) \times \mathrm{V}}{m}$$

where is:

V - the volume of sorbate solution - 50 ml;

m - mass of bisobent 0.2g / 50ml;

C_i i C_f - the concentrations at the beginning and end of the bisorption process (mg/L).

Removal efficiency is determined from the equation:

$$\% = \frac{(C_i - C_f)}{C_i} x100$$

where is:

C_i - the concentration of sorbate at the beginning of the bisorption process;

C_f - the concentration of sorbate at the end of the bisorption process.

The values of the Freundlich constants from the Freundlich adsorption isotherm were calculated [10]:

$$\log q_e = logKf + \frac{1}{n} S_e$$

where is:

q_e- amount of adsorbate adsorbed per unit weight of adsorbent (mg/g);

K_f- temperature-related parameter;

n- characteristic constant for the investigated adsorption system and are read from the diagram ($\ln q_e$) = f ($\ln C_e$).

Bisorption experiments were performed in batch mode.

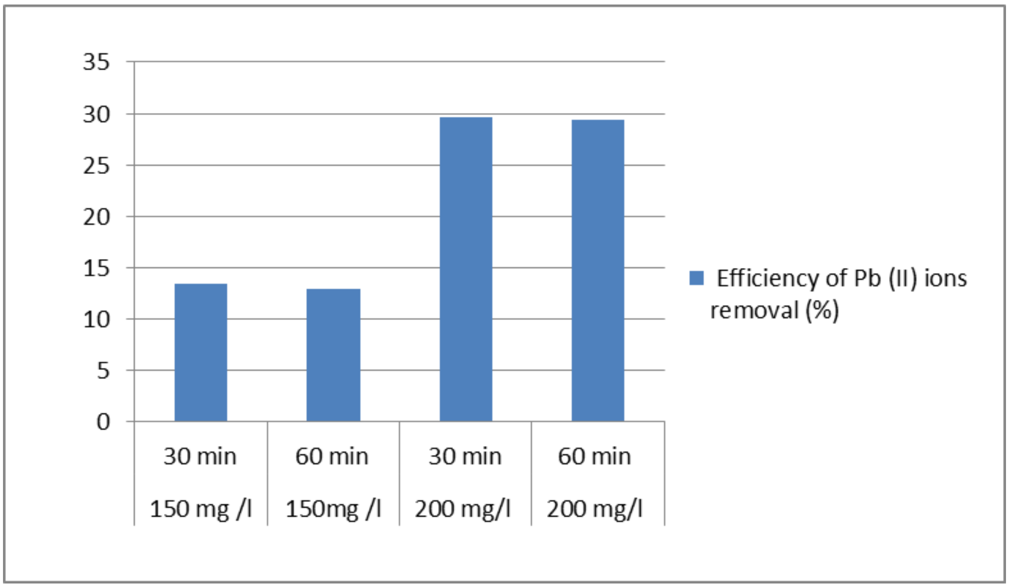
RESULTS AND DISCUSSION

The paper first determines the pH point of zero charge, a quantity that is of special importance when studying the phenomenon of adsorption in predicting the attractive or repulsive effects of the surface according to certain ionic species present in solution at a given pH value. [11]

Regarding this, the pH of the solution plays a significant role in determining both the degree of ionization of matter in solution and the dissociation of functional groups at the active sites of the adsorbent, and the chemical composition of the adsorbate particles [12].

The pH value that did not change after 24 hours was 4.5. This means that at all pH values of the aqueous solution lower than 4.5 the surface of the adsorbent will be positively charged, while at pH values above 4.5 the surface charge will be negatively charged.

The Graph 1. and Graph 2. show the values of the Pb (II) removal process for the unmodified and modified biosorbent.

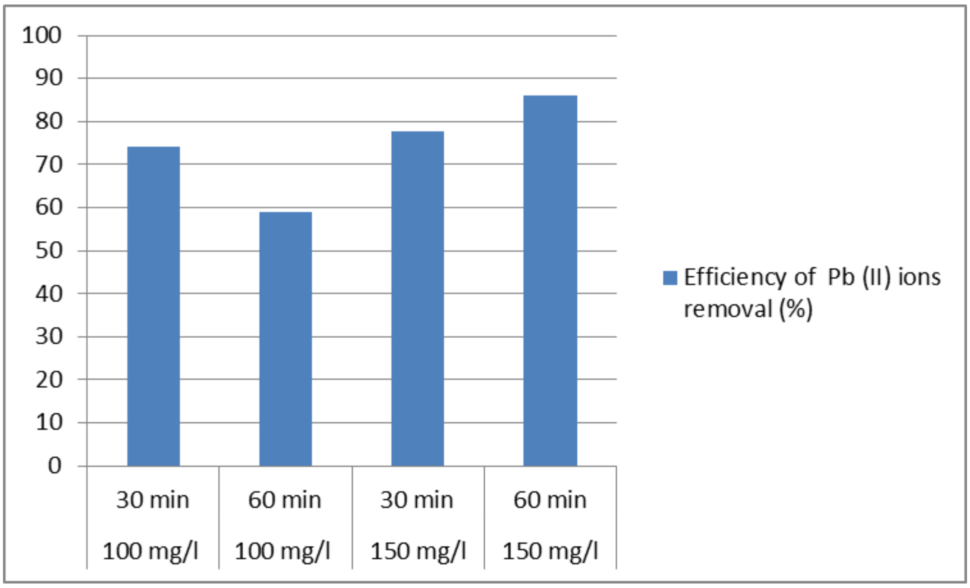


Graph 1. Removal efficieny of Pb (II) ions onto unmodified plum pits

As can be seen from the graph 1., at a contact time of 60 minutes there is a slight decrease in bisorption capacity compared to a contact time of 30 minutes. Some studies have shown that the effect of metal ion removal increases with the time of adsorption by applying almost all types of adsorbents.

For this reason, at the beginning of the treatment, the rate of removal of metal ions increases with the increase of the initial concentration, due to the large concentration of free binding sites on the surface. On the other hand, with the increase of the initial metal concentration, the active binding sites on the surface are saturated, so saturation appears as another important factor. [13]

However, the increase in the amount of adsorbed ions is proportional to the time to a certain maximum adsorption capacity, ie. the phase in which all available adsorption, active sites are filled under certain conditions, after which time is almost no longer affected. The results show that the equilibrium state in these tests is within 30 minutes during which most of the lead ions are adsorbed. By increasing the initial concentration of the pollutant of interest, it was found that the amount of adsorbed pollutant per unit mass of biosorbent usually increases. In this study, it was found that increasing the initial concentration of Pb (II) ions by 50 mg/L increases the sorption capacity more than twice.



Graph 2. Removal efficieny of Pb (II) ions onto modified plum pits

From Graph 2. it can be concluded that the removal efficiency of Pb (II) with the used modified plum pits sample % of removed Pb ions decreases significantly with increasing contact time at the initial Pb (II) concentration of 100 mg/L, while at the initial concentration of 150 mg/L and prolonged mixing, the removal efficiency increased to 86.032 %.

One of the most well-known isotherms often used by adsorption-desorption analyzes is the Freundlich isotherm [14], which was also used in this paper, and its values for the modified and unmodified biosorbent based on plum pits are shown in Tables 1. and 2.

Table 1. Freundlich adsorption isotherm constants for unmodified bisorbent base on plum pits

Number	The contact time (min)	The values of the Freundlich constants			
		lnK_f	K_f	1/n	R^2
1.	30	0,5387	1,71377	1,0782	1
2.	60	0,4698	1,59967	1,109	1

Table 2. Freundlich adsorption isotherm constants for modified bisorbent base on plum pits

Number	The contact time (min)	The values of the Freundlich constants			
		lnK_f	K_f	1/n	R^2
1.	30	2,4662	11,777	0,4526	1
2.	60	2,4516	11,606	0,5111	1

The value of the Freundlich constant indicates the relative adsorption capacity of the adsorbent, while the value of 1/n is an indicator of the strength of adsorption. If the value of 1/n is less than one, the adsorption process is considered to be of high intensity (Babaeivelni et al., 2013). A value of constant n greater than 1 indicates favored adsorption [15]. Some authors state the parameter 1/n as a heterogeneity factor, and the lower its value the greater the heterogeneity [16]. K_f is a parameter related to the binding capacity of the adsorbate, while the value of the constant n shows the affinity of the adsorbent for the adsorbate.

The calculated values for the biosorbent based on the unmodified biosorbent based on plum pits are presented in Table 1. As can be seen from the table, the value of the coefficients 1/n for the tested bisorbent is 1.0782 during a contact of 30 minutes and 1.109

during a contact of 60 minutes, which indicate the existence of high - energy absorption centers, while adsorption is more pronounced at lower concentrations.

From Table 2. it can be seen that the calculated values of the coefficients 1/n for the tested modified bisorbent based on plum pits indicate a moderate adsorption intensity, where at a contact time of 30 minutes the value of 1/n is 0.4526 and at a contact time of 60 minutes , 1/n is 0.5111.

CONCLUSION

The results of the examination of the possibility of application and sorption capacity of biosorbents based on modified and unmodified plum pits showed that the mentioned biosorbents can be used to remove Pb (II) ions, and that the pH point of zero charge is 4.5. The test results showed that there is an increase in the % removal with increasing concentration from 150 mg/L to 200 mg/L in the unmodified biosorbent where most of the lead ions are adsorbed within 30 minutes. It was found that increasing the initial concentration of Pb (II) ions by 50 mg/L increases the sorption capacity more than twice.

It has also been shown that the removal efficiency of Pb (II) with the modified biosorbent on based plum pits used % of removed Pb (II) ions decreases significantly with increasing contact time at an initial Pb (II) concentration of 100 mg/L, while at an initial concentration of 150 mg / L and prolonged mixing, the removal efficiency increases to 86.032 %.

The values of the coefficients 1/n from the Freundlich isotherm for unmodified biosorbent based plum pits are 1.0782 during a contact of 30 minutes and 1.109 during a contact of 60 minutes, indicating the existence of high-energy absorption centers, while adsorption is more pronounced at lower concentrations, while the values of the coefficients 1/n for the tested modified bisorbent based on plum pits indicate a moderate adsorption intensity, where at a contact time of 30 minutes the value of 1 / n is 0.4526 and at a contact time of 60 minutes, 1/n is 0.5111.

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WASTEWATER SLUDGE CONDITIONING WITH FLOCCULANT-NACL-STRAW TO IMPROVE SLUDGE DEWATERABILITY

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT:
One of the major improvement points in wastewater treatment processes is sludge treatment. The effectiveness of existing sludge treatment processes is highly limited due to poor dewaterability and compressibility of sludge. In this paper, a new sludge conditioning method was studied. The results show that combining NaCl and straw powder with commercial flocculant significantly improves sludge dewaterability and reduces moisture content, while increasing heat value. Adding NaCl in 0.25M dosage and 50% straw powder (dried and sieved to 0.125 – 0.063 µm) resulted in significant reduction of specific resistance to filtration and sludge moisture content. The results also suggest that it would be possible to partially substitute the flocculant with less expensive conditioners, which could potentially reduce the cost of sludge dewatering.

KEYWORDS: wastewater, flocculants, sludge

INTRODUCTION

Sludge is an inevitable by-product produced as a result of wastewater treatment processes. On average, sludge takes up around only 1% of treated water [1]. However, sludge management can take up to 60% of total operating costs of the wastewater treatment plant[2]. The high cost of sludge treatment is mainly due to its high water content (>92) and poor dewaterability[3].

For the purpose of sludge dewatering, chemicals such as calcium oxide, iron chloride, aluminum chloride and polyacrylamide are used[4]. However, these chemicals are expensive and reducing the need for these chemicals is economically important.

The aforementioned chemicals significantly reduce the moisture content of sludge and specific restistance to filtration (SRF) by forming larger flocs. However, a lot of the moisture is bound inside the sludge flocs. Thus, disintegrating the flocs before conditioning is key to enhancing sludge dewaterability[5]. It is understood that NaCl sludge condititoning is a cost-effective method of improving sludge dewaterability, with the reported optimal NaCl dosage of 0.25-0.30 mol/l[6, 7]. Furthermore, to improve sludge filter cake compressibility and mechanical strength some physical aids can be used. Zhu et al. reported using rice husk powders as physical conditioner, which lowered the moisture content of sludge filter cake to 62.50% [4]. Using physical conditioners can also increase the heat value of treated sludge, which is important for further sludge treatment i.e. incineration. Many physical conditioners such as lime, gypsum, fly ash and rice husk have been used as physical aids [8, 9, 10, 4]. However, currently there are no reports on using straw as a physical conditioner in sludge treatment.

The objective of this paper is to research the effect of straw powders on sludge dewaterability as well as researching the possibility of lowering the needed dosage of commercial flocculant by introducing alternative conditioners.

MATERIALS AND METHODS

Sewage sludge sample was collected from a local wastewater treatment plant in Živinice, Bosnia&Herzegovina. Raw sludge was stored at 4ºC and restored to room temperature before tests. The pH value of raw sludge was 7.16 with an initial moisture content of 94.50%.

NaCl was purchased as an analytical reagent. The flocculant was kindly donated by the wastewater treatment plant in Živinice. The flocculant solution (10 g/l) was prepared and mixed on a jar test apparatus 5 minutes at 80 r/min immediately before tests. Straw was collected from a local dairy cow farm. Prior to the tests, the straw was dried at 105°C, ground in a ball mill and sieved to 0.125 – 0.063 μm. Sludge filtration was conducted using a vacuum pump with a Buchner funnel at 600 mm Hg pressure.

SLUDGE CONDITIONING AND DEWATERING

The samples were as follows:

- Sample 1: Flocculant (10 g/l)
- Sample 2: Flocculant (10 g/l)+ NaCl (0.25M)
- Sample 3: Flocculant (10 g/l) + NaCl (0.25M) + straw (50%)
- Sample 4: Flocculant (10 g/l) + straw (50%).

All chemicals and physical aids were added to 300 ml of sludge in a 800 ml beaker. The prepared flocculant solution was added to the sludge (Sample 1) and mixed on a jar test apparatus for 60 s at 250 r/min, then 5 min at 80 r/min.

The samples containing NaCl (Sample 2 and Sample 3) were mixed for 120 mins at 80 r/min prior to adding the flocculant solution. In case of Sample 3, 50% wheat straw powder was added with NaCl and thus mixed for 120 mins at 80 r/min prior to adding the flocculant solution. After adding the flocculant, samples containing NaCl and NaCl+wheat straw powder were mixed for 60 s at 250 r/min, then 5 min at 80 r/min.

Sample 4 was prepared as follows: 50% straw powder was added to 300 ml sudge in a 800 ml beaker and mixed for 120 mins at 80 r/min. Then, the flocculant solution was added and the sludge was mixed for 60 s at 250 r/min, then 5 min at 80 r/min.

100 ml of each sample was filtered after mixing in a Buchner funnel with blue ribbon filter paper. The filtrate volume was recorded every 30 s for 4 min. Then, time to filter (TTF) was recorded as the time needed to collect 50 ml of filtrate.

ANALYTICAL METHODS

The effectiveness of sludge conditioning was measured in terms of moisture content, specific resistance to filtration (SRF) and net solids yield (Yn). Moisture content of sludge filter cake as well as moisture content of conditioned sludge before filtration was determined on a KERN moisture analyser.

The SRF of sludge was determined using the methods described by Coakley and Jones [11]. SRF is calculated by Eq (1),

$$\mathrm{SRF} = 2\,\frac{pA2b}{\mu c} \qquad (1)$$

where p is pressure (g/cm$^{2)}$, A is filtration area (cm^2), b is the slope calculated from the plot t/V vs. V (s/cm^6), μ is filtrate viscosity (P) and c is solids content (g/ml).

The Yn of sludge was calculated as described by Rehbun et al. [12]. Yn was calculated by Eq (2),

$$\mathrm{Yn} = F\,\left(2\,\frac{pc}{\mu t SRF}\right)^{1/2} \qquad (2)$$

where p is pressure (g/cm^3), c is solids content (g/ml), μ is filtrate viscosity (P), SRF is calculated from Eq. (1) and F is a correctional factor calculated from Eq. (3),

$$\mathrm{F} = \frac{SS\ original}{SS\ original + SS\ conditioner} \qquad (3)$$

where $SS_{original}$ is the original sludge solids (g/l) and $SS_{conditioner}$ is the conditioner solids (g/l).

Heat value and chloride and mercury contents of samples were also determined on an IKA calorimeter and Metronohm titrator.

RESULTS AND DISCUSSION

Sewage sludge was conditioned by single and combined processes described in section 2. and were as follows: flocculant conditioning with flocculant dosage of 10 g/l and 6 min total reaction time; flocculant-NaCl conditioning with a dosage of 10 g/l flocculant and 0.25M NaCl and 126 min reaction time total; flocculant-NaCl-straw powder conditioning with a dosage of 10 g/l flocculant, 0.25M NaCl and 50% powder straw (0.125 – 0.063 μm) and reaction time 126 min total; flocculant-straw powder conditioning with a dosage of 10 g/l flocculant and 50% powder straw (0.125 – 0.063 μm) with a reaction time of 126 min total.

The effectiveness of different conditioning methods in terms of SRF and moisture content is shown in Table 1, Figure 1. and Figure 2. shows the change of Yn with different conditioners. The SRF of raw sludge was 5.34 x 10^{10} s^2/g with a moisture content of 94.50%. Adding the flocculant decreased the SRF of sludge significantly to 3.59 x 10^{10} s^2/g, the moisture content dropped to 86.21% and the Yn was 7.49x10^{-4} g/cm^{2}s. The flocculant-NaCl sample displayed a further decreased SRF of 3.14 x 10^{10} s^2/g, 84.91% moisture content and the Yn increased to 3.63 x 10^{-3} g/cm^{2}s. In the flocculant-NaCl-straw powder conditioned sample the SRF was further reduced to 2.43 x 10^{10} s^2/g, the moisture content dropped to 79.87% and Yn further increased to 2.16 x 10^{-3} g/cm^{2}s. In the flocculant-straw powder conditioned sample the SRF was 2.73 x 10^{10} s^2/g, 83.78% moisture content and the Yn was 2.18 x 10^{-3} g/cm^{2}s.

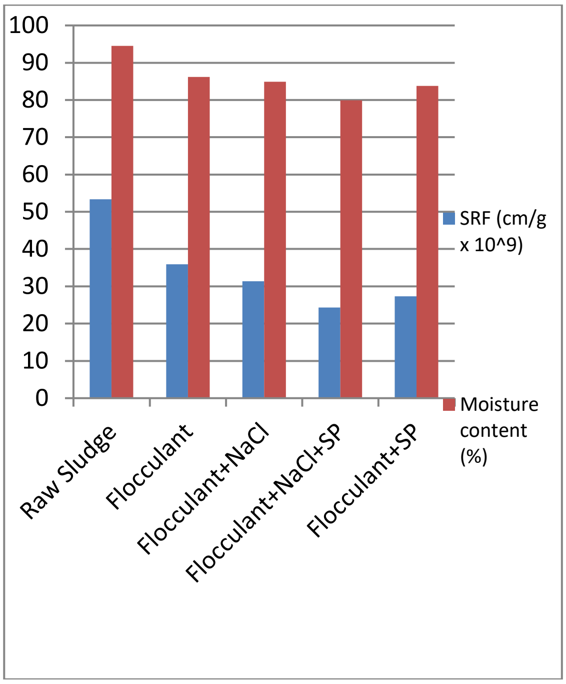

Fig 1. Effectiveness of different conditioning methods on SRF and moisture content of sludge

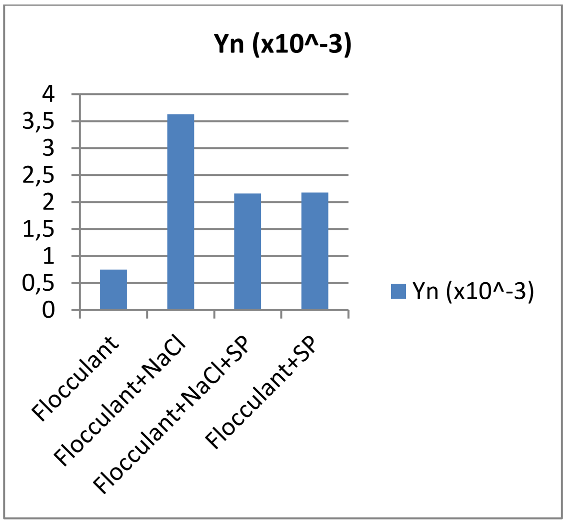

Fig 2. Effect of different conditioners on Yn of sludge.

Heat value of sludge samples conditioned with different conditioners was also considered. Heat values are presented in Table 2. Chloride and mercury contents in all samples were <0.1 and <0.54 respectively, meeting the requirements for incineration.

Table 1. SRF, Yn and moisture content of conditioned sludge

Sample	SRF ($x10^{10}$ s^2/g)	Yn ($x10^{-3}$ g/cm^2s)	Moisture content (%)
1. Flocculant	35.90	0.75	86.21
2. Flocculant + NaCl	31.40	3.63	84.91
3. Flocculant + NaCl + SP	24.30	2.16	79.87
4. Flocculant + SP	27.30	2.18	83.78

Table 2. Heat values of conditioned sludge.

Sample	Heat Value (MJ/kg)	Mercury (mg/kg)	Chlorine (%)
1. Flocculant	15.32	0.54	<0.1
2. Flocculant + NaCl	13.92	<0.54	<0.1
3. Flocculant + NaCl + SP	13.95	<0.54	<0.1
4. Flocculant + SP	16.12	<0.54	<0.1

CONCLUSION

In this paper, different sludge conditioning methods were studied in order to improve sludge dewaterability and lower the moisture content of sludge using alternative conditioners.

The highest SRF and moisture content reduction occured in the Flocculant+NaCl+SP conditioned sample, where SRF was 2.43 x 10^{10} s^2/g and moisture content was 79.87%. Yn was best in the Flocculant+NaCl conditioned sample, at 3.63 x 10^{-3}

g/cm^{2}s. Heat value was best in the Flocculant+SP conditioned sample, at 16.12 MJ/kg.

SRF, moisture content and Yn of sludge were significantly improved by combining different conditioners, compared to the sample conditioned only with flocculant. This suggests that combined conditioning highly benefits sludge dewaterability. Furthemore, it would also be possible to reduce the amount of flocculant needed by adding alternative conditioners.

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From this issue of Technologica Acta (vol. 10, no. 2) forward, the Journal will strictly follow the IEEE citation style. The brief explanation of IEEE citation style is given below.

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Journal article	[4] J. U. Duncombe, "Infrared navigation - Part I: An assessment of feasability," *IEEE Trans. Electron. Devices*, vol. ED-11, pp. 34-39, Jan. 1959.
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Conference paper	[7] L. Liu and H. Miao, "A specification based approach to testing polymorphic attributes," in *Formal Methods and Software Engineering: Proceedings of the 6th International Conference on Formal Engineering Methods, ICFEM 2004, Seattle, WA, USA, November 8-12, 2004*, J. Davies, W. Schulte, M. Barnett, Eds. Berlin: Springer, 2004. pp. 306-19.
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Technical report	[10] J. H. Davis and J. R. Cogdell, “Calibration program for the 16-foot antenna,” Elect. Eng. Res. Lab., Univ. Texas, Austin, Tech. Memo. NGL-006-69-3, Nov. 15, 1987.
Patent	[11] J. P. Wilkinson, “Nonlinear resonant circuit devices,” U.S. Patent 3 624 125, July 16, 1990.
Standard	[12] *IEEE Criteria for Class IE Electric Systems*, IEEE Standard 308, 1969.
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