



OPTIMIZING OF EXTRACTION OF BIOACTIVE COMPONENTS FROM SEA BUCKTHORN (*HIPPOPHAE RHAMNOIDES* L.) POMACE AND DEVELOPE OF ANTIOXIDANT-ENRICHED APPLE JUICE

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ABSTRACT

In our study, we were looking for an alternative to use of sea buckthorn pomace to open new opportunities. The dried pomace was extracted in a different method to achieve the highest antioxidant content. Ethanol and acetone were used as solvents, applied in different concentration. For the selection of the optimum extraction method, four spectrophotometric measurements were performed. With the best extract, three types of apple juice were made from apple juice concentrate by diluting it with different percentages of water and pomace extracts. The spectrophotometric measurements were also performed for juice samples to check the increase in amount of antioxidant components in the apple juice. Acceptability of enriched juices was determined by sensory evaluation and short market research. Based on the results the optimum extraction agent is 40 m/m % acetone for enriching apple juice. The results showed that there is a demand for the consumption of enriched juice with sea buckthorn pomace extracts and the fruit juice enriched with the 1:1 ratio of extract: water mixture is the most optimum according to sensory evaluators. Further examination could reveal whether the extracted antioxidant content of the pomace could be used as bio-preservatives in the food industry.

Keywords: sea buckthorn, pomace, apple juice, antioxidant, by-product, product-development

1. INTRODUCTION

The food waste is a critical subject in every industry, in every household; but in many cases by-products should not be considered as waste [1-3]. Fruit and vegetable wastes are produced in large quantities in food industry and constitute a source of nuisance in landfills because of their high biodegradability [4]. The nonedible portion of fruits and vegetables after processing (waste), such as peels, pods, seeds, skins, etc., accounts for about 10–60% of the total weight of the fresh produce. Because of the significant presence of pectin, minerals, vitamins, and bioactive molecules content, this waste offers a huge potential for its conversion into useful products, such as enzymes, ethanol, and biocolors [5]. The management of food processing by-products and wastes with reference to their reuse and recycling through value addition [6]. The European sea buckthorn (SB, *Hippophae rhamnoides* L.) is a deciduous shrub, which belongs to the *Eleagnaceae* family (*Rosales*). The berries of SB are rarely consumed fresh, but the fruit juice, pulp, and peel, and the seed oil are widely used in several countries. The SB is a good source of bioactive compounds as C-vitamin, carotenoid, flavonoid, polyphenolic content [7-9]. Processing of SB produces high amount of pomace, which are utilized rather inefficiently or discarded as a waste, so considerable amounts of nutrients are lost [10]. The pomace, which is left when berries are squeezed, is also a good source of vitamins and contains compounds that show antioxidant effects like flavonols, and phenolic acids are bioactive compounds. There is a growing interest in the utilization of antioxidant-rich plant extracts as dietary food supplements [11-12], so our goal is to find a method to extract this valuable antioxidant components and develop a delicious enriched apple juice with contain this pomace extracts.



2. MATERIALS AND METHODS

The “Ascora” sea buckthorn was collected from agricultural plots of Hungary at 2017. For the measurements the all chemicals were purchased by Sigma-Aldrich Chemie Ltd. All reagents used were of analytical grade.

2.1. Pre-treatment of sea buckthorn

Sea buckthorn was destemmed and heated to 80°C to inactivate their enzymes. The berries were squeezed, resulting in juice and pomace (skin and seed). In the next step, the sea buckthorn pomace (SBP) was dried by atmospheric dryer (LMIM, Esztergom, Hungary) at 80°C until moisture content became lesser than 10 (m/m) %. The moisture content was check by drying until constant weight at 121 °C using a MAC-50 moisture analyser (Radwag Waagen GMBH, Hilden, Germany). After that, the pomace was grinded. All SBP were stored in a freezer at -20 °C until ready for extraction, which was performed at room temperature.

2.2. Optimization of extraction condition

Optimization of conditions for the extraction of antioxidants and phenolics components from dried SBP was determined using water, ethanol and acetone as solvents, applied in different concentration (in case of ethanol and acetone: 20 (m/m) % and 40 (m/m) %). The ratio between pomace and solvent was 1:30 proportions. After half-an-hour of extraction, the samples were placed into a supersonic bath for another 30 minutes (*Bandelin Sonorex RK52*), to intensify the process. The tube is centrifuged (SIGMA 204) at 5000 1/min for 10 min to the phases separate and the supernatant is recovered. After the solvents were removed (by heating at 60°C) and replaced with water, the evaporated and back diluted sample was treated with bentonite to give translucent, completely clear liquid.

2.3. Measurements of antioxidant status of pomace extracts

Various spectrophotometric measurements were carried out to select the highest antioxidant content of pomace extracts. All spectrophotometry measurements were performed in triplicate.

- **TPC:** Total Polyphenol Content (TPC) was evaluated using a method by Singleton and Rossi [16]. The absorbance was measured at 765 nm. Results were specified in mg gallic acid equivalent/ 100 g dried pomace (mg GA/100g).
- **FRAP:** The antioxidant capacity of samples was determined by Benzie and Strain [13]. This method is based on reduction of Fe³⁺, TPTZ (2,4,6-tripyridyl-s-triazine) complex to the ferrous Fe²⁺ form at low pH. This reduction is followed by the measurement of absorption change at 593 nm. Ferric reducing antioxidant power assay was defined in ascorbic acid equivalent (mg ascorbic acid equivalent/ 100 g dried pomace; mg AA/100g).
- **DPPH:** The samples were measured in terms of hydrogen donating or radical scavenging ability using the stable radical DPPH (2,2-Diphenyl-1-picrylhydrazyl) [14]. The results were expressed as milligrams of Trolox equivalents (TE) per 100g dried pomace (mg TE/100g). Higher absorbance of the reaction mixture indicates lower free radical scavenging activity.
- **TEAC:** The free radical-scavenging activity was estimated by ABTS radical cation decolorization assay according to the procedure described by Re et al. [15]. The results were corrected for dilution and expressed as milligrams of Trolox equivalents (TE) per 100 grams of dried pomace (mg TE/100g).



2.4. Processing of enrichment of apple juice

With the best extraction method, three types of apple juice (11,2 Brix°, ATAGO PR-301) were made from apple concentrate (70 Brix°) by diluting it to minimum 11,2 Brix° [according to Hungarian regulation of 152/2009] with different mixture of water and pomace extracts (Tab. 1.).

Table 1. Ingredients and name of juices

Sample name		Apple juice	Water	Pomace extract
Control apple juice	CA	70 Brix°	100%	0%
50% - enriched apple juice	EA1		50%	50%
100% - enriched apple juice	EA2		0%	100%

The spectrophotometry methods were carrying out also for the juices, the results expressed mg per litre juice (mg/L).

2.5. Sensory evaluation of apple juice

Acceptability of enriched juices was determined by sensory evaluation and short market research. The sensory evaluation was carried out with 30 lay judges, the samples were coded with three-digit numbers. The evaluation was based on 100-point system, during the analysis the attributes were as follows: colour (max. 20 point) turbidity (max. 10 point) flavoured (max. 10 point) taste (max. 40 point) sea buckthorn taste (max. 10 point) of juices and overall impression. Evaluations of the samples were carried out separately and independently without any influence.

2.6. Statistical data evaluation

Single-factor ANOVA was used for monitoring the relations of the results of the individual analytical methods on different extraction conditions, separately. Correlation analysis was used to analyse the relation of the results of the antioxidant measurements. The significance level of all tests was specified to be $P=0.05$. The statistical evaluations were performed using Microsoft Excel.

3. RESULTS AND DISCUSSION

3.1. Results of antioxidant measurements

Dried SBP was extracted with different solvents (water, 20 and 40 (m/m) % ethanol and acetone), the samples were analysed to define total polyphenol content, as well as their antioxidant capacity (FRAP, DPPH, TEAC), to find the most effective method of extraction to achieve an extract rich in biological activity components (Tab. 2.).

Table 2. The average results of the spectrophotometry measurements of the pomace extracts (mg/100g pomace)

	Water	Acetone		Ethanol	
		20%	40%	20%	40%
TPC	1026.26±100.23	1587.54±164.61	2265.99±598.66	917.51±86.06	1146.46±338.38
FRAP	324.11±114.65	687.13±182.72	1925.59±49.52	486.47±403.95	1295.21±197.13
DPPH	4464.29±4.46	6422.99±6.42	10796.13±10.79	7047.99±7.05	5630.58±5.63
TEAC	302.36±0.30	687.86±0.68	9708.45±9.71	4931.78±4.93	7276.74±7.28

$x \pm SD$ (x: mean, SD: standard deviation)



Previous studies had also shown, that the fruits of SBT cultivars have strong antioxidant effect, and these results were right also in case of pomace extracts [17-19]. The results showed significant differences between the species ($p_{\text{TPC}}=2.5 \cdot 10^{-3}$, $p_{\text{FRAP}}=2.8 \cdot 10^{-5}$, $p_{\text{DPPH}}=7.4 \cdot 10^{-14}$, $p_{\text{TEAC}}=6.3 \cdot 10^{-19}$). Based on the results the water as a solvent was not efficiently, these results of antioxidant measurements were the lowest value in most cases. The optimum extraction agent is acetone to the highest antioxidant content of pomace extracts. Between the extraction efficient of two concentration of acetone was significantly difference ($p < 0.05$), so the best extraction solvent was the 40 m/m % acetone for extracting the valuable components from the pomace.

Table 3. The average results of the spectrophotometry measurements of the juice samples (mg/L)

	CA	EA1	EA2
TPC	372.80±11.57	329.68±72.63	462.15±19.79
FRAP	4338.54±477.06	10494.78±1039.99	14315.44±769.65
DPPH	150.67±2.01	196.61±1.70	398.56±1.87
TEAC	40.71±1.16	197.04±0.70	242.71±1.91

x±SD(x: mean, SD: standard deviation)

Based on the results of juices (Tab 3.), our desired goal - the enrichment of apple juice - was met, the antioxidant compounds, the antioxidant capacity value of FRAP, DPPH and TEAC method greatly increased by added the pomace extract. The all measurements showed outstanding results compared to the control sample. The antioxidant content of the sample increases in direct proportions with the amount of added pomace extract. The sample EA2 (enriched apple juice, with 100% pomace extract) had the most antioxidant content.

Table 4. Results of correlation analysis between the antioxidant methods.

	TPC	FRAP	DPPH	TEAC
TPC	1			
FRAP	0.79	1		
DPPH	0.84	0.78	1	
TEAC	0.49	0.87	0.74	1

This study assessed antioxidant potential of both extracts by using four different methods, which gave different antioxidant activity values (Tab. 2-3). From our values in Tab. 4, the greatest mutual correlation is shown between the results obtained by FRAP and TEAC methods, with the correlation coefficient being 0.87. In case of the most methods the coefficient was greater than 0.74, expect, the low correlation between TPC and TEAC was found.

3.2. Results of sensory analysis and market research

The enriched apple juices had beneficial sensory properties (Fig.1), the tasters were satisfied with finished products.

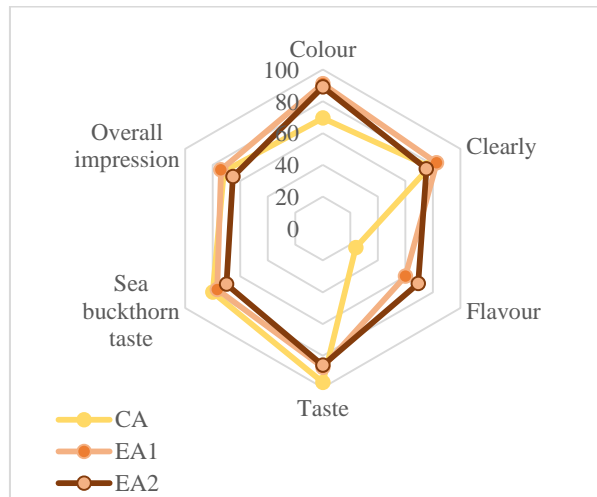


Figure 1. Results of sensory analysis

During product development, the flavour and sour flavour from SBP should be improved and decreased because the participants were the least satisfied with these parameters. According to the Fig. 2., apple concentrates dilute with 50% pomace extract (EA1 sample) is the most optimum according to evaluators. In case of this sample, the typical acidic flavour of the sea buckthorn did not yet negatively affect the taster and the ratio of apple and SBP was optimal and harmonic.

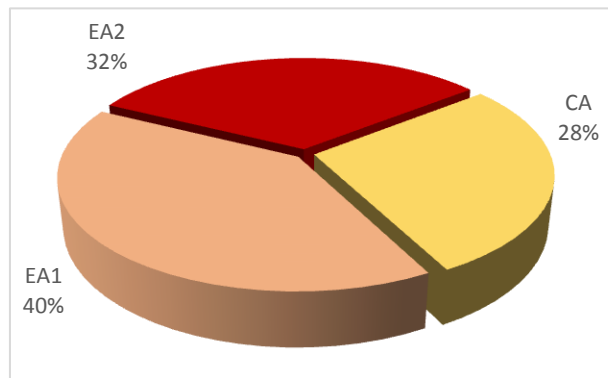


Figure 2. Results of market research, percentage distribution of popularity level

The results of the market research showed that there is a demand for the consumption of enriched juice. Overall, according to these data, consumers are open to new products, especially if they have a health benefit and are made up of natural materials. The 86 % of tasters are happy to buy the finished products. It can be assumed that consumers have strong connect between the healthy diet and sea buckthorn, so the young and health conscious consumer can be targeted with this product.



4. CONCLUSIONS

The aim of this research was to set up a technological process to obtain high-value biologically active extracts from sea buckthorn pomace, thereby helping to reduce waste from the juice industry. In the past few years, treating waste coming from the food industry, has become a remarkably important issue, due to environmental and economic reasons. Recycling waste should mean a satisfactory alternative, particularly, if we consider the amount of valuable components remaining in the waste of certain plants. On one hand, these could be retrieved using the proper method, and used again by the food industry. In our study, we have successfully recovered and recycled the antioxidant compounds from pomace of sea buckthorn to produce more valuable and special apple juice. These new aspects concerning the use of the pomace as by-products for further exploitation on the production of food additives with high nutritional value, their recovery may decrease quantity of a waste of valuable components and may be economically attractive.

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DEVELOPMENT OF MATZO MADE OF WHOLEMEAL RYE FLOUR AND ITS IMPLEMENTATION IN THE INDUSTRY

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ABSTRACT

In the baking industry, continuous development of products is required because consumers with different nutritional needs are pushing for new requirements for food. Along with the low caloric content, there is growing attention to the functional effects of foods.

The aim of our work is the development of a matzo made of wholemeal rye flour, which helps in healthy nutrition for the customer's and more economical from production's point of view. The main aim of the product development in our project is to increase the nutrient content by the raise of mineral and fibre content.

In the first part of our work we performed basic measurements with flours used during product development. We measured the quantity and quality of gluten protein with Glutomatic-Gluten Index System, the activity of amylase enzymes with Falling Number 1400 and we did complex dough monitoring with METEFÉM Valorigraphe FQA 205. In the second part of our project we compare the basic matzo with matzos made of 3 different recipes. Based on results of examinations it can be ascertain that the Sample 2 shows more advantageous values of the fibre content's and the prime cost's point of view.

Key words: trend, development, nutrition, matzo

1. INTRODUCTION

Bakery products are one of the most important food sources of the population [1]. Their protein, carbohydrate and vitamin content make their consumption an energy supplement in everyday life. The consumed foods help to maintain health, provide good physical and mental strength.

In the baking industry, continuous development of products is required because consumers with different nutritional needs are pushing for new requirements for food. Along with the low caloric content, there is growing attention to the functional effects of foods. Enriched bakery products are, overall, functional foods that have proven beneficial health effects along with their basic nutritional effects. It is important during nutrition that the process does not affect the basic organoleptic properties of the product [2].

In our work, we focused to increase the fibre content in a special bakery product which development is one of the main trends in the development of food in the baking industry [3]. Food fibers are complex, non digestible carbohydrates. The fibers are useful in preventing a number of diseases and abnormal conditions. Most importantly, they help reduce blood cholesterol levels, stabilize blood glucose, and also play a role in preventing colon cancer, obesity and constipation [4]. As a result, it is essential for the body to receive fiber in order to facilitate its normal operation.

We chosed the matzo for our work because, thank for its simple recipe and technology, it's very suitable for product development for consumers with different nutritional needs. Matzo is crisp and vesicular, unleavened bread made with water and flour, which is gastronomic and religiously important in Jewish culture. They can be consumed not only in bread form (Fig. 4), but are often used as raw materials for foods.



On the basis of the traditional recipe, matzo is characterized by a kind of neutral flavor, which is due to the fact that only flour and water are used during the preparation. The product does not contain added salt, sugar, spices or other substances. Thanks to the industrial revolution, when the mass production of matzo began, it was enriched with various materials to expand the customer circle. The reception of flavored products was different because of different world perceptions, but has now been accepted in several places. Bread consumption is now widespread and can be consumed by young children as it is easily digestible thanks to its simple composition. It is an ideal supplement to diets as opposed to traditional white bread, it does not contain yeast, fat, so its energy content is low.

2. MATERIALS AND METHODS

In the first part of our work we performed basic measurements with flours used during product development. We measured the quantity and quality of gluten protein with Glutomatic-Gluten Index System (Fig. 1), the activity of amylase enzymes with Falling Number 1400 (Fig. 2) and we did complex dough monitoring with METEFÉM Valorigraphe FQA 205 (Fig. 3) of BL80, BL160, RL90 and RLTK flours.

The gluten test was performed on the MSZ EN ISO 21415-1, MSZ EN ISO 21415-2 and MSZ EN ISO 21415-4 standards. During the study we determined the Gluten-index and the water absorption capacity of gluten protein from flours. By defining the Gluten-index, we can qualify the gluten proteins of the examined flours, thus determining the structure and physical properties of the dough and the degree of its gas retention, and the baking usability. The gluten test was performed only with wheat flours.



Figure 1. Glutomatic-Gluten Index System

The activity of amylase enzymes was tested according to the MSZ 6369-9:1977 standard. During the test, the enzyme content of the flours and their activity can be characterized, and the baking usability of flours.



Figure 2. Falling Number 1400

The complex dough monitoring was carried out according to MSZ 6369-6:2013 standard. During the measurement, the water absorption capacity and physical properties of the examined flour can be quantified.

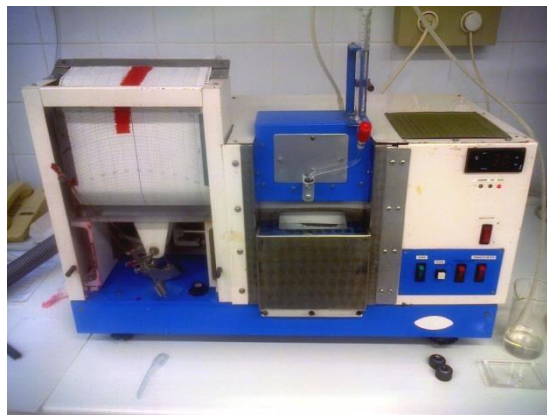


Figure 3. METEFÉM Valorigraphe FQA 205

In the second part of our project we compare the basic matzo with matzos made of 3 different recipes (Fig. 4). We named the basic matzo for Sample 1, and the 3 others for Sample 2, Sample 3 and Sample 4.

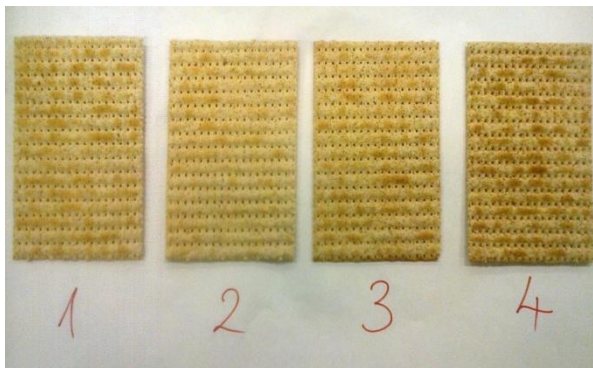


Figure 4. Comparison of basic matzo (No. 1) and matzos made of 3 different recipes (No. 2, 3, 4)

There was no change in the production method, for example baking temperature, only the composition was changed. During development, we must take into account that the new products meet the quality requirements of the basic matzo. The basic matzo contains only BL80 and RLTK flour, but the other 3 types of matzo contain different percentages of BL80, BL160, RL90 and RLTK flour. The composition of the new patterns is shown in Tab. 1. In view of the basic requirement, it is true for each product that its rye flour content is at least 40%. The amount of water used was determined by the quality of the dough made from different flours, and its suitability for further machining.

Table 1. Composition of the samples per 100 g finished product

Sample code	Materials [g/100 g of finished product]			
	BL80	BL160	RL90	RLTK
Sample 2	-	60	-	40
Sample 3	40	-	20	40
Sample 4	40	-	-	60

We measured the ash content according to MSZ 20501-1:2007 standard, the acid content according to MSZ 6369/11-87 standard, and fibre content with 2010 Fibertec System (Fig. 5) according to MSZ 6369/12-79 standard of matzo samples. We investigated the functional properties of the product under these tests. Then we made an organoleptic measurement and an economic calculation.



Figure 5. 2010 Fibertec System

3. RESULTS AND DISCUSSION

In the course of the studies we have found that BL80 and BL160 contain large amount of strong gluten proteins and each flour is low in enzyme content. In the baking industry flours with low enzyme content have negative impacts on the properties of the product but this feature doesn't matter to the matzo. In the dough monitoring it was found that each flour is suitable for matzo making, but RL90 is only slightly recommended because the large amount of water it absorbs reduces the efficiency of production.

During determining the ash content, we also determined the moisture content of the matzo samples. It can be concluded that none of the samples exceeds the moisture content of the Sample 1. Taking together the ash content and the moisture content, the most prominent data were found in Sample 4, but in measuring the acid content of matzos the results of Sample 4 are the worst. (Tab. 2) The reason for this is probably that Sample 4 contained large amounts of RLTK flour. The aim of our work is to find new recipes that result in higher fiber content. After determining the fiber content, it can be concluded that Sample 4 showed the best results during this study (Tab. 2). In addition, the fiber content test showed that the lowest value was shown in Sample 3. From this we can conclude that if some of the BL80 is replaced by RL90, the fiber content of the product decreases.



Table 2 Test results of the matzos

Sample Code	Moisture content [%]	Ash content [%]	Acid content [m/g]	Fibre content [%]
Sample 1	5,23	0,87	3,45	1,43
	5,33	0,86	3,55	1,41
Sample 2	5,02	1,00	3,70	1,45
	5,05	0,99	3,80	1,43
Sample 3	5,37	0,99	3,80	1,39
	5,37	0,97	3,90	1,42
Sample 4	4,70	1,06	4,05	1,73
	4,69	1,05	4,00	1,68

The organoleptic measurement included a critical group of 19 participants. During the organoleptic measurement, judges were asked to evaluate Samples 2, 3 and 4 from 1 to 3. Figure 6 shows that the most preferred sample for the consumer was the Sample 2. The least favoured product was the Sample 4.

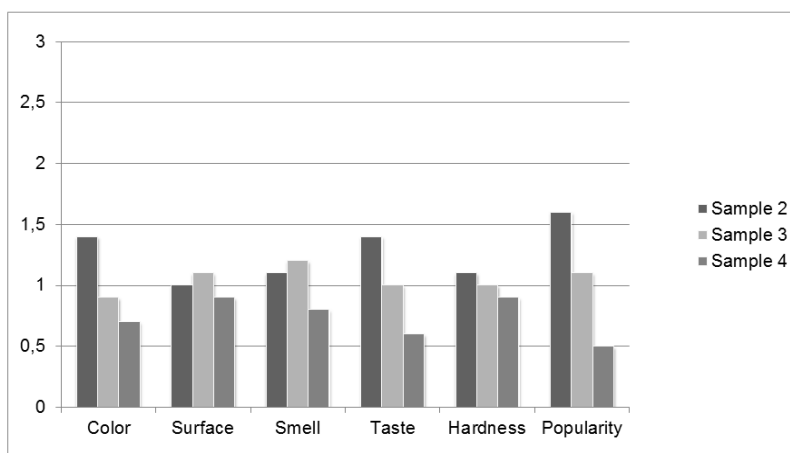


Figure 6 Compare the ranking of the samples made of new recipes

In the economic calculation, the direct material cost is determined by the quantity and knowledge of the flours used. The calculation shall take account of the loss of mass during baking and cooling. In the economic calculation it can be stated that Sample 2 requires the lowest production cost.



4. CONCLUSIONS

Based on our investigations we can conclude that the product development was successful, with the production of Sample 2 higher fiber content, popular and cheaper matzo can be produced. The sample complied with all requirements and fulfilled the goal of product development. The ash content and the fiber content of Sample 2 is the highest after Sample 4's, therefore our decision was greatly influenced by the opinion of consumers in organoleptic measurement. According to the organoleptic measurement, the 60:40 ratio of BL160 and RLTK in the product is the most favourable, which is manifested mainly in colour and taste scores, and the indicator of product popularity is higher than the others (min. 40 %).

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RESEARCH OF SATISFACTION BASED ON THE INVESTMENTS DONE IN SARKAD BETWEEN 2014 AND 2017

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ABSTRACT

We were searching for the first part of the development period from 2014 to 2020 in Sarkad, which mainly covers infrastructural investments. The purpose of our research is to investigate how the inhabitants think about the investments at a given time, and also to investigate the effect of the overall investments that they have experienced in Sarkad, in their own part of the city or in their own lives. The opinions of the participants in our questionnaire suggest that the upgrading's should be continued and, moreover, more investment for job facilities should be made by the local government in the city. This way, the satisfaction of the population could be maintained and the degree of emigration could be reduced.

Keywords: Sarkad, community development, hypothesis testing, infrastructural investment, Z-test, questionnaires, research of satisfaction

1. INTRODUCTION

On the one hand, our topic selection was based on the curiosity about the opinion of the residents of Sarkad on the local investments made since 2014, and since we have not found any relevant research work, we have found the right topic for our joint research. Our idea was given by the Integrated Urban Development Strategy in Sarkad published in 2010, which attracted our attention in how far this project has gone off. The following questions were asked: What does the local settlement development concept contain? How does the population assess the program? How do people from Sarkad get to know with the ongoing projects? Secondly, we chose this topic due to the fact that in 2016 several articles were published in the Local Newspaper that there are serious developments in the settlement. This was a great news for us, so we could ask the local population about some of the actual investments. It is true that the approval of most of the applications has been delayed and only took place in the second half of 2017, so we cannot cope with the ongoing investments in this research, but it will be a promising topic later. Similar residential satisfaction measurement documents have been revised such as [1], [2] and [3]. The selection also confirmed the fact that Máté Szigeti has been living in Sarkad for 22 years, and even his father and grandfather have grown up here, so they are known in the city. This factor has helped us to get as many people as possible, because today's people's trust is very difficult to earn, but everyone has their opinion, we just need time to listen to them.

2. MATERIALS AND METHODS

During the ground-scouting we visited the City Manager of Sarkad, MátyásCsepreghy and the Head of the Technical and Investment Department of Sarkad, Arnold Kővári, for more information on the investments made in the past few years and planned for next year. We have explained our research goals for both of them, and asked for their opinion on what would be the important factors for them, that are included in our research as a feedback to the local government.



We summarized our ideas and experiences gained from fieldwork. We prepared our questionnaire, which was signed on 25-26 March 2017 for a test question consisting of a ten person sample. For the sake of convenience, the participants in the trial questionnaire and the later respondents were selected from the same basic population. In addition, we did this in a similar environment [4]. The questionnaire was supplemented by protocol analysis and information summation, which provided us with relevant information about the mistakes of my questionnaire, which we could improve later on. Also, we could measure how much time it takes to fill in a questionnaire.

The responsible of the questionnaire was Máté Szigeti during the questionnaire survey, but her father helped us several times, which took place five consecutive Fridays, Saturdays and Sundays from 21 April to 21 May 2017. We have chosen the weekend days, because most of the population is not at work and there is no teaching. During our work, 365 questionnaires were filled in with the answers of the respondents.

To evaluate the data, we chose the Excel program, because we could use well-edited, varied diagrams and know the program well. [5] We applied the PSPP program to evaluate more complex relationships, such as to our hypotheses. Within this we created cross tables to get the data needed for the Z-test and a variance analysis was made to find that our hypotheses were correct or incorrect. The main thing is that it has a significant difference under the significance level of 0.05, whereas there is no significant difference above the 0.05 significance level.

3. RESULTS AND RATINGS

Most of the respondents are informed by Local Sarkad City Newspaper and, on average, about 1.32 sources, indicating that it is fairly unilateral for the population of Sarkad to be informed. Nearly one-fifth of the participants in our research are not satisfied with the amount of information we receive, which could be increased by getting Sarkad Tv into all households and increasing the number of resources available.

For most of the respondents (117 people), sewerage was the most important investment in the examined period. However, the restoration work was mixed, although most of them (135 people) considered this to be a bit positive, with the neutral (88 people) and negative responses (107 people) the whole. On average, the roads were refurbished, but the Roads of Sarkad were still poor or satisfactory.

It is true, that most people surveyed (135 people) put the equipment of surveillance cameras to the last place in the order of importance, but they still feel minimal improvement in the city's public security. Many respondents want to get feedback on whether cameras are effective and are suggesting an expansion of the number of cameras.

70% of the respondents were unable to judge the cost price of the allowance and the amount of support. Those however, who tried to do it rightly, overestimated the cost price twice.

Most of the respondents assessed the development of the local government positively, considering the impact of the investments on their own part of town and their own lives.

Respondents to the question of population retention were almost unanimous in answering the questionnaire, so we asked for their suggestions on how to improve this factor, which is outlined in Part 5 below.

4. HYPOTHESIS TESTING

Our first hypothesis, in which we hypothesized that most of the respondents living in the Old Town district made the installation of the cameras in one of the first three places in the order of importance, because we believe that this is the most important investment for them in comparison to other parts of the city. No part of our first hypothesis was justified.



For the first part of our hypothesis we used the Z-test for which the data was obtained from the questionnaire produced by the PSPP statistical program.

$$Z = \frac{p - p_0}{\sqrt{\frac{p_0 q_0}{n}}} = \frac{0,3489 - 0,50}{\sqrt{\frac{0,50 \cdot 0,50}{235}}} = -4.632638795207319 \quad (1)$$

The result of the Z-test (1) does not fall within the acceptance range between the -1.644853627 and $+\infty$ the significance level of 0.05. According to this, less than half of the respondents living in Old Town district ranked the cameras in the first three places.

Based on the variance analysis in the PSPP program, the second part of our hypothesis revealed a significant difference between the perception of the different neighbourhoods and the exception of a district, each of the districts placed the investment we have studied compared to Old Town district.

Our **second** hypothesis (2), in which we thought less than one third of the respondents were dissatisfied with the quality of the post-waste recovery work, proved to be true.

$$Z = \frac{p - p_0}{\sqrt{\frac{p_0 q_0}{n}}} = \frac{0,29315 - 0,33}{\sqrt{\frac{0,33 \cdot 0,67}{365}}} = -1.497237120104014 \quad (2)$$

For this hypothesis, we also used the Z-test for which the data was provided from the questionnaire, 7 questionnaire by the frequency, sample mean and spreadsheet of the PSPP program. The result of the Z-test was within the acceptance range between the -1.644853627 and $+\infty$ for the significance level of 0.05.

Our third hypothesis (3) is that the majority of respondents with at least matura examination and those with no matura examination did evaluate that their investments had a positive impact on their lives. Both parts are justified.

$$Z = \frac{p - p_0}{\sqrt{\frac{p_0 q_0}{n}}} = \frac{0,67907 - 0,50}{\sqrt{\frac{0,50 \cdot 0,50}{215}}} = 5.251365847793382 \quad (3)$$

For the first part of our hypothesis we used the Z-test, which verified both parts of the first half of the hypothesis because the results were within the acceptance range between -1.644853627 and $+\infty$. We also conducted a variance analysis on the hypothesis that there is a correlation between the maturity of the maturity and the impact of the respondents on their post-investment life. From the post-study results, it has been found that there is a significant correlation between the two variables (significance = $0.00 < 0.05$). This suggests that graduates with matura examination and non-holders differ in the impact of investments on their lives. While those with no matura examination were 3.42, then those with a matura examination had 3.75 of this value. Taking into account the average values of satisfaction (1-much worse, 2-bit worse, 3-same, 4-bit better, 5-better ratings) both positively evaluate the impact of investments on life, which is a justification for our hypothesis.



In our fourth hypothesis (4), in which we thought that the opinion of the respondents in the judgment of their own neighbourhood was different, the people in the Old Town district and Northern Quarter are more satisfied, but the inhabitants of the Newly District, Industrial Park and Outdoor Areas are less satisfied. The only factor that did not justify our hypothesis was that the inhabitants in the new district appreciated their own district just as we expected.

$$Z = \frac{p - p_0}{\sqrt{\frac{p_0 q_0}{n}}} = \frac{0,47333 - 0,50}{\sqrt{\frac{0,50 \cdot 0,50}{150}}} = -0.6532789144002736 \quad (4)$$

Based on our hypothesis we have analysed the variance in the PSPP program, whether there is a relationship between residence and residence satisfaction. As a result, it became apparent that there was a significant difference between the satisfaction of the inhabitants in the different parts of the city (significance = 0,000 < 0.5). Considering the average values of satisfaction (1-very negative, 2-rather negative, 3-neutral, 4-rather positive, 5-very positive rating). The average satisfaction of the Old Town residents is 3.57, which exceeds the highest and the total average of all the city districts by five hundredth. The average rating of residents in the Northern Quarter is 3.52. This is exactly the same as the total average and the same as the inhabitants in the New District. According to this, the previous three districts are more positive by the opinion of the inhabitants. The area of the Industrial Park has an average rating of 3.15, while the average number of residents in the Outdoor Area is 2.71. The last two results mean that industrial parks and those living in the Outside Region have had a neutral effect in their city area after the investments between 2014 and 2017.

All in all, it was found that our 1st Hypothesis as a whole and the part of our 4th Hypothesis based on the inhabitants in the New District did not prove to be true, while the 2nd and the 3rd Hypothesis as a whole, and one part of the 4th Hypothesis proved to be true.

5. CONCLUSIONS, SUGGESTIONS

Our traffic development proposals compared to the respondents and for our own opinion are the following. All streets of the city should be designed to be built with an asphalt pavement road. For cross-border connections, we consider it preferable to introduce a bus service to Nagyszalonta, as there are more relatives in the two countries. There should be a dense bus service between Sarkad and Doboz, as this would relieve and make the busses going to Gyula more comfortable. By doing so, it will shorten the reach of the county seat in time and distance.

A food processing plant based on local animal and plant breeding, but the canned and textile industry was also raised in the correspondents, by which providing long-term jobs and decent wages for the residents would be easier. Even with the abolition of sugar quota, the possibility of re-launching sugar could be explored.

Establishing a complex sport meeting for all needs, serving local sports clubs, such as tennis, football, table tennis, volleyball and women's' handball. Establishment of cultural entertainment venues. The actual construction of the long promised swimming pool. Increasing the tourist utilization of the Fekete Körös.

Among the proposals to extend existing institutions, we need to increase the extension of the Elderly Home, the expansion of the Nursery and the renovation of the school gymnasiums.



Suggestions related to the environment, to solve the problems of satisfied respondents after the sewage channelling in our second hypothesis, which means deficiently restored roads and repellent nuisances. Drinking fresh water in the Gyepes Stream for most of the year. Improving lighting in the industrial park area. The preservation of the further destruction of the uninitiated houses, the calling of the owners, and ultimate transformation into a local government apartment. Settling problematic areas with public workers. Increasing attention to stray animals. Increasing the number of scapegoats and increasing the number of cameras around the various institutions, which is needed to exceed the status of cleanliness and orderliness. Also, solar cells started to be installed or even supplemented with wind power plants.

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INVESTIGATION OF SORPTION OF 2,4-DICHLOROPHENOL ON SPECIAL HUNGARIAN OIL SHALE

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ABSTRACT

The development of efficient methods for the removal of different type of organic contaminates of natural waters is an ever challenging task in the modern environmental technology. The paper reports the physical characterization and adsorption properties of a Hungarian oil shale. Static equilibrium experiments were carried out to study the adsorption of 2,4-dichlorophenol (2,4-DCP) from aqueous solution. The obtained equilibrium data were satisfactorily fitted by a multistep adsorption isotherm within the concentration range of 0 to 100 mg/l. According to our laboratory scale experiments the studied row oil shale (OSR) adsorbent immobilizes the contaminants more efficiently than a number of other adsorbents applied in different remediation technologies. More than 90 % of the added 2,4-dichlorophenol was adsorbed by the studied oil shale. The contaminants are bound strongly by the sorbent therefore they cannot be washed out by the groundwater flow which, in turn, favors to the natural bacterial decomposition process of the polluting compound. This is considered as a significant advantage of the adsorbent because no chemical regeneration of the inexpensive oil shale is required. The reported results indicate that the oil shale can be used efficiently for the treatment of natural waters to remove their organic contaminants.

Keywords: oil shale, adsorption, 2,4-dichlorophenol

1. INTRODUCTION

Water pollution problems caused by organic contaminants emitted by the chemical industry and agricultural activity are especially severe because they threaten both soil and aquatic live too. Chlorophenols are chlorinated aromatic compounds. They are present in surface and subsurface waters as a result of natural degradation of different pollutants released by the agriculture and by various industrial plants (oil, plastics, pharmaceutical, wood preserving etc.) [1].

Chlorophenols are persistent in the environment [2] and can cause toxicity especially by bioaccumulation in animals and plants whereby threatening human health too [3].

The removal of these compounds from contaminated raw water as well as from industrial wastewater is a difficult task. The applied removal techniques typically include adsorption, photocatalytic decomposition and biodegradation as well as different combined methods [4]. The adsorption is one of the most common and established water purification processes [5]. Researchers tested many different types of adsorbents and ion-exchangers for removal of chlorophenols from contaminated waters [3].

The studied oil shale adsorbent contains considerable amounts of clay minerals as well as organic matter too which is finely dispersed in the macro- and micropores of the inorganic matrix. This rock could



therefore, be utilized as an inexpensive and efficient adsorbent for the removal of substituted phenolic compounds from contaminated waters [7].

Oil shale sources are located at several places of the Carpathian Basin, and especially large amounts can be found in the Hungarian mines. It is an algae based biomass fossil fine-grained sedimentary rock containing large amounts of organic matter, clay volcanic ash and calcium carbonate. The shale originates from the biomass of yellow green algae – genus *Botryococcus braunii* – accumulated in the volcanic craters over 4 to 5 million years [3].

The organic matter is composed of bitumen and large amount of kerogen [5]. The kerogen is an amorphous, three-dimensional polymer organic matter. It is insoluble in conventional organic solvents [5]. Much of the hydrocarbon is bound because of the low stage of thermal maturity, while the free hydrocarbon (HC) content ranges from 0.1 mg HC/g rock to 12.3 mg HC/g rock.

Since the 2,4-DCP is an intermediate in the production of different aryloxy alkanolic acid herbicides like the 2,4-dichlorophenoxy acetic acid (2,4-D) and it is also their important degradation product [2], the aim of our work is to investigate the sorption properties of Hungarian oil shale as an adsorbent for the removal of 2,4-DCP from model water samples, under laboratory conditions. The effect of the various parameters such as the initial concentration of the 2,4-DCP, the pH of the solution and the organic material content of the oil shale were examined.

2. MATERIALS AND METHODS

2.1. Materials and adsorbents

Analytical grade sodium chloride, sodium dihydrogen phosphate and disodium hydrogen phosphate were obtained from Reanal Chemical Co. (Hungary). The HPLC grade solvent (acetonitrile) was provided by VWR Ltd. (Hungary). The 2,4-DCP standard reference material (>99%) was the product of Sigma Aldrich. Hungarian oil shale samples were collected from different locations of the mine and were used in this work as adsorbent. The samples were first air-dried, then milled for 1 hour and sieved (particle size below 360 µm was used). Particle size distribution of OSR was measured using Mastersizer 2000 laser diffraction system (Malvern Instruments Ltd). Total organic carbon content (TOC) of adsorbents were determined by Apollo 9000 (TEKMAR DOHRMAN) TOC Analyzer. Nitrogen gas adsorption isotherms (BET surface) and pore size were obtained with ASAP 2000 apparatus.

The main mineral fraction of adsorbents was analyzed using the PHILIPS PW3710 X-ray diffractometer (K filter, Cu radiation (50 kV, 40 mA)). The crystalline phases were identified using the X'Pert Highscore Plus software. Scanning electron microscopy for oil shale samples was conducted using Thermo Fischer APREO SEM attached with EDX units, with accelerating voltage 20 kV.

The pH of OSR were measured by a Radelkis pH meter (OP-211) using a combined glass electrode (Radelkis, OP-0808P).

The measured physical and chemical properties of the studied OSR are summarized in Table 1.



Table 1. Characterization of the oil shale (OSR) sorbent

<i>Properties</i>	<i>OSR</i>
pH (1 mol/L KCl)	7.21
BET*, m ² /g	31.87
Typical pore size, nm	3.4
Main fraction, %	80.8
Particle size, μm	50-150
Organic content, %	9.79
Carbonate content, %	41.2
<i>Main mineral phases, %</i>	
	23.0
Calcite	7.3
Quartz	1.6
Siderite	6.2
Dolomite	2.5
Albite	1.8
Caolinite	0.6
Montmorillonite	38.7
Illite	0.7
Amorphous material	17.7

*Specific surface obtained by BET nitrogen adsorption method

In order to investigate the effect of organic matter content on the extent of adsorption 7 different samples were used (OS2, OS3, OS8, OS9, OS10, OS11, OS12). Their organic content, ignition loss and the main minerals are summarized in Table 2.



Table 2. The main components of different oil shale samples

Properties	oil shale adsorbent						
	OS2	OS3	OS8	OS9	OS10	OS11	OS12
Total organic carbon content of adsorbent (TOC, m/m %)	16,7	32,8	24,8	18,3	39,8	6,85	40,1
Main minerals							
Calcite	X	X	X	X	X	X	X
Quartz	X	X	X	X	X	X	X
Siderite	X	X	-	X	X	X	X
Dolomite	X	X	X	X	X	X	X
Albite	X	X	X	X	X	X	X
Caolinite	X	X	X	X	-	X	X
Montmorillonite	X	X	X	X	X	X	X
Illite	X	X	X	X	-	X	-
Aragonite	X	X	X	X	X	X	X
Gypsum	X	X	-	X	-	-	X

2.2. Adsorption studies

The adsorption isotherms were obtained in a series of batch experiments. The procedure is summarized in the scheme shown in Fig. 1. Static equilibrium experiments were carried out in a solution containing 0.1 mol/l NaCl and 0.01 mol/l phosphate buffer of three relevant environmental pH values ($\text{pH}_1=5.2$; $\text{pH}_2=7$; $\text{pH}_3=8.2$). 5-5 g of adsorbent were left to swell in 5 ml distilled water for 24 h at room temperature, then 65 ml of 2,4-dichlorophenol (solute) in appropriate buffer solutions (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mg/l) was added. The suspension was shaken for 1 hour in an orbital shaker then separated by centrifuge at 6000 rpm for 20 min. The supernatant was filtered then analyzed by HPLC.

The percentage removal of adsorbed 2,4-DCP was calculated using the relationship shown by Equ. (1), [4].

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \cdot 100 \quad (1)$$

where

C_0 and C_e (mg/l) are the initial and final (equilibrium) concentration of the 2,4-DCP respectively.

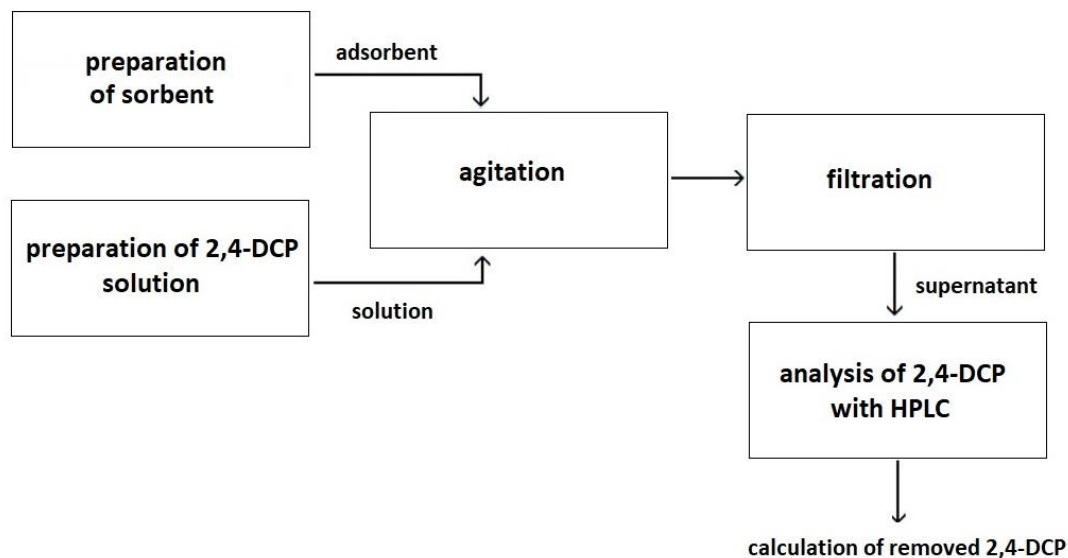


Figure 1. Scheme of the batch experiments

In the supernatant, the concentration of the 2,4-DCP was determined by a MERCK LaChrom HPLC system equipped with a LiChospher 100 column filled with 5 μm RP-18 packing material (125 mm x 4 mm) and with programmable UV detector. Samples of 10 μl injected by an autosampler were isocratically eluted by a hydro-organic eluent containing 65 % acetonitrile and 35 % water; flow rate: 0.7 ml/min; $\lambda=218$ nm. The concentration of the standard 2,4-DCP solution used for analytical calibration curve ranged from 1 to 50 mg/l ($R^2 > 0.99$). The standard deviations of the HPLC determinations ranged from ± 0.03 to ± 1.15 mg/l [3].

The pH of the solutions was measured by a Radelkis pH meter (OP-211) using a combined glass electrode (Radelkis, OP-0808P).



3. RESULTS AND DISCUSSION

The adsorption isotherms are important to describe the solute-adsorbent interaction. A multi-step isotherm model [8] was employed for the numerical fitting of the isotherm data to Equ. (2) by the Microcal TM, Origin 6.0 software.

$$q = \sum_{i=1}^s \left\{ \frac{q_{Ti} K_i (c - b_i + |c - b_i|)^{n_i}}{2^{n_i} + K_i (c - b_i + |c - b_i|)^{n_i}} \right\} \quad (2)$$

where

c is the equilibrium concentration of solution, [$\mu\text{mol/l}$],

s is the number of steps of the isotherm ($i = 1 \dots s$),

q_{Ti} is the adsorption capacity, [$\mu\text{mol/g}$],

K_i is the equilibrium constant, [$(\text{l}/\mu\text{mol})^{n_i}$],

b_i is the critical concentration limit, [$\mu\text{mol/l}$],

n_i is the average degree of association assigned to the i -th step of the adsorption curve.

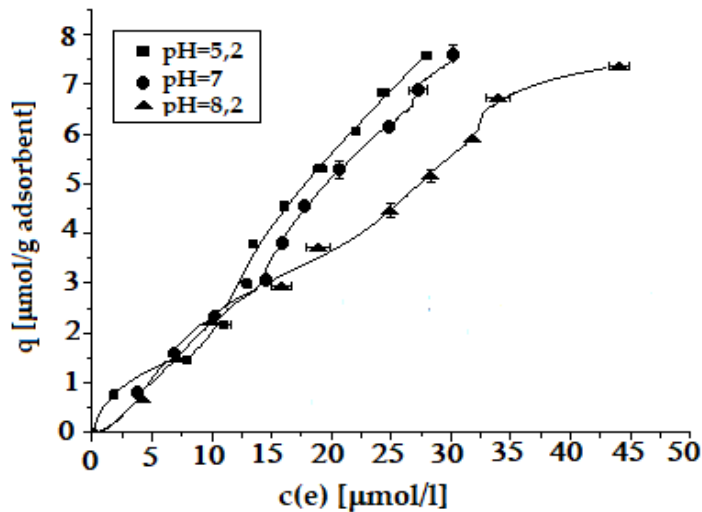


Figure 2. Effect of initial pH on sorption of 2,4-DCP by oil shale (OSR)



Adsorption isotherms for the 2,4-dichlorophenol on oil shale (OSR) at different initial pH values of the solution are shown in Fig. 2. These curves were fitted by Equ. (2) and the parameters were obtained by a least square procedure. The calculated equilibrium parameters of the adsorption and the related statistical measures of the goodness of fits are presented in Table 3.

Table 3. Calculated parameters of Eq.(2) for the adsorption isotherms of 2,4-DCP at various pH, at 25°C

Parameters	pH = 5.2	pH = 7.0	pH = 8.2
q_{T1} , $\mu\text{mol/g}$	54.15	11.05	7.53
q_{T2} , $\mu\text{mol/g}$	54.01	2.71	5.41
q_{T3} , $\mu\text{mol/g}$	5.09	1.62	-
K_1 , $(\text{l}/\mu\text{mol})^{n_1}$	$5.04 \cdot 10^{-2}$	$1.48 \cdot 10^{-2}$	$5.82 \cdot 10^{-3}$
K_2 , $(\text{l}/\mu\text{mol})^{n_2}$	$3.67 \cdot 10^{-3}$	0.21	0.12
K_3 , $(\text{l}/\mu\text{mol})^{n_3}$	$3 \cdot 10^{-5}$	0.32	-
b_1 , $\mu\text{mol/l}$	0	0	0
b_2 , $\mu\text{mol/l}$	48.88	56.84	70.60
b_3 , $\mu\text{mol/l}$	70.23	100.66	-
n_1	1.19	1.07	1.38
n_2	0.67	0.10	0.15
n_3	3.91	0.79	-
χ^2	$6.30 \cdot 10^{-2}$	$8.12 \cdot 10^{-2}$	$2.06 \cdot 10^{-2}$
R^2	0.99525	0.998	0.99795

3.1. The effect of pH

As can be seen in Fig. 3 and in Table 3, the pH of the aqueous phase is the most important parameter controlling the adsorption efficiency of the chlorophenols [9]. Since the 2,4-DCP is a weak acid ($\text{pK}_a = 7.85$, [10]), its speciation is governed by the pH. In the $\text{pH} < 7.85$ range the dominant form is the neutral, molecular species, while in the $\text{pH} > 7.85$, alkaline conditions the negatively charged anionic form dominates in the solution.

The initial parts of the isotherms indicate that in these regions the adsorbed amounts are not markedly influenced by the pH. This is due to the buffer capacity of the adsorbent itself which is efficient enough to maintain a uniform pH of the solution phase around its own pH value being ~ 7.2 . At this pH the 2,4-DCP is mostly occur in neutral form which favors the preferential uptake (sorption) of the contaminant ($7.2 < \text{pK}_a = 7.85$). At higher values of the adsorbed amount, however, the pH of the solution overwhelms the buffering effect of the adsorbent and the pH of the solution together with the ionization of the sorbed 2,4-DCP become the determinant factor and, as is expected, the adsorbed amounts decrease with the increase of pH. This is quantitatively shown in Table 3; the adsorption capacity (q_1) values of the first step of the isotherms are decreasing with the increase of pH. The reason is the electrostatic repulsion between the negatively charged surface of the rock and the phenolic anion.



3.2. Effect of organic material content of sorbent

Comparing the adsorption efficiency of various oil shale samples containing different amount organic phase, it can be seen that the higher is the TOC content the more 2,4-DCP is adsorbed (Fig. 4). It can be supposed that the apolar-apolar interaction works as an efficient sorption mechanism between the organic phase of the oil shale and the phenol species occurring at this pH dominantly in neutral form.

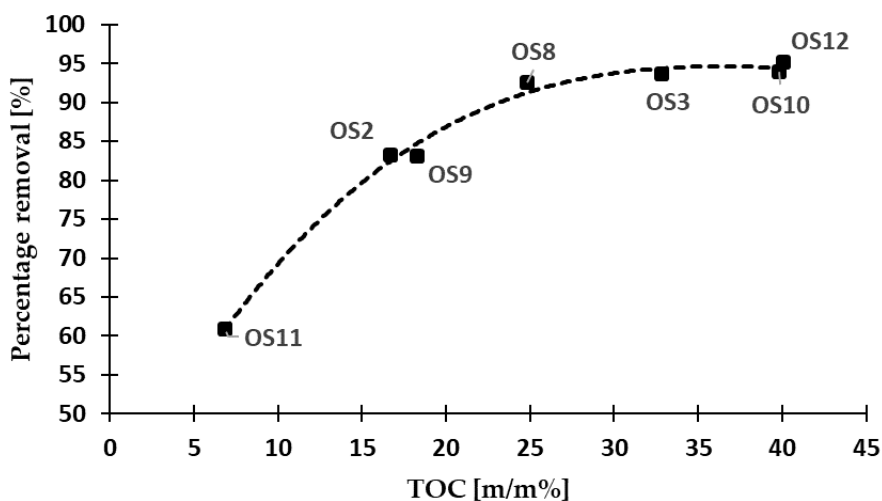


Figure 4. Effect of organic carbon content of oil shale adsorbent

3.3. SEM micrographs

The morphologies of the raw oil shale (OSR) and that of the adsorbent after the adsorption of 2,4-DCP were investigated by scanning electron microscope (SEM). The obtained micrographs are shown in Fig. 5. The SEM picture show well preserved fossil colonies of the *Botryococcus*. The cell content was removed during the fossilization while the outer walls of *Botryococcus braunii* colonies survived the diagenesis [11]. The SEM shows these empty cells voids surrounded by thick outer walls (Fig. 5 (1)), which were then filled with 2,4-DCP after the adsorption and cover the surface of adsorbent (Fig. 5 (2)).

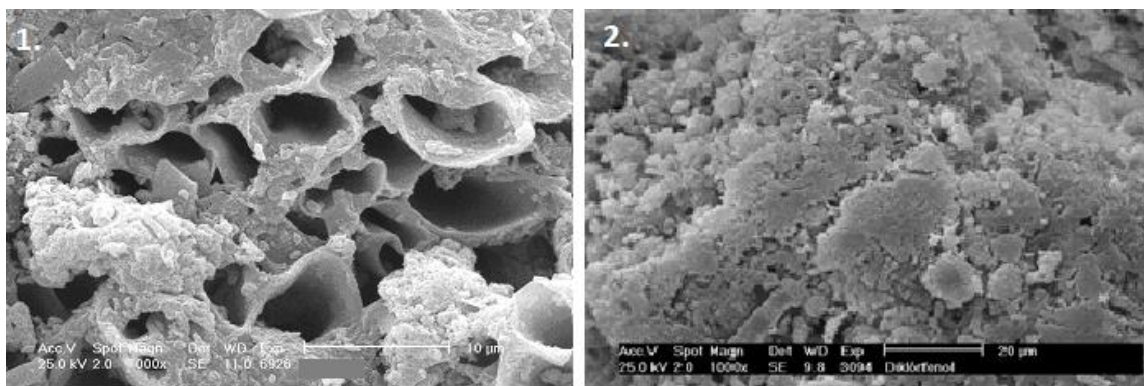


Figure 5. SEM micrograph of raw OSR (1) and with adsorbed 2,4-DCP (2)

4. CONCLUSION

Laboratory scale study of adsorption properties of the Hungarian oil shale revealed that it can be used as a low-cost adsorbent for the efficient removal of 2,4-dichlorophenol pollutant from surface and waste waters. Characteristic equilibrium parameters of the adsorption were obtained by fitting a multi-step isotherm equation to the experimental isotherms obtained at the pH values of 5.2, 7.0 and 8.2. The adsorption is favored by lower values of the pH and by the higher organic content of the oil shale. SEM micrographs clearly show the open barrel structure of the mineral phase which becomes highly covered after the adsorption of the organic contaminant.

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THE DEVELOPMENT OF FLY ASH – RED MUD BASED GEOPOLYMER

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ABSTRACT

Taking into account environmental considerations, such as decreasing CO₂ emission and the ecological footprint, the utilisation of secondary raw materials is essential for sustainable development. Fly ash is the product of coal combustion plants that is collected by various air cleaning equipment from flue gas, and red mud is the by-product of the Bayer-process, through which alumina can be produced from bauxite. Geopolymerisation is a process that is suitable for the utilisation of such wastes to produce ceramics, cement, concrete etc. with many advantageous properties.

The main objective of the article is to present data on the development and examination of geopolymer made out of deposited fly ash from Tatabánya and red mud from Almásfüzitő.

During the experiments, red mud was added to previously optimised fly ash geopolymer in various quantities and compressive strength tests were carried out to determine the optimal fly ash and red mud ratio. However, as the cracking of the specimens could be observed, further tests were carried out on the durability of the geopolymers. The effect of the sealing conditions and RM calcination was investigated, both via visual inspection and with FT-IR analysis at the ages of 3, 7, 14, 28 and 90 days.

Based on the results, it could be concluded that the sealing conditions have direct effect on the structural characteristics of fly ash – red mud based geopolymers, but further experiments should be carried out for the identification of the ongoing reactions.

Keywords: geopolymer, fly ash, FT-IR, red mud

1. INTRODUCTION

Geopolymers are inorganic polymers synthesized by the reaction of alumino-silicate and alkali compounds at ambient or near ambient temperature. As certain industrial wastes, such as fly ash, blast furnace slag and mine tailings contain sufficient amounts of reactive alumina and silica, they can be used as raw materials for geopolymerization. Therefore, geopolymerization can be considered a viable technology to transform industrial wastes into utilisable materials. Furthermore, geopolymers possess excellent physico-chemical and mechanical properties, e.g. low density, high strength, thermal stability, fire and chemical resistance. Thus, many industrial applications are viable in the areas of construction, road building, mining, metallurgy etc [1, 2, 3, 4, 5].

Fly ash is an industrial waste produced by coal-fired power plants and collected during flue gas cleaning, i.e. with filter bags, electrostatic separators etc. Its main constituents are SiO₂ and Al₂O₃, but other minor components can be frequently found in it as well, e.g. CaO, Fe₂O₃, MgO etc. [6, 7]. Red mud is the by-product of the Bayer-process, through which alumina can be produced from bauxite ore. It is a highly alkaline material, 11.3 ± 1.0 pH, with high moisture and very fine particle size. The main constituents include Fe₂O₃, Al₂O₃, SiO₂, CaO, Na₂O, TiO₂, K₂O and MgO [7, 8].

The aim of the experiments was to develop geopolymer with the synergic use of fly ash and red mud, and to examine its properties and durability.

2. MATERIALS AND METHODS

The main solid raw materials were landfilled brown coal fly ash (FA) from Tatabánya and red mud (RM) from Almásfüzitő. The particle size distribution of FA and RM was examined with a Horiba LA950 V2 type laser particle size analyser. The particle size distribution of both solid raw materials can be observed in Fig. 1. The median particle size of the FA was $x_{50}=24.28 \mu\text{m}$ and $x_{50}=3.09 \mu\text{m}$ for the RM.

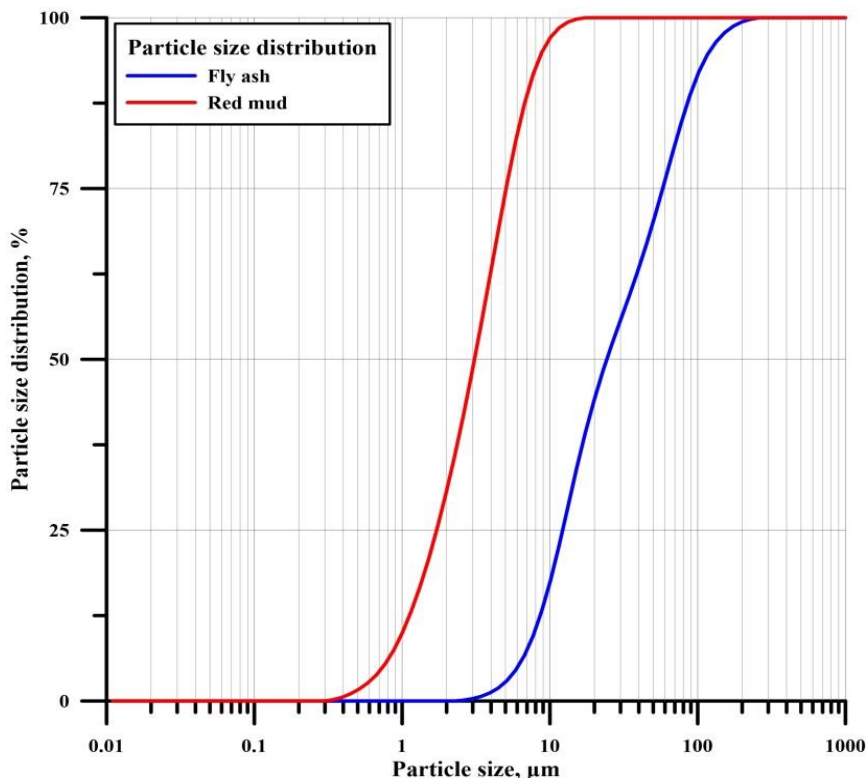


Figure 1. The particle size distributions of the fly ash and red mud samples

The moisture content of the FA samples was 28.80%, and the ignition loss was 0.75%. Based on the XRF analysis, the main oxidic components were SiO_2 (46.40%), Al_2O_3 (27.40%), Fe_2O_3 (6.96%), CaO (7.04%), MgO (2.23%), K_2O (1.65%) and TiO_2 (0.94%). The FA was first oven dried at 105 °C and then mechanically activated, i.e. ground for 10 minutes in a $\varnothing 305 \times 305$ mm ball mill.

The moisture content of the RM was 38.16%. After oven-drying at 105 °C, RM was pulverised in a mortar. For the durability tests, the dried and pulverised RM was also calcined at 850 °C for 1 hour.

The mineral composition of RM obtained from the XRD test is summarised in Tab. 1.



Table 1. The mineral composition of red mud

Phase	Ratio, wt. %
Hematite	38.4
Cancrinite (OH)	25.7
Cancrinite (CO ₃)	12.1
Katoite	7.6
Calcite magnesian	4.9
Gibbsite	4.2
Boehmite	0.6
Zircon	0.4
Amorphous	6.0

Based on previous experiments [9], the liquid/solid ratio was 0.82, with 8 M NaOH solution and Betol SB type water glass used as an activator solution; the composition of the water glass is SiO₂ (25.3%), Na₂O (13.7%) and K₂O (2.7%).

For geopolymer production, fly ash, red mud and the activator solution was mixed in 5 different ratios and 5 specimens were prepared from each paste. After holding the moulded geopolymer paste under sealed conditions for 24 hours, heat curing was carried out at 50 °C for 6 h. Then the specimens were left to cool down. After a five-day holding time, uniaxial compressive strength tests were carried out.

A Jasco FT-IR 4200 type Fourier transform infrared spectrometer was used for the structural analyses.

3. RESULTS AND DISCUSSION

3.1. The effect of red mud addition

At a constant solid matter quantity, fly ash was substituted with 0, 5, 10, 20 and 40 wt.% red mud. The obtained average uniaxial compressive strength values and specimen densities are illustrated in Fig. 2.

Without the addition of RM, over 20 MPa average compressive strength values could be achieved which was the highest among the examined mixtures. With the addition of 5, 10 and 20 wt.% RM, the uniaxial compressive strength decreased but remained around 15-20 MPa. However, the use of 40 wt.% RM drastically decreased the compressive strength of the specimens, but still reached over 9 MPa

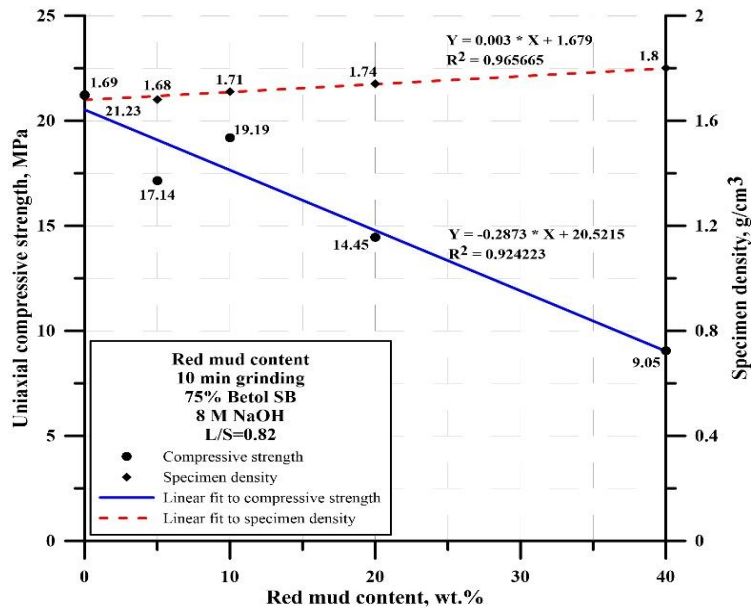


Figure 2. The effect of red mud on the average compressive strength and specimen density

The produced fly ash – red mud geopolymers had similar, or even higher compressive strength values than the geopolymers found in literature, produced under similar circumstances [7, 10 11].

In case of specimen density, the higher the red mud content in the geopolymer paste was, the higher the average specimen densities became.

3.2 Durability tests

As the cracking of the 20 and 40 wt.% RM content specimens could already be observed after the 5-day holding time, next, the durability of the specimens was examined.

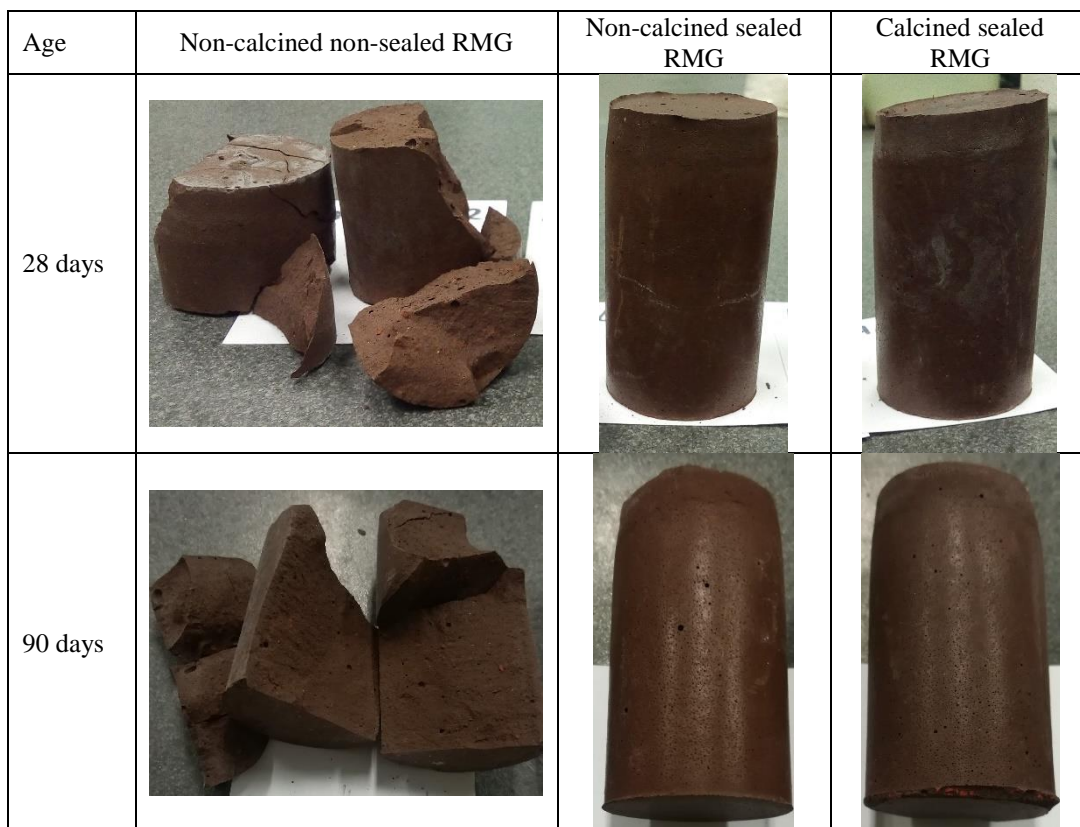
Three sets of geopolymers were produced using 20 wt.% RM to examine the effect of RM preparation and sealing conditions: non-calcined non-sealed red mud geopolymers (RMGs), non-calcined sealed RMGs and calcined sealed RMGs. Visual examination and FT-IR analysis was carried out at the ages of 3, 7, 14, 28 and 90 days. Photos of the specimens at the examined ages can be observed in Tab. 2.

In case of the non-calcined non-sealed RMGs, the cracking of the 3- and 7-day-old specimens could be observed and after 14 days, each specimen was fractured. On the other hand, all the RMGs held under sealed conditions were intact even after 90 days.

Table 2. The 3-, 7-, 14-, 28- and 90-day-old RMG specimens



Age	Non-calcined non-sealed RMG	Non-calcined sealed RMG	Calcined sealed RMG
3 days			
7 days			
14 days			



To identify and monitor the structural changes in the geopolymers, FT-IR analysis was carried out after the visual inspection. The wave numbers of the identified peaks and the assigned vibrations are summarised in Tab. 3.

Table 3. The characteristic wave numbers and the assigned vibrations of the RMGs

Wave number, cm^{-1}	Vibration
3600 – 2300	stretching –OH, HOH
1650 – 1630	bending HOH
1430 – 1410	stretching O–C–O
1090 – 990	asymmetric stretching Si–O–Si and Al–O–Si

The broad bands in the region between 3600 and 2300 cm^{-1} , i.e. the stretching vibrations of –OH and HOH, and the peaks between 1650 and 1630 cm^{-1} , i.e. the bending vibration of HOH groups, are associated with absorbed water on the surface and imprisoned water in the cavities of the specimens. The peaks between 1430 and 1410 cm^{-1} indicate the stretching vibration of the O–C–O bond of atmospheric carbonation, due to the reaction of NaOH with atmospheric CO_2 . Between 1090 and 990 cm^{-1} the peaks assigned to the asymmetric stretching vibrations of Si–O–Si and Si–O–Al bonds can be found, which are characteristic to geopolymers [2, 4, 12, 13, 14].

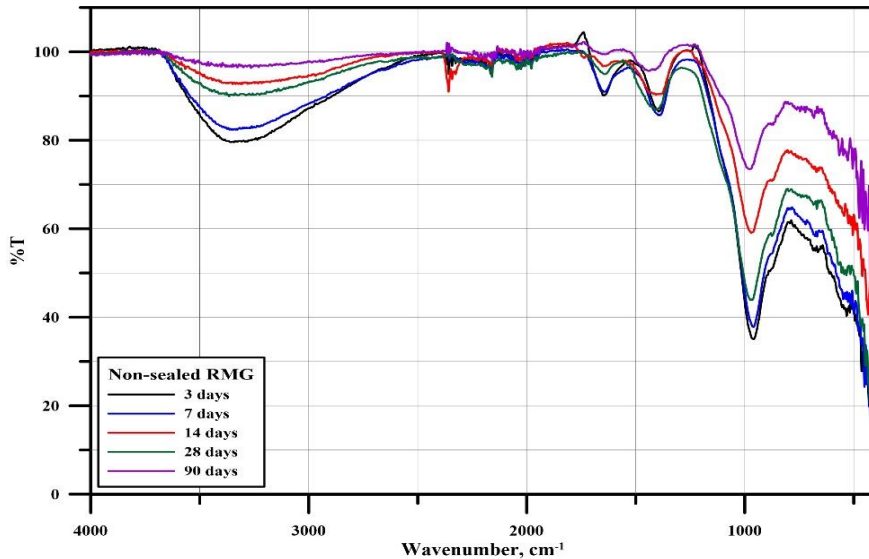


Figure 3. The FT-IR spectra of the non-calcined non-sealed RMG samples

In case of the non-calcined non-sealed RMGs (Fig. 3), the intensity of the peaks continuously decreased until 14 days, but at the age of 28 days, a small increase of each peak could be observed. However, by the 90-day analysis, all peak intensities lessened.

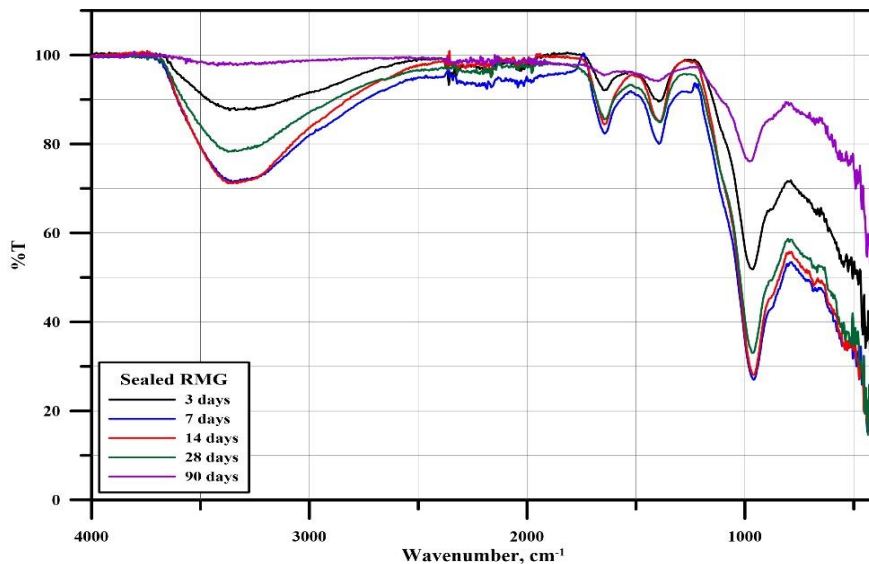


Figure 4. The FT-IR spectra of the non-calcined sealed RMG samples

As it can be observed in Fig. 4, the peak intensities of the non-calcined sealed RMGs increased after the first analysis at the age of 3 days. At 7 and 14 days, the intensities of the peaks associated with the stretching vibrations of the -OH and HOH bonds and the asymmetric stretching vibrations of Si-O-Si and

Si–O–Al bonds followed a similar trend, but the other peak intensities decreased at 14 days. After that, the intensity of every identified peak considerably decreased.

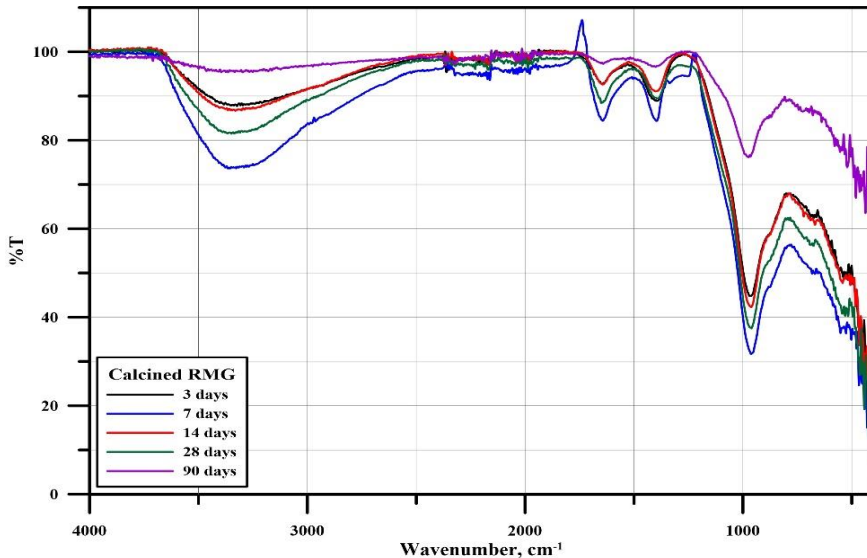


Figure 5. The FT-IR spectra of the calcined sealed RMG samples

The examination of the FT-IR spectra of the calcined sealed RMG samples (Fig.5) revealed no clear trends in relation to the ages of the specimens. The highest peak intensities can be observed after 7 days and the lowest intensities at 90 days. The 3- and 14-day spectra show a similar trend.

Based on the FT-IR analyses it can be stated that by the age of 90 days, the polymerization and polycondensation reactions die down and most of the water is consumed during the different reaction stages.

4. CONCLUSIONS

Based on the uniaxial compressive strength tests, it can be concluded that relatively high-strength geopolymer can be made at the age of 7 days from the combination of fly ash from Tatabánya and red mud from Almásfüzitő. However, the cracking of the specimens can be observed when higher amount – 20 and 40 wt.% – RM is added to the mixture. According to the durability tests, the sealing conditions have significant effect on the durability of the specimens. The non-calcined non-sealed geopolymers were fractured after 14 days, and the peak intensities of the FT-IR spectra showed lower intensities than the sealed specimens. When the specimens are sealed, calcination has no noticeable effect on the durability of the geopolymers.

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POSSIBLE IMPLEMENTATIONS OF THE CLOUD-BASED DATA-CENTRIC IOT PILOT PLATFORMS FOR SMART CITIES AND AGRICULTURE

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ABSTRACT

The Internet of Things (IoT) is starting to appear everywhere in many shapes and forms. But security is one of the most crucial thing that could trip up the growth of the IoT. Following security principles used in enterprise computing can help clear that issue. Already there are more connected devices than people on the planet, according to leading researchers in this area. By 2020, there will be 50 billion connected devices, outnumbering people by more than 6 to 1. Most of these devices will be controllable over the Internet, and they will increasingly be responsible for collecting and transmitting sensitive data. Today consumers might own an app that collects information on their exercise routine. In a few years, those same people might have an Internet-enabled medical device that continually delivers data to their doctor. In the wrong hands, data from home management systems could be used to assess user's whereabouts. Likewise, businesses could be vulnerable when they connect things like HVAC, irrigation, or commercial appliances.

Keywords: IoT, Smart city, Cloud platform

1. INTRODUCTION

Within this work, a documented remote control of heating via the http protocol has been made and a brief description of the Internet of Things paradigm and the smart home. The platform on which the work was made is the popular PC Raspberry Pi, with the Raspbian version of Linux [23]. Software has been written to run on Raspberry Pi (Python and bash shell) and a simple user interface in JavaScript and HTML. Raspberry Pi also spins the apache server on itself. There is also a simple demonstration with servos. PWM modulation was used to adjust the position of the valves. The introduction introduces a brief description of the fields to be processed, and IoT is described further. It is based on the technical performance itself and the description of the hardware part (Raspberry) and the software part with the code snippets. In conclusion, the proposed system improvements were suggested. [20]

Home Automation is the use and control of home appliances via remote control or automatically. For this purpose, the Internet of Things has recently started to be mentioned, ie, a network of sensors and actuators inside a home controlled by a central system that automates the home. It is estimated that by 2019, 68 million homes in America and Europe will be "smart homes". Also, it is assumed that up to 2020, 50 billion devices will be networked within the Internet of Things paradigm. Within this paradigm there is also the "smart lighting" discussed in this final work. 19% of the world's electricity consumption is used for lighting and 6% of greenhouse emissions comes from that energy. Smart lighting is a good way to minimize and save on lighting, with remote on and off lights. It also provides a greater level of comfort within the home itself. [22]

This theme was selected because of the ease of availability of the Raspberry Pi platform, due to the many open source codes and the interest of the same theme. The aim is to approach Raspberry Pi platform students, learn something about the Internet of Things paradigm and study smart homes as the coming new technology.



2. INTERNET OF THINGS PARADIGM

In general, the term Internet of Things (internet stuff) was coined by British entrepreneur Kevin Ashton 1999. It is a network of facilities (electronics, software, sensors) that allows data collection and processing [15] [17]. This allows objects to be controlled over the existing network infrastructure. Objects can be, for example, cardiac implants, car-built sensors, smart home appliances, etc.



Figure 1. Internet of things paradigm

3. SMART HOUSE BASICS

An intelligent or smart house is a house that has a built-in central control system. Such a system is able to integrate multiple systems (heating, hot water consumption, cooling, lighting, safety).

The market for smart homes in 2015 is worth \$ 5.77 billion, while the forecast for 2020 is \$ 10 billion. Early home automation has started with energy-saving machines [4] [24].

Independent household appliances with electricity or gas became viable during the 1900s with the introduction of electricity distribution and led to the introduction of washing machines (1904), water heater (1889), refrigerators, sewing machines, dishwashers and dryers for clothing. In 1975, the first home automation technology for general purpose X10 was developed. It is a communication protocol for electronic devices. Primarily uses wiring harness for signaling and control. By 2012, in the United States, according to ABI Research, 1.5 million households installed [2] [10] [13].

According to [7], there are 3 generations of smart homes:

- First Generation: wireless technology with a proxy server, eg Zigbee, Z-Wave
- Second Generation: Artificial Intelligence that manages electrical appliances, eg Amazon Echo
- Third Generation: a robotic friend who communicates with people, eg Robot Rovio, Roomba.

The apps and technology that the Smart House is having are: [14]

- heating, ventilation and air conditioning (HVAC): remote control of all home energy monitors over the internet with a simple and friendly user interface
- Lighting control system



- In-house control system: it is possible to know the current number of people using smart meters and environmental sensors such as CO₂ sensors that can be integrated into the building automation system to increase energy efficiency
- device control and smart grid integration with a smart gauge, by exploiting, for example, high solar panel output in the middle of the day to start washing machines
- security: home security system integrated with the home automation system can provide additional services such as remote surveillance of security camera over the internet or central locking of all external doors and windows
- Flood detectors, smoke detectors and CO detectors.

Smart homes could bump into two types: [3]

- Complete house automation - houses / apartments designed before construction to be smart. These are expensive and advanced solutions, which can be wireless (Wi-Fi, Zigbee, Z-Wave) or wired (PLC - Power Line Communication). Such systems work big companies, systems are closed and incompatible with others in the market. Examples of such systems are Creston, Control4, AMX, Elan Home Systems, HomeSeer.
- Non-invasive / consumer friendly home automation - inexpensive and user friendly solutions. The user usually obtains a central unit that collects data from the device and various plug and play devices that can be installed by themselves. Examples of such systems are Insteon, NEST, WeMo, Archos, Qivicon, Philips Hue, Iskon Smart Home.

The current biggest problem for smart home users is the unsafe systems (Wi-Fi and its vulnerability), and the fact that technology is still in peril, so users may buy devices, and after some time the manufacturer decides to abandon that service, shuts down servers and devices become useless [12][6] [18].

Also, the problem is lacking the right standards. There are many different and incompatible technologies where real IoT can not be achieved if all devices do not work together.

3. RESULTS AND DISCUSSION

MQTT is a communication protocol designed for use at the top of the TCP-IP protocol. It uses very little network traffic and is suitable for sensors that send their data to the "cloud". It requires connection to a type of dispatcher (Broker), who receives a subscriber of a particular sensor / device on a topic [5][16] [25].

The Message Queue Telemetry Transport Protocol (MQTT) was developed by Andy StanfordClark (IBM) and Arlen Nipper (Eurotech) in 1999 to track the pipeline in the middle of the desert. They needed a protocol that would enable efficient data transfer rates with low battery consumption and a cheaper overall system. Developed MQTT protocol with subscription - subscription to architecture has proven to be easier and more economical than HyperText Transfer Protocol (HTTP) protocol with request and response model. The Reveal Model - Subscription is triggered for events and allows customers to post messages without worrying about their final destination. The final destination of the posted message is determined by the MQTT broker who passes messages on the basis of client subscriptions and thus frees clients from sending requests for messages of interest, as opposed to the HTTP protocol where clients have to look for the information they need from the server. The MQTT protocol also features a small 2-byte fixed header size that further reduces network load [1][8][12].

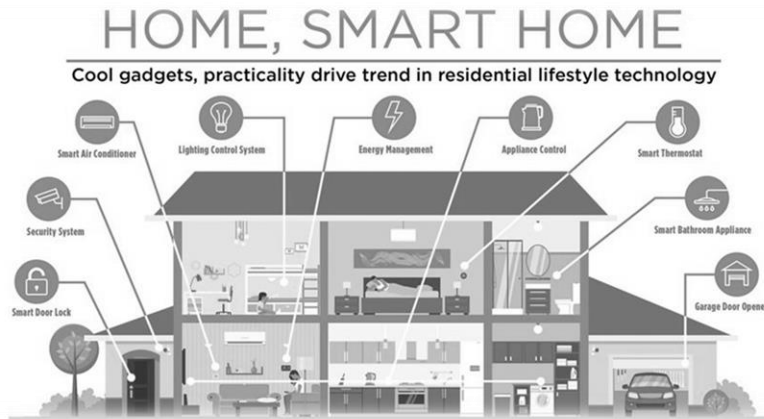


Figure 2. Smart home configuration

Raspberry Pi is a small-print computer that incorporates all the elements needed to work, created as a product of Raspberry Pi Foundation with the desire to encourage the development of computer literacy with emphasis on programming. The original model has become much more popular than it was expected to be sold out of a targeted market (eg in a robotics). By 2016, 11 million devices were sold, which is the best-selling British computer of all time [7][9].

The base of Raspberry Pi computers consists of Broadcom chips that are responsible for the central ARM processor (700 MHz ARM1176JZF-S core ARM11 family) and a graphical processor (Broadcom VideoCore IV, OpenGL ES 2.0, MPEG-2 and VC-1, 1080p30 h.264 / MPEG -4 AVC high-profile decoder and encoder). The operating memory is 256 MB (A model), ie 512 MB (B model).

The base also consists of 21 GPIO 3.3V data lines and 10/100 Ethernet module for wired network and USB hub with 2 external ports [21] [19].

4. CONCLUSIONS

This work has shown that Raspberry Pi as a widespread platform for IoT projects is very good for such projects. It has also been shown that MQTT as a system for connecting IoT devices is very flexible and easy to use. For the entire programming, Python programming language is used, which is convenient for such projects because it is very simple and easy to use. It has been shown to be well-used by a widespread platform such as Raspberry Pi because of its readability and a very large online community that allows sharing of ideas and programming code.

Testing was done so that Raspberry Pi was included in the home router. The power is supplied via a micro USB cable and a mobile charger. After booting, Raspberry sends its IP address to the selected e-mail. If this IP address is entered in a web browser, and if the computer / mobile phone is in the same local network as Raspberry, then the data management and visualization page is accessed. If your computer or cell phone is not in the local network, you must manually launch the file index.html. In this paper, it has been shown that easy-to-access platforms and open code can easily make visible results in the Internet of Things paradigms. Using easily accessible materials, it is possible to achieve results that are easy to apply in practice, industry and science.



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