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CONTENTS / SPIS TREŚCI

Papers

Artykuły

Proceedings of ECOpole

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Ewa BADOWSKA[1] and Dawid BANDZIERZ[1]

THE POSSIBILITIES OF LOCAL STORMWATER MANAGEMENT IN THE CONTEXT OF ITS QUALITY AND QUANTITY

MOŻLIWOŚCI MIEJSCOWEGO ZAGOSPODAROWANIA ŚCIEKÓW OPADOWYCH W KONTEKŚCIE JAKOŚCIOWYM I ILOŚCIOWYM

Abstract: On account of the previous attitude to urban land use by means of substantial building development and fast rainwater disposal the quantity of rainwater constitute increasing threat in the form of urban flooding. It results in financial loss connected with the removal of damage caused by cellar flooding in residential and office buildings in city centres. Also climate changes reveals appearing more frequent torrential rainfalls cause an increased frequency of flooding events. The local management of rainwater on site of its occurrence gives the possibility of reducing the amount of storm water discharged to the most overloaded storm and combined sewerage system, therefore the potential effects of flooding in urban areas can be reduced. The most important element in reducing the amount of stormwater from relevant area is the reduction of impervious surface in relation to permeable surface. Nowadays, due to land prices in urban areas, available building area is normally used in one hundred percent. At this point, so called alternative ways of rainwater management may be used. Very important for the selection of an appropriate solution for a given catchment area are soil and water conditions, terrain slope, but also the quality of rainwater that can be used for sanitary purposes and the maintenance of green areas. The surface from which rainwater is collected for its re-use can be contaminated with different types of substances. Water drops–are already contaminated in the atmosphere by dust suspended in the air. Then, depending on the surface, metals or petroleum substances may get into rainwater, but mainly pollution in the form of suspended solids is observed. Rainwater runoff may require a preliminary treatment before its re-using or introducing into the ground. All of the methods of stormwater treatment should not be overused due to the fact that it increases the cost of equipment, but also this equipment should not cause a negative impact on humans and the environment. The local management of stormwater can be a way to reduce the amount of waste water discharged from the catchment area. It can cause the reduction of consumption of potable water for sanitary purposes. Therefore, the selection of equipment and care to surface, from which rain water is managed, is very important. Without the change of attitude to the management of rainwater the effects of precipitation will become more severe and costly.

Keywords: management of rainwater, rainwater quality

Introduction

Nowadays urban areas are extensively built over by impervious surfaces. The local management of rainwater on site of its occurrence gives the possibility of reducing the amount of storm water discharged to the mostly overloaded storm and combined sewerage system, therefore the potential effects of flooding in urban areas can be reduced. The essence of suitable benefits is the correct selection of facilities for local rainwater management from the solutions available and possible to use. Important for the selection of an appropriate solution for a given catchment area are soil and water conditions, surface slope, but also the quality of rainwater that can be used for sanitary purposes and the maintenance of green areas. There are also guidelines for the use of rainwater instead of potable water for other purposes. The surface from which rainwater is collected for its

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re-use can contaminate it with different types of substances. Mixing the runoff from various types of surfaces can show both negative and positive effects, which also depends on its final use. Rainwater runoff may require a preliminary treatment before its re-using or introducing into the ground.

The quality of wastewater

The composition of rainwater undergoes the largest change during its contact with the surface. In urban areas a large part of the impervious surface belong to roofs and streets. The concentration of pollutants in runoff water from the roof and road surface may range greatly. In the literature the series of research results concerning selected pollutants: pH, suspended solids, COD, BOD, ammonia nitrogen, heavy metals (cadmium, zinc, copper, lead, nickel, chromium), PAHs, petroleum hydrocarbons, and bacteria are presented. Most of the literature data can be divided into the results from the roof surfaces and the road surfaces. But there are also the papers in which results from other surfaces such as pavements are presented. These articles constitute much smaller part.

The quality of wastewater from roofs

In case of roofs material from which the roof and the elements of gutters supplying are madet has a significant impact on the run-off quality. Also the roof slope, the location, the direction and intensity of wind have influence on the observed pollution concentration. The main reason for the increase in pollutant concentrations are in the case of roofing materials the substances that accumulate on the surface of the roof like bird droppings and plant particles and corrosion products. The literature data on this type of surface is divided into types of materials which roofs are made or because of the surrounding in which they are located. The diversity in index of pollutants in case of the specified surface includes, in some cases, only the suspended solids, and COD and in others a large number of other compounds including, for example, magnesium and sodium. For the purpose of current paper, the key indicators including pH, suspensions solids, COD, BOD, ammonia nitrogen, heavy metals, or in some cases petroleum substances known as PAHs and hydrocarbons of petroleum were selected.

Göbel [1] in his publication presents the results of 22 pollutants from 12 different areas and the runoff from roofs covered with tiles, concrete, fiber cement, bitumen, glass with zinc gutters. Selected average values amount: pH 5.7, suspended solids 43 mg/dm^3, BOD$_6$ 12 mg/dm^3, COD 66 mg/dm^3, heavy metals, cadmium (Cd) 0.8, zinc (Zn) 1851, copper (Cu) 153, lead (Pb) 69, nickel (Ni) 4, chromium (Cr) 4 µg/dm^3 ammonium nitrogen 3.39 mg/ dm^3, PAHs 0.39 µg/dm^3, petroleum hydrocarbons, 0.70 mg/dm^3. At the same time the mean values for identical roofing discharge runoff from roofs without zinc gutters are shown. In this case, the only difference in the average values is for zinc, where the average is 370 µg/dm^3. In the publication the roofs covered with copper, aluminum and zinc are distinguished. The only difference concerns the heavy metals and in the reference to roofs: with zinc gutter the values amount for the copper roof suitably copper 2600 µg/dm^3, for the zinc roof zinc 600 µg/dm^3. For aluminium roof mean values of selected indicators have the same value.

The data from Spain [2] from the four selected roofs that are located on the university campus and in the city of Barcelona with a variety of catchments from clay tiles, metal sheet, polycarbonate plastic and the catchment covered with gravel, the following results were obtained: pH 7.59, TSS 5.98 mg/dm^3 and ammonium nitrogen 0.50 mg/dm^3.

The confirmation of importance of determining the quality of rainwater from the roof is conducting the research in this subject around the world. In the Southwest China rainwater runoff from the roof of a university building covered with concrete and from roof covered with tiles located in a residential area was analyzed. The average concentration of TSS was 69 and 43 mg/dm^3 whereas COD 83 and 52 mg/dm^3. At the same time the runoff from roof that was located on the campus area was analyzed regarding heavy metals: copper 0.05, zinc 0.33, lead 0.54, cadmium 0.053 and iron 2.7 mg/dm^3 [3].

In Poland considerable interest in the subject area can be seen too. In the paper [4] the results of the runoff composition from the roof located in Czestochowa are shown. TSS was in the range of 20.5-62.3 mg/dm^3, BOD$_5$ 9.0-16.0 mg/dm^3 and COD from 12.1 to 24.8 mg/dm^3. In turn in one of the review articles [5] runoff from roofs was characterized by concentration in the range of pH 6.0-6.9, TSS 2.1-79 mg/dm^3, COD 6-230 mg/dm^3, petroleum substances 0.4-2.4 mg/dm^3. In the publication [6] hydrocarbon concentration of the three roofs located along the major transportation routes of Gdańsk was presented. The concentration range of petroleum hydrocarbons from these three facilities amounted from 24.98 to 64.42 µg/dm^3.

The number of available data and their diversity confirm the interest in the quality of stormwater. Based on the available data, it can be remarked additionally that the first flush of runoff brings the biggest pollution, so it is good to separate the first flush portion of runoff and stormwater prior to its release a management system. In the next portion of runoff in most cases low pollutant concentration occur, other than heavy metals, which is connected with the roof covering.

The quality of wastewater from roads

Runoff from roads as well as from roofs constitute significant share of total precipitation runoff. For safety reasons devoted to the receivers the rainwater from the lanes should be removed as soon as possible. Regarding roads, surrounding areas (city, industrial and green area) and density of traffic constitute the major factors to the quality.

One of German research on runoff from roads with annual daily traffic load of 57.000 vehicles/day in surrounding of residential housing, office buildings and a park showed the pH in the range 6.2-8.3, suspended solids 18.3-3165 mg/dm^3, COD 3.6-81 mg/dm^3, heavy metals cadmium <0.5-4.8 µg/dm^3, copper 24-604 µg/dm^3, zinc 128-3470 µg/dm^3, lead <0.5-405 µg/dm^3, nickel 4.2-403 µg/dm^3 [7].

In the paper [1] track records of runoff from road are divided into road area on the service road, main roads and motorways. The characteristics of pollution from road service were: pH 7.4, TSS 150 mg/dm^3, BOD$_6$ 11 mg/dm^3, COD 70 mg/dm^3, ammonium nitrogen 0.1 mg/dm^3, cadmium 1.6 µg/dm^3 , zinc 400 µg/dm^3, copper 86 µg/dm^3, lead 137 µg/dm^3, nickel 14 µg/dm^3, chrome 10 µg/dm^3, PAHs 4.5 µg/dm^3, petroleum substances 0.16 mg/dm^3. Characteristics of pollution from main road: pH 7.4, TSS 163 mg/dm^3, BOD$_6$ 11 mg/dm^3, COD 105 mg/dm^3, ammonium nitrogen 0.9 mg/dm^3, cadmium 1.9 µg/dm^3, zinc

407 μg/dm^3, copper 97 μg/dm^3, lead 170 μg/dm^3, nickel 11 μg/dm^3, chrome 11 μg/dm^3, PAHs 1.65 μg/dm^3, petroleum substances 4.17 mg/dm^3. For the motorway data are formed pH 7.4, TSS 153 mg/dm^3, BOD_6 32 mg/dm^3, COD 107 mg/dm^3, ammonium nitrogen 0.5 mg/dm^3, cadmium 3.7 μg/dm^3, zinc 345 μg/dm^3, copper 65 μg/dm^3, lead 224 μg/dm^3, nickel 27 μg/dm^3, chrome 13 μg/dm^3, PAHs 2.61 μg/dm^3, petroleum substances 4.76 mg/dm^3.

The results of runoff from roads in the Polish area of Czestochowa contain: pH, COD, BOD_5, TSS and heavy metals [4, 8]. The scope of the particular indicators amounted: pH 5.6-6.9, COD 22.8-215.0 mg/dm^3, 10-150 BOD_5 mg/dm^3, TSS 11-864.5 mg/dm^3, heavy metals suitably: copper 3.37-7.99 μg/dm^3, cadmium 0.47-0.77 μg/dm^3, lead 21.0-63.0 μg/dm^3, nickel 17.08-32.12 μg/dm^3, arsenic 11.97-28.24 μg/dm^3.

Other results from the road catchment area of Polish roads given in the collection of publications are summarized in the paper [5]. The roads are listed separately as expressways and city roads. In the case of expressways COD was 157 mg/dm^3, TSS 200 mg/dm^3. In the runoff from city roads COD amounted 270 mg/dm^3, TSS 320 mg/dm^3, petroleum substances 1.2 mg/dm^3. The list also presents results from residential roads where the value amounts pH 6.9-7.9, COD 161-247 mg/dm^3, TSS 61-292 mg/dm^3, petroleum substances 0.6-2.4 mg/dm^3.

The literature data show stormwater runoff from roads as mostly polluted. This is especially visible with reference to rainwater from the roofs. Runoff from roads is also characterized by higher levels of pollution concentration. Most of the pollution indicators (TSS, COD, metals) are observed in both types of runoff. However some pollutants are studied primarily in runoff from roads, but not in all. It is worth mentioning that petroleum substances whose origin results from flushing products is based on crude oil from road surface. The presence of these substances should be lower in runoff from roofs, as confirmed by the available data (0.02-2.4 mg/dm^3). In the runoff from roads scope of the presented results amounts 0.16-4.76 mg/dm^3.

The amount of stormwater

The location in the climatic zone and local conditions have the greatest impact on the occurrence of heavy rainfall events [9]. However, heavy rains in terms of daily total rainfall are barely differ in Poland and neighbouring countries [10].

The amount of stormwater is mainly connected with the intensity of precipitation, its duration, and surface runoff (surface impervious, pervious). The catchments with a high surface impervious generate greater amounts of rainwater due to a little opportunity for infiltration. Unfortunately, in urban areas, where rainwater can cause considerable damage, the ratio of the impervious surface and pervious ones is high. The management of rainwater runoff for each parcel individually would result in the stopping of the total runoff from small rainfall events, while the amount of stormwater from heavy rains would be reduced by the possibility of precipitation in collection systems. It should be noted that in the case of designing the facilities to stormwater management, the attention is mostly places on the quantitative balance. An important aspect is to create a balance of quality of stormwater due to the fact that the contamination the ground and ground water through stormwater are possible.

Systems for rainwater management

Before the cities rapidly developed it was common to use methods of rainwater management through the collection and using rainwater during dry weather as well as the surface disposal and infiltration into the ground. While the traditional approach to rainwater sewerage system designing based on the fastest disposal of rainwater out of the city is replaced by retention of excess rain water or management of rainwater in the site of precipitation, the earlier described methods are used again, but objects are optimized for maximum the appropriate use of storage capacity and the surface area for infiltration.

It should be remarked that the reasons for choosing a stormwater management system are miscellaneous and depend on the availability of drinking water, reflected in the price of water supply, environmental awareness, fees for discharge of stormwater into sewerage system, as well as the technical possibilities of the location and operation of facilities for each building object.

The principle of sustainable development extorts out of designers applying of the local devices and facilities for the management of rainwater. Through the processes which are involved in them the devices can be divided:

– Processes using detention:

- Open detention tanks (currently implement they have also the function of create landscaping)
- Closed detention tanks (usually installed in the existing sewerage system in order to relieve the overloaded part of a system and a in new sewerage system in order to optimize the sewer diameters and reduce the maximum flow discharged into a receiver)

– Processes using detention and ground infiltration:

- Lawns, surfaces of gardens, parks, green areas with the right kind of soil, that is pervious and has suitable level of ground water. A portion of the rainwater is evaporated in the process of evapotranspiration, which depends on the type and size of the flora covering green area.
- Car park areas, roadways with little road traffic, pavements, paved recreation areas

- using perforated modules made of concrete - the percentage parts of biologically active surface up to 50% of the total paved surface,
- using perforated elements made of plastic - the percentage parts of biologically active surface up to 95% of the total paved surface,
- using concrete, granite or paving blocks that are laid on the foundation with permeable substructure for example on a sand ballast without cement - a disadvantage of the solutions is the low degree of infiltration,
- using permeable asphaltic concrete on sand or gravel ballast - a disadvantage of the solution is silting-up process which makes the surface loses its conductivity properties.
- Absorptive tanks of the structure similar to the trough characterize by greater depth. The tanks are used for larger areas > 1 ha. Commonly used for drainage of motorways and expressways.

– Processes using deretention and underground infiltration:

- Receptive manholes, so far mainly been made from concrete. The diameter of wells is depended on flow and type of soil below the wells. Currently, the receptive manholes are made of plastic of various constructions depending on the manufacturer.
- Drainage boxes and chambers are mainly used for rainwater removal from large objects. They should be used in areas where there is a low level of groundwater. Due to the modularity and good strength they can be used to produce large retention-infiltration tanks. These devices are successfully used for rainwater removal from airports, industrial plants, sports facilities.
- Draining systems are used in good soil and water conditions - for small objects (*eg* detached house).

Above division was created on the basis of [11, 12].

The results of research

The research on the determination of the quality of storm runoff in urban areas was based on the small selected surface on roads. In the runoff of rainwater from definite surface the pollutants indicators as COD, TSS, petroleum hydrocarbons were determined. Sampling sites were located in the city of Lodz in a residential area and a residential area near the petrol station. Analyzed wastewater came from ten different rainfall events during 2012 and 2013.

Table 1

The ranges of pollutants concentrations (COD, TSS petroleum substances) occurred in stormwater runoff from roads

Type of surface	COD [mg O_2/dm^3]	TSS [mg/dm^3]	Petroleum hydrocarbons [mg/dm^3]
Urban roads	93-1000	40-1866	0.15-3.15

Table 1 shows the concentration of pollutants with the minimum and maximum values, which occurred in the effluent of the three collection points in the analyzed rainfalls. The results of the concentration of TSS and petroleum hydrocarbons correspond to the ranges found in the literature on the quality of rainwater runoff from roads. The only indication above the scope from literature is COD, the maximum value of the samples of the analyzed rainfall was 1000 mg/dm^3. Regarding for road surfaces as high COD value was not an exception. Therefore the analyzed surface is recognized as very polluted and the first flush runoff should be separated or the collected rainwater should be preliminarily removed before their reuse in order to ensure the proper sanitation and the comfort of retention devices.

The quality of sewerage has an influence on the proper selection of facility to stormwater management related to the exclusion of some of the solutions due to environmental contamination, clogging, contamination of soil and groundwater and increase investment and operating costs.

Conclusions

- The basis for the proper management of storm water is a sustainable strategy of development supported by properly accordant devices.

- Local stormwater management can distinctly reduce the amount of storm water brought to the sewerage systems.
- Local systems accordant to prevailing conditions can bring economic and social benefits.
- The quality of stormwater runoff is a major factor that may adversely affect on the facilities to rainwater management.
- The first flush of rainwater should be separated and treated.
- Further research on the quality of rainwater in order to control and prevent the accumulation of large amounts of harmful substances in environmental should be carried out.

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MOŻLIWOŚCI MIEJSCOWEGO ZAGOSPODAROWANIA ŚCIEKÓW OPADOWYCH W KONTEKŚCIE JAKOŚCIOWYM I ILOŚCIOWYM

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Abstrakt: Ze względu na dotychczasowe podejście do zagospodarowania terenu poprzez znaczną zabudowę powierzchni i systemy szybkiego odprowadzania wód opadowych z obszarów zurbanizowanych ilość ścieków opadowych stanowi coraz większe zagrożenie objawiające się tzw. powodziami miejskimi. Skutkiem tego są straty materialne związane z usuwaniem szkód wyrządzonych przez np. podtopienia piwnic budynków mieszkalnych czy biurowych w centrach miast. Jednocześnie zmiany klimatu objawiające się coraz częściej występującymi opadami ulewnymi powodują zwiększoną częstotliwość takich zdarzeń. Zagospodarowanie opadu w miejscu jego wystąpienia daje możliwości zmniejszenia ilości odprowadzanych ścieków deszczowych do (najczęściej przeciążonej) sieci kanalizacji deszczowej i ogólnospławnej, zatem zmniejsza ewentualne skutki zalewania obszarów zurbanizowanych. Najważniejszym elementem zmniejszającym ilość ścieków opadowych z danego terenu jest ograniczanie powierzchni przeznaczonej do zabudowy w odniesieniu do powierzchni nieuszczelnionej. Obecnie ze względu na ceny działek na terenach zurbanizowanych dostępna powierzchnia zabudowy zazwyczaj wykorzystywana jest w stu procentach. Znajdują tutaj zatem swoje zastosowanie tzw. alternatywne sposoby zagospodarowania wód opadowych. Bardzo istotne z punktu widzenia doboru odpowiedniego rozwiązania dla danej zlewni są występujące warunki gruntowo-wodne, spadek terenu, ale również jakość zbieranej wody opadowej, która może zostać wykorzystana do celów sanitarnych oraz utrzymania zieleni. Powierzchnie, z których woda opadowa zbierana jest do ponownego wykorzystania, mogą ją zanieczyszczać różnego typu związkami. Już w atmosferze krople wody zostają zanieczyszczone pyłami zawieszonymi w powietrzu. Następnie w zależności od powierzchni mogą być zanieczyszczone metalami lub substancjami ropopochodnymi, głównie jednak zanieczyszczenia występują w postaci zawiesin. Ścieki opadowe mogą wymagać pewnego podczyszczania przed ich ponownym wykorzystaniem lub wprowadzeniem do ziemi. Miejscowe zagospodarowanie wód opadowych powinno w jak najmniejszym stopniu wykorzystywać systemy oczyszczania, żeby nie powodować dodatkowego wzrostu kosztów urządzeń, ale jednocześnie nie wpływać negatywnie na człowieka i środowisko. Miejscowe zagospodarowanie wód opadowych może być sposobem na zmniejszenie ilości ścieków odprowadzanych z obszaru zlewni. Jednocześnie może pozwalać na zmniejszenie ilości zużywanej wody wodociągowej do celów sanitarnych. Istotny jest dobór urządzenia i dbałość o nawierzchnie, z których woda opadowa zostaje zagospodarowana. Bez zmiany podejścia zarządzania wodami opadowymi skutki opadów będą coraz bardziej dotkliwe i kosztowne.

Słowa kluczowe: zagospodarowanie wód opadowych, jakość ścieków deszczowych

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Tomasz CIESIELCZUK[1] and Czesława ROSIK-DULEWSKA[2]

POSSIBILITIES OF USING COMPOST AS OIL DERIVATIVES SORBENT IN SIMULATED CONDITIONS

MOŻLIWOŚCI ZASTOSOWANIA KOMPOSTU JAKO SORBENTU ROPOPOCHODNYCH W WARUNKACH SYMULOWANYCH

Abstract: Mineral oil products show a multisided negative impact not only on the environment but also to human beings. Oil products leaks are the result of traffic accidents and work done while handling fuels and lubricants. One method of limiting the spread of these substances is using sorbents. From a practical point of view the absorption rate of the sorbent is important, because it significantly determines the degree to limit their environmental impact. The tests of the ability to absorb gasoline and diesel were carried out on the reference surface - the glass and the actual surface - asphalt (asphalt specimen was taken from the so-called wearing course of a roadway lane). The rate of absorption was estimated on the basis of the test images that were automatically taken at intervals of 5 seconds. The study was conducted for commercial sorbents and compost from municipal waste. The study was conducted for the air-dry material and the humidity of 20, 30 and 40%. The best results were obtained with compost from mixed waste, and the worst for commercial organic sorbent. There were also no apparent effects of high humidity on the absorption rate of petroleum products. Thus, increased to 20% moisture of sorbent does not disqualify it from using it in practice. Only 40% moisture content lead to high decrease of sorption properties. On the basis of the research it was found that compost from municipal waste can be used to replace expensive commercial sorbents currently used both in professional rescue operations and in household use.

Keywords: compost, petroleum substances, sorption

Liquid fuels produced in the process of refining crude oil have become the basis for road transport - both truck and passenger. Daily consumption of oil in the world is estimated at about 10 million tones Mg. In Poland, liquid fuels sale is growing and according to Polish Organisation of Oil Industry and Trade in 2020 it will amount to 30 million cubic meters. Fuel production, its distribution, and in particular reloading generate threat of uncontrolled entry into the soil and ground water [1]. A threat of fuels and lubricants leak into the environment is also a problem that occurs while land traffic accidents (about 34.4 thow. in 2013), especially if a leak regards tank trucks carrying significant quantities of gasoline or other fuels. Production and utilization of sorbents for the removal of these impurities generate high costs, resulting in a constant search for substitutes for these materials.

The ever increasing quantity of urban waste forces society to seek new possibilities and new technologies for transforming wastes into reusable material. Composts made from municipal waste are real sources of biomass, however they often contain many harmful or toxic compounds [2]. However, using compost waste as a sorbent has many advantages. Compost is a natural product, which is manufactured microbiologically from mixed municipal solid waste stream or from segregated biodegradable fraction of municipal waste.

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What is more it is also biologically active product which supports the process of decomposition absorbed oil derivatives [3-5]. Its stability allows long-term storage and quick transport to any place by road or rail [6]. An additional advantage of this material is also its low price. It is important to launch a new cheap and environmental friendly sorbents which could be use in each place also by non high qualified personnel or people in private properties. It is especially chance for low-quality composts made of mixed MSW or biodegradable MSW with high content of impurities as glass, metal or plastics particles.

Material and methods

For the purpose of the research, the following materials were chosen: compost from mixed municipal waste created by technology MUT - Dano (marked “D”) and compost from segregated biodegradable fraction of municipal waste created by MUT - Herhof technology (marked “H”). Both tested municipal solid waste (MSW) composts had typical properties for products obtained in accordance with the above mentioned types of materials and technologies [7]. For comparison purposes, commercial sorbents were also tested: organic (marked “O”) and mineral (marked “M”). Basic parameters of investigated materials were analyzed by electrometric methods (pH and EC), and FES (Ca, K) after mineralization with aqua regia. Organic matter, TOC, N, P were analyzed with methodology according to Polish Standards.

Dynamic of sorption experiments were carried out on the reference surface - glass (sodium type) and the actual surface - asphalt (asphalt specimen was taken from the so-called wearing course) slanted at an angle of 5%. The tested sorbent was spread with a 3 mm thick layer on a surface (glass or asphalt) and then lead-free petrol (CAS: 86290-81-5, with density 742 g/dm^3) or diesel oil (CAS: 68334-30-5, with density 818 g/dm^3) was dispensed by burette on the upper edge of the layer. The quantity of dispensed organic liquid in each case was 50 cm^3. The rate of absorption was estimated on the basis of pictures taken automatically at intervals of 5 seconds. The study was conducted for the air-dry sorbents. For comparison purposes, the total sorption capacity of the tested dry materials was set and it was based on the difference in the weight of 10 g sorbent in a vessel after contact with the organic phase (gasoline or diesel). The experiments were carried out at 20°C.

Results and discussion

Basic characteristic of sorbents used in experiments is shown in Table 1. Both composts can be connect to organo-mineral materials, with high content of water soluble mineral compounds. High content of salts could be a phytotoxicological problem in case of use investigated composts as fertilizer or material for soil quality improve. Additionally a lot of composts produced from municipal solid waste (MSW) can contain a great number of impurities *eg* metal and glass particles, textiles or plastics. So, it is necessary to find other possibility of use low-quality composts. These materials contain both mineral and organic fraction and have different granulometric composition (Table 2) [8]. Especially high content of fine fraction (< 0.1 mm) was found in organic sorbent. Also compost D has characteristic composition with almost 35% content over 4 mm. Granulometric composition suggest that sorbent O with the fine particles could have the best sorption properties, however composts D and H with high organic matter content also could be suitable for organic liquids sorption. Different particles size in sorbent is an advantage because road surface has a lot of small holes and clefts, so it is important to fill up all hollows with sorbent.

Table 1

Main characteristic of sorbents used in experiments (*n* = 5)

Parameter	**H**	**D**	**M**	**O**
Organic matter [% d.w.]	34.4±1.47	42.2±3.38	0.86±0.02	98.8±0.10
TOC [% d.w.]	21.4±6.2	24.9±4.1	< 0.5	95.7±0.28
pH_{H2O}	7.74-7.92	7.89-8.12	6.22-6.28	3.76-3.78
EC [mS/cm]	4.16±0.10	3.05±0.41	0.69±0.12	0.09±0.02
N [% d.w.]	1.24±0.3	0.93±0.6	< 0.2	< 0.5
P_2O_5 [% d.w.]	0.75±0.2	0.82±0.3	< 0.3	0.42±0.1
K_2O [% d.w.]	2.15±0.6	3.65±0.8	7.9±1.2	1.2±0.2
CaO [% d.w.]	6.74±1.1	12.8±2.4	21.4±2.9	< 1.0

Table 2

Granulometric composition of investigated sorbents

Grain size [mm]	**H**	**D**	**M**	**O**
> 4	27.4	34.8	0.4	0.0
> 2	11.8	12.5	15.0	43.6
> 1	18.6	20.0	10.6	54.7
> 0.5	11.9	13.9	17.2	1.70
> 0.25	19.7	16.9	22.7	0.07
> 0.1	8.2	5.2	20.0	0.01
< 0.1	2.4	1.5	9.16	0.01

Commercial mineral sorbent M which is in common use in rescue actions in Poland. Pure mineral factory product contains low amount of organic carbon, nitrogen and phosphorus compounds. This material is time-stable easy to long-term store and use. It is suitable also for all common chemicals except hydrofluoric acid. After use it has to be stored on special landfill for hazardous wastes. Organic sorbent O contains low amount of nitrogen and phosphorus compounds. Moreover sorbent O made of peat has low amount of calcium and low pH value. After use it has to be burn in incineration plant or stored on landfill for hazardous wastes. Moreover, this material should be removed from hydrocarbons sorption purposes due to low global resources of peat.

Table 3

Total sorption capacity of dry tested materials at 20°C (*n* = 3) [g/kg d.w.]

	H	**D**	**M**	**O**
ES95	407 ±20	629 ±30	529 ±6.0	4638 ±138
ON	532 ±29	747 ±55	617 ±11	4224 ±117

The amount of absorbed substances over time is one of the most important parameters that indicate the effectiveness of the sorbent. The sooner petroleum substances is absorbed, the less likely it is to get into the environment. Thus, the sorbent which is being used should have the highest possible kinetic absorption of petroleum substances. From a practical point of view, sorption capacity is also essential because it determines the total amount of sorbent that must be used in order to eliminate a certain amount of oil derivatives. Table 3 shows the results of total sorption capacity of tested sorbents in room temperature.

In the case of compost and widely used by the emergency services mineral sorbent the results are similar, for both gasoline and diesel. However, organic sorbent absorbs gasoline in an amount of 7 to 11 times larger, and diesel fuel from 5.5 to almost 8 times higher as compared to other sorbents tested. These amounts are lower than the sorption capacity of hydrophobic fibers of the kapok tree (*Ceiba pentandra*) however kapok fibers after use should be incinerated what lead to increase of rescue action costs [9]. Figure 1 shows the results of the absorption capacity of gasoline ES95 by the sorbents and carried out within 50 seconds.

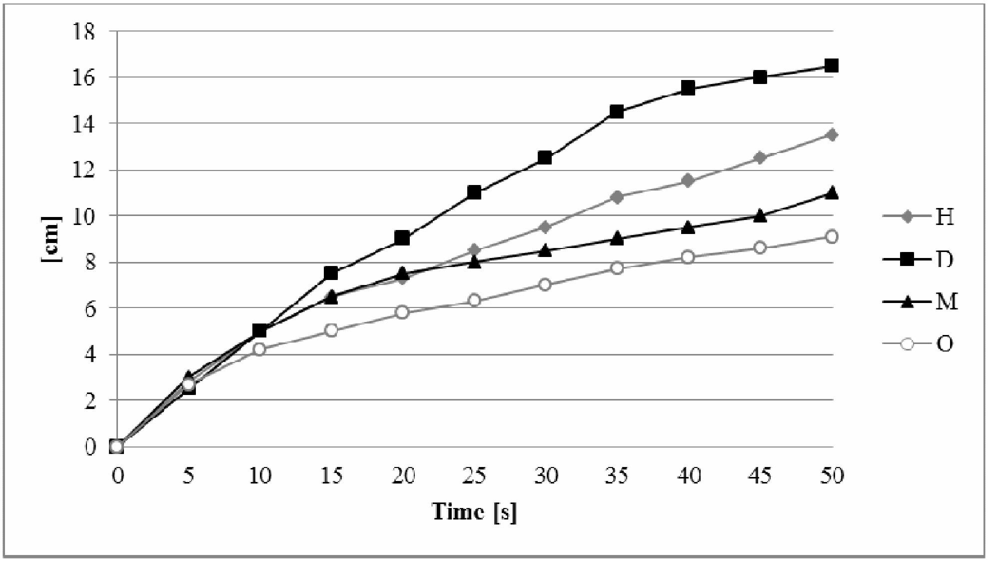

Fig. 1. Gasoline absorption possibilities by investigated sorbents in air-dry state (glass surface with slope 5%)

After the first 10 seconds of the contact between petrol and sorbents, the lowest growth rate was characterized by a sorbent O. In the 15th second of the contact of solid and liquid phase, the highest amount of gasoline ES95 absorbed was for sorbent D and the lowest for material O. In the 50th second of the test in the case of sorbents H and D 16.5 and 13.5 cm bed length was saturated. Surprisingly, the weakest result (9.1 cm) was recorded for the sorbent A. This material was originally expected to have much higher absorption rate, but because of its granulometric composition - a significant share of fine fraction - the achieved result was unsatisfactory. Figure 2 shows the results of the same test carried out on diesel.

The achieved results were worse than in the case of gasoline. This is due to the higher oil density (0.818 g/cm^3) than gasoline used in the experiment (0.742 g/cm^3). The best result (14 cm was achieved as in the case of gasoline for the sorbent D, and the worst (6.1 cm) similarly to previously reported result for the sorbent O. This may be due to the phenomenon of swelling the peat fibers, and thus sealing the sorbent bed what impedes the migration of organic liquid to a new bed. Sorbent H showed worse sorption capacity than gasoline - the absorption rate was only 8.3 cm/50 seconds and is worse than the one obtained by the sorbent M (10.5 cm).

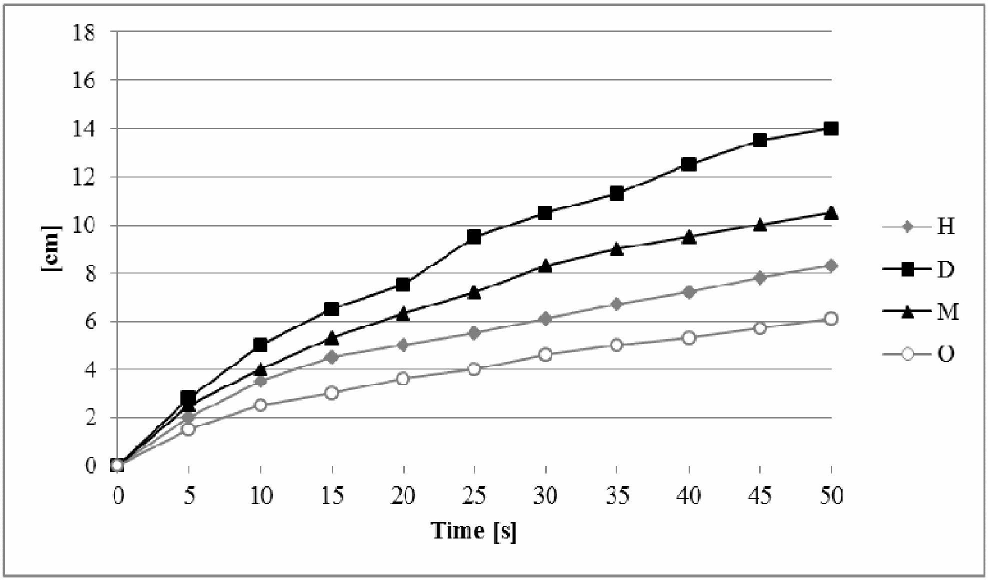

Fig. 2. Diesel oil absorption possibilities by investigated sorbents in air-dry state (glass surface with slope 5%)

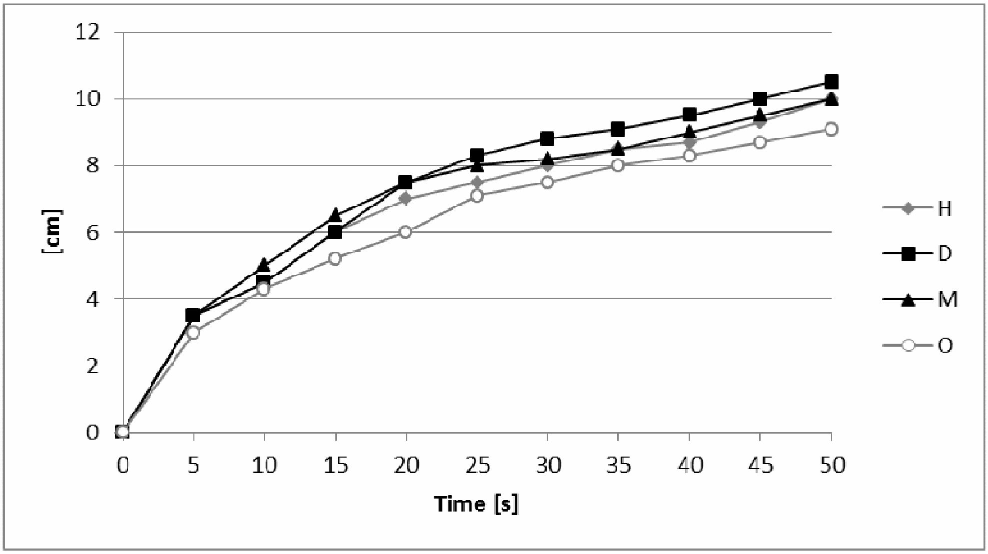

Fig. 3. Gasoline absorption possibilities by investigated sorbents in air-dry state (asphalt surface with slope 5%)

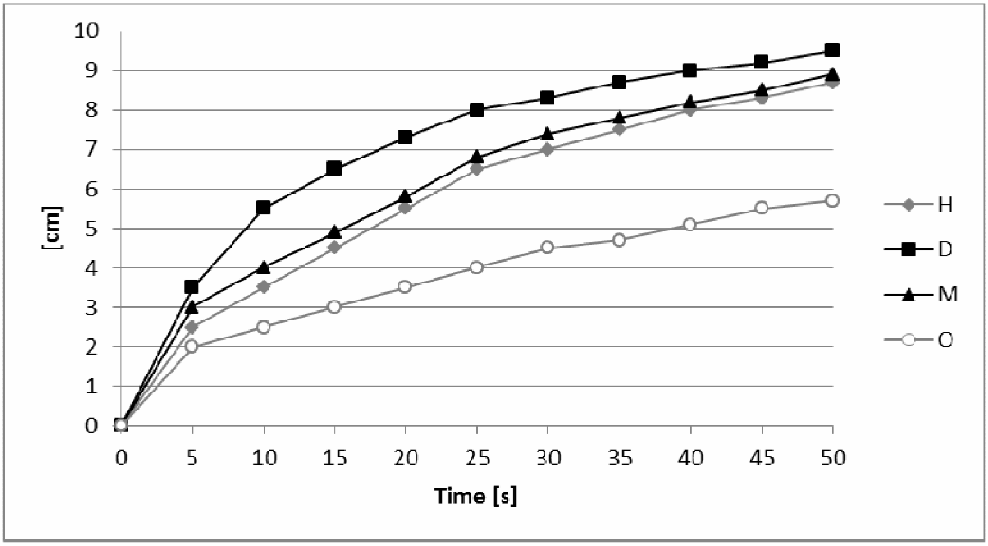

Fig. 4. Diesel oil absorption possibilities by investigated sorbents in air-dry state (asphalt surface with slope 5%)

In the tests carried out on the asphalt surface (Figs. 3 and 4), the obtained results demonstrate similar characteristics of absorption rate comparing the sorbents with each other. However, both in the case of gasoline and oil, on the asphalt surface the observed results were worse. It is probably due to a notable surface roughness, where in the slots the tested liquid may be collected before it will be absorbed by the sorbent. Moreover, both tested liquids as petroleum derivatives (like asphalt) have a far greater capacity of wetting asphalt compared to the glass surface. For both tested liquids (gasoline and diesel) after removal of the used up sorbent, surface contamination was observed for both glass and asphalt, which was the lowest for sorbent O, what resulted from a significant proportion of small organic fraction. Similar results in sorption capacity have been achieved carrying out the sorption by the capillary rise, but absorbed amount of oil was 3-4 times lower than the total sorption capacity specified here [8]. Mature composts have relatively high amount of water. It could be a disadvantage in use these materials as sorbents. Obtained results from pretests (Table 4), show that only high amount of water (40%) could lead to lower sorption properties. Especially commercial sorbent O had a good sorption capacity in all tested moisture levels. Poor results were obtained for sorbents M and H. Increase of water content lead rapidly drop of sorption capacity to level 3-4 times lower than in total dry state. This phenomenon was also observed in case of sorbent D, but sorption capacity was lower only two times. After that all further experiments were performed for tested sorbents with a water content of 20% (m/m). In the case of the reference surface (glass) the increase in water content in the tested materials did not affect negatively on the rate of absorption of petrol and diesel by commercial sorbents M, O and H. Sorbent absorption rate reduction was observed only for the sorbent D which was moistened with petrol at the length of 16.5 and 11 cm respectively for dry and wet material. In the case of diesel oil wetting, these values are 14 and 8.4 cm. The decrease of absorption rate was significant (respectively

33 and 40%), but recorded only in this case. Experiments carried out on the asphalt surface showed no negative effects of 20% water content in the absorbent material on wetting rate of the organic liquid. Probably the best sorption results observed in case of compost D is a result of high content of glass and metal impurities. This mineral particles lead go better contact of sorbed substance and solid organic matter contain in sorbent. It also reason of poor results achieved in case of sorbent O, where great amount of fine needle-like parts have a lot of very small There were an experiments made with other organic sorbents like coconut husk, rice husk, wood chips, kapok fiber, cattail fiber for oil removal from water stream [10]. Obtained results were good (comparable with polyester fiber) only in case of cattail fiber. However cattail is a wild plant which should be collected usually in wetland areas and dried before use. An additional disadvantage of this material is also its conflict with avifauna lifecycle - a lot of birds use cattail fields as reproduction areas. In case of high price of commercial sorbents, MSW composts appear as a real alternative in common use. Easy to made materials as composts have high stability allows long-term storage and this is cheap to transport them to any place. An additional advantage of this materials is high number of multi-microorganisms consortium which could effective accelerate petroleum products degradation process. In this case compost should be stored in wet state what can negatively lead on hydrocarbons sorption process as mentioned above. It is also possible to additional accelerate of decomposition hydrocarbons sorbed with MSW composts by using special enzyme preparations but in final effect total price of rescue action will be higher [11]. Compost is common material in each garden, so it could be use daily for sorption of oil products which leaking from old cars engines in garages or private park sites. Container with wet compost placed under oil leak point could appear as low-cost simple solution for catching and effective decomposing all drops of engine oil. It is especially interesting for truck and building machines park sites where engine and hydraulic oils leaks are very common.

Table 4

Total sorption capacity of tested sorbents in various moisture content for trade petroleum products

Moisture [%]	**ES95**				**ON**			
	H	**D**	**M**	**O**	**H**	**D**	**M**	**O**
0	407	629	529	4638	532	747	617	4224
20	345	596	274	4410	474	731	369	3870
30	226	556	190	4070	322	632	308	3600
40	105	328	116	3780	141	381	193	3550

Conclusions

In case of accidental oil leaks it is very important to quick and effective remove petroleum products from road surface to avoid soil or surface water contamination. The results demonstrate excellent absorption dynamics of petroleum liquid by compost sorbents. The highest absorption dynamics was recorded in the case of compost from mixed waste. This is probably the result of a high proportion of organic matter. The lowest dynamics (with the highest sorption capacity) was observed in the case of commercial sorbent O, which may be due to the seal of capillary between the sorbent particles on the way of swelling peat fibers, and as a result causing the migration of oil products in a direction parallel to the face of the sorbent bed. However, commercial sorbent O had the highest sorption capacity it is made of peat, so use of this sorbents type should be minimized due to global peat resources.

Moistness of tested sorbents did not affect negatively both the dynamics of the and the total length of the sorbent layer that is moistened by the tested liquid within 50 seconds. Thus, increased to 20 % moistness of the sorbent does not disqualify it from using it in practice. Due to keep rescue action cheap, it is very important to use compost without additional operations like sieving, drying or cleaning from impurities.

Obtained results show that compost could be an effective sorbent also for wide sorption purposes also in private garages and industrial areas.

Acknowledgments

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MOŻLIWOŚCI ZASTOSOWANIA KOMPOSTU JAKO SORBENTU ROPOPOCHODNYCH W WARUNKACH SYMULOWANYCH

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Abstrakt: Produkty przerobu ropy naftowej wykazują wielokierunkowe negatywne oddziaływanie nie tylko na środowisko, ale także na człowieka. W wyniku katastrof w ruchu lądowym lub prac związanych z przeładunkiem paliw i smarów dochodzi do wylewów produktów naftowych. Jedną z metod ograniczających rozprzestrzenianie się tych substancji jest zastosowanie sorbentów. Z praktycznego punktu widzenia istotna jest szybkość pochłaniania substancji ropopochodnych przez sorbent, co w znaczący sposób determinuje stopień ograniczenia ich szkodliwego oddziaływania na środowisko. Doświadczenia zdolności pochłaniania benzyny oraz oleju napędowego przeprowadzono na powierzchni wzorcowej - szklanej oraz powierzchni rzeczywistej - asfaltowej (próbkę asfaltu pobrano z tzw. warstwy ścieralnej pasa drogowego). Szybkość pochłaniania oszacowano na podstawie zdjęć testowych wykonywanych automatycznie w interwale co 5 sekund. Badania przeprowadzono dla sorbentów komercyjnych oraz kompostów z odpadów komunalnych. Badania prowadzono dla materiałów powietrznie suchych oraz o wilgotności wynoszącej 20, 30 i 40%. Najlepsze wyniki uzyskano dla kompostu z odpadów zmieszanych, a najgorsze dla komercyjnego sorbentu organicznego. Nie zanotowano także wyraźnego wpływu podwyższonej wilgotności na szybkość pochłaniania produktów naftowych. Zatem podwyższona do 20% wilgotność sorbentu nie dyskwalifikuje go z zastosowania w praktyce. Dopiero wilgotność na poziomie 40% znacznie obniża właściwości sorpcyjne badanych materiałów. Na podstawie przeprowadzonych badań stwierdzono, iż komposty z odpadów komunalnych mogą z powodzeniem zastąpić drogie sorbenty komercyjne stosowane obecnie zarówno w czasie akcji ratowniczych, jak i w warunkach domowych.

Słowa kluczowe: kompost, substancje ropopochodne, sorpcja

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CONTENT OF POLYCYCLIC AROMATIC HYDROCARBONS IN SOILS EXPOSED TO TRAFFIC POLLUTION

ZAWARTOŚĆ WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH W GLEBACH NARAŻONYCH NA EMISJE ZANIECZYSZCZEŃ KOMUNIKACYJNYCH

Abstract: The aim of the research was to determine the impact of traffic pollution on the content of 11 polycyclic aromatic hydrocarbons (PAHs) in soils: naphtalene, acenaphtene, acenaphtylene, fluorene, phenantrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene as well as benzo[a]pyrene. The research material consisted of soil samples collected from 13 points located along regional road No. 957 passing through Zawoja (southern Poland, Malopolska region). In each point the soil samples were collected from sites located 5 and 200 m from the road edge. The PAHs content was determined using gas chromatography with mass detection, after solid phase extraction. Mean contents of individual PAHs in samples collected closer to the roadway were higher than mean contents in samples collected farther. Differences in the content of PAHs between samples collected at a distance of 5 m and 200 m from the edge of the roadway were increasing along with the increase of number of rings in the PAHs, i.e. soils located at a distance of 5 m from the edge of the roadway contained 9% more naphtalene, 37-294% more 3-ring compounds, 260-333% more 4-ring compounds, and 324% more benzo[a]pyrene.

Keywords: polycyclic aromatic hydrocarbons, soil, transportation

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that are harmful to living organisms (they have a carcinogenic effect) [1 based on various sources]. One of the main anthropogenic sources of PAHs is road transportation. PAHs are emitted during combustion of fuels (gasoline, diesel), use of engine oils as well as during abrasion of tyres and asphalt [2-4]. As a result, these compounds are present in road dust as well as in soil in areas neighbouring with traffic routes [4, 5]. Excessive content of polycyclic aromatic hydrocarbons in soil (particularly in soil used agriculturally) constitutes a threat to living organisms because these compounds are accumulated in the links of the food chain [6].

The aim of the research was to determine the impact of traffic pollution on the content of 11 polycyclic aromatic hydrocarbons in soils.

Material and methods

The research material comprised soil samples collected from a site located in southern Poland (from the Suski district which is situated in the Malopolska region). The samples were collected from 13 grass covered points located along regional road No. 957 passing through Zawoja. In each point the soil samples were collected from places located 5 m and 200 m from the road edge, from a 0-10 cm deep layer. A characteristic of the research

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material collection sites (including information on traffic intensity) as well as data on the properties of the analyzed soils are shown in the article by Filipek-Mazur et al [7].

The content of the following 11 compounds from the PAH group was determined in the soil samples:

- 2-ring compound: naphtalene,
- 3-ring compounds: acenaphtene, acenaphtylene, fluorene, phenantrene, anthracene,
- 4-ring compounds: fluoranthene, pyrene, benz[a]anthracene, chrysene,
- 5-ring compound: benzo[a]pyrene.

The content of PAHs was determined on the Varian 4000 GC/MS system using gas chromatography with mass spectroscopy, after solid phase extraction (SPE) using Bakerbond C18 500 mg, 3 cm^3 columns. FactorFour VF-5ms capillary column was used. The determination of the PAHs content in each sample was conducted in two replications. In order to perform calibration, a method of comparison with an external reference standard was used. Restek 610 PAH Calibration Mix standard was used.

Statistical analyzes were performed using the data analysis software system STATISTICA version 10 (StatSoft, Inc.).

Results and discussion

Soils located 5 m from the edge of the roadway had a higher mean content of each of the 11 determined polycyclic aromatic hydrocarbons than the soils at a distance of 200 m (Tables 1 and 2). The studied soils, particularly the ones collected at the distance of 5 m from the edge of the roadway, had a high diversification in the content of hydrocarbons. The variability coefficient of the PAHs content was 68-230% for the soils collected closer to the roadway, and 46-138% for the soils located farther from the edge of the roadway.

Table 1

PAHs content in soils located 5 m from edge of roadway

PAH	**Arithmetic mean**	**Minimum**	**Maximum**	**Standard deviation**	**Variability coefficient**
	[mg · kg^{-1} d.m.]				**[%]**
Naphthalene	0.107	0.053	0.342	0.073	68.4
Acenaphthylene	0.012	ND *	0.036	0.010	81.8
Acenaphthene	0.059	0.006	0.318	0.087	147.2
Fluorene	0.053	0.007	0.228	0.065	122.7
Phenanthrene	0.923	0.095	4.361	1.261	136.7
Anthracene	0.197	ND	1.023	0.299	151.9
Fluoranthene	2.240	0.048	14.349	3.841	171.4
Pyrene	1.905	0.034	12.762	3.405	178.8
Benz[a]anthracene	0.789	ND	5.585	1.495	189.5
Chrysene	1.132	ND	8.337	2.227	196.7
Benzo[a]pyrene	1.251	ND	10.701	2.880	230.2
Two-ring compound	0.107	0.053	0.342	0.073	68.4
Three-ring compounds	1.244	0.114	5.654	1.684	135.4
Four-ring compounds	6.066	0.082	41.033	10.957	180.6
Five-ring compound	1.251	ND	10.701	2.880	230.2

* ND - not detected (value “0.000” was used to do the statistical calculations)

Table 2

PAHs content in soils located 200 m from edge of roadway

PAH	Arithmetic mean	Minimum	Maximum	Standard deviation	Variability coefficient
	[mg · kg^{-1} d.m.]				[%]
Naphthalene	0.098	0.068	0.231	0.045	46.3
Acenaphthylene	0.009	ND*	0.019	0.005	56.9
Acenaphthene	0.024	ND	0.070	0.022	90.7
Fluorene	0.025	ND	0.063	0.018	73.2
Phenanthrene	0.414	0.041	1.403	0.370	89.4
Anthracene	0.050	ND	0.170	0.059	118.2
Fluoranthene	0.622	0.023	2.786	0.715	115.1
Pyrene	0.500	ND	2.215	0.573	114.5
Benz[a]anthracene	0.182	ND	0.805	0.215	118.2
Chrysene	0.277	ND	1.442	0.383	138.0
Benzo[a]pyrene	0.295	ND	1.212	0.340	115.2
Two-ring compound	0.098	0.068	0.231	0.045	46.3
Three-ring compounds	0.522	0.049	1.685	0.459	87.9
Four-ring compounds	1.581	0.023	7.248	1.878	118.8
Five-ring compound	0.295	ND	1.212	0.340	115.2

* see Table 1

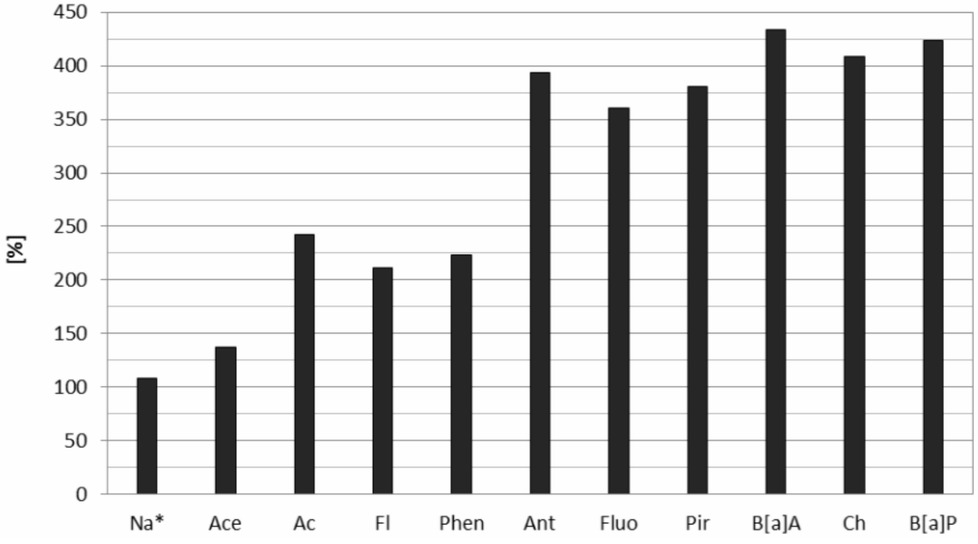

Fig. 1. Average PAHs content in soils located at a distance of 200 m from the edge of the roadway presented in relative values (with assumption that the content of individual PAHs in the soils located at a distance of 5 m is 100%); *Na - naphthalene, Ace - acenaphthylene, Ac - acenaphthene, Fl - fluorene, Phen - phenanthrene, Ant - anthracene, Fluo - fluoranthene, Pyr - pyrene, B[a]A - benzo[a]anthracene, Ch - chrysene, B[a]P - benzo[a]pyrene

The mean content of individual PAHs in soils located closer to the edge of the roadway was higher by 9 to 333% than the mean content in soils located at a distance of 200 m from the roadway. As a rule, differences in the PAHs content between soils located 5 and 200 m from the edge of the roadway were increasing along with the increase in the number of rings in the molecule of a compound. In Figure 1, the PAHs content in soils located 5 m from the edge of the roadway is presented in relative values - assuming that the content of individual hydrocarbons in the soils located at a distance of 200 m is 100%. Soil located closer to the edge of the roadway contained 9% more naphthalene (2-ring compound), 37-294% more 3-ring PAHs, 260-333% more 4-ring PAHs, and 324% more benzo[a]pyrene (5-ring compound).

As specified in the regulation on soil and earth quality standards [8], 1 kg of dry matter of soil from agricultural lands, taken from a depth of 0-0.3 m may contain no more than 0.1 mg of naphthalene, 0.1 mg of phenanthrene, 0.1 mg of anthracene, 0.1 mg of fluoranthene, 0.1 mg of chrysene, 0.1 mg of benzo[a]anthracene, and 0.03 mg of benzo[a]pyrene. In total, the permissible content of PAHs was exceeded in 11 soil samples collected at a distance of 5 m from the edge of the roadway and in 11 samples collected at a distance of 200 m (Table 3). That excess concerned, above all, the contents of phenanthrene, fluoranthene, benzo[a]anthracene, chrysene, and benzo[a]pyrene (between 7 and 11 soil samples), in other words compounds containing between 3 and 5 rings. Fewer soil samples were polluted with naphthalene and anthracene, that is compounds containing, respectively, 2 and 3 aromatic rings in a molecule.

Table 3

Number of soil samples where permissible content of PAHs, specified in regulation on soil and earth quality standards [8], was exceed

PAH	**Distance from the roadway**	
	5 m (*n* = 13)	**200 m (*n* = 13)**
Naphthalene	0	1
Phenanthrene	10	9
Anthracene	4	2
Fluoranthene	11	11
Benzo[a]anthracene	9	7
Chrysene	9	7
Benzo[a]pyrene	10	8

In own research, soil pollution particularly with compounds with a greater number of rings was found. It is an unfavorable situation, because the greater the number of rings in a molecule of aromatic hydrocarbon, the more harmful effect it has on living organisms [1 based on various sources, 9 based on various sources, 10].

Conclusions

1. Soils located closer to the edge of the roadway had a higher mean content of each of the 11 determined PAHs (naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, and benzo[a]pyrene) than soils located farther from the edge of the roadway.
2. Soils located at a distance of 5 m from the edge of the roadway contained 9% more naphthalene, 37-294% more 3-ring compounds, 260-333% more 4-ring compounds, and 324% more benzo[a]pyrene.

Acknowledgements

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ZAWARTOŚĆ WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH W GLEBACH NARAŻONYCH NA EMISJE ZANIECZYSZCZEŃ KOMUNIKACYJNYCH

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Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie

Abstrakt: Celem badań było określenie wpływu emisji zanieczyszczeń komunikacyjnych na zawartość 11 wielopierścieniowych węglowodorów aromatycznych (WWA) w glebach, tj.: naftalenu, acenaftenu, acenaftylenu, fluorenu, fenantrenu, antracenu, fluorantenu, pirenu, benz(a)antracenu, chryzenu oraz benzo(a)pirenu. Materiał badawczy stanowiły próbki gleb pobrane z 13 punktów położonych wzdłuż drogi wojewódzkiej nr 957 na terenie Zawoi (południowa Polska, województwo małopolskie). W każdym punkcie próbki gleb pobrano z miejsc odległych o 5 i 200 m od brzegu jezdni. Zawartość WWA oznaczono techniką chromatografii gazowej z detekcją masową, po ekstrakcji do fazy stałej. Średnie zawartości poszczególnych WWA w próbkach pobranych bliżej jezdni były większe od średnich zawartości w próbkach pobranych w większej odległości. Różnice w zawartości WWA pomiędzy próbkami pobranymi w odległości 5 i 200 m od brzegu jezdni zwiększały się wraz ze zwiększaniem liczby pierścieni w cząsteczkach WWA - gleby położone w odległości 5 m od brzegu jedni zawierały o 9% więcej naftalenu, o 37-294% więcej związków 3-pierścieniowych, o 260-333% więcej związków 4-pierścieniowych i o 324% więcej benzo(a)pirenu.

Słowa kluczowe: wielopierścieniowe węglowodory aromatyczne, gleba, transport

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EFFECT OF *Bacillus subtilis* EXOMETABOLITES ON THE GROWTH RATE OF *Rhizoctonia solani*

WPŁYW METABOLITÓW *Bacillus subtilis* NA TEMPO WZROSTU *Rhizoctonia solani*

Abstract: The aim of the research was to assess a potential biological activity of cell-free supernatants (CFS) obtained from 4, 6, 8, 10 and 24-hour culture of *Bacillus subtilis* against 4 pathogenic strains of *Rhizoctonia solani* marked as R1, R2, R3 and R4. The antagonistic properties of metabolites were assayed by the dual-culture technique on PDA medium. Fungistatic activity of *B. subtilis* was determined on the rate of mycelia growth inhibition. On the basis of obtained results, it has been proved that fungistatic activity of *B. subtilis* is varied and depends on the age of the bacterial culture and susceptibility of the fungus. Taking into consideration all the analyzed parameters, *R. solani* R1 was the most sensitive but R3 lest sensitive to the metabolites produced by *B. subtilis.* The highest inhibition of the growth rate was obtained for *R. solani* R1 and the decrease of index amounted between 72-87%, whereas a lower inhibition was noted for strain R3 (44-78%), depending on the age of the bacterial cultures. *B. subtilis* may find a wide range of application in the process of plant protection against diseases caused by *R. solani.*

Keywords: *Bacillus subtilis*, *Rhizoctonia solani*, antifungal activity

Plant diseases caused by fungi as *Rhizoctonia solani* constitute the most numerous and the significant group of diseases taking into account an economic aspects. *Rhizoctonia solani* and other pathogenic *Rhizoctonia* species cause pre- and post-emergence damping-off of beet sugar, which can reduce seedling stands and yield. They can survive over winter and between sugar beet crops as sclerotia and melanized mycelium. Under conditions of high temperature and high soil moisture can cause seedling blight and subsequently brown root rot [1, 2]. Current agriculture is based largely on the application of synthetic pesticides and fungicides. The exercise use of agrochemicals lead to the emergence of pathogen resistance and serve negative impacts on the environment, cause serious effect to human health and non-target organisms. Therefore, it is a growing demand for new and safer methods to reduce, replace or at least supplement the existing control strategies. In recent years, there has been a growing interest in potential use as plant protection non-pathogenic microorganisms, such as bacteria of *Bacillus* kind, as promising alternatives to synthetic chemicals. They are an eco friendly and generally safe microorganisms that are ubiquitous in nature [3-5]. One of the most promising means to achieve this is the use new tools based on biological agents (BCAs) for disease control. Biological control agents interact with phytopathogens directly or indirectly to reduce the population of pathogens or reduction in the ability of the pathogens to cause disease. *Bacillus* spp. strains developed different mechanisms which limit pathogenic activity of fungi and show antifungal activity with varying degrees of antagonism. Several studies have found that some strains of the genus *Bacillus* eg. *B. megaterium*, *B. pumilus*,

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B. cereus. *B. subtilis* have a broad spectrum of activities and were reported to suppress the growth of pathogens such as: *Pythium* spp., *Fusarium* spp., *Aspergillus* spp. *Botritis cinerea* [4, 6-10]. Antagonistic properties of the *Bacillus* spp. is strongly conditioned by factors such as the strain of the bacteria, the chemical composition of the medium and the incubation conditions (the incubation time, temperature, aeration) as well as susceptibility of fungi. Therefore, the possibility of controlling soil-borne pathogens by introducing specific antagonistic bacteria to infested soil has been extensively investigated during the past decades [4, 6, 7, 11-14].

Therefore the aim of conducted research was to determine how metabolites produced by strain *Bacillus subtilis* affect the growth *Rhizoctonia* strains.

Materials and methods

The involvement of antifungal activity compounds produced by *Bacillus subtilis* strain in the inhibition of fungal growth was confirmed by the ability of cell-free culture filtrate of these strain to inhibit of hyphal growth of *Rhizoctonia solani* strains marked as R1, R2, R3 and R4.

Fungistatic activity of *B. subtilis* was determined with the culture-plate method on PDA medium containing glucose as carbon source. Fungal mycelial-discs (diameter of 10 mm) obtained from growing cultures of tested fungal isolates were placed in the centre of PDA medium containing 0,5 ml working cultures obtained from 4, 6, 8, 10 and 24-hour culture of *Bacillus subtilis*. The control plate contained *R. solani* cultures and aseptic broth medium in place of the supernatant. All plates were incubated at 26 ±2°C for 4-6 days and the diameters of fungal growth was measured every days. The experiment was performed in triplicate, where one repeat was represented by a one plate containing the growth medium with one mycelia disc. The influence of metabolites produced by *B. subtilis* on the growth of *R. solani* strains was determined as the growth rate index as described previously [15]. The inhibition of fungal growth was evaluated as the percentage reduction of the growth rate index in the treated plate versus the growth rate index in the control plate.

Results and discussion

Bacillus spp. can occur in the plant rhizosphere soil and exercise an antagonistic and competitive effect on the fungal communities. They have ability to produce biologically active compounds or plant growth regulators, which seem to play a major role in biological control of plant pathogens [3]. The mechanisms of antagonism of the biocontrol strains against the pathogens included competition for nutrients or space, production several different non-volatile and volatile of antimicrobial compounds, mycolytic enzymes, induction of defence responses in plant [3, 7, 11]. In this study the antifungal activity of *B. subtilis* was evaluated against 4 pathogenic strains of *Rhizoctonia solani* as the growth rate index (Figs. 1 and 2). The *Rhizoctonia* spp. strains showed different sensitivities and responses to the metabolites produced by *Bacillus subtilis* depending on the age of the culture. In this experiment 4, 6, 8, 10 and 24-hour culture of *B. subtilis* were used as an inhibitory factor. It was observed that the linear growth of the mycelium of *R. solani* R1 and R2 on PDA medium was inhibited most efficient by adding supernatants from 8-10 hours bacterial cultures to the growth medium compared to the control. The value of the growth rate index of strains R1 and R2 amounted 1.19 and 2.09, respectively (Fig. 1). The highest reduction of the growth rate index was noted for *R. solani* marked as R1 and obtained reduction amounted 87%. Whereas the highest degree of inhibition the strain R2 was 11% lower than the strain R1 and achieve the value about 76% (Fig. 3).

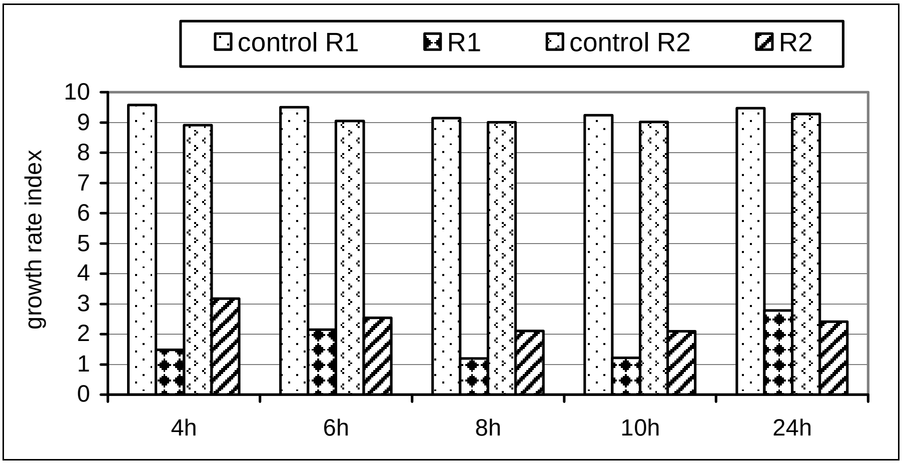

Fig. 1. The influence of *Bacillus subtilis* on mycelial growth of *Rhizoctonia solani* strains R1 and R2 on PDA medium

Significantly smaller effect of the tested bacteria on the growth of fungi was found in the case other strains of *R. solani* (Fig. 2).

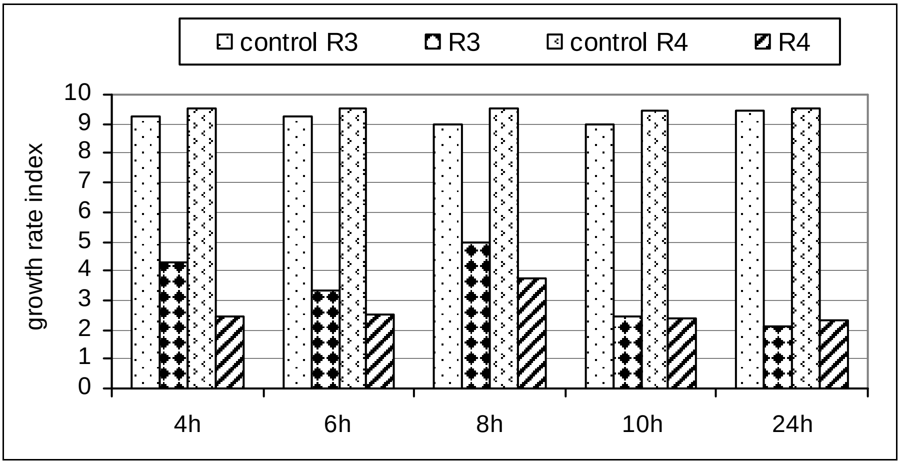

Fig. 2. The influence of *Bacillus subtilis* on mycelial growth of *Rhizoctonia solani* strains R3 and R4 on PDA medium

The growth of strains marked as R3 and R4 was strongly inhibited, when *B. subtilis* was applied as 24-hour supernatants, where the index growth rate amounted to 2.08-3.30, respectively. The range of percentage inhibition varied from 76-78 for this strains. The lowest reduction in the growth rate index was obtained in case of *R. solani* marked as R3 and achieved the value between 44-78% compared with the control (Fig. 3).

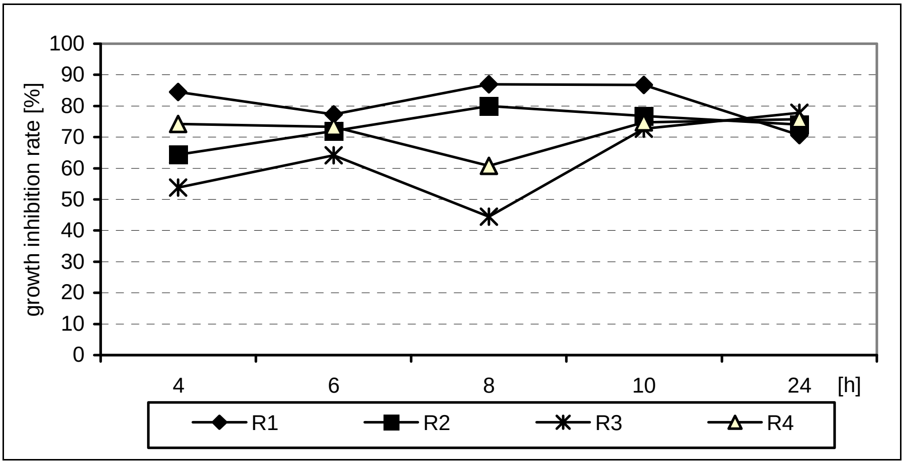

Fig. 3. Inhibition effect of *B. subtilis* on mycelial growth of *R. solani* strains

The largest differences in the effects of metabolites of *B. subtilis* on growth of *R. solani* was observed after application of 8-hour culture. The percentage inhibition of the growth rate index varied from 44 to 87. Whereas, the most similar inhibitory effects against all the tested strains *Rhizoctonia* spp. was observed after application suppernatants of 24-hours of culture *B. subtilis.* The inhibition of the growth of these fungi ranged from 71 to 78 percent (Fig. 3).

These inhibitive activities of *B. subtilis* against the hyphal growth of *R. solani* may be due to the production of hydrolytic enzymes, that can degrade structure of cell wall viz. β-1,3 glucanase, chitinase, protease and/or secretion of several cyclic lipopeptides, diffused and dissolved into the culture media. Some of this bioactive substances can cause induce hyphal deformation, enlargement of cytoplasmic vacuoles and cytoplasmic leakage, inhibit sclerotial germination of *R. solani.* Moreover most of these compounds are produced at the late growth stage or at logarithmic growth phase then they lost its antibiotic efficiency in stationary phase [3, 4, 7, 11].

Conclusions

Conducted research confirmed fungistatic properties of *Bacillus subtilis* against *Rhizoctonia solani* strains and prove that growth inhibition of the fungi depends not only on the biological properties and age of the bacterial culture and also susceptibility of the fungus to bacterial metabolites. Taking into consideration all the analyzed parameters, *R. solani* R1 was the most sensitive but R3 lest sensitive to the metabolites produced by

B. subtilis. The highest decrease of index was obtained for *R. solani* R1 and amounted between 72-87%, whereas a lower decrease of index was noted for strain R3 (44-78%). These studies confirm the sensitivity the different strains of *R. solani* on the metabolites secreted by *B. subtilis*. Therefore, this bacterium may found application as an antifungal agent, to protect of plants against diseases caused by *Rhizoctonia solani*.

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WPŁYW METABOLITÓW *Bacillus subtilis* NA TEMPO WZROSTU *Rhizoctonia solani*

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Abstrakt: Celem badań była ocena biologicznej aktywności supernatantów otrzymanych z 4-, 6-, 8-, 10- i 24-godzinnej hodowli *Bacillus subtilis* wobec 4 szczepów *Rhizoctonia solani* oznaczonych jako R1, R2, R3 i R4. Antagonistyczne właściwości metabolitów *B. subtilis* oznaczono metodą hodowlano-płytkową na podłożu PDA i oceniono na podstawie indeksu tempa wzrostu. Z uzyskanych wyników badań wykazano, że fungistatyczna aktywność *B. subtilis* jest zróżnicowana i zależy od wieku hodowli bakteryjnej oraz wrażliwości grzybów. Biorąc pod uwagę wszystkie analizowane parametry, szczep *R. solani* R1 był najbardziej wrażliwy, natomiast R3 najmniej na metabolity produkowane przez *B. subtilis*. Największe zahamowanie indeksu tempa wzrostu, w wysokości 72-87%, stwierdzono w przypadku *R. solani* R1, natomiast najmniejsze w przypadku szczepu R3 (44-78%) w zależności od wieku hodowli bakterii. *B. subtilis* może znaleźć szerokie zastosowanie w ochronie roślin przed chorobami wywołanymi przez *R. solani*.

Słowa kluczowe: *Bacillus subtilis*, *Rhizoctonia solani*, aktywność przeciwgrzybowa

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and Teresa KRZYŚKO-ŁUPICKA[1]

MICROBIOLOGICAL ANALYSIS OF BIOAREOSOL IN FOOD INDUSTRY

ANALIZA MIKROBIOLOGICZNA BIOAEROZOLU W ZAKŁADACH PRZEMYSŁU SPOŻYWCZEGO

Abstract: Presence of bacteria and fungi in the food processing plants influence on quality and stability of products. Fungal contaminants are especially dangerous because fungi produce mycotoxins and allergens. The aim of this study was assessed microbial contamination of the air in food industry and determining the dominance of bacteria or fungi in various closed spaces. The bioaerosol was tested by the Koch sedimentation method by using Petri dishes (90 mm) which were located hight at 1.3 m and incubated 15 min. Air analysis was performed in various closed spaces: production hall (HP, HP3, HP4), aseptic production hall (AC, AU), packing department (PD), cloak rooms (CL i CM1, CM2), two production storages (PS1, PS2), technical storage (TS) and canteen (CA). The results were given in CFU/m^3 of air. Preliminary analysis showed that the most polluted bioaerosol was observed in cloak room for men (CM1, CM2) and production storages (PS1, PS2). The highest total number of microorganisms in air (4.5 103 CFU/m^3) was observed in cloak room (CM2). The number of microorganisms - from 102 to 103 CFU /m^3 of air was in production zone.

Keywords: food industry, bioareosol, airborne microorganism, fungal contaminants

Implementing a system to ensure the quality of the product described in ISO 22000:2006 and forced to have a HACCP system in the food industry [1] resulted in increased interest in monitoring the microbiological purity of the air and surfaces in the technology halls. Despite the indication of both the ISO 22000 and the code of Good Manufacturing Practice (GMP) to monitor the microbiological purity of the air in the Polish law is the lack of normative reference to the content of specific groups of microorganisms in bioaerosol [2, 3]. The problem with the content of microorganisms and especially filamentous fungi in the environment of production in the food industry is real and the lack of reference values makes, that food factories do not take preventive measures. In recent years, there have been reports on the sanitary conditions of the dairy and wine industry [4, 5], and in 2006, the plant produces packs for the food industry [3]. The above reports indicate, that the halls and usable areas are contaminated with fungi such as *Penicillium*, *Aspergillius*, *Cladosporium* and *Fusarium* [3, 6]. They influence on the contamination of food products, as well as a potential threat to human health.

The aim of this study was to evaluate the sanitary conditions of indoor air in food industry plants in Opole region.

Materials and methods

The assessment of air quality in the food plant with both preservatives and in aseptic conditions (generated in the production machine) was conducted in the spring in the

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[*] Contribution was presented during ECOpole'13 Conference, Jarnoltowek, 23-26.10.2013

following areas: the main production hall (HP, HP3, HP4) and packing department (PD), clean (AC) and unclean (AU) aseptic production halls, ladys' cloak room (CL) and the two men's locker rooms (CM1, CM2), a technical storage (TS), production storages (PS1, PS2) and in the canteen (CA).

Bioaerosol analysis was carried out by Koch's sedimentation method, placing a Petri dish at a height of 1.3 m for 15 minutes [7]. Each culture was incubated at 25ºC for 48 hours - bacteria (in the BTL agar) and filamentous fungi (in Czapek BTL medium) for 7 days. Content of microorganisms in air, using the Omeliański formula, was calculated and expressed as the number of colony forming units (CFU) in 1 m^3 of air [8]. The results are given in [%] as the ratio of the number of bacteria and fungi in the air in the test areas of food production plant.

Subsequently we performed a preliminary qualitative analysis of isolated filamentous fungi [9, 10].

Results

Preliminary microbiological analysis of the bioaerosol showed, that the most polluted areas in the plant were men's cloak rooms (CM, CM2) and warehouses of finished products (PS1, PS2) and the highest total number of microorganisms in the air ($4.5 \cdot 10^3$ cfu/m^3) was observed in men's cloak room (CM2). However, the air in the production area the total number of microorganisms (TNM) ranged from $3.49 \cdot 10^2$ cfu/m^3 (in HP space) to $1.34 \cdot 10^3$ cfu/m^3 (in HP4 space) (Fig. 1).

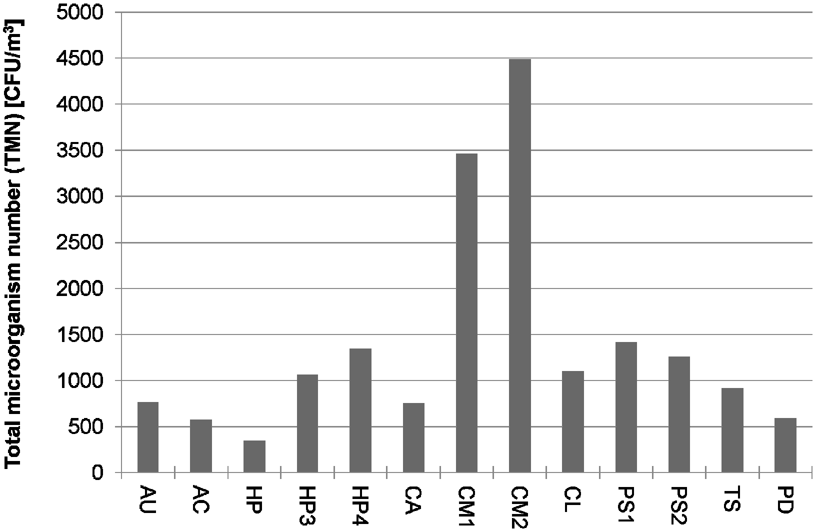

Fig. 1. The total number of microorganisms in 1 m^3 of air [cfu/m^3] in the production areas (AU, AC, HP, HP3, HP4, PD); men's cloak rooms (CM, CM2); - ladys' cloak room (CL); production storages (PS1, PS2); technical storage (TS)

The changing rooms (CM1, CM2), which were the most microbiologically contaminated, as well as the production areas (HP, AU, HP4) were dominated by bacteria and they were in 70-80% and 60-70% of the air, respectively. Only in the case of the HP3 production line and the line which prepares packaging materials (PD) filamentous fungi accounted for over 80% of the total number of microorganisms in the air (Fig. 2).

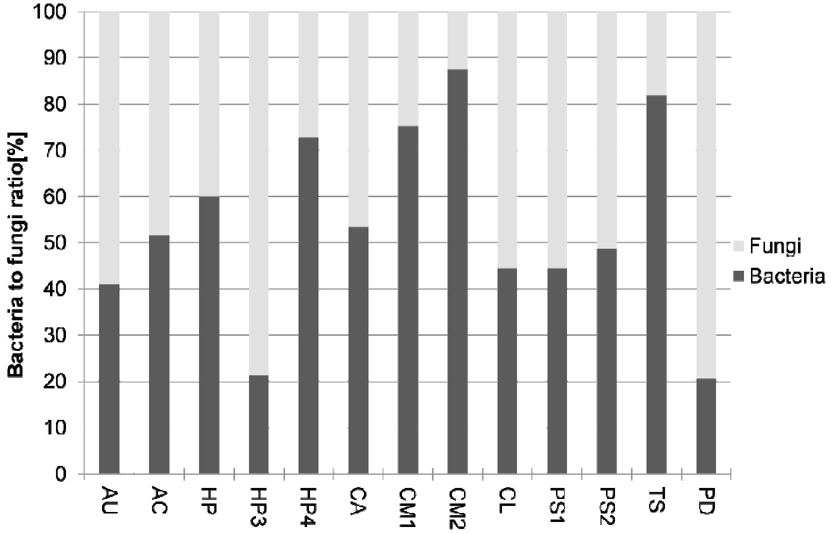

Fig. 2. Bacteria to fungi ratio in the air in a different rooms of the food production plant [%]

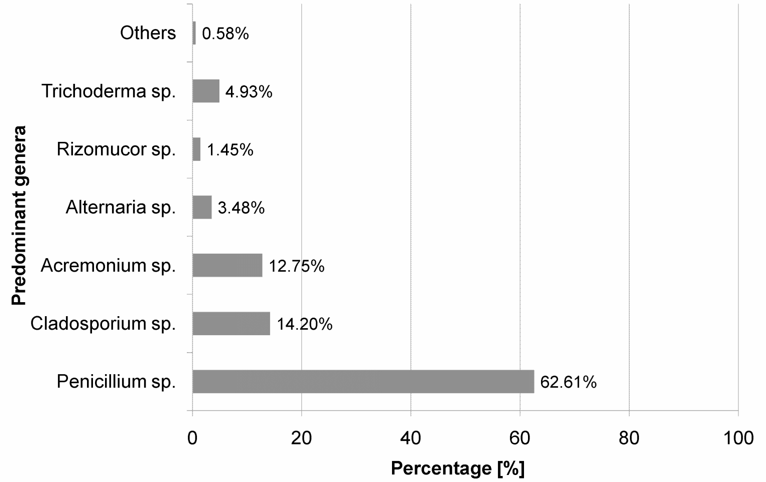

Fig. 3. Predominant genera of filamentous fungi in the air of the food production plant [%]

The greatest species diversity of filamentous fungi was found in the rooms such as men's and women's cloak rooms and production storages. Isolated on the plant area fungi were classified into genus: *Penicillium* (63%), *Cladosporium* (14%), *Acremonium* (13%), *Trichoderma* (5%), *Alternaria* (3.5%) and others (1.5%) (Fig. 3).

Many authors seeks to provide reference values for the content of microorganisms in bioaerosol but various studies, however, use different methodology which causes difficulty in their comparison [2, 11]. Also there is a lack of the specific normative values for air microbial contamination in different sectors of the food industry, with emphasis on the nature of the production and the technology used [3]. The only general description for the food industry are the recommendations proposed by Krzysztofik [12], where permissible concentration of the total number of microorganisms in 1 m^3 of air should not exceed $6 \cdot 10^2$ CFU, and does not allow for a growth of filamentous fungi on Sabouraund medium [12]. In the case of the analyzed plant, the parameters adopted above, the permissible level of microbial contamination satisfy only rooms HP and AC. Both study by Kręgiel [3] in a technology hall and analyzed by Dioguardieg and Franzetti [13] regional dairies in northern Italy does not satisfy this criterion [3, 13]. Therefore, it is important to analyze the risks resulting from microbial pollution in different sectors of the food industry and the establishment of individual standards including the impact of bioaerosol on the quality of the product and its possible contamination.

Conclusions

Conducted a preliminary study showed that the most microbiologically polluted areas in the plant does not belong to the area of production but the locker rooms and warehouses. Reducing the number of microorganisms present in these areas will prevent the spread of them to the production area. The lack of appropriate reference values and the poor number of studies on microbiological contamination in food industry causes the difficulties in comparing the results.

The next stage of research will be screening of antimicrobial substances. The research will be conducted on strains isolated from air and surface of a plant. After finding the essential oil and its concentration will be carried out a study in one of the social rooms.

Acknowledgements

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ANALIZA MIKROBIOLOGICZNA BIOAREOZOLU W ZAKŁADACH PRZEMYSŁU SPOŻYWCZEGO

Samodzielna Katedra Biotechnologii i Biologii Molekularnej, Uniwersytet Opolski

Abstrakt: Obecność bakterii i grzybów strzępkowych w zakładach przemysłu spożywczego wpływa zarówno na jakość, jak i na stabilność produktów spożywczych. Niebezpieczne jest zwłaszcza zanieczyszczenie grzybami strzępkowymi ze względu na produkowane przez te drobnoustroje alergeny i mikotoksyny. Celem przeprowadzonych badań była ocena skażenia mikrobiologicznego powietrza oraz wskazanie dominujących grup mikroorganizmów w poszczególnych pomieszczeniach zakładów przemysłu spożywczego. Analiza bioareolozu była prowadzona metodą sedymentacyjną Kocha - umieszczone na wysokości 1,3 m szalki Petriego (90 mm) eksponowano przez 15 min. Analiza czystości mikrobiologicznej powietrza była prowadzona w różnych pomieszczeniach zakładów produkcji spożywczej: hali produkcyjnej (HP, HP3, HP4), hali produkcji aseptycznej (AC, AU), hali przygotowania opakowań jednostkowych (PD), szatniach (CL, CM, CM2), magazynach produkcyjnych (PS1, PS2), magazynie technicznym (TS) i stołówce (CA). Wyniki zostały przedstawione w jtk/m^3 powietrza. Wstępne badania wskazały, że najbardziej zanieczyszczone mikrobiologicznie były szatnie męskie (CM1, CM2) i magazyny produkcyjne (PS1, PS2). Najwyższą ogólną liczbę mikroorganizmów w powietrzu (4,55 10^3 jtk/m^3) odnotowano w jednej z szatni (CM2). Ogólna liczebność mikroorganizmów w powietrzu strefy produkcji wahała się od 10^2 do 10^3 jtk/m^3.

Słowa kluczowe: przemysł spożywczy, bioaerozol, mikroflora powietrza, zanieczyszczenia grzybami

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ASSESSMENT OF THE IMPACT OF SEWAGE SLUDGE COMBUSTION TECHNOLOGY ON THE PROPERTIES OF ASHES

OCENA WPŁYWU TECHNOLOGII SPALANIA KOMUNALNYCH OSADÓW ŚCIEKOWYCH NA WŁAŚCIWOŚCI POPIOŁÓW

Abstract: The amount of sewage sludge produced at Polish and foreign sewage treatment plants constantly increases. Polish and European Union regulations on sewage sludge treatment lead to higher popularity of thermal treatment methods. Thermal methods cover among others incineration of sewage sludge in the fluidised bed or grate furnaces. The paper presents the test results of ashes produced from sewage sludge from Polish sewage sludge incineration plants equipped with fluidised bed - sewage treatment plant in Sitkowka-Nowiny near Kielce and with a stoker - sewage treatment plant in Olsztyn. The mobility of heavy metals from ashes from sewage sludge was investigated. The tests were performed using a methodology proposed by Community Bureau of Reference (BCR). It has been stated that the dominant fraction of heavy metals in ashes from sewage sludge taken at both plants was immobile.

Keywords: sewage sludge ash, mobility, heavy metals

Introduction

In Poland main methods of municipal sewage sludge utilization are applied in agriculture (22.4% of dry mass of sewage sludge generated in the year 2011), applied in land reclamation including reclamation of land for agricultural purposes (10%) and landfilled (10.4%) [1]. The environmental use of sewage sludge is seasonal and is regulated by waste act [2], regulations [3, 4], and the directive [5]. Furthermore, there are no suitable areas for this purpose. According to the National Waste Management Plan, only 7.5% of total number of sewage treatment plants provide sludge which can be used in agriculture [6]. Furthermore, from 1st January 2016 landfilling of unprocessed sewage sludge will be prohibited [7].

The consequence of these situations is an increase of the amount of thermal sewage sludge utilization, especially in big agglomerations [8, 9]. The thermal disposal of sewage sludge includes main methods: combustion (grate furnace, fluidized bed, smelting and rotary furnace), co-combustion (with: coal, other fuels, municipal solid waste), alternative processes (for instance, pyrolysis) [10]. In Poland the dominant combustion technology of sewage sludge is fluidized bed furnace (8 - installations). Combustion of sewage sludge in grate furnace is in 4 municipal waste water treatment plants [11].

The incineration does not provide a zero-waste disposal method since approximately 30% of the solids remain as ash [12]. The ash forming as a result of sewage sludge combustion process is included into the landfilled waste depending on the criteria it fulfils: non hazardous waste, hazardous waste or inert waste. One of the criteria is the limit of heavy metals [7, 13]. The concentration of heavy metals is not a sufficient indicator of

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waste environmental harmfulness. The mobility and bioavailability of heavy metals in the environment depends on the forms of their occurrence.

The use of sewage sludge ash in agriculture has been reported [14], processing sewage sludge ash to form materials like: brick [15, 16], glass-ceramics [17], lightweight aggregate [18, 19], asphalted paving mixes [20], cement mortars [21, 22].

The chemical and mineral composition of sewage sludge ash depends on. the thermal sewage sludge disposal technology [23].

The aim of this research was the evaluation of impact of combustion technology on sewage sludge ash properties, like heavy metals mobility. The analysed technologies of sewage sludge combustion were combustion in fluidized bed furnace and combustion in grate furnace.

Materials

Sewage sludge ash from combustion in fluidized bed

One of the waste water treatment plants with combustion sewage sludge in fluidized bed is installation in Sitkowka-Nowiny. This waste water treatment plant receives waste water from the sewer system in Kielce - capital of this region, Sitkowka-Nowiny municipalities and part of the Masłów municipality. The nominal flow capacity of this sewage treatment plant equals 270 000 PE. The total amount of waste water influent is municipal waste water 85% and 15% of industrial waste - mainly from the food and metal industries. This waste water treatment plant releases around 12 000 Mg/a [24]. The maximum amount of combustion sludge equals 88.8 Mg/d. This sludge thermal utilization installation is composed of main elements:

- receipt and storage of sewage sludge,
- sludge drying in discs dryer - drying at 215ºC, after drying sewage sludge has 36% d.m. Dried sludge after leaving the drier is directed to the mixing tank. In this tank dried sludge is mixed with screenings, sand and fat,
- combustion in fluidized bed - combustion at 850ºC.

Sewage sludge ash from combustion in grate furnace

One of the Polish sewage treatment plants in which the sewage sludge is incinerated in grate furnace is the sewage treatment plant in Olsztyn. The sewage is transported to the sewage treatment plant by means of a separate sewage system. The capacity of the sewage treatment plant equals 350 000 RLM. The amount of sewage sludge intended for combustion equals 760 Mg d.m. of sewage sludge. The maximum capacity of sewage incineration plant equals 15 Mg/d. The installation of sewage sludge combustion consists of belt drier and the combustion chamber with a grate.

Methods

The chemical composition of examined sewage sludge ashes was determined by means of emission spectroscopy method in XRF infrared. The phase composition of sewage sludge ash was determined with the use of XRD X-ray diffraction methodology. Grain size distribution of sewage sludge ash was made by laser diffractometer.

Mobility of heavy metals from sewage sludge ash

The BCR test was applied to determine the heavy metal fraction in sewage sludge ashes. The sequential extraction method used allows one to determine the mobility degree of metals which are present in the matrix. The methodology suggested by European Community Bureau of Reference was used. The tests were conducted in accordance with the four-step BCR sequential extraction procedure [24], introducing a change in the method of residual fraction mineralisation, *ie* aqua regia was used in the process of mineralisation [12]. The heavy metals in the obtained extracts were determined using an optical spectrometer with inductively coupled plasma ICP Perkin-Elmer Optima 8000.

Results and discussion

The chemical composition of sewage sludge ash is presented in Table 1. The compositions of both examined types of sewage sludge ash showed the dominance of silicon dioxide, calcium oxide and phosphorus oxide. The presence of both silicon dioxide and aluminium oxide is the result of rain water carrying mineral contamination into the sewage system, street cleaning as well as water-supply and sewer pipes corrosion [25].

Table 1

Chemical composition of sewage sludge ash

Component	**Sewage sludge ash from Sitkowka-Nowiny (SSA1)**	**Sewage sludge ash from Olsztyn (SSA2)**
	[%]	**[%]**
SiO_2	35.72	25.77
Al_2O_3	6.70	9.54
Fe_2O_3	9.56	5.12
CaO	17.46	20.70
MgO	4.51	4.48
SO_3	1.21	0.30
K_2O	1.61	1.87
Na_2O	0.52	0.55
P_2O_5	19.0	21.58
TiO_2	1.00	0.77
Mn_2O_3	0.14	0.13
SrO	0.05	0.10
ZnO	0.37	0.41
BaO	0.11	0.09
CuO	0.06	0.13
TOC	0.09	5.39

In both types of sewage sludge ash, in comparison to literature data [26], a large portion of biophile element - phosphorus was discovered. A high concentration of phosphorus in the ash is the effect of i.a using detergents by the inhabitants, sewage treatment method, especially with the use of coagulants for phosphorus precipitation.

The sewage sludge ash (SSA1) from fluidized bed incineration presented a high degree of mineralization (TOC - 0.09% d.m.), in contrast to grate furnace sewage sludge ash (SSA2) (TOC - 5.3% d.m).

Sewage sludge ash SSA1 presented the following phase composition: quartz, $Ca_9Al(PO_4)_7$, hematite, orthoclase, albite. The phase composition of sewage sludge ash SSA2 included quartz, $Ca_9Al(PO_4)_7$, feldspars. Both quartz and hematite are the typical sewage sludge ash as well as carbon fly ash phases.

Grain size distribution of both types of sewage sludge ash was shown in Figures 1 and 2. In sewage sludge ash SSA1 x_{50} equals 58.78 µm, x_{99} - 319.39 µm. Whereas in the sewage sludge ash SSA2 x_{50} equals 1480.77 µm, x_{99} - 2267.73 µm.

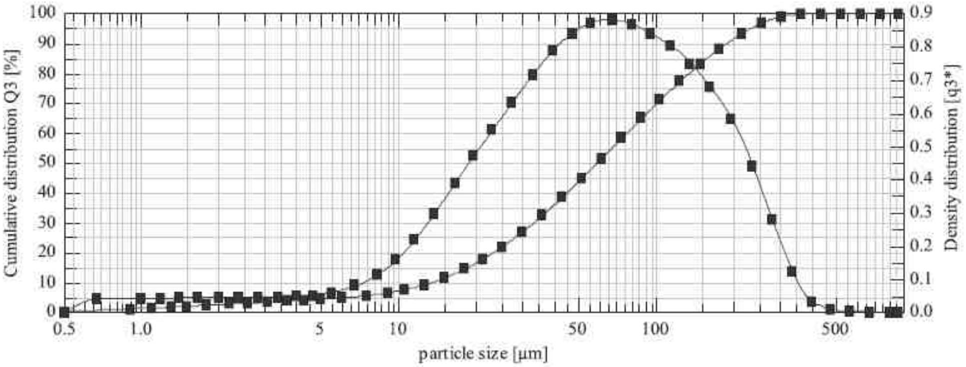

Fig. 1. Cumulative distribution and density distribution of sewage sludge ash from waste water treatment plant in Sitkowka-Nowiny

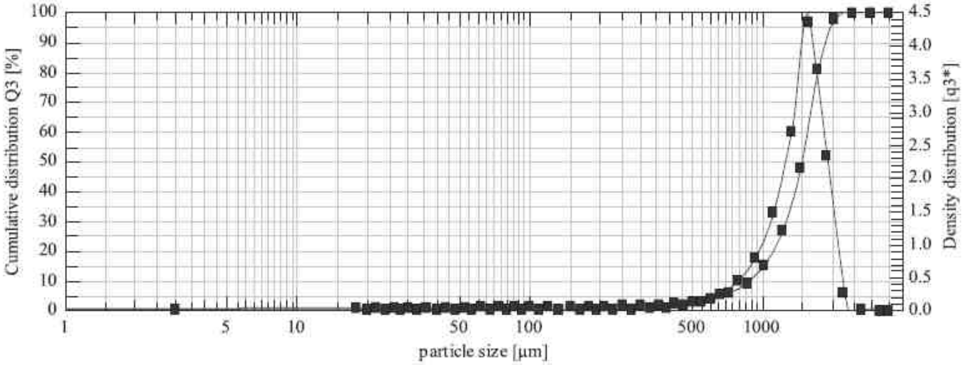

Fig. 2. Cumulative distribution and density distribution of sewage sludge ash from waste water treatment plant in Olsztyn

The heavy metals mobility of examined sewage sludge ash is presented in Tables 2 and 3 and Figures 3 and 4. The sewage sludge ash SSA2 presented a lower content of cadmium, lead and zinc in comparison to sewage sludge ash SSA1. As far as sewage sludge ash SSA1 is concerned, copper, chromium, nickel, zinc were present mainly in the immobile form - FIV. Whereas lead and cadmium dominated in a potentially immobile form (FIII). In sewage sludge ash SSA2 the dominant fraction of copper, chromium, nickel, lead and zinc was the immobile fraction (FIV). While the dominant fraction of cadmium in ash SSA2 was the mobile fraction (FI).

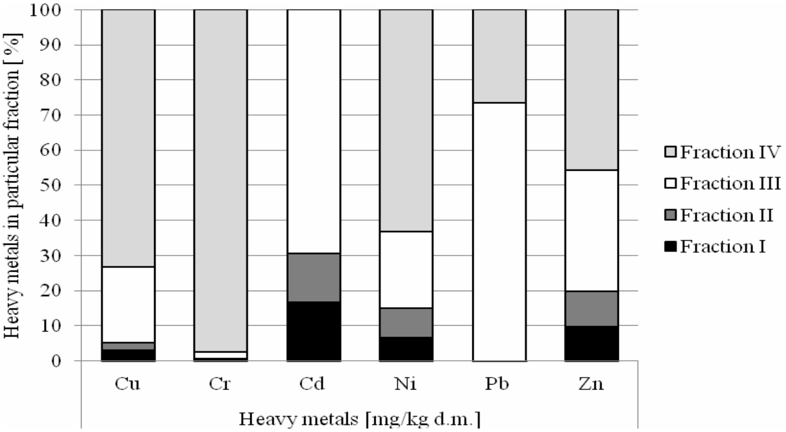

Fig. 3. The contribution percentage of heavy metals in particular fraction in sewage sludge ash from waste water treatment plant in Sitkowka-Nowiny

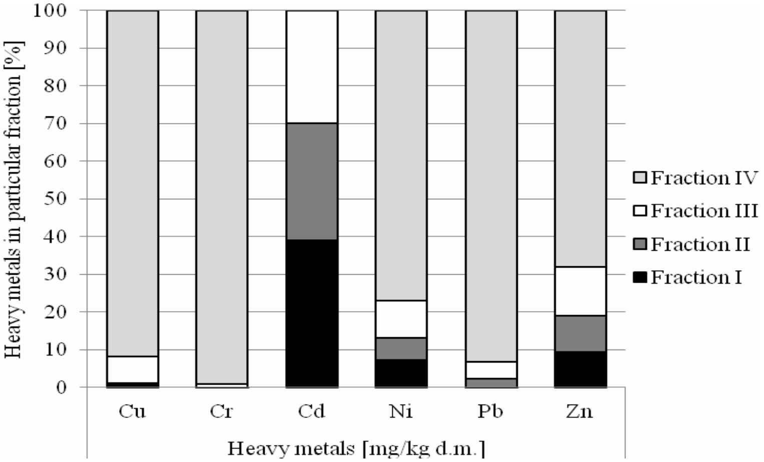

Fig. 4. The contribution percentage of heavy metals in particular fraction in sewage sludge ash from waste water treatment plant in Olsztyn

Table 2

Speciation of heavy metals sewage sludge ash from waste water treatment plant in Sitkowka-Nowiny

Speciation	**Heavy metals [mg/kg d.m.]**					
	Cu	**Cr**	**Cd**	**Ni**	**Pb**	**Zn**
FI	11.98±0.21	0.33±0.02	0.90±0.01	2.97±0.02	0.01±0.09	71.65±1.02
FII	8.24±0.08	0.08±0.08	0.74±0.01	3.81±0.04	0.16±0.18	72.96±0.35
FIII	85.42±1.26	1.49±0.13	3.76±0.05	9.92±0.02	310.89±2.02	256.21±2.82
FIV	290.99±6.40	73.92±5.29	0.00±0.00	28.90±0.05	112.47±0.97	336.85±5.49
ΣFI-IV	396.63	75.82	5.40	45.60	423.53	737.67

Table 3

Speciation of heavy metals sewage sludge ash from waste water treatment plant in Olsztyn

Speciation	**Heavy metals [mg/kg d.m.]**					
	Cu	**Cr**	**Cd**	**Ni**	**Pb**	**Zn**
FI	8.52±0.23	0.29±0.03	0.33±0.01	4.22±0.03	0.16±0.12	56.58±0.74
FII	1.11±0.08	0.27 ±0.05	0.27±0.02	3.34 ±0.02	0.64±0.11	58.48±1.33
FIII	58.10±1.72	0.54±0.08	0.22±0.02	5.77±0.08	1.50±0.22	78.28±0.22
FIV	757.26±16.89	110.01±10.48	0.00±0.00	44.58±0.39	31.94±0.34	410.09±5.37
ΣFI-IV	824.99	111.11	0.82	57.91	34.24	603.43

Conclusion

- The sewage sludge ash from fluidized bed incineration installation presented a high degree of mineralization. The conditions in the combustion chamber clearly influenced the incinerated sewage sludge mineralization degree.
- The incineration technology significantly influenced the grain size distribution and the size of incinerated sewage sludge ash fractions. The ash from fluidized bed installation presented minor grain size distribution whereas the grain size distribution of ash from grate furnace installation was considerably homogeneous. According to literature data the grain size distribution of sewage sludge ash fractions is an important factor influencing the choice of ash neutralization method *ie* the usage as an additive to a particular building material.
- The incineration technology of examined sewage sludge did not have a significant influence on the mobility of heavy metals from the sewage sludge ash. In the examined sewage sludge ash the heavy metals dominated in the immobile phase (FIV). Cadmium was an exception which at low concentration, especially in the grate furnace installation ash, dominated in a mobile phase (FI).

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OCENA WPŁYWU TECHNOLOGII SPALANIA KOMUNALNYCH OSADÓW ŚCIEKOWYCH NA WŁAŚCIWOŚCI POPIOŁÓW

Wydział Inżynierii Środowiska, Geomatyki i Energetyki, Politechnika Świętokrzyska w Kielcach

Abstrakt: Ilości osadów ściekowych powstających w krajowych i zagranicznych oczyszczalniach ścieków komunalnych stale wzrastają. Obowiązujące w Polsce i Unii Europejskiej normatywy prawne regulujące postępowanie z osadami ściekowymi przyczyniają się do wzrostu popularności metod termicznych. Stosowane metody termiczne obejmują między innymi spalanie osadów ściekowych w piecu ze złożem fluidalnym lub w piecu rusztowym. W pracy przedstawiono wyniki badań popiołów z osadów ściekowych pochodzących z krajowych instalacji spalania osadów ściekowych: ze złożem fluidalnym - oczyszczalnia w Sitkówce-Nowiny k. Kielc oraz z rusztem - oczyszczalnia w Olsztynie. Zbadano mobilności metali ciężkich z popiołów z osadów ściekowych. Badania przeprowadzono, wykorzystując metodykę proponowaną przez Community Bureau of Reference (BCR). Stwierdzono, że dominującą frakcją metali ciężkich w popiołach z osadów ściekowych pochodzących z obu instalacji była frakcja niemobilna.

Słowa kluczowe: popiół z osadów ściekowych, mobilność, metale ciężkie

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APPLICATION OF NUMERICAL MODELING TO STUDY OF DISPERSION OF BHT IN POLIETHYLENE PIPES

ZASTOSOWANIE MODELOWANIA NUMERYCZNEGO DO BADANIA TRANSPORTU BHT W PRZEWODACH POLIETYLENOWYCH

Abstract: PE-HD water pipes are exposed to adverse environmental conditions, both during production and their subsequent use in the construction industry. Organic compounds migrating into water may lead to deterioration of water quality, especially its taste and odor. Commonly used antioxidant BHT and its products of degradation are leaching into water as a result of degradation of the pipes material. This paper presents the results of laboratory tests considering changes of BHT concentration in the water circulating in the PE-HD pipe of 30 m length as well as our numerical studies. Numerical calculations were performed using the commercial software Fluent, Ansys Inc., based on the computational fluid dynamics (CFD). The analyses of water samples confirmed the migration of the tested antioxidant from the pipe material into water. The results of numerical analysis showed the good agreement with the measured values.

Keywords: antioxidants migration, BHT, PE-HD pipes, numerical modeling

Introduction

Polyethylene is nowadays the material which application to the construction of new and renovation of old networks and water supply systems [1]. Water pipes made of PE-HD are exposed to the adverse environmental conditions, both at the production and their later use in construction. Polyethylene pipes exposure to UV radiation, high temperature, mechanical stress, oxidative compounds used for water disinfection may lead to damage and degradation of pipes material and release of organic compounds form the material of water pipes [2, 3].

In order to improve the mechanical and physical properties and to extend the life of pipes made of PE-HD, the organic and inorganic compounds such as: stabilizers, dyes, fillers are added to the material at the stage of production [3-7]. Stabilizers are substances designed to improve polymer resistance to aging in time of its processing as well as during the use of material. Among stabilizers the following can be distinguished: thermal stabilizers, light stabilizers, antioxidants and biological stabilizers [8]. Antioxidants are used in the production of almost all commercial polymers in the amount of up to 2% [9].

Researches in numerous scientific reports show that organic compounds migrating into the water can cause changes of its organoleptic properties, deterioration of taste and smell [5, 7, 10-12]. Compounds responsible for the deterioration of the organoleptic properties of water include BHT antioxidant (4-methyl-2,6-di-tert-butyphenol), or products of its degradation as well as alkylobenzenes, ketones or esters [13]. Researches performer by *eg* Mikami et al [14], Matsuo et al [15], Fernandez-Alvarez et al [16] shown that BHT released into water is degraded as a result of oxidation reaction and the following compounds may

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be formed: BHT-COOH (3,5-di-tert-butyl-4-hydroxybenzoic acid), BHT-OH (2,6-di-tert-butyl-4-(hydroxymethyl)phenol), BHT-CHO (3,5-di-tert-butyl-4-hydroxybenzaldehyde), BHT-Q (2,6-di-tert-butylcyclohexa-2,5-diene-1,4-dione).

BHT is a fat-soluble antioxidant which found wide application in the polymer, fuel, food and pharmaceutical industry [17]. According to the Directive 67/548/EWG on the classification of dangerous chemicals, BHT is a flammable, toxic and irritant compound. This compound is considered as safe to use if the amount of the antioxidant in food does not exceed 0.02% of the total fats and oils [17]. BHT is also used to improve the stability of pharmaceuticals, fat-soluble vitamins and cosmetics [18]. Addition of BHT to plastics prevents polymer decomposition during its processing, and extends life of the finished products [19].

Modeling of water quality in distribution networks is now becoming a very useful tool supporting designing process and network management. Computational Fluid Dynamics methods (CFD) allow to calculate dispersion of contaminants in water pipes at different flow conditions, having regard to chemical reactions in the water and on the walls of pipes [12, 20]. CFD is now being used with great success in many areas of science and technology, including the modeling of hydraulic parameters in water supply systems, as well as in the sewer systems [21, 22]. One of the most popular commercial CFD software with wide range of computing capabilities is Fluent, Ansys Inc. [23, 24]. The literature contains many examples of use of Fluent software in a variety of fluid flow simulation calculations [23-25].

Mathematical description of water movement in water pipes applied in Fluent model is based on the laws of mass and momentum conservation and the Navier-Stokes equation. These equations are solved with the proper set of computational simplifications, boundary conditions and initial data. [23, 26]. Qualitative calculations including transport, mixing and disintegration of chemical compounds in the water, reacting or not with other components of the mixture, are usually based on the equation of mass conservation for a given component of the mixture [27].

This paper presents the laboratory tests of BHT concentration changes in the water circulating in the loop with a length of 30 m, made of new PE-HD pipes, and numerical investigations reflecting the laboratory experiment. Numerical calculations were performed using the commercial software Fluent, Ansys Inc., on the computational fluid dynamics (CFD). Numerical calculations were used for quantitative evaluation of the analyzed antioxidant in the water having contact with the PE-HD pipes.

Materials and methods

Measuring installation

Laboratory measurements of changes in the concentration of BHT in the water were carried out on a specially prepared laboratory installation (Fig. 1). It was built with new PE-HD 80 pipes, PN 12.5, with a diameter of 32x3.0 mm produced in Poland in accordance with PN-EN 12201-2:2011 purchased directly from the manufacturer. Pipeline length was 30 m, inner surface of pipes was equal to 2.45 m^2, and the volume of water in the analyzed system - 15.9 m^3.

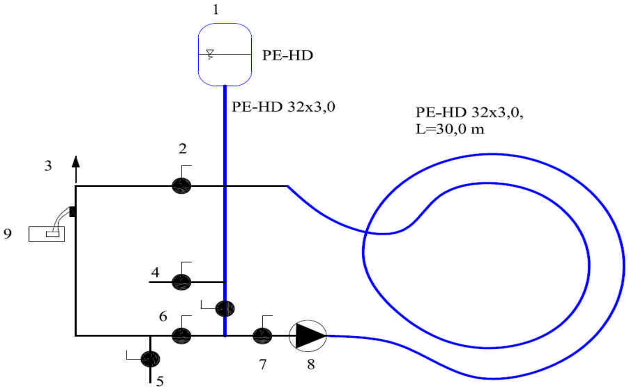

Fig. 1. Scheme of the measuring installation: 1 - water tank to fill up installation, 2, 6, 7 - stop valve, 3 - deaerator, 4, 5 - drain valve, 8 - centrifugal pump, 9 - PortaFlow 300 ultrasonic flowmeter

Before testing, measuring installation was rinsed with the deionized water prepared with Milli-Q (Millipore, Molsheim, Germany) providing at least 3-fold exchange of water in the system. Then, the system was filed with test water. Basic parameters of deionized water used for rinsing and then for filling the system were as follows: TOC ≤ 0.5 ppb, resistivity 18.2 MΩm. Setting of water flow in the system equal to 0.6 m/s (Re = 13650) was maintained with the help of WILO MVIe 203-1/16/E/3-2/B centrifugal pump. Water samples were collected into testing glass vials with a capacity of 40 ml in accordance with the schedule of research, and then they were subjected to the analyses by gas chromatography Trace Ultra Thermo coupled with Polaris Q (GC-MS) mass spectrometer. Prepared samples were subjected to stationary phase extraction using a blue SPME fiber. Gas chromatography working conditions were as follows: analytical column RTx5 (Dioxin) 60 m × 0.25 mm *df* = 0.15 μm by Restek, as a carrier gas He (99.9996%) was used flowing with intensity of 1.2 cm^3/min. Working conditions of Polaris Q-Thermo mass detector were as follows: ion source temperature - 250°C, transfer line temperature - 275°C. Results of the analysis were retention spectra (area under peak of characteristic ion - base peak - 205) and mass spectra confirming the presence of the analyzed compound.

Results of laboratory measurements

Results of laboratory measurements of water samples, carried on GC-MS are shown in Table 1.

Table 1

BHT concentration in the water from the measuring stand

Sample No	A	B	C	D	E	F	G	H	I	J
Time [hr]	0	2	4	6	11	24	48	72	100	147
BHT concentration [μg·dm^{-3}]	20.8	19.8	41.1	49.5	60.9	93.9	115.3	138.4	177.6	194.2
Water temperature [°C]	21.6	22.2	22.4	22.9	23.5	22.3	22.5	23.0	24.1	25.0

Detectability limit for water samples marked by GC-MS was 2.7 ng·dm^{-3}, while quantification limit (*QL*) was 8.1 ng·dm^{-3}.

For the first 40 hours of measurements (samples from A to G, samples marking in accordance with Table 1), counting from the start of the experiment, the fastest BHT growth in the water was observed.

The revealed results of measurements of the BHT concentration in the water indicate that after about 70 hours, counting from the start of the stand, in the samples relatively small increase of antioxidant content has been observed. During the duration of measurement, 10-fold concentration increase was observed, from 20.8 μg·dm^{-3} (in the first hour of measurement, $t = 0$) to 201.8 μg·dm^{-3} (in the last hour of measurement $t = 147$ h). Obtained results of BHT concentration in water are comparable with the values obtained by Widomski et al [25] for BHT migrating from PE-HD 100 pipes.

CFD modeling

Numerical modeling of selected antioxidant (BHT) propagation in the analyzed water, moving with constant mean velocity, was performed using the finite element method in a commercial program Fluent 6.3 which is the part of Ansys 14.0 computational package, Ansys Inc. Computational domain range reflecting the capacity of water filling measuring installation consisted of 149783 finite elements and 179090 junctions. While creating geometric model reflecting measuring installation, necessary assumptions and simplifications were accomplished. The model does not include centrifugal pump - water movement with constant rate in the model was obtained by giving a constant flow rate to selected, small control volume [25].

In numerical research, in order to determine BHT concentration in the water the following assumptions were made: simulation time according to the duration of the laboratory measurements; numerical calculations were carried out on the basis of the law of conservation of mass, momentum and energy, as well as in relation to viscous, dual-equation model of turbulence k-ε [28]; the assumed value of the diffusion coefficient of BHT from the material surface into the water equal 7.15E-16 m^2·s^{-1} [29]; time step length - 60 s; boundary condition of contaminants transport: variable in time, reflecting concentration value of BHT in the boundary layer, described as the mass fraction of the analyzed antioxidant.

Table 2

Input data to simulation calculations

Average flow rate	**Water temperature**	**Water viscosity coefficient**	**BHT molar mass**	**Coefficient of BHT diffusion from the material into the water**	**Boundary condition Dirichlet, mass fraction**	**Time**
[m·s^{-1}]	**[K]**	**[Pa·s]**	**[g·mol^{-1}]**	**[m^2·s^{-1}]**	**[-]**	**[hr]**
0.63	288	0.001308	220.35	7.15E-16	9.15E-07	$t = 0$ - $t = 24$
					2.37E-07	$t = 25$ - $t = 147$

Changes of BHT concentration caused by water sampling for chemical analyses, and the addition of ultrapure water in order to fill the capacity of measuring stand was not included in the calculation, due to its negligible values. The model does not take into account the chemical reaction of antioxidant degradation in the water. Input data assumed for the calculation is presented in Table 2.

Results and discussion

The calculation results of BHT transport in water included three-dimensional distribution of mass fraction of the analyzed antioxidant inside the polyethylene pipe. The results of numerical calculations of BHT concentration changes in water are presented in Table 3.

Table 3

Results of numerical calculations of BHT concentration changes in water

Time	**[hr]**	0	2	4	6	11	24	48	72
BHTconcentration	**[$\mu g \cdot dm^{-3}$]**	0	71.5	76.6	77.7	79.1	82.2	109.0	134.0

The BHT mass fraction distribution in water for the flow rate v = 0.63 $m \cdot s^{-1}$ indicates that the concentration increases during the time duration of experiment. During the simulation calculations, the increase of mass fraction value has been observed from $7.15 \cdot 10^{-8}$ (in the 2nd hour) to $1.85 \cdot 10^{-7}$, which corresponds to the following concentrations: from c = 71.5 $\mu g \cdot dm^{-3}$ to c = 185.0 $\mu g \cdot dm^{-3}$.

Figure 2 shows BHT concentration changes in time for the measured and calculated values obtained in the experiment.

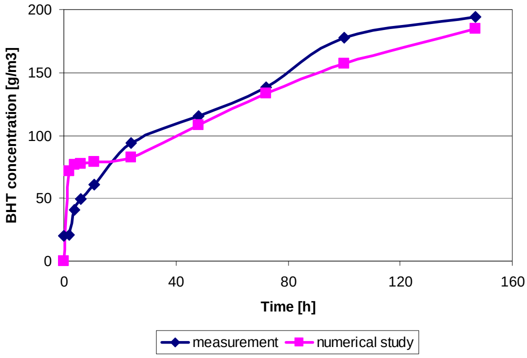

Fig. 2. BHT concentration change in time obtained for the measured and calculated values

Increase of BHT content in water observed during numerical calculations, is consistent with the measured values. In both cases, more than 2.5-fold increase of BHT in the water has been observed.

Average values of the BHT concentration in water obtained by numerical calculations, show quite good agreement with the measured values. Correlation coefficient R = 0.92343 and determination coefficient R^2 = 0.83436871 were determined in Statistica 7.1 for p = 0.05.

Conclusions

The conducted laboratory measurements and numerical calculations show an increase of BHT concentration in water. During laboratory research, in 147th hour, counting form the start of our experiment almost 10-fold increase of BHT in the water (from $c_0 = 19.8$ μg·dm^{-3} to $c_{147} = 194.2$ μg·dm^{-3}). The range of obtained calculation value were $c_2 = 71.5$ μg·dm^{-3} to $c_{147} = 185.0$ μg·dm^{-3}. Numerical calculations of BHT spreading in the water conducted by finite elements method allowed to obtain the results characterized by the considerable compliance with the values of laboratory measurements. The calculated final BHT content was lower that the measured value by 4.7%. Values of the coefficients of: correlation $R = 0.92346$ and determination $R^2 = 0.83436871$ confirmed that a good agreement with compared sets has been achieved. Calculated values of mean square error RMSE = 0.024644861 and Nash-Sutcliff's coefficient $E = 0.761738$ reveal good prognostic ability and efficiency of the model. However, to obtain such a good agreement of the results, it was necessary to introduce the two values of boundary condition for mass transport (t = 0-24 h - $9.15\cdot 10^{-7}$, t = 25-147 h - $2.37\cdot 10^{-7}$). It may be caused by omitting the chemical reaction of BHT decomposition in the water with oxygen in the numerical model. The presented measurements and numerical calculations shown the necessity to conduct further research with regard to chemical models of the analyzed contaminant mass transport, as well as to examine and describe the kinetics of the reaction of BHT decomposition in the flowing water and further including the received results into the developed numerical model.

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ZASTOSOWANIE MODELOWANIA NUMERYCZNEGO DO BADANIA TRANSPORTU BHT W PRZEWODACH POLIETYLENOWYCH

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Abstrakt: Przewody wodociągowe wykonane z PE-HD narażone są na wpływ niekorzystnych warunków zewnętrznych zarówno na etapie produkcji, jak i ich późniejszego wykorzystania w budownictwie. Związki organiczne migrujące do wody mogą powodować zmianę jej właściwości organoleptycznych, pogorszenie smaku i zapachu. W wyniku degradacji materiału przewodów do wody wymywany jest m.in. powszechnie stosowany przeciwutleniacz BHT lub produkty jego degradacji. W pracy przedstawiono wyniki badań laboratoryjnych zmian stężenia BHT w wodzie krążącej w przewodach z PEHD oraz badań numerycznych. Obliczenia numeryczne wykonano z wykorzystaniem komercyjnego programu Fluent, Ansy Inc., bazującego na obliczeniowej dynamice płynów (CFD). Analiza próbek wody potwierdziła migrację przeciwutleniacza z materiału rury do wody. Wyniki analiz numerycznych dały dobrą zgodność z wartościami pomierzonymi.

Słowa kluczowe: migracja przeciwutleniaczy, BHT, rury PEHD, modelowanie numeryczne

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ANTIFUNGAL ACTIVITY OF *Pseudomonas fluorescens* AGAINST PHYTOPATHOGENIC STRAINS OF *Rhizoctonia solani*

AKTYWNOŚĆ PRZECIWGRZYBOWA *Pseudomonas fluorescens* WOBEC FITOPATOGENNYCH SZCZEPÓW *Rhizoctonia solani*

Abstract: The aim of conducted research was to determine the influence of metabolites of *Pseudomonas fluorescens* on the growth of 4 pathogenic strains of *Rhizoctonia solani* marked as R1, R2, R3 and R4 infesting sugar beet. The antagonistic properties of metabolites were assessed after 4, 6, 8, 10 and 24 hours of culturing of *P. fluorescens* with a culture-plate method on Czapek medium. The bacterial strains were cultured at 25ºC for 4-7 days. Fungistatic activity of *P. fluorescens* was determined on the rate of mycelial growth inhibition and of the growth rate index. Obtained results have proved that the strains of *Rhizoctonia* spp. under study were sensitive to *P. fluorescens* metabolites. The highest inhibition of the linear growth of fungi was noted for *R. solani* R1 and R3. In all cases the highest inhibition of the growth rate was obtained after 4 and 6 hours of culturing and the lowest was noted after 10 or 24 hours of culturing. After supplementing the growth medium of *P. fluorescens* the drop of the growth rate index was noticeable and reduction amounted between 78 and 89%. Conducted research confirmed fungistatic properties of *P. fluorescens* strains against *R. solani* strains. The tests showed that growth inhibition of the mycelium depends not only on the type of metabolites produced by a specific bacterial strain but also on the length of culturing.

Keywords: fungistatic activity, growth rate index, *Pseudomonas fluorescens, Rhizoctonia solani*

Introduction

Diseases of cultivated plants caused by *Rhizoctonia solani* Kühn are controlled mainly by an application of chemical substances or agronomic techniques (proper crop rotation, avoiding excessively moist and clumped soil) [1]. However, the residues of chemical substances in plants and the environment and the risk of pathogens' growing resistance to the treatment bring about the need to search for new protection methods. The methods include among others biological measures. According to the Directive 2009/128/EC of the European Parliament and of the Council, sustainable biological methods, employing microorganisms residing in a rhizosphere which are able to degrade toxins produced by pathogens, should be preferred to chemical methods.

The biological protection of plants includes different types of amensalism, especially antybiosis as well as a competition between protective microorganisms and pathogens for nutrients, energy and habitat [2]. When biological methods are considered, special attention is paid to PGPR microorganisms (*plant growth promoting rhizobacteria*) which produce enzymes performing hydrolysis of the cell wall of pathogenic fungi resulting in its degradation and consequently termination of the pathogens. PGPR microorganisms include bacteria such as: *Pseudomonas, Bacillus, Paenibacillus, Brevibacillus, Agrobacterium, Burkholderia, Pantoea, Lysobacter* [2-5].

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The aim of conducted research was to assess the usefulness of *Pseudomonas fluorescens* strain against phytopathogenic strains of *R. solani.*

Materials and methods

In the experiment, a fungistatic activity of *P. fluorescens* against 4 strains of *R. solani* marked R1, R2, R3 and R4 has been assessed. The strain *P. fluorescens* was isolated from soil and identified with the use of ID32GN tests (Biomerieux). The strains of tested fungi were isolated from the infested bulbs of sugar beetroot and diagnosed on the basis of their macro- and microscopic features.

The bacteria were cultured in the broth medium for 48 hours at 30°C. Next, the broth was inoculated with the suspension of 10^6 cfu/ml density and incubated for the time period from 4 to 24 hours. After the incubation it was centrifuged at 10 000 rpm and obtained supernatant underwent further analysis.

Conducted tests employed a culture-plate method applied on Czapek growth medium consisting of [g/dm^3]: sucrose 30.0, $MgSO_4 \times 7H_2O$ 0.5, KH_2PO_4 1.0, KCl 0.5, $NaNO_3$ 3.0, $Fe_2(SO_4)_3 \times 7H_2O$ 0.01, agar 15.0. Tested growth media were inoculated with supernatants obtained after 4, 6, 8, 10 and 24 hours of culturing of *P. fluorescens* rods. Next, the media were inoculated with 10mm discs overgrown with 7-days old mycelium of tested *R. solani* strains. The control trials contained only tested *R. solani* strains with no addition of supernatant. All plates were incubated at 25ºC for 5 days. The diameters on the plates were measured every day until the mycelium of *R. solani,* in the control trial, reached the edge of the plate. The experiment was conducted in 6 trials, where one trial was represented by one culturing plate with the growth medium and the mycelial disc.

The influence of metabolites produced by *P. fluorescens* on the growth of *R. solani* strains was determined against the growth rate index, calculated according to the formula [6]:

$$T = \frac{A}{D} + \frac{b_1}{d_1} + \frac{b_2}{d_2} + \ldots + \frac{b_x}{d_x}$$

where: T - growth rate index, A - mean value of diameter measurements [mm], D - the length of the experiment (number of days), b_1, $b_2 \ldots b_x$ - increase in a diameter size since the last measurement, d_1, $d_2 \ldots d_x$ - number of days since the last measurement.

The fungistatic properties of the supernatant have been assessed on the basis of the linear growth inhibition of the fungus.

Results and discussion

In the conducted research, presented in this paper, strains *Pseudomonas fluorescens* were tested in terms of their applicability to control phytopathogenic strains of *R. solani*. Laboratory tests allowed to determine the direct influence of metabolites produced by *P. fluorescens* on the growth pace of tested fungi illustrated by calculated growth rated indexes and an inhibition of the mycelial growth (Figs. 1-3).

The analysis of the mycelial growth of *Rhizoctonia* spp. strains showed that in all control trials its pace was very fast in time (Fig. 1).

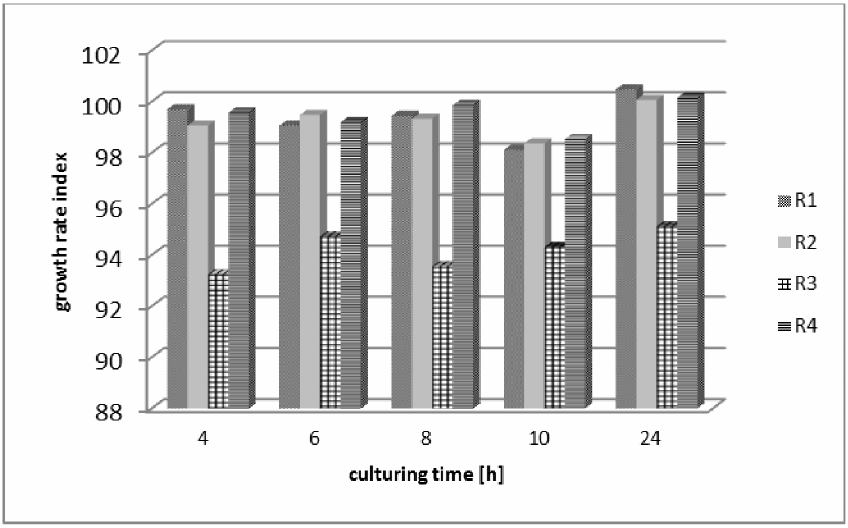

Fig. 1. The growth rate index of *R. solani* for the control trials

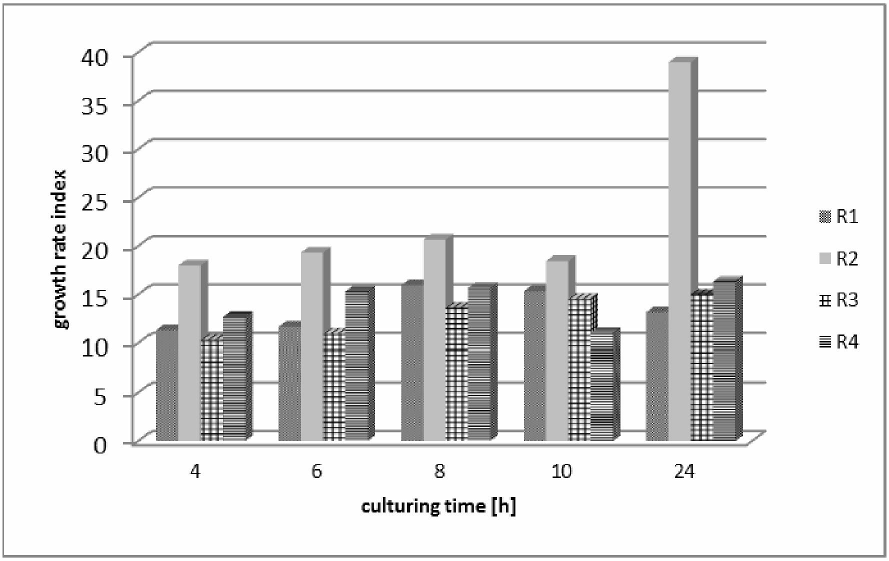

Fig. 2. The growth rate index of *R. solani* for the proper trials

The plate with growing medium was fully covered with the fungus after 3 days in case of the strains: R1, R2 and R4, for which the value of the growth rate index ranged between 98.11 and 100.47. The highest measured values were obtained after 24 hours of culturing and the lowest after 10 hours of culturing. The recorded values of the growth rate index were similar after 4, 6 and 8 hours of culturing and amounted around 99 units. The control strain, marked R3 covered the whole surface of the plate after 4 days of culturing.

Therefore, in this case the values of the growth rate index were lower and fluctuated between 93.24 and 95.11 after 4 hours and 24 hours of culturing respectively.

Metabolites produced by *P. fluorescens* were collected after 4, 6, 8, 10 and 24 hours of an incubation process and then added to the growing media which significantly affected an inhibition of the growth rate index of tested *R. solani* strains (Fig. 2). Regardless of the culturing time of *P. fluorescens* and the type of the fungi strains applied, obtained results of the growth rate index were lower in comparison with the results recorded for the control trials. The results presented in Figure 3, prove unquestionably that the highest inhibition of the growth rate index has been obtained after the application of metabolites obtained after 4 and 6 hours of bacteria culturing, except for the strain R2, for which the most effective were metabolites produced after 4 hours and 10 hours. The strain *P. fluorescens* applied in the research was the most active in case of the strains: R1 and R3 and the recorded value of the reduction of the growth rate index amounted over 88% after the application of the metabolites produced after 4 and 6 hours of the incubation. It seems that the same bacterial strain was least active in case of the strain R2, although the reduction of the growth rate index amounted between 79.19 and 83.18% (Fig. 3).

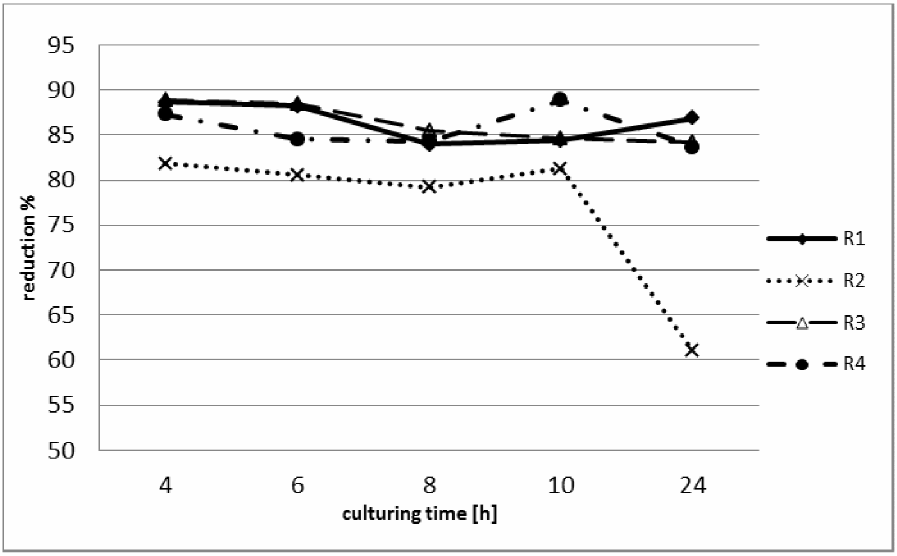

Fig. 3. Influence of *P. fluorescens* on the linear growth rate index of tested fungi *R. solani*

The analysis of obtained results prove that each tested strain of *R. solani* showed a different reaction towards applied metabolites of *P. fluorescens* obtained at its different growth phase. The bacterial strain under study did not inhibit the growth rate index of *R. solani* completely but only restricted it to the range of 78.24-88.95%. Therefore the question has arisen of whether obtained results allow to classify *P. fluorescens* as a useful strain in the process of biological protection against Rhizoctonia diseases? Although many authors [4, 7-10] confirm antagonistic activity of *P. fluorescens* strains towards *R. solani*, conducted tests should be treated as pilot research which requires further confirmation.

Conclusions

1. Obtained results show significant efficiency of *P. fluorescens* against phytopathogenic strains of *R. solani.*
2. The differences concerning the growth inhibition degree noted in the research for individual strains allow to state that the process depends on the strain itself and the length of culturing process.
3. The highest antifungal activity was noted after an application of the supernatants of *P. fluorescens* obtained after 4 and 6 hours of culturing, which corresponds with the early phase of the logarithmic growth.
4. Significant differences obtained during the tests and lack of complete growth inhibition of *R. solani* prove that further large-scale laboratory tests including different strains of *P. fluorescens* should be conducted prior to field tests.

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AKTYWNOŚĆ PRZECIWGRZYBOWA *Pseudomonas fluorescens* WOBEC FITOPATOGENNYCH SZCZEPÓW *Rhizoctonia solani*

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Abstrakt: Celem podjętych badań było określenie wpływu metabolitów *Pseudomonas fluorescens* na wzrost 4 fitopatogennych szczepów buraka cukrowego *Rhizoctonia solani* oznaczonych jako R1, R2, R3 oraz R4. Ocenę właściwości antagonistycznych metabolitów przeprowadzono metodą hodowlano-płytkową na podłożu Czapka dla 4-, 6-, 8-, 10- i 24-godzinnych hodowli *P. fluorescens*. Hodowle prowadzono w temperaturze 25ºC przez 4-7 dni. Na podstawie stopnia zahamowania wzrostu grzybni oraz indeksu tempa wzrostu określono aktywność fungistatyczną *P. fluorescens*. Wyniki doświadczenia wskazują, że wśród badanych szczepów *Rhizoctonia* spp. były szczepy wrażliwe na działanie metabolitów *P. fluorescens*. Największą inhibicję rozrostu liniowego grzybni zaobserwowano dla szczepów *R. solani* R1 oraz R3. W obu przypadkach najwyższe zahamowania wzrostu grzybni uzyskano dla 4- i 6-godzinnej hodowli, a najniższe dla hodowli 10- i 24-godzinnej. Po wprowadzeniu do podłoża hodowli *P. fluorescens* zaobserwowano spadek indeksu tempa wzrostu, uzyskując redukcję od około 78 do 89%. Przeprowadzone badania potwierdzają fungistatyczne działanie szczepów *P. fluorescens* wobec szczepów *R. solani*. Przeprowadzone analizy wykazują, że inhibicja wzrostu grzybni uzależniona jest nie tylko od rodzaju metabolitów wydzielanych przez dany szczep bakterii, ale również od wieku jej hodowli.

Słowa kluczowe: aktywność fungistatyczna, indeks tempa wzrostu, *Pseudomonas fluorescens*, *Rhizoctonia solani*

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THERMAL DECOMPOSITION OF SELECTED CHLORINATED ALIPHATIC HYDROCARBONS IN THE FLUIDIZED BED REACTOR WITH CHEMICALLY ACTIVE BED MATERIAL

TERMICZNY ROZKŁAD WYBRANYCH CHLOROWCOPOCHODNYCH WĘGLOWODORÓW ALIFATYCZNYCH W REAKTORZE FLUIDYZACYJNYM Z CHEMICZNIE AKTYWNYM MATERIAŁEM ZŁOŻA

Abstract: Combustion of fuels, including renewable fuels, is associated with emissions of various gaseous compounds containing chlorine. The reversible sorption / desorption of hydrogen chloride, in a fluidized bed reactor, while combustion of Cl-containing substances, was carried out. Dichloromethane (DCM) was used as the source of chlorine. DCM thermal decomposition in a sand bed and then in a fluidized bed containing hydroxyapatite was investigated. In both series: process temperature was 930ºC, the air excess 1.3, the concentration of DCM 2900 ppm. The concentration of components containing chlorine such as HCl, CH_2Cl_2, CH_3Cl, $CHCl_3$, CCl_4, $COCl_2$ in the flue gases were monitored by FTIR analyzer. The main chlorine product was HCl. Samples of the hydroxyapatite before the process of thermal decomposition of DCM, taken from the bed during the process, and after the thermal decomposition of chlorapatite at 1050°C were analyzed by X-ray diffraction (XRD). The content of chlorapatite in the analyzed samples was respectively 10, 53 and 18%. X-ray fluorescence (XRF) analysis showed the molar ratio of Ca:P:Cl was: 1.12:0.41:0.01, 1.01:0.36:0.09, 1.10:0.40:0.05 respectively. The hydroxyapatite can be used as an absorbent of the $HCl_{(g)}$ during combustion of materials containing chlorine.

Keywords: chlorine, chemically active fluidized bed, hydroxyapatite

The chlorine content in coals varies and is dependent on where coal seams were formed and its degree of coalification. Mass fraction of chlorine in lignite is < 0.005-0.029%, and in bituminous coal 0.02-0.159%. In biomass used as additive to conventional fuels content of chlorine is also various, woody material contains less (less than 0.05% chlorine), a material derived from annual plants more (> 1%) of this element [1]. The most chlorine is included in the wastes and its proportion in total weight of the wastes is difficult to define. Textiles contain only 0.02% of the chlorine while PVC pipe scraps 46% of this element [2]. All of these substances are the source of chemical energy and can be converted into energy in power plants. Chlorine is mainly released as HCl, but the chloride emission standards are limited only for incinerators of waste [3]. The presence of chlorine in the combustion zone may be the source of not only HCl but also polychlorinated dibenzo-para-dioxins and dibenzofurans [4, 5], as well as leads to intensification of high-temperature chlorine corrosion of the superheater tubes [6, 7]. The source of molecular chlorine required to initiate corrosion may be chlorides present in the exhaust gas, or settling on the boiler’s walls in the form of sodium and potassium chloride [8]. Chlorine compounds are undesirable substances not only in power plants, but also as

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a product of combustion in the environment [9]. It seems appropriate to search for methods to reduce the formation of the chlorine compounds in the combustion chamber and transform them into possible least environmentally harmful substances.

The processes of thermal decomposition of DCM and chlorobenzene in a reactor with a fluidized bed of sand have been described at work by Olek et al [10]. It has been shown that in the bubbling fluidized bed degradation of total chlorine takes place in the bubbles flowing through the bed, in which the temperature of combusted gaseous mixture (LPG or propane with air) exceeds 1200°C, while the mean fluidized bed temperature is about 850°C. It was also found that the Cl introduced into the reactor in the form of DCM or chlorobenzene, leaving it in the form of HCl.

HCl emissions can be reduced by sorption to the gaseous products on calcium carbonate, hydroxide or calcium acetate. The product of this reaction is calcium chloride, however, efficiency of the method decreases with increasing temperature [11]. Zhang et al found that for the most effective calcium acetate process efficiency drops greatly from 99% to 13.52% with the increase of temperature from 200 to 1000°C [12]. Fujita et al investigate the possibility of high temperature HCl removal by using hydrogrossular $Ca_3Al_2(SiO_4)(OH)_8$ [13]. Hydrogrossular is effective for HCl sorption in temperature from 400 to 1000ºC. Tanahashi et al used dry-sorbent based on coal fly ash with slaked lime to remove HCl during pyrolysis of PVC [14]. They achieved 99.8% efficiency of HCl sorption in pilot scale reactor under pyrolysis conditions.

In this work an attempt is undertaken to determine the possibility of carry out a reversible sorption/desorption of hydrogen chloride in a stationary fluidized bed, during the thermal decomposition of substances containing chlorine. The possibility of use of hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) as a sorbent for HCl removal has been proven. Methods of the preparation of synthetic hydroxyapatite and possibility of replacement the hydroxyl group by chlorine are known. Kannan et al reported the results of studies on the preparation chloroapatites through aqueous precipitation method [15]. Thermal stability of chloroapatite is up to 1200°C.

HAp is decomposed in two stages. In the temperature range 900-1360ºC undergoes dehydroxylation, that is, removal of the hydroxyl groups without loss of crystal structure of mineral [16]. At temperature above 1430ºC mineral loses thermal stability and decomposes into calcium phosphates. The conditions for dehydroxylation of HAp have been created in the stationary fluidized bed of sand. The average temperature of the bed of quartz sand should not exceed 1100°C, but inside the bubble temperature reaches value about 400ºC higher than the average temperature of the bed material [17]. Under conditions formed in the fluidized bed, in the atmosphere enriched in chlorine, the OH groups in hydroxyapatite may be substituted by chloride atoms to form chloroapatite.

The aim of present work is to determine the chemical composition of gases produced from the decomposition of chlorinated hydrocarbons in a fluidized bed made of sand and supplemented by chemically active substance (hydroxyapatite). The effect of adding chlorine and hydroxyapatite on the combustion process is monitored by measurement of the concentration of CO_2, CO and NO_x in the flue gases. Special attention is paid to the chlorine compounds such as HCl, CH_2Cl_2, CH_3Cl, $CHCl_3$, CCl_4, $COCl_2$.

In order to verify the transformation of HAp into the chloroapatite: for the starting material, received from the bed during the process and after the process, the elemental composition and phase composition were specified. In order to detect the physical changes undergone in the material during the thermal treatment SEM scans and porosimetric analysis were carried out.

Experimental

Materials and apparatus

The bed material was quartz sand (200 g, particle size 0.3 to 0.385 mm). Initially sand was fluidizing by air, then by a LPG and air mixed in plenum chamber. Dichloromethane (DCM) - technical grade - was chosen as sources of chlorine. Sorbent material was hydroxyapatite in the form of feedstock bone (100 g, particle size 0.6 to 0.75 mm). The bone material was obtained in the process of mineralization of solid waste from meat and bone meal in a fluidized bed reactor at a temperature of 1000°C [18].

The observations were made using a laboratory with a stationary fluidized bed of a solid material. The 5-20 kW fluidized bed reactor with the set of analyzers has been described in detail before [10]. From the set of analyzers two of them were used. Concentration of O_2, CO, CO_2 and NO_x was controlled by Horiba PG250 analyzer. Concentration of O_2 was measured by electrochemical sensor (EC), CO and CO_2 by the non-dispersive infrared detectors (NDIR), NO_x by chemiluminescence detector (CLA). Standard library of IR spectra of FTIR analyzer (Gasmet DX-4000) was extend to include selected gaseous components. The concentration of the substances characterizing the combustion process, CH_4, C_2H_6, C_3H_8, C_2H_4, C_6H_6, C_2H_2, C_6H_5OH, CH_3OH, C_2H_5OH, CHOH, C_3H_4O and chlorine compounds HCl, CH_2Cl_2, CH_3Cl, $CHCl_3$, CCl_4, $COCl_2$ were controlled. Concentration measurements were accurate to no less than 2 ppm_v.

The chemical composition of solid products was analyzed by X-ray fluorescence (XRF). The phase composition was studied by X-ray diffraction. The porosimetric analysis was determined by the BET method, based on isotherms of nitrogen sorption obtained by the Micromeritics analyzer, model ASAP2020. Microscopic examination of surface structure was done by using SEM TM3000 Tabletop Microscope.

Research methodology

The experiment was initiated by fluidizing sand bed by air at temperature of 20ºC, then to the air LPG was added and ignition was initiated. The tests were carried out at an air excess ratio of $\lambda = 1.3$. The bed was gradually heated to 930°C at rate ~1.5 K/s. After the bed temperature reached 930ºC dosage of 2900 ppm_v of DCM to the fuel-air mixture was started. After stabilization the flow of DCM, 100 g of bone material was added to the reactor (Fig. 1), which caused rapid decrease of HCl at the outlet of reactor. Process was carried out until HCl achieved level before hydroxyapatite was added to the bed. Then DCM was turned off.

The possibility of desorption of chlorine from chloroapatite was investigated by the raise of the bed temperature to about 1050ºC, for a period of time. The samples of the sorbent before dosing into the reactor (P1), at the end of the sorption process (P2), and after the process of thermal decomposition of chloroapatitie at 1050°C (P3) were analyzed.

Results and discussion

As expected, in presence of Cl radicals the combustion process of hydrocarbons fuel has been partially inhibited. However, this was not apparent in changes in the bed temperature (Fig. 1a). An increase of the concentration of CO from 17 to 120 ppm_v is the characteristic phenomena of inhibitory effect of Cl radicals. Concentration of NO_x did not change and was not more than 15 ppm (Fig. 1b). Detailed explanation of the phenomena associated with the introduction of both DCM and chlorobenzene to the mix air + LPG combusted in the fluidized sand has been presented by the authors in an earlier work [10]. After injection of the hydroxyapatite to the reactor temporary decrease of mean bed temperature was observed (due to ambient temperature of added material) followed by decrease in the concentration of CO_2 and increased concentrations of CO and NO_x. Along with the addition of hydroxyapatite new equilibrium was settled down in the reactor, the CO concentration was stabilized at a higher level of 350 ppm_v. Over time, the concentration of NO_x was lowered to 15 ppm_v, and after turning off the dosage of DCM decreased to 13 ppm_v.

Hydroxyapatite particles compared to the sand have greater specific surface area. The introduction into the combustion chamber the substances with strongly developed surface area promotes recombination reactions of radicals OH and HO_2 occurring mainly on the surface of a solid. The effect was to inhibit the oxidation of CO to CO_2, wherein the radicals OH and HO_2 play a crucial role.

Throughout the whole combustion process DCM was detected in the flue gases (Fig. 1c), the mean concentration was 32 ppm_v, the background level was 17 ppm_v. A 99.5% level of thermal decomposition of DCM was obtained, which is consistent with previous studies [10]. During the combustion of LPG with DCM the main gaseous product containing chlorine was hydrogen chloride. Concentration of HCl was 5700 ppm_v. After introduction of HAp rapid and significant decrease in the concentration of HCl (Fig. 1c) to 950 ppm was observed and not more than 20 ppm_v increase in the concentration of chloromethane (Fig. 1c, gray line). The achieved degree of reduction of HCl concentration in the flue gases was 33%. The presence of chloromethane in the flue gases after the introduction of hydroxyapatite is related with a temporary increase in concentration of CH_4 from 0 to 160 ppm_v. As a consequence methyl radical may recombine with chlorine to form methyl chloride:

$$CH_3 + Cl + M \rightarrow CH_3Cl + M \qquad (1)$$

After saturation of whole hydroxyapatite introduced in to reactor by chlorine, the mean concentration of HCl has returned to the level of 5700 ppm_v. Due to the delays in the analytical sensors, measured concentration of HCl did not reach the background concentration immediately after switching off the supply of DCM. The increase of the bed temperature from 930 to 1050°C caused an increase in concentration of HCl from 240 to 330 ppm_v. The concentration of phosgene, $CHCl_3$ and CCl_2 did not exceed 2 ppm_v, these compounds were omitted in the graphs.

Figure 2-4 show the microscopic (SEM) images of bone material taken from the reactor at different stages of the process of thermal decomposition of DCM.

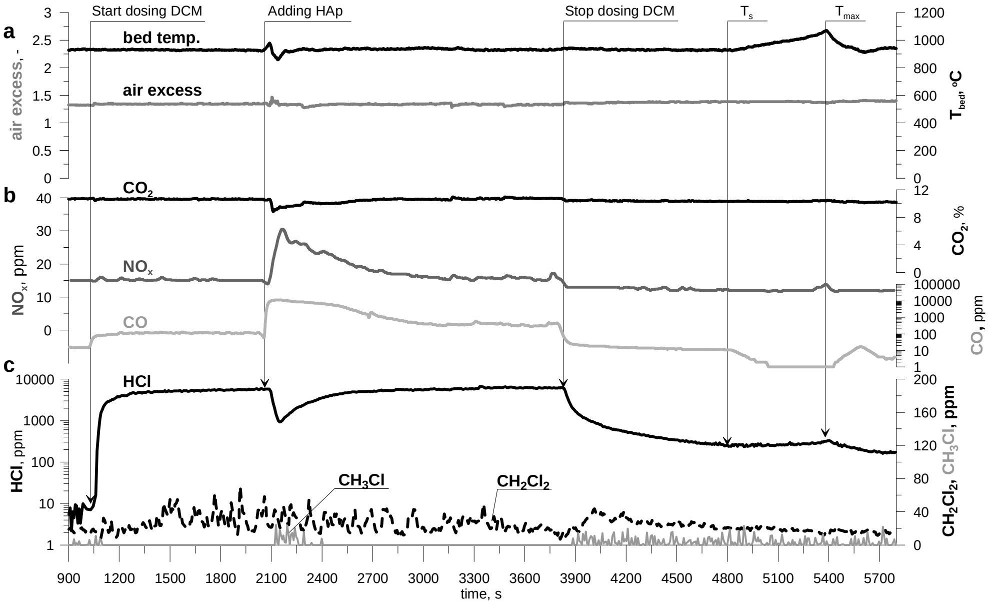

Fig. 1. Selected parameters of the process of thermal decomposition of DCM in bed material enriched by hydroxyapatite, the concentration of NO_x, CO and CO_2, and the concentration of chlorine products of decomposition process mixture of DCM + LPG

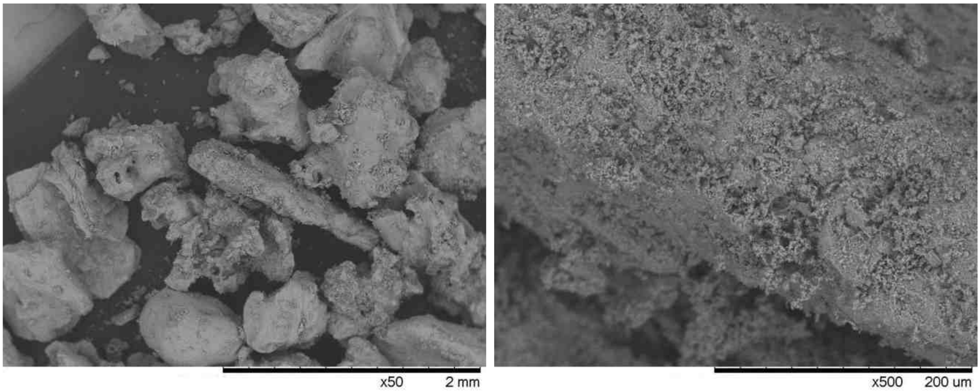

Fig. 2. Microscopic images of HAp from the sample P1

Low magnification (x50) makes it possible to show the shape of the grains. The oval-shaped granules form the dominant fraction. Along with the lengthen the residence time of HAp in the fluidized bed gradual changes can be seen as influence of hydrodynamic effects of the bed. The erosion of the material was seen as smoothing and rounding of the edges of the particles were observed. In the sample P1 predominate in narrow range of particles size from 0.6 to 0.75 mm, while for the samples P2 and P3 wider range of particle size was observed. The surface of grains in the P1 sample was covered with small particles.

In the sample P2 small particles were uncommon, it could be seen a smooth homogeneous surface. In case of the sample P3 which has the longest residence time in the reactor undergone a process of chlorine desorption (above 1000°C) consequently there a tendency to detachment the flat blades of the material from the mineral surface was observed.

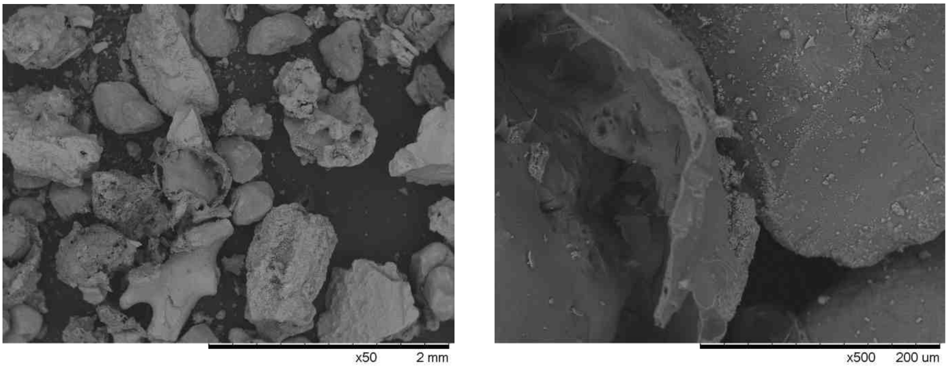

Fig. 3. Microscopic images of the HAp from sample P2

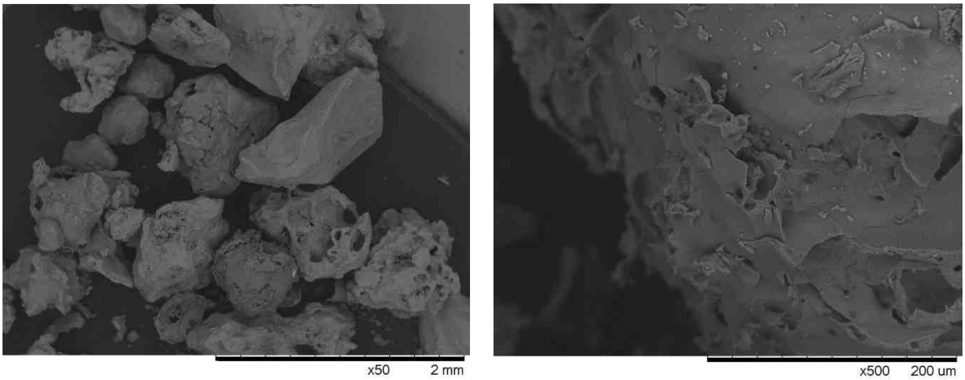

Fig. 4. Microscopic images of the HAp from sample P3

As a result of progress of sorption and desorption processes, surface area and pores size of the sorbent were decreased. As demonstrated in the work [19] after the process of calcination at 600°C BET surface area is 21.75 m^2/g, but if calcination temperature was increased to 950°C the surface area is reduced to less than 7 m^2/g. Material P1 was earlier calcined in a rotary kiln, then mineralized at 900°C in a fluidized bed incinerator, so the value of 3 m^2/g of BET surface area it was not surprising. The porous material can be obtained at a temperature not higher than 900°C, above it the sintering process is observed [20], which is confirmed by the analysis of samples of P2 and P3. The process of desorption at a temperature above 1000°C resulted in sintering of the bone material and decrease in the size of surface area as well as the pore diameter of the sample P3 in comparison to sample P1.

Table 1

Porosimetry analysis of samples of materials before introduction into the reactor (P1), received from the bed during the adsorption process (P2), sifted from the bed after decomposition process of chloroapatite (P3)

	The specific surface	**The average pore volume**	**Average pore diameter**
	[m^2/g]	**[cm^3/g]**	**[Å]**
P1	3	0.024	547
P2	2.5	0.025	508
P3	1.3	0.003	132

In Table 2 the mass fractions of elements in samples P1, P2 and P3 was shown. Base chlorine content in the analyzed material was 0.45%, which is three times higher than the literature data indicate 0.13-0.15% [21]. The share of chlorine in the sample P2 in relation to P1 increased more than 7 times, which indicates the inclusion of chlorine in the structure of HAp. In the sample P3 amount of the chlorine was still higher than in the material P1, only a part of the chlorine has been desorbed. Increased level of calcium in sample P2, in comparison of other samples, can be noticed. This is due to slightly contamination of the analyzed sample by bed material (SiO_2) in the sample P2. For this reason, the actual content of chlorine in the sample P2 may be slightly higher than the measured 3.26%.

Table 2

Elemental composition of samples P1 (before introduction into bed), P2 (material extracted during the process), P3 (sifted from the field after the completion of the decomposition of chloroapatite)

Element	**Ca**	**O**	**P**	**Si**	**Na**	**Fe**	**Mg**	**Cl**	**K**
	Conc. [%]								
P1	44.8	37.5	12.6	1.39	1.05	0.77	0.50	**0.45**	0.43
P2	40.3	37.8	11.2	5.01	0.48	0.91	0.37	**3.26**	0.12
P3	43.9	37.5	12.4	2.37	0.42	1.07	0.36	**1.65**	0.06

Table 3

Phase composition of the sample before introduction into the reactor (P1) received from the bed during the adsorption process (P2), sifted from the bed after completion of the decomposition process of chloroapatite (P3)

	Hydroxyapatite	**Orthophosphate(V) calcium**	**Chloroapatite**	**Calcium oxide**
	Weight fraction [%]			
P1	**74.5**	13.6	10.6	1.3
P2	31.4	16.0	**52.6**	0
P3	**62.1**	19.4	18.5	0

The X-ray analysis showed that the main crystalline phase in samples P1 and P3 was HAp (Table 3). In the sample P2 decreased share of HAp was determined, the dominant component was chloroapatite. The content of this mineral was 52.6% compared to 10.6% in the sample P1 and 18.5% in the sample P3. This shows that carrying out the sorption of HCl in bed material in the presence of HAp is possible. Due to the HAp being at a temperature ~1000°C (emulsion), and as shown in previous works [17] temporarily at higher temperatures (bubbles) increased content of orthophosphate(V) calcium was observed. Calcium phosphates were produced by partial disintegration of HAp.

XRD and XRF analysis of samples P2 and P3 showed that the controlled desorption of chlorine from the chloroapatite was approximately 50%.

Conclusions

The study confirmed the possibility of carrying out the process of thermal decomposition of dichloromethane in fluidized bed reactor. Degree of DCM decomposition was 99%. The main chlorine component of the process was gaseous HCl. Thermal degradation of DCM produces the Cl radicals which leads to the radical processes with the participation of OH radicals. As a result an increase of CO was observed. Also some increase in the concentration of CO occurred after introduction of hydroxyapatite into the bed. However, under conditions of an excess of oxidant, while residence time will be appropriate, *eg* 2 s, CO should be burnt out in the freeboard.

The results showed that HCl released during thermal decomposition of DCM is absorbed by hydroxyapatite at the bed temperature of 930ºC. This flue gases dechlorination process occurring in the fluidized bed is analogues to dry desulphurization process which also can be achieved in the fluidized bed using calcium carbonate.

This method could be used in installations of thermal treatment or incineration, where wet flue gas cleaning systems would not be reasonable due to high costs. Chlorine is bound in a product which is stable at ambient temperature. Obtained chloroapatite may be used in the industry. Sorption process can also be partially reversed at a temperature above 1000°C, although the process is accompanied by cracking of the mineral surface (Fig. 4) and material sintering. Theoretical calculations show that with HAp amounts of used in this research, the retained mass of chlorine may be higher - hydroxyapatite sorption capacity is not utilized in 100%.

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TERMICZNY ROZKŁAD WYBRANYCH CHLOROWCOPOCHODNYCH WĘGLOWODORÓW ALIFATYCZNYCH W REAKTORZE FLUIDYZACYJNYM Z CHEMICZNIE AKTYWNYM MATERIAŁEM ZŁOŻA

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Abstrakt: Spalanie paliw, w tym paliw ze źródeł odnawialnych, związane jest z emisją gazowych związków zawierających chlor. Wykonano badania sprawdzające możliwość odwracalnego procesu sorpcji/desorpcji chlorowodoru w stacjonarnym złożu fluidalnym podczas spalania substancji zawierających chlor. Jako źródło chloru zastosowano dichlorometan. Proces termicznego rozkładu DCM przeprowadzono w złożu piaskowym, a następnie w złożu piaskowym z dodatkiem biohydroksyapatytu. W obu seriach pomiarowych temperatura procesu wynosiła 930°C, współczynnik nadmiaru powietrza 1,3, a stężenie DCM 2900 ppm. Za pomocą analizatora FTIR monitorowano stężenia następujących związków chloru w gazach poprocesowych: HCl, CH_2Cl_2, CH_3Cl, $CHCl_3$, CCl_4, $COCl_2$. Dominującym związkiem chloru w gazach był HCl. Metodą XRD przeanalizowano biohydroksyapatyt przed procesem termicznej dekompozycji DCM, odebrany ze złoża w trakcie procesu, oraz po zakończeniu dozowania DCM i procesu termicznej dekompozycji chloroapatytu w 1050°C. Zawartość chloroapatytu w analizowanych próbkach wynosiła odpowiednio 10, 53 oraz 18%. Analiza XRF wykazała następujące stosunki molowe Ca:P:Cl w próbkach: 1,12:0,41:0,01, 1,01:0,36:0,09, 1,10:0,40:0,05. Przeprowadzone badania wykazały możliwość wykorzystania biohydroksyapatytu jako materiału sorpcyjnego w stosunku do gazowego chlorowodoru powstającego w gazach spalinowych podczas utylizacji materiałów organicznych zawierających chlor.

Słowa kluczowe: chlor, chemicznie aktywne złoże fluidalne, hydroksyapatyt

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Zbigniew SUCHORAB[1]

MONITORING OF CAPILLARY RISE PHENOMENON IN CALCIUM SILICATE BOARD USING THE SURFACE TDR PROBES SET

MONITORING PROCESU PODCIĄGANIA KAPILARNEGO W SILIKACIE WAPIENNYM ZA POMOCĄ POWIERZCHNIOWYCH SOND TDR

Abstract: Capillary rise phenomenon is a process threatening many building objects. It is mainly caused by the capillary structure of most building materials. The described phenomenon relies on water flow against gravity forces and hydrostatic pressure. The problem of capillary uptake is especially visible in case of lack of horizontal or vertical water isolation layers, their damage or natural wear during long time exploitation. The sufficient condition for capillary rise phenomenon appearance is constant contact of the building barriers to the moist ground. Described phenomenon is dangerous because the range of its influence can reach even 2.5 m or more above ground level, depending on building material. Capillary uptake is a dangerous process, because it runs to barriers destruction and decrease of its strength and heat parameters. Excessive water is the reason of biological strokes of the buildings, mainly caused by mould. The article presents the experimental research of capillary rise phenomenon in a sample of autoclaved calcium silicate. For the experiment it is applied the setup of TDR sensors prototypes which enable constant monitoring of the described phenomenon in non-invasive way.

Keywords: capillary rise, calcium silicate, surface probes TDR, monitoring

Introduction

This article is devoted to the capillary rise phenomenon and the possibility of its monitoring in autoclaved calcium silicate being an insulating material.

Capillary rise is one of the most threatening problems observed in many buildings [1, 2]. It causes the damage of external barriers, funds and runs to many exploitation problems like biological corrosion [3, 4], decrease of indoor air parameters and the decrease of thermal parameters of the materials [5-8].

A very interesting building material is autoclaved calcium silicate sold in Polish market as Renovario/Calsitherm and distributed by Ecovario Ltd Company [9]. It was elaborated in Germany by Häupl [10] at the end of the previous Century. Autoclaved calcium silicate is produced in form of plates with the dimensions of $1250 \cdot 1000$ mm and 25, 30 or 50 mm thickness [9]. The plates are made of calcium silicate being the mineral based material. Crystals of calcium silicate form the microporous shell, which provides the great capillarity of the ready material [11]. The most important parameters of Calsitherm plates, influencing their application are bulk density, porosity, compression strength and heat conductivity coefficient. All of them are set together in the Table 1, following the distributor webpage [9].

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Table 1

Technical data of autoclaved calcium silicate plates [9]

Parameter	Unit	Value
Bulk density	[kg/m^3]	200-240
Porosity	[%]	over 90
Compression strength	[MPa]	1
Heat conductivity coefficient (dry plate)	[W/(m · K)]	0.060
Heat conductivity coefficient (wet plate)	[W/(m · K)]	0.059

From the technical data presented in the table above it is visible that Calsitherm plates can be considered as insulation material with average insulating parameters (significantly lower, comparing to the other common materials like mineral wool or polystyrene). On the other hand their great porosity, exceeding 90% and microporous structure (Fig. 1) causes that they can be applied for internal insulation of the walls which should not be insulated from the outside. This is especially applicable for the old historical objects.

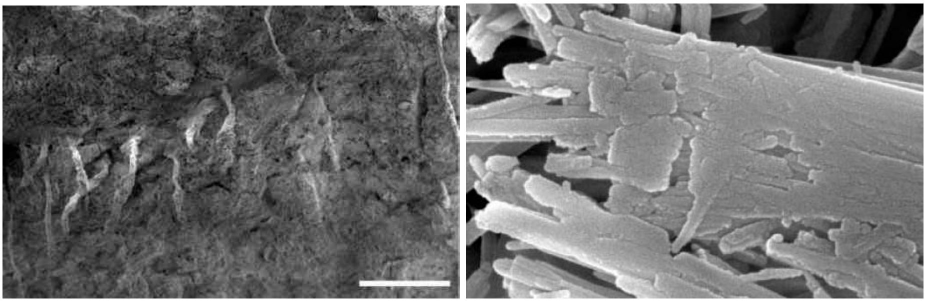

Fig. 1. SEM photography of autoclaved calcium silicate structure [12]

Indoor insulation layer, comparing to the traditional external insulation techniques does not provide suitable temperature distribution inside the building envelopes. In most cases this runs to water vapor condensation inside of them. It must be underlined here, that great porosity and water absorptivity of calcium silicate forces the wall to transfer condensed water into the insulation material which can be safely removed to the indoor air during dry periods of the year [2].

Materials and methods

As it was underlined in the above chapter, autoclaved calcium silicate is characterized by strong capillary forces and great water absorptivity. This paper presents research of water absorptivity of autoclaved calcium silicate.

For the experiment, the autoclaved calcium silicate (Calsitherm plate) sample was put to the container with constant water level and exposed to water uptake process (Fig. 2). Dimensions of the sample (Fig. 3) were the following: 580 mm (height) × 280 mm (width) × 50 mm (thickness). Bottom 20 mm of the sample was submerged into water, and moisture sensors were placed at the following heights over water level: 100 mm (probe 00), 200 mm (probe 16), 300 mm (probe 32), 400 mm (probe 48), 500 mm (probe 64).

For the experiment it was applied the TDR (Time Domain Reflectometry) methodology, previously applied by the author of this paper for moisture determination in soils [13] and building materials and envelopes [14-17]. The application of the TDR methodology was strongly limited to soils and light building materials due to its invasive character and the necessity to install the measuring elements into the structure of measured barrier. This ran to measured material destruction and readouts falsification because of the steel elements internal installation.

To obtain the possibility of noninvasive, constant monitoring of the described phenomenon it was used an unique system of modified TDR probes (Figs. 2-4). The traditional TDR probes were reduced to measuring bars, which were separated with plastic dielectric material, that enabled to keep constant, parallel bars distribution and made it easier to attach the measuring elements to the sample. Measuring elements were made of brass angle-bars with the following dimensions: 200 mm (length), 10 mm (sides of the bars). Space between the bars was 40 mm and the total width of the probe was 60 mm. The terminations of the angle bars were connected to the concentric cable which distributed the electromagnetic signal from the described sensors to the TDR multimeter presented at Figure 2. Such prepared probes attached to the material sample and the whole measuring setup are presented at Figures 2 and 3.

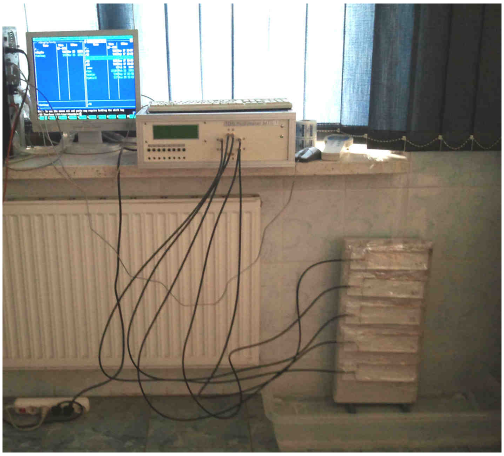

Fig. 2. Measuring setup during experiment

To avoid any influence of the external conditions on the sample and uptake process, the sample, together with the probes was covered with insulating foil. Sensors were connected to the typical TDR multimeter (EasyTest/Lublin/Poland) which was controlled by PC computer. Measurement sequence was repeated every 15 minutes and the readouts were made at each attitude (every probe). Modified system of the TDR probes required to elaborate special software which enabled to control the device and interpret the obtained results. The redouts from the multimeter were obtained as the TDR reflectograms, that, after suitable postprocessing (location of signal peaks and calculation of time intervals) and empirical calibration (Fig. 2) enabled to monitor moisture changes at each level of the examined sample.

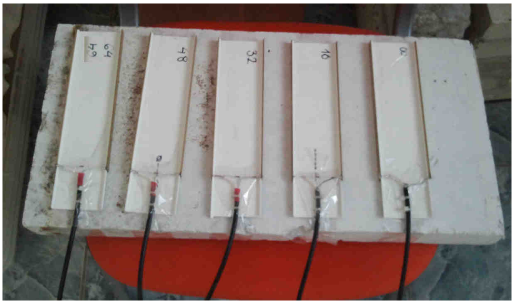

Fig. 3. Probes attached to the examined material

Results

Before the experiment started all probes were calibrated for moisture. Probe during calibration procedure is presented at Figure 4.

Fig. 4. Surface probe calibration for autoclaved calcium silicate

Calibration experiment of surface TDR probes is presented in the following paper [18]. After calibration procedure was conducted, the equation (1) was elaborated, which was then applied to recalculate moisture from the TDR readouts:

$$\Theta = -0.0023 \cdot t^2 + 1.4227 \cdot t - 127.74 \qquad (1)$$

where: t - signal travel time along the angle bar of the sensor [ps], Θ - volumetric water content [% vol.].

The diagram presented at Figure 5 represents the progress of the water uptake phenomenon in Calsitherm sample. It is clearly visible that water quickly appears at Probe 00 placed 100 mm above water level. Rate of the moisture increase is very high and after 2 hours a state near maximum water content is reached. Moisture increase read by the above probes is postponed for average period of 5 hours but still is very rapid and quickly after water appears, maximum moisture is reached. Moisture increases appear after 4 hours at Probe 16, after 9 hours at Probe 32, after 13 hours at Probe 48 and finally after 20 hours at Probe 64.

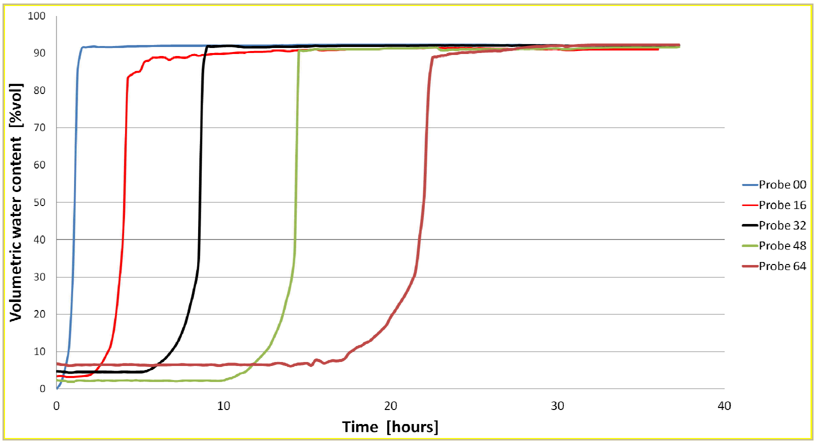

Fig. 5. Water uptake process determined in calcium silicate

Presented research confirms high water absorptivity of autoclaved calcium silicate (Calsitherm plates) declared by the producers and distributors. Modified TDR sensors confirmed that maximum water content for the described material exceeds 90% and maximum moisture states are achieved quickly after water appears. This confirms high capillary forces and unique capillary structure of the discussed material.

Conclusions

Basing on the conducted experiment the following conclusions may be drawn:

- described experiment proved high potential of the TDR method for monitoring of moisture changes phenomena in building materials,
- setup applied for the described experiment is unique and its application required modification of applied probes construction and special software,
- conducted research confirmed high water absorptivity of autoclaved calcium silicate,
- uniform porous structure causes a predictive water uptake process which runs rapidly and quickly after water appears, maximum water content is reached.

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MONITORING PROCESU PODCIĄGANIA KAPILARNEGO W SILIKACIE WAPIENNYM ZA POMOCĄ POWIERZCHNIOWYCH SOND TDR

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Abstrakt: Podciąganie kapilarne jest procesem dotykającym wiele obiektów budowlanych. Przyczyną jego występowania jest kapilarna struktura większości materiałów budowlanych. Zjawisko to polega na przepływie wody w kierunku niezgodnym z siłami grawitacji, wbrew ciśnieniu hydrostatycznemu. Omawiany problem podciągania kapilarnego jest szczególnie widoczny w przypadku braku poziomych i pionowych izolacji przeciwwilgociowych, ich uszkodzenia lub przy naturalnym ich zużyciu w czasie wieloletniej eksploatacji. Warunkiem wystarczającym do rozpoczęcia procesu podciągania kapilarnego wody do wyższych partii ścian jest styczność przegród budowlanych z gruntem o naturalnej wilgotności. Zjawisko to jest niezwykle niebezpieczne, ponieważ zasięg jego oddziaływania może osiągać nawet wysokość do 2,5 m od poziomu gruntu lub więcej w zależności od materiału budowlanego. Podciąganie kapilarne jest procesem szkodliwym, ponieważ prowadzi do degradacji przegrody, obniża jej właściwości konstrukcyjne oraz cieplne. Nadmierna ilość wody w przegrodzie jest przyczyną porażeń biologicznych budynków, z których najczęściej spotykanym problemem jest zagrzybienie. W artykule przedstawiono badania eksperymentalne procesu podciągania kapilarnego w próbce z autoklawizowanego silikatu wapiennego. Do badań zastosowano zestaw prototypowych czujników TDR, dzięki którym możliwy jest ciągły monitoring zjawiska w sposób bezinwazyjny.

Słowa kluczowe: podciąganie kapilarne, autoklawizowany silikat wapienny, powierzchniowe sondy TDR, monitoring

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DO THE DEGRADABLE/BIODEGRADABLE PLASTIC MATERIALS DECOMPOSE IN DOMESTIC COMPOST BIN?

CZY DEGRADOWALNE/BIODEGRADOWALNE TWORZYWA SZTUCZNE ROZKŁADAJĄ SIĘ W DOMOWYM KOMPOSTOWNIKU?

Abstract: Biodegradation of plastic materials advertised as degradable/biodegradable or certified as compostable was tested in composting conditions (domestic compost bin). This study was carried out in order to assess the biodegradability of the samples under real conditions of home composting, and to find out whether there were any physical changes in terms of their thickness when exposed to natural composting environment. The samples were obtained from retail chains in the Czech Republic, Poland, Slovakia and the UK. The experimental samples were placed in home compost bins and were checked and visually assessed during the experiment, which lasted 14 weeks. From the results it can be concluded that the polyethylene samples with the additive (samples A, B and E) have not decomposed, their colour has not changed and that no degradation neither physical changes has occurred. Samples C, F have not decomposed. Samples certified as compostable G, H and I have not decomposed. Sample D exhibited the highest decomposition rate. The main conclusion from this study is that degradable/biodegradable plastics or plastics certified as compostable are not suitable for home composting.

Keywords: biodegradable waste, biodegradability, compostability, degradation, home composting, plastic

Introduction

The management of the organic fraction of municipal solid wastes (OFMSW) is a growing problem due to the rapid collapse of landfills, the “not in my backyard” practice and the potential contamination and loss of organic resources derived from landfilling [1]. Furthermore, in 1999, the European Union Landfill Directive [2] required the Member States to reduce the amount of biodegradable waste being dumped, promoting the adoption of measures to increase and improve sorting activities at the origin, such as recovery and recycling. Composting is one of the most frequently used alternatives to landfill [3, 4]. Compost can be applied as a fertilizer, organic amendment or growing medium, improving soil physical properties and increasing both water retention and the supply of essential nutrients [1, 5-8].

Composting of OFMSW has been considerably developed and studied at industrial level and it is widely reported in literature [4, 9-14]. However, at a smaller scale, composting can be developed at home, a process that has been scarcely studied from a technical and scientific point of view [11, 15, 16]. Home composting, or backyard composting [3], presents some potential benefits in comparison to industrial composting. Home composting avoids the collection of an important part of municipal solid wastes, thus reducing the economic, material and energetic investments in infrastructures [15, 17, 18]. It implies less land use and, finally, it allows a more specific control of the composting process and the organic materials treated [1].

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Although these benefits are evident, home composting can present some concerns. In recent years, biowaste has been collected in single-use plastic bags. Manufacturers claim that these bags can be composted (inserted into compost pile). However, not all of these materials are truly biodegradable and therefore may pose problems within home composting. The aim of this paper is to provide information about biodegradability of polymeric (biodegradable/degradable) materials advertised as 100%-degradable or certified as compostable, which may be a part of biodegradable waste, in home composting conditions.

Experimental procedures

The aim of the experiment was to expose samples labelled as degradable or biodegradable to the process of composting at home compost bins and to prove whether the information stated on the wrappers is true and testifies the features of the particular materials. The evaluation of the disintegration of the samples was carried out according to ČSN EN 14806 a ČSN EN ISO 20 200. In the course of the experiment photographic documentation was realized and the experiment diary into which data were regularly recorded was created.

Description of the samples

As research samples were selected carrier bags, which are commonly available in retail chains in the Czech Republic, Poland, the Slovak Republic and the UK, while they state that they are biodegradable, degradable or other designation. In addition, 2 bags certified for composting were chosen. One of them was a carrier bag from a Czech manufacturer and the other sample came from the UK. In total, the experiment contained 9 samples of carrier bags. Types and descriptions of the samples are listed in Table 1. The examined samples were labelled with letters A - I. At the beginning of the experiment, all 9 samples were photographically documented.

Table 1

Types and descriptions of the samples

Sample	Type	Descriptions
A	PE HD + TDPA ADDITIVE	100% degradable
B	PE-HD + ADDITIVE	100% degradable, after certain period of time degrades itself
C	PE-HD	Degrades into CO_2 and H_2O within 3 years
D	N/A	-
E	PE-HD	100% degradable
F	N/A	Biodegradable
G	Starch	Compostable
H	Starch	Compostable
I	Bioflex-219F	In compost biodegrades within 90 days

Preparation of the samples

Samples were weighed on a scale model AND HF 200V in laboratory at the Department of Applied and Landscape Ecology, Mendel University in Brno. Weights of all

9 samples were recorded in the experiment diary. Measured values are stated in Table 2. Subsequently, the samples were inserted into a mesh pocket with meshes of dimension 1 x 1 mm. These mesh pockets were then secured with metal frames at all sides. The samples in mesh cases were weighed. The obtained values were recorded in the experiment diary. Samples were provided with descriptions in order to secure their identification during and after the termination of the experiment.

Table 2

Weights of the samples

Sample	**m_i [g]**
A	5.1
B	7.6
C	5.1
D	8.1
E	7.5
F	8.6
G	9.6
H	14.8
I	12.0

m_i - initial weight of the samples

For the purpose of the experiment two plastic garden compost bins (bins A and B) were used, with capacity: 270l, height: 70 cm, base: 63 x 63 cm. The composition of the compost pile was chosen to resemble the most favourable materials that normally people use for composting. The compost pile consisted of horse manure, soil and grass, mixed with sawdust at a ratio of 1:3.

The initiation of the experiment

Compost bins were placed next to a wall of a house, on southeast side, in order to be protected from weather conditions and to prevent excessive drying out of the compost pile. Each compost bin was layered with the same amount of material. The bottom layer of the compost pile in the bin consisted of 20 dm^3 of horse manure mixed with garden soil. Horse manure, a mixture of manure and bedding, in this case consisted of horse manure together with a combination of sawdust and shavings. On the top of it were subsequently placed layers consisting of a mixture of grass and sawdust. The samples were put among single layers. After filling the compost bins, each was sealed by 20 dm^3 of rainwater.

The experiment took place from 07.2012 until 10.2012. Temperatures in compost bins were measured and recorded at regular intervals. The first 4 weeks the temperature was measured daily, afterwards every second day. When the temperature dropped to 20°C, temperatures were measured once a week. The compost pile was periodically dug over and dampened when necessary in order to achieve and maintain optimal humidity. During the experiment three visual inspections of the samples took place. Samples were taken out of the compost, their condition was visually checked and photographs were taken. Table 3 shows time schedule of the experiment.

The graph (see Fig. 1) shows the development of ambient air temperatures within monitored period of time.

Table 3

Time schedule of the experiment

Day of the experiment	**Date**	**Operation**
0	20.07.2012	Initiation of the experiment
29	18.08.2012	Sample checking
58	16.09.2012	Sample checking
66	23.09.2012	Sample checking
101	28.10.2012	Termination of the experiment

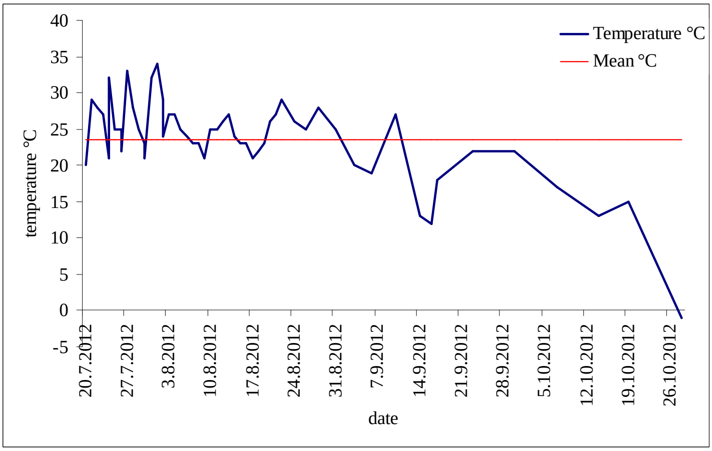

Fig. 1. The development of ambient air temperatures within monitored period of time

The following graph shows the development of temperatures in compost bins (see Fig. 2).

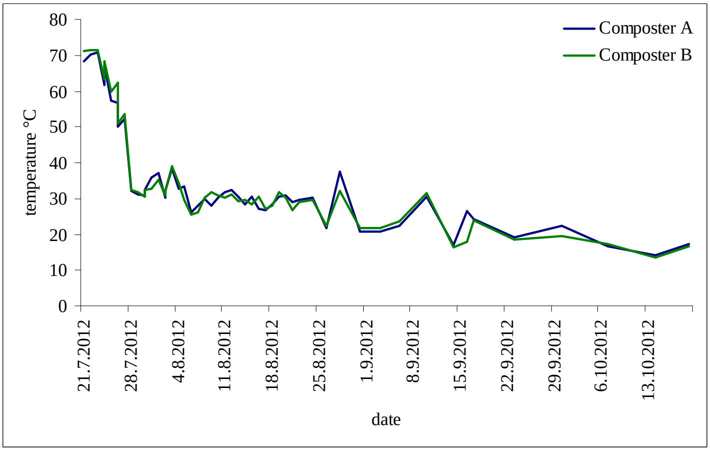

Fig. 2. The development of temperatures in both compost bins

In compost bins the thermofilic phase of the experiment lasted 7 days and the temperature reached and then surpassed 70°C, as shown in Figure 2. The highest temperature in the compost bin A was 71.3°C, in bin B it was 71.4°C. After 7 days, the temperatures in the bins dropped and the compost pile got to the stage of transformation. At the beginning of the phase of transformation the following temperatures were measured in compost bin A: 32.1°C and compost bin B: 32.3°C, in the next days temperatures in the range of 27-39°C were measured. This phase lasted 29 days. During this phase the appearance of the samples was checked and photographs taken. Samples A, E, F, G, H and I showed no visual change by visual observation. Samples B and C showed certain change in colour. The printing on the examined samples changed colour. Sample D showed signs of advanced disintegration, decay in small separate pieces, in some places the original material was entirely absent. In the phase of ripening, the temperature of material in the compost bins approximated to ambient air temperature. Temperatures ranged from 30.3 to 14.3°C in bin A and from 32.1 to 13.6°C in bin B. The compost pile was kept at this stage until the end of the experiment. In this phase, two visual inspections of the samples took place. The first one was conducted after 8 weeks of the experiment. Samples A, E, F, G, H showed no changes when controlled. Samples B and C showed more intense change in colour, but there was no sign of degradation or disintegration. Sample D showed signs of advanced disintegration and signs of occurring disintegration were also observed at sample I.

Within the second inspection, the samples were removed from mesh pockets and photographed. Small fragments occurred only in sample D (these were apparent already at the first inspection). Samples G, H and I also succumbed to disintegration, the sample split into large parts, cracks emerged. Samples A, E and F showed no change in colours or signs of disintegration, their condition at this stage was the same as their initial condition (prior to being placed into the compost pile). Samples B and C show changes in colour printing, some colours disappeared, others changed shades.

Termination of the experiment

The experiment was terminated after 14 weeks, after the expiration of the composting process. Samples were removed from the compost bins and transported to the laboratory of the Department of Applied and Landscape Ecology, Mendel University in Brno, where they were prepared for further research. At the stage of completion and evaluation of the experiment, the samples were treated in accordance with standards of ČSN EN 14806 and ČSN EN ISO 20 200.

The samples were weighed and cleaned in the laboratory. After thorough washing, the samples in mesh pockets were placed in the oven with air circulation and the temperature was set to 58°C. The samples were left for 24 hours at this temperature (set by the Standard ISO 20200). After drying the samples to constant weight, they were removed from mesh pockets. At sample D, all small parts were collected using tweezers. In order to avoid loss of material, this sample was placed into a container for the purpose of weighing and subsequent handling. The same procedure was repeated with samples G and H. The samples were weighed and the weights recorded in the experiment diary.

Results and discussion

Determination of the degree of degradation and samples evaluation

All data recorded in the experiment diary (see Table 4) were used for the calculation determining the degree of degradation of plastics (hereinafter referred to as D) according to the norm. In order to calculate D, mathematical formula (1) was used:

$$D = \frac{m_i - m_r}{m_i} 100 \tag{1}$$

where: D - degree of disintegration [%], m_i - initial weight of dry tested material [g], m_r - weight of tested material after washing and drying to constant weight [g].

Table 4

Weights and degree of degradation

Sample	m_i [g]	m_r [g]	m_x [g]	m_y [g]	D [%]
A	5.060	5.090	10.5	17.2	–5.9
B	7.638	7.805	13.5	23.3	–2.1
C	5.327	5.188	-	17.9	2.6
D	8.643	3.115	16.7	23.9	63.9
E	7.462	9.878	16.8	31.1	32.3
F	8.076	7.635	-	23.1	5.4
G	9.595	8.693	-	25.5	9.4
H	14.805	14.818	-	37.9	0.0
I	12.031	12.236	-	32.2	–1.7

m_i - initial weight of dry tested material [g], m_r - weight of tested material after washing and drying to constant weight [g], m_x - weight of tested material in netpockets after drying [g], m_y - weight of tested material after removal from compost pile [g], D - degree of disintegration [%]

According to calculations using formula 1, degradation occurred at 4 of the observed samples: Sample C: D = 2.6%. This sample during interim controls exhibited only colour alterations, remained in one piece, and showed no signs of significant damage. Sample D: D = 63.9%. Degree of decomposition was high. Sample F: D = 5.4%. Besides low degree of decomposition this sample showed no other modifications. Sample G: D = 9.4%. There were visual signs of decay, integrity and structure is impaired. Sample H: D = 0%. No degradation occurred. The sample showed changes in structure, the material lost strength and peripheral parts showed signs of decay. Sample I: The sample exhibited negative stage of decomposition, initial signs of degradation occurred. Samples A, B and E showed no signs of degradation neither during the composting process nor at its end, only sample B changed the colour of printing.

Conclusions

This study was carried out in order to assess the biodegradability of the above-described samples under real conditions of home composting, and to find out whether there were any physical changes in terms of their thickness when exposed to a natural composting environment. The experimental samples were placed in the home compost bin and were checked and visually assessed during the experiment that lasted 14 weeks (standards for the laboratory test required 12 weeks).

From the results obtained during the biodegradability test, it can be concluded that the PE samples with the additive (samples A, B and E) have not decomposed, their colour has not changed (except sample B) and that no degradation neither physical changes (thickness) has occurred. Therefore, the samples made of PE with additives cannot be claimed to be biodegradable. They should have exhibited at least some changes or signs of the occurring decomposition (similarly as common organic waste), which were however not observed. Similar results are described in study carried out by Davis et al [19], where it has been found that shredded PE sacks in an open windrow composting did not degrade, thus resulting in fragments of PE being highly visible within the windrow throughout the composting process. Samples C, F, G, H and I have not decomposed. Sample D exhibited the highest decomposition rate.

In contrast to the laboratory conditions, the real conditions (including home composting) are affected by a number of factors that cannot be influenced such as air temperature, pH of the environment, water content of the compost pile, precipitation etc. It is necessary to emphasize that the nature of the compost’s raw material plays an important role in polymers’ degradation since different compost systems (*ie*, manure, yard, and food waste) produce different microbiological activity [20]. All these factors can significantly affect the rate and degree of degradation.

The main conclusion from this study is that degradable/biodegradable plastics or plastics certified as compostable are not suitable for home composting and that in home composting bin they do not degrade. However, according to Kale [20], an overall conclusion cannot be exclusively derived, since all the variables in real composting, such as compost raw materials, enzymes, ambient atmosphere, etc., and their interaction with biodegradable plastics, should be considered and explored for better understanding and insight of the biodegradation process.

Acknowledgements

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CZY DEGRADOWALNE/BIODEGRADOWALNE TWORZYWA SZTUCZNE ROZKŁADAJĄ SIĘ W DOMOWYM KOMPOSTOWNIKU?

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Abstrakt: Biodegradacja materiałów sztucznych reklamowanych jako degradowalne/biodegradowalne oraz certyfikowanych jako kompostowalne była badana w przydomowych warunkach kompostowania (w kompostownikach). Badania zostały przeprowadzone w celu oceny rozkładu próbek w rzeczywistych warunkach kompostowania oraz w celu sprawdzenia, czy badane próbki wykazują jakiekolwiek zmiany fizyczne. Badane materiały pochodziły z sieci sklepów handlowych w Czechach, Polsce, Słowacji i Wielkiej Brytanii. Umieszczone w domowym kompostowniku próbki sprawdzano i oceniano wzrokowo podczas eksperymentu, który trwał 14 tygodni. Na podstawie wyników można stwierdzić, że próbki wykonane z polietylenu z dodatkami (próbki A, B i E) nie uległy rozkładowi, ich barwa nie zmieniła, jak też nie wystąpiła degradacja fizyczna, nie rozłożyły się także próbki C, F. Również próbki certyfikowane jako kompostowalne G, H i I nie uległy rozkładowi. Próbka D wykazywała najwyższy stopień rozkładu. Z przeprowadzonego doświadczenia wynika, że degradowalne/biodegradowalne oraz certyfikowane jako kompostowalne tworzywa sztuczne nie nadają się do przydomowego kompostowania.

Słowa kluczowe: odpady biodegradowalne**,** biodegradacja, kompostowalność, degradacja, przydomowe kompostowanie, tworzywa sztuczne

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MOLDING WATER CONTENT OF CLAY SOILS AND HYDRAULIC PROPERTIES OF MINERAL LINERS OF WASTE LANDFILLS

WILGOTNOŚĆ ZAGĘSZCZANIA MATERIAŁÓW ILASTYCH A WŁAŚCIWOŚCI HYDRAULICZNE PRZESŁON MINERALNYCH SKŁADOWISK ODPADÓW

Abstract: Municipal landfill cells as engineering constructions highly dangerous to the natural environment have to be isolated by liners in order to prevent the anthropogenic pollutants transport, together with *eg* landfill leachates. Mineral liners, properly prepared and compacted, sealing the bottom, sides and top of the landfills are one of the most popular manners of landfills isolation. The mineral liners are usually constructed of compacted clay soils to obtain, the required by Polish Decree of Minister of Environment of 3rd April 2013 and Council Directive 1999/31/EC of 26th April 1999 on the landfill of wastes, value of liner's saturated hydraulic conductivity lower than $1 \cdot 10^{-9}$ m·s^{-1}. The value of hydraulic conductivity of saturated soils is directly affected by the conditions of soil compaction, especially the molding water content. This paper presents an attempt of determination of the effects of molding water content of a selected clay soil on its saturated hydraulic conductivity and hydraulic properties of the sealing liner, constructed according to the actual standards, of the compacted clay material. Range of our studies covered the in situ and laboratory measurements as well as numerical modeling. Saturated hydraulic conductivity under natural conditions was measured by BAT probe, (GeoNordic) while the hydraulic conductivity of the compacted clay soils was tested by Humboldt Mfg. Co. permeameters for compacted soils, according to ASTM D5856. The assessment of hydraulic properties of a liner made of the clay material under study was performed by the method of numerical modeling of infiltration process with the assumed value of groundwater head with application of the FEFLOW, DHI-WASY modeling software. The lacking validation of our modeling attempt influences the fact that our studies should be treated as preliminary.

Keywords: clay materials, mineral lines, hydraulic conductivity, numerical modeling, waste landfill

Introduction

Landfilling of municipal wastes poses a considerable threat to the natural environment caused by migration of numerous pollutants by air, surface runoff, and leachates. The environmental impact of landfills depends on the efficiency of limiting the pollution of air, water and soil by the applied techniques of sealing [1]. Prevention of leachate seepage and migration is realized by barriers, known as liners, utilizing various technical solution based on natural and geosynthetic materials. One of the most popular and durable solution are mineral clay liners meeting the requirements of the local standards [2, 3]. These barriers are constructed of natural clays of permeability capable to secure the required value of hydraulic conductivity [4, 5]. In the European Union it should be lower than $1 \cdot 10^{-9}$ m·s^{-1}. The saturated hydraulic conductivity of clayey soils under natural conditions may be higher than the above value [6-8] so the application of compaction process may be required. The compaction increases the resistance of soil to water flow, thus, in the effect, the saturated hydraulic conductivity is reduced [9], however, the degree of reduction depends on the

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molding water content of the soil. So the molding water content becomes one of the most important factors influencing the hydraulic characteristics of compacted clay liner [10-14]. On the other hand, molding water content affects also the swelling and shrinking properties of clays, influencing the sustainability of the liner [15-17].

This paper presents an attempt of recognition of a selected clay soil molding water content effects on its saturated hydraulic conductivity and hydraulic properties of the sealing liner, constructed according to the actual standards, of the compacted clay material. Our studies were based on *in situ* and laboratory measurements, as well as on numerical modeling method.

Materials and methods

The presented studies were focused on mineral clay soil sampled in the open pit of a former brickyard in Łążek Garncarski, approx. 90 km south of Lublin, Poland. The particle size composition of the sampled soil and its basic characteristics such as bulk density, saturated hydraulic conductivity and water content under natural conditions are presented in Table 1.

Table 1

Characteristics of the clay soil sampled in Łążek Garncarski, Poland

Particle fraction name	**Sand [%]**	4.5
	Silt [%]	51
	Clay [%]	44.5
Solid particle density [Mg m^{-3}]		2.614
Bulk density [Mg m^{-3}]		1.693
Gravimetric water content [%]		21.18
Total porosity [m^3 m^{-3}]		0.352
Saturated hydraulic conductivity [m s^{-1}]		$1.37 \cdot 10^{-10}$

The particle size distribution of the soil was determined by the standard areometric method according to PN-B-04481:1988 [18], solid particle density was measured in le Chatelier flask and gravimetric water content was obtained by the standard weight method according to ASTM C566-13 [19]. The saturated hydraulic conductivity of the tested soil under natural, undisturbed conditions was measured by a field permeameter for fine grained soils GeoN by Geo Nordic, Stockholm, Sweden.

Laboratory measurements of saturated conductivity of the soil compacted at various water contents were carried out in the permeameters for compacted soils by Humboldt Mfg. Co, USA. The H-4145 compaction permeameters and the falling water head method of measurements meeting requirements of ASTM D5856-95 [20] were applied to our studies. The soil was compacted, with different molding water contents, according to PN-B-04481:1988 [18]. The following values of molding water contents (by weight) were applied during our laboratory studies: 14, 17 and 19%.

Numerical modeling of hydraulic efficiency of a mineral liner constructed of the compacted clayey soil was performed by FEFLOW, WASY-DHI, Germany modeling software. FEFLOW is a well known and successfully verified numerical tool, based on the finite elements/volumes method allowing calculations of water and mass transport in saturated, unsaturated or variably saturated porous medium [21-25]. The developed two dimensional model represented a 1 m wide mineral liner of 1 m thickness, required by the actual Polish and European standards [2, 3]. The prepared model consisted of 2831 nodes and 5472 elements.

Numerical calculations of the two dimensional water flow in FEFLOW were based on standard forms of Darcy's and Richards' equations [26-28]:

$$\boldsymbol{q}_i = -\boldsymbol{K}_{ij} \frac{\partial h}{\partial x_j}$$

$$S_0 \frac{\partial h}{\partial t} = -\frac{\partial \boldsymbol{q}_i}{\partial x_i} \mp Q$$

where: $\boldsymbol{qi}$ - groundwater flux vector [m s^{-1}], h - hydraulic pressure head [m], t - time [s], $\boldsymbol{K}_{\mathrm{ij}}$ - hydraulic conductivity tensor, i, j = 1, 2, [m s^{-1}], Q - sink or source term [s^{-1}], S_0 - specific storage compressibility [m^{-1}], $S_0 = 1 \cdot 10^{-4}$ m^{-1}.

Mathematical description of water retention curve to our simulations was presented by van Genuchten [29]:

$$\theta = \frac{\theta_s - \theta_r}{[1 + (ah)^n]^m} + \theta_r$$

where: θ_s - saturated volumetric water content [m^3 m^{-3}], θ_r - residual volumetric water content [m^3 m^{-3}], θ_r = 0 m^3 m^{-3}, h - pressure head [m], a - fitting parameter [m^{-1}], n, m - fitting parameters, $m = 1 - n^{-1}$.

Hydraulic conductivity of unsaturated soils K was calculated in the presented model according to van Genuchten's formula [26]:

$$K = K_s S_e^i \left[1 - \left(1 - S_e^{\frac{1}{m}} \right)^m \right]^2$$

where: K_s - saturated conductivity [m s^{-1}], l - fitting parameter, l = 0.5 [28], S_e - dimensionless effective saturation defined as:

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r}$$

The retention characteristics of the soil described by van Genuchten model [29] applied to numerical calculations are presented in Table 2. The isotropic soil was assumed to our calculations due to the developed small scale model [25].

Table 2

Retentional characteristics of the soil applied to numerical calculations

	Saturated volumetric water content $\boldsymbol{\theta_s}$ [$\mathbf{m^3\,m^{-3}}$]	**Fitting parameter *a* [$\mathbf{m^{-1}}$]**	**Fitting parameter *n* [-]**
Parameter value	0.352188	0.0269	1.354476

The required input data for water retention characteristics were determined by laboratory measurements including a sand box in the range of $h < 0.1$ bar as well as pressure chambers with 1 bar, 2 bar, 5 bar and 15 bar ceramic plates, produced by Soil Moisture Equipment Corp, USA. Numerical modeling of two dimensional gravitation water flow through the mineral liner required assumption of the necessary initial and boundary conditions. The initial condition was assumed as full liner's soil saturation, *ie* $S = 1.0$. The bottom boundary condition was assumed as the constant Dirichlet type condition in which the water head was equal to –5.0 m. The variable Dirichlet type top boundary condition represented by various values of water pressure head over the modeled liner was selected to our calculations. The applied values of assigned pressure head were assumed as 0.01, 0.5, 1 and 5 m. The assumed time of simulation covered one hydrologic year, *ie* 365 days.

Results and discussion

The results of saturated hydraulic conductivity measurements as well as bulk density and total porosity tests for the applied molding water contents are presented in Table 3.

Table 3

Saturated hydraulic conductivities, total porosities and bulk densities of the soil dependently on molding water content

	Molding water content [% by weight]		
	14	**17**	**19**
Saturated hydraulic conductivity [$\text{m}\cdot\text{s}^{-1}$]	$3.936\cdot10^{-9}$	$1.000\cdot10^{-10}$	$7.325\cdot10^{-11}$
Soil bulk density after compaction [Mg m^{-3}]	1.83	1.97	2.02
Total porosity after compaction [$\text{m}^3\,\text{m}^{-3}$]	0.300	0.246	0.227
Bulk density after swelling [Mg m^{-3}]	1.66	1.85	1.88
Total porosity after swelling [$\text{m}^3\,\text{m}^{-3}$]	0.365	0.292	0.281

The data presented in Table 3 show a clear decrease of the saturated hydraulic conductivity with the increase of bulk density resulting from the increase of the molding water content. The presented results show that in all three cases compaction was performed on the left side of the standard Proctor's curve. Additionally, it is visible that saturation of compacted clay material, leading to swelling of soil, affects its bulk density and total porosity. The degree of bulk density reduction and total porosity increase is related to molding water content.

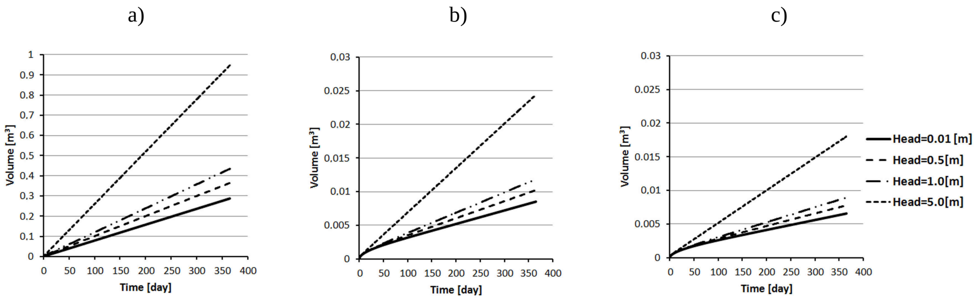

Fig. 1. Calculated cumulative volume of seepage through mineral liner made of the clay soil compacted at different water contents: a) seepage volume for molding water content $u = 14\%$, b) seepage volume for molding water content $u = 17\%$, c) seepage volume for molding water content $u = 19\%$

The results of numerical calculations of water seepage through a 1 m thick layer of the clayey material compacted with various molding water contents are presented in Figure 1.

The results presented in Figure 1 shows that hydraulic properties of the mineral clay liner as a barrier for pollutants propagation made of the compacted clay material directly depend on molding water content. The lower the molding water content, the higher saturated hydraulic conductivity and the higher infiltration rate for the same value of water head applied to the upper boundary of the liner. Table 4 shows the observed mean values of daily seepage volume for all the applied values of water head and the molding water contents under consideration.

Table 4

Mean daily seepage volume [m^3] for all the tested molding water contents and the applied water pressure head values

Molding water content [% by weight]	**Water pressure head [m]**			
	0.01	**0.5**	**1.0**	**5.0**
14	$0.792 \cdot 10^{-3}$	$0.999 \cdot 10^{-3}$	$1.191 \cdot 10^{-3}$	$2.597 \cdot 10^{-3}$
17	$0.023 \cdot 10^{-3}$	$0.028 \cdot 10^{-3}$	$0.032 \cdot 10^{-3}$	$0.067 \cdot 10^{-3}$
19	$0.018 \cdot 10^{-3}$	$0.021 \cdot 10^{-3}$	$0.024 \cdot 10^{-3}$	$0.049 \cdot 10^{-3}$

The results of the mean daily water seepage related to the water pressure head values triggering infiltration flow show that better sealing of landfill waste body by natural liner constructed of the compacted clay material is obtained when the clay material is compacted at higher value of water content. Increase of molding soil water content from 14 to 19% allowed to reduce the volume of seepage by approx. 98% in cases of all applied values of pressure head.

Summary

Our studies support literature reports proving that there is a direct relation between molding water content in a clay soil during compaction and its saturated water conductivity (inducing modification of its general hydraulic characteristics). This relation allows to obtain better sealing properties, *ie* lower permeability, of the compacted mineral liner when soil was compacted with higher values of water content. In our case, the increase of molding water content from 14% to 19% resulted in a decrease of saturated hydraulic conductivity of the compacted soil from $3.936 \cdot 10^{-9}$ to $7.325 \cdot 10^{-11}$ m s^{-1}. Additionally, the performed numerical modeling of infiltration through the compacted clay liner showed that the approx. 98% decrease of daily infiltration rate through the 1.0 m thick clay liner was possible due to increase of molding water content by 5% (from 14 to 19%) for all the values of water pressure head under consideration (0.01-5 m). The above shows that selection of the proper molding water content during construction of the municipal landfill cell liner of compacted clay material is crucial because it may significantly influence the effectiveness of the sealing preventing migration of the pollutants into the natural environment. On the other hand the increase of molding water content may result in an increase bulk density and decrease of total porosity after swelling of the clay material after saturation by water. Thus, the possibility of soil cracking, reducing the sealing properties of the liner becomes significant. Our studies should be extended to include different types of clay soils and to cover the second part of the Proctor's curve, however, compaction of clay material at high molding water content may be impractical. The lacking validation of our simulation calculations influences the fact that our modeling studies should be treated as preliminary.

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WILGOTNOŚĆ ZAGĘSZCZANIA MATERIAŁÓW ILASTYCH A WŁAŚCIWOŚCI HYDRAULICZNE PRZESŁON MINERALNYCH SKŁADOWISK ODPADÓW

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Abstrakt: Składowiska odpadów jako szczególnie uciążliwe dla środowiska budowle inżynierskie muszą być izolowane przesłonami w celu zapobiegania rozprzestrzeniania się wraz z m.in. odciekami zanieczyszczeń antropogenicznych pochodzących ze składowiska. Jednym ze sposobów zapewniania izolacji składowisk są przesłony mineralne odpowiednio przygotowane i zagęszczone, zabezpieczające dno, boki oraz powierzchnię składowiska. Przesłony minerale są najczęściej wykonywane z odpowiednio zagęszczonych gruntów ilastych, tak aby, zgodnie z Rozporządzeniem Ministra Środowiska z 30 kwietnia 2013 r. w sprawie składowisk odpadów oraz Council Directive 1999/31/EC z 26 kwietnia 1999 w sprawie składowania odpadów, przepuszczalność hydrauliczna przesłony była niższa niż $1{\cdot}10^{-9}$ $\text{m}{\cdot}\text{s}^{-1}$. Bezpośredni wpływ na wartość współczynnika przewodnictwa wodnego w stanie pełnego nasycenia mają warunki, w których przeprowadzane jest zagęszczenie gruntu, a dokładnie wilgotność ośrodka porowatego w czasie zagęszczania. Praca niniejsza przedstawia próbę określenia wpływu wilgotności zagęszczania wybranych gruntów ilastych na ich przepuszczalność w stanie pełnego nasycenia oraz właściwości hydrauliczne wykonanej z nich, zgodnie z obowiązującym stanem prawnym, przesłony składowiska odpadów. Zakres pracy obejmował badania terenowe, laboratoryjne oraz modelowe. Przewodnictwo hydrauliczne gruntów w stanie naturalnym określono za pomocą polowej sondy BAT, GeoNordic, przewodnictwo zaś w stanie pełnego nasycenia po zagęszczeniu mierzono za pomocą przepuszczalnościomierzy Humboldt Mfg. Co. do gruntów zagęszczonych wg ASTM D5856-95. Ocenę właściwości hydraulicznych przesłon wykonanych z badanych materiałów ilastych zrealizowano poprzez modelowanie numeryczne procesu infiltracji przy zadanej wysokości naporu wód gruntowych zrealizowane za pomocą programu obliczeniowego FEFLOW, DHI-WASY. Ze względu na brak walidacji modelu otrzymane wyniki należy traktować jako wyniki badań wstępnych.

Słowa kluczowe: materiały ilaste, przesłony mineralne, przewodnictwo hydrauliczne, modelowanie numeryczne

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BIOSORPTION OF Cu(II) BY LIVE AND DEAD CELLS OF *Yarrowia lipolytica*

BIOSORPCJA Cu(II) PRZEZ ŻYWE I MARTWE KOMÓRKI *Yarrowia lipolytica*

Abstract: The biosorption characteristic of Cu(II) using live and dead cells of *Yarrowia lipolytica* as biosorbents have been investigated in the present research. Biosorption of Cu(II) was enhanced with an increase in pH, temperature, agitation, contact time and initial concentration of the metal ion. It was observed that dead and live biomass efficiently removed copper at 30 min at an initial pH of 5.0. Temperature of 35ºC was optimum at agitation speed of 150 or 200 rpm. For initial copper concentrations of 1-200 mg · dm^{-3}, the adsorption data provide an excellent fit to the Langmuir isotherm. Experimental maximum biosorption capacity turned out to be 12.56 mg · g^{-1} for living material and 14.31 mg · g^{-1} for dead sorbents, respectively.

Keywords: biosorption, copper, *Yarrowia lipolytica*, live cells, dead cells

Conventional physiochemical methods for metals remediation include precipitation, filtration, coagulation, evaporation, ion exchange, membrane separation and solvent extraction. However, application of such processes is always expensive and ineffective in terms of energy and chemical products consumption, especially at low metal concentrations of 1-100 mg · dm^{-3} [1]. Therefore, there is a great need for an alternative technique, which is both economical and efficient. Biosorption, based on live or dead biosorbents, has been regarded as a cost-effective biotechnology for the treatment of complex wastewater containing heavy metals at high volume and low concentration [2]. Biosorption can be defined as the property of certain biomass to bind and concentrate selected ions or other molecules from aqueous solutions [3]. In general, yeasts belonging to the genera *Saccharomyces*, *Candida* and *Pichia* are considered to be valuable adsorbents for metal ions [4]. However, in the recent years, there are reports on different strains of the non-conventional yeast *Yarrowia lipolytica* tolerating, resisting and accumulating metal ions [5]. This microorganism utilizes a variety of renewable carbon sources and its use in the waste water treatment processes generates a large quantity of biomass [5-7].

The biosorption characteristic of Cu(II) using live and dead cells of *Y. lipolytica* as biosorbents have been investigated in the present research.

Material and methods

In this work, the strain of *Y. lipolytica* Polish Collection of Microorganisms was used. First of all, effects pH, temperature, agitation speed and biosorbent dose on copper biosorption and removal by live and dead cells were examined to find optimum conditions. All the samples were incubated for 24 h in 50 mg · dm^{-3} of Cu(II). Unless otherwise stated, standard conditions for biosorption experiments included an initial pH 5.0, being agitated at 150 rpm and having a dosage of 1.0 g · dm^{-3}. Effects of 3.0-7.0 pH values, temperature

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from 15-35°C, agitation speeds from 50 to 200 rpm and different biomass densities (0.5-2.5 g · dm^{-3}) were tested in parallel. The concentrations of copper solutions were determined in aqueous solutions spectrophotometrically by measuring the absorbance of complex formed between rubeanic acid and Cu(II) at 390 nm.

Both the values of biosorption capacity and removal ratio of Cu(II) were evaluated as follows (1):

$$q_e = \frac{(C_0 - C_e)}{X} \tag{1}$$

where q_e is the equilibrium Cu(II) concentration on the biosorbent [mg · g^{-1} dry cell]; C_0 and C_e is the initial and residual metal concentration [mg · dm^{-3}]; X is the biomass concentration [g dry cell · dm^{-3}].

The familiar of the Langmuir isotherm is expressed as follows (2):

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \tag{2}$$

where q_{max} represents the maximum monolayer biosorption capacity of the biosorbent [mg · g^{-1}] and K_L [dm^3 · mg^{-1}] is related to the affinity of the binding sites.

The general Freundlich equation is written as follows (3):

$$q_e = K_F C_e^{1/n} \tag{3}$$

where K_F [dm^3 · g^{-1}] is a constant related to the biosorption capacity and n is an empirical parameter representing the biosorption intensity.

Results and discussion

The resulted response surface plots shown in Figures 1-4 indicate the influence of the experimental factors on biosorption process.

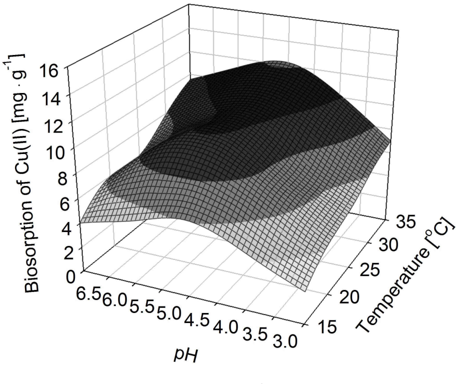

Fig. 1. Effect of pH and temperature on biosorption capacity of Cu(II) by live cells *Y. lipolytica*

It was found that the optimum pH for Cu(II) removal by live and dead cells was 5.0. The maximum biosorption of Cu(II) by living cells was 12.56 mg · g^{-1} while that was

13.41 mg · g^{-1} for dead cells. As reported by Li et al [8] and Vasquez et al [9], pH has a significant effect on the solubility, speciation and biosorption capacity of heavy metals. The dependence of metal uptake on pH is related to both the surface functional groups on the biomass and the metal chemistry in solution. Kiran et al [10] reported that as the pH increased to 5.0, more functional groups with negative charge such as carboxyl, amine or hydroxyl became exposed with subsequent increase of attraction sites to positively charged ions, and thus enhanced the biosorption capacity. At lower pH in this research, the effect of pH could be explained as the competition for active sites between H_3O^+ and positive copper ions.

Figures 1 and 2 shows the biosorption of Cu(II) ions at different temperatures for the yeast cells. An increase in temperature showed a positive effect on metal biosorption process. This result suggested that the biosorption process was endothermic in nature.

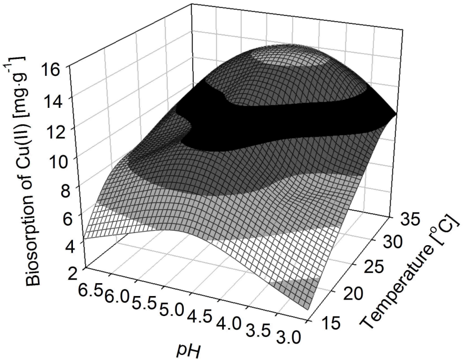

Fig. 2. Effect of pH and temperature on biosorption capacity of Cu(II) by dead cells *Y. lipolytica*

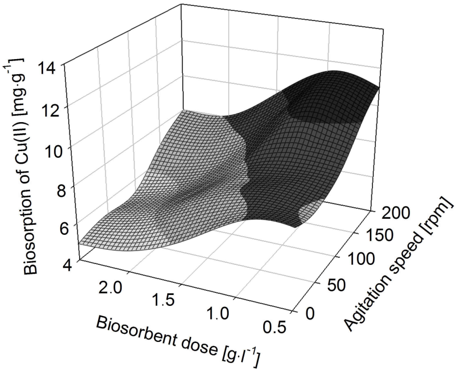

Fig. 3. Effect of biosorbent dose and agitation speed on biosorption capacity of Cu(II) by live cells *Y. lipolytica*

As can be seen in Figures 3 and 4, the effect of agitation speed on Cu(II) biosorption by live and dead cells had similar trends, where maximum biosorption capability was found at 150-200 rpm. An increase in agitation speed is known to enhance interactions of metal ions with the binding sites on the yeast biomass [7, 8].

The effect of cell biomass quantity on biosorption was studied by varying the dose of the sorbent. From Figures 3 and 4, it was observed that specific uptake of Cu(II) decreased significantly with an increasing yeast biomass. This observation is possibly due to the enhanced number of binding sites that were available for complexation of Cu(II) ions and due to increased electrostatic interactions with large quantities of biomass [7].

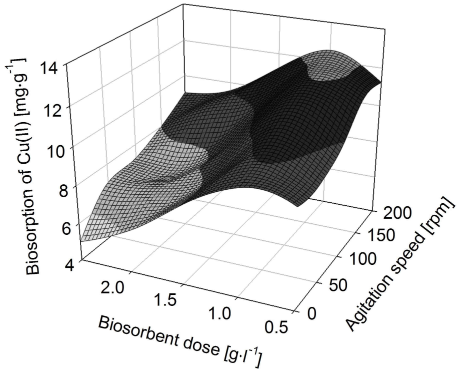

Fig. 4. Effect of biosorbent dose and agitation speed on biosorption capacity of Cu(II) by dead cells *Y. lipolytica*

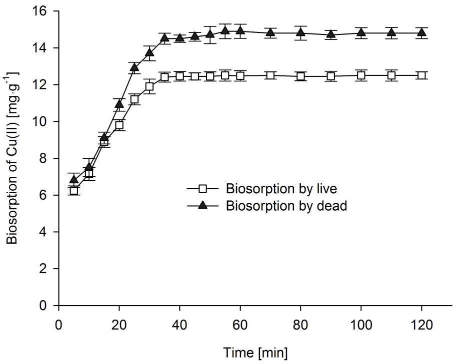

Fig. 5. Effect of contact time on biosorption capacity of Cu(II) by live and dead cells *Y. lipolytica*

The effect of contact time on biosorption equilibrium by live and dead cells of *Y. lipolytica* were represented in Figure 5. The effect of contact time on biosorption of Cu(II) ions by live and dead cells was studied under favorable conditions. From Figure 5, it is evident that the uptake of Cu(II) was rapid during the time frame of 25-30 min. The biosorption process was slower at later stages (30 min-2 h). Li et al [8] indicates that the first phase of biosorption is always rapid, and it is considered to be a spontaneous process with no energy consumed.

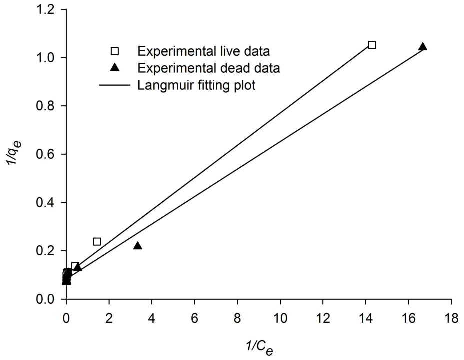

Fig. 6. Langmuir fitting plots of biosorption of Cu(II) onto live and dead cells *Y. lipolytica*

Table 1

Constans simulated with Langmuir and Freudlich models
for Cu(II) biosorption using live and dead cells *Y. lipolytica*

Strain	**Langmuir model**			**Freudlich model**		
	K_L [dm^3 · mg^{-1}]	q_{max} [mg · g^{-1}]	R^2	n	K_F [dm^3 · g^{-1}]	R^2
	$q_e = q_{max}K_LC_e/(1+K_LC_e)$			$q_e = K_FC_e^{1/n}$		
Live	0.6034	9.8231	0.9967	1.0511	1.7142	0.9139
Dead	0.5935	12.0336	0.9941	1.1511	1.8254	0.8762

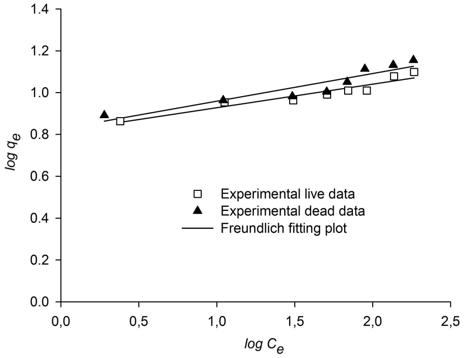

Fig. 7. Freundlich fitting plots of biosorption of Cu(II) onto live and dead cells *Y. lipolytica*

The linearized Langmuir and Freundlich adsorption isotherms on Cu(II) biosorption for live and dead *Y. lipolytica* were show in Figures 6 and 7. The adsorption constants, metal binding constant and correlation coefficients for the metals obtained from Langmuir, Freundlich isotherms analysis are given in Table 1. The adsorption data with respect to copper provide an excellent fit to the Langmuir isotherm. In the experiments of Cu(II) biosorption, the q_{max} value of live cells was 9.82 mg · g^{-1}, compared to 12.03 mg · g^{-1} of dead cells.

Conclusions

The biosorption of Cu(II) by live and dead cells *Y. lipolytica* has been investigated at optimum conditions determined in advance. Batch biosorption experiments with regard to pH, temperature, agitation, biomass dose, initial metal concentration, contact time, competitive biosorption analysis were performed in this study. When live and dead cells of *Y. lipolytica* were employed as biosorbents, the experimental maximum biosorption capacity turned out to be 12.56 and 14.31 $\text{mg} \cdot \text{g}^{-1}$, respectively. At various initial copper concentrations, batch biosorption data of live and dead cells preferred to be simulated with Langmuir isotherm. Taking into consideration of present finding, dead cells of *Y. lipolytica* proved to be more efficient and low-cost biosorbents than live ones, which can be utilized as an alternative for the treatment of wastewater.

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BIOSORPCJA Cu(II) PRZEZ ŻYWE I MARTWE KOMÓRKI *Yarrowia lipolytica*

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Abstrakt: Przedstawiono charakterystykę biosorpcji Cu(II) przy użyciu żywych i martwych komórek *Yarrowia lipolytica* jako biosorbentu. Biosorpcja Cu(II) zwiększała się wraz ze wzrostem pH, temperatury, szybkości mieszania, czasu kontaktu i początkowego stężenia jonu metalu. W pracy zaobserwowano, że żywa i martwa biomasa skutecznie usuwa miedź w ciągu 30 minut przy początkowym pH 5,0. Temperatura 35ºC była optymalna przy szybkości mieszania wynoszącej 150-200 rpm. Dla początkowego stężenia miedzi z zakresu 1-200 $\text{mg} \cdot \text{dm}^{-3}$ uzyskane dane biosorpcji były doskonale dopasowane do modelu Langmuira. Uzyskane w trakcie doświadczeń maksimum biosorpcji dla żywego i martwego sorbentu wynosiło odpowiednio 12,56 i 14,31 $\text{mg} \cdot \text{g}^{-1}$.

Słowa kluczowe: biosorpcja, miedź, *Yarrowia lipolytica*, żywe i martwe komórki