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TREATMENT OF INDUSTRIAL WASTEWATER IN ACCORDANCE TO 'ZERO WASTE' STRATEGY

Abstract

An integrated system combining volumetric coagulation and nanofiltration (NF) was proposed as the high-efficiency wastewater treatment technology. In this study, biologically treated coke wastewater (after denitrification and nitrification processes) coming from a coke plant located in Silesia (southern Poland) was used. The results indicate that the use of integrated membrane processes allows to achieve high efficiency of wastewater treatment. The treated wastewater can be converted back and used as technical water in the coke plant, in accordance to 'zero waste' strategy.

Key words

industrial wastewater, coke plant, wastewater treatment, zero waste, circular economy

Introduction

According to the Polish legalisation, industrial wastewater is 'effluent discharged from the areas where any trade or industry is carrying on, other than domestic wastewater or rainwater' (Journal of law 2011, no. 115, item. 1229) [1]. Industrial wastewater is one of the important contaminants sources in the pollution of the water environment. Therefore these wastewater, before being discharged to the receiver, must be treated [2], whereby the degree of cleaning depends upon the type of receiver:

- sewer equipment (Journal of law 2006, no. 136, item. 964) [3];
- environment (natural receiver: water or earth) (Journal of law 2014, item. 1800) [4].

Due to the fact that the requirements for treatment of industrial wastewater are continuous dokręcania, development of new concepts and technological solutions to ensure the highest possible flexibility of treatment installation is very important and necessary. It is recommended to use an integrated systems, connecting together the classic unit processes used in wastewater treatment technology, ie. biological, chemical and physical [5, 6].

There are many types of industrial wastewater based on the different industries and the contaminants; each sector produces its own particular combination of pollutants. In most industry sectors, wastewater effluents result from the following water uses: sanitary wastewater (e.g. from washing, drinking, etc.), cooling (eg. from disposing of excess heat to the environment), process wastewater (water used for making and washing products, water used for removal and transport of waste and by-products) and cleaning (including wastewater from cleaning and maintenance of industrial areas) [7]. In the group of most hazardous industrial effluents, the wastewater generated during the process of coke production and the treatment and processing of coking by-products is mentioned. This wastewater contains sizable amount of ammonia salts and compounds such as phenols, oils, tars, suspensions, polycyclic aromatic hydrocarbons (PAHs), toxic organic nitrogen compounds, cyanide, ammonia, hydrogen sulfide. Due to raw coke wastewater contains toxic impurities, it can not be introduced into the receiver without purification. Therefore, the wastewater is pretreatment at the coking plant, mostly in biological wastewater treatment installations. However, after the biological processes, coke wastewater is often insufficient treated and pollution caused by coke wastewater is a significant problem all over the world. Therefore, it is necessary to develop concepts of wastewater treatment properly to avoid any adverse longterm environmental and ecological impacts to the receiver, in a sustainable way [8].

The aim of the paper was to examine an integrated system: coagulation-nanofiltration for the removal of organic and inorganic pollutants from industrial wastewater, discharged from the coke plant located in southern

Poland. Recirculation and usage of treated wastewater at the plant is proposed as new, innovative solution in accordance to the 'zero waste' strategy.

'Zero waste' strategy

The European Union (EU) in 2014 in Communication no. 398: '*Towards a circular economy: A zero waste programme for Europe'* emphasized issue of the more efficient use of waste [9]. 'Zero waste' strategy as one of the most visionary concepts for solving waste problems assumes that moving towards a more circular economy (CE) is an essential way to deliver the resource efficiency agenda established under the Europe 2020 Strategy for smart, sustainable and inclusive growth. Higher and sustained improvements of resource efficiency performance may bring large economic benefits and seems to be promising in the future waste management [10].

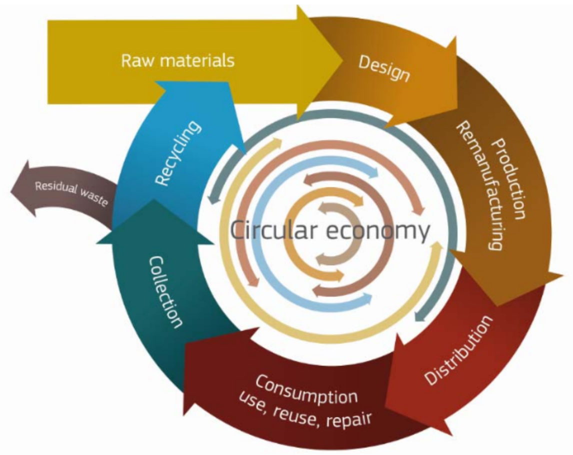

Fig. 1. Strategy of circular economy
Source: COM 398, 2014

Transition to a more circular economy requires many changes throughout value chains, including new ways of turning wastewater into a resource. This implies systemic change, and innovation not only in technologies, but also in organisation, society, finance methods and policies. Moreover, it should be mentioned that even in a highly circular economy there will remain some element of linearity as virgin resources are required and residual waste is disposed of – figure 1 [9]. Targeting the whole system means striving for:

- Zero waste of resources: energy, materials, human;
- Zero emissions: air, soil, water;
- Zero waste in activities: administration, production;
- Zero waste in product life: transportation, use, end of life;
- Zero use of toxics: processes and products [11].

There are many possible in-plant changes, process modifications and water-saving measures through which industrial wastewater loads can be significantly reduced. Up to 90% of recent wastewater reductions could be achieved by industries employing such methods as recirculation, operation modifications, effluent reuse or more efficient operation. In the case of industrial wastewater, assumptions of 'zero waste' strategy could be obtained by recycling treated wastewater for technological cycle at the plant [7].

Materials and methods

The coke wastewater was collected from coke plant located in Silesia, southern Poland. Production capacity of plant is 600,000 tonnes of coke per annum. These wastewater was treated in the treatment plant: biological processes involving the separate denitrification, nitrification and oxidation of organic carbon. Diagram showing individual stages of coke wastewater treatment in the analyzed plant is shown in Figure 2.

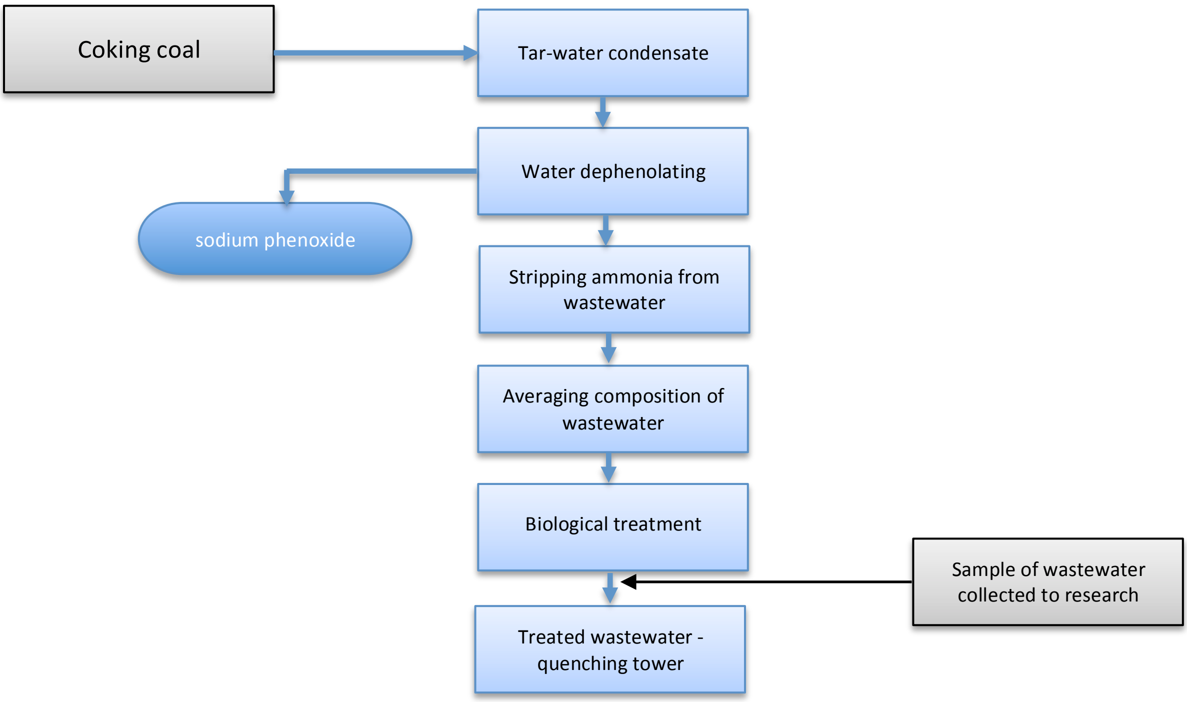

Fig. 2. Stages of coke wastewater treatment in analyzed plant
Source: Author's research

The samples were characterized for the concentration of selected physiochemical indicators: pH, temperature, chemical oxygen demand (COD), ammonium nitrogen, nitrate nitrogen, total organic carbon (TOC), total carbon (TC), total suspended solids and 16 PAHs listed by Environmental Protection Agency (USEPA). Common standard method given by Hermanowicz et al. [12] was used in the laboratory to determine physiochemical indicators. Temperature was measured at the plant (*in situ*). The value of pH was performed using a potentiometric method (pH-meter Cole Palmer). For the indication of COD a test method was performed using a spectrophotometer HACH DR 4000th. The concentration of nitrate nitrogen and ammonium nitrogen was established using cuvette tests of HACH LANGE firm on a spectrophotometer DR 2800th. The determinations of TOC and TC indicators where performed by high temperature catalytic oxidation using GC Multi N/C 2100 apparatus and determination of suspended solids was performed by gravimetric method. Qualitative and quantitative PAHs identification was carried out using high performance liquid chromatography HPLC with fluorescence detection (FL 3000) - THERMO Scientific HPLC.

Experimental Procedure

In the first stage of the research, wastewater was treated in coagulation process. The process of volumetric coagulation was conducted using the jar test with the reactors of capacity 1.0 L. In this study, aluminum sulphate $Al_2(SO_4)_3 \cdot 18H_2O$ (alum) as coagulant was used. In the study, experimentally determined optimum dose was equal to 130 mg/L 1% solution of alum. The experimental process consisted of the initial rapid mixing stage that took place for 60 sec, the following slow mixing stage for 30 min and the final settling step for 1 h. After 1 hour settling period, samples were withdrawn from supernatant for second step of research. After the coagulation, the wastewater was directed to the membrane module. The following equipment was used in the nanofiltration treatment of coke wastewater: an apparatus with a slab-type membrane module SEPA CF-NP (GE Water, USA), tank of wastewater (8 L) with a cooler, rotameter, high-pressure pump and pressure gauges as well as valves. The membrane module consisted of two steel plates with a flat membrane [13]. One commercial polymer membrane (DK), produced by GE Water (USA) was used for nanofiltration. The surface of the membrane was 144 cm^2. Cross-flow setting was used to close the system and direct wastewater to the feed tank. The transmembrane pressure of the process was 1.5 MPa and the linear flow velocity over the membrane surface was 2 $m \cdot s^{-1}$. The obtained equilibrium streams were up to $12.54 \cdot 10^6$ $[m^3/m^2 \cdot s]$ after 140 minutes of filtration. The process parameters are shown in Figure 3.

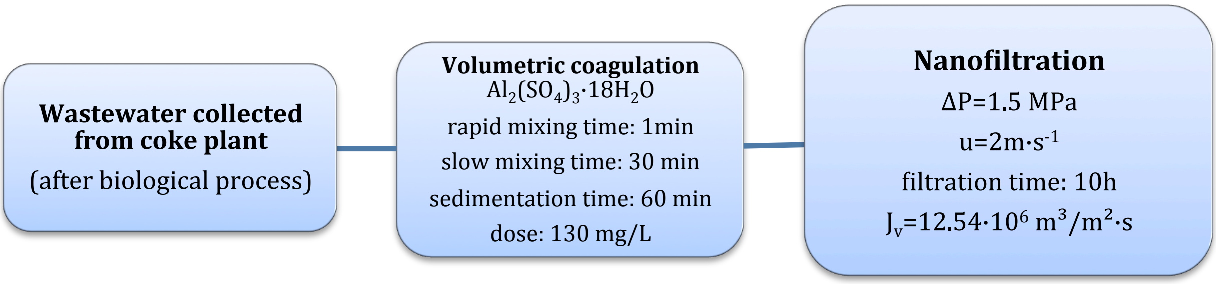

Fig. 3. The process parameters during coke wastewater treatment
Source: Author's research

Results

The changes in the composition of coke wastewater during technological research are shown in Table 1. In wastewater collected from coke plant, all values significantly exceeded the standards of quality and this prevents their direct discharge into an environment and to sewage system.

Table 1. The composition of the treated coke wastewater

Indicator [unit]	Wastewater collected from coke plant (after biological process)	Treated wastewater		Allowable values of wastewater pollution	
		after coagulation	after nanofiltration	discharged into the environment (water and soil) [4]	discharged into the sewage system [3]
Temperature[°C]	43	20	20	35	35
pH	7.2	5.1	6.6	6.5-9.0	6.5-9.5
COD [mg O_2/L]	6072.4	2973.1	938.2	125	[1]
Ammonium nitrogen [mg NH_4^+/L]	334.5	228.8	78.3	10.0	100.0[2] 200.0[3]
Nitrate nitrogen [mg NO_3-/L]	35.7	29.2	18.8	30.0	
TOC [mg C/L]	411.1	277.9	128.1	30	-
TC [mg C/L]	717.5	310.4	130.7	-	-
Total suspended solids [mg /L]	132.6	70.1	3.1	70.0	-
PAHs [µg/L]	95.0	53.0	15.0	-	20 [4]

[1] values of indicators should be based on permissible load of these pollutants for individual treatment plant;
[2] for wastewater discharged to the treatment plant for an area with a population> 5000;
[3] for wastewater discharged to the treatment plant for an area with a population ≤ 5000;
[4] expressed as carbon content

Source: Author's research

The pH of the coke wastewater was equal to 7.7. In the coagulation process, pH value decreased to 5.1 and increased to 6.6 after nanofiltration. It did not exceed the permissible values of 6.5–9.0 [4] and 6.5-9.5 [3] in the treated wastewater. This value of pH was also in the range characteristic for coke wastewater, given by Bartkiewicz (7.5–9.1) [14]. Temperature of raw wastewater reached 43°C. During the experiment, the wastewater was cooled to room temperature 20°C. Initially, the value of COD was equal to 6072.4 mg O_2/L, ammonium nitrogen - 334.5 mg NH_4^+/L, nitrate nitrogen - 35.7 mg NO_{3-}/L, TOC - 411.1 mg C/L, TC- 717.5 mg C/L and total suspended solids - 132.6 mg/L. The concentration of 16 PAHs (2-rings: naphthalene; 3-rings: acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene; 4-rings: fluoranthene, pyrene, benzo(a)anthracene, chryzen; 5-rings: benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene; 6-rings: indeno(1,2,3,c,d)pyrene, benzo(g,h,i)perylene) reached 95 µg/L.

Efficiency of coke wastewater treatment was evaluated on the basis of the degree of pollution load removal, based on the following equation:

$$R = \left(1 - \frac{C_p}{C_n}\right) \cdot 100$$

where:
c_n – concentration of the compound in the feed solution, mg/L;
c_p – concentration of the compound in the permeate, mg/L.
The results of the coke wastewater treatment efficiency is shown in Figure 4.

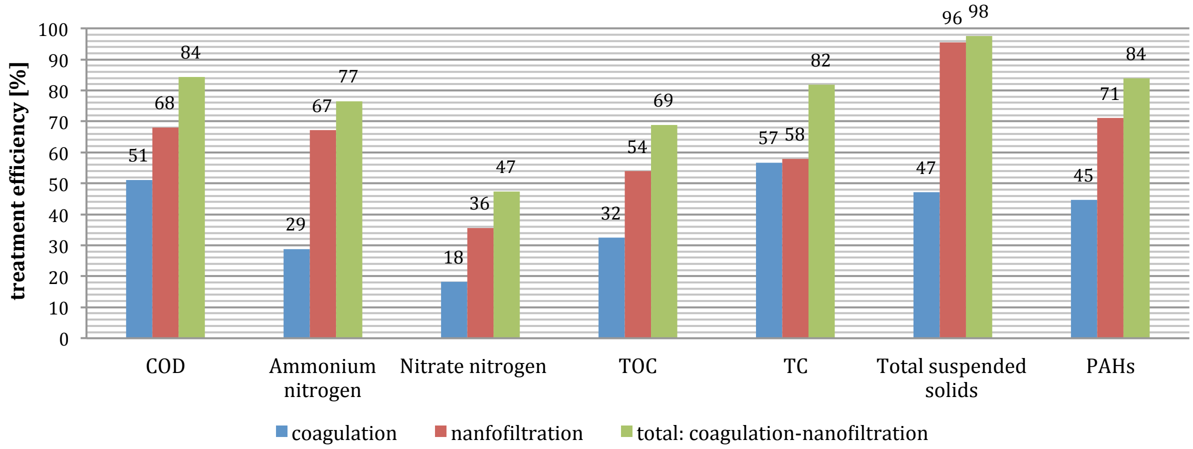

Fig. 4. The effectiveness of coke wastewater treatment
Source: Author's research

During the technological research, high treatment efficiency was achieved. The results show that the best efficiency is represented by integrated system: coagulation – NF for total suspended soils – 98%. The high removal efficiency was also obtained for 16 PAHs – 84%. The removal of polycyclic aromatic hydrocarbons from wastewater is very important due to their toxic properties [15]. There is also a high degree in removal of: COD – 84%, ammonium nitrogen - 77%, TC - 82% and TOC - 69%. The obtained high retention coefficients during nanofiltration result from the cut-off of used DK membrane, which is adapted to retain compounds with a molecular weight of 150-300 g / mol.

The obtained results may lead to the conclusion that the wastes additionally treated in the process of nanofiltration still did not meet the standards of quality since the concentration of ammonium nitrogen and COD were too high [4]. However, treated wastewater can be converted back and used as technical water in the coke plant, in accordance to 'zero waste' strategy. Zero waste in industrial networks can therefore be understood as a new standard for efficiency and integration [11]. It should also be noted that the area of application and thus the market for membranes is developing dynamically in recent years, which may positively affect growth in the use of membrane technology [22]. A significant improvement in environmental protection through the use of the highly effective methods of industrial wastewater treatment that meets the standards and requirements of Polish and EU environmental law, defined by the IPPC Directive, is possible. Therefore, it is required further research on the use of membrane processes in coke wastewater treatment.

Summary and conclusions

The findings show that the use of integrated membrane processes allows to achieve high efficiency of coke wastewater treatment, which was repeatedly confirmed [16, 17]. An important advantage of membrane technology is the ability to carry out separation of impurities in a continuous manner and the ease of integration of membrane processes with other unit processes - integrated of hybrid processes. Therefore, there is need to pay attention to the possibility of introducing membrane modules to the technological system of existing and planned wastewater treatment plants [5, 6, 18]. The analyzed membrane technology reduces the pollutant load in wastewater and allows to recycling of recovered water - to quenching of coke [19]. In the water sector, industries have a duty to optimize their water cycle within the water basin in which they are located. A resource efficient approach to wastewater treatment could up new possibilities for sustainable and more bio-based economic growth, including the recovery of valuable resources embedded in wastewater steams [20, 21]. Moreover, reusing wastewater increases the productivity of the abstracted water. The time to invest in building circular economy for industrial plant is now due to high European Union support for new eco-innovation solutions. Due to the managing the production of wastewater from industrialized area has always received a great deal of scientific, technical, and regulatory attention, high-efficiency wastewater treatment technology are constantly being invented and applied. Currently, emphasis is placed on possible reuse of treated wastewater at the plant in accordance with the circular economy assumptions.

Currently eco-innovativeness is an important factor owing to which industrial plants are competitive on the national and international markets. Some EU policies and instruments already provide tools and incentives in line with the circular economy model. All of Member States have a consultation points where entrepreneurs can obtain information about current programs, supporting the development of eco-technologies under the EU Research and Innovation Programme (Horizon 2020) and its instruments, including the European Institute of Innovation and Technology, the European Structural and Investment Funds, the Eco-innovation Action Plan, the Green Action Plan for small and medium-sized enterprises (SMEs), and the European Consumer Agenda [9]. The innovative projects receiving financial support could be both investment and modernization projects of wastewater plants. The industrial plants which decide to introduce new eco-technologies will obtain the confidence and capacity to move to circular economy solutions. For the potential beneficiaries, it is required to take into account whole life cycle in the investments projects, in accordance with the 'zero waste' strategy. These solutions will be in the first place supported by European funds at the national and international level in new programming period 2014-2020.

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HUMAN CAPITAL
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References

[1] The Water Law (Journal of law 2011, no. 115, item. 1229). (in Polish).

[2] W. Wolf, Innovative methods of wastewater processing in agri-food industry (Innowacyjne metody przetwarzania ścieków przemysłu rolno-spożywczego), Acta Innovations, 11 (2014) 39-42. (in Polish).

[3] The Minister of Housing of 14 July 2006 on how the responsibilities of suppliers of industrial wastewater and conditions for entry wastewaters into sewers (Jurnal of law 2006 no. 136, item. 964). (in Polish).

[4] The Minister of Environment of 18 November 2014 on conditions to be met for the introduction of sewage into the water or the ground, and the substaces particulary harmful to the aquatic enviroment (Jurnal of law 2014, item. 1800). (in Polish).

[5] B. Tomaszewska, The use of ultrafiltration and reverse osmosis in the desalination of low mineralized geothermal waters, Archives of Environmental Protection, 37 (3) (2011) 63–77.

[6] B. Tomaszewska, M. Bodzek, Desalination of geothermal waters using a hybrid UF-RO process. Part II: Membrane scaling after pilot-scale tests. Desalination, 319 (2013) 107-114.

[7] A. Alturkmani, Industrial wastewater, www.4enveng.com.

[8] X. Jin, E. Li, S. Lu, Z. Qiu, Q. Sui, Coking wastewater treatment for industrial reuse purpose: Combining biological processes with ultrafiltration, nanofiltration and reverse osmosis. Journal of Environmental Sciences, 25(8) (2013) 1565-1574.

[9] Commission of European Communities. Communication No. 398, 2014. Towards a circular economy: A zero waste programme for Europe.

[10] M. Smol, J. Kulczycka, A. Henclik, K. Gorazda, Z. Wzorek, The possible use of sewage sludge ash (SSA) in the construction industry as a way towards a circular economy. Journal of Cleaner Production, 95 (2015) 45-54.

[11] T. Curran, T., I.D. Williams, A zero waste vision for industrial networks in Europe. Journal of Hazardous Materials, 207 (2012) 3-7.

[12] W. Hermanowicz, J. Dojlido, W. Dożańska, B. Koziorowski, J. Zerbe, Physico - chemical studies of water and wastewater (Fizyczno-chemiczne badanie wody i ścieków), Arkady, Warszawa, 1999. (in Polish).
J. van der Geer, J.A.J. Hanraads, R.A. Lupton, The art of writing a scientific article, J. Sci. Commun. 163 (2010) 51–59.

[13] M. Smol, M. Włodarczyk-Makuła, J. Bohdziewicz, K. Mielczarek K., The use of integrated mambrane systems in the removal of selected pollutants from pre-treated wastewater in coke plant, Monographs of the Environmental Engineering Committee Polish Academy of Sciences, Warsaw-Gliwice, Membranes and Membrane Processes in Environmental Protection, 119 (2014) 143-152.

[14] B. Bartkiewicz, Industrial wastewater treatment (Oczyszczanie Ścieków Przemysłowych), Polish Scientific Publishers, Warszawa, 2006 (in Polish).

[15] E. Wiśniowska, Effect of chemical stabilisation of sewage sludge on the fate of PAHs, Archives of Environmental Protection, 3 (2008) 249-257.

[16] M. Smol, M. Włodarczyk-Makuła, Effectiveness in the removal of Polycyclic Aromatic Hydrocarbons from industrial wastewater by ultrafiltration technique, Archives of Environmental Protection, 38(4) (2012) 49-58.

[17] M. Smol, M. Włodarczyk-Makuła, J. Bohdziewicz, K. Mielczarek, D. Włóka, The use of coagulation and reverse osmosis for the removal of pollutants from industrial wastewater (Zastosowanie koagulacji oraz odwróconej osmozy do usuwania zanieczyszczeń ze ścieków przemysłowych), Monografia Interdyscyplinarne zagadnienia w inżynierii i ochronie środowiska, Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław, 4 (2014) 747-759. (in Polish).

[18] J. Bohdziewicz, E.Kudlek, M. Dudziak, Analytical control of diclofenac removal in the photocatalytic oxidation process. Civil and Environmental Engineering Reports, 23 (2013) 23-30.

[19] Best Available Techniques for coking plant (BAT), Najlepsze dostępne techniki (BAT) wytyczne dla branży koksowniczej, Ministerstwo Środowiska, Warszawa, 2005. (in Polish).

[20] T. Porębski, S. Tomzik, W. Ratajczak, M. Talma-Piwowar, W. Capała, The use of membrane processes in the chemical industry-recycling of raw materials, energy saving (Zastosowanie procesów membranowych w przemyśle chemicznym—recykling surowców, oszczędność energii). Polimery, 57(5) (2012) 382-388. (in Polish).

[21] Methodological Guide - the release and transfer of pollutants to the environment resulting from the coke plant operating in Poland (Przewodnik metodyczny – uwalnianie i transfer do środowiska zanieczyszczeń będących efektem eksploatacji instalacji koksowniczych w Polsce), Wydawnictwo Instytutu Chemicznej Przeróbki Węgla. Zabrze, 2010. (in Polish).

[22] T. Porębski, S. Tomzik, W. Ratajczak, M. Talma-Piwowar, W. Capała, The use of membrane processes in the chemical industry-recycling of raw materials, energy saving (Zastosowanie procesów membranowych w przemyśle chemicznym—recykling surowców, oszczędność energii). Polimery, 57(5) (2012) 382-388.

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ELIMINATION OF PHARMACEUTICAL COMPOUNDS FROM MUNICIPAL WASTEWATER BY PHOTOCATALYSIS, MICROFILTRATION AND NANOFILTRATION

Abstract

The aim of the study was to develop an innovative method for the removal of selected pharmaceuticals from biologically treated municipal wastewater. The photocatalytic oxidation in the presence of TiO_2 was carried out in a reactor irradiated with a UV lamp (power 150 W) and two-stage membrane filtration was also applied. In the first stage the catalyst particles were separated using a microfiltration membrane. In the second stage the wastewater was polished in a semi-industrial installation equipped with a flow-through tubular membrane module with a filter surface area of 240 cm^2. The system combining photocatalysis and membrane filtration allowed for complete elimination of the pharmaceuticals.

Key words

pharmaceuticals, sequential system, photocatalysis, microfiltration, nanofiltration

Introduction

Nowadays, more and more attention is paid to organic micropollutants classified as a group of xenoestrogens present in the aquatic environment. This group contains phenols, non-biodegradable halogenated organic compounds, pesticides, polycyclic aromatic hydrocarbons, surfactants, endocrine disrupting compounds but also pharmaceutical compounds. The main sources of pharmaceuticals in the aquatic environment are the waste waters from the pharmaceutical and cosmetic industry but also municipal waste water [1]. The growing problem of the presence of pharmaceutically active compounds in the environment is especially related to increasing production and consumption (even excessive) of drugs, especially those available over the counter. The pharmaceuticals that are the most commonly detected in the influent and effluents of waste water treatment plants include non-steroidal analgesic and anti-inflammatory drugs, namely diclofenac, naproxen and ibuprofen, psychotropic drugs represented by carbamazepine, as well as antibiotics, beta-blockers, hormones, and chemotherapeutic agents [2,3].

Directive of the European Parliament and of the Council 2013/39/EU of 12 August 2013 [4] amending Directive 2000/60/EC and 2008/105 /EC as regards priority substances in the field of water policy ordered the preparation of a substance watch list for monitoring purposes throughout the Union, which, according to the decision of the Executive Commission (EU) 2015/495 of 20 March 2015 [5], apart from nine other organic micropollutants includes diclofenac. The data obtained during the monitoring will determine whether this compound will be classified as one of the priority substances. The presence of these substances in the environment has a negative effect on the overall balance of the whole ecosystem including also human health and life. For example, the exposition of rainbow trout and salmon trout to diclofenac at 0.5 to 1.0 $\mu g/dm^3$ concentration can result in the formation of negative changes in kidneys, liver and gills [6,7]. Ibuprofen concentration range from 1 to 1000 $\mu g/dm^3$ can lead to a limitation of photosynthetic water organisms growth [8]. Thus, it is necessary to ensure complete elimination of this type of compounds from the aquatic environment, and especially from the water bodies that may be the source of drinking water.

The waste water treatment systems based mainly on biological treatment processes do not guarantee an effective removal of pharmaceutical micropollutants because of their polar structure and low susceptibility to biochemical degradation. The observed removal efficiencies are in the range of 40 to 60% depending on the type of a pharmaceutical compound [9]. The concentrations of these substances detected in effluents from municipal waste water treatment plants can therefore be as high as 2.6 µg/L [10]. Even such small concentrations of chemically active substances can exert detectable biological effects on living organisms depending on the type of the compounds [11]. The advanced oxidation processes, which include ozonation, Fenton reaction, ultraviolet radiation, heterogeneous photocatalysis using semiconductors as catalysts, sonolysis, radiolysis and a number of electrical and electrochemical methods that are an alternative to the commonly used biological waste water treatment methods [12]. Rapid and non-selective oxidation of organic compounds is possible due to the reactions occurring in the presence of highly reactive free radicals such as hydroxyl radicals ($OH^{\bullet}$) and $O_2^{\bullet}$, $OH^{\bullet}$ and $ROO^{\bullet}$ radicals [13]. The effect of hydroxylation or dehydroxylation of organic compounds should be their complete mineralization to CO_2 and H_2O [14]. However, the degradation by-products generated in these processes are often more toxic than the parent compound.

High-pressure membrane techniques such as nanofiltration and reverse osmosis have been also widely used for the removal of pharmaceutically active organic micropollutants [15,16]. The removal efficiency of micropollutants in membrane processes depends on several factors, which include hydrophobicity, charge and pore size of the membrane, but also the operating conditions such as temperature, flow rate and transmembrane pressure. The retention of the compounds is also dependent on their physicochemical properties, concentration and chemical composition and pH of the solution in which they are present [17]. However, it should be mentioned that membrane separation generates not only the treated stream of permeate but also the retentate, which is a hazardous waste due to the high concentration of micropollutants removed in the process.

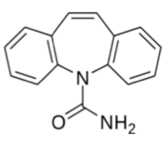
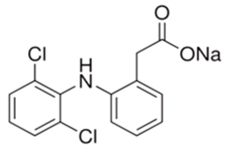
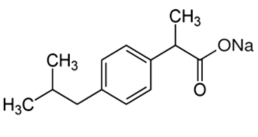
The integration of the advanced oxidation processes with the pressure membrane techniques offers satisfactory removal efficiency of organic micropollutants and their degradation by-products, which are formed not only in the treatment systems but also in the natural environment. Sequential systems based on the advanced oxidation processes can also be used to treat highly concentrated retentate stream, which is generated during the membrane filtration.

The aim of the study was to develop and evaluate a method allowing for the removal of pharmaceutical compounds from biologically treated municipal waste water. This treatment method was based on heterogeneous photocatalysis process and pressure membrane techniques. Specifically, the studied compounds included non-steroidal anti-inflammatory drugs (diclofenac and ibuprofen) and psychotropic drugs (carbamazepine).

Materials and methods

In this study, the secondary effluent from an activated sludge waste water treatment system was spiked with pharmaceutical compounds at a concentration of 1 mg/dm^3 and was subjected to the investigated treatment processes. Analytical standards of sodium salts of diclofenac (DCL) and ibuprofen (IBU), and carbamazepine (CBZ) (table 1) with a purity > 98% were purchased from Sigma-Aldrich (Poznan, Poland).

Table 1. The chemical characteristics of chosen pharmaceuticals

Compound			
Name	Carbamazepine	Diclofenac sodium salt	Ibuprofen sodium salt
Structural formula			
Characteristics			
Molecular formula	$C_{16}H_{12}N_2O$	$C_{14}H_{10}Cl_2NNaO_2$	$C_{13}H_{17}O_2Na$
Molecular weight, g/mol	236.3	318.13	228.26
Solubility in water, mg/L	17	50	100
pK_a	2.30	4.15	4.91
log K_{ow}	2.45	4.51	3.97

Source: own compilation on the basis of Bohdziewicz at al. 2015 [18]

The photocatalysis process was conducted in a 10-L batch laboratory reactor manufactured by Avantor Performance Materials Poland S.A. The reaction mixture was irradiated with a medium-pressure immersion lamp with a power of 150 W, which was introduced into the reactor. The lamp was placed in a cooling jacket, which provided a uniform temperature of the process 21±1°C. In order to provide sufficient amount of oxygen for the photocatalytic oxidation the reaction mixture was aerated with an aeration pump with a capacity of 4 dm^3 of air per minute. The reactor was placed on a magnetic stirrer, which prevented sedimentation of the catalyst particles. Commercial titanium dioxide purchased from Evonik Degussa GmbH was used as a catalyst. The dose of the catalyst was determined experimentally and fixed at 50 $mgTiO_2/L$. The contact time of the catalyst with the aqueous mixture prior to the irradiation process was 15 min. The irradiation was carried out continuously for 60 min. The separation of the catalyst from the reaction mixture was carried out using a membrane filtration system equipped with a 0.45 µm cellulose acetate microfiltration membrane from Millipore, which was connected to a vacuum pump from AGA Labor.

The nanofiltration process was conducted using a semi-industrial installation TMI 14 from J.A.M INOX Produkt, which was equipped with a tubular flow-through membrane module with a polyamide membrane AFC80 from PCI Membrane System Inc. (USA) with a filter surface area of 240 cm^2. The process of membrane filtration was performed until 20% of the feed was collected at a transmembrane pressure of 2 MPa.

The analytical monitoring of the investigated processes was performed using qualitative-quantitative analysis of pharmaceuticals by the GC-MS (EI) technique. In order to determine the analytes by chromatography, the studied pharmaceuticals were extracted by solid phase extraction (SPE) from 20 ml water samples using the SupelcleanTM ENVI-8 cartridges (volume 6 ml, 1.0 g bed weight) from Supelco. The filling of the cartridges prior to the extraction was washed with methanol (5 ml) and with deionized water (5 ml) at pH = 7. Next, water sample was added to the extraction cartridge. After the extraction the packing was dried for 5 min under vacuum. The extract was eluted with 3 ml of methanol and subjected to drying in a stream of nitrogen. Next, the extract was dissolved in methanol and subjected to chromatographic analysis. The analyses were performed using the Saturn 2100 T Varian (Warsaw, Poland) analytical system, which comprises a capillary gas chromatograph (GC) coupled on-line with an ion trap type mass spectrometer (MS). The eluent was separated in the SLBTM-5 ms column from the Supelco Company (Poznan, Poland) with dimensions of 30 m x 0.25 mm x 0.25 µm at the following temperature settings of the column oven: 80°C (8 min), 10°C/min up to 300°C (5 min). The other temperature parameters were as follows: injector - 230°C, ion trap - 180°C, ion source - 290°C. Helium was the carrier phase and the flow rate was 1.1 ml/min. Injections of the sample with a volume of 1µl were performed manually using a 10 µl Hamilton microsyringe. The qualitative GC-MS analysis was carried out using the selected ion monitoring mode (SIM) in the range of 70 to 400 m/z.

Results and discussion

In the first stage of the study, a single step membrane filtration was assessed for its efficiency in removing the selected pharmaceuticals from the treated waste water. The microfiltration process did not allow for the reduction of concentrations of the pharmaceuticals. However, in the case of nanofiltration the concentration of micropollutants decreased in the course of the process (Fig. 1). The retention coefficient for CBZ and DCL after 15 minutes of filtration was over 90%. The concentration of IBU decreased by 50% and it increased with increasing filtration time and increasing fouling intensity. This phenomenon consisted in deposition of organic and inorganic substances on the surface of the membrane. After 2h of the process the retention coefficient for all the three pharmaceuticals exceeded 91%.

However, it should be mentioned that membrane processes generate not only the treated stream of permeate but also the retentate, which contains elevated concentration of the compounds that are removed from the feed. Thus, the retentate is a toxic waste that requires further treatment and disposal steps.

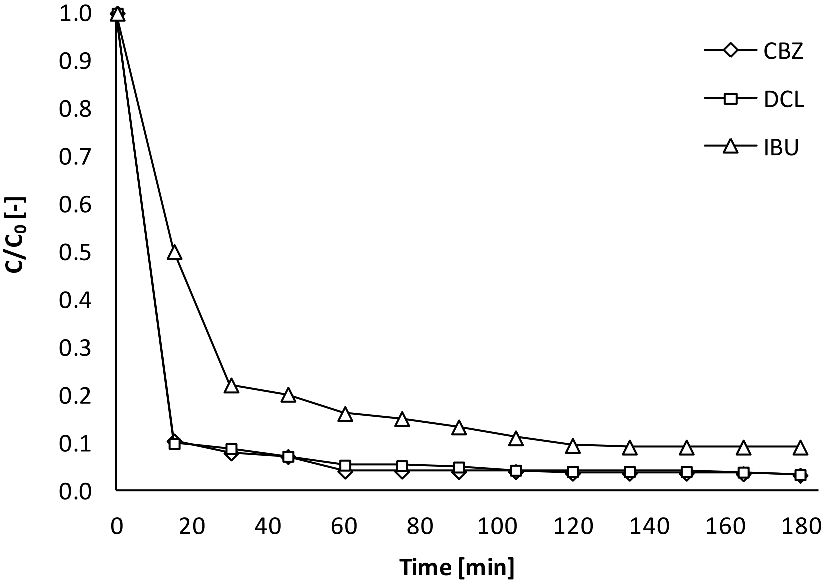


Fig. 1. Change of pharmaceuticals concentrations during the nanofiltration process
Source: own compilation

Figure 2 shows the removal efficiency of the pharmaceutical compounds during the process of heterogeneous photocatalysis. Time 0 corresponds to the reduction in the concentration of micropollutants achieved due to the sorption on the photocatalyst molecules. The degree of adsorption of the micropollutants on the surface of the catalyst particles has an impact on the efficiency of the photocatalysis process. Greater susceptibility for adsorption on the catalyst surface was observed for the compounds belonging to the group of non-steroidal analgesic and anti-inflammatory drugs - DCL and the IBU. This is due to increased hydrophobicity of these drugs (Table 1) compared to the psychotropic drug. Different degree of adsorption of the studied compounds can also predict the efficiency of their photocatalytic decomposition.

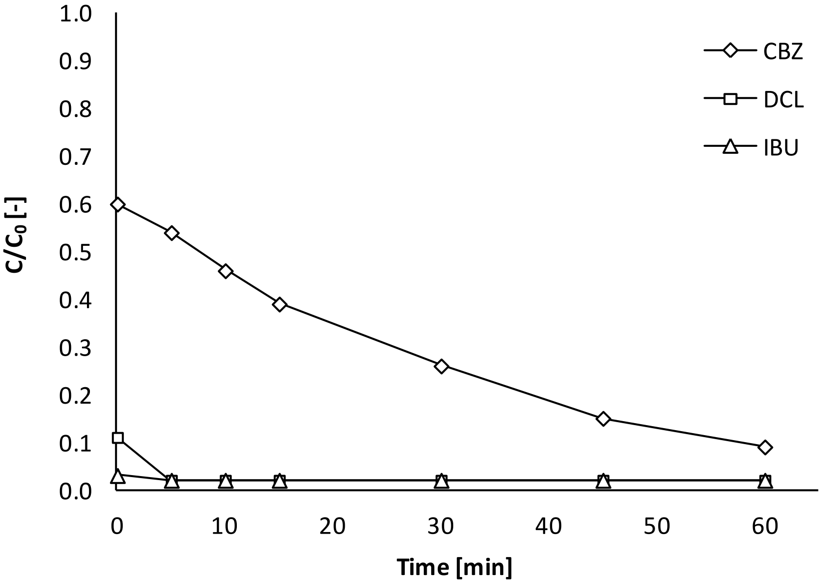


Fig. 2. Change of pharmaceuticals concentrations during the photocatalysis process
Source: own compilation

The efficiency of the removal of the compounds in the process of photochemical oxidation increased with increasing duration of irradiation. The removal efficiency of IBU and DCL after 5 min of the process was over 98%. The concentration of CBZ was reduced by 46% after the same irradiation time, and at the end of the irradiation process the removal efficiency of this pharmaceutical exceeded 91%.

It should be emphasized that the TiO_2 photocatalyst has a high chemical stability and it can be reuse after the separation in the microfiltration process. In some experiments the photocatalyst was reused up to five times without reducing the efficiency of treatment processes [19].

Chromatographic analysis showed that by-products of oxidation and reduction of the studied micropollutants were generated during the photocatalysis process. In the initial stage of the photocatalysis process (up to 10 min) three derivatives of diclofenac, among others, were identified: 4'-hydroxydiclofenac, 1-(2,6-dichlorophenyl)indolin-2-one and N-(2,6-dichlorophenyl)-2-aminotoluene, and 1-hydroxyibuprofen and 4-(1-carboxyethyl)benzoic acid, which are derivatives of ibuprofen. The following degradation by-products of CBZ: oxcarbazepine, 10,11-dihydro-10-hydroxycarbamazepine and carbamazepine-10,11-epoxide were identified at all stages of the photocatalytic oxidation process. The oxidation by-products can be much more toxic than the parent compound, which as a result can negatively affect the quality of the treated water.

The combination of the photocatalytic oxidation process with the process of two-stage membrane filtration appears to be a solution allowing to remove the oxidation and reduction by-products generated in photocatalysis processes and polish the retentate generated during the nanofiltration process. Therefore, in the further step of this study only the sequential combination of the process was considered. The schematic illustration in figure 3 shows a layout of the sequential system photocatalysis/microfiltration/nanofiltration for wastewater treatment. In the first treatment step the wastewater was subjected to the photocatalytic oxidation during 15 minutes, and then it was subjected to microfiltration to separate the catalyst particles from the mixture. The obtained permeate is directed to the second stage of membrane filtration in which nanofiltration membrane was used. The retentate generated during the process was recycled to the photocatalytic reactor.

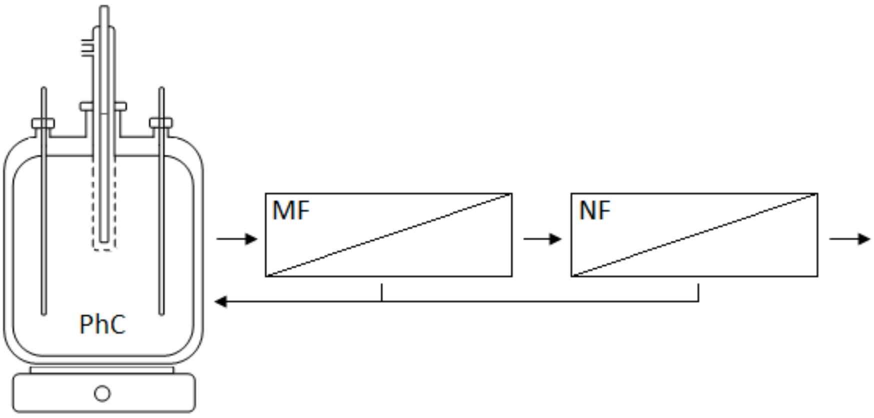


Fig. 3. Simplified scheme of the sequence system photocatalysis/microfiltration/nanofiltration (PhC – photocatalytic reactor; MF – microfiltration membrane; NF- nanofiltration membrane)
Source: own compilation

The wastewater treatment in the sequential system allowed to achieve complete elimination of pharmaceutical compounds (Fig. 4).

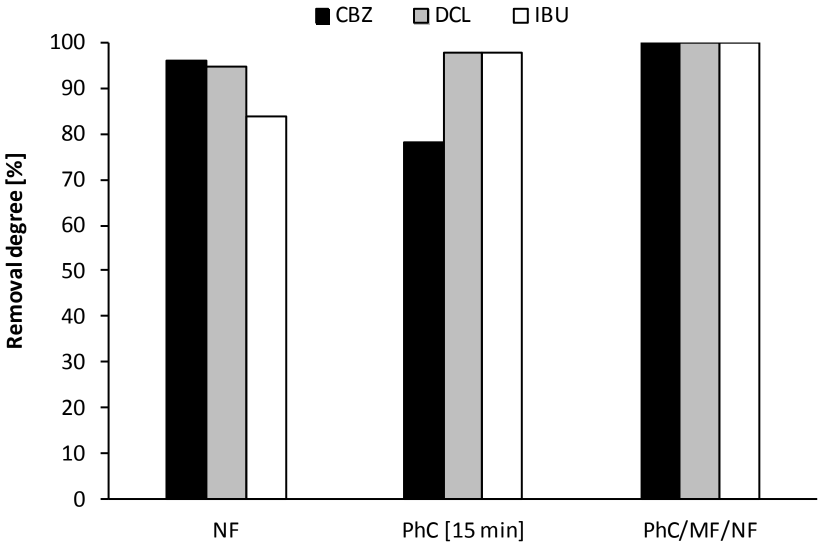


Fig. 4. Degree of pharmaceutical removal in single processes and in the sequence system
Source: own compilation

The pharmaceuticals and the by-products of oxidation and reduction of the drugs that were not mineralized in photocatalysis process were retained during nanofiltration already after 30 minutes of operation. Chromatographic analysis showed that the onset of the fouling phenomenon resulting in an increase of filtration resistance led to the elimination of both the parent forms of the pharmaceutical compounds, as well as their oxidation products that are characterized by significantly lower molecular weights and less complex structure of the molecule. This fact is attributed to formation of a so-called secondary membrane, which has lower porosity than the nanofiltration membrane on which it was formed. It can therefore be concluded that fouling caused by inorganic and high-molecular-weight subjected to chemical oxidation has positive effect on the retention of pharmaceuticals regardless of steric effects associated with the structure of micro-pollutants.

The efficiency of the sequential system after recycling the retentate from the mikro- and nanofiltration process was measured for three times. The obtain results do not indicate a reduction of the degree of removal of tested pharmaceutical micropollutants. Additionally, the filtration resistance noted in the third treatment process was about 1.5% higher than in the first process. In order to evaluate the economic feasibility of considered technology, further studies concerning inter alia the determination of the reduction of generated treated wastewater streams and the possibility of regeneration of membranes will be undertaken.

Summary and conclusions

The presence of pharmaceutical compounds in the aquatic environment may lead to an imbalance in the dynamic equilibrium within the entire ecosystem. Unit water treatment processes do not offer satisfactory removal efficiencies of organic micropollutants and their metabolites or generate toxic waste streams that require further purification. In contrast, the proposed wastewater polishing system that combines sequential processes of heterogeneous photocatalysis and micro- and nanofiltration allowed complete elimination of the investigated pharmaceutical compounds and their decomposition by products (both physiological metabolites and waste water treatment by-products). The obtained results can be used in the future as a basis of a technological design, which is a key element in designing or upgrading modern waste water treatment plants to meet increasingly stringent requirements for the elimination of organic micropollutants from the treated waste water.

References

[1] L.H.M.L.M. Santos, A.N. Araújo, A. Fachini, A. Pena, C. Delerue-Matos, M.C.B.S.M. Montenegro, Ecotoxicological aspects related to the presence of pharmaceuticals in the aquatic environment, J. Hazard. Mater. 175 (2010) 45–95.

[2] N.M. Vieno, H.Härkki, T. Tuhkanen, L. Kronberg, Occurrence of pharmaceuticals in river water and their elimination in a pilot-scale drinking water treatment plant, Environ. Sci. Technol. 41 (2007) 5077–5084.

[3] J.L. Santos, I. Aparicio, E. Alonso, Occurrence and risk assessment of pharmaceutically active compounds in wastewater treatment plants. A case study: Seville city (Spain), Environ. Inter., 33 (2010) 596–601.

[4] Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy (Dz. Urz. L 226 z 24.8.2013, s.1).

[5] Commission Implementing Decision (EU) 2015/495 of 20 march 2015 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council (Dz.U.UE.L.2015.78.40).

[6] R. Triebskorn, H. Casper, A. Heyd, R. Eikemper, H.R. Kohler, J. Schwaiger, Toxic effects of the non-steroidal anti-inflammatory drug diclofenac. Part II. Cytological effects in liver, kidney, gills and intestine of rainbow trout, Aquat. Toxicol., 68 (2004) 151-166.

[7] B. Hoeger, B. Kollner, D.R. Dietrich, B. Hitzfeld, Water-borne diclofenac affects kidney and gill integrity and selected immune parameters in brown trout (*Salmo trutta f. fario*), Aquat. Toxicol., 75 (2005) 53-64.

[8] F. Pomati, A.G. Netting, D. Calmari, B.A. Neilan, Effects od erythromycin, tetraycline and ibuprofen on the growth of *Synechocysts sp*. and *Lemna minor*, Aquat. Toxicol., 67 (2004) 387–396.

[9] C. Miège, J.M. Choubert, L. Ribeiro, M. Eusèbe, M. Coquery, Fate of pharmaceuticals and personal care products in wastewater treatment plants. Conception of a database and first results, Environ. Poll., 157 (2009) 1721–1726.

[10] A. Jelic, M. Gros, A. Ginebreda, R. Cespedes-Sánchez, F. Ventura, M. Petrovic , D. Barcelo, Occurrence, partition and removal of pharmaceuticals in sewage water and sludge during wastewater treatment, Water Res. 45 (2011) 1165–1176.

[11] N.A. Doerr-MacEwen, M.E. Haight, Expert stakeholders' views on the management of human pharmaceuticals in the environment, Environ Manage. 38(2006) 853–866.

[12] A. Rey, J. Carbajo, C. Adán, M. Faraldos, A. Bahamonde, J.A. Casas, J.J. Rodriguez, Improved mineralization by combined advanced oxidation processes, Chem. Eng. J. 174 (2011) 134–142.

[13] L. Feng, E.D. van Hullebusch, M.A. Rodrigo, G. Esposito, M.A. Oturan, Removal of residual anti-inflammatory and analgesic pharmaceuticals from aqueous systems by electrochemical advanced oxidation processes. A review, Chem. Eng. J. 228 (2013) 944–964.

[14] J.-C. Sin, S.-M. Lam, A.R. Mohamed, K.-T. Lee, Degrading Endocrine Disrupting Chemicals from Wastewater by Photocatalysis: A Review, International Journal of Photoenergy 2012 (2012) 1-23.

[15] H. Ozaki, N. Ikejima, Y. Shimizu, K. Fukami, S. Taniguchi, R. Takanami, R.R. Giri, S. Matsui, Rejection of pharmaceuticals and personal care products (PPCPs) and endocrine disrupting chemicals (EDCs) by low pressure reverse osmosis membranes, Water Sci. Technol., 58 (2008) 73–81.

[16] A. Simon, L.D. Nghiem, P. Le-Clech, S.J. Khan, J.E. Drewes, Effects of membrane degradation on the removal of pharmaceutically active compounds (PhACs) by NF/RO filtration processes, J. Membr. Sci., 340 (2009) 16–25.

[17] M. Dudziak, Separacja mikrozanieczyszczeń estrogenicznych wysokociśnieniowymi technikami membranowymi, Wydaw. Politechniki Śląskiej, Gliwice, 2013. (in Polish)

[18] J. Bohdziewicz, E. Kudlek, M. Dudziak, Influence of the catalyst type (TiO_2 and ZnO) on the photocatalytic oxidation of pharmaceuticals in the aquatic environment, Des. Wat. Treat. (in press)

[19] D. Suryaman, K. Hasegawa, S. Kagaya, T. Yoshimura, Continuous mineralization of concentrated phenol dissolved in an electrolyte-containing tap water by integrating biological–photocatalytic treatment with TiO_2 separation: utilization of sunlight and reuse of TiO_2, Environ. Technol., 30 (2009) 215–224.

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RATING AGENCIES ON FINANCIAL MARKET

Abstract

The article deals with genesis of rating agencies, their development and influence on the state of the local economy. This knowledge is crucial while conducting financial operations on any market. The article treats also about the most important issues related to the rating agencies. Article researches historical data based on financial reports published by Polish financial institutions. Conclusions of this research will help to understand the significance of rating agencies acting on financial markets, to judge rules of their operations and the quality of delivered ratings.

Key words

rating agencies, securities, investment risk

Introduction

Name of rating agencies comes from English “to rate” – meaning to measure the value or character of someone or something. It means the qualitative measure, based on overall analytical procedures, but covers a subjective opinion of analyst, who executes this procedure. Credit rating is a factor, described based on qualitative and quantitative data, which allow for grouping particular rated subject into one of several previously defined levels of credit capacity. Based on such a grade, lenders are able to estimate the level of risk of their current and potential borrowers. The concept of rating may be described as “including the borrower / issuer or a particular financial operation into one of many classes of credit risk, predefined within organized hierarchy, usually marked by letters and numbers with assigned levels of insolvency or loss”[1]. Rating agencies are autonomic institutions with their operational objective, being measuring and publishing the credit credibility of business entities, by estimating their defaulting risk.

The genesis of rating agencies

The birth of the credit rating agencies is associated with the trust crisis in United States during the great investments in post-crisis era with the beginning of XIX century. At this time there was a huge demand for objective and professional investment risk analysis that would be delivered by impartial organizations. Since then and until late 20th century, the credit rating sector has developed only in the United States. Enormous national investment projects planned for different fields of economy, delivered by private contractors and financed by government bonds that boosted the economy, became a cradle and natural place of evolution for rating agencies.

The purpose of rating agencies operation was to limit the risk related to investments by estimating and publishing information about the risk. The goal was not only to limit the risk related to investment in some specific single entity but first of all – limit the overall market risk estimated for many securities issuers. This was the reason why the credit rating phenomenon, as a measure of investment risk, appeared in state regulations relevant for economically and socially crucial institutions, such as: banks, insurance companies and pension funds. The bodies, supervising these institutions wanted them to invest only in the safe securities. Regulations forbade the institutions to invest in “speculative securities” [3], as they were defined in “recognized rating manuals”[3]. “Speculative” securities (currently known as junk bonds) were ones below the secure level of investment. Banks, insurance companies and pension funds were obliged to invest only in securities at the investment level – currently these would be securities rated BBB- or higher in Standard & Poor’s scale. With such regulations, institutions were forced to base their decisions on the data published by rating agencies in “recognized rating manuals”[3]. Thereby the rating agencies grades became a standard, which significantly increased the position of commercial companies engaged in rating market. At this time, it became bedrock for safety of the United States financial system.

In the history of rating agencies there are several phases of development to be outlined. At the beginning they acted as commercial inquiry offices, then specialized financial and business press, and finally they became the credit rating agencies of contemporary times. Table 1 shows this chronology.

Table 1. The history of rating agencies

<table>
<tr><td colspan="5">Pre-CRA</td></tr>
<tr><td>1832</td><td>1849</td><td colspan="2">1841</td><td>1849</td></tr>
<tr><td>The American Railroad Journal</td><td>„Poor's Manual of the Railroads of the United States"</td><td colspan="2">First informational agency that rated the financial liabilities of merchants (bought in 1859 by Robert Dun)</td><td>John Bradstreet agency</td></tr>
<tr><td colspan="5">CRA</td></tr>
<tr><td colspan="5">Phase 1 (1909-1943): creation and establishing of rating agencies sector</td></tr>
<tr><td>1909</td><td>1916</td><td>1930</td><td>1933</td><td>1941</td></tr>
<tr><td>Establishing John Moody's agency</td><td>Poor enters the rating sector.
John Knowles Fitch established Fitch Ratings</td><td>First legal regulations appearance</td><td>Dun&Bradstreet (D&B) consolidation</td><td>Fusion of Poor Company and Standard Statistics</td></tr>
<tr><td colspan="5">Phase 2: (1944-1969): economic stabilization – low demand for credit ratings</td></tr>
<tr><td>1962</td><td></td><td></td><td colspan="2"></td></tr>
<tr><td>D&B buys Moody's Investor Services</td><td></td><td></td><td colspan="2"></td></tr>
<tr><td colspan="5">Phase 3 (1970-2001): time of great economical turbulences and high demand for credit ratings</td></tr>
<tr><td>1970</td><td>1975</td><td>1995</td><td colspan="2">2000</td></tr>
<tr><td>Penn Central securities insolvency
Introduction of *issuer-pays* model</td><td>SEC provides the list of Nationally Recognized Statistical Rating Organization (NRSRO)</td><td>Fitch Ratings becomes a part of Fimalac S.A.</td><td colspan="2">Fitch Ratings buys Duff & Phelps Credit Rating Co.</td></tr>
<tr><td colspan="5">Phase 4 (2002-today): fast development of financial innovations, rating agencies expand beyond the US market. Financial crisis of 2007/2008 and new legal changes related to rating agencies.</td></tr>
</table>

Source: Langohr H. M., Langohr P. T., *The rating agencies and their credit ratings. What they are, how they work and why they are relevant*, John Wiley and Sons Ltd., Chichester, 2008, page 376.

Today's rating agencies sector is divided between three agencies of global scope: Moody's Investor Service (Moody's), Standard and Poor's Rating (S&P) and Fitch IBCA (Fitch), which is the smallest of them [4].

Role of ratings and rating agencies.

Rating agencies can be defined as commercial investment consulting enterprises, which run qualitative classification of entities and financial instruments in order to mark each of them with the financial trust grade, expressed in letter code [2]. Rating agencies describe themselves as independent institutions providing information about financial credibility. To achieve this goal, they provide estimations on current and prospective financial condition of business entities and financial instruments issued by them. However, the grade, yet never free from subjective opinion, might be a reason for a loss caused by misjudged rating. Unfortunately, this is not included in the contract between the evaluator and graded party, so possible loss cannot be fulfilled. Therefore, it can be claimed that there are no legal mechanism to control the ratings, so value and quality of ratings depend on the good will of rating agencies and their motivation to uphold solid reputation on the financial markets. Credit rating is a universal tool to measure the level of investment risk, which allows comparing the financial credibility of entities operating on different markets. The same process applied to different entities constitutes a certain standard for grading the financial risk [6]. It is embraced as a grade of financial credibility, a financial credibility itself, financial standing, current estimation of credit credibility, including the character of obligations and qualitative measure of securities, based on issuer's reliability in the past and forecasting his future financial condition as well [6].

Table 2. Rating agency functions

	Issuers	Investors	Supporting institutions
Informative function	Informative brokaring: ▪ Production of information ▪ Contribution to reputation growth		
		Economies of scale in information production	
	Public information announcement		
Rating function			Regulations based on credit rating
	Private risk management		
Monitoring and standarization function	Credit / Investment process		
		Risk comparizon	

Source: Dittrich F., The Credit Rating Industry: Competition and Regulation, University of Cologne, 4 June 2007, p. 14: http://papers.ssrn.com/sol3/papers.cfm?abstract_id=991821, 14.04.2011.

As described in Table 2, there are three roles of rating agencies. First of all, they provide information, which strengthens the financial standing of issuers and allows investor to derive benefits from economies of scale. Secondly, rating agencies have a certification role – rating allows managing private risks and is a regulatory instrument. Thirdly, by standardization, rating provides overall view on issuance of debt securities and allows comparing the risk. There are also some factors, perceived within the economic and political framework that is based on intuition, therefore they cannot be proved.

The credit rating market is an oligopoly of top three agencies: Standard & Poor's, Moody's and Fitch. This is the result of natural accumulation processes, but also entry barriers instituted by NRSRO (Nationally Recognized Statistical Rating Organization), which weakened the competition between agencies. According to The Economist publishers this is caused by the Securities and Exchange Commission (SEC). However, as it was already mentioned, that this situation has also some advantages, because limited competition allows the rating agencies to remain resistant to issuers influence. It also became a principle already that issuers require ratings from all three agencies.

Table 3 shows symbols used by rating agencies. They represent grades – alone or modified with additional marks. Moody's uses symbols starting with AAA up to C for long-term securities and from P-1 to NP for short-term securities. Standard & Poor's classifies ratings from top grade AAA to minimum D for long-term securities, but for short-term securities these are A1 to D. Fitch is very similar to Standard & Poor's for long-term securities, but short-term securities are graded between F1 and F3 (investment category) and between B and D (speculative category).

Table 3. Rating classes

	Moody's		Standard & Poor's		Fitch Ratings		Profile
	long-term	short-term	long-term	short-term	long-term	short-term	
Investment level	Aaa	P-1	AAA	A-1+	AAA	F1+	„Prime". The highest safety of the investment.
	Aa1		AA+		AA+		High investment quality.
	Aa2		AA		AA		
	Aa3		AA-		AA-		
	A1		A+	A-1	A+	F1	Average-high rating. Average quality investment.
	A2		A		A		
	A3	P-2	A-	A-2	A-	F2	
	Baa1		BBB+		BBB+		Average low rating. Average-low investment quality.
	Baa2	P-3	BBB	A-3	BBB	F3	
	Baa3		BBB-		BBB-		
Speculative level	Ba1	Not Prime	BB+	B	BB+	B	Speculative level
	Ba2		BB		BB		
	Ba3		BB-		BB-		
	B1		B+		B+		Highly speculative level
	B2		B		B		
	B3		B-		B-		
	Caa1		CCC+	C	CCC	C	High investment risk
	Caa2		CCC		CCC		Extremly high investment risk
	Caa3		CCC-		CCC-		Risk of losing invested capital
	Ca1		CC+		CC+		
	Ca2		CC		CC		
	Ca3		CC-		CC-		
	C		C		C		
	/		D	SD/D	DDD	RD/D	Issuer's insolvency
/					DD		
					D		

Source: own work, based on Dziawgo D., Credit Rating na międzynarodowym rynku finansowym, Polskie Wydawnictwo Ekonomiczne, Warszawa, 2010, page 152-171, Fitch Ratings, Fitch ratings definitions: International short term ratings, „Re Library", March 26, 2007, page 1-3 and data available atMoody's Investors Service http://www.moodys.com/researchdocumentcontentpage.aspx?docid=PBC_79004

Rating for Poland and Polish financial institutions

In 1997 Polish Bank Association supported by United States Agency for International Development (USAID) initiated establishing of Central-European Center for Rating and Analysis S.A. (CERA). Shortly after it started to operate, CERA was taken over by Thomson Financial BankWatch, and afterwards by Fitch – as mentioned currently one of the biggest rating agencies in the world. Thereby, originally Polish company lost its local nature and became a part of international corporation. A Table 4 below shows reversed chronology of facts related to rating Poland by Fitch. Data indicate slight progression in ratings issued for Poland. The long-term ratings stabilize at BBB+ level and the sort-term at F2.

Table 4. History data for rating of Poland by Fitch

		Foreign currency rating			Local currency rating	
Country	Date	Long-term	Short-term	outlook/watch	Long-term	outlook/watch
Poland	18 Jan 2007	A+	F2	stable	A	stable
Poland	23 Mar 2005	BBB+	F2	positive	A	stable
Poland	6 May 2004	BBB+	F2	stable	A	stable
Poland	4 Nov 2003	BBB+	F2	positive	A+	stable
Poland	21 Sep 2000	BBB+	F2	stable	A+	stable
Poland	19 Nov 1998	BBB+	F2	-	A+	-
Poland	7 Jun 1996	BBB	F3	-	A-	-
Poland	29 Apr 1996	BB+	B	Rating Watch positive	-	Rating Watch positive
Poland	26 Oct 1995	BB+	B	-	-	-

Source: Fitch – Complete Sovereign Rating History 10.11.2012.

Tables 5a and 5b show ratings of Poland against ratings of other countries of European Union, all issued by Standard & Poor's allows picturing economic situation of Poland. Current S&P rating defines Poland as a financially stable country, which for many economists seems to be an overestimated grade. As an argument they point out Poland's high unemployment, low birth-rate, high work emigration, growing foreign and domestic debt and tremendous negligence in developing road infrastructure. As shown in Table 5a Poland has low Gross Domestic Product per capita in relation to other countries of the European Union and quite high, but lowering GDP growth; moderate public debt; high unemployment rate – but not the highest in the EU, and fairly high interest rates comparing to other European countries, but also globally[1].

Table 5a. Ratings of Poland against ratings of other member states of the European Union

	GDP (bln EUR)		GDP per capita EU=100		Public debt (% GDP)		Unemployment rate (%)		S&P country rating	
	2006	2011	2006	2011	2006	2011	2006	2011	2006	**2012**
Austria	259	301	126	126	62,3	72,2	4,4	4,1	AAA	**AA+**
Belgium	319	368	118	119	88	98,2	7,9	7,1	AA+	**AA**
Bulgary	26	38	38	44	21,6	16,3	8,2	11,8	BBB+	**BBB**
Cyprus	15	18	91	99	64,7	71,6	4,4	9,5	A	**BB+**
Czech Republic	118	155	80	80	28,3	41,2	6,4	6,7	A-	**AA-**
Denmark	219	240	124	127	32,1	46,5	3,9	7,8	AAA	**AAA**
Estonia	13	16	66	64	4,4	6	5,7	11,7	A	**AA-**
EU	11695	12629	100	100	-	-	7,8	10	-	**-**
EURO zone	8565	9414	109	108	-	-	8	10,6	-	**-**
Finland	166	192	114	115	39,6	48,6	7,3	7,6	AAA	**AAA**
France	1798	1997	108	108	64	86	8,8	9,9	AAA	**AA+**
Germany	2314	2571	115	118	68,1	81,2	9,6	5,6	AAA	**AAA**
Greece	209	215	92	90	107	165	8,7	21	A	**CCC**
Hungary	90	101	63	65	65,9	80,6	7,5	11	BBB+	**BB+**

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[1] According to data available on October 2012 basic interest rates in non-European countries were: Australia 3,75; Japan 0,10; Canada 1,0; Norway 1,75; New Zealand 2,50; Switzerland 0,25.

Irland	178	156	146	128	24,5	108	4,3	14,7	AAA	**BBB+**
Italy	1493	1580	105	101	106	120	6,3	9,3	A+	**BBB+**
Latvia	16	20	51	51	10,7	42,6	6,2	14,6	A-	**BBB-**
Lithuania	24	31	56	57	17,9	38,5	4,9	14,3	A	**BBB**
Luxemburg	34	43	270	271	6,7	18,2	4,6	5,1	AAA	**AAA**
Malta	5	6	76	83	64,4	72	6,8	6,7	A	**A-**
Netherlands	540	602	131	133	47,4	65,2	4	4,9	AAA	**AAA**
Poland	**272**	**370**	**52**	**63**	**47,7**	**56,3**	**11,9**	**10**	**BBB+**	**A-**
Portugal	161	171	79	80	69,3	108	9,2	14,6	AA-	**BB**
Romania	98	136	38	46	12,4	33,3	7,2	7,5	BBB-	**BB+**
Slovakia	45	69	63	74	30,5	43,3	12	14,1	A	**A**
Slovenia	31	36	88	85	26,4	47,6	5,4	8,7	AA	**A+**
Spain	986	1 073	105	100	39,7	68,5	8,3	23,2	AAA	**BBB+**
Sweden	318	387	123	123	45	38,4	6,4	7,5	AAA	**AAA**
United Kingdom	1949	1737	120	112	43,4	85,7	5,5	8,3	AAA	**AAA**

Source. Own work based on: Raport o sytuacji banków w 2011 r. KNF, Warszawa 2012; Monitor konwergencji nominalnej MF DPF AS 9 / 2012;http://www.money.pl/gospodarka/unia-europejska/statystyka; Money.pl.

Table 5b. National economy performance indicators of Poland and other member states of the European Union

	GDP growth rate (%)							Inflation	reference rate %	Long-term interest rate %	Inflation HICP y/y	General government deficit (%GDP)
	2007	2008	2009	2010	2011	2012	2013	2011	10 /12	06 /12	06 /12	2011
Austria	3,7	1,4	-3,8	2,3	3,1	0,8	1,7	0,7	1,00	2,1	2,1	-2,6
Belgium	2,9	1	-2,8	2,2	1,9	-0,1	0,2	0,5	1,00	2,7	2,0	-3,7
Bulgary	6,4	6,2	-5,5	0,4	1,7	0,6	0,9	0,5	-	4,9	2,4	-2,1
Cyprus	5,1	3,6	-1,9	1,1	0,5	-2,4	-5,4	-1,5	1,00	7,0	3,8	-6,3
Czech Republic	5,7	3,1	-4,7	2,7	1,7	-1	-0,9	-0,7	0,50	2,6	3,3	-3,1
Denmark	1,6	-0,8	-5,8	1,3	1	-0,4	0,4	0,4	0,45	1,1	2,1	-1,8
Estonia	7,5	-3,7	-14	2,3	7,6	3,9	0,8	3,7	1,00	-	4,1	1,0
EU	3,2	0,3	-4,3	2	1,5	0	1,3	2,9	-	4,2	2,5	-
EURO zone	3	0,4	-4,3	1,9	1,5	-0,3	1	2,8	1,00	3,8	2,4	-
Finland	5,3	0,3	-8,4	3,7	2,9	-1	-1,4	1,7	1,00	1,6	3,1	-0,5
France	2,3	-0,1	-3,1	1,7	1,7	0	0,2	0,3	1,00	2,3	2,2	-5,2
Germany	3,3	1,1	-5,1	3,7	3	0,7	0,4	1,2	1,00	1,2	1,9	-1,0
Greece	3	-0,2	-3,3	-3,5	-6,9	-7	-3,9	3,5	1,00	25,8	0,9	-9,1
Hungary	0,1	0,9	-6,8	1,3	1,7	-1,7	1,1	-1,4	7,0	1,5	2,6	-8,3
Irland	5,2	-3	-7	-0,4	0,7	0,2	-0,3	2,6	1,00	6,1	2,0	-13,3
Italy	1,7	-1,2	-5,5	1,8	0,4	-2,4	-1,9	-1,4	1,00	6,0	3,6	-3,9
Latvia	9,6	-3,3	-18	-0,3	5,5	5,2	4,1	5,6		4,7	1,9	-3,5
Lithuania	9,8	2,9	-15	1,4	5,9	3,7	3,3	4,4		4,8	2,9	-5,5
Luxemburg	6,6	0,8	-5,3	2,7	1,6	-0,2	2,1	0,0	1,00	1,7	2,7	-0,6

Malta	4,3	4,1	-2,7	2,3	2,1	0,6	2,4	-,0,4	1,00	4,2	4,2	-2,7
Netherlands	3,9	1,8	-3,5	1,7	1,2	-1,2	-0,8	-0,8	1,00	1,8	2,6	-4,7
Poland	6,8	5,1	1,6	3,9	4,3	2	1,6	3,8	4,75	5,0	4,0	-5,1
Portugal	2,4	0	-2,9	1,4	-1,6	-3,2	-1,4	-2,20	1,00	10,5	2,8	-4,2
Romania	6,3	7,3	-6,6	-1,6	2,5	0,6	3,5	0,8	-	6,5	3,1	-5,2
Slovakia	10,5	5,8	-4,9	4,2	3,3	1,8	0,9	-0,8	1,00	4,4	3,8	-4,8
Slovenia	6,9	3,6	-8	1,4	-0,2	-2,5	-1,1	3,2	1,00	6,3	2,6	-6,4
Spain	3,5	0,9	-3,7	-0,1	0,7	-1,6	-1,2	-0,4	1,00	6,8	2,2	-8,5
Sweden	3,3	-0,6	-5	6,1	3,9	0,9	1,5	1,5	1,5	1,3	0,7	0,3
United Kingdom	3,5	-1,1	-4,4	2,1	0,7	0,3	1,7	-0,2	0,5	7,6	5,7	4,3

Source. Own work based on: Raport o sytuacji banków w 2011 r. KNF, Warszawa 2012; Monitor konwergencji nominalnej MF DPF AS 9 / 2012; http://www.money.pl/gospodarka/unia-europejska/statystyka; Money.p

Table 6 shows historical data of ratings for economically weaker European countries, delivered by all three agencies. As it can be seen, regardless of issuer, the ratings are very similar.

Table 6. Ratings of Poland against ratings of selected European countries.

	Moody's			S&P			Fitch		
	2012 July	2010 July	2007 July	2012 July	2010 July	2007 July	2012 July	2010 July	2007 July
Greece	C (Ca)	Ba1 (A3)	A1 (A2)	CCC			CCC (B-)	BBB- (BBB+)	A (A)
Ireland	Ba1 (Baa3)	Aa2 (Aa1)	Aaa (Aa1)	BBB+			BBB+ (BBB+)	AA- (AA+)	AAA (AAA)
Spain	Baa3 (A3)	Aaa (Aa2)	Aaa (Aa2)	BBB+ (A)	AA		BBB (A)	AA+ (AAA)	AAA (AAA)
Portugal	Ba3 (Ba2)	A1 (Aa2)	A1 (Aa2)	BB (BBB-)			BB+ (BBB-)	AA- (AA)	AA (AA)
Italy	Baa2 (A3)	Aa2 (Aa3)	Aa2 (Aa3)	BBB+ (A)			A- (A+)	AA- (AA)	AA- (AA)
Poland	A2 (Baa1)	A2 (Baa1)	A2 (Baa1)	A-	A-	A-	A- (BBB+)	A- (BBB+)	A- (BBB+)
Czech Republic	A1 (Baa1)	A1 (Baa1)	A1 (Baa1)	AA-			A+ (A+)	A+ (A+)	A (A-)
Hungary	Ba1 (Baa3)	Baa1 (A3)	A2 (A1)	BB+ (BBB-)	BBB-		BB+ (BBB-)	BBB (BBB)	BBB+ (BBB+)

Source : Own work based on data available at: http://www.moodys.com, http://www.standardandpoors.com http://www.fitchratings.com.

Ratings shown in Table 6 do not seem to relate to economy performance indicators shown in Table 5b. This might determine that either the ratings were not based on the same indicators or the update of those ratings was delayed significantly.

Table 7 Polish banks' ratings according to Moody's and Fitch

Moody's	Financial strenght rating	Long-term deposit rating	Short-term deposit rating	Forecast
PKO BP	C- (C-)	A2 (A2)	P-1 (P-1)	STA (STA)
Pekao	C- (C-)	A2 (A2)	P-1 (P-1)	STA (STA)
ING Bank Śląski	D+ (D+)	A2 (A2)	P-1 (P-1)	NEG (STA)
BRE Bank	D (D)	Baa1 (A3)	P-2 (P-2)	STA (DNG)
BZ WBK	D+ (D+)	Baa2 (Baa2)	P-2 (P-2)	NEG (NEG)
Bank Millennium	D (D)	Baa2 (A3)	P-3 (P-2)	DNG (DNG)
Bank Handlowy	D+ (D+)	Baa1 (Baa1)	P-2 (P-2)	NEG (NEG)
BGŻ	D (D)	A3 (A3)	P-2 (P-2)	STA (STA)
Getin Noble Bank	D- (D-)	Ba2 (Ba3)	NP (NP)	STA (NEG)
BPH	D (D-)	Baa2 (Baa2)	P-2 (P-2)	STA (UPG)
Lukas Bank	D+ (C-)	A3 (A2)	P-2 (P-1)	NEG (STA)
BRE Bank Hipoteczny	E+ (E+)	Baa3 (Baa3)	P-3 (P-3)	STA (DNG)
Fitch	Individual rating	Long-term rating	Short-term rating	Forecast
Pekao	C (C)	A- (A-)	F2 (F2)	NEG (NEG)
ING Bank Śląski	C (C)	A (A)	F1 (F1)	STA (STA)
BRE Bank	C/D (C/D)	A (A)	F1 (F2)	STA (STA)
BZ WBK	C (C)	BBB+ (BBB+)	F2 (F2)	STA (NEG)
Bank Millennium	C/D (C/D)	A (A)	F1 (F1)	NEG (STA)
Getin Noble Bank	D (D)	BB (BB)	B (B)	No indication ()
BOŚ	D (D)	BBB (BBB)	F3 (F3)	STA (STA)

Source: Own work based on data available at: http://www.moodys.com, http://www.standardandpoors.com http://www.fitchratings.com.

Summary

Rating agencies are definitely useful and beneficial for financial markets. Information published by these agencies allows both parties of financial transactions to secure their business. However, there are several issues related to the way rating agencies operate. First, they are not subject to liability. They are able to have significant influence on the market by publishing the credit rating as a protection of investors business, but there is no guarantee of accuracy of such rating and rated entity has no power to appeal. The rating itself becomes a subjective opinion. The evidence for this statement might be historical data, showing that several subjects with high and safe ratings became bankrupt. Another significant issue is excessive rating unanimity. By comparing ratings of the biggest rating agencies (Moody's, S&P's and Fitch) it is obvious that grade differ very rarely when issued to the same subjects. It may raise suspicions of collusion between them. Third problematic area is bias caused by social and cultural conditions. The ratings might be based on preferred economic policy and American originated agencies seem to discriminate issuers that do not follow Anglo-American management and financial policies. This kind of subjective way of granting the ratings might indirectly influence on rated countries or entities. As indicated before – the rating is not always adequate to the condition of rated country. Another issue, worth mentioning is a tendency to grant the ratings without any request from the rated entity.

When the entity stops to order ratings from agency, the free of charge non-requested low quality rating might be a way of retaliation.

It is highly important, that rating agencies describing themselves as independent institutions providing information about financial credibility, provide not only accurate estimations, but also up to date. Credit ratings – when not updated quickly enough – may affect the business cycles. On one hand they may slow down the reaction before the crisis and on the other, they may delay the market boom. The gaps in correlation between significant changes within the national economy of some countries listed in Table 5b and their ratings show that such situations already happened. This may lead to situations when investors decisions are made based on misleading information, which doesn't include changes in the level of risk.
However the rating, when issued, will be considered up to date until publishing the next one. The suggested solution for this issue might be providing each rating with its validity, which will alert the investors, when expired.

References

[1] De Laurentis G., *Rating interni e credit risk management*, Bancaria Editrice, Roma, 2001, p. 103.

[2] Dziawgo D., Credit Rating na międzynarodowym rynku finansowym, Polskie Wydawnictwo Ekonomiczne, Warszawa, 2010, p. 124.

[3] White L. J., Markets. The Credit Rating Agencies, "Journal of Economic Perspectives", Volume 24, nr 2, Spring 2010, pp. 211-226.

[4] White L. J., The credit rating industry: an industrial organization analysis, [w]: Levich R. M., Majnoni G., Reinhart C., Ratings, rating agencies and the global financial system, Kluwer Academic Publishers, Boston, 2002, p. 44.

[6] Dziawgo D., *op. cit.*, p. 69.

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APPLICATION LCA FOR ECO-EFFICIENCY ASSESSMENT OF INVESTMENTS PROJECTS

Abstract

Eco-efficiency which takes into account the life cycle idea is a relatively new concept described by ISO International Standard 14045:2012. It can be used in environmental management by integration environmental considerations with economic analysis to improve products and technologies. Nowadays, eco-efficiency is a strategic tool and it is one of the key factors of it sustainable development. In the investment decision-making process, to assess new technology solutions and to choose the best options, the eco-efficiency account should be introduced. Life Cycle Assessment (LCA) as a method used to assess environmental aspects and quantified impacts of investment project is proposed. Life cycle cost analysis being the combination of Net present value (NPV) with life cycle cost (LCC) was chosen for quantifying their financial effects. The eco-efficiency analysis based on LCA can be recommended not only as a decision support tool for individual investors, but also for ranking of investment projects when applying of financial support from structural or other national funds, as well in sustainable public procurement.

Key words

eco-efficiency, environmental protection, investment project, Life Cycle Assessment (LCA)

Introduction

In economic policy of many countries, and in the strategies of institutions and international organizations (European Union, United Nations), along with the increase in consumer awareness, attention paid to the issue of product quality improvement and environmental protection has begun to grow. Consequently, economic operators, particularly from the EU countries, must meet specific requirements for high quality products, applying the technologies intended to further reduce environmental impacts [1]. The environmental technology sector is perceived worldwide as one of the most dynamically developing areas of the economy. Currently, the investments in environmental protection project registered an increasing trend all around the world. Studying their efficiency provides insights for further developing of new investments. The investments efficiency issue is very complex, based on a large number of generated effects. It covers three distinctive concepts:

- economic efficiency of investments;
- environmental (or ecological) efficiency of investments;
- social efficiency of investments [2].

This work is focused on economic and environmental efficiency of investments concepts. It has to be mentioned that environmental performance can, and should be used to assess the planned investment projects, especially those designed to protect the environment. In the investment decision-making process, to assess new technology solutions, the eco-efficiency account should be introduced. In the present paper, Life Cycle Assessment (LCA) as a method used to assess environmental aspects and quantified impacts of investment project is proposed.

Eco-efficiency of investment projects

In the literature, the term ‘eco-efficiency’ has been given a range of different meanings [3], e.g. in Cicea et al. studies, an environmental efficiency is found as ecological efficiency or eco-efficiency [2]. A general definition of eco-efficiency is contained in the report of the World Business Council for Sustainable Development [4]. Eco-efficiency is considered as a management philosophy that focuses on reducing environmental intensity and increasing environmental productivity while also reducing costs and creating value [5-8]. It has been recognized that for many of consumer products, a large share of the environmental impacts is not only in the use of the product but in its production, transportation or disposal. Therefore, in choosing an investment project, environmental impacts generated by all parts of a product's life cycle, from acquisition of materials through manufacture a recovery or disposal, must be considered. In ISO 14045:2012 it was proposed to take into account the whole value chain in eco-efficiency assessment, including environmental and product-system-value assessment. The key objectives of ISO 14045 are to present clear terminology and a common methodological framework for eco-efficiency assessment, practical use of eco-efficiency assessment for a wide range of product (and service) systems, including interpretation of eco-efficiency assessment results and transparent and informative reporting of eco-efficiency assessment results. Environmental assessment in eco-efficiency evaluation shall be based on Life Cycle Assessment (LCA) according to ISO 14040:2006.

In practice, eco-efficiency is best understood as an efficient use of natural resources, minimization of waste and pollution at every stage of production while ensuring quality of delivered goods and services, and providing cost-effectiveness. Nowadays, eco-efficiency is one of the key goals in corporate environmental management, which brings together economic and ecological issues [9-11]. It is worth to note that in the countries of the European Union in recent years the dynamic growth of expenditures on environmental protection was observed. According to EUROSTAT database (2015) in EU (28 countries) between 2004 and 2011 expenditures on environment protection increased from 133.4 to 171.0 EUR per inhabitant [37]. Environmental fees and penalties as well as access to EU funds allowed to accumulate significant resources to finance investment and ecological activities. Initially, the criteria for the granting of financial assistance were very mild, but over time more and more attention has been paid to the selection of investment projects, which meet both economic and ecological criteria. Given the importance of public procurement, there is certain that increased focus on environmental performance in the public sector will have a great impact on business. The companies that are not able to provide information about the environmental performance and the life cycle costs (LCC) of products have face difficulties in getting contracts with the public sector now and still in the future. Consequence of this is steadily more common measures of eco-efficiency in industry [12]. For example, an evaluation of the economic and ecological feasibility of new and existing mining projects using a combination of environmental goals expressed in life cycle assessment (LCA) results with economic goals expressed within life cycle costing (LCC) was proposed in [35] study. The authors emphasize that mining producers can reasonably expect that implementation of LCA and LCC will lead to minimisation of environmental impact of their activities and to more effective environmental, cost and waste management. This means savings through reducing the amount of waste emissions and a decrease in fees and fines [35].

In Poland, environmental performance (cost) is defined as the discounted net benefit streams, attributed per unit of physical environmental effects, for example on the pollution reduction. In this perspective, it can be a tool for ranking and evaluation of protective projects, according to the relationship:

$$EE = \frac{NPV}{eWC}$$

where:
EE - environmental performance,
eWC - ecological material effects in natural units,
NPV - net present value (discounted cash flows).

The condition of efficiency should be at least zero and positive NPV value, and a similar value per unit of environmental effects. In case of difficulty in assessing the value of the cash inflows (or profits) of the proposed investment, the analysis can be limited to comparing the discounted value of the expenses (costs), which includes external costs, per unit of environmental effects [13]. In the Adeoti et al. study, the discounted cash flow micro-economic assessment to evaluate the 6.0 m^3 family-sized biogas project in Nigeria, based on the NPV values was used. The results shows that the 6.0 m^3 family-sized biogas project using cattle dung as substrate in Nigeria has a good economic potential [33]. In another work, the authors indicated that addressing social and environmental concerns makes financial sense in the analyzed investment project (Camisea project). In present value terms (based on NPV values), the benefit of managing these concerns was expected to surpass the cost investment by approximately US$50 million [34]. It need to be noticed that using the life cycle net present value (LCNPV) method it is possible to compare different investment options, and this method can be treated as a tool that can help producers to make better decisions pertaining to environmental protection. Study of the influence of the environmental cost of projects should be based on long-term analysis of environmental investment [35].

Implementation of eco-innovative technologies

The dissemination and implementation of eco-innovative technologies is essential because of growing legal requirements and increased competition [14]. In this respect, technologies increasing productivity, minimising the amount of recycling and waste, reducing energy and material consumption (low-input technologies) should be sought and implemented [15]. Implementation of such measures will depend on business strategy and environmental, economic and social objectives set out therein. Integration and effective identification of those objectives usually requires conducting additional activities relating to:

- extension of corporate financial reporting by environmental protection aspects, and identifying the environmental protection costs of individual unit processes,
- application of investment effectiveness calculation from the perspective of the life cycle of the object, i.e. the investment phase, service phase (e.g. greater capital expenditures on buildings can result in a significant reduction in operating costs such as heating), and post-production phase (such as closing costs, rehabilitation and monitoring of waste disposal facilities),
- inclusion of environmental aspects in the design phase, i.e. the implementation of innovation technologies based on the eco-balance of the entire life cycle of the product (eco-design),
- incurring higher costs for research and implementation of new and innovative technological solutions and marketing costs to market new products (e.g. in the case of those derived from waste, it is necessary to demonstrate that they have no longer the status of waste according to law).

External factors pose also some difficulty to the entrepreneurs, namely:

- lack of system solutions relating to the environmental protection and rapidly changing legal provisions,
- diversity of multiple indicators to assess the ecological effects, in the absence of universally accepted, standardised model of ratio analysis for their quantification,
- lack of support mechanisms that would promote seeking comprehensive solutions, taking into account environmental, economic and social aspects.

Although, in Poland for years there have been grants or loans for environmental project available from the national funds (such as the National Fund for Environmental Protection and Water Management), and, recently, also from the EU funds (e.g. Structural Funds), the business operators fund the majority of such projects with their own resources. Supporting eco-innovative projects designed to reduce negative environmental impacts, at every stage of the product life cycle, requires the development and implementation of rules for their evaluation, taking into account the technical feasibility, economic and ecological efficiency, and consideration to social aspects. The selection of such investment solutions should be made based on:

- analysis and assessment of possible technological solutions, such as with the cumulative account method, the technological quality, best available techniques (BAT),
- assessment of environmental impacts of the project, based on the eco-balance developed,
- assessment of potential environmental impacts of various processes, including pre-production activities (so called upstream, for example transportation of raw materials), and post-production activities (so called downstream, such as the operation phase of a manufactured product), this way, transfer of environmental effects from one phase process to another (e.g. from the production to operation phase), from one region to another, or from one preserved area (water) to another (air), is avoided. The LCA method could be applied for that,
- account of project eco-efficiency, taking into account the synchronisation of economic and environmental effects [13].

Taking into account the above considerations, for the assessment of new technology solutions during the investment decision-making process, the eco-efficiency account should be introduced. It uses dynamic methods, combined with eco-balance methods, particularly the LCA and LCC. Such approach allows the assessment of eco-efficiency of the planned projects by quantifying their financial and environmental effects, and then, their prioritisation, depending on the adopted criterion.

Life Cycle Assessment method (LCA)

Currently, different approaches for eco-efficiency analysis are suggested: cost-benefits analysis CBA, life-cycle analysis LCA, contingent valuation CV [16]. According to the International Organization for Standards (ISO), Life Cycle Assessment is a method used to assess environmental aspects and impacts of products [17]. According to the official definition given by the European Commission, LCA is the process of collecting and evaluating data "input" and "output" of the product, as well as the potential impact on the environment throughout its life cycle: production, use and disposal (Figure 1) - estimating environmental effects caused by products and processes from ‘cradle to grave’ or ‘cradle to cradle‘ [18]. In recent years, the perspective that LCA provides on the environmental performance of products had been made it a central concept for both environmental management in industry and environmental policy-making in public government [19]. The development and harmonization has occurred resulting in an international standard (ISO), complemented by a number of guidelines and textbooks. This has increased the maturity and methodological robustness of LCA. However, this method is still under development [20, 21].

Introduction of LCA in investment projects will allow taking into account all the factors that could potentially affect the environment and which are associated with the product. However, it should be noted that in LCA analysis the product can be a particular item/ product, an entire or part of a production process or use of the product, as well as the particular service or even an economic system [20]. Analyses with the LCA method involve quantification and assessment of the environmental effects during the entire life cycle, based on the developed material and energy balance [23].

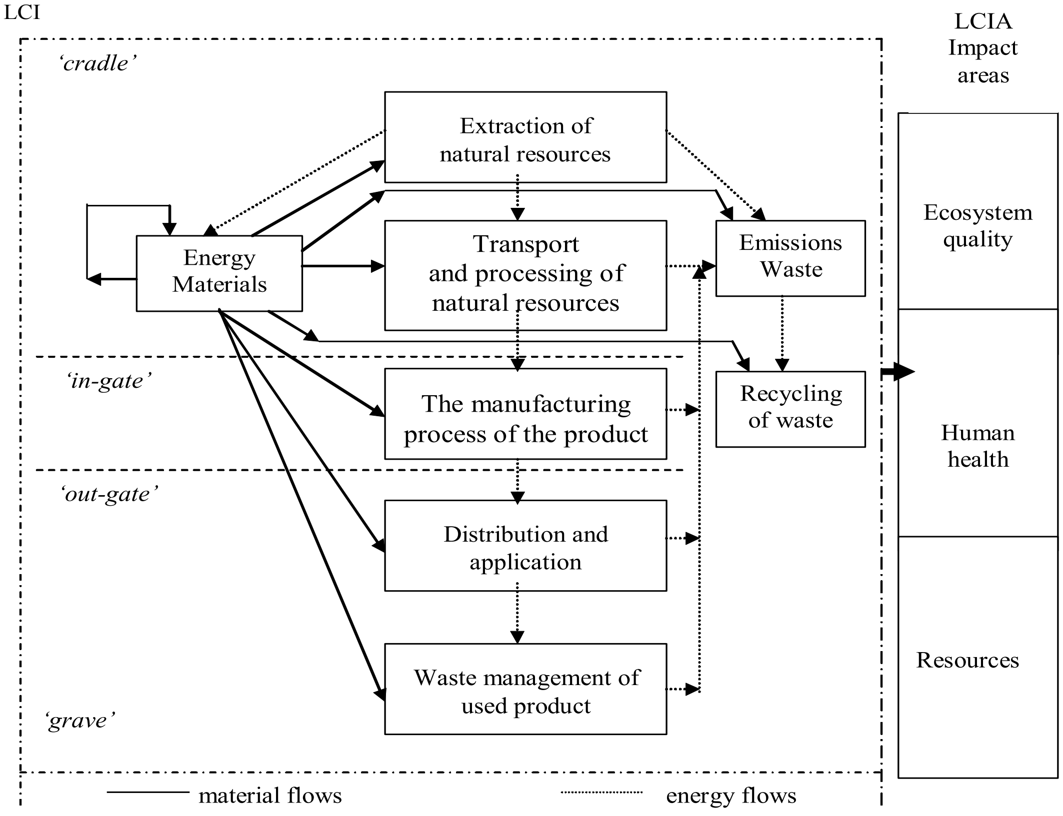

Fig. 1. LCA life cycle scheme
Source: [13]

The magnitude and significance of environmental, economic or social costs associated with specific life cycle activities are identified during the Life Cycle Impact Assessment (LCIA) phase. According to analyze the existing impact assessment methods, Society of Environmental Toxicology and Chemistry (SETAC) and the European Platform on Life Cycle Assessment (EPLCA) have made initial selection of 11 different categories of impact – Figure 2 [13, 24]. LCA includes impact categories on a global scale (climate changes, ozone layer depletion) as well as on a regional or even local scale (acidification, eutrophication, photochemical oxidation). Various temporal horizons of impact modelling enable to recognise the phenomenon of impact accumulation in time [25]. For each category of impact, based on scientifically valid models, the value of indicators is developed. However, their value is determined in another unit (kg of CO_2 equivalent, kg of PO_4 equivalent, kg of SO_2 equivalent), therefore it is not possible to directly compare them. However, they allow for assessing the impact of the product/process on the environment by determining the share of each emissions and each of the unit processes analyzed in this impact category. LCA, as one of the techniques of environmental management, is recognized and recommended in the EU as a tool for assessing environmental projects in many areas of economic activity [13].

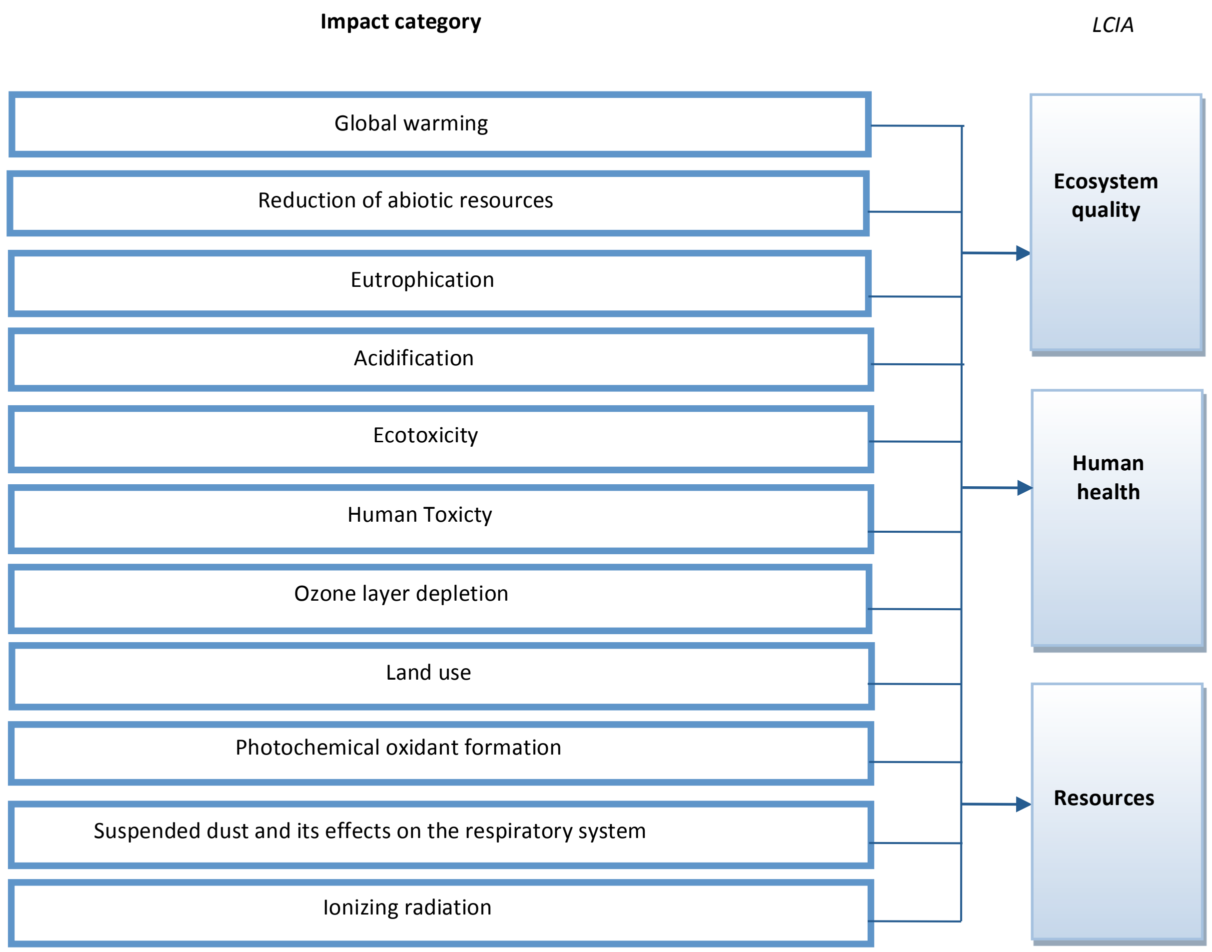

Fig. 2. The 11 different categories of impact
Source: [24]

The LCA results are presented in figures in specified categories of impact or on the basis of the calculated eco-indicator. This allows to compare the environmental impact of the proposed activity, e.g. a variant of omission or any other defined effect (such as a competitive manufacturer), which may be used to determine the ecological effect of the planned investment activities [26].

Cost efficiency assessment - using a dynamic unit cost method to evaluate the efficiency of environmental investments

Environmental performance can and should be used to assess the planned investment projects, especially those designed to protect the environment. Entities providing financial support usually define it as the relationship between the set ecological targets and expenditures incurred to reach them [27]. This approach defines the purpose as a selected area of the environment such as air protection and does not take into account the efficiency (cost-effectiveness) of planned economic development projects. However, when the eco-efficiency is defined as the relationship between discounted net benefits and environmental effects (e.g. reduction of pollution), there are clear difficulties in interpreting the results, especially for products/processes with significantly different impacts on the environment, but the same calculated indicator. Moreover, evaluation of the environmental effect is carried out in a protected area, such as air, which may cause an environmental problem in another area. Therefore, introduction of the eco-efficiency method of Life Cycle Assessment assesses the impact on the environment in integrated terms and allows the quantification of the results, is proposed. The combination of the methods of economic evaluation of the effectiveness of investment (discount method) enables the assessment of the eco-efficiency for both planned (*ex ante*) and made (*ex post*) investments.

It should be noticed that the use only the cost-benefit analysis is not a relevant method for making economic appraisal of investments that respond to compulsory ecological standards. Since the ISPA (Instrument for Structural Policies for pre-Accession) serves as a measure that helps accession countries to comply with EU ecological standards, the appraisal procedure should rely rather on the cost-effectiveness analysis [28]. To evaluate the effectiveness of environmental protection investments it is proposed to use cost-effectiveness ratio, created on the basis of cost per unit of dynamic methods (DGC - Dynamic Generation Cost) [29]. This is an indicator developed and used in the German bank KfW [28]. It determines the relation between the costs of the project and the effects coming from its use. This cost is equal to a price which allows for discounted revenues equal discounted costs. DGC shows what is the technical cost of obtaining environmental effect unit (product), expressed in local currency (e.g. EUR euro, US dollars, PLN zloty) per unit of environmental effects. It takes into account the current value of the investment and running costs. The obtained results are expressed in natural units, while the lower cost of obtaining environmental effect unit means more cost-effective investment. The mathematic notations of eco-efficiency as a combination of economic performance as DGC and ecological performance as LCA are expressed by the ratio as follows:

$$Eco-efficiency = \frac{1}{DGC \cdot LCA}$$

DGC indicator can be used at various stages of preparation and selection of investment projects, especially at:

- comparing alternative solutions for a given problem;
- limiting the scope of the investment,
- selecting of investment projects.

DGC ratio can be calculated from formula [13, 29]:

$$DGC = p_{EE} = \frac{\sum_{t=0}^{t=n} \frac{KI_t + KE_t}{(1+i)^t}}{\sum_{t=0}^{t=n} \frac{EE_t}{(1+i)^t}}.$$

where:
KI_t - capital costs incurred during the year;
KE_t - operating costs incurred during the year;
PEE - production in the year;
i - discount rate;
t - year, ranges from 0 to n, where 0 is the year of the first bear the costs, while ‘n’ is the last year of installation.

DGC indicator can be considered from two points of view:

- company, which wants to achieve a certain goal and considers choosing the best option; analysis of the technical cost allows to sort the options (from cheapest to most expensive);
- society, which as an investor can support the selected project.

The main problem in resolving the discussed issues are:

- determine the measurement of the environmental effect, which has a significant impact on the surrounding of the planned investment. E.g. an environmental impact of $1m^3$ of wastewater discharged into the lake, in which there is no outflow, is quite different than when the receiver is large river. In practice, only a few areas of environmental protection selection of projects may be based only on the cost-effectiveness indicator. It is possible, e.g. in the case of climate protection (global warming), because it does not matter the place of emission but only the amount of greenhouse gases enter into the atmosphere.
- selection the environmental effect indicator – there is no generally accepted methodology for assessment of the integrated environmental effect, and focus on indicator characterizing just one area of protection.
- approval the discount rate at the same level for environmental effects and financial effects. It is assumed that the environmental effects expressed in physical quantities can and should be discounted, but the discount is much lower than adopted in financial terms. This is due to the fact that the ecological effects of property are not subject to the same rules as the amount of capital used in economic processes. Here it is important to answer the question whether the resulting environmental effect in future years is worth less than that achieved in the current year. In the literature there is no

consensus on this issue, but generally lower levels of environmental or social discount rate are offered in comparison to those taken into account in the financial assessment. For example, the Stern report on climate change (i.e., the costs of CO_2) [30] proposed a discount rate of 1.4% with 1.3% due to the expected growth and 0.1% of the possible annihilation of mankind.

The analysis of alternative solutions for investments should be carried out in practice only during the formulation of the concept. Therefore, the design office, preparing the concept of investment, should describe all possible options to achieve the objective set by the investor and the estimate for each investment and operating costs. As a result, DGC pointer enables the cheapest solution to be chosen. Therefore, comparison of alternative solutions is the best use of the DGC pointer. Selection and qualification of projects for funding is a difficult task. The DGC pointer allows the creation of a ranking of projects for groups of homogeneous environmental effect, so projects may be prioritized according to their size and value. This procedure will ensure the lowest cost of obtaining the environmental effect [13]. Czaplicka-Kolarz et al. [36] were conducted eco-efficiency analysis on the basis of LCA and DGC of high density polyethylene (HDPE) and low density polyethylene (LDPE) production. Using DGC and LCA analysis, which allows to compare production technologies of chosen polyolefins, and it was adopted methodology for eco-efficiency calculating. The results allow a statement, which technology is more eco-efficient. Eco-efficiency indicators presented in this paper could be used as a benchmark for eco-efficiency assessment of polyethylene production by chosen technologies in existing installations [36].

The assessment of the profitability projects co-financed by the Structural Funds are carried out on the basis of detailed recommendations, e.g. for investment in environmental protection, described in the publications developed for the European Commission in the form of guides. For large infrastructure project, in accordance with Art. 26 of Council Regulation 1260/99/EC (Journal of Law 161 of 26 June 1999) laying down general provisions on the Structural Funds, preparation of cost analysis and benefits (CBA), analysis of risk factors, environmental impact assessment (EIA), and evaluate the impact of investments on equal opportunities and employment, is required. The aim of CBA is to demonstrate whether the project leads to an increase in welfare of the community affected by its consequences. The widely understood socio-economic CBA should take into account not only the financial costs and benefits expressed as cash flows, but also provide information about the impact of these aspects of the project that are not subject of the transaction on the market. For such projects, both (real) financial rate of return of the total investment and economic rate of return, taking into account social and environmental aspects through the use of shadow prices account, is calculated [31]. The CBA method is appropriate for the assessment of economic efficiency and in some extent - an integrated economic efficiency, environmental and social - but only for investment project [32].

While at the EU level, there are generally accepted guidelines for financial analysis economic and investment projects, as well as the detailed requirements for the preparation of the EIA, the method of calculating the ecological effects for the evaluation and implementation of various programs is determined at the level of individual country or region. This approach allows for the prioritization of national or regional authorities, which are subject to specific financial support from designated areas of environmental protection. The choice of the method of determining how the effect will be calculated should be based on ecological principles and objectives of the environmental policy of the country and provide a basis for the implementation of the principles of sustainable development [13].

Summary

According to ISO International Standard 14045:2012, eco-efficiency assessment is a necessary management tool to decrease the overall environmental impact and is increasingly becoming a key requirement for success in business. Eco-efficiency is the function of life cycle assessment and life cycle cost and it connects the basic business target (profit) and the basic production system target (costs) with environmental approach. This allows to the possibility to create innovative products fulfilling environmental criteria by decision-makers in companies. In this paper, environmental assessment in eco-efficiency evaluation based on Life Cycle Assessment (LCA) according to ISO 14040:2006 was proposed. Moreover, it was highlighted that environmental performance should be more frequently used to assess the planned investment projects, especially those designed to protect the environment.

References

[1] E. Kochańska, Analysis of the development of technological innovation in the context of international cooperation between science and the economy (Analiza rozwoju innowacji technologicznych w kontekście międzynarodowej współpracy nauki i gospodarki). CBI PRO-AKADEMIA, (2015) 7-20. (in Polish)

[2] C. Cicea, C. Marinescu, I. Popa, C. Dobrin, Environmental efficiency of investments in renewable energy: Comparative analysis at macroeconomic level. Renewable and Sustainable Energy Reviews, 30 (2014) 555-564.

[3] R.L. Burritt, C. Saka, Environmental management accounting applications and eco-efficiency: case studies from Japan. Journal of Cleaner Production, 14(14) (2006) 1262-1275.

[4] World Business Council for Sustainable Development. 2000. Measuring eco-efficiency - a guide to reporting company performance. Conches-Geneva, Switzerland: WBCSD.

[5] E. Lorek, The development of the market of goods and ecological services in the Silesia region. UE Katowice, 2004.

[6] A. Kicherer, S. Schaltegger, H. Tschochohei, B.F. Pozo, Eco-efficiency. Combining Life Cycle Assessment and Life Cycle Costs via Normalization. The International Journal of Life Cycle Assessment, 12(7) (2007) 537-543.

[7] A.J. Picazo-Tadeo, J.A. Gómez-Limón, E. Reig-Martínez, Assessing farming eco-efficiency: A Data Envelopment Analysis approach, Journal of Environmental Management, 94 (2010) 1154-1164.

[8] C. Sinkin, C.J. Wright, R.D. Burnett, Eco-efficiency and firm value. Journal of Accounting and Public Policy, 27(2) (2008) 167-176.

[9] J. Kulczycka, E. Pietrzyk-Sokulska, Evaluation of minerals in Poland, Publisher IGSMiE Academy of Sciences, Cracow, 2009.

[10] I. Zabalza Bribián, A. Valero Capilla, A. Aranda Usón, Life cycle assessment of building materials: comparative analysis of energy and environmental impacts and evaluation of the eco-efficiency improvement potential. Building and Environment, 46(5) (2011) 1133-1140.

[11] Z. Zhu, K. Wang, B. Zhang, Applying a network data envelopment analysis model to quantify the eco-efficiency of products: a case study of pesticides. Journal of Cleaner Production, 69 (2014) 67-73.

[12] O. Michelsen, A.M. Fet, A. Dahlsrud, Eco-efficiency in extended supply chains: a case study of furniture production. Journal of Environmental Management, 79(3) (2006) 290-297.

[13] J. Kulczycka, Eco-efficiency of investment projects using the concept of product life cycle (Ekoefektywność projektów inwestycyjnych z wykorzystaniem koncepcji cyklu życia produktu), IGSMiE Academy of Sciences, Monographs 169, Cracow, 2011. (in Polish).

[14] E. Kochańska, P. Makowski, Economic and technological aspects of distributed energy systems based on biomass – case of a small country in Poland (Ekonomiczne i technologiczne aspekty rozwoju rozproszonej energetyki opartej o biomasę na przykładzie małej gminy). Acta Innovations, 6 (2013) 24-31.

[15] Z. Kowalski, A. Makara, Methods of ecological and economic evaluation of technology, Chemik, 64 (2010) 3, 158-167.

[16] T. Kuosmanen, Measurement and Analysis of Eco-efficiency: An Economist's Perspective. Journal of Industrial Ecology, 9(4) (2005) 15-18.

[17] BS EN ISO 14040:2009: Environmental management - Life cycle assessment - Principles and framework, Warsaw, 2009.

[18] J. Reap, F. Roman, S. Duncan, B. Bras, A survey of unresolved problems in life cycle assessment-Part I goals and scope and inventory analysis. The International Journal of Life Cycle Assessment, 13(4) (2008) 290-300.

[19] Z. Kowalski, J. Kulczycka, A. Skowron, A. Sobczak, Comparative evaluation of calcium feed phosphate production methods using Life Cycle Assessment. Archives of Environmental Protection, 33 (2007) 83-94. a

[20] Z. Kowalski, J. Kulczycka, Z. Wzorek, Life cycle assessment of different variants of sodium chromate production in Poland. Journal of Cleaner Production, 15(1) (2007) 28-37. B

[21] E. Loiseau, G. Junqua, P. Roux, V. Bellon-Maurel, Environmental assessment of a territory: An overview of existing tools and methods. Journal of Environmental Management, 112 (2012 213-225.

[22] H. Baumann, A.M. Tillman, The Hitch Hiker's Guide to LCA. An orientation in life cycle assessment methodology and application. External organization, Lund , Sweden, Studentlitteratur, 2004.

[23] A. Lewandowska, P. Kurczewski, J. Kulczycka, K. Joachimiak, A. Matuszak-Flejszman, H. Baumann, A. Ciroth, LCA as an element in environmental management systems—comparison of conditions in selected organisations in Poland, Sweden and Germany. The International Journal of Life Cycle Assessment, 18(2) (2013) 472-480.

[24] N.L. Pelletier, N. W. Ayer, P.H. Tyedmers, S.A. Kruse, A. Flysjo, G. Robillard, F. Ziegler, A.J. Scholz, U. Sonesson, Impact categories for life cycle assessment research of seafood production systems: review and prospectus. The International Journal of Life Cycle Assessment, 12(6) (2007) 414-421.

[25] A. Lewandowska, A. Matuszak-Flejszman, K. Joachimiak, A. Ciroth, Environmental life cycle assessment (LCA) as a tool for identification and assessment of environmental aspects in environmental management systems (EMS). The International Journal of Life Cycle Assessment, 16(3) (2011) 247-257.

[26] R. Koneczna, Ł. Lelek, Ekologiczna ocena przedsiębiorstw sektora motoryzacyjnego–zastosowanie metody LCA. Prace Naukowe Uniwersytetu Ekonomicznego we Wrocławiu, (220) (2011) 408-418.

[27] X. Olsthoorn, D. Tyteca, W. Wehrmeyer, M. Wagner, Environmental indicators for business: a review of the literature and standardisation methods. Journal of Cleaner Production, 9(5) (2001) 453-463.

[28] J. Rączka, Cost-efficiency analysis based on dynamic rate of unit cost. Training materials developed under the Transform Advice Programme - Investment in Environmental Infrastructure in Poland, 2002 (in Polish).

[29] K. Czaplicka-Kolarz, D. Burchart-Korol, P. Krawczyk, Ecoefficiency analysis methodology on the example of the chosen polyolefins production. Journal of Achievements in Materials and Manufacturing Engineering, 43(1) (2010) 469-475.

[30] N. Stern, The economics of climate change: the Stern review. Cambridge University Press, 2007.

[31] A. Markowska, T. Żylicz, Introduction Polish. Cost-benefit analysis of investment projects: A Guide to the cost-benefit analysis of investment projects Structural Funds, the Cohesion Fund and the Instrument for Pre-Accession (Wprowadzenie polskie. Analiza kosztów i korzyści projektów inwestycyjnych: Przewodnik do analizy kosztów i korzyści projektów inwestycyjnych fundusze strukturalne, Fundusz Spójności oraz Instrument Przedakcesyjny), European Commission, Brussels, 2008, pp. 18. (in Polish)

[32] F. Piontek, Methodology for assessing the environmental effectiveness of spending appropriated funds (Metodyka oceny efektywności wydatkowania ekologicznego funduszy celowych), AE, Katowice, 1999. (in Polish)

[33] O. Adeoti, M.O. Ilori, T. O. Oyebisi, L. O. Adekoya, L. O. Engineering design and economic evaluation of a family-sized biogas project in Nigeria. Technovation, 20(2) (2000) 103-108.

[34] A. Dabbs, M. Bateson, The corporate impact of addressing social issues: a financial case study of a project in Peru. Environmental monitoring and assessment, 76(1) (2002) 135-156.

[35] M. Góralczyk, J. Kulczycka. LCC application in the Polish mining industry. Management of Environmental Quality: An International Journal, 16(2) (2005) 119-129.

[36] K. Czaplicka-Kolarz, D. Burchart-Korol, P. Krawczyk. Eco-efficiency analysis methodology on the example of the chosen polyolefins production. Journal of Achievements in Materials and Manufacturing Engineering, 43(1) (2010) 469-475.

[37] ec.europa.eu/eurostat/data/database, 10.08.2015.

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PREDICTION OF CHANGES IN PROPERTIES OF PIPES FROM POLYETHYLENE IN THE RESEARCH OF SIMULATION OF AGEING

Abstract

This study presents a comparative analysis of specimens before and after photochemical and electrochemical ageing processes. The specimens were cut out of the pipes obtained through extrusion. The examinations were carried out for two commercial grades of polyethylene. Ageing with UV radiation was carried out using a gas discharge lamp, whereas simulation of electrochemical ageing was performed in a water solution of NaCl. Tensile strength testing, differential scanning calorimetry, colour and gloss measurements and hardness testing using the method of ball indentation were carried out for both types of specimens (after ageing and without ageing). Analysis of the results of the examinations revealed that ageing caused significant changes in properties of the specimens. In the samples after ageing was observed decrease in tensile strength. Found a decrease in the degree of crystallinity and changing temperatures physical changes. In the samples after ageing was observed different values of the parameters describing the colour. In samples after ageing also reported a reduction in gloss and hardness.

Key words

pipes, polyethylene, ageing, thermal properties, mechanical properties, colour, gloss

Introduction

Simulations of the ageing process allow for determination of changes in thermomechanical properties of the components made of polymeric plastics [1]. Properties of pipes made of polymeric plastics substantially depend on conditions of their storage and use. Working environment and medium that flows through the pipe cause its degradation. As a result of ultraviolet radiation and depending on the chemical composition of the soil in which the pipe is placed, the chain in the plastic might be torn, which leads to a reduction in the molecular mass of the plastic. These processes result in deterioration of mechanical properties of the pipe, which might lead to the breakdown of the whole system of piping [2-7]. Pipes made of polypropylene, which is the material from the group of polyolefin plastics, can be manufactured in various sectors of the industry. The pipes made of polyethylene are characterized by e.g. insignificant mass, high smoothness of surface and easiness of installation [6-10].

The aim of the examinations was analysis of the effect of ageing conditions on thermomechanical properties of pipes made of polyethylene. The examinations used two different commercial grades of polyethylene. Differential scanning calorimetry examinations and tensile strength testing were also carried out for specimens before and after the ageing process.

Research methodology

The examinations were carried out for the specimens made of two different types of polyethylene with commercial names of: PE 3802 YCF used for transport of gas and PE XSC 50 Blue for transport of water, manufactured by Total Petrochemicals. The specimens were cut out from extruded pipes with the following parameters:

- rotational speed of the feed screw: 69.2 [1/min],
- pull-off speed: 1.208 [m/min],
- mass flow intensity: 76.1 [kg/h],

- temperature in individual zones of cylinders in the extrusion machine: t_1 – 180 [^{o}C], t_2 – 181 [^{o}C], t_3 – 182 [^{o}C], t_4 – 183 [^{o}C], t_5 – 185 [^{o}C],
- extrusion machine head temperature: 185 [^{o}C].

Simulation of ageing with ultraviolet radiation was carried out for the polyethylene 3802 YCF in a specialized chamber with an arc tube of high-pressure mercury vapor lamp. It was calculated based on the data concerning power of solar radiation that the time of simulated ageing corresponded to a half-a-year ageing under natural conditions [12, 13]. The examinations of accelerated electrochemical ageing used specimens made of XSC 50 Blue polyethylene. The test stand was equipped with a glass vessel filled with water solution of NaCl with concentration of 35 per mille with specimens placed inside. The ageing process occurred under following conditions: direct current with current intensity of 0.3 A, time: 700h, temperature: 20°C and pH: 7. The equipment used graphite electrodes.

The following examinations were carried out for tensile strength, tensile stress at break and elongation at break. Tensile strength examinations were carried out using a tensile strength testing machine (Inspekt Desk 20 manufactured by Hegewald&Peschke). Examinations of thermal properties were carried out using (DSC Phox 204 PC manufactured by NETZSCH). The measurements were carried out with the specimen heating rate of 10^{o}C/min in the range of temperature of from 50 to 190^{o}C. Evaluation of the crystallinity degree used the Netzsch-Proteus software. This software allows for examination of the course of specimen melting at the specific range of temperatures and determination of the surface area between the thermographic curve and the base line in the range of endothermic reflex. The specimens before placing in the measurement chamber were weighted using SARTORIUS scales with precision of 0.01 mg with internal calibration option and closed weighing chamber. The mass of specimens was within the range of from 7 to 10 mg. The colour of the specimens was measured using X-Rite spectrophotometer. The examinations were carried out using CIELAB model (Fig. 1). This model describes the colour by means of three coordinates, *a*, *b* and *L*. The values of *a* coordinate determine the colour from green to red, while the *b* coordinate defines the colour from blue to yellow. Parameter *L* (luminance) characterizes brightness of the colour from black to white [11]. Gloss was measured by means of ELCOMETER equipment, with the refraction angle of 20^O.

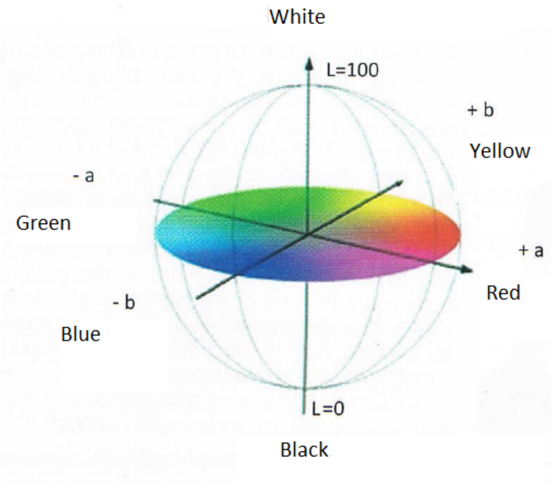

Fig. 1. CIELAB space [12]

Results and discussion of research

Results obtained for tensile strength are presented in Table 1 and Figs. 2 and 3. Both processes of photochemical ageing and electrochemical ageing caused changes in strength properties of commercial polyethylene grades studied. Lower value of tensile strength was recorded for the aged specimens. Elongation and tensile stress at break were also reduced.

Table 1. Results of tensile strength investigations for polymers before and after ageing

Polymer	**Tensile strength, MPa**	**Elongation at break, %**	**Stress at break, MPa**
Polyethylene 3802 YCF	17,8	370	12,55
Polyethylene 3802 YCF after ageing	18,1	56	5,3
Polyethylene XSC 50 Blue	25,3	457	16,44
Polyethylene XSC 50 Blue after ageing	23,3	421	14,91

Source: Author's

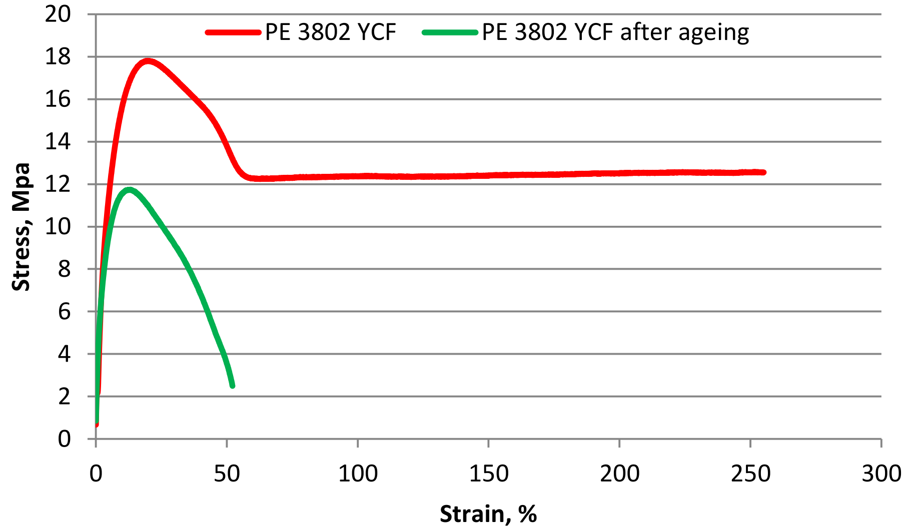

Fig. 2. Tensile strength for polyethylene 3802 YCF before and after ageing
Source: Author's

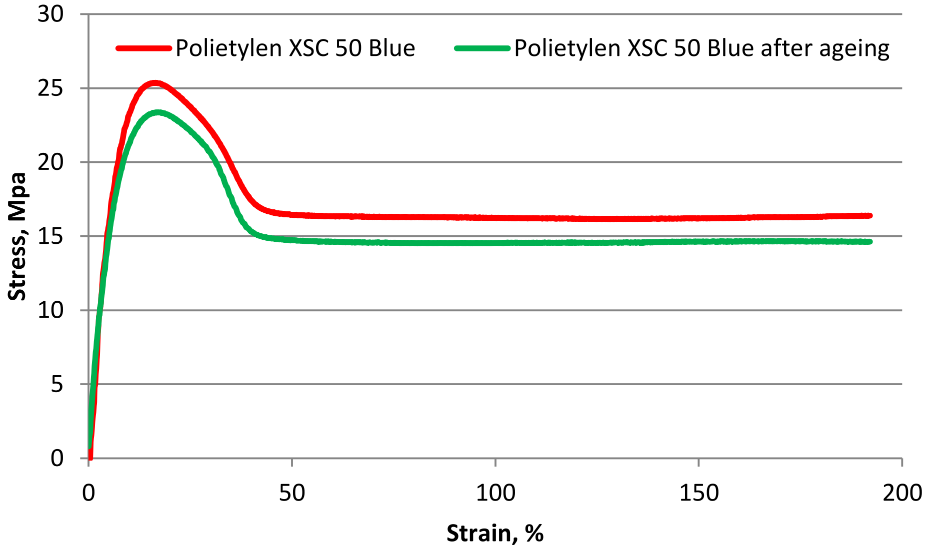

Fig. 3. Tensile strength for polyethylene XSC 50 Blue before and after ageing
Source: Author's

Table 2 and Figs. 4 and 5 present the results obtained from differential scanning calorimetry of the plastics studied. The process of electrochemical ageing caused a decline in the degree of crystallinity of the polymers analysed. Extension of the range of melting point and a shift towards higher temperatures with melting of crystalline phase occurring at the fastest rate were observed for both 3802 YCF polyethylene and XSC 50 Orange polyethylene.

Table 2. Results of DSC investigations

Polymer	***Degree of crystallinity, %***	***Melting range, °C***	***Max. melt temperature, °C***
Polyethylene 3802 YCF	47,9	127,1 – 138,1	131,2
Polyethylene 3802 YCF after ageing	46,2	121,2 – 138,9	134,2
Polyethylene XSC 50 Blue	39,8	125,7 – 139,2	135
Polyethylene XSC 50 Blue after ageing	33,2	124,6 – 141,3	136,7

Source: Author's

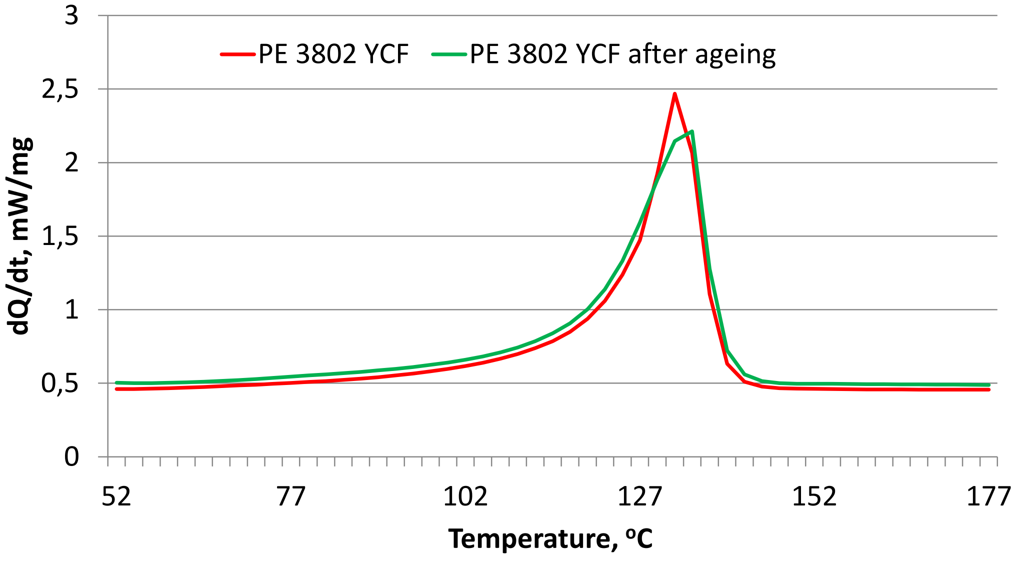

Fig. 4. Thermograms for polyethylene 3802 YCF before and after ageing

Source: Author's

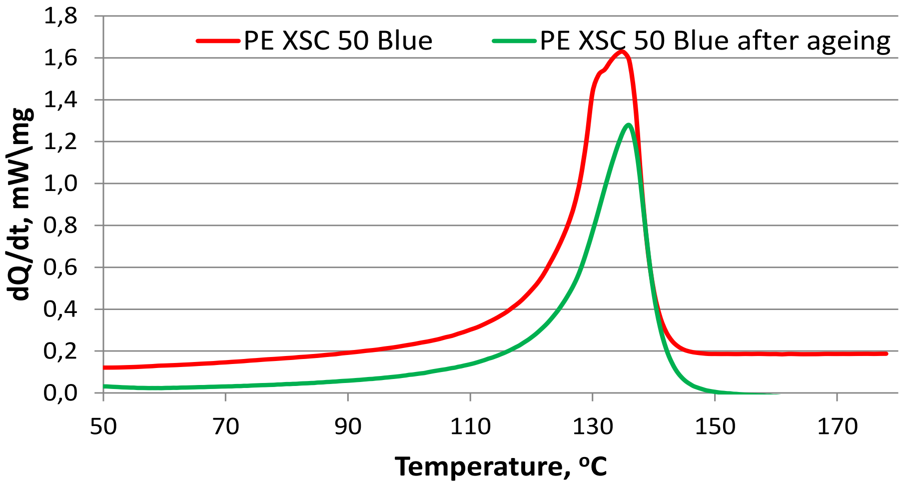

Fig. 5. Thermograms for polyethylene XSC 50 Blue before and after ageing

Source: Author's

Results of colour measurement for the materials analysed in the study are presented in Table 3 and Figs. 6 and 7.

Table 3. Results of colour investigations before and after ageing

Polymer	***L***	***a***	***b***
Polyethylene PE 3802 YCF	71,83	-1,18	52,37
Polyethylene PE 3802 YCF after ageing	72,4	-2,2	48,67
Polyethylene XSC 50 Blue	38,9	-3,5	-35,6
Polyethylene XSC 50 Blue after ageing	37,4	-3,6	-34,9

Source: Author's

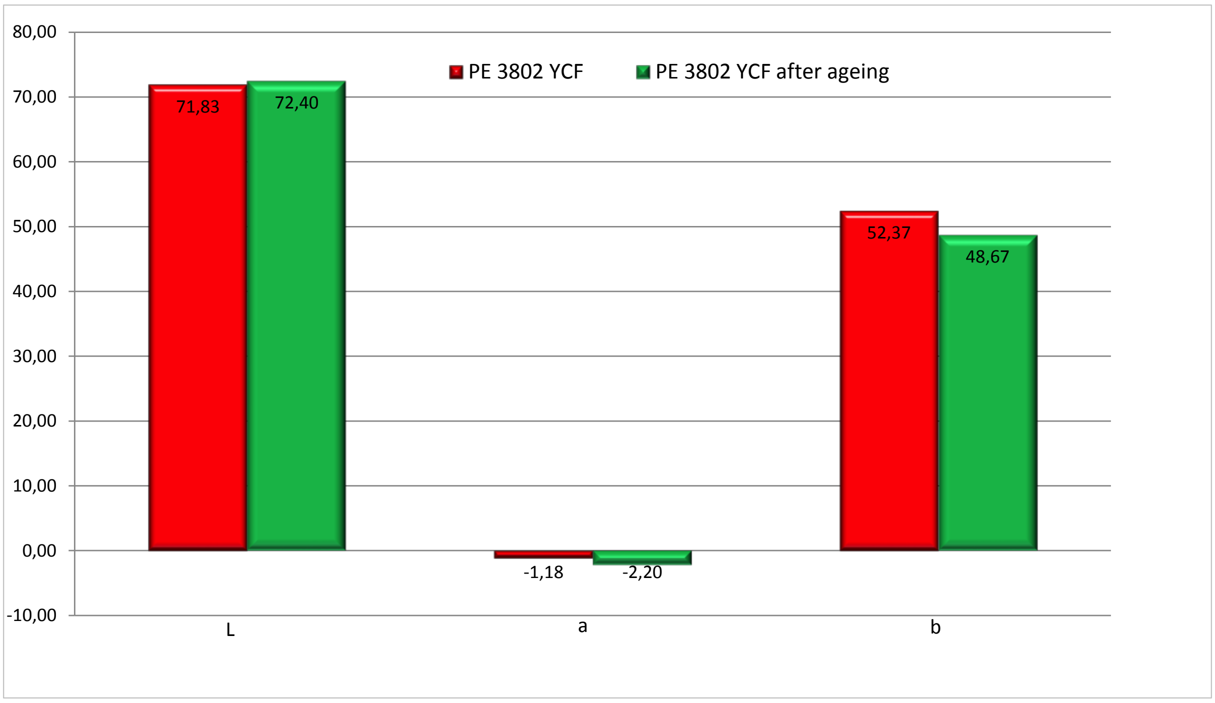

Fig. 6. Colours investigations for polyethylene 3802 YCF before and after ageing

Source: Author's

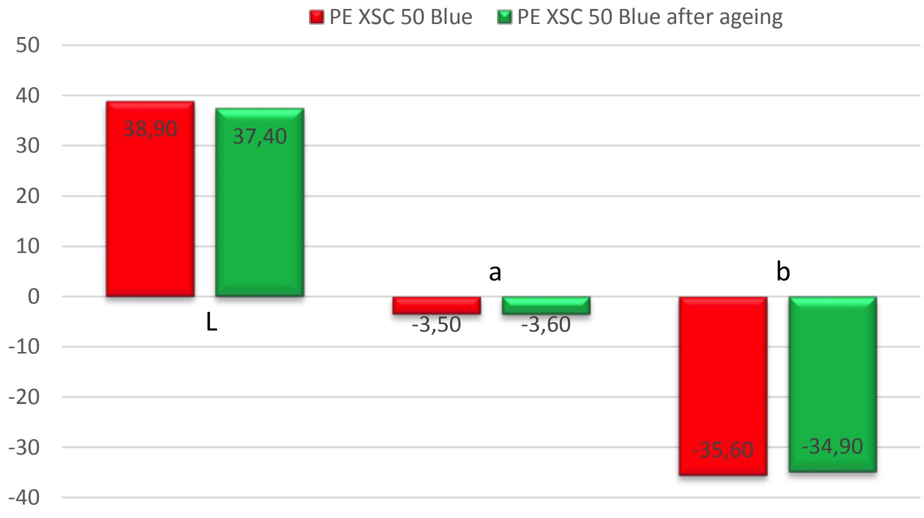

Fig. 7. Colours investigations for polyethylene XSC 50 Blue before and after ageing
Source: Author's

The specimens subjected to the process of ageing had different values of the colour coordinates compared to the non-aged specimens. The colour of pipes in the case of polyethylene 3802YCF after ageing was moved towards green and blue colours. A shift in the coordinates towards green and yellow colours was observed for the XSC 50 Blue polyethylene after ageing. Luminance of specimens as a result of ageing was reduced. The results of examinations of the luminance were presented in Fig. 8 and 9. The process of electrochemical ageing caused a decline in luminance of the specimens studied both in the case of 3802 YCF and XSC 50 Blue polyethylene.

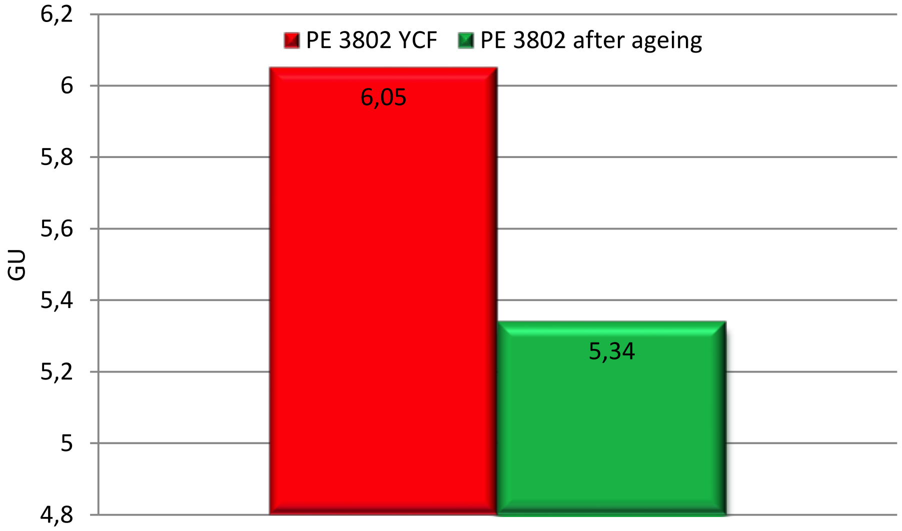

Fig. 8. Gloss investigations for polyethylene 3802 YCF before and after ageing
Source: Author's

Fig. 9. Gloss investigations for polyethylene XSC 50 Blue before and after ageing
Source: Author's

Figs. 10 and 11 present the results of hardness measurements using ball indentation. A decline in hardness was recorded as a result of electrochemical ageing. Lower values of hardness were found for both specimens after ageing with UV radiation and specimens after chemical ageing process compared to the specimens before ageing.

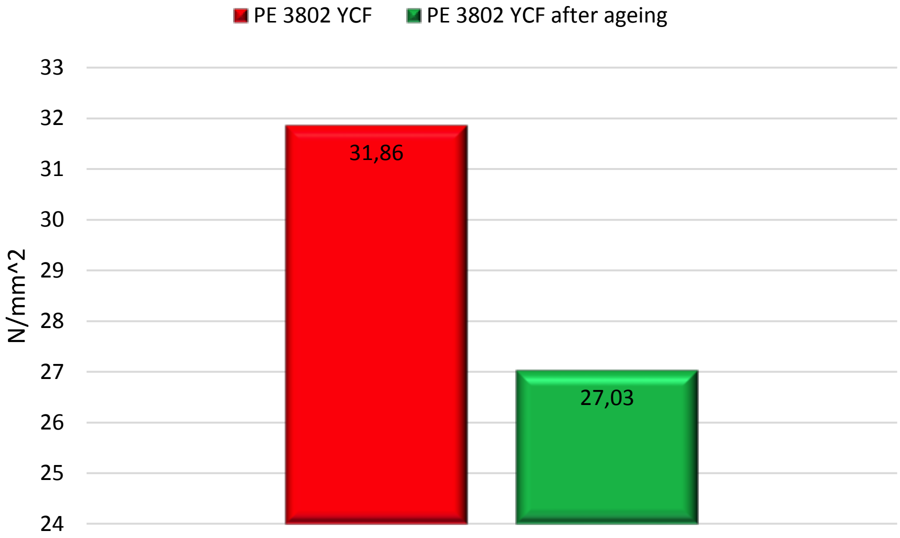

Fig. 10. Hardness investigations for polyethylene 3802 YCF before and after ageing
Source: Author's

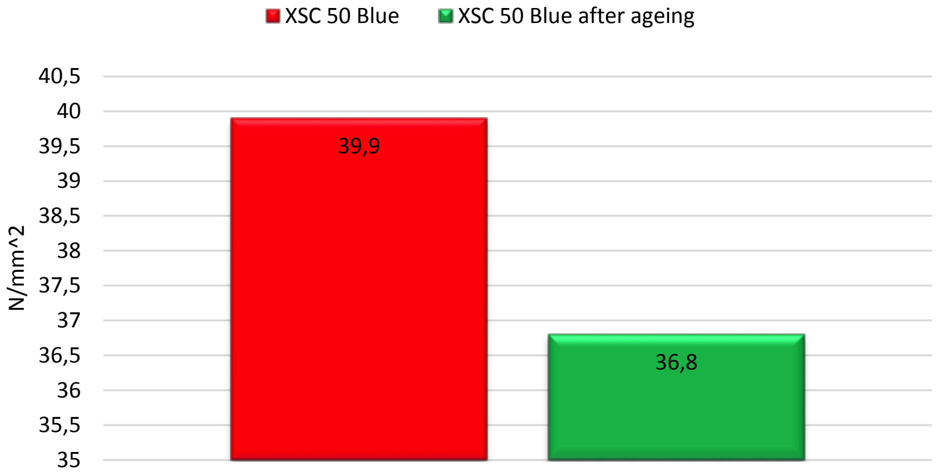

Fig. 11. Hardness investigations for polyethylene XSC 50 Blue before and after ageing
Source: Author's

Summary and conclusions

Analysis of the examinations carried out in this study demonstrates that photochemical and electrochemical ageing affected the properties of the two grades of polyethylene used for the tests. Aged specimens were characterized by lower tensile strength and lower elongation at break compared to non-aged specimens. Lower degree of crystallinity was also found. Ageing caused changes in parameters of colour and luminance. A decline in hardness was observed compared to non-aged specimens. The study allows the determination of changes occurring in the pipes of plastics due to the impact of degradation factors. They open the way to further studies aimed at reducing the impact of ageing and allow extend the time of using of polymer pipes.

References

[1] Z. Dobkowski, Lifetime prediction for polymer materials using OIT measurements by the DSC method, Polimery 3 (2005) 213-215.

[2] D. Sobków, K. Czaja, Wpływ warunków przyspieszonego starzenia na proces degradacji poliolefin, Polimery 9 (2003) 627-632.

[3] A. Gnatowski, Badania struktury i właściwości termicznych polietylenu i kompozytów polietylenu z włóknem tekturowym po procesach wygrzewania i starzenia promieniami UV, Composites Theory and Practise (2009) 3 238-243.

[4] T. Jachowicz, A. Krzyżak, Wpływ starzenia naturalnego na wybrane właściwości rur z polietylenu, Matrol (2009) 70-76.

[5] A. Pusz, K. Michalik, Creep damage mechanisms in gas pipes made of high density polyethylene, Archives of Materials Science and Engineering 2 (2009) 89-95.

[6] M. Maity, B.B. Khatua, C.K. Das, Effect of processing on the thermal stability of the blends based on polyurethane, Polymer degradation and stability 72 (2001) 499-503.

[7] Brabowska B.: Biodegradacja tworzyw polimerowych, Archives of Foundry Engineering 10 (2010) 57-60.

[8] K. Czaja K.: *Poliolefiny*, WNT, Warszawa, 2005.

[9] M. Kwacz, J. Zadrosz, Przykłady zastosowań rur z tworzyw sztucznych w sieciach podziemnych cz. II, Nowoczesne Budownictwo Inżynieryjen 3 (2008) 66-71.

[10] E. Piekarska, Rury z polietylenu – niezawodność funkcjonowania w wodociągach, sieciach paliw gazowych i kanalizacji, Przetwórstwo Tworzyw 2 (2008) 39-44.

[11] J. Molenda, M. Wrona, E. Siwiec, Zastosowanie modelu CIE lab w badaniach barwy lotnych popiołów, Problemy Eksploatacji 3 (2012) 177-187.

[12] A. Gnatowski, Influence of injection moulding conditio and annealing on thermal properties, structure, color and gloss of composite polyamide 6 with glass beads, Composites Theory and Practise 2, (2012) 115-120.

[13] M. EL-Nouby, M. El Shazy, Attenuation of UV-B radiation in the atmosphere: Clouds effect, at Qena (Egypt), Atmospheric Environment, 41 (2007) 4856-4864.

[14] F. Joao, N. Eduardo, P. Amauri, J. Soares, Modeling hourly and daily fractions of UV, PAR and NIR to global solar radiation under various sky conditions at Botucatu, Brazil, Applied Energy, 86 (2009) 299-309.

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POTENTIAL OF LOW CONCENTRATION NANOFLUIDS IN HEAT TRANSFER

Abstract

The main purpose of conducted studies was recognition of low concentration nanofluid under the influence of magnetic field potential applications. The investigations are having fundamental character but Authors keep in mind better energy utilization through the heat transfer enhancement. The examined fluid was composed of water and Cu/CuO nanoparticles. Three temperature differences were imposed on the system. The results did not give unequivocal answer on possible utilization of studied phenomena, but there is open scene for the studies of particle-fluid interaction and flow structure. The main conclusion is that the magnetic properties of base fluid and particles are crucial for such analysis.

Key words
weakly-magnetic nanofluid, heat transfer phenomena, strong magnetic field, thermo-magnetic convection

Introduction

Nowadays, there are great numbers of electronic devices that surround us. Their proper operation depends on many factors, for example optimal temperature, humidity, cooling media, etc. The operational conditions are very important; therefore their selection and optimisation are significant [1]. From other point of view the energy itself is valuable. Many research subjects are related to its better utilization, more efficient devices or optimized systems [2-3]. The most important factor in the efficient energy usage corresponds to the efficient heat transfer. Traditional coolants have meaningful limitation, which is coming from their low thermal properties. There are many research works done on the heat transfer processes intensification [4-7]. Various passive and active methods are applied to augment the transfer of high heat fluxes. One of the passive methods resulted in an appearance of nanofluids. The idea of nanoparticles addition to the base fluid was born hundred years ago, but it was possible to realize it now due to the technological development. The first report on nanofluid successful preparation was published in 1995 [8]. Since then, interest in such fluids is constantly growing. There are more and more possible applications, among others: in solar systems [9], medicine [10] and in daily life [11-12]. Another way to enhance the heat transfer is application of the magnetic field. Several experimental and numerical studies were conducted [13-16]. It has been proven that the usage of an external, strong magnetic field could intensify or completely suppress the natural convection of one-phase paramagnetic fluid [17-18].

The demand of better energy utilization through the more efficient heat transfer was an origin of present investigations. Since the nanofluids and the magnetic field could enhance the processes, the idea of their combination seemed to be the logical consequence. However the cost of nanofluids is pretty high, therefore the low particle concentration fluids were firstly considered as the working media and the copper nanofluid was produced and studied. Although the results were different than expected, they have given insight on the phenomena occurring in the system. They can be explained through the forces acting on the base fluid and the particles. The reason was that the copper nanofluid turned to be copper oxide one. The difference in the magnetic properties caused very complex force system and difficulties in the results interpretation.

Experimental setup and research methodology

Experimental equipment and enclosure are schematically shown in Fig.1. Experimental stand was consisted of an enclosure, filled with a working fluid, placed in the bore of a superconducting magnet, a heater control system, a thermostating bath and a data acquisition system connected to a personal computer. To achieve the highest magnetic buoyancy force acting on the investigation system, the enclosure was placed at the location of grad$\mathbf{B}^2_{max}$ maximal value occurrence [18]. The bottom wall of the experimental enclosure was heated (with constant heat flux) and the top one was cooled, both of them were made of copper. A nichrome wire was used as a heater, connected to a DC power supply and placed under copper plate. The heating power was monitored with multimeters. The water flowing through the cooling chamber was maintained at constant temperature by a thermostating bath. Three thermocouples were placed in heated and cooled plates each, while six thermocouples inside cubical enclosure (shown in Fig. 1(b)). The signals of measured temperature were stored in a computer through a data acquisition system and were used to analyze the heat transfer and flow structure.

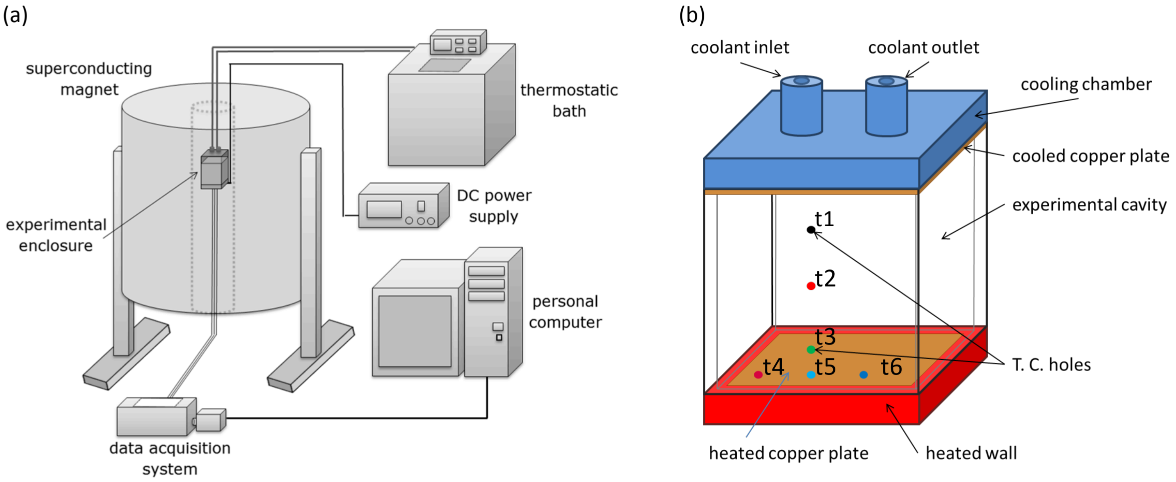


Fig. 1. Experimental (a) setup and (b) enclosure.

Source: [16]

Table 1. Formulas applied for the calculation of nanofluids thermo-physical properties

Property	Formula
Thermalconductivity	$k_{nf} = k_{bf}\dfrac{k_p + 2k_{bf} + 2\varphi\left(k_p - k_{bf}\right)}{k_p + 2k_{bf} - \varphi\left(k_p - k_{bf}\right)}$
Density and specific heat product	$\rho c_{p,nf} = \varphi\left(\rho c_p\right)_p + \left(1-\varphi\right)\left(\rho c_p\right)_{bf}$
Thermal expansion coefficient	$\beta_{nf} = \varphi\beta_p + \left(1-\varphi\right)\beta_{bf}$
Dynamic viscosity	$\mu_{nf} = \dfrac{\mu_{bf}}{\left(1-\varphi\right)^{2.5}}$
Electrical conductivity	$\sigma_{nf} = \sigma_{bf}\left[1 + \dfrac{3\left(\dfrac{\sigma_p}{\sigma_{bf}} - 1\right)\varphi}{\left(\dfrac{\sigma_p}{\sigma_{bf}} + 2\right) - \left(\dfrac{\sigma_p}{\sigma_{bf}} - 1\right)\varphi}\right]$

Source: [19]

Table 2. Thermo-physical properties of working fluids

Property	Unit	Value
Thermalconductivity	k_{nf} [W·(mK)$^{-1}$]	0.601
Density	ρ_{nf}[kg·m^{-3}]	1019
Specific heat	$c_{p,nf}$ [J·(kg·K)$^{-1}$]	4177
Thermal expansion coefficient	β_{nf}[K^{-1}]	$19.78\cdot10^{-5}$
Dynamic viscosity	μ_{nf}[kg·(m·s)$^{-1}$]	$10.07\cdot10^{-4}$
Electrical conductivity	σ_{nf}[S·m^{-1}]	$5.52\cdot10^{-6}$
Mass magnetic susceptibility	χ_m[m^3·kg^{-1}]	$12.4\cdot10^{-9}$*

Source: Authors - values calculated in the basis of Tab. 1, * - measured values

Examined nanofluid consisted of distilled water with addition of 1% weight (corresponding to 0.112 vol.%) copper/copper oxide particles of 40-60 nm size. Nanofluid was prepared by a two-step method with ultrasonic agitation (Sonics & Materials Inc. model: VCX 130 PB, 130 W, 20 kHz) lasting about 10 minutes. The obtained liquid was opaque and stable for the duration of the experiment. To define the nanofluid thermo-physical properties the formulas listed in Table 1 were used. The magnetic susceptibility was determined experimentally. All properties applied in the analysis are presented in Table 2.

The interaction of the gravitational and the magnetic buoyancy forces

The acting forces on the fluid (the gravitational and the magnetic buoyancy ones) can act in the same or in a different directions depending on some parameters. Thus, their mutual orientation, which effects on the total acting force, will be larger or smaller. Experimentally verified magnetic property of nanofluid indicated that it was diamagnetic (negative value of the magnetic susceptibility), therefore the maximal gradient of magnetic induction square was located on the cooling plate. Such arrangement should orient the forces in the same direction, and therefore the total acting force on the nanofluid should be higher. However added particles were paramagnetic and even they did not change much the bulk fluid magnetic susceptibility, the magnetic field was influencing them in different manner. Probably the additional force (magnetic buoyancy force for paramagnetics) appeared, what resulted in complex force system and the unequivocal results of the heat transfer. The schematic relationship of the force system is presented in Fig. 2.

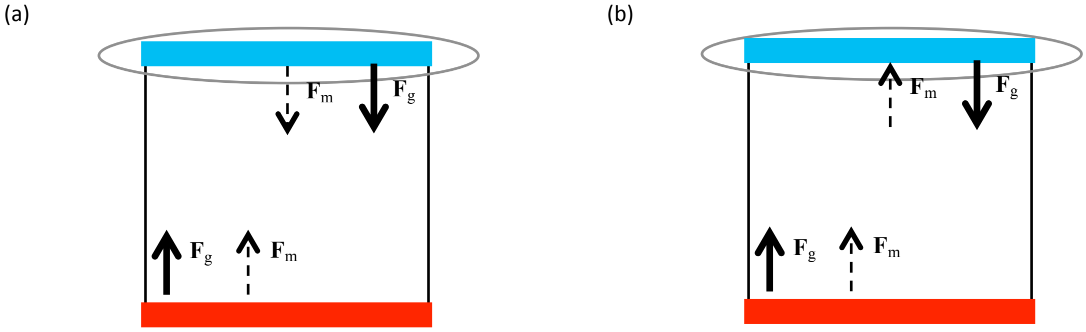


Fig. 2. Reciprocal relation of the gravitational (**F**$_g$) and magnetic (**F**$_m$) buoyancy forces for (a) diamagnetics and (b) paramagnetics.
Source: Authors

Values of the forces could be calculated by following formulas:

- the gravitational buoyancy force:

$$\mathbf{F}_g = -\mathbf{g}\rho_0\beta(T-T_0)\ , \tag{1}$$

- the magnetic buoyancy force for diamagnetics:

$$\mathbf{F}_m = \frac{\chi_m\rho_0\beta(T-T_0)}{2\mu_0}\nabla\mathbf{B}^2_{max} \tag{2}$$

- the magnetic buoyancy force for paramagnetics:

$$\mathbf{F}_m = -\left(1+\frac{1}{\beta T_0}\right)\frac{\chi_m\rho_0\beta(T-T_0)}{2\mu_0}\nabla\mathbf{B}^2_{max}\ . \tag{3}$$

The T_0 indicated reference temperature equal to the arithmetical average of cooled and heated walls' temperature.

Effect of magnetic field on heat transfer processes and flow structure is presented in Figs. 3-5.

Signal analysis methodology

For each temperature difference methodology was the same. The first part of the analysis was related to the heat transfer and the first undertaken step was measurement of the conduction state to determine the heat loss in the system. Experimental enclosure was inverted in the position that the hot plate was at the top and cooled one at the bottom, then it was placed in the selected location in the magnetic field. The chosen test section corresponded to the place of maximum $\mathrm{grad}\mathbf{B}^2_{max}$ occurrence. The ambient temperature in the magnet was 18°C, therefore, cooled wall temperature was set at the same level and only the heated wall temperature could be changed. The next step was related to the measurement of convection state without and with magnetic field utilization. Taking into account convective and conducted heat fluxes, the Nusselt number could be defined:

$$\mathrm{Nu} = \frac{Q_{\mathrm{net\_conv}}}{Q_{\mathrm{net\_cond}}}. \tag{4}$$

According to the adopted assumption, that the heat loss would be the same regardless of the phenomenon occurring inside the enclosure, particular term could be calculated in the basis of following formulas:

$$Q_{\mathrm{loss}} = Q_{\mathrm{cond}} - Q_{\mathrm{theor\_cond}}, \tag{5}$$

$$Q_{\mathrm{net\_conv}} = Q_{\mathrm{conv}} - Q_{\mathrm{loss}}. \tag{6}$$

A linear dependence of heat losses on the temperature difference was obtained in the form:

$$Q_{\mathrm{loss}} = 0.06398 \cdot \Delta T. \tag{7}$$

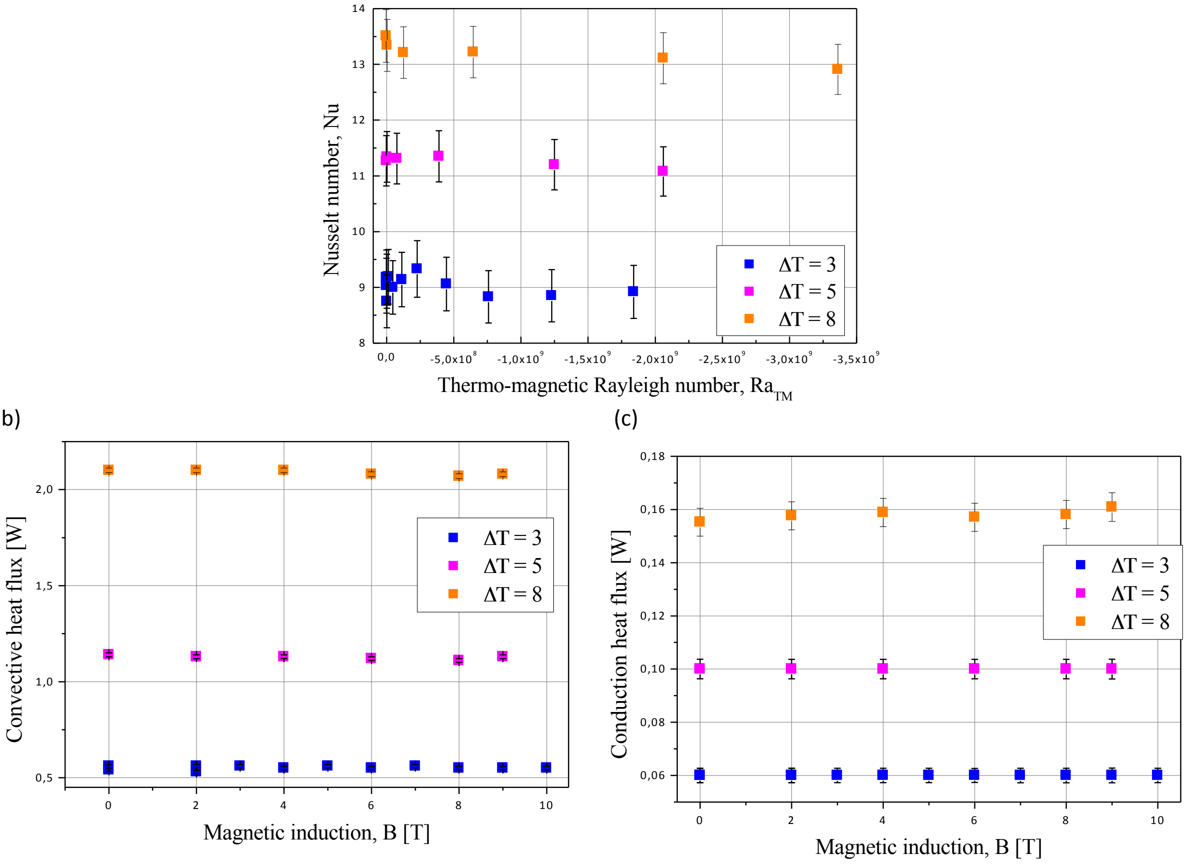
Knowing all of necessary components it was possible to calculate the Nusselt number.

The next part included the flow structure analysis with Fast Fourier Transformation utilization. Due to the nanofluid opaqueness there was no possibility to conduct an optical visualization. Therefore, the signal analysis using the FFT was the only way to get information about the flow structure. The results were demonstrating the peaks, which were associated with certain periodic phenomena. In the light of analyzed convection phenomenon a characteristic frequency could be interpreted as the occurrence of vortex structures. The FFT analysis was conducted with an algorithm presented in [20]. The representative results are shown in Figs. 4 and 5.

Result discussion

In Fig. 3 (a) exemplary results of heat transfer analysis are shown. They are represented by the Nusselt number dependence on the thermo-magnetic Rayleigh number.

(a)



(b)

(c)

Fig. 3. (a) The Nusselt number versus the thermo-magnetic Rayleigh number; (b) convective and (c) concduction heat fluxes depended on the magnetic induction for various temperature differences.

Source: Authors

There is a clearly visible increase of the Nusselt number value at the magnetic induction up to 6T for the lowest temperature difference. However, at higher magnetic fields induction slight decrease of its value is observed. For higher temperature difference (5 degrees), increase of the Nusselt number is smaller, but still can be found. Whereas for the highest of examined temperature differences the Nusselt number decreased. The most likely, it could be explained by an increase of magnetic field influence on paramagnetic particles in nanofluid. The magnetic force was acting in the opposite way on the diamagnetic base fluid and the paramagnetic nanoparticles, at the upper part of the enclosure. Hence, with the increasing magnetic induction and the temperature difference an effect of paramagnetic nanoparticles became visible in the transport processes. The convective and conduction heat fluxes were analyzed for a better understanding of the issues in the corresponding temperature differences and shown in the Figs 3 (b) and (c). Convective heat flux did not change for the lowest temperature difference, while for the higher temperature difference a slight decrease at 6T of magnetic induction and its higher values could be observed. It should be noted that, the convective and conduction heat fluxes took higher values at the higher temperature differences, respectively. The conduction heat flux could be considered as almost constant, however with increasing magnetic induction it increased slightly for the highest temperature difference.

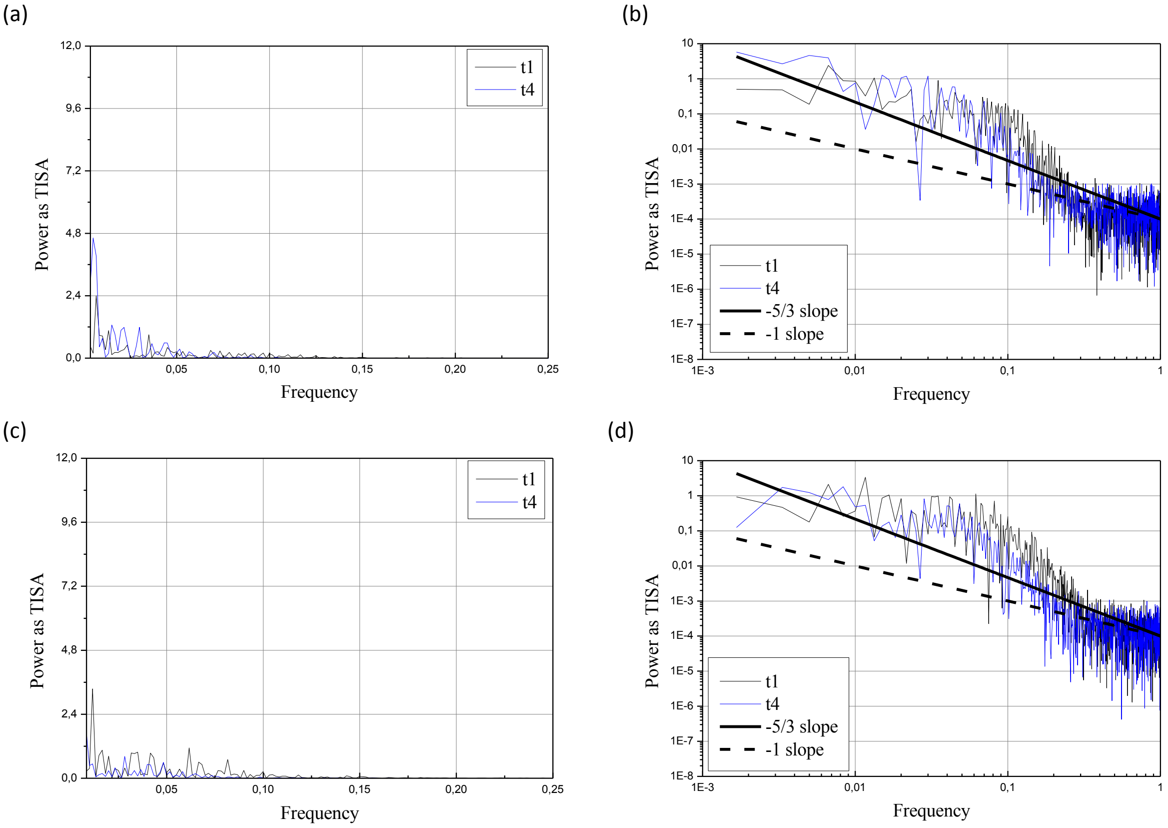


Fig. 4. The powerspectrum versus frequency (a) at 2T of magnetic induction,Ra_{TM}= $-2.51\cdot10^{6}$, (b) log-log scale at 2T of magnetic induction,,Ra_{TM}= $-2.51\cdot10^{6}$, (c) at 6T of magnetic induction,Ra_{TM}= $-3.90\cdot10^{8}$, (b) log-log scale at 6T of magnetic induction,Ra_{TM}= $-3.90\cdot10^{8}$, for temperature difference of ΔT = 5.

Source: Authors

Examples of spectral analysis as linear and log-log scale diagrams at 2T and 6T of magnetic induction are presented in Figs 4 and 5 for selected temperature differences, respectively. The various kind of power spectrum for 5 degrees of temperature difference are visible. The multiple peaks are shown at 2T of magnetic induction, which could indicate a multiscale structure of the swirls, while at 6T of magnetic induction the magnitude of the peaks is slightly smaller. The few clear peaks and many smaller ones are visible for 8 degrees of temperature difference at 2T of magnetic induction, which could point out on few large swirls and many small vortices present in the experimental enclosure. At higher value of magnetic induction the magnitude of peaks was reduced. Hence it could be stated that the increase of magnetic induction calmed down the fluid flow. The straight lines (-5/3 and -1 slopes) did not match the power spectrum distribution in any range for any presented temperature difference, what suggested that the flow did not occur in the inertial-convective turbulent regime [21]. However, the change in nanofluids flow structure was noticeable.

On the basis of presented and all performed graphs and analyzes of the power spectrum versus frequency, it could be said that the magnetic field affected the flow structure and therefore energy transport within the nanofluid.

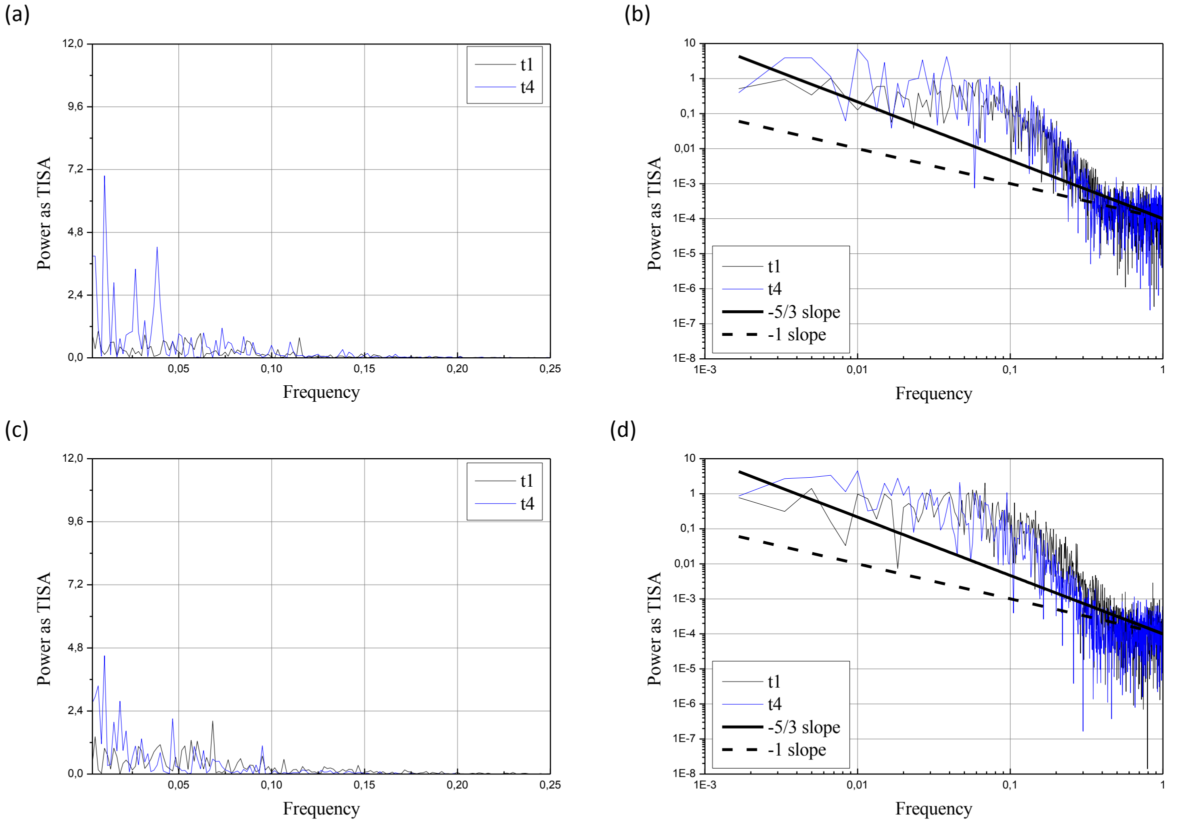


Fig. 5. The power spectrum versus frequency (a) at 2T of magnetic induction,Ra_{TM}= -4.09·10^6, (b) log-log scale at 2T of magnetic induction, Ra_{TM}= -4.09·10^6, (c) at 6T of magnetic induction,Ra_{TM}= -6.44·10^8, (b) log-log scale at 6T of magnetic induction, Ra_{TM}= -6.44·10^8, for temperature difference of ΔT = 8.

Source: Authors

Summary

In the paper the experimental analysis of thermo-magnetic convection of 0.112 vol.% Cu/CuO nanofluid was presented. The impact of magnetic field and various temperature differences on the heat transfer and the fluid flow structure was investigated. The recorded signal allowed analysis of the phenomena during the nanofluid thermo-magnetic convection. System of the gravitational and magnetic buoyancy forces, caused by different magnetic properties of base fluid and nanoparticles, was very complex. Therefore, the unequivocal answer on the question of potential utilization of low concentration nanofluid cannot be given. Such composition of nanofluid does not lead to a great effect, but it shows in which direction should go the next studies. In the next stage of study the nanofluids with the same magnetic properties of components will be considered to achieve the maximum magnetic field influence. Additionally, the interaction between fluid and particles in the magnetic field will be analyzed.

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Nomenclature

B - magnetic induction, T

c_p - specific heat, $\mathrm{J\cdot(kg\cdot K)^{-1}}$

F - force, $\mathrm{N\cdot m^{-3}}$

g - gravitational acceleration, $\mathrm{m\cdot s^{-2}}$

k- thermal conductivity, $\mathrm{W\cdot(m\cdot K)^{-1}}$

$Q_{\mathrm{net\_cond}}$- conduction heat flux, W
$Q_{\mathrm{net\_conv}}$- convective heat flux, W
Q_{loss}-heat loss flux, W
Nu - Nusselt number, dimensionless
T- temperature, K
T_0- reference temperature, K

Greek symbols

β - thermal expansion coefficient, $\mathrm{K^{-1}}$

ρ - density, $\mathrm{kg\cdot m^{-3}}$

μ - dynamic viscosity, $\mathrm{kg\cdot(m\cdot s)^{-1}}$

μ_0 - magnetic permeability of vacuum, $\mathrm{H\cdot m^{-1}}$

σ - electrical conductivity, $\mathrm{S\cdot m^{-1}}$

χ_m - mass magnetic susceptibility, $\mathrm{m^3\cdot kg^{-1}}$

Superscripts

bf - base fluid
g - gravitational buoyancy force
m - magnetic buoyancy force
nf- nanofluid
p - particles

References

[1] A. Ijam and R. Saidur, "Nanofluid as a coolant for electronic devices (cooling of electronic devices)," Appl. Therm. Eng. 32 (2012) 76–82

[2] N. Putra, W. N. Septiadi, R. Sahmura, and C. T. Anggara, "Application of Al2O3 Nanofluid on Sintered Copper-Powder Vapor Chamber for Electronic Cooling," Adv. Mater. Res. 789 (2013) 423–428

[3] M. Rasponi, F. Piraino, N. Sadr, M. Laganà, A. Redaelli, and M. Moretti, "Reliable magnetic reversible assembly of complex microfluidic devices: fabrication, characterization, and biological validation," Microfluid. Nanofluidics, vol. 10, no. 5 (2010) 1097–1107

[4] M. T. H. Mosavian, S. Z. Heris, S. G. Etemad, and M. N. Esfahany, "Heat transfer enhancement by application of nano-powder," J. Nanoparticle Res., vol. 12, no. 7 (2010) 2611–2619

[5] Y. Xuan and Q. Li, "Heat transfer enhancement of nanofluids," Int. J. heat fluid flow 21 (2000) 58–64

[6] K. Khanafer, K. Vafai, and M. Lightstone, "Buoyancy-driven heat transfer enhancement in a two-dimensional enclosure utilizing nanofluids," Int. J. Heat Mass Transf., vol. 46, no. 19 (2003) 3639–3653

[7] D. Wen, G. Lin, S. Vafaei, and K. Zhang, "Review of nanofluids for heat transfer applications," Particuology, vol. 7, no. 2 (2009) 141–150

[8] S. U. S. Choi and J. A. Eastman, "Enhancing thermal conductivity of fluids with nanoparticles," 1995

[9] R. S. Shawgo, A. C. Richards Grayson, Y. Li, and M. J. Cima, "BioMEMS for drug delivery," *Curr. Opin. Solid State Mater. Sci.*, vol. 6, no. 4, pp. 329–334, Aug. 2002.

[10] O. Mahian, A. Kianifar, S. A. Kalogirou, I. Pop, and S. Wongwises, "A review of the applications of nanofluids in solar energy," *Int. J. Heat Mass Transf.*, vol. 57, no. 2, pp. 582–594, 2013.

[11] Y. He, Y. Jin, H. Chen, Y. Ding, D. Cang, and H. Lu, "Heat transfer and flow behaviour of aqueous suspensions of TiO2 nanoparticles (nanofluids) flowing upward through a vertical pipe," *Int. J. Heat Mass Transf.*, vol. 50, no. 11–12, pp. 2272–2281, 2007.

[12] R. Taylor, S. Coulombe, T. Otanicar, P. Phelan, A. Gunawan, W. Lv, G. Rosengarten, R. Prasher, and H. Tyagi, “Small particles, big impacts: A review of the diverse applications of nanofluids,” J. Appl. Phys., vol. 113, no. 1 (2013) p. 011301

[13] T. Bednarz, E. Fornalik, H. Ozoe, J. S. Szmyd, J. C. Patterson, and C. Lei, “Influence of a horizontal magnetic field on the natural convection of paramagnetic fluid in a cube heated and cooled from two vertical side walls,” Int. J. Therm. Sci., vol. 47, no. 6 (2008) 668–679

[14] T. P. Bednarz, C. Lei, J. C. Patterson, and H. Ozoe, “Enhancing natural convection in a cube using a strong magnetic field — Experimental heat transfer rate measurements and flow visualization,” Int. Commun. Heat Mass Transf., vol. 36, no. 8 (2009) 97–102

[15] E. Fornalik, P. Filar, T. Tagawa, H. Ozoe, and J. S. Szmyd, “Effect of a magnetic field on the convection of paramagnetic fluid in unstable and stable thermosyphon-like configurations,” Int. J. Heat Mass Transf., vol. 49, no. 15–16 (2006) 2642–2651

[16] A. Roszko, E. Fornalik-Wajs, J. Donizak, J. Wajs, A. Kraszewska, and L. Pleskacz, “Magneto-thermal convection of low concentration nanofluids,” MATEC Web Conf., vol. 6, no. 18 (2014) 1–8

[17] T. Bednarz, E. Fornalik, T. Tagawa, H. Ozoe, and J. S. Szmyd, “Experimental and numerical analyses of magnetic convection of paramagnetic fluid in a cube heated and cooled from opposing verticals walls,” Int. J. Therm. Sci., vol. 44, no. 10 (2005) 933–943

[18] E. Fornalik, Magnetic convection of paramagnetic fluid in an enclosure. AGH Uczelniane Wydawnictwa Naukowo-Dydaktyczne, 2009

[19] Y. Xuan and W. Roetzel, “Conceptions for heat transfer correlation of nanofluids,” Int. J. Heat Mass Transf., vol. 43 (2000) 3701–3707

[20] http://www.fftw.org/.

[21] K. R. Sreenivasan, “The passive scalar spectrum and the Obukhov – Corrsin constant,” Phys. Fluids, vol. 8 (1996) 189–196