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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].

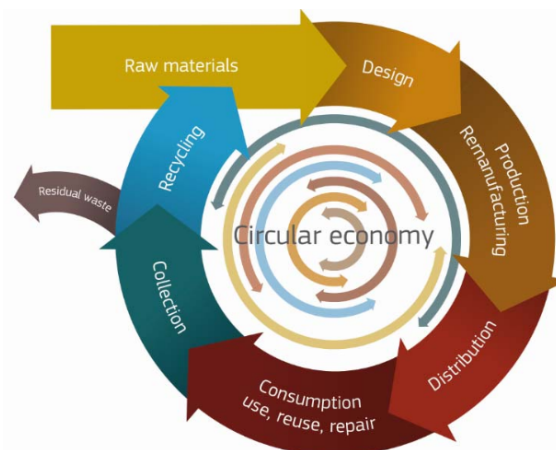


Fig. 1. Strategy of circular economy

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.

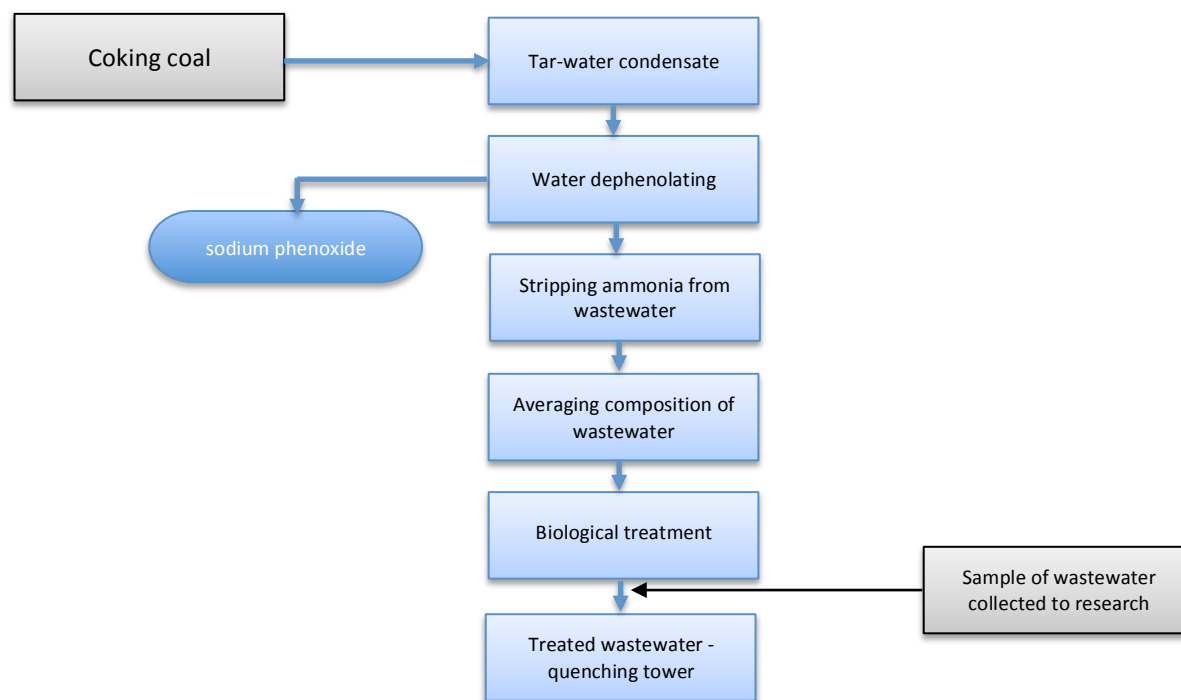


Fig. 2. Stages of coke wastewater treatment in analyzed plant

Source: Author's research

The samples were characterized for the concentration of selected physicochemical 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 physicochemical 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 were 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 $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (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 cm². 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·s⁻¹. The obtained equilibrium streams were up to $12.54 \cdot 10^6$ [m³/m²·s] after 140 minutes of filtration. The process parameters are shown in Figure 3.

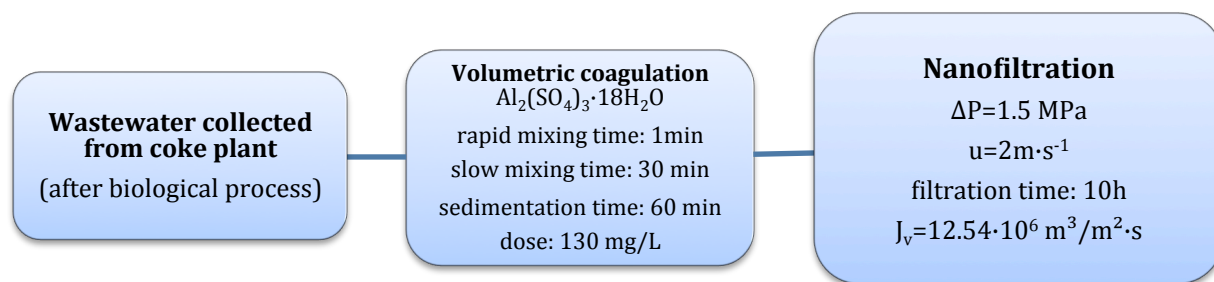


Fig. 3. The process parameters during coke wastewater treatment

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 O₂/L, ammonium nitrogen - 334.5 mg NH₄⁺/L, nitrate nitrogen - 35.7 mg NO₃⁻/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.

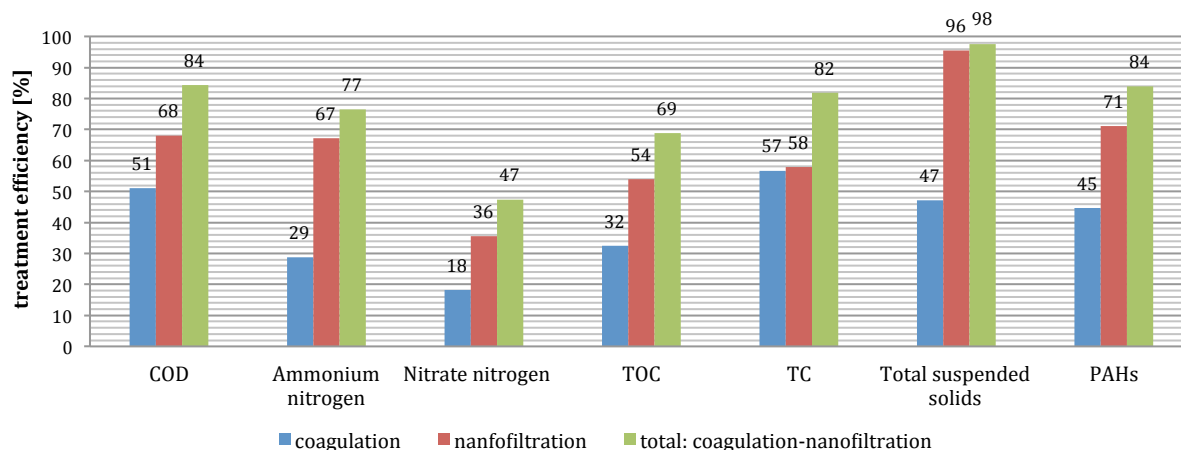


Fig. 4. The effectiveness of coke wastewater treatment

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 solids – 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 or 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 streams [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.

Acknowledgements

This research was supported by BS/MN-401- 313/12. Author Marzena Smol is a beneficiary of the project DoktoRIS – Scholarship Program for Innovative Silesia (DoktoRIS – Program Stypendialny Na Rzecz Innowacyjnego Śląska) funded by the European Union under the European Social Fund



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