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# Wastewater treatment in coke plants in the aspect of a circular economy

Marzena Smol[a,*], Maria Włodarczyk-Makuła[b], Jolanta Kozak[c]

[a]*Mineral and Energy Economy Research Institute of the Polish Academy of Sciences, Cracow, Poland, email: smol@meeri.pl, https://orcid.org/0000-0001-5833-2954*
[b]*Czestochowa University of Technology, Czestochowa, Poland, email: maria.wlodarczyk-makula@pcz.pl, https://orcid.org/0000-0002-3978-2420*
[c]*Chief Inspectorate for Environmental Protection, Central Research Laboratory, Czestochowa, Poland, email: jolanta.kozak@poczta.onet.pl, https://orcid.org/0000-0001-6816-4966*

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**ABSTRACT**

Nowadays, more and more attention is dedicated to the possibility of implementation of the circular economy (CE) solutions in various sectors. One of the interesting examples are wastewater treatment plants (WWTPs) – both industrial and municipal, where it is possible to recover valuable raw materials, energy and water, in accordance with the CE concept. This paper presents a review of possible technological solutions that can be implemented in the coke WWTPs, as a way toward a CE, that is the main economic policy of the European Union (EU). The special focus is dedicated to treatment methods of coke wastewater, which are integral part of environmental management in industrial plants. Scope of paper includes a short characteristic of coke plants and coke wastewater and an overview of treatment technologies that are used to remove various pollutants (including toxic organic substances) from this wastewater. Moreover, water and wastewater flows in coke plants are presented. There are several recovery and recycling possibilities of useful components and treated wastewater in coke plants. Currently, closing water and materials loops in the industrial plants, including coke plants, is forced by legal regulations and European recommendations regarding the CE implementation. Therefore, further development of innovation in this area, and the implementation of CE solutions in coke plants can be expected in the coming years.

*Keywords:* Coke plant; Wastewater treatment; Water recovery; Circular economy (CE)

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## 1. Introduction

In the European legislation, industrial wastewater is defined as “any wastewater that is discharged from premises used for carrying on any trade or industry, other than domestic wastewater and run-off rain water” [1]. Chemical composition of industrial wastewater is varied, depending on the production profile of the company and the technologies used [2,3]. Industrial wastewater may be a source of environmental pollutants for soil, surface water and groundwater [4], therefore, a composition of wastewater discharged to receivers must meet certain requirements [5], announced in the European [6,7] and national regulations. Currently, effective controlling of hazardous industrial discharges into sewers is crucial measure for protecting the environment – in the case of discharge of wastewater into natural reservoirs [8,9], for the effective and sustainable operation of the wastewater treatment plant (WWTP) – in the case of discharge of wastewater into sewage system [10]. It is also important to meet standards indicated in the Industrial Emissions Directive [11]. Currently, there is also strong need to be in the line with the assumptions of the European Green Deal (EGD), that was published in the European Union (EU), as official growth strategy in 2019

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* Corresponding author.

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[12]. The EGD covers all sectors of economy [13], therefore, they have been obliged to actively support a green transition, through actions aimed at protecting the environment and striving for climate neutrality by 2050 in Europe [14]. In March 2020, the European Commission (EC) adopted the EU industrial strategy, which is a plan for so-called "future ready" economy, to address challenge of green transformation [15]. Together with this industrial strategy, a second circular economy (CE) package – action plan was proposed, to modernise the EU's economy and support transformation toward CE in EU's countries [16]. A key objective of this new CE policy framework is to stimulate developing markets for circular products and services, in Europe and beyond [17]. In the latest EC documents on EGD and CE, a special attention is dedicated to possibility of using wastewater, including industrial wastewater, as a possible source of water, energy, as well as raw materials that can be recovered, according to the idea of more sustainable management of primary and secondary sources – as a practical example of CE implementation [18,19]. Therefore, in recent years, recirculation of process water, that is, water and wastewater generated in industrial plants in production processes, has been used more and more often. This approach to process water reuse is in line with the Zero Waste Europe agenda, which emphasises that sustainable economic growth is possible by moving to CE [20]. In the first European communication on CE, the EC emphasised that more efficient use of waste (including post-process water) may bring high economic benefits to the Member States. First and second CE action plans [20,21] support activities aimed at implementing CE in the industrial sector in various areas, including water, sewage and waste management [22]. Circular economy systems make it possible to preserve an added value of materials (or products) for the longest possible time and eliminate waste. Under Horizon 2020 and Horizon Europe initiatives, the EU presented opportunities for the transition to CE at national and international level through large-scale eco-innovation projects, while promoting the uptake of eco-innovative solutions in the market [23].

Currently, one of key areas of improvement is the industrial sector, as it uses the largest amount of resources (which as primary raw materials can be used in a more rational way), while generating the largest amount of waste (which as secondary raw materials should be managed in a more sustainable way) [12,21]. In the case of industrial wastewater, the condition for water recovery is the use of closed circuits, so-called zero liquid discharge (ZLD), where it is possible to recycle treated wastewater and reuse it as process and/or feed water [24]. The most important benefits of reusing treated wastewater include reduced costs of water collection and wastewater disposal, no environmental fees, increased reliability of existing systems, environmental and economic benefits via limited consumption of water, and independence due to the lack of need for a nearby water source [25]. For large plants, reusing water or treated circulating wastewater as a source in the production process is usually a much more appropriate solution than using surface water resources. This method is currently used in many industrial plants in the energy, refining, paper and microelectronics sectors [26]. Particularly noteworthy are industrial wastewaters that contain ingredients dangerous to human health and life, such as, for example, carcinogenic micropollutants [27].

The group of the most dangerous industrial wastewater includes wastewater generated during the coke production process as well as purification and further processing of selected by-products from coking [28]. Depending on the type of pollutants, the methods of coke wastewater purification should be selected in such a way as to ensure the highest degree of contamination removal at the lowest possible cost. Increasing the efficiency of wastewater treatment is associated with the expansion of wastewater treatment systems with new unit processes or it comes down to the modification of already operating systems [29]. This creates new opportunities for the implementation of CE solutions, in which there is not only the need to treat wastewater, but also to recover valuable raw materials and water (including recycling process water to industrial processes in the coking plant) [30].

There are several possibilities of closing materials and water loop in coke plans. The wastewater flow, that is usually discharged separately after pre-treatment, can be recirculated from the oxidative desulfurisation processes. BTX (mixtures of benzene, toluene, and the three xylene isomers, all of which are aromatic hydrocarbons) can be recovered from wastewater which is led to the tar or water separator [31]. An important element in the coking plant is phenol, which causes serious problems in the technology of coke wastewater treatment [32]. It can be recovered from the coal water with the use of solvent extraction process, before the coal water is directed to ammonia liquor storage tank.

As a consequence of legal demands, coke plant operators are obliged to improve technologies for emissions control, to revamp batteries, or even built a new battery if the latest standards may not be fulfilled under economic and technical reasons [33]. Moreover, due to the restrictions for treatment of industrial wastewater are constantly tightening [14], it is recommended to develop concepts and technological solutions ensuring the highest possible flexibility of the treatment and recovery installation, for example, through the use integrated systems that combine classic unit processes used in wastewater technology, that is, biological, chemical and physical [34,35].

The current paper presents the possible technological solutions that can be implemented in the coke wastewater treatments plans, as a way toward CE. The special focus is dedicated to treatment methods of coke wastewater (including biological methods), which are integral part of environmental management in industrial plants. The work contains review of applied solutions for coke wastewater treatment, recovery of useful components as well as recycling and use of treated wastewater from the perspective of CE transition. A comprehensive analysis of various data sources was conducted. They focused on following areas: industrial plants, coke plants, coke wastewater and circular economy. The reviewed databases included official EU' documents (regulations, directives, communications, working documents and reports), as well as available peer review publications available in selected scientific databases.

The new approach is to collect and present various possibilities of implementing CE solutions in the area of circular management of water and raw materials in the coke WWTPs.

## 2. Characteristics of coke plants

### 2.1. General information on coke plants

Coke production is associated with the process of high temperature pyrolysis of the coal in coking chambers. A final product is a coke (that constitutes approx. 75% of the efficiency of all coke plant products) and raw coke oven gas. Apart from coke and coke oven gas, there are tar and coke oven benzene as well as various, depending on the technologies used, products of desulfurisation and binding ammonia from coke oven gas – ammonium sulfate, sulfur, sulfuric acid. The amount of coal derived products is closely associated with volume of coke production. An average mass yields of the main products in coal-derived coke plants, calculated on dry coal charge, are as follows [36]:

- coke tar 3.5%–4.5%,
- decomposition water 3%, contained in tar and benzene,
- coke benzene 1%,
- ammonia 0.4% removed in the form of ammonium sulfate or decomposed in a nitrogen desulfurisation plant,
- purified coke oven gas 16.5%, approx. 315 $m^3$/Mg of dry charge.

In the global scale, there is about 560 coke oven plants globally. The significant part of them occur in Asia (China). Annual production of coke in the world reached 716 Tg in 2015. The highest volume was produced in plants in Asia, it was equal to 582 Tg. In Europe, approx. 6% of total world coke production was reported. The production capacity of EU coke plants was equal to 44 Tg in 2015. Out of the European plants, approx. 19 Tg of coke was produced, including 9.7 Tg in Germany, and 9.6 Tg in Poland. Currently, in Poland 9 coke oven plants are in operation. The largest one is plant Zdzieszowice, with annual capacity reaching 4.2 Tg. It is also the largest coke oven plant in the EU [37]. The main activity is the production of foundry and metallurgical coke, which (simplified) is produced in processes of degassing coal at high temperatures (in the range of 900°C–1,200°C) without air access. In addition to coke, the product is coke oven gas, which can be used in the economy after prior preparation (cooling and cleaning). During these multi-stage processes, tar, benzol, ammonium sulfate and sulfuric acid are separated from coal water, as useful components [38]. According to the applicable law, coke plants have to operate in accordance with the Best Available Techniques (BAT), which is a standard defining limit values of several emissions for huge industrial plants, as for example coke plants. BAT norm is based on Directive 96/62/EC on Integrated Pollution Prevention, so-called “IPPC Directive” – Integrated Pollution Prevention and Control. Characteristics of BAT in the coke industry in the EU are included in the BREF reference document [39]. Based on BAT standards, the technical and technological solutions aim to minimize the emission of impurities to soil, air and water [31,40].

### 2.2. Characteristics of coke wastewater

The amount of coke wastewater depends on the amount of raw material and production volume. In addition, the quantity is influenced by the type of gas and by-product treatment processes and the water and wastewater management used in the plant. The average amount of technological wastewater from coke plants ranges from 0.15 to 0.35 $m^3$/Mg of coal. Regarding the volume of coke production, the estimated amount of wastewater is in the range from 0.35 to 0.45 $m^3$ of wastewater [41,42].

The mainstream of wastewater in the coke plant is the outflow from the technological process, coke oven gas treatment and the processing of coking by-products. This is usually done at the carbon-based products department. The main wastewater streams are presented in Table 1.

Wastewater generated in the coke plant is characterised by a different composition, which depends not only on the type of raw material for coke production but also on the technological process. Among the pollutants in high concentrations are organic and inorganic pollutants. The basic organic pollutants in coke wastewater include: tar, oils, volatile and non-volatile phenols with steam as well

Table 1
Main wastewater streams in coke plants

| No. | Main wastewater streams in coke plant |
|---|---|
| 1 | Ammonia water, which is a mixture of ammonia water used in the initial cooling of coke gas, condensed water vapor released from the feed mixture and pyrogenic water |
| 2 | Outflows from benzol rectification and benzol condensation |
| 3 | Outflows from tar processing |
| 4 | Wastewater from gas desulphurization, transformation of hydrogen sulphide into sulfuric acid |
| 5 | Steam condensates used to heat media in technological processes |
| 6 | Outflows from ammonia stripping from coal water |
| 7 | Outflows from hydraulic closures of gas pipes |
| 8 | Steam condensates from cleaning devices and pipes |
| 9 | Wastewater draining from periodic cleaning of floors, apparatus, devices, drainage of installation trays |
| 10 | Ammonia water, which is a mixture of ammonia water used in the initial cooling of coke gas, condensed water vapor released from the feed mixture and pyrogenic water |

as aromatic hydrocarbons, including polycyclic. The inorganic ones are cyanides, sulfides, ammonium nitrogen and ammonium salts as well as anions such as chlorides, sulfates, sulfides, thiosulfates, rhodides. It should be emphasized that coke wastewater is listed as the most onerous industrial wastewater. The general qualitative characteristics of coke wastewater are presented in Table 2.

The selected pollutants in coke wastewater are toxic to aquatic organisms, therefore wastewater cannot be discharged into the sewage system or receiver. In accordance to the current legislation, it is necessary to carry out multi-stage wastewater treatment, which is carried out in integrated physico-chemical and biological processes [34].

Currently, in the most of coke plants a modernisation of the gas and wastewater treatment installations is being carried, using BAT, which have a significant ecological aspects. Among the recommended solutions should be listed: intensive gas cooling, gas desulfurisation using the ammonia method with catalytic decomposition of ammonia and utilisation of sulfur compounds using the Claus method as well as air-tight sealing of process equipment, and the expansion and modernisation of the biological wastewater treatment plant [36]. Those activities are integral part of water and wastewater management in coke plants.

## 3. Water and wastewater management

The method of water and sewage management in coke installations depends on technological conditions applied in given plant. Wastewater coming from larger plants is directed to multi-stage treatment processes, while wastewater from small plants, after initial treatment, is turned back to the technological cycle. It can be used for wet coke quenching or discharged to municipal treatment plants. Due to the tightening of requirements regarding the protection of water against pollution and limiting conditions for discharged wastewater into water and soil, there is a strong need to undertake technological activities related to continuous improvement of wastewater treatment efficiency in the existing coke wastewater treatment plants. At present, most coke plants modernise gas and wastewater treatment installations, taking into account the biological removal of nitrogen compounds (nitrification and denitrification), in accordance with BAT guidelines [47]. Considering WWTPs in coke plants as a part of CE, attention is now paid primarily to recovery of carbon derivatives and the use of treated wastewater and purified coke oven gas. Liquid phase management in coke plant depends on main coke production technology and technologies for recovery of useful components from the coke gas stream. As it has already been mentioned, components that can be used in the economy are separated from the processes of cooling and cleaning coke gas. These are products such as: tar, benzol and ammonium sulfate, sulfur and sulfuric acid [40]. Fig. 1 shows a simplified diagram of coke gas treatment and component recovery from coke oven gas.

By Regulation (EC) No. 1907/2006 of the European Parliament and of the Council of 2006, the REACH

Table 2
General qualitative characteristics of coke wastewater

| Index | References | | | | | |
|---|---|---|---|---|---|---|
| | Ranade et al. 2014 [43] | Mishra et al. 2021 [42] | Mielczarek et al. 2014a [44] | Sindera et al. 2011 [45] | Mielczarek et al. 2014b [46] | Kwiecińska et al. 2017 [37] |
| Temperature, °C | | 36 | | | | |
| pH | 6.5–10.9 | 7.5–9.1 | | 7.4–11.9 | 9.1–9.4 | 7.0–9.5 |
| Volatile phenols, g/m$^3$ | 18–2,026 | 260–3,000 | 200–2,925 | | | |
| General phenols g/m$^3$ | | | 1,343–6,630 | 31–2,027 | 381–534 | 500–1,500 |
| Organic compounds labeled as oxidizability, g·O$_2$/m$^3$ | | 2,500–10,000 | | | | |
| COD$_{Cr}$, g·O$_2$/m$^3$ | 770–4,200 | | 2,500–14,600 | 693–6,494 | 3,489–4,520 | 200–6,500 |
| BOD$_5$, g·O$_2$/m$^3$ | | | 800–5,840 | | 50 | 800–3,500 |
| TOC, g·C/m$^3$ | 126–1,182 | | | 72–1,489 | | |
| Oils and tars, g/m$^3$ | 2.2–175 | 100–240 | 60–998 | | | |
| Volatile ammonia calculated as NH$_4^+$, g/m$^3$ | | 110–900 | 100–1,165 | | | |
| Total ammonia expressed as NH$_4^+$, g/m$^3$ | 276–2,100 | 980–6,500 | | | | 50–200 |
| Rhodizonates, g/m$^3$ | 330–532 | 100–1,500 | 60–372 | 1.8–532 | | |
| Cyanides, g/m$^3$ | 10–80 | 10–100 | 10–80 | 1.6–18.1 | 11–27 | 5–20 |
| Sulfides, calculated as H$_2$S, g/m$^3$ | | 10–600 | | | | 10–50 |
| Chlorides, g/m$^3$ | 260–3,620 | 1640 | | | | 2,500–3,500 |
| Sulfates, g/m$^3$ | | 1,480 | | | | 900–1,200 |
| Thiosulfates, g/m$^3$ | | 290 | 369–1,000 | | | |
| Suspension, g/m$^3$ | | | 250–1,000 | | | |

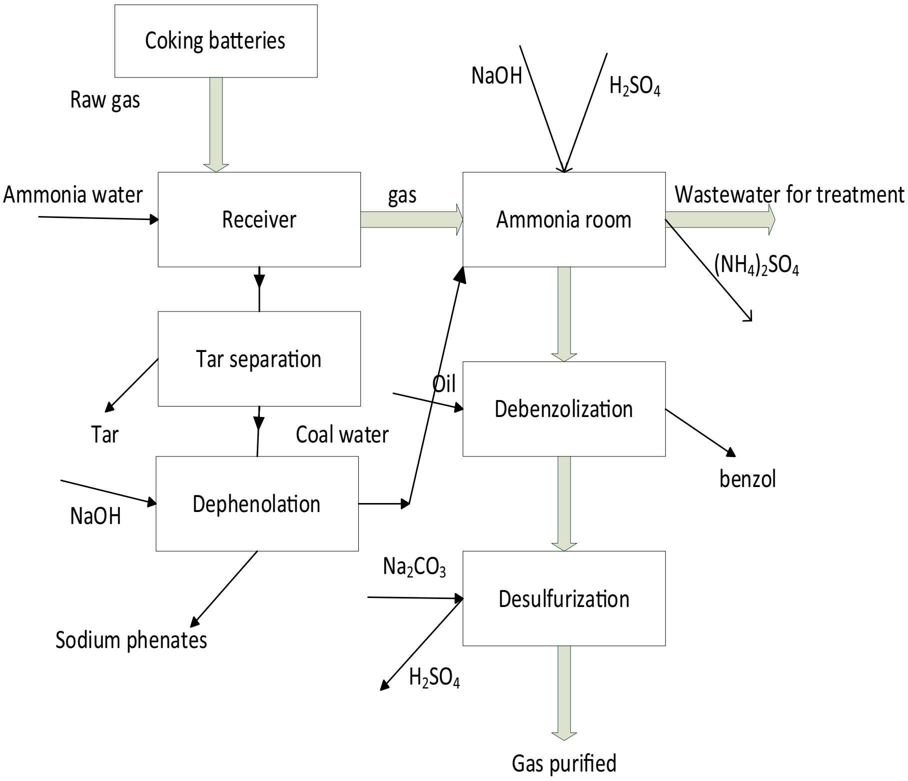

Fig. 1. A simplified diagram of coke gas cleaning and component recovery from coke gas (own, based on [42,43]).

(Registration Evaluation and Authorization of Chemicals) system was introduced in the EU countries. According to this document, each chemical product placed on the market must be registered, assessed, classified and authorised. Regarding the coke industry, coke as a major product does not have to be registered under the REACH system. But other products, such as coke oven gas, tar and coke oven benzol as well as ammonium sulfate, sulfur, sulfuric acid, are subject to registration [36]. These products can be useful in the chemical industry. For example, sodium phenolate can be used to produce phenol, cresols and xylene [Industry Standard]. On the other hand, benzol which is subjected to distillation may be a substrate for the production of benzene and its derivatives (SDS 2010). Cleaned coke oven gas is used in the technological process.

### *3.1. Treatment of coke wastewater taking into account biological processes*

The level and type of pollutants in the coke wastewater exclude the possible discharging it into water or soil without treatment [34]. Therefore, the coke plants are equipped with on-site coke wastewater treatment plants. They aim to minimise pollution load to the values required by legal regulations and hydro-legal permission. The functioning of WWTP on the site corresponds to the scope and level of BAT in the coke. However, often despite the use of highly effective solutions in the treatment technology of post-process coke wastewater its discharge to natural reservoirs is not possible, due to exceeded standards in the scope of selected physicochemical indicators. Even a multi-stage wastewater treatment process does not eliminate pollutants to a level that would allow the treated wastewater to be discharged to receivers. The multi-stage processes include chemical treatment and biological treatment preceded by the removal of ammonia and tar. Biological wastewater treatment can be carried out by means of activated sludge or activated sludge combined with the nitrification process, or activated sludge combined with preliminary denitrification and nitrification [36,45,48]. Wastewater is treated in several stages in large installation and plants, or directed to technological purposes (in closed cycle – after initial treatment). It can be recycled to coke wet quenching or to complement cooling circuits. If, on the other hand, wastewater cannot be used on-site the plant, or it is insufficiently treated, then it is necessary to transfer it off-site. Off-site transfer can be implemented via a sewer or any other ways, for example, with the use of specially adapted containers or road tankers. Fig. 2 shows the general scheme of coke wastewater treatment developed in the BAT document [31]. BAT guideline covers preliminary removal of tars, phenol and ammonia prior to the main wastewater treatment processes. A special role is played by biological processes, in which biodegradation of organic compounds, nitrification of ammonium nitrogen and denitrification of nitrates (V) take place under appropriate conditions. Fig. 3 shows a general example of a coke wastewater treatment scheme. A final stage of coke wastewater treatment is biological process or extraction dephenolation method. This method is a two-step method – in the first stage, phenols are extracted with the use of benzol, and in the second stage, sodium phenates are generated as a result of reaction of phenol-benzol with sodium

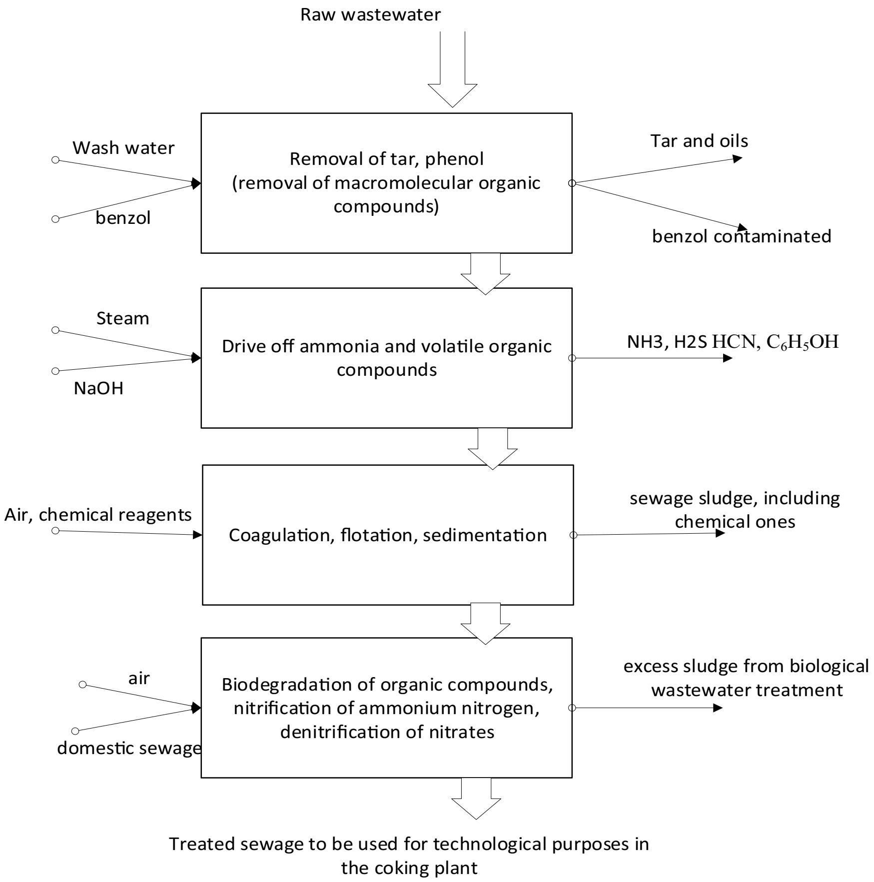

Fig. 2. General scheme of coke wastewater treatment (own, based on [40]).

hydroxide solution (lye) [31]. The technological system of the two-stage biological treatment with usage of activated sludge allows for the oxidation of organic compounds and nitrification of ammonium nitrogen and denitrification of nitrates. The degree of coke wastewater treatment in terms of organic compounds expressed by the chemical oxygen demand (COD) index may reach 96%, and with regard to volatile phenols – 99.9%. The concentration of organic compounds expressed by COD index usually does not exceed 250 g/dm$^3$, the concentration of ammonium nitrogen and rhodate does not exceed 10 g/m$^3$, the concentration of cyanides usually does not exceed 5 g/m$^3$, and volatile phenols and sulfides – 0.1 g/m$^3$ [42,43,49]. Vazquez et al. [50] studied laboratory-scale activated sludge plant to investigate the biodegradation of coke wastewater. This research was conducted with and without bicarbonate addition of. The presence of source of inorganic carbon was included to favor nitrification, due to alkalinity of coke wastewater was quite low. It was stated that maximum removal efficiency was observed for COD, thiocyanates and phenols without bicarbonate addition. The highest nitrification efficiency was obtained with addition of bicarbonate, while removal efficiency of phenols and COD was similar to those observed without nitrification [50].

In research of Wang et al. [28], the use of oxic biological pretreatment (OP) for removal of impurities form coke wastewater was effective (>80%) in the case of COD and SCN$^-$, but marginal for N. In the work by Bai et al. [35], bioaugmentation of phenolic compounds (showing high toxicity index) was studied. The study liquid was semi coke wastewater. The initial content of phenols was equal to 2,450 ± 1.2 mg/dm$^3$. In the removal process, high efficient was obtained, with content of phenols reaching 200 ± 0.9 mg/dm$^3$. Moreover, the observed removal efficiency of petroleum hydrocarbons by microorganisms was equal to 97.08% ± 0.09%. Wastewater after treatment showed more biodegradable effect, while its water quality showed significant improvement [35]. A novel integrated system that contains biological – electrocatalytic process was studied by [51]. The integrated process include: 2 three-dimensional electrochemical reactors (3DERs), three-dimensional biofilm electrode reactor (3DBER) and two biological aerated filters (BAFs). In the 3DERs system, 73.21% of COD was removed, 91.46% of NO$_3^-$–N, and 38.02% of NH$_4^+$–N. In BAFs system, NH$_4^+$–N was transferred to NO$_3^-$–N via microbial nitrification. In 3DBER system, residual NO$_3^-$–N was removed by bio-electrochemical denitrification. This system could remove 99.38%–99.74% of NH$_4^+$–N, 74.72%–83.27% of COD, and 69.64%–99.83% of TN from coke wastewater. Moreover, a significant reduction of wastewater toxicity was observed [51]. It is worth to notice that in the early 1990s, coke WWTPs showed significant modernisation related to the implementation of biological processes based on the activated sludge method, that is, specially selected microorganisms

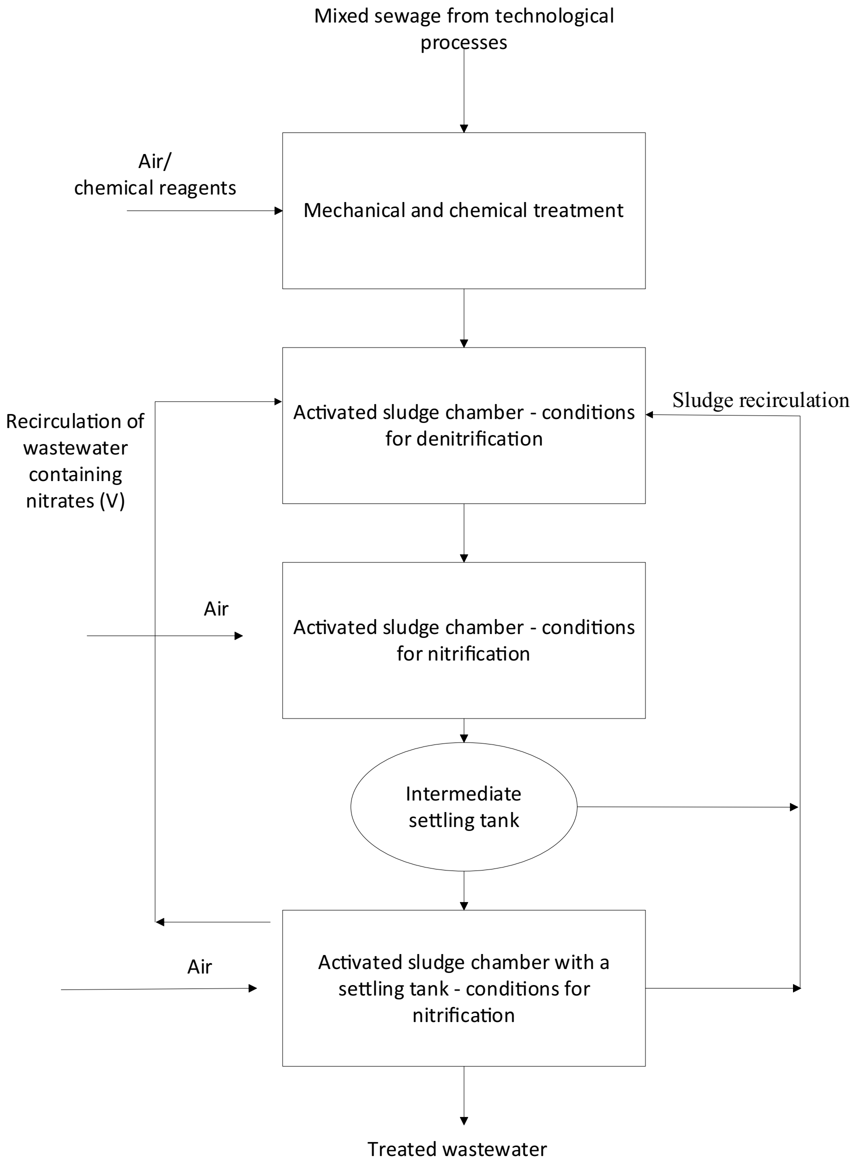

Fig. 3. An exemplary technological and process diagram for the treatment of mixed wastewater flowing out of the coke plant processes (own, based on [42,43,49]).

capable of removing nitrogen compounds and organic compounds. As a consequence of several further changes and improvements introduced to the coke technologies (related to the purification and recovery of raw materials from coke oven gas) a composition of coke wastewater was subject to further improvements, which required the introduction of additional methods of pollutants removal. The threats associated with limited access to good quality water observed in recent years have prompted not only research, but also government and economic institutions to look for and develop solutions related to reducing water consumption and recovering water from waste sources (including sewage), also in coke industry [37]. In the international project, entitled "Innowatreat – An Innovative System for Purification and Recovery of Water From Coke Wastewater Using Clean Technologies", it was shown that thanks to the currently used coke wastewater treatment processes, it is possible to implement more advanced solutions, thanks to which the wastewater can be a source of water necessary for the proper functioning of the plant (itpe.pl/innowatreat). This is in the line with CE assumptions, and should be promoted among all coke plants in Europe and aboard.

### *3.2. Methods of post-treatment coke wastewater*

Coke wastewater treatment processes are carried out in several stages, however in many cases the used treatment methods are not sufficient to remove all pollutants, especially those difficult to decompose. The removal of polycyclic aromatic hydrocarbons (PAHs) as well as cyanides and sulphides can be particularly troublesome. PAH concentration even in treated coke wastewater may exceed 1 mg/dm$^3$. This is particularly problematic when this wastewater is used in the coke plant for wet quenching (cooling) of coke. The extinguishing process can thus become a potential source of PAHs that are released into the atmosphere [46]. Also, the introduction of treated wastewater to the receiver or sewage system is not a good solution due to its toxicity. Research on the treatment of raw and treated coke wastewater was carried out various researchers [44,52,53]. These studies involved the application of the process, adsorption, coagulation and membrane processes to the treatment of raw wastewater. In the case of biologically treated wastewater, processes such as reverse osmosis, ultrafiltration in a system integrated with coagulation and methods of advanced oxidation were used [54,55], to support the biological processes in coke wastewater. In general, the composition and specificity of coke pollutants require a necessity of appropriate selection of treatment method [42].

### *3.2.1. Advanced oxidation methods*

The methods of advanced oxidation include various techniques, and their common feature is the generation of radicals as compounds with strong oxidizing properties [56]. They are proposed as the last stage of wastewater treatment, after treatment with biological methods, or as a preliminary stage of treatment to remove organic impurities from coke wastewater. The mentioned process could increase biodegradation and may be integrated with conventional biological process to obtain high quality wastewater. The main objective is to remove pollutants from wastewater, including toxic volatile organic compounds such as PAHs. A set of technological parameters of advanced chemical and photochemical oxidation to effectively reduce the content of these compounds in coke wastewater was proposed in [55]. With the use of modified Fenton reaction, a concentration of PAHs, mainly with the heavier fraction, was reduced by nearly 99%. Calcium peroxide was used as the source of hydroxyl radicals. In other studies, using sodium percarbonate also obtained similar results, with 4–6 rings hydrocarbons being removed with greater efficiency than the lighter PAHs [57,58]. The classic Fenton's reagent, as hydrogen peroxide, iron ions in an acidic environment was studied by Chu et al. [59]. COD value decrease by 50% compared to the initial values. The rate of oxygen uptake in the wastewater (reaction time 1 h) increased by about 65% compared to the raw coke wastewater. The results indicate a significant improvement in biodegradation of coke wastewater [59]. Currently, removal of nitrogen from coke wastewater is problematic due to conventional biological methods could be not sufficiently effective in the presence of concentrated biotoxic components, including for example phenolic compounds or thiocyanide ($SCN^-$). The advanced oxidation processes (with Fenton and photo-Fenton reaction) were used also by Krzywicka and Kwarciak-Kozłowska [60] to remove pollutants from coke plant wastewater. Authors confirmed that the usage of Fenton process with ultraviolet radiation shown a better result in removal of selected impurities. Oulego et al. [61] studied wet oxidation process to remove pollutants from coke wastewater containing high content of thiocyanate. There was significant effect of temperature and oxygen concentration on thiocyanate wet oxidation observed – higher in raw coke wastewater then in synthetic wastewater containing only thiocyanate. It was also proven that carbonates, sulfate, and ammonium are the main products of reaction of thiocyanate wet oxidation. In work of Li et al. [62], a supercritical water oxidation (SCWO) method was used to treat semi coke wastewater. It was shown that changes in the key operating parameters (as oxidation coefficient, temperature of reaction residence time) could positively impact on reaction mechanism for organic compounds in semi coke wastewater. The findings shown 99.02% and 63.94% removal for COD and $NH_3^-N$ under the condition of 25 MPa, 600°C, 1.3 times oxidation coefficient and 10 min [62]. Wang et al. [28] proposed a novel ternary process to remove nitrogen from coke wastewater, which is based on combined Fenton pretreatment, biological pretreatment, as well as final partial nitrification–denitrification (PN) process. Authors indicated that oxic biological pretreatment may remove approx. 80% of $SCN^-$ and COD in coke wastewater, through usage of pristine coke wastewater sludge. In this process, Fenton pretreatment could further degrade a residual toxic organic substances, while protecting the metabolism of denitrobacteria and nitrobacteria. It could allow to efficient reduction of $NH_4^+$–N and TN content (which appears in final PN process with self-cultivated sludge). This research presents integrated biological – physicochemical systems for removal of nitrogen from toxic coke wastewater [28].

### *3.2.2. Adsorption, coagulation and membrane processes*

Adsorption is a method that is widely used in wastewater treatment. Materials with high sorption properties are used as adsorbents. Usually it is activated carbon, but it can also be ashes, pumice stone, fruit kernels, and carbon nanotubes [63,64]. In the research, where coke coal was used as an adsorbent, COD was reduced by over 76%, moreover, the addition of coke coal before the biological process allowed to removal of biodegradation inhibitors, which created more efficient conditions for microorganisms present in the activated sludge and intensified the processes of biodegradation, nitrification and denitrification [65]. One of the most commonly used pollutants (including PAHs) adsorbents from aqueous solutions, as coke wastewater, is activated carbon. Vázquez et al. [66] studied coke wastewater (after biological treatment) that still contained small amounts of phenolic compounds. The following adsorbents were used: granular activated carbon, the resins XAD-2, OC-1074, AP-246. Authors indicated that activated carbon was the most effective to remove residual phenols from coke wastewater. The final concentration of impurities permits effluent to be directed to sewage system for further treatment at WWTP. The other tested adsorbents (XAD-2, AP-246, OC-1074 resins) were less effective, especially XAD-2, what was correlated with their lower adsorption capacities [66]. It has been shown that the degree of PAH removal with the use of activated carbon depends on following factors: concentration of PAH compounds in the solution, contact time, carbon type and its dose [67]. An important factor was also size of the adsorbate particles, which determines their transport inside the adsorbent. Activated carbons catalyze the formation of hydroxyl radicals [68], which simultaneously results in the oxidation of organic compounds adsorbed on their surface. Coagulation is an important process in soluble containments removal and both solid–liquid separation in water solutions [69]. In recent years, advanced work has been carried out to improve and modify coagulation process. It consists in the usage of new coagulants (pre-hydrolyzed salts) and flocculants, which accelerates the process and minimizes the required doses of reagents. Li et al. [70] proposed an integrated system of coagulation and adsorption for treatment of biologically pretreated coke wastewater in the laboratory, pilot, as well as industrial scale experiments. High efficiency of pollutants removal was obtained in this one-step novel process, reaching 85.3% and 99.4% for COD and cyanide, respectively [70]. Coagulation and zero-valent iron (ZVI) processes were studied to remove of COD from coke wastewater. The findings indicated that ZVI was more effective, with COD removal efficiency reaching 43.6%. The determined optimal condition of coagulation (400 mg/L of $Fe_2(SO_4)_3$ as coagulant at pH 3.0–5.0) shown efficiency of COD removal in the range of 27.5%–31.8% [69]. Liu et al. [71] studied three kinds of micro-bubbles on the coagulation flotation process to treat coke wastewater under optimum coagulation conditions, that were obtained from zeta potential measurement. It was shown that micro-bubble flotation integrated with ozone indicated the highest efficiency of pollutants removal. The used ozone micro-bubbles showed high absolute zeta potential values, producing repulsion forces, and therefore – avoiding the coalescence of bubbles. Moreover, attractive interaction between bubbles and particles in coke wastewater was observed. It was also indicated that the ozone micro-bubble system generated the most hydroxyl radicals, which positively effect on degradation of organic material in analysed wastewater samples [71]. Smol and Włodarczyk-Makuła [72] investigated coagulation as pre-treatment method for coke wastewater. The decrease in the concentration of studied indicators was observed with the use of alum (aluminum sulfate $Al_2(SO_4)_3{\cdot}18H_2O$) as coagulant: COD – 26.8%, ammonium nitrogen – 35.7%, TOC – 28.1%, TC – 39.1%, SS – 39.5% and 16 PAHs – 57% [72]. Wang et al. [73] studied an oxic-anoxic-oxic (O-A-O) processes, integrated with coagulation and ozonation to treat coke wastewater. High removal efficiency was obtained for $NH_4^+$–N (91.5%–93.3%) total nitrogen (91.3%–92.6%) and COD (89.1%–93.8%). It was proven that high removal of $NH_4^+$–N was observed due to the location of an aerobic tank in front of A-O system (which may mitigate the inhibitory effect of toxic pollutants in coke wastewater on nitrifying bacteria.

In the case of using physical processes, high pollutants removal effects from wastewater are often not achieved. Greater efficiency is achieved by integrating biological processes with physicochemical processes. Literature data indicate that the use of membrane processes is effective in removing of pollutants, including PAHs from coke wastewater [46]. In membrane techniques, a driving force is a difference in pressure across the membrane. They are usually used in the aqueous solutions [34]. The highest efficiency in pollutants removal from industrial wastewater have reverse osmosis (RO) and nanofiltration (NF), followed by ultrafiltration (UF) and microfiltration (MF). The membrane techniques showed the high efficiency in the treatment of coke wastewater [34]. The use of integrated coagulation systems – RO and coagulation – NF for post-treatment coke wastewater allowed to reduce the concentration of the tested indicators (COD, TOC, TN, turbidity, Σ16 PAHs). In the case of PAHs removal, the reverse osmosis coagulation system proved to be more effective. The total content of Σ16 PAHs after nanofiltration reached 18.69 μg/L and after RO 5.94 μg/dm³. The average value of the retention coefficient for RO was 89.9% [74]. In other studies, the use of integrated membrane processes (filtration on sand bed—reverse osmosis), in the case of sand bed filtration, the COD value decreased by 39.1% and after RO by 84.6%. The initial concentration of PAHs in coke wastewater was almost 95 μg/dm³. After filtration on the sand bed, the concentration of the tested PAHs decreased gradually by 52.3%, and after reverse osmosis by 94%. The efficiency of removal of individual hydrocarbons was in the range of 19%–100% [75]. Research on separation of cyanide from coke wastewater was carried out by Kumar et al. [76] in a cross-flow NF membrane module following MF of coke wastewater. Approx. 94% of cyanide was removed during this process. The results showed that MF and NF with properly selected membranes in dedicated module may lead to a help to solve a problem with cyanide removal from coke wastewater. Kumar et al. [77] studied integrated membrane – hybrid process that ensures reuse of water and recovery of ammoniacal nitrogen as struvite from coke wastewater was proposed. It is an example of good practices in the CE implementation in coke plants. In the membrane module more than 95%, 96%, 90% of the cyanide and phenol, and $NH_4^+$–N, respectively, were removed.

### *3.3. Circular water and wastewater flows in coke plants*

There are some CE solutions for water and wastewater in coke plants. The possible flows of water in coke plant are presented in Fig. 4. In general, there are water flows in coke plants, that can be drained from the coke oven results from ammonia liquor or steam. These substrates are mainly used in goosenecks for suction and direct cooling of charging gases, as well as moisture of coal and chemical water (water generated in cooking process). Other condensates are formulated from the coke oven gas treatment in the by-product plant (in case of direct cooling, in electrostatic precipitator and scrubbing units). This condensed water and tar from the collecting main (downstream of the gooseneck), the coolers and the electrostatic precipitator are led to the tar/water separator. The primary cooling could be conducted by direct, or indirect cooling (which is more popular). During indirect cooling, water is circulated in a closed cycle and does not affect wastewater quantity, while during direct gas cooling – the cooling water is considered to be a washing liquor and is eventually drained via the still. The possible water losses could occur during the recooling of cooling waters as well as condensates by evaporation of cooling waters. This water from the tar or water separator, so-called 'coal water' shows high content of ammonia, and is directed to ammonia liquor storage tank [40]. Usually, in coke plants, most of water flows (excluding water from indirect cooling systems as well as wet oxidative desulfurisation systems) are eventually drained from the ammonia still and led to WWTP. There are high concentrations of $NH_3$ in the ammonia still. There is need to decrease ammonia concentration before discharging the water to a WWTP or to natural reservoirs.

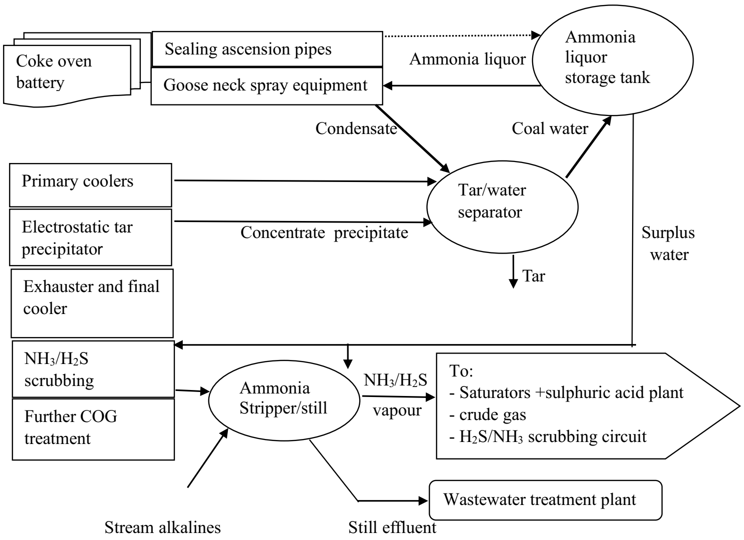

Fig. 4. Scheme of example water flows in a coke oven plant (own, based on [40]).

Table 3
Possibilities of circular economy implementation in water flows in coke plants (own based on [40])

| Coke plant area | Circular economy solution example |
|---|---|
| Circular flow of wastewater | BTX recovery from wastewater which is led to the tar or water separator<br>Circular flow of wastewater from the oxidative desulfurisation processes (that is usually discharged separately after pre-treatment) |
| Circular flow of phenol | Circular flow of phenol (with concentration >3 g/dm$^3$) could be recovered from the coal water with the use of solvent extraction process, before the coal water is directed to ammonia liquor storage tank |
| Circular flow of chemical water | Circular flow of chemical water from (optional) sulphuric acid plant (that is usually led to the still)<br>Circular flow of chemical water from (optional) Claus process which usually is not condensed but directed to the atmosphere via a stack; other alternative is injection of this water into the raw gas, before treatment |
| Indirect gas cooling water | Indirect gas cooling water which is recirculated and does not affect wastewater quantity; during direct gas cooling, the cooling water is treated as washing liquor and it could be drained via the still |

The circular management of ammonia includes its recovery (as valuable by-product) in the form of anhydrous ammonia or ammonium sulfate. Moreover, there is strong need to remove of ammonia is extremely because of highly toxicity of free ammonia for water environment, as well as biological WWTPs. It is also wort to notice that ammonia shows quite very oxygen demand, therefore there is a justified risk of oxygen depletion in WWTPs or the recipient water [40]. The presented aspects affected installation of ammonia strippers in most of coke oven plants. Ammonia strippers strip $NH_3$ and $H_2S$ from liquid phase by alkaline additions and steam. Then, vapours are directed to a crude gas or to scrubbing circuit of $NH_3/H_2S$ (in order to improve efficiency of $H_2S$ scrubbing) or to a sulfuric acid plant, where $H_2S$ and $NH_3$ can be together incinerated. There are also other possibilities of CE implementation in water flows in coke plants, as presented in Table 3. During direct gas cooling, the cooling water is treated as washing liquor and it could be drained via the still.

It is also worth to notice that more and more coke plants try to adapt their technological lines to the need to recover raw materials and water in the plant, very often in the area of water and sewage management. However, in the case of these enterprises, it requires significant financial outlays related to investments (new installations or modifications of existing installations), which is still the main barrier to the implementation of such solutions. Undoubtedly, the driving force behind the implementation of CE model in coke plans are changes in the law, especially in the field of more pro-environmental technologies, recovery of raw materials, energy and water in industrial plants, as well as numerous EC's postulates in the field of transformation towards the CE model.

## 4. Conclusion

- Closing water and materials loops in the industrial plants, including coke plants, is forced by legal regulations and the European recommendations regarding CE implementation.
- The group of the most dangerous industrial wastewater includes wastewater generated during the coke production process.

- Highly efficient treatment processes allow the treated wastewater to be reused for technological purposes.
- The chemical or biological methods of coke wastewater treatment are high effective in the context of pollutants removal.
- One of the most important challenges for the coke industry are the growing requirements related to the reduction of adverse environmental impact.

## Author contributions

Conceptualization M.S. & M.W-M.; methodology M.S.; validation M.S., M.W-M.; investigation M.S., J.K., M.W-M.; resources M.S., J.K., M.W-M., writing—original draft preparation M.S., J.K., writing—review and editing M.S., visualization M.S. & M.W-M.; project administration M.S.; funding acquisition, M.S.

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## Data availability statement

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

## Ethical approval

Not applicable.

## Conflicts of interest

The authors declare no conflict of interest.

## Consent to participate

Not applicable.

## Consent for publication

Not applicable.

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