The innovative system for coke oven wastewater treatment and water recovery with the use of clean technologies

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1. Introduction

Coke oven wastewater formation is connected with the production of coke carried out at number of coke oven plants over the world. The wastewater is highly loaded stream contaminated with a range of organic and inorganic substances, and requires sophisticated methods of treatment before its further utilization. Within this report, current situation of coke production and related amount of coke oven wastewater are shown together with description of the stream formation, methods of treatment and utilization.

2. Coke production process and application

Coke is produced by the destructive distillation of coal in coke ovens. Specially prepared coal blend comprising of various types of coals of desired coking parameters is heated in an oxygen-free atmosphere (coked) until most volatile components in the coal are removed [1-3]. The process is carried out in battery, which contains twenty or more tall, wide and narrow ovens arranged side by side. After charging, a coke oven is heated for twelve or more hours, during which a variety of volatile compounds evolves from coal. If these volatiles are further recovered, there is a by-product process arrangement. In a non-recovery battery, released volatiles are burned in space above coke or in flues, which heat the oven. The material remaining after coking process is a carbon mass called coke, and it is used in various processes, among which pig iron production is the most significant one [4-8]. All areas of possible coke application are shown in figure 1.

Over 90% of worldwide coke production is used in blast furnace process. Coke is the most important reducing agent in hot metal production. It removes the oxygen either indirectly by forming carbon dioxide or directly using its inherent carbon content. Coke functions as both a support material and a matrix through which gas circulates in the stock column. So far, coke is the most appropriate agent for blast furnace operations and it cannot be replaced by coal or other fuels [8-12].

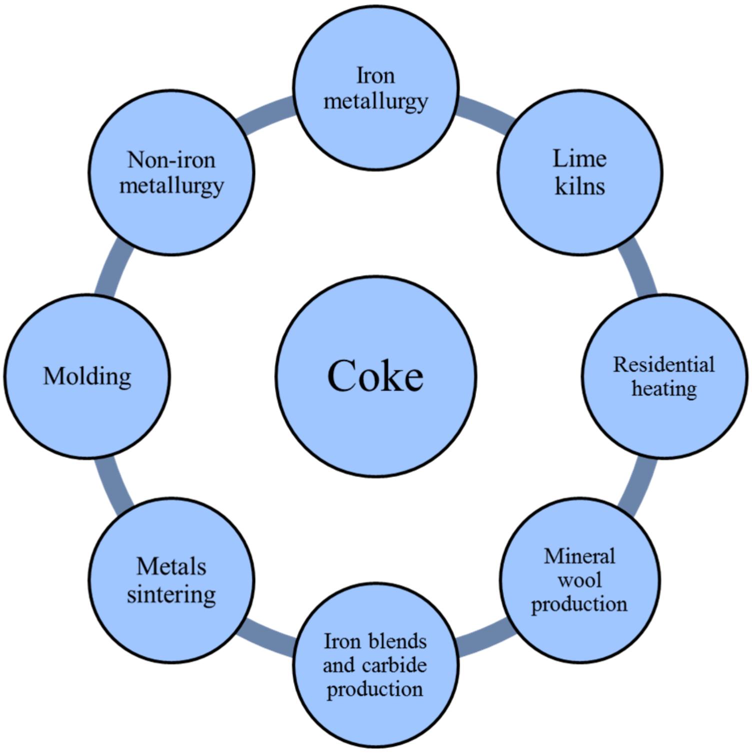

Figure 1. Areas of coke application [1-11]

3. Worldwide and European coke production

There are over 560 coke plants in the world (fig.2). Most of them (ca. 400, with over 600,000 t/y capacity each) are located in China. Approximately 6% of total world coke production is generated in Europe at 59 coke oven plants (fig.3). In 2015, the worldwide production of coke reached 651 Mt, while in EU it was 44 Mt, among which above 19 Mt were generated in Germany (9.7 Mt) and Poland (9.6 Mt) [13-15].

Figure 2. Number of coke oven plants over the world [13-15]

Figure 3. Number of coke oven plants in Europe [13-15]

4. Coke oven plant operation

Coke oven plants are complex technological plants, which comprise of different technological sites, where coal preparation, coking and coal by-product recovery and upgrading occurs. The scheme of coke oven plant is presented in figure 4.

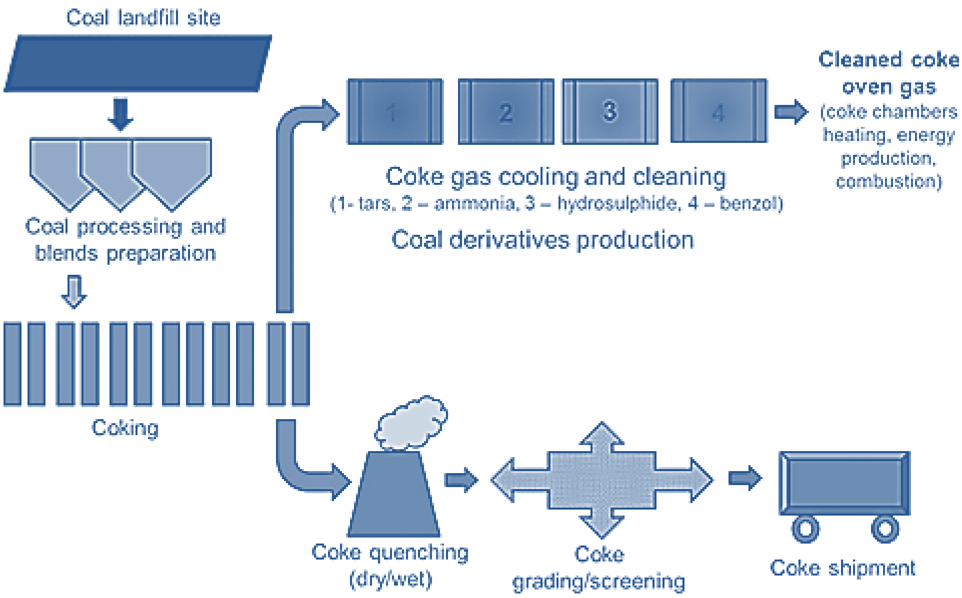

Figure 4. The basic scheme of coking plant

Processes performed at coking plants comprise of several technological operations, among which one can distinguish [15-18]:

- preparation of coal blend from coals deposited at the coal site;
- supply of coal blend tower with coal;
- drawing of coal from coal tower and charging of coke ovens with coal;
- heating of coke ovens with coke oven gas and coal blend coking;
- coke pushing;
- coke quenching (wet or dry);
- collection of raw coke oven gas;
- coke oven gas cleaning;
- coal by-product processing.

Except of coke, the coke making process results in formation of other products, the share of which depends on coking coal properties and coking process conditions, but in general it can be established at [15-18]:

- Coke – 70-80%
- Tar – 2.5-4.5%
- Pyrogenetic water – 3-5%
- Ammonia – up to 0.4%
- Benzole – up to 1.3%
- Clean COG – 12-18%

5. Coke oven wastewater formation

The processing of coke oven gas and the recovery of coal derivatives results in the formation of highly contaminated liquor which, after separation of tars and ammonia, becomes coke oven wastewater. The liquor is formed during coke oven gas cooling stage (gas cooling/condensation unit), where tars, water vapor and other substances present in the gas condensate or are partially washed out from the gas. The liquor is firstly directed to tars separation unit, at which two major streams are formed: organic (tars) and aqueous. The latter phase is partially used to provide water for the gooseneck spray equipment, while the rest can be involved in further gas treatment for removal hydrogen sulphide by means of absorption. The surplus amount of the liquid is directed to ammonia stripping, and the stripping column effluent (so called still effluent) is introduced to coke oven wastewater treatment plant [20-23]. The formation of coke oven wastewater at coking plant is shown in figure 5, while its typical composition is presented in table 1. It is assumed that 0.6 to 1.6 m^3 (in some cases even 4 m^3 is reported) of wastewater is generated per every ton of coke. It means that ca. $750 \cdot 10^6$ m^3 of coke oven wastewater is annually generated at coke oven plants around the world, while in Europe it is ca. $92 \cdot 10^6$ m^3 (in Poland ca. $10 \cdot 10^6$ m^3).

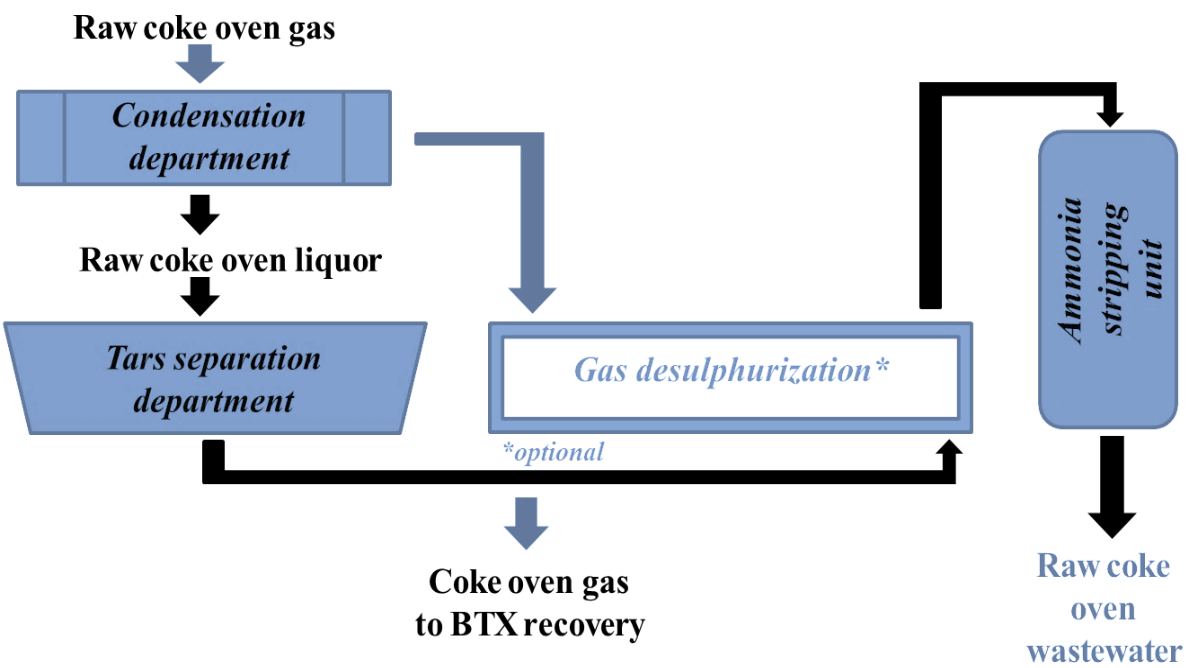

Figure 5. The scheme of formation of coke oven wastewater

Table 1. Typical composition of raw coke oven wastewater[15-23]

Parameter	**Unit**	**Concentration in raw coke oven wastewater**
pH	-	7-9.5
Specific conductivity	µS/cm	5000-12500
COD*	mgO_2/dm^3	200-6500
BOD_5**	mgO_2/dm^3	800-3000
PAHs***	mg/dm^3	5-150
Sulphides	mg/dm^3	10-50
Cyanides	mg/dm^3	5-20
Thiocyanates	mg/dm^3	50-420
Phenols	mg/dm^3	500-1500
Ammonia	mg/dm^3	50-200
Chlorides	mg/dm^3	2500-3500
Sulphates	mg/dm^3	900-1200

* Chemical oxygen demand; ** Biological oxygen demand; ***6 Borneff

6. European regulations and documents on coke oven wastewater

6.1. BAT conclusions

Having regard to Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions, the Commission established the best available techniques (BAT) conclusions on industrial emissions for iron and steel production, which can be found in Commission Implementing Decision of 28 February 2012 (2012/135/EU).

BAT conclusions are defined as reference standards for permissible emissions established for a given branch of industry defined for a best available technique applied in a given process. They determine the reference points used to set permit conditions for installations covered by the IED. Within a range of conclusions for coke oven plants, points 55 and 56 are devoted to coke oven wastewater, in which one can find that [24]:

> 55. BAT is to pretreat wastewater from the coking process and coke oven gas (COG) cleaning prior to discharge to a wastewater treatment plant by using one or a combination of the following techniques:

- using efficient tar and polycyclic aromatic hydrocarbons (PAH) removal by using flocculation and subsequent flotation, sedimentation and filtration individually or in combination;
- using efficient ammonia stripping by using alkaline and steam.

> 56. BAT for pretreated wastewater from the coking process and coke oven gas (COG) cleaning is to use biological wastewater treatment with integrated denitrification/nitrification stages. The BAT-associated emission levels, based on a qualified random sample or a 24-hour composite sample and referring only to single coke oven wastewater treatment plants, are:

- chemical oxygen demand (COD) < 220 mg/dm^3
- biological oxygen demand for 5 days (BOD_5) < 20 mg/dm^3
- sulphides, easily released < 0.1 mg/dm^3
- thiocyanate (SCN^-) < 4 mg/dm^3
- cyanide (CN^-), easily released < 0.1 mg/dm^3
- polycyclic aromatic hydrocarbons (6 PAH Boerneff) sum of Fluoranthene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene and Benzo[g,h,i]perylene) < 0.05 mg/dm^3
- phenols < 0.5 mg/dm^3

- sum of ammonia-nitrogen (NH_4^+-N), nitrate-nitrogen (NO_3^--N) and nitrite-nitrogen (NO_2^--N) < 15 – 50 mg/dm^3.

Regarding the sum of ammonia-nitrogen (NH_4^+-N), nitrate-nitrogen (NO_3^--N) and nitrite-nitrogen (NO_2^--N), values of < 35 mg/dm^3 are usually associated with the application of advanced biological wastewater treatment plants with predenitrification/nitrification and post-denitrification.

Hence, it can be sum up that point 55 refers to the preliminary treatment of raw coke oven liquor, while point 56 is devoted to coke oven wastewater treatment.

6.2. BREF documents

Best Available Technique (BAT) Reference Document (BREF) is a publication resulting from a series of exchanges of information between a variety of stakeholders, including regulators, industry and environmental non-governmental organizations [25]. BREF for coke oven plant can be found in chapter 5 of Best Available Techniques (BAT) Reference Document for Iron and Steel Production, which was revealed in 2013. In subchapter 5.1 applied processes and techniques are shown, in subchapter 5.2. current emission and consumption levels are given, while in subchapter 5.3. techniques to consider in the determination of BAT are presented. For coke oven wastewater, the documents clearly defines the need for tars separation and ammonia stripping from raw coke oven liquor, before further stream treatment in biological or biochemical coke oven wastewater treatment plant. Available systems and their operation efficiencies are described, together with operational data, achieved environmental benefits, economics, cross-media effects and applicability (subchapter 5.3.21). The driving force defined for coke oven wastewater treatment is that the demand for low discharges of nitrogen compounds requires a suitable wastewater treatment system.

7. Conventional coke oven wastewater treatment and utilization methods

The proper treatment of coke oven wastewater is an important topic not only from a point of nitrogen discharge decrease pointed in BREF document, but also of destruction of other hazardous contaminants, which appear in the stream (ca. cyanides, thiocyanates, sulphides, phenols and PAHs). Hence, in order to assure proper treatment effect and achieve environmental targets, at nowadays operated coke oven wastewater treatment plants two main technological sites can be found:

- chemical treatment;
- biological treatment.

At some plants, chemical site is preceded with physical separation, in order to remove larger particulates (e.g. large particles of tars), while biological site can be followed by polishing stage, which assures the removal of eventual refractory compounds, over amount of ammonia or phenols [25-27].

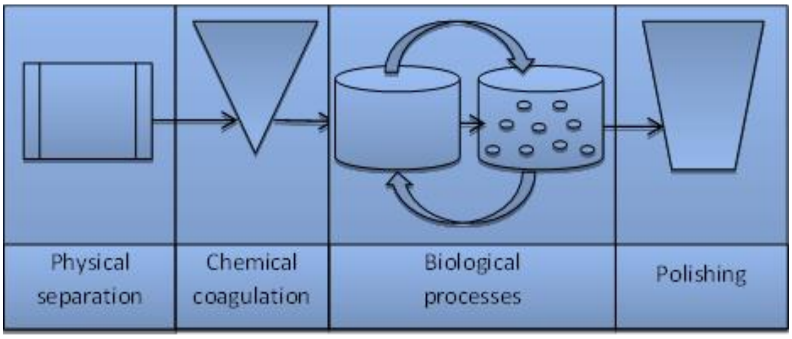

Figure 6. The scheme of conventional coke oven wastewater treatment plant

Chemical site of a coke oven wastewater treatment plant is operated with the use of coagulation followed by sedimentation and/or flotation. At the site, iron-based coagulant is added to the influent and the mixing of the stream with the reagent is performed. Usually, in order to assure proper performance of coagulation, pH of the stream needs to be adjusted (decreased). The addition of a coagulant results in hydrolysis of the metal present in the compound (i.e. iron) followed with formation of flocks, aggregation of which can be enhanced by addition of organic flocculant. Depending on the flocks properties (affinity to sedimentation), the stream is directed either to a flotation unit or to a settling tank, at which separation of sediments formed during the process takes place. The main aim of chemical treatment of coke oven wastewater is the removal of cyanides, sulphides and suspended tars particles, which reveal toxic effect to microorganisms used in further biological processes [26-28].

After chemical site, the stream of coke oven wastewater is directed to biological treatment, which is based either on single stage aerobic activated sludge method or its combination with nitrification and/or denitrification processes.

In an aerobic system with activated sludge, biodegradable contaminants are biologically degraded to carbon dioxide, water and minerals and the non-degradable, non-polar components are completely or partially removed from the wastewater by adsorption on the activated sludge flocks. For aeration purposes, ambient air is most commonly used, however there exist systems which are supplied with oxygen. The latter solution increases process control and reduces stripping of volatile components from the wastewater [25-26]. The exemplary data on the efficiency of aerobic activated sludge treatment systems is given in table 2.

Table 2. Parameters of effluent of biological treatment plant based on aerobic activated sludge [25]

Parameter	Unit	Plant effluent
COD	mg/dm^3	140-700
Phenol	mg/dm^3	<0.1-10
Thiocyanates	mg/dm^3	<0.1-35
Ammonia	mg/dm^3	<1-100
Cyanides, easily released	mg/dm^3	<0.1
PAHs (6 Borneff)	$\mu g/dm^3$	3-200

Some wastewater treatment plants are designed to remove ammonium (NH_4^+) efficiently by means of nitrification. The traditional design of an aerobically activated sludge system can be taken as a starting point for this kind of plant. The nitrification bacteria convert the ammonium into nitrate (NO_3^-). However, sensitive biological reactions such as nitrification are always endangered by shock loads of critical constituents such as cyanides. Hence, separation of the treatment process into a first activated sludge method for COD removal and hydrolysis followed by nitrification of ammonia protects slow growing, sensitive, autotrophic bacteria from inhibitory and toxic effects of respective pollutants. Nevertheless, there exists coke oven wastewater treatment plants, at which nitrification and COD removal takes place simultaneously in the aerobic part of the installation. The end-products from this conversion are carbon dioxide, water and nitrates. Nevertheless, such systems are usually preceded with preliminary chemical treatment of the stream [25-32].

Denitrification is the biological process where nitrates are converted by bacteria into nitrogen gas. This process take place under anaerobic or anoxic conditions. During denitrification, bacteria use the nitrate as terminal electron acceptors instead of molecular oxygen (O_2). The nitrogen is emitted as molecular nitrogen (N_2). The overall reaction is:

$$5\ C_{organic} + 2\ H_2O + 4\ NO_3^- \rightarrow 2\ N_2 + 4\ OH^- + 5\ CO_2$$

However, denitrifying bacteria require COD as feed. Hence, part of biological treatment influent is directed to the anoxic part of the installation together with nitrified wastewater. Thus, both COD and nitrate are present in the reactor. On the other hand, denitrification can be applied as a preliminary biological process, in the treatment cycle. Hence, in such a system it is called predenitrification [25-32]. The exemplary data on the efficiency of nitrification/denitrification treatment systems is given in table 3.

Table 3. Parameters of influent and effluent of biological treatment plant based on nitrification/ denitrification [25]

Parameter	**Unit**	**Plant influent**	**Plant effluent**
pH	-	8.5-9.5	7.6-8
Suspended solids	mg/dm^3	30-40	42-75
COD	mg/dm^3	2000-6500	45-800
BOD_5	mg/dm^3	800-3000	<20
Phenol	mg/dm^3	500-1500	0.1-<2
Thiocyanates	mg/dm^3	150-380	<4
Ammonia	mg/dm^3	50-200	0.6-80
Nitrite	mg/dm^3	n/a	<1.3
Nitrate	mg/dm^3	n/a	<27
PAHs (6 Borneff)	$\mu g/dm^3$	200	0.2-<50

After the treatment, there exist three basic methods, with the use of which the coke oven wastewater treatment plant can be utilized. In case when the treatment enables to decrease the amount of contaminants to the permissible level established in proper regulations, the stream may be directly deposited to the environment. If the applied treatment technology is incomplete (e.g. it does not comprise of denitrification unit) or the overall efficiency of treatment is not enough sufficient, the stream may be deposited to municipal sewage. Finally, if the proper quality stream is obtained, it can be used to supply wet coke quenching loop. However, one should be aware in case of the latter method that eventual disruptions during the treatment may lead to increased emissions at quenching tower, while high salinity usually revealed by the stream may affect the final coke quality (especially in case of large concentrations of chlorides and sodium ions) [33-35].

8. Evaluation of conventional coke oven wastewater treatment technology

Despite the fact that the coke oven wastewater treatment process is the complex operation, it is often not enough sufficient to remove all the contaminants present in the treated stream to the limits given in a range of regulations (on quality of wastewater deposited to the environment, industrial wastewater standards, etc.). The most problematic treatment operation is connected with the efficient removal of cyanides. They appear in the raw wastewater as a simple CN^- ions and their removal should be obtained during chemical coagulation. However, the efficiency of traditional process is poor, especially in the case of high load of the stream with dispersed organic contaminants (tars). In such a case, the stream requires the addition of high amounts of chemicals. The insufficient removal of cyanides during chemical treatment stages is highly undesired, especially considering proceeding biological processes. Cyanides, as well as sulphides, are known to be toxic to active sludge microorganisms, and their presence in the influent to biological treatment stage results in the inhibition of the process and its improper run [36-39]. Additionally, standards on cyanides content in coke oven wastewater treatment plant effluent are very sharp and the permissible levels are usually established below 0.1 mg/dm^3 for free form of the compound and 5 mg/dm^3 for its complexes.

Chemical coagulants, which are used for dispersed tars removal and cyanides and sulphides precipitation, comprise of a metal ion (ferrous or ferric ion), which is responsible for the coagulation process performance, and inorganic ion carrier (usually chloride Cl^- or sulphate SO_4^{2-}).

If the coke oven wastewater treatment influent contains high amount of tars, cyanides and sulphides, the efficient run of coagulation requires the addition of significant amount of chemicals. Hence, the excess of inorganic ions, the amount of which is already quite high in the raw stream, is introduced to the wastewater. The high salinity of purified wastewater possesses many disadvantages considering their further utilization methods. If the stream is used in wet quenching of coke, the presence of inorganic ions, especially chlorides, may seriously affect the quality of the final product. On the other hand, the regulations of purified industrial wastewater quality, which is deposited to the environment, limit the maximum contents of salts at the level of 1500 mg/dm^3 [40-41].

The water/wastewater management of coke oven plant do not only face the efficient treatment and utilization of wastewater, but also needs to assure huge amount of properly treated water dedicated to various technological purposes (heating/cooling systems, steam generators, wet gas cleaning, etc.). Hence, there exists a high demand for fresh water, which need to be up-taken either from the municipal water network or from natural sources (surface or ground water). Depending on the further destination, the water needs to be softened or completely demineralized, what requires the use of sophisticated treatment techniques and results in generation of additional waste streams (e.g. effluent from washing of ionites). The most favorable solution would be the recovery of technological grade water from the wastewater stream [42-44].

9. Review of ongoing or finished European projects on coke oven wastewater

Coke oven wastewater treatment has already been a subject of several projects funded by European Commission. The main objectives and short descriptions of those projects are given in next sections together with INNOWATREAT project added values.

Enhanced treatment of coke oven plant water, acronym ECOWATER, project reference: RFCR-CT-2010-00010, 1.07.2010-31.12.2013.

Main project objective: to reduce discharges of PS and PHS substances in coke oven wastewaters by investigation of mechanisms of their biological decomposition and application of effluent polishing by photo-oxidation, filtration and adsorption technique.

Description: With the introduction of the European Union Water Framework Directive (WFD), the steel industry is facing significant challenges to reduce wastewater emissions of Priority Substances (PS) and Priority Hazardous Substances (PHS) including trace metals (i.e. Cd, Ni, Pb, Hg) and PAHs (i.e. Benzo[a]pyrene). With the WFD coming into force, tighter environmental quality standards were introduced for these substances in local river basins. The first objective of ECOWATER was to address the challenges faced by the steel industry to fulfil the requirements of the WFD. At the beginning of the project, there was a significant gap in the knowledge across the steel industry on the emissions of these substances in wastewater effluents from cokemaking and ironmaking /steelmaking operations. Research was required in this area to identify the main emission sources, determine effluent toxicity, quantify emissions and measure the environmental impacts of steelworks. The second aspect of ECOWATER was concerned with the investigation of the potential of state-of the-art molecular biology techniques for understanding further biodegradation processes in coke oven biological effluent treatment (BET) plants. In recent years, there has been an explosion in microbial molecular biology techniques. The environmental sector is well placed to adapt many of these techniques to gain efficiencies across a range of biological treatment streams. Novel molecular biology techniques could not only provide the flexibility and adaptability that is required in treatment but could deliver significant environmental improvements by enhancing the biodegradation capabilities of bacteria therefore minimizing the use of other less cost-effective abatement solutions. In the project ECOWATER, it was proposed, for the first time, to use a range of novel state-of-the-art molecular biology techniques to identify uncultivable microorganisms that plays a major role in the degradation of organic pollutants such as phenols and PAHs. The third important aspect of the

ECOWATER project was concerned with the development of innovative technological solutions for the removal of PS and PHS in wastewater effluents from the steel industry in order to ensure that integrated steelworks comply with the final discharge consent in the future. In particular, the potential application of a photocatalytic oxidation process using anatase (TiO_2) was studied. Photocatalytic oxidation is an interesting approach for water treatment because the process gradually breaks down the contaminant molecules and therefore no sludge requiring disposal to landfill is produced. In parallel, work was carried out at the pilot scale to investigate the potential of advanced adsorption techniques using sorbents such as powdered activated carbon (activated lignite) and zeolites which present high adsorption capabilities, respectively, for the removal of organic and inorganic pollutants. Finally, pilot scale tests were also carried out to investigate the potential for coke oven effluent treatment of a new high efficiency filtration technology (Fuzzy filtration), which has only been used in municipal waste biological effluent treatment plants and oil refineries to date [45].

Chemical treatment for specific destruction of cyanides, project reference: 7261-02/412/03, funded under: ECSC-WORKENV SC, 01.07.1986-30.06.1989.

Main project objective: to develop the method of cyanides removal from steel industry wastewater by means of addition of organic compounds.

Description: The problem of appearance of cyanides in various wastewater streams is the topic of many studies focused on their effective removal from the aqueous stream. The conventional method i.e. chemical coagulation, is so far the most popular at industrial wastewater treatment plant, however, it requires some modification and improvement in order to obtain higher effectiveness of the process. There is at present no treatment for the specific removal of cyanides. The aim of the project is to explore the possibilities of such a treatment involving the chemical transformation of cyanide into glyconitrile, and then its polymerization to allow easy removal or prevent any impact on the water environment. The first stage will comprise the development of a method of transforming cyanides by polymerization and examination of the possibilities of direct separation of the product thus formed, in applications involving various types of effluents (blast-furnaces, coking plants, surface treatment, etc.). The second stage will consist of an evaluation of the behavior of the polymer in the natural environment at an urban biological treatment plant and/or industrial plant. A similar approach will be followed with a treated effluent but one whose polymer has been separated (toxicity of reaction by-products, etc.) [46].

Investigation of technical and economic benefits associated with the use of pure oxygen in the biological treatment of carbonization effluents, project reference: 7621-02/416-08, funded under: ECSC-WORKENV SC, 01.01.1987-31.05.1988.

Main project objective: to improve the performance of biological treatment of carbonization effluence by using pure oxygen instead of air based system.

Description: To impartially investigate the technical and economic benefits associated with the use of pure oxygen in the treatment of carbonization effluents.

Following the installation of a British Oxygen Company 'Vitox' pure oxygen injection system on the biological effluent treatment plant serving a UK coking works, the performance of the plant was closely monitored over an 18 month period and compared with the treatment performance achievable via conventional air-based effluent treatment. The conversion from conventional surface aeration to pure oxygen injection coincided with a very dramatic improvement in effluent treatment performance at the works, part of the improvement being due to a general tightening-up over plant surveillance and operating discipline. The BOC Vitox process proved to be a reliable and controllable means of providing mixing, sludge suspension and oxygen transfer in coke oven effluent treatment, however, at an oxygen consumption of 1.0-1.2 kg O_2 per kg COD removed. Reduced sludge wastage and antifoam requirement were obtained and the need to heat the aeration tank contents in winter months was totally eliminated. In addition COD removal proved to be 2-6% better than that achieved via conventional aeration and a less colored final effluent was produced. A pure oxygen injection unit (British Oxygen Company, 'Vitox' system) will be installed in the biological effluent treatment plant at a UK Coking works, with the full installation and operating costs of the unit being borne by the Monckton Coke and Chemical Company Limited. Under financial assistance from the ECSC, the performance and economics of the modified effluent plant will be comprehensively monitored over a period of 15 months and will be compared with the performance and economics of the conventional effluent plant [47].

The project was continued with: **Further investigation of technical and economic benefits associated with the use of pure oxygen in the biological treatment of carbonization effluents**, Project reference: 7261-02/452/08, funded under: ECSC-WORKENV 5C, 01.01.1990-31.12.1991.

Description: To ensure avoidance of any commercial bias in the study, an independent expert body (BCRA Scientific and Technical Services Limited) will oversee and assist in the investigation and will be responsible for producing a final report to the ECSC within three months of the monitoring programmes completion.

The enhancement of biological stage, which is crucial for ammonia and dissolved organic compounds removal from wastewater, is very important for every industrial and municipal wastewater treatment plant. Hence, every modification of treatment technology aiming the support of this stage is desired. The project goals were to examine the stability of biological treatment with pure oxygen injection at increased influent strengths and biological loadings, to examine the ability of biological treatment with pure oxygen injection to produce a treated effluent with a more generally acceptable, low level of suspended solids and, finally, to examine the influence of aeration tank pH regulation on the performance of both pure-oxygen and air-based activated-sludge systems. Overall, it was concluded that pure oxygen injection provided a very versatile means of oxygen transfer enabling higher organic loads to be accommodated than would be possible with many conventional aeration systems. Pure oxygen injection also provided benefits in terms of eliminating foam production minimizing heat losses, and providing favorable conditions for nitrification. The study did not corroborate claims that the use of pure oxygen reduces excess sludge production or treated effluent suspended solids concentrations. By operating the activated-sludge process at different aeration tank pH levels over the range 5.9-8.0 it was concluded that the pH within this range had no significant effect on chemical oxygen demand removal. With regard to treated effluent suspended solids concentration, however, the aeration tank pH did appear to exert an influence although the optimum pH varied from one effluent to the other. Scale-up of the laboratory-scale data to full-scale BET plant operation was found to be extremely good thereby confirming the accuracy and validity of the laboratory-scale approach. Although pure oxygen injection has allowed a higher COD removal to be achieved at a given biological loading than that achieved in a conventional air-based system, it has yet to be demonstrated that treatment can remain stable at the much higher influent strength and biological loadings that have been maintained successfully in a conventional air-based system during the previous 18 month research period. When considering the capital cost of an effluent plant, the maximum biological loading that can be maintained, and therefore the plant size, is obviously of great importance. The relative merits of pure oxygen and air in this respect must therefore be quantified. In addition, the high COD removal obtained at MC & CC with pure oxygen injection (based on filtered samples) has been achieved at the expense of a fairly high concentration of suspended solids in the final effluent. It is doubtful whether this level of suspended solids in the final effluent would be consistent with the discharge consent conditions imposed on some coking works within the European Community. It is especially interesting to note the very substantial and consistent difference in aeration tank pH levels recorded between the pure oxygen and air-based treatment systems over the 18 month research programme. This observation must lead one to question whether the differences in COD removal and final effluent color recorded between the pure oxygen injection and the conventionally aerated systems might be due simply to an aeration tank pH effect. In other words, could some of the benefits of pure oxygen injection be achieved perhaps more cost-effectively and perhaps even more strikingly via automatic pH regulation of a conventional air-based system [48].

Coke-oven effluent purification: an examination of methods for improving quality after biological treatment, project reference: 7261-02/493/08, funded under: ECSC-WORKENV SC, 01.01.1992-31.12.1994.

Main project objective: to investigate a range of techniques aiming the removal of suspended solids and insoluble pollutants as well as soluble and COD-generating contaminants.

Description: The aim of this research was to examine the technical capability of various technologies to produce further purification of biologically treated coke-works effluents, and to make projections regarding the economics of their full-scale implementation. After the initial removal of tars and the majority of ammonia by traditional physical and chemical means, the residual aqueous effluent arising from the coke manufacturing process is conventionally purified further by aerobic biological treatment before being allowed to discharge to a watercourse, and well designed and operated biological treatment is capable of removing pollutants such as phenol, thiocyanate and ammonia down to trace concentrations. In addition, approximately 85-90% of the chemical oxygen demand of the effluent will be removed. Notwithstanding the high degree of purification effected by the conventional route, there are pressures to further purify coke works effluents before discharge, examples being the mooted imposition in certain instances of discharge limits of <20 mg/dm^3 suspended solids, <0.5 μg/dm^3 Benzo-a-pyrene and the need to achieve $> 95\%$ removal of the chemical oxygen demand. Seven technologies were considered. These were:

- Gravity sedimentation, sand filtration, dissolved air flotation and cross-flow microfiltration to remove suspended solids and insoluble pollutants.
- Absorption onto carbon, oxidation by hydrogen peroxide and oxidation by ozone, to remove soluble pollutants and their associated chemical oxygen demand.

In examining these technologies, tests were conducted on the biologically treated effluents from three separate coke works and, where practicable, large pilot scale plants were operated for extended periods on site to collaborate data from smaller scale work [49].

Techniques or the identification and removal of the residual soluble COD of biologically purified coke oven waste water, project reference: 7261-02/496/02, funded under: ECSC-WORKENV SC, 01.01.1993-31.12.1995.

Main project objective: to identify substances, which remain in the effluent after biological treatment of coke oven wastewater in order to improve their degradation.

Description: Organic contaminants present in coke oven wastewater are very diversified due to a range of factors i.e. molecular weight, susceptibility to biological decomposition, solubility in water, toxic effect, etc. Nevertheless, the former parameter i.e. molecular weight, is crucial considering the further decomposition of the compound. Even if the substance is biodegradable, its decay may be a time consuming process. By obtaining an insight into the residual COD levels present in the biologically purified coke-oven waste water, the authors hope to increase the degree of purification still further, thus ensuring that contamination of the aqueous environment is kept to a minimum. Biologically purified coke-oven wastewater has a soluble unidentifiable COD averaging 150 mg/dm^3. To date, there has not been a single instance anywhere in the world involving the successful identification of the constituents. It is assumed that this soluble COD could well be attributable to the presence in the water of humic acids and pyrolysis products caused by carbonization. Given that the identification of these products is a highly cumbersome and intricate task, appropriate help should be sought from specialized research centres. Research of this kind requires not only up-to-date analysis apparatus (GC/MS), but also a great deal of investigatory work that can be carried out only by highly trained personnel. Using substance identification techniques, substances can be characterized further with a view to their removal and/or transformation into less harmful products. These removal methods may take the form of chemical (e.g. enforced oxidation), physicochemical (eg. photolysis) or biological (specialized bacteria) processes and must all be tested in order to determine their environmental acceptability (toxicity tests) [50].

10. Review of recent researches on coke oven wastewater treatment

The treatment of coke oven wastewater, as one of the most complex and problematic industrial waste stream, is often discussed in the literature and widely investigated by many scientific and industrial R&D centres all over the world. Different processes are used for purification of wastewater are investigated.

In recent publications, electrochemical processes are proposed to decompose and destruct a range of contaminants (cyanides, sulphides, thiocyanates) present in coke oven wastewater. **Ozyonar and Karagozogly** [51] compared treating of pretreated coke wastewater by electrocoagulation process (EP) and electrochemical peroxidation process (ECP) using direct pulse current. They used air stripping process of ammonia as a physicochemical process for this purpose. The efficiency of the process and settling characteristic of waste sludge were investigated through changing some operating parameters such as initial pH, initial H_2O_2 concentration and current density. Direct pulse current was used to prevent the passivity or polarization of electrodes and to increase removal efficiency. They found that ECP was more efficient than EP in removing of COD, total organic carbon, phenol, cyanides and thiocyanates, but at higher operating costs. **Pillai and Gupta** [52] applied anodic oxidation of industrial wastewater from a coke oven plant having cyanide including thiocyanate (280 mg/dm^3), chemical oxygen demand (COD 1520 mg/dm^3) and phenol (900 mg/dm^3) using a novel PbO_2 anode. From univariate optimization study, low NaCl concentration, acidic pH, high current density and temperature were found beneficial for the oxidation. Optimization was performed for maximizing the removal efficiencies of these three parameters simultaneously. The optimum condition was obtained as initial pH 3.95, NaCl as 1 g/dm^3 and current density of 6.7 mA/cm^2, for which the predicted removal efficiencies were 99.6%, 86.7% and 99.7% for cyanide including thiocyanate, COD and phenol respectively.

Water reclamation from coke oven wastewater effluent or introduction of membrane processes arranged in a different modes to the coke oven wastewater treatment is also a subject of many researches, within which very interesting and promising results are obtained. **Kumar and Pal** [53] designed and investigated new system using forward osmosis–nanofiltration in flat-sheet cross-flow module to separate reusable water from coke-oven wastewater with reduced concentration polarization and high flux using low energy. They analyzed different sets of operating conditions (pressure, cross-flow rate, pH of the feed solution, run time) for better understanding of the phenomena of concentration polarization and reverse salt diffusion in the system. Polyamide composite membranes were studied to select the best performing ones. In effect, 1.5M NaCl was found to be the best for forward osmosis while investigating effects of different draw solutions on the water flux and rejection of target contaminants. Removal of about 96–98% of cyanide, phenols, NH_4^+–N and chemical oxygen demand from real coke-oven could be achieved along with pure water flux of 46 $dm^3/(m^2h)$ in forward osmosis system under optimized conditions. Downstream nanofiltration module ensured continuous recovery and recycle of 99% of the draw solute while ensuring recovery of reusable water at the rate of 45 $dm^3/(m^2h)$. **Jin et al.** [54] investigated a full-scale plant using anaerobic, anoxic and oxic processes (A1/A2/O), along with a pilot-scale membrane bioreactor (MBR), nanofiltration (NF) and reverse osmosis (RO) integrated system to treat coking wastewater for industrial reuse over a period of one year. The removal of pollutants (TCN, COD, BOD, ammonium nitrogen, SCN-, fluoride) efficiency reached very high values during the A1/A2/O biological treatment stage, and all parameters were further reduced by over 96.0%, except for fluoride (86.4%), in the final discharge effluent from the currently operating plant. The pilot-scale MBR process reduced the turbidity to less than 0.65 NTU, and most of the toxic organic compounds were degraded or intercepted by the A1/A2/O followed MBR processes. In addition, parameters including COD, TCN, total nitrogen, fluoride, chloride ion, hardness and conductivity were significantly reduced by the NF-RO system to a level suitable for industrial reuse. However, the concentrates from the NF and RO units were highly polluted and should be disposed of properly or further treated before being discharged. **Yin et al.** [55] applied a membrane process of nanofiltration (NF) to separate high concentration of ammonium thiosulfate from ammonium thiocyanate in coking wastewater. The experimental results showed that the NF membrane selectively retained $(NH_4)_2S_2O_3$ with a rejection of 95.0% at a concentration of more than 60 g/dm^3. Meanwhile, the permeation of NH_4SCN was 120.0% at a concentration of nearly 120 g/dm^3. Diafiltration was optimized to ensure a high average salt rejection of 93.4% for $(NH_4)_2S_2O_3$. The results reveal that the NF membranes are successful in separating high concentration of bi-component ammonium salt solutions into mono-component ones.

Many studies found in the literature are devoted to application of advanced or alternative processes dedicated to the treatment of coke oven wastewater, with the enhancement of removal of target contaminants. **Chang et al.** [56] investigated the biological and chemical characteristics of coke-oven wastewater after ozonation treatment through the examination of selected parameters in a bench-scale bubble column reactor. They found that color and TCN could be removed almost entirely, but organic matter and cyanide could not, due to the inadequate oxidation ability of ozone to remove ozonation by-products under experimental conditions. It appeared that removal of cyanide and total organic carbon were pH-dependent and were found to be efficient under neutral to alkaline conditions. The removal rate for TCN was about five times that of cyanide and mostly ozone was used to oxidize the pollutants. The results indicated that the contribution of ozonation to inhibition reduction was very significant, but limited to the enhancement of biodegradation. The operation for ozonation of coke-oven wastewater was feasible under neutral condition and short ozone contact time in order to achieve better performance and cost savings. **Shao et al**. [57] investigated application of pulsed corona discharge process, in which simultaneous SO_2 removal from simulated flue gas and coke-oven wastewater degradation. They indicate that coke-oven wastewater has good desulfurization ability and pulsed corona discharge enhances the removal efficiency of SO_2 up to 85%, which is removed through absorption, neutralization and radical reactions. Coke-oven wastewater can also be degraded by pulsed corona discharge, and SO_2 injection is helpful to the degradation process, where almost all cyanide and over half of phenols can be decomposed. The obtained experimental result suggests the possibility of the simultaneous processing of desulfurization and decontamination of coke-oven wastewater. This research may provide a new technology for desulfurization and coke-oven wastewater treatment in integrated steel plants. **Wang and Wang** [58] reviewed microwave (MW) chemistry in the field of organic wastewater treatment due to its rapid heating at the molecular level and its ‘‘hot spots’’ effect on the surface of an MW absorbent. MW was successfully combined with many kinds of organic wastewater treatment methods. The recent application status of MW irradiation, the MW heating mechanism, and the relevant theory in organic wastewater treatment are introduced, and then combinations of MW irradiation with different organic wastewater treatment methods were addressed in detail. After that, the energy efficiency of MW-enhanced organic wastewater treatment methods were calculated, discussed, and compared with that of some other organic wastewater treatment methods. The MW non-thermal effect was also discussed. Finally, the possible future research directions and some guidelines for MW-enhanced organic wastewater treatment were given.

The general idea of the treatment technology is based on the conventional solution, in which a series of physical, chemical and biological methods is applied. However, their detail recognition and introduction of modification methods aiming the improvement of their operation and efficiency are also seek for. **Ghose** [59] analyzed physico-chemical treatment wastewater from coking plant as a suitable option for the treatment of coke plant effluents.

For this purpose ammonia removal by synthetic zeolite, activated carbon for the removal of bacteria, viruses, refractory organics, etc. were analyzed. The complete physico-chemical treatment was proposed, which can be suitably adopted for the recycling, reuse and safe disposal of the treated effluent. The process may be useful on industrial scale at various sites. **Vazquez et al**. [60] analyzed laboratory-scale activated sludge plant to study the biodegradation of coke wastewater. The study was undertaken with and without the addition of bicarbonate. The addition of this inorganic carbon source was necessary to favor nitrification, as the alkalinity of the wastewater was very low. The authors stated that maximum removal efficiencies were obtained for COD, phenols and thiocyanates without the addition of bicarbonate. A maximum nitrification efficiency was achieved when bicarbonate was added, the removals of COD and phenols being almost similar to those obtained in the absence of nitrification. **Staib and Lant** [61] determine the reaction pathway and kinetics of thiocyanate (SCN^-) degradation during mixed culture (activated sludge) treatment of coke-ovens wastewater. The effect of phenol and cyanide, both present in coke-ovens wastewater, on thiocyanate degradation was also to be determined. The degradation of thiocyanate was quantified by identification of specific rates of removal and oxygen uptake rate. The results indicated that thiocyanate was removed via microbial growth using thiocyanate as a substrate, and that SO_4^{2-}, NH_4^+ and CO_2 are the reaction products. None of the results obtained showed inhibition of thiocyanate degradation due to phenol. In contrast, cyanide was found to have a significant inhibitory effect on the degradation of thiocyanate. Thiocyanate removal could totally inhibited in coke-ovens wastewater at concentrations of CN^- in excess of 1 mg/dm^3. Thiocyanate degradation was defined as the slowest and most sensitive process, compared with the removal of phenol and cyanide, and would be the determining factor when identifying the hydraulic residence time required for treatment of coke-ovens wastewater (excluding nitrification).

Due to the continuous sharpening of regulations on the quality of finally purified stream the wastewater treatment systems needs to be extendedly modified. In general, there is a group of five basic contaminants present in raw coke oven wastewater, which are of the greatest interest and attention, i.e. dispersed tars (including PAHs), phenols, ammonia, sulphides and, the worst of all, cyanides. Numerous papers are devoted to application of different methods of their removal from wastewater, basing on conventional and alternative techniques. **Shen et al.** [62] investigated the effects of organic polymers with different charge density on the removal mechanisms of TCN in coking wastewater by polyferric sulfate with a cationic organic polymer or a non-ionic polymer. The results showed that residual concentrations of TCN after polyferric sulfate with a cationic organic polymer flocculation are much lower than that after those with non-ionic polymer precipitation. It was attributed to the different TCN removal mechanisms of the individual organic polymers. Using polyferric sulfate with a cationic organic polymer, TCN adsorbed on ferric hydroxides can be removed via charge neutralization and electrostatic patch flocculation, while non-ionic polymer has little influence on TCN removal. **Wei et al.** [63] investigated the change of hazardous materials in coking wastewater at different treatment stages (anaerobic, anaerobic/aerobic, anaerobic/aerobic/photo degradation, anaerobic/aerobic/ozone oxidation treatment) and their effects on the development of maize embryos. The results showed that the biodegradable organic compounds in the wastewater can affect maize embryo development and that in the process of coking wastewater treatment no new toxic chemicals were produced**. Zhang et al.** [64] conducted batch experiments to determine the effects of metal loading and fixing methods on the capacity of granular activated carbon for removing cyanide from KCN. Adsorption was the primary mechanism of cyanide removal, and after period of less than 3 weeks the effluents became stable and met the discharge limits. **Another group** of scientists studied activated coke (AC) to adsorb organic pollutants from coking wastewater [65]. This study initially focused on the sorption kinetics and equilibrium sorption isotherms of AC for the removal of COD from coking wastewater. The results showed that almost all COD an color may be removed with dose of AC was 200 g/dm^3 after 6h of agitation at 40°C. The adsorption of COD onto AC was enhanced with an increase of temperature, indicating that the adsorption process would be a chemical adsorption rather than a physical one. Park et al [66] used pre-denitrification process to treat coke wastewater containing toxic compounds such as phenols, cyanides and TCN and showed very good removal efficiencies in carbon and nitrogen removals. However, a considerable amount of cyanides in the form of ferricyanide remained in the effluent of biological treatment process. But ferric chloride solution has been used as a chemical precipitant. In conclusion, economic assessment indicated that ferrous iron is more economically profitable than ferric iron in spite of its high cost. **Vasquez et al. [67]** used laboratory-scale biological plant composed of two aerobic reactors operating at 35^{o}C to study the biodegradation of coke wastewater and to remove organic matter, especially phenols, TCN and ammonium nitrogen. The biodegradation of these pollutants was studied employing different hydraulic residence times (HRT) and final effluent recycling ratios in order to minimize inhibition phenomena attributable to the high concentrations of pollutants. The removal of COD, phenols and thiocyanate was carried out in the first reactor and the nitrification of ammonium took place in the second. The best results were obtained when operating at HRT of 98 h in the first reactor and 86 h in the second reactor, employing a recycling ratio of 2. In order to remove nitrate, an additional reactor was also implemented to carry out the denitrification process, adding methanol as an external carbon source. Very high removal efficiencies were achieved. **The same group** of scientists [68] studied the removal of phenols and COD from coke wastewater subjected to biological treatment. The adsorbents used were granular activated carbon and the resins XAD-2, AP-246 and OC-1074. The best results were obtained with GAC, which presented higher adsorption capacities. In the equilibrium assays, the adsorption capacities (Q) found were 1.48 mg/g for GAC versus 0.07 and 0.04 mg/g for resins AP-246 and OC-1074, respectively. In the kinetic assays, the values of the Lagergren adsorption parameter, qe, were 1.69, 0.15 and 0.14 mg/g for GAC, AP-246 and OC-1074, respectively. In the column assays, the dynamic capacity of GAC for up to 480 bed volumes was 1.82 mg/cm^3. No saturation was obtained for this volume due to the asymptotic shape of the breakthrough curve, whereas for the same percolated volume, the resins AP-246 and OC-1074 were saturated. These two resins presented similar saturation capacities of around 1.1 mg/cm^3. **Maron et al.** [69] studied the treatment of coke wastewater in a pilot plant equipped with a 400 dm^3 stripping tank, a 350 dm^3 neutralization/homogenization tank and a 6 m high 1500 dm^3 sequential batch reactor (SBR), controlled by a PLC. Ammonia stripping efficiencies of 96% were obtained for HRT of 66 h. The biological treatment in the SBR led to removal efficiencies of 85% COD, 98% thiocyanate and 99% phenols for HRT of 115 h. Final concentrations in the effluent of 1.8 mg phenols/dm^3, 5.4 mg SCN/dm^3, 206 mg COD/dm^3 and 78 mg $N–NH_4/dm^3$ were obtained.

It is clearly seen that coke oven wastewater treatment and improvement of applied operations is a topic of interests of many researches. The discussed studies indicate on a strong need for novel and efficient solutions elaboration, which would limit the environmental impact of the coke oven plant effluent on the aquatic environment and also that would improve the overall cycle operation, especially with the possibility of water reclamation and effective reuse.

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