Review

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Physicochemical methods for process wastewater treatment: powerful tools for circular economy in the chemical industry

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Abstract: In the chemical industry, a typical problem is the appropriate treatment of the process wastewaters. The biological treatment cannot be usually applied because of the high content of organochemical compounds. However, phsycicochemical methods can significantly contribute to the proper treatment of the process wastewater and usually also allows the recovery of the polluting materials. This phenomenon opens the application area of physicochemical methods for the treatment of process wastewater and can contribute not only to the aims of the circular economy but also to the zero liquid discharge. Besides literature studies, authors' own results and innovations have been also presented. The treatment strategy for pharmaceutical process wastewater is reviewed in detail, which also serves to point out that hybrid methods can be usually efficient to solve the primary goal–maximum recovery and reuse of polluting materials.

Keywords: chemical industry; circular economy; physicochemical methods; process wastewater; zero liquid discharge.

1 Introduction

Industrial processes need to be carefully designed and operated to provide conditions for sustainable living on our planet. This thinking requires the analysis of the cycles of nature and translating the concept into industrial practice since no waste is present in nature; all matter is used in a consequent process (Tong and Elimelech 2016). This principle can be expedient for the treatment of process wastewater (PWWs) from the chemical industry containing many valuable substances. Fan et al. (2020) highlighted the importance of waste management and environmental sustainability, especially during the COVID-19 pandemic.

1.1 Problem background

Following this principle, the European Commission (EC) adopted a package to promote the transition to a circular economy at the end of 2015 (International Environmental Technology Centre 2015). This draft encourages companies and consumers to use resources more economically. A circular economy recognises that, in many cases, environmental impact cannot be reduced within a single production process since waste generation is inevitable (Kakwani and Kalbar 2020). Consequently, production, consumption and waste generation processes need to be linked, and nature's inherent cycle needs to be implemented in the industry (Andrews et al. 2011). Klemeš et al. (2021) emphasised the importance of implementation of the circular economy concept in the aspect of plastic waste recycling too. Industrial symbiosis, which implies the use of waste from one sector as a raw material in another sector, should be promoted (International Environmental Technology Centre 2015). Figure 1 illustrates the circular economy (Gai et al. 2021).

The action plan of the program includes, among others, a legislative proposal on minimum requirements for the reuse of wastewater (Willet et al. 2019). The program also encourages recycling in other sectoral areas,

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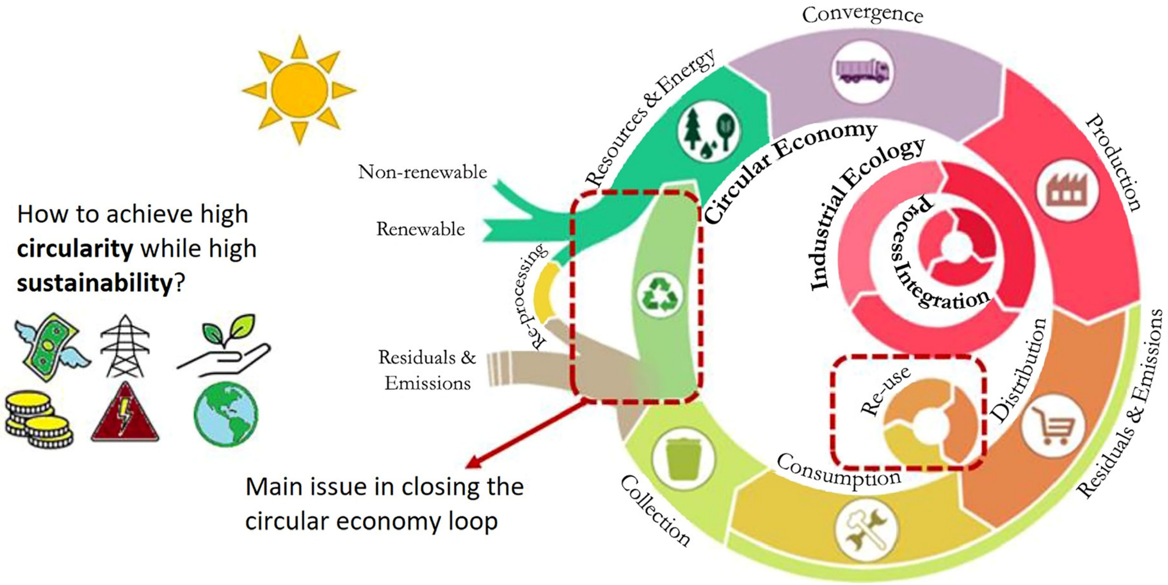

Figure 1: Representation of the circular economy (Gai et al. 2021), amended from (Walmsley et al. 2019).

with the ultimate goal of reducing the proportion of waste placed in landfills to less than 10% by 2030 (Schellekens et al. 2020).

In the recent period, environmental protection has become increasingly more important also in the chemical industry (Awaleh and Soubaneh 2014). Although the goal of environment-oriented process design is to prevent waste generation, in many cases, its occurrence is unavoidable (Tyagi and Lo 2013). A typical manifestation of this is the example of process wastewaters, generated especially in fine chemical industries, among them, mainly in the pharmaceutical industry (Lawrence et al. 2005). In the latter case, efficient end-of-pipe liquid waste management is required instead of direct discharge (Mizsey 1994). In connection with end-of-pipe waste treatment methods, it is important to take into account potentially recoverable materials and their recirculation (Diaz-Elsayed et al. 2019). It is important to mention that PWWs are generated in extremely large quantities and can contain many valuable chemicals. Thus, following the concept of a circular economy, it is worth dealing with their management, extracting valuable materials and utilizing them locally.

According to (Shahedi et al. 2020), wastewater treatment methods can be categorised into three classes, biological, physical, and chemical processes. As regards organic contaminant removal from wastewater (Alipour and Azari 2020), we usually talk about biological wastewater treatment, which can be combined with mechanical operations (Hao et al. 2019). On the one hand, biological wastewater treatment is a typical end-of-pipe waste treatment in which recirculation is almost completely impossible. On the other hand, it is not always applicable due to operational limitations in the case of technological wastewaters with high organic content (Belis-Bergouignan et al. 2004). In populated areas, municipalities also do not allow its use due to the possibly insufficient safety distance. Therefore, in chemical plants, especially in populated settlements, other water treatment alternatives should be considered, e.g. physicochemical methods. As incineration excludes the possibility of recycling and is also a typically polluting process and expensive for aqueous waste, it is the least preferred solution (Sahu and Chaudhari 2013).

Possible physicochemical methods include separation units which operate on the basis of differences in relative volatility. Potentially occurring volatile substances include volatile organic compounds (VOC) and adsorbable organically bound halogens (AOX). The advantage of applying these physicochemical methods lies in the possibility of recovery and recycling of organic pollutant components mentioned above (Dursun and Sengul 2006).

Valentini and Vaccaro (2020) summarised the powerful tools of waste minimisation in chemical industries. Through the example of separation of azeotropic mixtures, the authors emphasise the solvents recovery methods as environmentally effective and sustainable protocols. Karimi Estahbanati et al. (2021) mentioned the physicochemical processes as technologies, which are able to recover resources from industrial wastewater. The research also highlights that conversion from the linear economy toward the circular economy is a preferential and promising strategy.

The discussion of the problem is first approached from the perspective of waste management, and then the pollution problems and the methods for solving them are gradually presented. At first, the work approaches the environmental aspects of the chemical industry sector. Thereafter, waste reduction strategies of this sector are described. The following chapter consists of the introduction of wastewater features and main treatment methods. The main part of the work is represented by the detailed introduction and evaluation of physicochemical methods for the treatment of chemical process wastewaters. At last, the specificities of liquid waste in the pharmaceutical sector are demonstrated, where the use of physicochemical methods can be highly recommended.

2 The environmental factors, impact on the chemical industry

Economic and technological systems operate by collecting information, energy and matter from the environment in order to transform and return them. The material leaving the technosphere can fall into one of the following categories: product, waste or by-product.

The biosphere, namely the natural environment, has been subject to greater use since the second half of the 20th century due to the intensive development of the economy. This was also reflected in the fact that the interaction between the biosphere and the technosphere has become much more intense. However, the risk of some irreversible or potentially irreversible environmental changes, the overburdening of the biosphere and the limited availability of raw materials are raising more and more questions about the current pace of economic development. Consequently, it is an important task to reconcile social needs with the possibilities offered by the natural environment. In fact, the concept framed by these considerations is that of sustainable development.

According to the first law of thermodynamics, specifically, the law of conservation of energy, the implementation of waste-free technology is theoretically impossible. Complete (100%) product yield is, in principle, not attainable, as the detection of by-products depends on the analytical accuracy. The “environmental factor” is an indicator used for chemical waste, which marks the amount of waste per ton of product (Sheldon, 1992). Table 1 shows the typical environmental factor values for some sectors of the chemical industry.

Table 1: Industries and environmental factors (Toth 2020).

Industry	Product volume (t)	Environmental factor
Oil refining	10^6–10^8	0.1
Manufacture of chemical raw materials	10^4–10^6	<1–5
Fine chemicals manufacture	10^2–10^4	5–50
Pharmaceutical industry	10^1–10^3	25–100 <

Based on Table 1, it can be stated that in many chemical sectors (e.g. the pharmaceutical industry), the yield of the main product often shows only a few % efficiencies, and a large amount of by-products and waste is typically generated. In view of this tendency, the modern approach to problem-solving is to prevent adjoining products in their source (producing) point. Reducing waste is also a major economic interest for producers (Buruzs et al. 2012). However, the production costs can significantly be increased by strict environmental regulations and chemicals, and environmental protection is not only a problem of technological, chemical, biological, biochemical, etc., importance but also an economic issue. Economic and environmental aspects are closely linked by these correlations. Requirements formulated by society towards the chemical industry would, over time, force manufacturers to make technological improvements and produce more environmentally friendly products. This trend has also led to the development of naturally degradable plastic bags.

Traditionally, the chemical industry is more prone to pollution, and it counts as a material and energy-intensive industry. However, along with the accession to the EU, the protection of the environment is mandatory for all domestic companies (Buruzs et al. 2012). The chemical industry also uses a significant amount of energy, as well as a wide variety of raw materials in a large amount, for its production. Consequently, it puts a significant burden on the environment on both the input and output sides. Technological developments and modernisation do not only reduce such burden but also serve to elaborate more efficient material and energy management, as a result of which waste can be gradually reduced.

The production and use of certain chemical products pose a serious environmental risk due to their high active agent content. From this point of view, plant protection products can also cause serious problems.

The US National Research Council (2013) examined how the above-mentioned harmonisation could be achieved, namely, how the environmental goals of the economic sector could be combined with the opportunities offered by technology and research. Based on their professional opinion, the goal can be achieved through the successful cultivation of the following research and development areas:

(i) The environmental impact of production, use and disposal of chemicals have to be reduced.
(ii) A comprehensive risk assessment is required to provide socially acceptable environmental and technical solutions, which includes the consideration of economic and social factors.
(iii) For the purpose of acquiring more accurate knowledge of the processes in nature, suitable observation methods have to be developed and improved. With the development of monitoring systems and a deeper understanding of ecological processes, it is easier to determine the appropriate level of interventions.
(iv) Efficient and environmentally friendly energy production methods should be developed and put into practice.
(v) Technical developments should be coordinated with ecological considerations. The environmental impact of the technosphere and the use of energy sources and raw materials have to be reduced. Production shall be directed towards industrial ecology.
(vi) More accurate knowledge of the correlation between population growth and consumption trends is needed for the exact assessment of resulting environmental impacts.

Further narrowing the circle, the authors highlight the following key environmental issues in relation to the chemical industry:

a) It is a need to differentiate between the ways to reduce the environmental impact of chemical technologies, depending on whether we need to treat waste from a previous operation or due to product wear, study the environmental impact of current technology, or develop a new, environmentally friendly process.
b) It is important to know the mechanism and evolution in time of the interaction between chemicals and the environment as accurately as possible in order to eliminate adverse effects to the greatest extent. Mapping of actual stages of product and waste should also be part of the assessment process.
c) It is also important to decide how and when it is necessary to measure the state of the environment.
d) Care should be taken to keep the environmental impact at a minimum level, in connection with the use of raw materials and technological processes, and throughout the entire life cycle of products.

The book of Heaton (2012) summarises the environmental challenges of the chemical industry. These include more efficient use of raw materials and energy sources, reduction and avoidance of environmental impact through the development of "clean" technologies, continuous expansion of the range of recycled materials, elimination of existing environmental damage, and development of environmental monitoring.

A comprehensive analysis of the environmental impacts of chemical processes is needed to follow the previously mentioned strategies (Čuček et al. 2012). Many types of environmental footprints and the life cycle assessment (LCA) can help with proper planning and efficient operation of industrial processes.

Fan et al. (2018) reported a substantial carbon emission and even greenhouse gas (GHG) footprints calculation based on energy consumption. Jiang et al. (2020) demonstrated the efficiency of the management cycle and analytical framework during a waste case study. Fan et al. (2021b) developed a graphical decision-support method for determining carbon management of biomass resources, which can even be extended to other waste areas. The study of Fan et al. (2021a) highlighted the GHG footprint calculation to help decision making through the example of bioenergy analysis.

Life Cycle Assessment is a generally approved tool to evaluate the environmental impacts of industrial processes. Environmental ranking and analysis can be formed of different treatment methods. Szabados et al. (2018) compared different treatment methods of ethanol-like pharmaceutical process wastewater with the aggregated (single) score impact assessment method (IMPACT2002+). The environmental impacts were analysed by LCA software (SimaPro). The comparison highlighted that the best option is the physicochemical method (distillation and wet oxidation) for chemical oxygen demand (COD) reduction of the examined chemical wastewater. It was determined the conventional (biological) treatment, including incineration, has a much higher adverse environmental impact than an untreated option. The advantage of physicochemical methods was the recyclability of chemicals. Furthermore, it was found, that incineration of process wastewater is an extremely polluting method. There is a potential risk of air pollution and thus climate change.

It can be seen that a multitude of definitions and parameters are necessary in order to perform a comprehensive analysis in the complex, overall, environment-focused assessment of each technology.

3 Waste reduction strategies in the chemical industry

It can be stated that the chemical industry and all industrial activities, in general, are associated with the generation of unavoidable wastes, as today there is no existing technological process in which only and exclusively the desired end-product is generated. In the past, at the time of less stringent environmental regulations and a lower level of industrial development, the so-called end-of-pipe solutions were used.

Directions generally applied were measures for waste disposal (landfilling of solid waste, treatment of wastewater, treatment of process flue gases) and their possible recycling. These operations were often completely independent of the technological processes that "produced" the waste. From the 1990s onwards, environmental protection independent of chemical technologies was gradually replaced by the concept of environmental protection linked to and integrated into technologies. The main objectives of environmental protection inherently built into chemical technologies are:

- Recycling of production waste and used products.
- Reducing the use of raw materials and energy.
- Reducing the potential contaminants at the source.

It is important to note that a shift in the focus of environmental protection towards waste reduction requires a change in the modality of chemical processes. Technological changes in the chemical industry, for the purpose of environmental protection, can be classified into two groups:

- Modernisation of existing plants, or
- Construction of new plants integrating environmental protection into basic technologies.

As a heuristic rule, it is more viable to take waste reduction principles into account when designing and building a new plant than to modernise technologies in an existing one.

In the case of a multi-unit chemical plant, if the plant units are studied individually, only a local optimum can be obtained, which is not sufficient to reduce global (total) waste emissions. The local developments of each plant part have to be coordinated and monitored at the level of the chemical plant, in which process all units has to be involved.

Initially, environmental development in the chemical industry was carried out on an "ad hoc" basis. The main ways to reduce waste were accurate industrial practice, small changes in operations, and strict adherence to raw material standards and production standards. However, by systematically exploring opportunities to reduce environmental impact, results can be significantly better. This operation is based on hierarchical chemical process design, which can be used either for designing new technologies or for upgrading existing ones.

Hierarchical process design can be described with an "Onion Diagram" method published by Linnhoff et al. (1994). The diagram illustrates the main elements of the chemical production process in different layers, which represent the consecutive steps of hierarchical process design. Process design begins with the innermost layer of the onion, i.e. the reactor. Moving outwards, it then continues with the separation/recirculation system, followed by the system of heat exchanger network (HEN), energy, raw and auxiliary material systems. The process has to always be examined as a whole since there are close interactions and correlations between the different levels of process planning. For example, the process of separation and recirculation cannot be ignored in the design of an optimal reactor.

It should be emphasised, that heat exchanger network retrofit is also an important task in environmental benign process design. Yong et al. (2015) proposed an extended version of the Grid Diagram, which is able to calculate the loads and thermodynamics simultaneously. Wang et al. (2020a) improved the Shifted Retrofit Thermodynamic Grid Diagram. This tool is suitable for the selection of the heat exchanger type during the retrofit plan of HEN.

The Onion Diagram should be supplemented by an additional fictitious layer, which symbolises further operations necessary for the smooth operation of the chemical production process (Mizsey 1994). It constitutes the environment necessary for the implementation of a complex process. This includes treatment, recycling, disposal of generated waste, product change, raw material exchange, equipment maintenance, storage, process start-up, and shut-down, among others.

In the planning process, the waste generated has to also be taken into account. In the reactor and separation layer, principally process waste is expected to be generated, while in the outer layers, we have to reckon mainly with utility waste. According to another grouping, the waste of the server environment can be called extrinsic waste, and the waste generated in the process planning steps can be referred to as intrinsic waste.

The extended Onion Diagrams are illustrated in Figure 2. The original diagram was improved by Klemeš et al. (2018) by accounting for emissions and supply chains (Figure 2b).

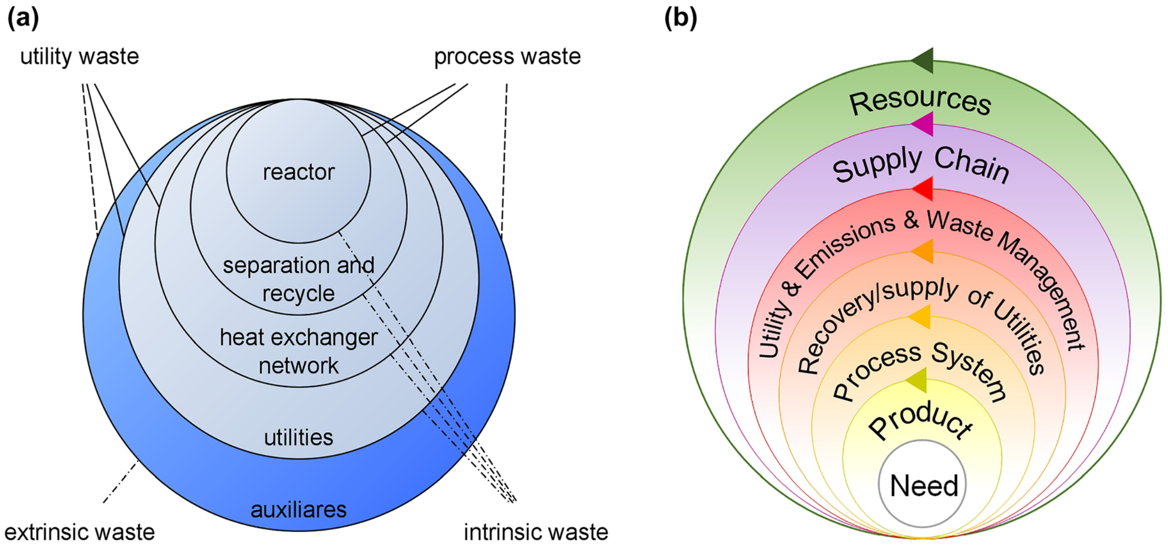

Figure 2: Extended Onion Diagrams.

The green chemistry principles contain useful recommendations for chemical process design and for liquid waste management (Anastas and Warner 1998). Some principles provide an instruction directly to solve the waste problems of the chemical industry:

- Waste prevention (Principle 1): It is better to prevent waste than to treat it after it has been generated.
- Atom economy (Principle 2): The maximum use of starting materials in chemical processes should be sought.
- Safer solvents and auxiliaries (Principle 5): Auxiliaries (solvents, reagents, etc.) should be used in the smallest possible amount; if necessary, be environmentally friendly materials.
- Use of renewable feedstocks (Principle 7): Renewable raw materials should be used as chemical feedstocks.
- Design for degradation (Principle 10): Chemical products has to be designed in such a way that they do not remain in the environment after use. If for some reason, they remain there; their decomposition will lead to the formation of environmentally friendly products.

The EU Green Deal provides a framework for present and future challenges. EU rules on industrial emissions need to be modernized in order to achieve the main goal of reducing greenhouse gases (Rivas et al. 2021). In the future, investment by industrial members to promote a circular economy should be supported. New best available techniques can address mandatory resource utilization performance levels. Existing environmental management systems need to be upgraded to reduce the use of toxic chemicals (Jahnz and Stoycheva 2022).

3.1 Systematic strategy to reduce material waste

Waste reduction changes need to be coordinated at the highest level, i. e. the level of the company. First-generation methods can be used to reduce material waste during the operation of each plant. The methods include making operational changes, taking into account production regulations and standards, and accurate plant management. The required raw materials, as well as the utility waste materials, can therefore be identified (Mizsey 1994).

The next phase of the strategy is economic analysis, in which the costs of end-of-pipe waste treatment methods (incineration, disposal) that are completely independent of the underlying technology has to first be estimated. When comparing the individual alternatives, in the absence of special environmental and liquid waste management regulations, the economy should be the main viewpoint.

Before making significant changes to the technology in a plant, it has to be examined whether the waste from one unit can be recovered as a raw material in another unit within the chemical plant (Mizsey 1994). Attempts should be made to develop closed-loop technologies where possible. The most important goal is to design chemical factories in a conscious way so that the waste can be utilized in another plant as raw material. If closed system production or technology cannot be realised within the company, efforts should be made to minimise the occurrence of waste at the plant level. Finally, as mentioned above, nondisposable waste has to be incinerated or treated (landfill). In the case of process wastewaters, the circuit has to also be closed in order to minimise the release of pollutants into the environment. It is advisable to extract recyclable material from PWW so that it can directly contribute to waste reduction.

4 Features of wastewater in the chemical industry sector

Data analytics in social media may be able to interpret household liquid waste management (Jiang et al. 2021). However, if the aim is the collection of information on industrial waste, an accurate database should be used. The European Pollutant Release and Transfer Register (European Pollutant Release and Transfer Register 2020) is Europe's largest database of industrial emissions, providing information on more than 90 compounds and 45 economic sectors. The data is compiled with the contribution of 33 countries, represented by the Member States of the EU, Iceland, Liechtenstein, Norway, Serbia and Switzerland, and the UK. The E-PRTR classifies chemical wastewater pollutants into the following categories:

a) chlorine-containing organic compounds,
b) other organic compounds,
c) inorganic compounds,
d) heavy metals.

The collected wastewater emissions of the chemical sector can be found in Table 2.

In the year 2017, the total emission of these 33 countries was as much as 11 Mt, 92% of which can be considered direct, while 8% is defined as indirect. In the case of direct emission, the generated wastewater is treated onsite by the chemical plant and subsequently discharged into public sewers. During indirect discharge, the wastewater reaches the residential wastewater treatment plants through the municipal sewer system. Following proper treatment, wastewater can be released into the open. Among the treatment options, local factory treatment methods are predominantly used (European Environment Agency 2018).

The vast majority of wastewater produced by the chemical industry does not directly originate from chemical reactions, although they can naturally occur as condensates or reaction products. More often, the wastewater is produced subsequent to the reaction, during the processing steps, by chemical operations (filtration, centrifugation, extraction, distillation). The types of wastewater typically occurring in the chemical industry are listed in the following paragraphs.

a) Examples of "process wastewater" types more closely related to the chemical process (Brinkmann et al. 2016):
- mother liquors
- product cleaning wash waters
- condensates of technological vapors
- quench water (waters from the cooling or treatment of gas streams by direct water injection)
- polluted water of end-gas and flue gas washing
- water from equipment washing
- waters from vacuum production (condensate from water ring vacuum pump or gas jet injector)

These waters makeup as much as 10–30% of chemical wastewater (Brinkmann et al. 2016) but can account for up to 90% of total pollutant emissions.

Table 2: Pollutant categories in wastewater of chemical industry sector between 2007 and 2017 (European Pollutant Release and Transfer Register 2020).

Emission	Chlorine-containing organic compounds (kt)	Other organic compounds (kt)	Inorganic compounds (kt)	Heavy metals (kt)	Sum (kt)
2007	1.36	480	11,675	2.27	12,159
2008	1.41	168	10,261	2.14	10,432
2009	1.06	141	7,158	2.02	7,302
2010	1.81	157	8,790	1.15	8,950
2011	1.64	154	10,282	1.20	10,439
2012	1.57	150	10,166	1.22	10,319
2013	1.54	147	10,924	1.01	11,073
2014	1.46	148	10,722	1.00	10,873
2015	1.50	254	9,770	0.90	10,026
2016	1.49	149	9,730	0.90	9,881
2017	1.52	146	10,786	0.81	10,934
Average	1.49	190	10,024	1.33	10,217

b) Other examples of wastewaters that are less closely connected to the production process but ultimately lead to water pollution:
- waters for clearance of flue gas of combustion processes
- heat exchanger water effluents (often containing corrosion inhibitors)
- partial streams from the water exchange of external circuits
- wastewater from filter backwash
- polluted waters of laboratory and semi-industrial experiments
- municipal wastewater
- rainwater from contaminated areas
- leachate from landfills

Approximately 70–90% of the amount of wastewater falls into this category, generally causing less pollution.

In terms of the pollutants contained, chemical wastewater can originate from:
- unreacted raw material or reagent,
- product residues,
- parts of excipients not recovered from effluents,
- intermediate (reaction) products,
- products or by-products of undesirable processes.

5 Wastewater treatment processes of the chemical industry sector

In waste management, the IPPC Directive (Integrated Pollution Prevention and Control) applies to industrial companies, which is based on the application of “Best Available Techniques” (BAT). EU Council Directive 96/61/EC is intended to ensure the protection of the environment as a whole, and it is mandatory for all Member States to transpose into national law (4th modification, 2006). The regulation has to take into account the geographical location of the industrial plant and local environmental conditions. The directive aims at the integrated management of soil, air and water pollution, industrial safety, and energy use.

BAT Reference Documents (BREFs) are a collection of comprehensive information on the Best Available Techniques. As a general guideline, 90% chemical oxygen demand removal is a desirable goal for chemical wastewater treatment. Another principle is that it is expedient to treat wastewater with efficient pretreatment solutions in its most concentrated state before dilution and mixing, as it provides a simpler and cheaper alternative to conducting to the central wastewater treatment plant.

Wastewater free of suspended solids can be divided into biodegradable and nonbiodegradable parts. If the contaminants are toxic, they are separated before further treatment. Procedures for the treatment of nonbiodegradable wastewater are based on physical and/or chemical processes. After proper pre-treatment, the wastewater can be discharged to the respective catchment, the central biological wastewater treatment plant, or the municipal wastewater treatment plant in connection with the type of contaminant. Figure 3 introduces the recommended methods for the treatment of wastewater in the chemical sector.

At first, mechanical methods are recommended for the treatment of chemical process wastewaters due to potentially occurring solid pollutants. In the chemical industry from the various processes, there can be a wide variety of solids, even suspended substances in wastewaters. It contains generally insoluble salts and catalyst residues. In any case, due to possible scaling, fouling and/or pumping problems, the initial wastewater should be pretreated using the mechanical methods in Figure 3. If the solid pollutant content of wastewater is very low and it is

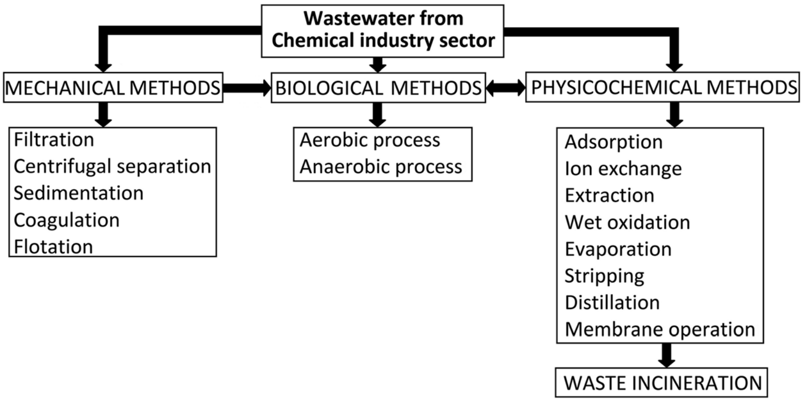

Figure 3: Classification of treatment methods of wastewaters from the chemical industry sector, amended from Gupta et al. (2012).
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biodegradable, the application of biological methods is recommended, followed by the physicochemical methods. If the Biochemical Oxygen Demand (BOD) is negligible, biological methods are not required, and the physicochemical methods can be applied; however, this is a very rare case in the chemical sector.

Generally, chemical process wastewater is not biodegradable or only to a limited degree, and biological methods are very often unsuitable for its treatment. It is usually polluted by toxic organic and inorganic compounds, metal ions and anions, therefore in many cases; the application of physicochemical methods is unavoidable. If PWW may become biodegradable after the physicochemical step, it is worth trying out biological methods. If the contamination is still above the emission limit value or applying physicochemical methods is not possible, wastewater has to be incinerated (Hosseini et al. 2011a).

It has to be also mentioned, that the final disposal of the salinity of the concentrated streams that are generated means can be a serious problem. In the case of saline effluents, the goal is to obtain the purest possible solid waste that can be recycled, based on the circular economy. This can be accomplished by using zero or near-zero liquid discharge (ZLD) procedures, which remove all the liquid waste from the system and produce solid waste (Ahirrao, 2014). Several physicochemical methods described later can be used on this principle, mainly thermal technologies (Liang et al. 2021).

Hereinafter, physicochemical methods for the treatment of chemical PWWs are presented and evaluated in light of applicability aspects. Further physicochemical or tertiary wastewater methods are the following: Crystallisation, precipitation, and electrolysis. The mentioned methods are less significant in the wastewater treatment practice, and they are not presented in detail.

5.1 Main physicochemical methods for the treatment of process wastewaters

There is a number of physicochemical methods that can be used to treat process effluents, essentially with the aim to remove organic solvents and reduce Chemical Oxygen Demand (COD) (Singh et al. 2012). The choice between these methods depends on more factors, such as:

(i) the composition of process wastewaters, and pollutants to be removed;
(ii) environmental regulations;
(iii) economic parameters;
(iv) local conditions.

Table 3 summarises the physicochemical methods and incineration used to reduce emissions of PWW as a function of the pollutant to be removed.

In the following, the applicability of the most important physicochemical methods is presented, along with the associated advantages and disadvantages.

5.1.1 Adsorption

Among technologies for liquid waste treatment, adsorption has high separation efficiency and a good rate of material recovery (Guillossou et al. 2019). However, organic material content can significantly reduce adsorption capacity, and the used adsorbent has to be regenerated or disposed of (Dai et al. 2019). During regeneration, some loss should always be expected (Simandi 2011). The most frequently applied adsorbents are activated carbon, metal oxides (Cyr et al. 2002), fly ashes, zeolites, goethites, and biomass (Gupta et al. 2012).

There are different chemical processes in which the resulting wastewater contains phenol. A widely known

Table 3: Physicochemical methods and incineration for emission reduction (Toth 2020).

	TSS	BOD COD TOC	Refractory COD/ TOC	AOX	NH_4-N	PO_4-P	Heavy metals	Phenols	Oil
Adsorption		X	X	X	X	X	X	X	X
Ion exchange		X					X		
Extraction		X	X	X				X	
Wet oxidation		X	X	X				X	
Evaporation		X		X	X	X	X		
Stripping		X		X	X		X	X	
Distillation		X	X	X					
Membrane filtration (MF, UF)	X	X					X		X
Membrane filtration (NF, RO)		X	X	X	X	X	X	X	
Incineration		X	X	X	X		X	X	X

process is the production of phenol from cumene hydroperoxide (by cleavage, in which the final products are phenol and acetone). The effluents from such chemical syntheses typically contain phenol, which has to be removed before releasing into natural water bodies (Caetano et al. 2009).

In the past, many methods have been developed for the removal of phenols (and cresols), such as adsorption by ion exchange resins. Moreover, a number of studies are underway to determine the most suitable conditions and functional groups for adsorption columns that can be most effectively used to bind phenol on a molecular level. In a series of experiments, a resin with two functional groups was used (a strong anion exchanger: Dowex XZ and a weak anion exchange resin: AuRIX 100), along with a polymer resin having no functional groups (crosslinked polymer Macronet MN200). It was found that the adsorption of phenol is greatly influenced by the pH of the solution, and the polymer resin without functional groups adsorbed phenol much better under acidic conditions. In contrast, the resin with two functional groups performed similarly well under basic conditions (Caetano et al. 2009).

Nowadays, adsorption is used effectively as a complex treatment process. Qin et al. (2021) decreased the TOC of coking wastewater by 69% with coal adsorption and electrochemical/UV/H_2O_2 treatment. Yang et al. (2021) reached a drastic reduction in COD of the initial wastewater (above 99%) using a combination of acidification, adsorption, and photocatalysis methods (Rathi and Kumar 2021). found that by using magnetic adsorbents, metal oxide adsorbents, and nano adsorbents, the effectiveness of adsorption capacity can be improved for the removal of emerging contaminants. The examination of Acosta-Herrera et al. (2021) showed that principal anions and cations could be removed effectively by adsorption from anodising wastewater. Singh et al. (2021) used nanomaterials for the adsorption and detoxification of pharmaceutical compounds from wastewater. Chai et al. (2021) summarized the application of novel materials for heavy metal adsorption in wastewater treatment. Some promising adsorbents were found, such as MXenes, UiO-66 and graphitic carbon nitride.

Finally, the advantages of PWW treatment with adsorption are the following:

- possible recovery of compounds (mainly with zeolites),
- generally low extra space requirements,
- possible removal of toxic organic compounds,
- high removal efficiency (expect lignite coke).

The disadvantages are included in the following list:

- spent adsorbent has to be regenerated (high energy consumption) or disposed of (generating waste to be incinerated). Regeneration is highly recommended and of paramount importance for feasibility and environmental sustainability.
- A major erosion problem can be caused by the scouring effect in the activated sludge,
- irreversible blockage of active sites may be caused by a high content of macromolecular compounds decreasing efficiency,
- significantly reduced desorption capacity may be caused by mixtures of organic compounds,
- the adsorption capacity loss with the cycles,
- the management of adsorbent post-adsorption and environmental impacts of the adsorbent are necessary.

5.1.2 Ion-exchange

Ion exchangers can be classified into two types: anion and cation exchangers. The most commonly applied ion exchangers are the following: polystyrene sulfonic acid, zeolites, sodium silicates, metha acrylic resins, and acrylic. It has to be mentioned that ion exchange requires low energy and process reversibility. It is applied for the removal of low concentrations of organic and inorganic compounds. The concentration of mentioned compounds can be reduced by up to 95% with ion exchange. Occasionally, pretreatment of the water is required (Gupta et al. 2012).

With ion exchange operations, toxic or hazardous ionic constituents of liquid waste can be replaced. By their application, theoretically, all ions and/or ionic particles can be removed with high efficiency. However, a major disadvantage of the process is that the regeneration of ion exchange resins produces wastewater (regenerating liquid) containing concentrated contaminants, toxic elements, and acidic or alkaline substances, which has to be treated. In addition, ion exchange materials are highly sensitive (Johir et al. 2011). Some materials bind irreversibly on the resin and continuously reduce the ion exchange capacity of the resin (Simandi 2011).

Ma et al. (2021b) demonstrated the effectiveness of magnesium and calcium ion removal from chemical wastewater with the combination of coagulation and ion exchange. Reclaimed water can be recycled with their integrated process, thus achieving near-zero liquid discharge. Camacho et al. (2021a) used novel ion exchange resins for the recovery of the phenolic fraction of wastewater. Above 50% COD removal was reached. The process was also optimized and modelled by Camacho et al. (2021b).

It is worth highlighting as a summary, that emissions can be significantly reduced in addition to COD reduction using processes combined with ion exchange. The advantages of PWW treatment with ion-exchange can be found in the following list:

- relatively insensitive to flow variations,
- a wide variety of specific resins are available,
- possible water recovery,
- possibly high efficiency,
- all ions or ionisable species can be removed from their aqueous liquids (in principle).

The disadvantages are the following:

- sludge and brine resulting from regeneration has to be treated,
- regeneration is necessary and may cause attrition of resin particles by mechanical impacts,
- competing ions can cause interference in the wastewater,
- precipitation can cause bacteria growth on the resin surface and fouling,
- refiltration is mandatory.

5.1.3 Extraction

Extraction refers to the dissolution of specific components from the mixture of solid or liquid materials using a suitable solvent. In the extraction operations, the resulting solution is called the extract, while the remaining solid builder and the mother liquor are called the raffinate.

In general, one of the types of extraction, namely liquid-liquid extraction, is used to regenerate water-immiscible organic solvents. Within this process, it is important to note that if a volatile substance needs to be handled, it is rather recovered by distillation. However, if it has a high boiling point, it can be extracted with water without further ado.

Another type of extraction, solid–liquid extraction, can be used to remove toxins in cases where solid waste cannot enter the sewage sludge due to its toxin content. Another application is the removal of contaminants from heavy metals, which, if released to the biological treatment line, would cause the destruction of microorganisms present at this stage.

In order to develop an appropriate treatment sequence for wastewater, it is necessary to consider the relationship between the pollutant and the treatment process related to it. As the first step in wastewater treatment, suspended solids and water-immiscible, nonpolar contaminants should be separated from the main water stream. For this purpose, different filtration methods, flotation, and gravity separation are available. The resulting solid-free wastewater can be broken down into biodegradable and nonbiodegradable parts. Within this classification, for the treatment of nonbiodegradable contaminants, the extraction process is applied by industry.

Patent of Monzyk et al. (2014) disclosed a highly efficient method for removing one or more ionic components (NO^{3}-, NO^{2}-, $PO_{4}{}^{3}$-, polyphosphates or a mixture of these) from nutrient-rich wastewater effluents, using liquid–liquid extraction. The result of the process is an ion-rich solution, and the extractant can also be recovered by stripping. The treatment process can be divided into two phases: The extraction phase and the stripping/regeneration phases. The preferred extractant is methyl-tri- (n-octyl) -ammonium ion. The effluent to be treated is contacted with the fresh extractant, and after phase separation, the wastewater is repeatedly exposed to an already regenerated extractant until an adequate degree of purification is achieved.

In many areas of the chemical sector, including the pharmaceutical industry, rubber industry, paint industry, as well as the preparation of corrosion-resistant galvanic coatings, generation of chromium-containing wastes and wastewater can often occur. The use of chromium trioxide as an organic solvent in the organic chemical industry also results in wastewater containing such heavy metals. In these process effluents, chromium is present in various forms: chromium (III) and chromium (VI) ions.

Due to detrimental health effects, these wastewaters has to be disposed of, preferably by recovering the chromium content for further reuse. As a first step, the chromium (VI) ions contained in the mother liquor are reduced to chromium (III) ions. This is followed by the extraction of organic impurities. The extractant used in this step is subsequently recovered by distillation. The extracted solution is treated with NaOH, and a chromium sulfate solution is formed as a final product, which is an excellent tanning agent. A great advantage of the technology is that it significantly reduces the related environmental impact, and by-products generated can be utilised in commonly used chemical equipment, so selling them can generate additional profits for the company (Toth 2020).

A suitable method for removing phenols is liquid-liquid extraction. In this case, the contaminated water is treated with an extractant that is immiscible with water, but the phenol is more soluble in it than in the polar phase, which is the effluent to be treated (Panditrao et al. 2004).

In other patents, phenol is extracted with cumene and then removed from the extractant in salt form by treatment with sodium carbonate and sodium hydroxide (Hauschulz et al. 1972); yet another patent mentioned ethers as extracting agents (Bondy et al. 1998).

Subsequent regeneration of the solvent is necessary, which can be accomplished by stripping in more steps. The ions are thus placed in an aqueous phase, and they become concentrated. The biggest problem with the extraction method is that the water-soluble substance(s) to be recovered can only be obtained with a solvent. As a consequence, to achieve recovery of one solvent, application of another solvent is required, which also necessitates further treatment. Moreover, the residue has to always be deposited or disposed of. A further disadvantage is that it is not always possible to select the right solvent. Its use is reasonable in cases where distillation is not an available option, or the cost of distilling the original liquid mixture is higher than that of extraction, including the cost of solvent recovery (Simandi 2011).

Wang et al. (2021a) have developed magnetic responsive nanocomposites (CNTs/MNPs@NH_2) for the enrichment and extraction of estradiol as a typical steroid hormone drug in pharmaceutical industry wastewater. Zhang et al. (2020) demonstrated the main advantages of solvent extraction, which are high efficiency and renewability, as well as its impressive effect on high concentration chemical wastewater, through the example of purification of chlorine-containing wastewater using trioctylamine (TOA) diluted in sulfonated kerosene as the extractant. Sunsandee et al. (2021) separated homogeneous palladium catalysts from pharmaceutical industry wastewater with a hollow fiber supported liquid membrane, which was impregnated with Aliquat 336 as an extractant. An extraction rate of above 99% was achieved.

Summarizing the case studies, it can be concluded that it is expedient and economical to use extraction where a large amount of solvent is available locally in the industry for the process. The advantage of PWW treatment with extraction is the following:

- possible removal and recycling of toxic organic compounds and some metals.

The disadvantages are the following:

- residues have to be disposed of or incinerated,
- limited applications due to solvent characteristics.

5.1.4 Wet oxidation

Significant amounts of volatile and nonvolatile contaminants can also be present in PWW, so wet oxidation can be applied after distillation (Méndez-Arriaga et al. 2009). The degree of oxidation is determined by the used temperature, the oxygen partial pressure and, in certain cases, the catalyst (Wang et al. 2012). PWWs freed from volatile components, but containing dissolved higher molecular weight organic materials (Kanakaraju et al. 2018), are expedient to oxidise, namely in wet oxidation, i.e. in the aqueous solution itself (Szabados et al. 2016). Air or, more recently, oxygen can be used as an oxidising agent. Although the latter is more expensive than the air, the total pressure used during the operation can be much lower (Kim and Ihm 2011). This operation, combined with distillation, is a highly effective solution for the treatment of PWW that cannot be biologically treated due to its concentration and is still too dilute for incineration (Levec and Pintar 2007). The pharmaceutical industry sector has numerous operative wet oxidation processes for the treatment of PWWs (Hosseini et al. 2011b). Table 4 summarises the possible (wet) oxidation processes in the case of PWWs.

Szabados et al. (2018) investigated wet oxidation for COD reduction of chemical PWWs. It was found that COD values can be decreased by 10–60%. COD reduction was only 30% higher by increasing residence time from 2 to 8 h. An approximately proportional increase in COD reduction was obtained by increasing mass flow oxygen and partial pressure. Figure 4 shows the industrial implementation of wet oxidation by Szabados et al. (2018).

Table 4: Oxidation processes for the treatment of process wastewaters (Debellefontaine and Foussard 2000, Tungler 2020).

Name	Average conditions	Process type
Wet air oxidation (WAO)	200–350 °C, 70–230 bar, air/O_2	Thermal oxidation
Catalytic wet air oxidation (CWAO)	<200 °C, <50 bar, air/O_2 and catalizator	
Supercritical water oxidation (SCWO)	>374 °C, >221 bar, air/O_2 or H_2O_2 (and catalysation)	
Wet peroxide oxidation (WPO)	>100 °C, >1 bar, H_2O_2	Wet peroxide oxidations
Fenton wet peroxide oxidation (FWPO)	~25 °C, ~1 bar, H_2O_2 and Fe^2+	
Advanced oxidation processes (AOP)	•OH–hydroxyl radical (electrolysis, UV light electrolysis, gamma radiation, O_3)	Special processes
Combined advanced oxidation processes (combined AOP)	O_3 + UV, H_2O_2, biological processes + AOPs + activated carbon + CWAO	Combined processes

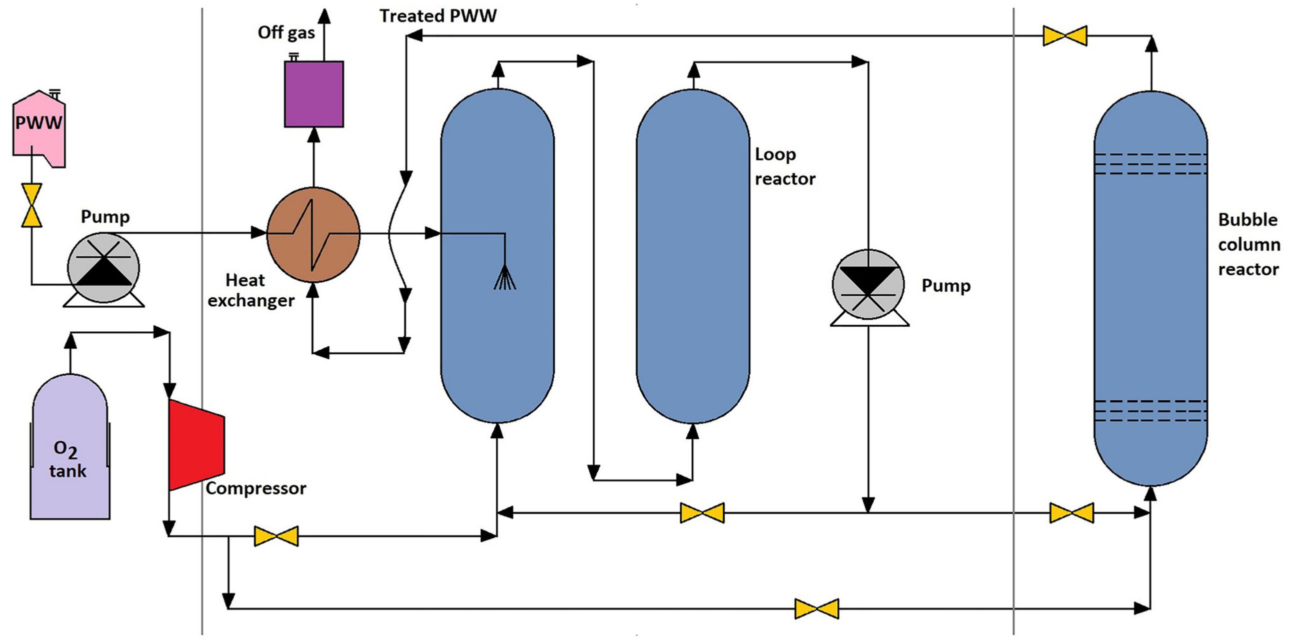

Figure 4: Flowsheet of the wet oxidation plant, amended from Szabados et al. (2018).

Berkün et al. (2021) demonstrated the CWAO method's high COD removal efficiency (83.1%) during catalysis of real pharmaceutical wastewater. Giannakis et al. (2021) introduced that sulfate radical-based advanced oxidation processes (SR-AOPs) are suitable for wastewater treatment in many industries, among which the chemical sector. Nair et al. (2021) determined that advanced oxidation processes are emerging as preferred methods for reducing the toxicity of the various components of the paint industry wastewater.

Ma et al. (2021a) emphasized that advanced oxidation processes have no secondary pollution, and they have high oxidation efficiency compared with other chemical wastewater treatment methods. Furthermore, the development trends were also summarized. The hotspot of future research is the development opportunity of low-cost, high-efficiency catalysts. Achieving a green and efficient preparation of catalysts is also very important, besides the exploration of active centers and further reaction conditions. Last but not least, the investigation of the toxicological character of catalysts in the environment is substantial.

The advantages of PWW treatment with wet oxidation can be found in the following list:

- organic and inorganic compounds can be transformed into less hazardous substances or removed,
- can be combined/integrated with other processes,
- high flow rate fluctuations can be managed,
- solid waste can be made up of inert metal salts in many cases,
- wastewater with relatively high refractory COD can be treated.

The disadvantages are the following:

- hydrogen peroxide requires appropriate storage (well-defined by standards) and handling to avoid the risk of explosive decomposition,
- high energy consumption: ozone generation, UV light generation, pressure, and heating for chlorine oxidation,
- when using halogenated oxidizing agents, organic halides may be formed.

5.1.5 Evaporation

Today, it is a realistic alternative to remove most of the water in an evaporator, and only small amounts of waste need to be treated in further steps, e.g. by incineration. This solution has been made competitive by the increase in various costs and fines (Simandi 2011).

Evaporation is a thermal process for components separation, in which valuable components are recovered from the solution of a non-volatile solute by evaporating the solvent.

Evaporation of PWW is carried out for the following purposes:

- preparation of a more concentrated solution,
- further use of the solute in dry form,
- recovery of the valuable pure solvent.

Evaporation of PWW is a distillation method in which water stands for the volatile substance while the concentrate is discharged as the bottom product. The aim of this operation is either a volume reduction of PWW or concentration of mother liquors. Volatile water vapor is collected in a condenser, and–after proper treatment, if necessary – it can be subsequently recirculated. The operation performed under vacuum reduces boiling temperature, allowing the recycling of materials that would otherwise decompose.

Evaporation is used when a concentrated form of PWW is required or advisable to obtain for further processes, when:

- The goal is to concentrate liquids from mother liquors and waste gas scrubbers to a level that allows valuable materials to be recycled.
- The aim is to evaporate and crystallise solids, either for material recovery or removal from the effluent, in which case the operation is used as pretreatment before the waste stream is subjected to thermal utilisation, incineration or disposed of as hazardous waste.

The evaporator unit has to be operated in such a way that the required thermal energy is provided by the utilisation of waste heat from production processes. Evaporation is rarely used as a separate operation; it is usually part of a technological process.

Yu et al. (2021) investigated a novel double-stage solar air evaporating separation system through an experiment in order to significantly reduce the energy demand for evaporation of saline wastewater. Liu et al. (2021a) successfully applied rotary spray for evaporation of high salinity wastewater to improve the mass and heat transfer characteristics and the evaporation rate. Yu et al. (2019) examined computer simulations and experiments on evaporating wastewater. It was determined that the gained output ratio (GOR) of the method could be significantly increased with a counter-flow spray concentration tower system.

It is important to emphasize that, thermal technologies such as evaporators means the conventional way to reach ZLD. Finally, the advantages of PWW treatment with evaporation are the following:

- volume and amount of hazardous waste can be reduced,
- wastewater amount can be reduced,
- possible recovery of material,
- possible removal of toxic organic compounds from wastewater,
- opportunity for zero liquid discharge.

The disadvantages are included in the following list:

- high energy consumption,
- sensitive to foaming, fouling and corrosion,
- volatile contaminants are emitted as a waste gas or they may pollute the condensate,
- residues, if not suitable for recycling, has to be disposed of usually by incineration.

5.1.6 Stripping

The stripping method is one of the most regularly applied tools for the removal of VOC from PWW (Brinkmann et al. 2016). The stripping aims to remove volatile organic and/or inorganic contaminants, such as organic solvents, hydrogen sulfide, ammonia, chlorinated hydrocarbons, aryl/aromatic compounds, and hydrocarbons (Başakçilardan-Kabakci et al. 2007). Generally, air or steam is applied to strip the less volatile compounds and VOCs (Gmehling et al. 1994).

In the stripping method, the PWW is brought into contact with a high amount of hot gas, vapor or steam to bring the volatile organic and/or inorganic compounds into the gas/vapor phase from the aqueous phase (Toth and Mizsey 2015). In the case of air stripping, usually, water is also transferred to the gas phase, which lowers the temperature of the hot air and therefore lowers the volatility of the impurities (Toth 2015). Impurities are removed from the gas phase used for stripping so that the gas/air can be applied again. Stripping can be performed as either a continuous or a batch method (Driscoll et al. 2008).

Depending on the volatility of the organic compound and the nature of the method, several types of stripping apparatus can be chosen (Ecker and Winter 2000). In the case of easily removable compounds, a stripping tank can be applied, where steam or air is bubbled into the wastewater (Toth and Mizsey 2015).

Tray and packed columns can be accurately applied to remove the polluting contaminants. The PWW is preferably pumped at the top of the column, and the steam or air is pumped at the bottom. The treated PWW is typically removed at the bottom, and the pollutants can be found in the top product, as it can be called a distillate product (Toth and Mizsey 2015). Figure 5 shows a general scheme for process wastewater stripping.

If the wastewater contains solid contaminants, it can cause fouling and breakdown of the heat exchangers and the column, which means a general problem with the stripping method.

It is worth mentioning that air stripping is not to be applied alone because the vapors and output gases can possibly enter the atmosphere and, as a consequence, the pollution is just transformed from the liquid into the air

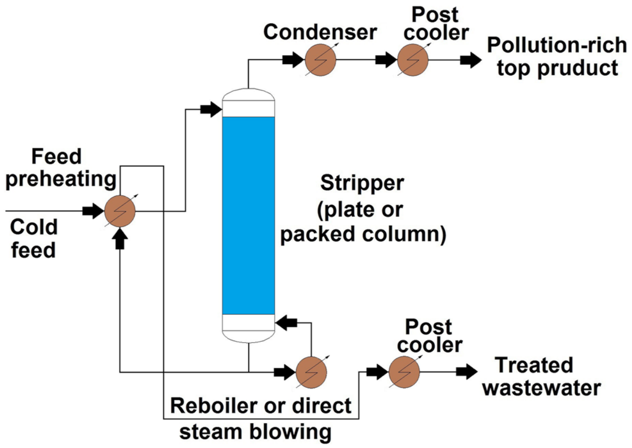

Figure 5: General scheme for process wastewater stripping after Toth (2015).

(Toth 2015). Gases and vapors have to be treated in order to avoid environmental pollution. Thermal or catalytic oxidation, adsorption, absorption, chemisorption, condensation and membrane separation may be possible purification methods (Sackewitz 1999). In many cases, these added methods are regularly more expensive and complicated than the stripping method itself (Toth and Mizsey 2015).

Air and steam stripper types were compared to remove AOX from pharmaceutical wastewater in an industrial case study by Toth and Mizsey (2015). It was found that both strippers are capable of reducing the dichloromethane content of the treated wastewater under the emission limit, of 8 ppm. The offered method was steam stripper, despite the fact that using steam was more expensive than air because the additional gas-treatment cost of air stripping was too high and the procedure too complex.

Li et al. (2020) demonstrated that the modelling of ammonia recovery from wastewater could already be solved in-process simulator environment. The air stripping process is applicable for ammonia removal, also in the case of municipal wastewater (Zangeneh et al. 2021). Cheng et al. (2021) integrated air stripping and calcium hydroxide precipitation for the treatment of flue gas desulfurization wastewater, which is suitable for COD removal of over 90%.

The advantages of PWW treatment with stripping can be found in the following list:

- low energy consumption,
- low-pressure drop,
- possible recovery of material,
- high removal efficiency.

The disadvantages are the following:

- usual column cleaning is mandatory,
- stripping gas has to be treated,
- in many cases, injection of anti-fouling agents is necessary.

5.1.7 Distillation

Among the various liquid waste treatment technologies, distillation is the most common method (Gorak and Sorensen 2014). In practice, if it is about distillation, rectification is meant. So these names are considered in practice as synonyms. The reasons for the application of the distillation are the following: material recovery can be solved practically without waste, organic pollutants can be recovered, distilled material can be reused, and pollutants can be deposited and disposed of in a concentrated form (Ge et al. 2021). In addition, the related investment cost is reasonable and affordable for various industrial frames (Kister 1992).

The disadvantage of this operation is that separation of mixtures of several solvents with similar boiling points by distillation is usually a very difficult task, and the separation of azeotropic substances by simple distillation is not possible (Arlt 2014). For this purpose, various hybrid separation operations have been developed, such as extractive heterogeneous azeotropic distillation (EHAD) (Haaz et al. 2020) and the combination of distillation with the hydrophilic pervaporation process (Skiborowski et al. 2013).

In reference to technological wastewater generated in numerous sectors of the chemical industry, extraction of volatile and distillable organic components (VOCs) significantly reduces the COD of PWW. In many cases, the value of adsorbable organically bound halogens (AOX) can also be reduced by distillation below 10 ppm, but processing should be done carefully. COD rejection opportunities can be seen in Table 5.

It may occur that the bottom product obtained during distillation no longer contains volatile organic matter, but its COD value does not reach the emission limit yet. In such

Table 5: COD reduction effect of the distillation of process wastewater from the chemical industry.

Process wastewater	Koczka and Mizsey (2010)	Szabados et al. (2018)	Toth et al. (2018a)
Initial COD mg/L)	15,000–500,000	12,000–300,000	15,000–17,000
Bottom product COD (mg/L)	Under 1000	3,600–22,000	500
COD rejection (%)	93.3–99.8	70.0–92.7	96.7–97.1

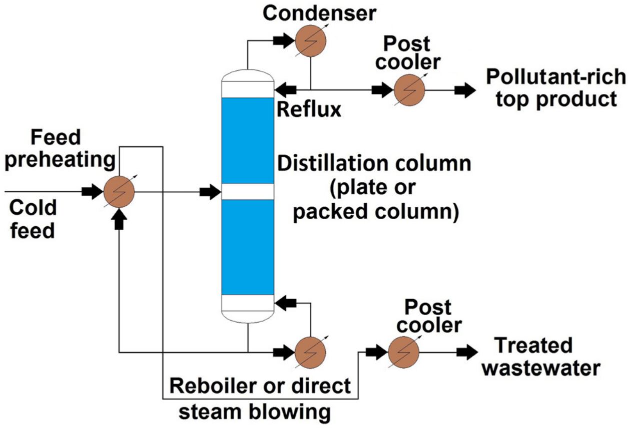

Figure 6: General scheme for process wastewater distillation, after Toth (2015).

a case, additional procedures would be required. In combination with membrane operations, not only larger molecules but even monovalent ions can be removed (Simandi 2011). Figure 6 shows a general scheme for PWW distillation.

Toth et al. (2018a) presented in detail the AOX and COD removal distillation column for the treatment of chemical PWW, starting with laboratory and pilot experiments, all the way to design and industrial implementation. As a novelty, it can be stated that innovative engineering solutions result in an economical and suitable method to reduce the AOX and COD content below the emission limit value of the bottom product of the distillation column:

- The direct steam injection can be used for the heating of the kettle, as a result of which the condensing steam dilutes the bottom product.
- The hot effluent PWW can be applied for feed preheating. 90% of energy savings can be reached with heat integration.
- The distillate product (mainly dichloromethane) can be utilised due to the application of the column rectifying section. *This reuse/recycling option can adapt the method of the circular economy concept.*

Figure 7 introduces the column for the separation of process wastewaters from the chemical industry.

Zhu et al. (2021) investigated the recovery of cyclohexane and sec-butyl alcohol azeotropic mixture from wastewater with thermal coupling extractive distillation combined with a heat pump. It was found that extractive distillation with ethylene glycol extractive agent is a suitable process for the recycling of organic solvents, based on the investigation of composite energy-saving process design, CO_2 emission, and thermoeconomic analysis. Ma et al. (2021c) proved that vapor recompression assisted extractive distillation is a suitable solution for the recovery of benzene and n-propanol from wastewater. The energy integration, according to pinch technology and economic optimisation, also justifies the great significance of the process. Wang et al. (2020b) investigated different methods for the separation of a binary azeotropic system of n-heptane and isoamyl alcohol from wastewater. The results have shown that compared with extractive distillation and pressure-swing distillation, the thermal integrated pressure-swing distillation had the lowest total annual cost, the lowest carbon emission and the highest thermodynamic efficiency. Guo (2021) confirmed that single column extractive distillation of ionic liquids integrated with a heat pump is a promising method for the recovery of isopropanol and ethanol from wastewater, both in economic and energy aspects.

Figure 7: Industrial distillation column for the treatment of chemical wastewaters, from Toth (2015).

Finally, the advantages of PWW treatment with distillation are the following:

- wastewater with relatively high COD can be treated,
- possible recovery of material,
- possible removal of refractory and/or toxic organic compounds.

The disadvantages are included in the following list:

- high energy consumption,
- residues has to be disposed of, usually by incineration.

5.1.8 Membrane operations

The advantages of membrane separation include high separation efficiency (Baker 2012), flexible application possibilities, and energy-saving features, by means of which high-purity product can be obtained in one step, without the use of a foreign organic compound as an excipient (Fane et al. 2011).

During its operation, care has to be taken to avoid fouling, scaling, and the phenomenon of concentration polarisation (Song and Elimelech 1995). It is also important to point out that membrane separation provides an opportunity to separate materials, which separation could not be accomplished by any other method. Its spread would be very beneficial from an environmental point of view because no additional waste is generated during its use (Baker 2012).

Membrane filtration is a realistic solution for the treatment of chemical PWW (Obotey Ezugbe and Rathilal 2020) because it is suitable for.

(i) Elimination of heavy metals from PWW (Koczka 2009).
(ii) Reduction of the amount of PWW, using hybrid separation technology (Toth et al. 2018b).
(iii) Reduction of the COD value of PWW (Cséfalvay et al. 2008).

These methods have not yet been widely used yet to treat wastewater from various industrial processes (Abdel-Fatah et al. 2021), but their application is spreading rapidly in the chemical sector (Shojaee Nasirabadi et al. 2016).

Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), or hyperfiltration (Kucera 2015) belong to the group of pressure-driven membrane methods, where the driving force is the transmembrane pressure between the two sides of the membrane (Bélafiné 2002).

Ultrafiltration is applied in chemical and electronic industries, as well as biochemical and food industries for the separation of particulate matter from soluble compounds (Ohanessian et al. 2020). UF is mostly used for pretreatment of desalination and wastewater reclamation (Brover et al. 2022). Nanofiltration is used for the desalination and removal of salt-like chemical pollutants (te Brinke et al. 2020). It has to be mentioned that the major application area of reverse osmosis is desalination (Greenlee et al. 2009) of sea-water and brackish waters (Baker 2012), but the COD reduction of PWW (Haaz et al. 2019) and removal of chemical pollutants are also processes that can utilise RO.

Table 6 summarises the information about the types of pressure-driven membranes, the values of transmembrane pressure and applicability.

These membrane operations can be applied for COD removal from PWW of chemical and similar industries. Table 7 introduces some reference work about the treatment of different industrial wastewaters with their maximum available COD rejection.

It can be seen that high COD rejection can be achieved with a combination of pressure-driven membrane processes in the aspect of the treatment of chemical wastewaters (see Table 7).

Organic solvent nanofiltration (OSN) means really a breakthrough in the last decade for the food, pharmaceutical, and petrochemical industries, to deal with organic solvents and promote valorization routes, where the main option proposed is the incineration. These novel, energy-efficient technologies based on polymer membranes are emerging as a viable alternative to thermal processes (Galizia and Bye 2018). Shi et al. (2021a) summarized that integrally skinned asymmetric, thin-film composite and nanocomposite are the most common types of membranes for OSN. Lai et al. (2022) prepared a novel PPTA/PPy composite OSN hollow fiber membrane for the treatment of organic dye wastewater. Using the procedure, the rejection of negative dyes was higher than 93.4%. Different membrane cascade configurations were investigated as a possible direction of development for yield improvement in solvent recovery (Ghazali and Lim 2022).

At last, the advantages of PWW treatment with membrane operations (MF, UF, NF and RO) are the following:

- possibility of totally automatic operation,
- low operating cost and temperatures,
- possible recycling of permeate and concentrate,

Table 6: Microfiltration, ultrafiltration, nanofiltration, reverse osmosis, and their applicability (Csefalvay 2009).

Membrane Processes	Type of Membrane	Transmembrane pressure (bar)	Applicability
Microfiltration (MF)	Symmetrical, asymmetrical, microporous	1–3	Particles, starch, pigments, bacteria
Ultrafiltration (UF)	Asymmetrical, microporous or composite	1–10	Macromolecules, polysaccharides, colloids, vira, proteins
Nanofiltration (NF)	Asymmetrical, nanoporous or dense	5–35	Mono-, di-, and oligosaccharides, dyes, multivalent ions
Reverse osmosis (RO)	Asymmetrical, dense or composite	15–80 (200)	Monovalent ions, glucose, amino acids

Table 7: COD rejection of different process wastewaters with membrane filtration (based on Toth (2015).

Treatment	Wastewater	Max. COD rejection (%)	References
NF	Wastewater with solvent content	80	Premachandra et al. (2021)
NF	Coal chemical industry	70	Shi et al. (2021b)
RO	Dairy industry	90	Del Re et al. (1998)
RO	Detergent wastewater	91	Haaz et al. (2019)
UF	Milking plant	87	Reimann and Yeo (1997)
UF + NF	Seafood processing	93	Ferjani et al. (2005)
UF + NF	Liquid detergent plant	96	Forstmeier et al. (2002)
UF + NF	Soybean process water	98	Pauer et al. (2013)
NF + RO	Alcohol manufacturing plant	52	Madaeni and Mansourpanah (2003)
NF + RO	Dumpsite leachate	90	Rautenbach and Linn (1996)
NF + RO	Pharmaceutical industry	94	Cséfalvay et al. (2008)
NF + RO	Dairy industry	99	Balannec et al. (2005)
NF + RO	Pharmaceutical industry	78	Toth (2015)
UF + NF + RO	Dumpsite leachate	96	Rautenbach et al. (2000)
UF + NF + RO	Phenolic wastewater	95	Sun et al. (2015)

- flexible in usage, because it has a modular structure,
- high separation efficiency,
- state-of-the-art opportunity for zero liquid discharge.

The disadvantages are included in the following list:
- risk of fouling,
- short membrane lifetime,
- in many cases low permeate fluxes,
- high-pressure application is mandatory,
- cleaning is necessary.

The electrochemical based membrane technologies, such as electrodialysis (ED) and bipolar membrane electrodialysis (BMED), could provide routes with the possibility of the creation of zero liquid discharge processes. Chen et al. (2022b) proposed electrodialysis metathesis for high-salinity wastewater, which proved a near-zero discharge desalination process without scaling potential. Lv et al. (2022) also proposed a ZLD technology, combining macroporous resin adsorption and desorption, BMED, and ED. During the electrodialysis process, the COD rejection rate reached above 93%. It has to be mentioned, that the macroporous resin and the used solvents were recycled, which achieved the closed-loop ZLD of salt recycling and reuse in wastewater. Furthermore, techno-economic analysis of ED and BMED was also justified that the process was promising for industrial application. Hung et al. (2022) examined the effects of process conditions on the removal and recovery of boron from boron-laden wastewater using BMED. During the investigation, 98.6 and 86.5% can be achieved in boron removal and recovery efficiencies.

Integration of membrane and crystallization processes providing also the possibility of circular solutions. Membrane distillation crystallization (MDCr) is an emerging hybrid method synergising membrane distillation (MD) and crystallization, thus achieving ZLD. MDCr method can be applied to increase water recovery and to yield useful solids of industrial wastewater. MDCr has low energy consumption and high efficiency and it can consider environment-friendliness. It has to be mentioned, that currently still most of the application of MDCr is limited to laboratory and pilot scales (Yadav et al. 2022).

One of the most dynamically developing membrane separation operations is pervaporation (Van der Bruggen and Luis 2014), which can also be used as a unit of various hybrid operations (Toth et al. 2018b). Pervaporation is the preferred solution for dewatering/dehydration of solvents, including alcohols (Wang et al. 2018). Wang et al. (2021b) developed the combination of steam recompression assisted distillation and pervaporation technology for recycling acetonitrile and n-propanol from wastewater based on environmental and thermoeconomic analysis. Cui et al. (2021) proved that the pervaporation–distillation hybrid process is energetically favorable and suitable for the recovery of ethyl acetate and isopropanol from wastewater.

5.2 Incineration of process wastewater–waste-to-energy option

Incineration is the most common (almost exclusive) treatment of PWWs, which is an accepted method for disposal. In many cases, the water content of the initial process wastewater is really high. In this case, it is advisable to use an enrichment process (e. g. stripping, and distillation) before incineration, which can increase the content of organic substances. The process can be advantageous because, due to their relatively high heat of combustion, these wastes are not only capable of self-combustion, they can also be used as energy carriers in waste incineration plants so that the thermal energy produced can be utilised afterwards (Holler et al. 2005).

This recovery option is called as "waste-to-energy" concept (Rogoff and Screve 2019), and there are many examples in the case of incineration. Chen et al. (2022a) developed a construction for the exploitation of organic waste and municipal solid waste, which combine anaerobic digestion and incineration for waste-to-energy. The suggested hybrid system based on biogas utilization proved to be energetically useful and economical. The comprehensive study by Escamilla-García et al. (2020) demonstrated the feasibility and the effectiveness of waste-to-energy in the case of incineration on the examination of the Mexican population. It can be strengthening the renewable energy sector, and significantly improvement for the waste management system. Liu et al. (2021b) confirmed the public acceptance of waste-to-energy incineration projects, based on society research in China.

The possibility of incineration of waste solvents is determined by their halogen (I-, Br-, Cl-) and sulfur content. If the solvent does not contain such components, it can be incinerated in energy-producing boilers without the risk of corrosion (Wang et al. 2007). However, the latter case is quite rare, so waste solvents are usually disposed of by incineration in facilities built for this purpose or in existing hazardous waste incinerators (Cheremisinoff 1992c).

The calorific value of halogen-free solvent wastes (without water or with low water content) reaches or approaches the calorific value of mineral oil-based fossil liquid wastes (30–40 MJ/kg). Such wastes can be used as auxiliary fuels in several high-temperature industrial technologies (cement production, power boilers, ceramics industry, etc.), or for the combustion of low calorific wastes in hazardous waste incinerators, in which they are used to feed the supporting flame and to provide the required temperature in afterburners (Cheremisinoff 1992a).

Technologies for the treatment, thermal disposal, and selling of hazardous wastes are very diverse. Depending on their toxicity, hazard, and quantity, a wide variety of preparation, incineration, and residue cleaning technologies can be distinguished. Combustion technologies can be separated, but joint solutions are also very common (Cheremisinoff 1992b).

To sum up, it should be highlighted that incineration is not a recommended tool for the treatment of PWWs, from an environmental viewpoint. It means the most unfavorable solution from the aspect of the circular economy concept.

Finally, the advantages of PWW treatment with distillation are the following:

- Waste heat can be utilised.
- With high salt concentration, the elimination of pollutants is possible.
- High organic content can be completely removed.

The disadvantages are included in the following list:

- Incineration of halogenated and sulfur compounds demands flue-gas treatment, causing solid waste and wastewater.
- Disposition of bottom and fly ashes (solid waste) is necessary.
- Supporting fuel has to be added to waste with low organic concentrations.

6 Process wastewater from the pharmaceutical industry and recommended treatments

The physicochemical methods can be properly illustrated by the treatment of pharmaceutical PWWs because their composition is the most compatible with the application of these methods. It is particularly important to deal with pharmaceutical waste because the sector has a very significant environmental factor.

When examining the causes of waste generation during pharmaceutical production, the typical emissions can be traced back to general environmental problems of the sector (Gupta et al. 2018):

(i) A large number of complex technologies are used, along with a wide variety of raw materials.
(ii) The starting materials (chemicals) used are incorporated into the product in a very small proportion (often below 10%). This sector has the highest environmental factor in the chemical industry.
(iii) Possibilities for recycling are limited by extremely strict quality assurance (GMP) regulations.
(iv) International standards make it difficult to modify production procedures, as it is often linked to a detailed review and approval procedure.

It can be stated that the environmental burdens of pharmaceutical production are the most significant during active ingredient production since the pharmaceutical forms are produced in extremely clean spaces by physical operations (Main operations: dissolving, pressing, mixing, drying, grinding, sieving, homogenising, etc.) (Ódor et al. 2005). Strade et al. (2020) pointed out that the pharmaceutical industry is water demanding industry and a producer of a high amount of water (wastewater) which is the reason for the environmental burden. The main environmental loads typical of pharmaceutical factories are the following (Rana et al. 2014):

a) Organic solvents: Most of the emissions can be attributed to the excessive use of organic solvents. Their high COD value is a serious problem.
b) Other organic substances: nonsolvent residual reagent, intermediate product, a by-product. They are characterised by high COD values; in addition, they have a high degree of diversity, which makes them difficult to manage.
c) Dissolved inorganic salt: It may occur due to the usage of absorption equipment for the capture of acid vapors, neutralisation of process effluents, and in mother liquors of organic reactions.
d) Ammonia-ammonium ion: It may occur in saturated absorption waters and mother liquors of reactions.
e) Organic solvent extraction: This method can dissolve several unwanted solvents during application.
f) Metals: They may appear in mother liquors of metal catalytic reactions. Their removal is often solved in a process closely related to technology.
g) Adsorbable organically bound halogens (AOX): They can cause a serious problem when released into the air or water. Strict emission values also force the industry to reduce the amount of chlorinated solvents (Ribeiro et al. 2020).

Table 8 shows some compositions of PWWs from the pharmaceutical industry.

Typical emission stages of wastewater in the pharmaceutical industry are summarised in Table 9 (Neuwahl et al. 2019).

Typical process effluents, i. e. process wastewaters (Neuwahl et al. 2019).

- Aqueous mother liquors: They may occur after drug recovery, e.g. during operations of phase separation, filtration and centrifugation. The main types of pollutants are: organic solvents (most common: methyl alcohol, ethyl alcohol, acetone, isopropyl alcohol, acetic acid, methylene chloride, formic acid), total salt, ammonia, organic solvent extract, undefined organic substances, etc.
- Vacuum waters: They can come from water ring vacuum machines. Typical pollution: organic solvents.
- Washing and rinsing water: It may result from cleaning and rinsing of production equipment. In this case, a typical form of contamination cannot be determined.

Other wastewater effluents may include (Backhaus and Karlsson 2014):

- Communal: not an industry-specific issue
- Flow-through cooling waters: In the case of a properly closed system, they can be considered uncontaminated. They may dilute technological wastewater, depending on the method of drainage. From the flow-through system, the sector switched to the principle of recycling, which meant a reduction in water consumption.
- Rainwater: Its drainage does not take place in a separate system at each site, so accidental contamination cannot be ruled out.

Table 8: Typical composition of pharmaceutical process wastewater.

	Gupta et al. (2019)	Gadipelly et al. (2014)	Wei et al. (2012)	Lokhande et al. (2011)	Saleem (2007)
Characteristics			**Range of parameters**		
PH	3.7–8.5	3.9–9.2	7.2–8.5	3.69–6.77	6.2–7.0
TSS (mg/L)	48–1,113		48–145	280–1,113	690–930
TDS (mg/L)	600–1,770	675–9,320		1,770–4,009	600–1,300
Total solids (mg/L)	880–4,934			2,135–4,934	
BOD (mg/L)	20–1,800	200–6,000	480–1,000	995–1,097	1,300–1,800
COD (mg/L)	128–3,500	375-32,500	2,000–3,500	2,268–3,185	2,500–3,200
Alkalinity (mg/L)	90–564				90–180
Total nitrogen (mg/L)	80–164	165–770	80–164		
Ammonium nitrogen (mg/L)	74–116	148–363	74–116		
Total phosphate (mg/L)	18–47		18–47		
Turbidity (NTU)	2.2–138		76–138		2.2–3.0
Chloride (mg/L)	205–261			205–261	
Oil and grease (mg/L)	0.5–2.9			0.5–2.9	
Phenol (mg/L)	95–125				95–125
Conductivity (μS/cm)	157–1,673				
Temperature (°C)	32–46				

Table 9: Typical wastewater emissions of the pharmaceutical industry.

Process	Input materials	Wastewater
Reaction	Solvents, e.g. benzene, chloroform, methylene chloride, toluene, methanol, ethylene glycol, methyl isobutyl ketone, xylenes, hydrochloric acid, catalysts, reagents	Used solvents, catalysts, reagents in water; water seals of pumps; wet washing tower wastewater; effluents from equipment cleaning *BOD and COD high; pH: 1-11*
Separation	Separator and extraction solvents, e.g. toluene, hexanes	Equipment-cleaning wash waters, rinsing waters, spills, residues of used separating solvents in the aqueous phase
Cleaning	Cleaner solvents, e.g. methanol, toluene, acetone, hexanes	Equipment-cleaning washing waters, rinsing waters, spills
Drying	Products and intermediates	Equipment-cleaning washing waters, rinsing waters
Natural products extraction	Plant and animal fabrics, extraction solvents, e.g. ammonia, chloroform, phenol, toluene	Equipment-cleaning washing waters, used solvents *BOD and COD low; pH: 6-8*
Fermentation	Vaccine, sugars, starches, nutrients, phosphates, fermentation solvents, e.g. ethanol, amyl alcohol, methanol, acetone	Fermentation broth (which contains sugars, starches, nutrients etc.) *BOD and COD high; pH: 4-10*
Formulation	Drugs, binders, sugar, syrups and fillers, granulation, excipients	Equipment-cleaning washing waters, used solvents *BOD and COD low; pH: 6-8*

According to as stated above, efforts should be made to extract materials from process effluents. Material recovery can make the process more economical in the long run because extracted materials can be used as starting materials or intermediate products in other production processes (Ódor et al. 2005). As a matter of fact, in addition to by-products, the resulting wastewater also contains starting materials and final products (Kadam et al. 2016). In many cases, pharmaceutical effluents may also carry catalysts, emulsifiers, and other components as well (Khetan and Collins 2007).

Some of these contaminants are very difficult to biodegrade, and the degradation process happens at a slow pace. Some components cannot be broken down at all and may even prevent the biological removal of other components (Strade and Kalnina 2019). As a result, these wastewaters differ significantly from municipal wastewaters and even other wastewaters of industrial origin, mainly due to their higher content of nonbiodegradable components. Contaminants of organic origin, contained in them, often occur in molecularly dispersed form, in contrast to, e.g. municipal wastewater, in which about 60% of organic pollution is present in colloidal form, which facilitates destabilisation and flocculation (Miarov et al. 2020).

There is a two-way approach to the treatment of such wastewaters. On the one hand, efforts should be made to minimise the release of nonbiodegradable contaminants into the effluent and to remove such components from the water as efficiently as possible by physical or chemical treatment before biological treatment takes place (Kaczala and Blum 2016). The other aim is to ensure the highest possible COD removal in the biological treatment, even in the case of quantitative or qualitative fluctuations in the composition of wastewater (Kavitha et al. 2012).

Some of the contaminated solvents can be regenerated by various treatment methods (Patneedi and Prasadu 2015). In some cases, the regenerated solvent can be used in other industries. In practice, however, a cross-industry solvent transfer is not typically used due to the variations in the quality of regenerated and recycled raw materials, and pollutants interfere with the continuous sustainability of quality (Toth 2015).

If these pharmaceutical effluents enter the surface waters, it can lead to changes in flow conditions and morphology, endangering habitats or even making them disappear. They can cause poisoning of river wildlife and can also create heat pollution. As a result of warming, the oxygen content of the water decreases, and aerobic organisms become damaged, resulting in their significantly reduced number. The lack of oxygen favors anaerobic degradation processes, which leads to the disruption of biological balance. Some thermophilic algal species may also multiply to a great extent. In consequence, waters will be richer in organic matter, which can lead to the process of eutrophication (Khan et al. 2021).

Figure 8 shows a strategy developed for the treatment of process effluents containing volatile organic components and AOX. The strategy follows the principle of sustainability and circular economy, according to which the extraction of valuable materials in wastewater should be

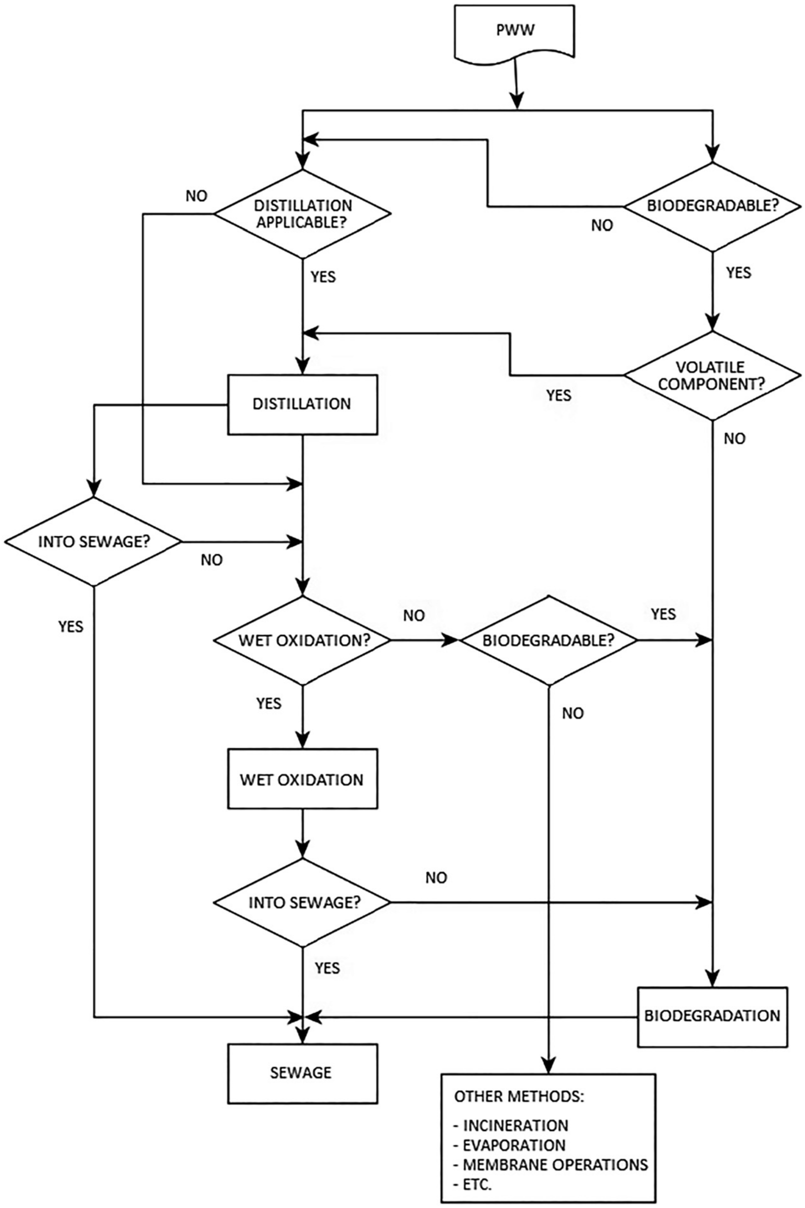

Figure 8: Treatment strategy for pharmaceutical process wastewater, amended from Hosseini et al. (2011a) and more recently (Toth 2015).

considered a primary goal. The last step is the drainage of wastewater into the sewer. An important aspect of technology selection is that wastewater properties should meet the criteria for discharge into the sewer. The relevant limit values are laid down in the US EPA regulation about pharmaceutical manufacturing (Browner et al. 1998).

It has to first be decided, on the basis of available data, whether the wastewater contains components that cause an above-limit COD and AOX value. If so, and the components in question are volatile, distillation is advisable for the removal of such volatile content. Following distillation, it is necessary to test the distillate product due to its concentrated volatile solvent content, which may be reused or recycled (Perez-Vega et al. 2013). After removing the volatile content, if the recovered solvents have a low COD value and they are biodegradable, they can be reutilised.

The toxic waters require wet oxidation, which does not have to be carried out to complete mineralisation; it is enough if the toxic components are degraded. The partly oxidised PWWs contain biodegradable compounds, usually small carbon atom number carboxylic acids such as acetic acid, which are an excellent carbon source for denitrification. Complex physicochemical and biological treatment offers a sustainable and competitive alternative to incineration (Hosseini et al. 2011a). It needs to be mentioned, that incineration is much more economical due to the much lower water content, contrary to raw and dilute wastewater. In order to determine a safe treatment method, an appropriate combination of the aforementioned techniques and detailed characterization of the PWWs would be needed, including the quantification of their biodegradability when diluted with domestic wastewater at different ratios (Hosseini et al. 2011a). The expenditure arising from environmental fines should be compared to the cost of cleaning technology.

7 Conclusions

The chemical industry is still considered to be one of the industries with the highest environmental impact, mainly due to several unfavorable experiences. However, this opinion is not entirely justified today because the pollution caused by the sector has significantly decreased as a result of technological development and structural transformation in the chemical industry. The environmental factor can show a wide range of values based on the type of chemical industry. It can vary from 0.1 to as high as over 100. In the decade between the years, 2007 to 2017, the average pollutant emission (comprising the organic, inorganic compound and heavy metals) in wastewater of the chemical industry sector was as high as 10,217 kt. There are also tendencies for environmental considerations and process wastewater reduction aspects to become more and more important both in relation to existing chemical processes and when designing new ones. It is important to note that more and more severe environmental regulations force such development. Active environmental protection has become an integral part of the chemical industry sector. Numerous industrial developments and scientific achievements have been published with the aim to reduce the use of raw materials and energy and recovering and recycle the process of wastewater polluting compounds and by-products. Developments and research in the field of environmental and technical chemistry have a significant role in diverting the chemical industry to a greener path and waste reduction.

In this research work, some development proposals are collected that could be worth focusing on in the near and distant future in order to develop a more environment-oriented chemical industry. The recommended methods are represented by the physicochemical methods, as they offer the possibility to recover the polluting materials from PWW, which are usually valuable substances. The main physicochemical methods (adsorption, ion exchange, extraction, wet oxidation, evaporation, stripping, distillation, membrane operations) were examined in an aspect of their pros and cons. Very often, the level of initial chemical oxygen demand of process wastewater goes beyond 10,000 mg/L; it can ever reach 100,000 mg/L or above. As it was determined, every mentioned tool is able to drastically reduce the chemical oxygen demand and total organic carbon of PWW, which are the key parameters in terms of environmental impact. Numerous case studies demonstrate that a reduction of more than 90% can be achieved by hybrid technologies based on distillation and membrane unit operations.

This work critically evaluates the main criteria for the selection of procedures, which involve the assessment of process wastewater properties, local conditions, economic parameters and environmental regulations. It is becoming increasingly important to find appropriate treatment methods for processing wastewater in the chemical sector to cope with the more and more severe environmental regulations. On the other hand, such methods are getting more and more based on physicochemical methods that also offer the recycling and reuse of the polluting materials opening new horizons for the circular economy and also zero-emission liquid discharge technologies.

Abbreviations

AOP	Advanced oxidation processes
AOX	Adsorbable organically bound halogens
BAT	Best available techniques
BMED	Bipolar membrane electrodialysis
BOD	Biochemical oxygen demand
BREF	BAT reference document
COD	Chemical oxygen demand
CWAO	Catalytic wet air oxidation
EC	European Commission
ED	Electrodialysis
EHAD	Extractive heterogeneous azeotropic distillation
FWPO	Fenton wet peroxide oxidation
GHG	Greenhouse gas
GMP	Good manufacturing practice
GOR	Gained output ratio
HEN	Heat exchanger network
IPPC	Integrated pollution prevention and control
LCA	Life cycle assessment
MD	Membrane distillation
MDCr	Membrane distillation crystallization
MF	Microfiltration
NF	Nanofiltration
OSN	Organic solvent nanofiltration
PWW	Process wastewater
RO	Reverse osmosis
SCWO	Super critical water oxidation
TDS	Total dissolved solids
TEA	Techno-economic assessment
TOC	Total organic carbon
TSS	Total suspended solids
UF	Ultrafiltration

VOC	Volatile organic compounds
WAO	Wet air oxidation
WPO	Wet peroxide oxidation
ZLD	Zero liquid discharge

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