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# Report

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# Innovative Techniques for Effluent Treatment for Specific Pollutants

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# Innovative Techniques for Effluent Treatment for Specific Pollutants

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## ABSTRACT

This report identifies twenty-seven (27) innovative techniques to treat a selected list of organics substances, inorganic substances and heavy metals, based on a literature review, consultation with Concawe member companies and waste water treatment equipment suppliers and vendors. Some of these have Best Available Techniques (BAT)- Associated Emission Levels (AELs), while others are listed in the Refinery Reference document (REF BREF) but have no BAT-AELs in the current BAT conclusions of the REF BREF. This report provides a description of each technique, the substances targeted by each technique, their efficiencies and their main advantages and disadvantages, as well as an evaluation of their level of maturity in its application in industry and capital and operational costs. A smaller number of techniques were then selected based on their maturity and commercial availability for which their environmental footprint and cross media effects were assessed and overall capital and operational costs identified. These techniques may be considered for further testing to gain a better understanding of their applicability to a fuel manufacturing effluent. A main conclusion of this study is that high TRLs for techniques applied to a specific sector or to several sectors do not necessarily translate into a similar level of application to the fuel manufacturing wastewaters in terms of their efficiencies, costs, and general applicability. Such techniques will need to be tested in an operational environment to assess such applicability.

## KEYWORDS

BAT, best available technology (BAT), capital cost, operational costs, effluents, emissions, innovative techniques, refinery, REF BREF, water treatment, waste water.

## INTERNET

This report is available as an Adobe pdf file on the Concawe website (www.concawe.eu).

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## SUMMARY

This report presents the findings of the identification and assessment of innovative wastewater treatment techniques to treat a range of selected organics substances, inorganic substances and heavy metals. Some of these have BAT-AELs while others are listed in the REF BREF but have no BAT-AELs in the current BAT conclusions of the REF BREF. The Industrial Emissions Directive (IED; 2010/75/EU) sets the framework for permitting of industrial facilities in the EU.

The identification of innovative treatment techniques for refinery wastewaters was based on a literature review of scientific journal publications, online technical websites, contractors' information and previous Concawe commissioned work on the topic, together with information provided by Concawe member companies related to the testing or use of such techniques at their refineries. Where possible, information was also obtained from wastewater treatment specialist companies.

The BAT for refineries' wastewater discharge control mentioned in the BAT Reference Document for the Refining of Mineral Oil and Gas (REF BREF) is a three-stage WWTP. However, the REF BREF does not prescribe the exact configuration of the wastewater treatment system that should be used, only that discharges concur with the BAT-AELs mentioned in the associated Commission Implementing Decision 2014/738/EU (EU, 2014). Refinery wastewater treatment systems are designed to remove inorganic and organic constituents to reduce the contaminant loads to the limits set in the refinery's operating permits. However, further reductions are likely to be required as the European Commission implements the EU Action Plan: "Towards a Zero Pollution for Air, Water and Soil", adopted in 2021.

Twenty-seven (27) innovative techniques were identified as part of this work, encompassing a wide range of technique types including advanced oxidation techniques, electrical/electrochemical techniques, membrane-based techniques, adsorption-based techniques, extraction techniques, precipitation techniques and others. The report provides a description of each technique, the substances targeted by each technique, their efficiencies and their main advantages and disadvantages. An evaluation of their Technology Readiness level (TRL), i.e., an indication of their level of maturity in its application in industry and to which industrial sector, is also provided and used to select a smaller number of techniques for further assessment of their environmental footprint, cross media effects and capital and operational costs.

The selected techniques assessed have demonstrated their capability to treat one or more of the target substances discussed in this report. Some have been tested in refineries while others are used in industries containing such substances. Fuel manufacturing sites differ in their size, complexity, the types of processes they operate, and the types of crude oil they process. In addition, the techniques selected cannot treat refineries effluents on their own, as they will typically form part of a combination of techniques to achieve the desired effluent quality. Consequently, the cost of using a technique is significantly impacted by all these variables. Also, cross media impacts can often result from the application of new techniques, and these should be considered when assessing the applicability of a technique at a given location and in a specific industrial sector. Further testing of such techniques to assess such applicability at specific fuel manufacturing facilities is therefore necessary.

# 1. INTRODUCTION

This report presents the findings of the identification and assessment of innovative wastewater treatment techniques to reduce the concentrations of several organic and inorganic substances and heavy metals in fuel manufacturing sites' wastewater discharges. Some of these have BAT-AELs while others are listed in the REF BREF but have no BAT-AELs in the current BAT conclusions of the REF BREF. The Industrial Emissions Directive (IED; 2010/75/EU) sets the framework for permitting of industrial facilities in the EU. With respect to the IED, the minimum parameters that refineries are obliged to monitor and control are laid down in a Best Available Techniques (BAT) Reference document (BREF) for the mineral oil and gas refining sector – the so-called REF BREF[1]. The REF BREF also includes the BAT Conclusions (BATc; 2014/738/EU), published in 2014, which is a legal binding document setting out minimum requirements for the EU for the refining sector. The BAT conclusions shall be the reference for setting emission limits and issuing operating permits. It is anticipated ("current best estimate") that a formal decision on the need to revise the REF BREF will be given by the European Commission (EC) in the coming years.

From recent updates on the directive recast, it is expected that the emission limit values in a permit would be set at the strictest achievable associated emission levels (AELs) considering the entire range of the emission levels taking into account the best overall performance of the installation and having regard to possible cross-media effects. It is also expected that it will include binding AELs for emerging techniques, applicable within 6 years of the publication of the BAT Conclusions with a possible temporary derogation for testing the emerging technique for a period of time not exceeding 30 months. Future revisions will increasingly focus on the control and restrictions of hazardous substances and on seeking increasing alignment with groundwater and surface water 'target' values. Installations should expect increased attention from competent authorities with a revalidation of discharge permits to ensure alignment with REF-BREF requirements and local requirements for improvements of water quality in a River Basin.

The identification of innovative treatment techniques for refinery waste waters was based on a literature review of scientific journals, technical papers, online technical websites, contractors' information and previous Concawe commissioned work on the matter, together with information provided by Concawe member companies related to the testing or use of such techniques at their refineries. Where possible, information was also obtained from wastewater treatment specialist companies.

**Section 2** of this report provides an introduction and general description of refinery wastewater treatment techniques with special emphasis on techniques classified as BAT in the REF BREF. This Section also discusses overall efficiencies of current wastewater treatment configurations and the main refinery processes sources from which the selected substances originate from.

**Section 3** provide a list of innovative techniques identified during the literature review, Concawe members survey and interviews with wastewater treatment specialist including their mode operation, applicability, advantages and disadvantages, overall environmental footprint, cross-media effects and technical maturity.

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[1] Best Available Techniques (BAT) Reference Document for the Refining of Mineral Oil and Gas, EU-JRC 2015. (http://eippcb.jrc.ec.europa.eu/reference/BREF/REF_BREF_2015.pdf)

**Section 4** provides an assessment of the identified techniques Technology Readiness Levels (TRLs), an indication of their maturity and commercial availability.

**Section 5** provides a qualitative environmental/sustainability assessment, applicability to refinery effluents and costs for a smaller number of selected techniques.

Finally, **Section 6** provides a summary of the previous sections and some final observations and conclusions resulting from the review of the available information.

# 2. REFINERY WASTEWATER TREATMENT

## 2.1. GENERAL DESCRIPTION OF REFINERIES' WASTE WATER TECHNOLOGIES

The BAT for refinery discharge control mentioned in the BAT Reference Document for the Refining of Mineral Oil and Gas (REF BREF) is a three-stage WWTP. However, the REF BREF does not prescribe the exact configuration of the wastewater treatment system that should be used, only that discharges concur with the BAT-AELs mentioned in the associated Commission Implementing Decision 2014/738/EU (EU, 2014). The WWTP can be extended with a fourth stage, called a polishing step, to further reduce nitrogen or carbon compounds, if deemed required. The steps themselves can be described as follows:

- Step 1: Recovery of free phase oil and solids by static physical separation of oil from the water.

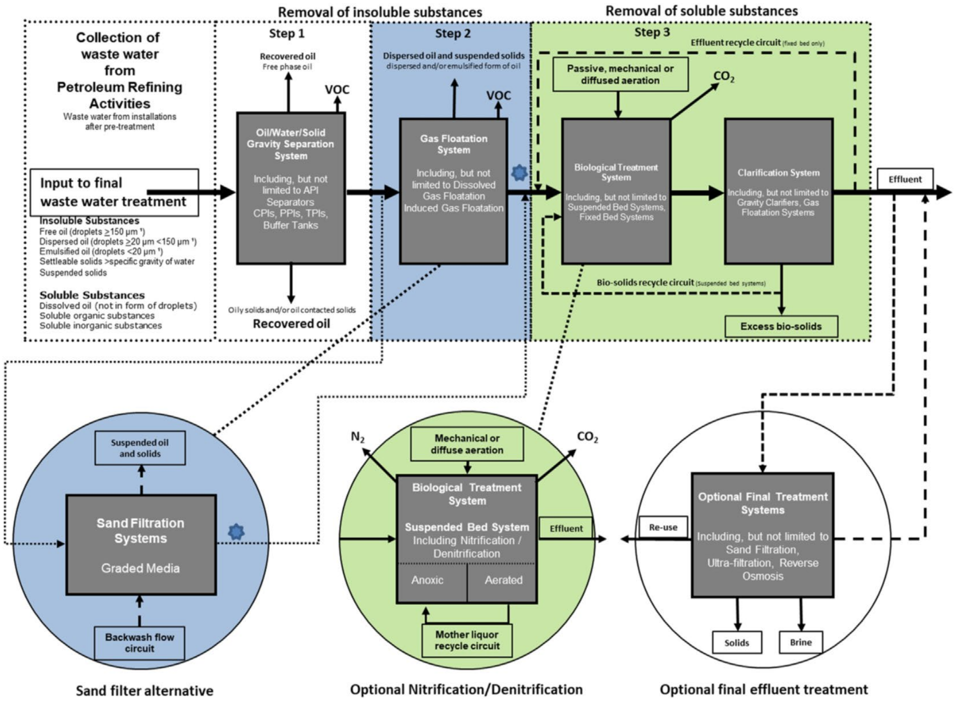
- Step 2: Removal of dispersed oil by active physical-chemical separation/ flotation of oil, water, and suspended solids.

- Step 3: A biological treatment to remove biodegradable substances, such as hydrocarbons (HCs), and other organic and inorganic substances. Step 3 includes a clarification system.

- Step 4: An additional polishing step (optional according to the REF BREF), including, but not limited, to sand filtration, ultrafiltration and reverse osmosis.

The REF BREF also list other options for step 3 such as heterotrophic denitrification, granular activated carbon (GAC), Micro Porous Polymer Extraction (or MPPE for the removal of BTEX, Phenol and PAHs). The REF BREF further mentions a combination of sand filtration, ultrafiltration, activated carbon and reverse osmosis to treat waste waters to cooling water or boiler feed quality, in particular for areas where water resources may be scarce. A schematic representation of such a three-stage WWTP is provided in **Figure 1**.

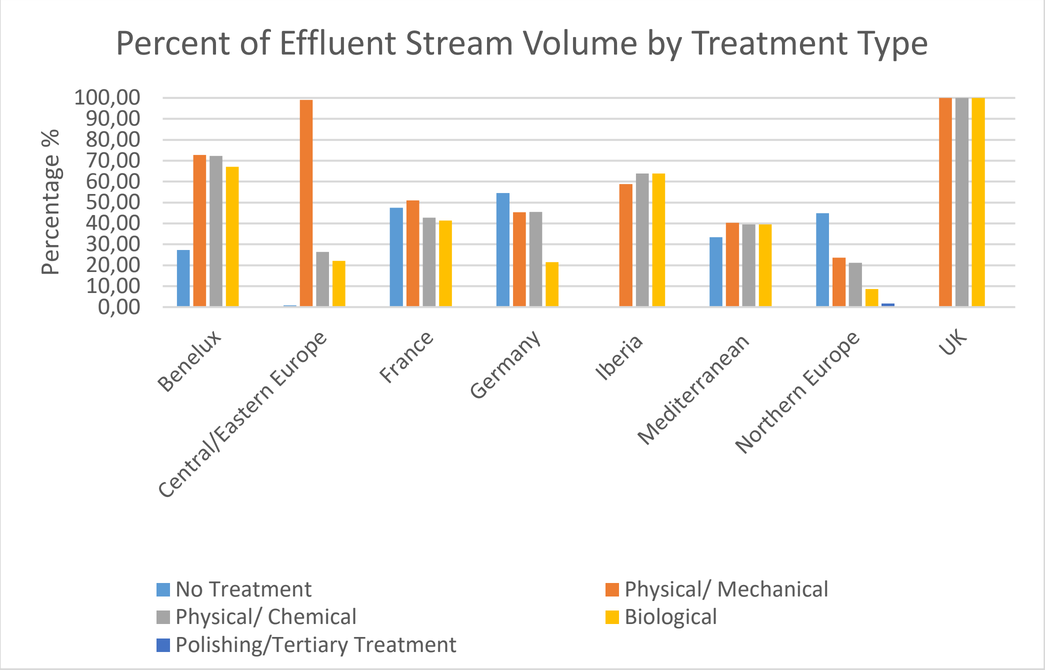
*Figure 1:* Schematic three-stage WWTP with optional polishing options (JRC, 2015).



Refinery wastewater treatment systems are designed to remove inorganic and organic constituents to reduce the contaminant loads to the limits set in the refinery's operating permits based on Best Available Technique Associated Emission Levels (BAT-AELs). In addition, those permits indicate which parameters should be monitored.

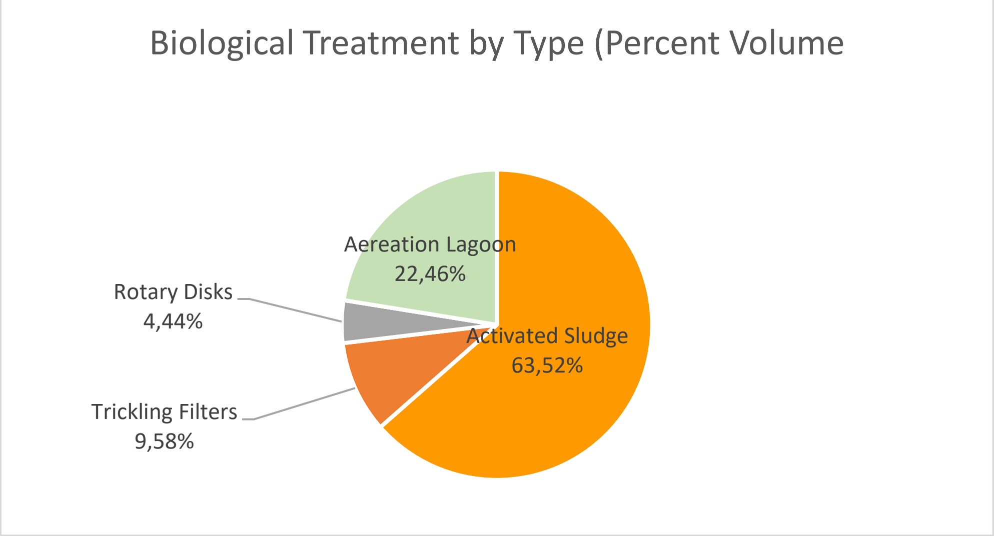
**Figure 2** shows the percentage of effluent by treatment type, for European refineries in 2022 (Concawe Water Survey 2022). Note that some sites may have multiple effluent streams with different treatment types. Physical/mechanical treatment (such as API separators), physical/chemical treatment (such as DAF) and biological treatment all presented similar volumes representing a three stage WWTP. Final polishing was reported by two refineries (out of a total of 48 reporting refineries), representing a small volume with some 4,6 million m$^3$.

***Figure 2:*** Percent of effluent stream volumes by treatment type (excluding once-through cooling volumes). Concawe Water Survey 2022. It includes data from 48 reporting refineries.



In terms of the biological treatment applied by the reporting refineries the activated sludge process was by far the most common biological treatment technique applied (63% of treated volume), followed by aeration lagoons (22.5%), trickling filter (9.5%) and rotary disks with just 4.5% of the treated volumes (see **Figure 3**).

***Figure 3:*** Percent of effluent stream volumes with biological treatment (by biological treatment type). Concawe water survey 2022.



A study carried out by Hjort et al. 2021 has looked at the performance of a number of European refineries with regards to the waste water treatment techniques and the relevant reductions in water emissions of hydrocarbon pollutants such as Total Petroleum Hydrocarbons (TPH), BTEX, dissolved PAHs and Naphthalene. The study showed high total reduction factors for TPH between 97% and >99%. These values show that the 3-stage refinery WWTP trains, as expected, are very efficient in removing HCs. These reductions are consistent with literature data (Mahmoudkhani et al. (2012) and Santos et al. (2015)). The largest reductions of TPH were found in the physical-chemical separation/flotation step (where DAF systems were used), where 81-94% reduction of TPH influent concentration was observed. These values represent the removal of whole oil, and thus represent physical removal processes. It should be noted that such efficiencies are conditioned by the particular quality of the effluents such as pH and conductivity, and by the chemical additives used to assist separation.

## 2.2. CURRENT TREATMENT OF SELECTED SUBSTANCES

**Table 1** lists the substances selected for this study. The main reason for their selection is the fact that these substances are toxic for biological systems above certain concentrations and potentially prevent achieving the desired effluent quality. A brief description of current treatment practices and efficiencies using 3-stage waste water treatment systems is provided below.

***Table 1:*** List of Substances Targeted in this Report

| Parameter | | Parameter | |
|---|---|---|---|
| Organics | Phenol Index | Metals | Nickel |
| | BTEX | | Arsenic |
| | PAHs | | Chromium |
| | AOX | | Cobalt |
| Inorganics | Total Phosphorous | | Copper |
| | Cyanides (as Total CN) | | Manganese |
| Metals | Cadmium | | Selenium |
| | Lead | | Vanadium |
| | Mercury | | Zinc |

### 2.2.1. Organic Substances

**Phenols** can be toxic to bacteria in concentrated solutions. However, they can serve as food for aerobic bacteria without serious toxic effects at levels as high as 500 mg/l. A phenol threshold concentration of 200 mg/l was reported to have an inhibitory effect on the activated sludge process (REF BREF). High concentrations of phenols can also affect the removal efficiency of carbon and nitrogen in the biological treatment stage. Abatement efficiencies reported for five WWTPs were in the range of 90-99.9%, where four of those reported 99% (REF BREF). Emission data for phenols provided in the REF BREF had a 0.01 to 0.04 mg/l range (5th to 95th) and a 50th of 0.1 mg/l (2008 data). Data reported by fuel manufacturing sites in Europe in 2022 showed a 5th percentile of less than detection limit and a 95th percentile of 0.29 mg/l with a 50th percentile value of 0.01 mg/l (Concawe Water Survey 2022).

High concentrations of phenols in the influent normally correspond to final WWTPs treating waste waters from installations where phenolic compounds are used/produced. Techniques reported to reduce phenols in waste water include a range of techniques such as;

- Pretreatment at the installation(s) from which the waste waters originate, via extraction or adsorption with activated carbon;
- Treatment at the WWTP.

The trickling filter and the activated sludge process are generally in use for the treatment of phenolic waste water. The removal of phenols is effective only up to a certain level. Some discharged effluent standards are set at 0.1 mg/l (CWW BREF). Thus, the conventional methods may not be sufficient to bring down the phenol concentration to such a low level in the treated effluent.

Hjort et al. 2021 showed that European refineries waste water treatment techniques were efficient at reducing **BTEX**, dissolved **PAHs** and Naphthalene. In particular, it showed that biological treatment was highly effective for removing volatile BTEX and Naphthalene (>98% removal). The study showed that the main reduction of low molecular weight PAHs occurred during the biological treatment step. An issue with regards to the treatment of PAHs is that there are many more easily degradable hydrocarbons that would evolve dominant strains of the micro-organisms in the bioreactor that would result in the PAHs almost being left untouched. Moreover, it should not be overlooked that besides degradation, the PAHs may be adsorbed by the suspended organic matter. In such circumstances, a polishing step like a sand filter or activated carbon can substantially reduce the PAH emission load.

BTEX effluent concentrations from European refineries reported in the REF BREF were 0 to 0.43 mg/l (5%-95% percentiles), with an average of 0.03% for 2008 data. Data for 2022 (18 refineries) had a range of 0 to 0.1 mg/l (5% to 95% percentiles) and an average of 0.0218 mg/l.

**AOX** is a sum parameter which indicates the overall level of organohalogen compounds (chlorine, bromine and iodine) in water samples. Many organohalogen compounds are toxic (especially the fat-soluble chlorinated group – dioxins, furans, and polychlorinated phenolic compounds) and/or persistent. However, as a sum parameter, AOX does not give information on the chemical structure of organohalogen compounds present or on their toxicity. AOX is mainly associated with the production of organic chemicals and silicones. Waste water streams containing high AOX loads are preferably pretreated or recovered separately, e.g. by (chemical) oxidation, adsorption, filtration, extraction, (steam) stripping, hydrolysis (to improve biodegradability), distillation, membrane processes or anaerobic pretreatment. Stripping and adsorption to activated carbon have been reported as techniques used to remove AOX at WWTPs. A certain share of the AOX is also removed during final treatment (e.g. due to biodegradation or due to adsorption to particles). Organohalogen compounds are part of the organic load of waste waters and is therefore a part of COD/TOC, and, if biodegradable, also of $BOD_5$. Therefore, techniques that reduce COD/TOC will also contribute to AOX reduction.

### 2.2.2. Inorganic Substances

**Phosphorus** is present in waste waters in inorganic and organic forms. The inorganic forms are orthophosphates (i.e., $H_2PO_4$-) and polyphosphates. Organically bound phosphorus is usually of minor importance. Phosphorus discharge has to be controlled in the same way as nitrogen discharge in order to avoid eutrophication of surface waters.

Microorganisms utilise phosphorus for cell synthesis and energy transport. As a result, 10–30% of the influent phosphorus is removed during traditional biological treatment (REF BREF]. When the industrial waste waters do not contain enough phosphorus for optimum growth of the organisms used in treatment, the addition of inorganic phosphates may be necessary. Data reported by 39 refineries in 2022 showed a range of concentrations from less than detection limits (5% percentile) to 1.76 mg/l (95% percentile).

Abatement efficiencies for loads reported for 21 WWTPs range from -13.3% to 98.8%, but more generally from 46% to 97.7% (10th to 90th percentile) with a median of 77.7% (CWW BREF). These values suggest that chemical precipitation of phosphorus is often carried out in addition to biological phosphorus removal. The negative value of -13.3%, reflects a higher concentration of Total Phosphorous in the effluent due to the addition of TP as a nutrient to the biological treatment (CWW BREF).

Removal of phosphorous at the WWTP can occur biologically (i.e., incorporated into cell biomass), or by precipitation (with ferric chloride, lime, etc) before, during or after the biological treatment. It can also be done by precipitation in physico-chemical WWTPs, although it should be noted that physico-chemical treatment only removes orthophosphates but no other forms of phosphorous. Chemical precipitation for phosphorus removal increases the volume of sludge produced and often results in a sludge with poor settling and dewatering characteristics. With biological phosphorus removal, the need for chemical addition is reduced or eliminated. The Concawe water survey 2022 reported an average of 0.22 mg/l total phosphorous for 20 reported outlets with 7 reporting concentrations below detection limits.

**Cyanides** can be present in water in dissolved or particulate form. They can be found as cyanide ions (CN-), hydrogen cyanide (HCN), complex bound cyanides, organically bound cyanides, and other inorganic forms. Many cyanide-containing compounds are highly toxic, but some are not. A primary concern regarding aqueous cyanide is that it could volatilise, especially when the pH is below 8. The cyanide ion (CN-) has a relatively short half-life because it can serve as a source of energy for aerobic bacteria, provided the concentration is kept below its toxic threshold.

Data reported by European refineries in 2022 showed emissions of total Cyanide range from less than detection limit to 0.1905 mg/l (5% to 95% percentiles) with a 50% percentile of 0.006 mg/l for a total of 20 reported outfalls. At low level, cyanides are biodegradable in adapted WWTPs (CWW BREF). The rate of biodegradation depends on the activity and adaptation of the WWTP. When influent concentrations are high (in the range of 4–5 mg/l), there is a risk of toxicity for the bacteria of the biological treatment. Biological treatment is not usually used to reduce cyanides, however, depending on the individual case, it may also be possible to enable safe degradation of cyanides in a biological WWTP. The following pre-treatment techniques were reported (CWW BREF):

- Conversion to glyconitrile with formaldehyde and sodium hydroxide;
- Oxidation with hydrogen peroxide;
- Complexation with iron and oxidation with ozone;
- Oxidation with hypochlorite;
- Oxidation under alkaline conditions.

The removal of cyanides is complex and compound specific. Cyanides may be complexed either with organics or with metals. In the case of metal complexes, depending on the metal and its state of oxidation may require different treatment techniques.

### 2.2.3. Metals

The waste waters of many chemical/petrochemical processes contain metals that are contained in the materials used for chemical processing such as feedstock and catalysts. The corrosion of pipes and equipment is also an important source of metals (especially Cu, Cr, Ni, Zn) in effluents of WWTPs. Metals are not degradable and almost all of them are adsorbed to the sludge or passed through the biological WWTP. High levels of metals can inhibit the biological processes in WWTPs, but certain concentrations are needed for the growth of the organisms. High metal loadings in waste water sludge can cause problems for disposal. Once discharged to water they can be retained in sediments from where they can remobilise in the water body (river or sea).

Techniques to abate heavy metals are well established (particularly as regards As, Ag, Cr, Cu, Cd, Hg, Ni, Pb and Zn where BAT-AEL are adopted). Metals are typically separated by precipitation, flotation, extraction, ion exchange or vacuum distillation, typically after segregation and selective pretreatment of waste water streams from processes where metals are an issue. During biological treatment of waste water, metals can be removed by biomass as a positive side effect either through an active uptake (bioaccumulation) or by passive biosorption. The extent to which metals are removed depends on several factors, for example pH, nature and concentration of biomass and inorganic particles, and the chemical state of the metal ion (oxidation state, complexation). Organometallic compounds may be more difficult to remove from waste waters (this depends on the compounds and the waste water composition). Under unfavourable conditions, the achievable elimination may be lower and/or the treatment more difficult/expensive. The reported emissions concentrations of metals by Concawe refineries in 2022 are listed in **Table 2**.

*Table 2:* Refineries Reported Metals Emissions Values (Concawe Water Survey 2022)

| **Metal** | **Monitoring Values** | | |
|---|---|---|---|
| | **Number of Sources** | **Percentile 5$^{th}$ (mg/l)** | **Percentile 95% (mg/l)** |
| Arsenic | 39 | 0.000549 | 0.011803 |
| Cadmium | 49 | <DL | 0.000866 |
| Chromium | 39 | <DL | 0.011118 |
| Cobalt | 13 | <DL | 0.002258 |
| Copper | 44 | <DL | 0.021 |
| Lead | 48 | <DL | 0.0086 |
| Manganese | 40 | 0.003185 | 0.18613 |
| Mercury | 47 | <DL | 0.01827 |
| Nickel | 46 | 0.000525 | 0.06522 |
| Selenium | 11 | 0.00275 | 0.1378 |
| Vanadium | 36 | <DL | 0.243833 |
| Zinc | 36 | 0.005593 | 0.1299 |

DL - Detection Limit

# 3. INNOVATIVE TECHNOLOGIES FOR INDUSTRIAL WASTE WATERS TREATMENT

## 3.1. INTRODUCTION

The review carried out as part of this report shows that innovative identified abatement techniques are generally limited to waste water treatment techniques (rather than abatement at the source of pollution). Some innovative upstream abatement technique exists, such as techniques to remove dissolved mercury from incoming feedstock, but they are not commonly employed by fuel manufacturing sites as it is not an easy process, and the mercury content of incoming crudes to refineries is generally low (less than 10 ppb, on a month-average basis) as reported in IPIECA's Good Practices Guidelines. The process is typically deployed before the cryogenic distillation. More recently, fuel manufacturing sites have started employing mercury removal beds upstream in the process ahead of acid gas removal and dehydration (thus reducing the risk of fugitive mercury emissions) (UNEP, 2022).

Pre-treatment techniques (i.e., treatment at source) are therefore quite mature. Similarly, techniques related to step 1 (recovery of dispersed oil and solids) and step 2 (removal of dispersed oil and suspended solids) of the WWTP are also mature and no innovative techniques were identified. There are however some examples of innovative techniques that could be used in both pre-treatment and polishing settings, and these are described in this report.

A literature search of technologies applied to refinery effluents specifically, and to industrial waste waters more generally, identified a number of innovative technologies encompassing a variety of modes of action, maturity level and specificity in relation to the substances they can treat. The information obtained from the search was complemented with information provided by Concawe members via a survey questionnaire, and from interviews with specialist WWT vendors. The review also looked at techniques used in other sectors (chemical, fine chemicals, non-ferrous metals, etc) that are not currently in fuel manufacturing sites. Many of these techniques can reduce general organic load (COD, TOC), increase the biodegradability of persistent substances and/or reduce their toxicity, and in occasions reduce concentrations of inorganics at the same time. Others, such as Super Critical Water Oxidation (SCWO) can reduce most organics substances including recalcitrant/persistent ones due to its great oxidative characteristics. The search found most technique can remove several substances at the same time. **Table 3** provides a list of the technologies identified during the search and the main substances targeted by each technique. The techniques have been loosely grouped by their main mode of action to facilitate their description and assessment in later sections.

*Table 3:* Innovative Techniques Identified for the treatment of Selected Substances (substances in red are those selected as part of this study)

| Technology | Targeted Substances |
|---|---|
| **Advanced Oxidation Techniques** | |
| Ultrasonic Reactors | Sulphates, COD, phosphates, heavy metals, phenols, MTBE |
| Photocatalytic Oxidation with TiO2 | General organic substances, BOD/COD removal, biodegradability improvement, specific pollutants (pharmaceutical, pesticides), toxicity reduction, phenols. |
| Supercritical water oxidation (SCWO) | Organic compounds, BTEX, phenols, recalcitrant substances such as PAH, PCBs, dioxins, AOX, etc |
| Wet Air Oxidation | COD, TOC, AOX |
| Wet oxidation with $H_2O_2$ | COD, TOC, phenols, AOX, PAH |
| Photo-Fenton method | COD, TOC, Phenols, BTEX |
| $H_2O_2$/UV | COD, BOD, TPH, MTBE, |
| Ozonation | COD, BOD, improve biodegradability |
| **Electrical/Electrochemical Techniques** | |
| Electrocoagulation/electroflotation | General COD, Suspended Solids, toxic and non-biodegradable substances, heavy metals, phosphates, Cyanides |
| Electrodialysis | Inorganics, TDS, heavy metals, Oil & Grease. |
| Combined Electrochemical Oxidation | Biodegradability improvement, TOC, COD reduction, pesticides and herbicides, VOCs, PFAS, PAH. |
| **Membrane-Based Techniques** | |
| Membrane distillation | Ions, acids, colloids, VOCs, BTEX, phenols |
| Membrane Bioreactor (MBR) | COD, BOD, TSS, TN, BTEX, metals, PAHs |
| Microfiltration + Ultrafiltration | Particulate material and colloids up to 0.1 um (MF) and 0.01 um (UF). |
| Nanofilatration + Reverse Osmosis | Large organic molecules, multivalent ions, dissolved constituents, heavy metals, AOX, Phosphate/Total Phosphorous, phenols |
| **Adsorption Techniques** | |
| Granulated Activated Carbon | COD, metals, phenols |
| Novel adsorption materials (hydrogels, nano adsorbents) | Heavy metals, Phenol, Cyanides |
| Ion Exchange | Heavy metals, some phenols |

| | |
|---|---|
| **Extraction Techniques** | |
| Extraction | Phenols |
| Micro Porous Polymer Extraction | Dissolved/dispersed hydrocarbons, BTEX, PAH, Phenols |
| Pertraction | Organic compounds, pesticides, halogenated hydrocarbons, PAHs |
| **Precipitation Techniques** | |
| Chemical Precipitation | Heavy metals |
| Crystallisation (METCLEAN) | Heavy metals, fluoride, phosphate, sulphate |
| **Other** | |
| Evaporation | None identified |
| Naturally improved microorganisms | Refractory TOC/COD |
| Falling film contactor | Hydrocarbons |
| ABMET | Selenium, BOD, TSS |

**Table 4** uses the information included in **Table 3** but looks at the various techniques that can be used to treat each of the target substances.

***Table 4:*** Applicable Technique per Selected Substance

| Substance | Technique | | Substance | Technique |
|---|---|---|---|---|
| **Phenol Index** | Ultrasonic Reactors | | **AOX** | SCWO |
| | Photocatalytic Oxidation | | | Wet Oxidation w/$H^2O^2$ |
| | Photo-Fenton | | | Wet Air Oxidation |
| | SCWO | | | NF + RO |
| | Wet Oxidation | | **Total Phosphorous** | Ultrasonic reactors |
| | NF + RO | | | Electrocoagulation |
| | GAC and advanced adsorption materials | | | NF + RO |
| | Ion Exchange | | | Crystallisation |
| | Extraction | | **Total Cyanides** | Electrocoagulation |
| | MPPE | | | Bio/Nano adsorbents |
| | Membrane distillation | | **Metals** | Ultrasonic Reactors |

| Substance | Technique | | Substance | Technique |
|---|---|---|---|---|
| **BTEX** | SCWO | | | Electrodialysis |
| | Membrane Distillation | | | Electrocoagulation |
| | MPPE | | | Bio/nano-adsorbents |
| | Electrocoagulation | | | GAC |
| | Wet Air Oxidation | | | MBR |
| **PAH** | Combined Electrochemical Oxidation | | | NF + RO |
| | SCWO | | | Ion Exchange |
| | MPPE | | | Chemical precipitation |
| | MBR | | | Crystallisation |
| | Pertraction | | | ABMET (Se) |

The following Section provides a general description of the technologies included in **Table 3**. More detailed descriptions of each technique listed about can be found in Annex A.

## 3.2. GENERAL DESCRIPTION OF IDENTIFIED INNOVATIVE TECHNIQUES

A technical summary of the techniques listed in **Table 3** is provided in this Section to gain a general understanding of their main mode of action, their targeted substances and efficiencies and their degree of technical maturity. For convenience, they have been grouped into general categories based on the main mode of action. The groupings are not strict, and other groupings are possible since some of these technologies use a combination/integration of different techniques whose efficiencies are based on their combined action.

### 3.2.1. Advanced Oxidation Techniques

Advanced Oxidation Processes (AOPs) are the methods based on the creation of hydroxyl radicals (•OH) by various methods. The hydroxyl radical has great oxidation potential (E0 = 2.8 V) and reacts with almost all types of organic compounds, leading to their full mineralization resulting in carbon dioxide ($CO_2$), inorganic salts, and water, or their transformation into less toxic or persistent substances. Hydroxyl radicals have a higher oxidation potential than substances such as $KMnO_4$ (potassium permanganate) or $H_2O_2$ (hydrogen peroxide). The produced hydroxyl radicals can remove the organic chemicals in different ways such as radical addition, hydrogen extraction, or electron transmission. The creation of hydroxyl radicals is generally enhanced by merging oxidants such as $O_3$ (ozone) and $H_2O_2$, catalysts such as $TiO_2$ (titanium oxide), UV (ultraviolet) radiation, ultrasound, and electricity.

Advanced oxidation methods are highly efficient techniques for the treatment of several waste water types, including waste waters from the oil and gas industry, and are capable of treating a wide range of organic substances, inorganic substances and metals. Of the techniques listed in Table 3 under Advanced Oxidation Techniques, Super Critical Water Oxidation (SCWO), Photocatalytic Oxidation and Ultrasonic Reactors have been identified as emerging techniques in the CWW BREF 2016.

**Supercritical Water Oxidation (SCWO)** is a technique where waste water is brought to the supercritical region of water, i.e. temperatures over 374°C and pressures above 22.1 MPa. Under these conditions water becomes a fluid with unique properties that can be used to advantage in the complete mineralization of organic substances into carbon dioxide ($CO_2$), water and nitrogen. The process causes salts to precipitate out of solution, meaning they can be treated using conventional methods for solid-waste residuals and oxidises metals to their highest oxidation state while destroying all volatile solids. Given its great oxidation potential, this technique can be used to treat any organic substances.

**Wet Air Oxidation** involves the reaction of oxygen in the aqueous phase under high pressure and temperature, to increase the solubility of oxygen in water (CWW). It is a treatment technique identified in the CWW BREF. The reaction often takes place in the presence of catalysts. Reaction products are dependent on the waste water content and can include carbon monoxide and carbon dioxide from organic content; nitrogen from ammonia/ammonium and organics which contain nitrogen; nitrates from nitrite and organics which contain nitrogen; hydrogen chloride from chlorinated organic compounds; sulphate from sulphides and sulphites; and phosphate from compounds which contain phosphorus.

There are two types of water air oxidation processes: low-pressure (0.5-2 MPa and 30ºC to 200ºC) and high-pressure water air oxidation (>2 MPa and 150ºC to 340ºC). The equipment necessary for wet air oxidation is similar to that used in SCWO and include the reactor vessel, high pressure for waste water and sludge movement, compressor for air/oxygen supply, gas/liquid separator, exchanger with preheating capability and pressure reducing valves. As per SCWO, the material specification requirements are high given the high pressures and temperatures involved, requiring enamelled parts or PTFE lining, and metals parts may be of titanium or its alloys.

Wet air oxidation is used to treat refractory organic contents and/or inhibitors to subsequent biological treatment. Thus, the performance of the system is not assessed by looking just at the efficiency of the oxidation process, but also by taking into account the efficiency of the subsequent biological process. Therefore, wet air oxidation can be used upstream the biological treatment or downstream of the biological system as a polishing step to remove remaining harmful substances. Its application is recommended for waste waters with COD concentrations of between 5000 mg/l to 50,000 mg/l.

**Photocatalytic Oxidation** is a low-temperature system based on photocatalysis that can degrade a range of organic compounds as well as destroy microorganisms in aqueous effluents. With the suspended catalyst type, waste water and a catalyst are passed as a thin slurry film over a series of plates and exposed to UVA light. With an immobilised catalyst type, the catalyst is coated on an inert substrate. This type is simpler to operate and has, in general, a lower destruction efficiency than the former, but reduces the need for a recovery plant. The technique can be used on either a batch or continuous flow mode. If further treatment of the effluent is needed the system can be operated in a loop. Photocatalytic Oxidation can be applied to industrial waste waters for general organic pollutant destruction; specific pollutant degradation such as pharmaceutical- or pesticide-contaminated waters; toxicity reduction; biodegradability improvement; general BOD/COD removal and odour and colour improvement. No data on efficiency for the above elements was found. A removal efficiency of 99% has been reported for Phenols. (Elmobarak et al 2021).

**Ultrasonic Reactor** was identified as an Innovative technique in the CWW BREF for the treatment of sulphate-rich waste waters where after treatment with aluminium oxide under acidic conditions and the pH neutralise with lime slurry or liquid lime. The effluent is then passed through an ultrasonic reactor at a controlled rate where sulphate can precipitate as calcium aluminium sulphate oxide in a very fine precipitate. The process follows with clarification where sludge is removed and treated in a filter press and can then be disposed of or reused/recycled. As stated in the CWW BREF 2016, this technique is also able to remove phosphates, heavy metals and results in general COD reduction. The acoustic cavitation created in the reactor causes water molecules and dissolved oxygen to split into •OH and O2- •. Thus, organic pollutants can break down and inorganic pollutants can oxidise in this reactive environment. Typical ultrasonic systems consist of a generator, one or more transducers, a booster, an emitter and the reactor vessel. The reactor’s configuration has an essential role regarding the cavitation activity and are designed to reduce dead zones and increase active cavitation zones.

AOPs such as **photo-Fenton, hydrogen peroxide ($H_2O_2$)** and **ozone** have been proposed as tertiary treatments for urban effluents due to their ability to detoxify wastewater streams containing persistent contaminants. Treatment by activated sludge is more efficient and less expensive for removing high concentrations of organic compounds. However, there are some circumstances where these techniques offer some advantages such as a small footprint and the ease in which they can be integrated with other treatment processes. They can be used to remove non-biodegradable substances that persist after biological treatment or used prior to biological treatment to partially degrade toxic and persistent substances and increase their biodegradability that could otherwise be toxic to activated sludge. The removal of contaminants and the inhibition of toxic compounds are some of the major advantages of these AOPs. For example, more conventional techniques such as filtration, adsorption, and flotation do not destroy the pollutants, but they transport them to other mediums (solid residues) which need to be further managed.

**Fenton** is a mixture of hydrogen peroxide (**$H_2O_2$**) and ferric ions. This mixture has great oxidising potency in an acid medium. The standard reaction of the Fenton process leads to breaking of $H_2O_2$ into a hydroxyl ion and a hydroxyl radical, and the oxidation from Fe2+ to Fe3+. The standard pH in Fenton’s reaction observed in several reports is 3. While the Fenton’s reaction has been extensively reviewed and showed to give good results in the treatment of waste waters, its effectiveness increases when UV radiation is applied to the system (Photo-Fenton). The UV irradiation greatly increases the organic contaminants degradation rate of Fenton, which is susceptible to UV emissions with wavelengths over 300 nm. Fenton and Photo-Fenton techniques have shown promising results in treating COD and BOD with up to 92% and 90% reported abatement efficiency, respectively. The technology is however shown to be sensitive to the process conditions, particularly the pH of the environment, to operate effectively.

**Hydrogen peroxide ($H_2O_2$)** is a powerful oxidant with a standard reduction potential of 1.77 V that is used to reduce concentrations of organic compounds in waste waters. However, $H_2O_2$ is less effective in treating more persistent substances presenting a low reaction rate. The application of $H_2O_2$ to degrade organic compounds is more efficient when it is performed in combination with other components or sources of energy that are competent at producing hydroxyl radicals ($^{\bullet}OH$), such as UV radiation in wavelengths >300 nm typically achieved using mercury vapor lights. The technique is used to degrade organic compounds in waste waters. Studies have shown using $H_2O_2$ in combination with UV showed a reduction of phenol of 99% with an influent of 100 mg/l and a reduction of COD of 36% and 40% with influents of 350 mg/l and 9000 mg/l respectively When a catalyst $TiO_2$ was used in combination with UV, COD saw a reduction of 93% on an influent of 970 mg/l.

**Wet oxidation** is another oxidation technique based on the Fenton reaction where organic matter is oxidised by hydroxyl radicals formed from the reaction of hydrogen peroxide with a ferrous ion (i.e. Fe2+) catalyst. The reaction is also carried out in an acidic medium but under mild conditions of temperature (100-150°C) and pressure (2-4 bar). The use of a strong oxidant (radical) at higher temperatures and pressures than in the conventional Fenton reaction significantly improves the grade of mineralisation of most organic compounds with short residence times and more efficient usage of hydrogen peroxide.

A typical wet oxidation with hydrogen peroxide plant consists of an acidification tank, heat exchangers, one or more stirred reactors, pH increase to allow subsequent catalyst precipitation, a decanter for solid separation and flocculation and centrifuges of filter presses for sludge dewatering.

The main use of wet oxidation is the reduction of COD and TOC and the increase in the biodegradability of a waste water stream. It is primarily applied to the pesticides and pharmaceutical sectors and specialist chemicals production. An example of a chemical plant using the wet oxidation with hydrogen peroxide technique is Repsol Química in Tarragona, Spain.

The use of **ozone ($O_3$)** has been extensively applied to eliminate undesirable organic pollutants in both purification of drinking water and wastewater treatment. Ozone is a selective oxidant that reacts with electron-rich organic compounds. Hydroxyl radicals ($^{\bullet}OH$) produced from the consumption of ozone is a nonselective oxidant, which quickly reacts with several organic compounds. The ozone oxidation rate in water is improved at a greater pH. The ozone oxidation potential can be improved by adding hydrogen peroxide ($H_2O_2$). In fact, ozonation using $H_2O_2/O_3$ systems was found to be the best AOP method for the disinfection of water. Similarly, the combination of ozone with a catalyst was found to be more efficient for COD and TOC reduction, than ozone oxidation only. The ozone process can also be improved through the decomposition of ozone with direct radiation ($\lambda$ = 254 nm) which produces $H_2O_2$ as a transitional compound which then decomposes to $^{\bullet}OH$ radicals. A study conducted on wastewater from a sewage treatment plant that uses a combination of $O_3$/UV advanced oxidation process showed COD and BOD reductions of 43% and 32% respectively. Derco et al, 2021 showed efficiencies of using ozone 80% to 90% for benzene after 40 min in a waste water containing petrol, and a 81% removal of xylene after 20 minutes. When combined with UV, removal efficiencies for xylenes increased to 96%, with toluene showing a similar removal efficiency.

The techniques described above rely on the formation of hydroxyl radicals, strong oxidants that result in the total mineralisation or partial degradation of organic compounds. **Table 5** provides additional information regarding general advantages and disadvantages of each technique together with a brief description of their commercial availability and treatment capacity. Advantages of these techniques include their efficiency to degrade/remove organic compounds and the fact that they are overall simple to operate with few mobile parts. In the case for SCWO, the potential to generate energy is a particular advantage. Disadvantages include the fact that are mostly cost efficient for low flow effluents given the cost of chemicals increase significantly with increase capacities. In the case of SCWO, salt deposition and corrosion are one of the main issues that caused several plants to stop operation in the past. New designs are been developed to minimise these issues. Ultrasonic reactors still suffer from high energy dissipation rates that reduces overall efficiency.

***Table 5:*** Advantages and Disadvantages of Advanced Oxidation Techniques

| Technique | Advantages | Disadvantages | Maturity/ Applicability |
|---|---|---|---|
| | | | |
| **SCWO** | High destruction efficiency (>99.9%) | High corrosion levels | Commercial operating plants available for range of contaminants. Mostly low-capacity plants although Chematur in Sweden claims a capacity of 3000 l/h. Harlingen WWTP in US treats municipal sludge (50 l/min). Plant design and construction offered by SCFI (trade name AcquaCritox). Not known use on refinery effluents. |
| | Complete solubilisation of organics | Precipitation of salts and fouling | |
| | Oxidation of metals | High energy requirements | |
| | Potential for energy production | High capital and maintenance costs | |
| | Small Footprint | Heat loss | |
| | Do not fall under incineration regulations | Several plants reportedly closed due to design issues | |
| | No odour issues associated with the technique | Low flow (max reported 306 t/d) | |
| | Can generate electricity when COD>100 g/l and volume >3 $m^3$/hr | | |
| | | | |
| **Wet Air Oxidation** | Waste water with relatively high refractory COD concentrations can be treated | Dioxins can be generated | Mainly used for the treatment of spent caustics therefore small capacity (3 $m^3$/hr). Commercial plants operating in India, US, Spain. |
| | Inorganic contaminants can either be eliminated or transferred to less hazardous substances | Due to acidic pH stainless steels is required which makes it inconvenient for effluents containing chlorides. | |
| | Can be combined with other treatments | | |
| | | | |
| **Ultrasonic Reactors** | High efficiency destruction for several substances: phosphates, sulphates, phenols, heavy metals. | High investment cost | Used commercially for the treatment of sewage sludge. Installed at Rimex UK for the treatment of heavy metals. Capacity of 40 $m^3$/h reported. Can be higher by adding more reactors. Not |
| | Filter cake produced is non-hazardous. Can be reused in cement | Precipitate slow to settle requiring additional tank/clarifier | |

| Technique | Advantages | Disadvantages | Maturity/ Applicability |
|---|---|---|---|
| | industry or as waste stabilizer | | known use on refinery effluents |
| | Higher efficiency in combination with other AOPs | High dissipation rate reduces efficiency. | |
| | | | |
| **Photocatalytic Oxidation** | No chemicals consumed | Applicable to small scale specialist treatment | No known commercial application at industrial scale. |
| | General organic pollutant destruction | Need to remove catalyst after treatment when using a suspended catalyst type | |
| | Continue or batch mode. Can potentially be scaled up from l/d to $m^3$/d. | Can coagulate and loose activity (for slurry type) | |
| | Simple, few moving parts | High capital cost and operational costs | |
| | | | |
| **Fenton/Photo-Fenton/$H_2O_2$-UV/Ozonation** | Can reduce waste water with high refractory COD concentrations of g/l to less than 1 ug/l. | High energy consumption: ozone generation, UV generation, | Typically applied to low volume effluents. An ozonation plant is part of a reuse water stream with capacity of 2500 $m^3$/h at a refinery in China. |
| | Can cope with large fluctuations in incoming concentrations | High feed quality demands | |
| | Small residence time and thus small tank volume | Generally high cost per unit removal | |
| | Process can be combined with any others to achieve optimum results (GAC adsorption, stripping, activated sludge) | Due to acidic pH stainless steels is required which makes it inconvenient for effluents containing chlorides. | |
| | | | |
| **Wet Oxidation with $H_2O_2$** | Can treat refractory organics from 2g/l to 100 g/l | pH and flocculation required | Applied to various chemical petrochemical processes |
| | $H_2O_2$ is safe to use | Sludge generation | |
| | Short residence time requiring small vessels. | Due to acidic pH stainless steels is required which makes it inconvenient for effluents containing chlorides. | |
| | Easy to integrate | | |
| | Solid waste is inert salts | | |

**Table 6** provides a summary of removal efficiencies as reported in the literature.

***Table 6:*** Advanced Oxidation Techniques Efficiencies and Point of Treatment.

| **Technique** | **Reported Efficiencies** | **Point of Treatment** |
|---|---|---|
| Ultrasonic Reactors | Phenol 99%<br>Total phosphorous 99.9%<br>Sulphate 99.7%<br>COD 55%<br>Heavy Metals up to 99.7%<br>MTBE 98% | End or Pipe<br>Pre-treatment for sewage sludge |
| | | |
| Photocatalytic Oxidation | Phenols 99%<br>MTBE 98% | Prior to biological treatment to reduce toxicity and increase biodegradability.<br>End of Pipe for polishing small volume effluents. |
| | | |
| SCWO | Phenol likely >99.9%<br>PAH likely >99.9%<br>AOX likely >99.9% | End of pipe/in combination with other treatment.<br>Removing toxic COD/AOX prior to biological treatment. |
| | | |
| Wet Air Oxidation | COD 77%-99%<br>TOC 12%-95%<br>AOX 80%,<br>AOX 60% to 90% | At source to treat spent caustics.<br>Prior to biological treatment to reduce COC and refractory substances. |
| | | |
| Wet Oxidation with $H_2O_2$ | Phenols 99.8%<br>Toluene 98.5% | On its own to treat refractory compounds or as a pretreatment to relieve biological treatment. |
| | | |
| Fenton/Photo-Fenton | Phenol 95%-99% | Prior to biological treatment to reduce toxicity and increase biodegradability.<br>End of Pipe for polishing small volume effluents. |
| | | |
| $H_2O_2$/UV | Phenol 99% | Prior to biological treatment to reduce toxicity and increase biodegradability.<br>End of Pipe for polishing small volume effluents. |
| | | |
| Ozonation | Benzene 80%-90%<br>Toluene 95%<br>Xylene 95%-96% | Primarily end of pipe. In real case example is used as part of a reuse water configuration involving membranes and biological treatment. |

### 3.2.2. Electrical/ Electrochemical Techniques

The electrolytic treatment of wastewater presents an innovative technology in which a sacrificial metal anode and cathode produce electrically active coagulants and tiny bubbles of hydrogen and oxygen in water. It includes a variety of techniques based on electrochemical technology, such as electrocoagulation, electroflotation, electrodialysis and combined electro oxidation. Although electrodialysis uses a combination of electrolysis and membrane technology it has been included in this section giving the importance of electrolysis in the technique. Electrolysis literally means “to break substances apart” by using electricity. The process occurs in an electrolyte, a watery or a salt solution that makes possible the transfer of ions between two electrodes. When an electrical current is applied, the positive ions move to the cathode while the negative ions move to the anode. At the electrodes, the cations are reduced and the anions are oxidized.

**Electrocoagulation (EC)** is a technology that involves the release of a coagulant by the electrolytic dissolution of metal ions from metal electrodes following application of an electric current, resulting in simultaneous formation of hydroxyl ions and hydrogen gas production. The coagulants aggregate and precipitate suspended solids with a simultaneous adsorption of dissolved pollutants (Cerqueira et al. 2012), which can be filtered as a precipitate or skimmed as a float in the case of **electroflotation**. Small bubbles of hydrogen and oxygen gas that are released from the electrodes collide with air bubbles causing pollutant particles to float. The process does not require any chemicals addition (except for pH control) and can tolerate a broad range of pollutants and fluctuation in influent quality. Electrocoagulation has been used to treat organic and suspended solids from a variety of industrial waste waters. The technology reduces COD, oil and grease (O&G) and suspended solids with high removal efficiencies for COD, BOD, TPH and O&G. High removal efficiencies have been reported also for specific organic substances such as phenols, phosphate, free cyanide, BTEX and metals.

Electrocoagulation can be used on its own or in combination with other techniques. Laboratory tests on refinery effluents tend to place the technique after the API and before biological treatment. Examples of small scale commercial applications include the treatment of produced water from oilfields, the treatment of liquid waste from the decommissioning of a petrochemical facility and the treatment of runoff from a fracking operation. One manufacturer in the US claimed they have scaled up the technique to 15,000 $m^3$/d. Electrocoagulation produces less sludge than conventional chemical coagulation. Some reports claimed it is cheaper too but the replacing of electrodes is a main operating cost.

**Electrodialysis** is a type of electro-membrane technology that separate ions by selective transport of a fluid through ion-exchange membranes under the influence of an electric field. In particular, electrodialysis produces two streams of different concentrations flowing in alternate compartments separated by cation and anion exchange membranes. In this way, when an electrical current is applied to the cell, positively charged cations in the waste water migrate towards the cathode through the cation exchange membranes, and are rejected by the Anion exchange membranes, and vice versa. This results in the generation of diluted and concentrated solutions between the membranes. Electrodialysis processes are different from distillation techniques and other membrane-based processes (such as reverse osmosis) in that dissolved species are moved away from the feed stream, whereas other processes move away the water from the remaining substances allowing the process to be scaled up to high treatment volumes. Electrodialysis is mainly applicable for the removal of inorganic minerals, dissolved solids (TDS), and heavy metals for which high removal efficiencies are reported. Consequently, electrodialysis is mainly used to desalinate brackish water and it holds 4% of the market share in the desalination industry. It is generally cheaper than RO but for lower TDS effluents (<3000 ppm). Fouling of the membrane together with electricity consumption are the main operational costs. It can achieve treatment capacities of up to 20,000 $m^3$/day.

**Combined Electrochemical Oxidation** is a technique identified as an emerging technique in the CWW BREF 2016. The electrochemical processes can be classified into two main groups: direct electrolysis and indirect electrolysis. Direct electrolysis (also called ‘anodic oxidation’, ‘direct oxidation’ or ‘electrochemical incineration’) is where a pollutant reacts at the anode surface with adsorbed hydroxyl radicals. Indirect electrolysis is where the pollutant reacts in the solution with an electro generated reagent produced at the anode (e.g., $O_3$, ClO-, $Cl_2$, $ClO_2$) or at the cathode (e.g. $H_2O_2$). Combined electrochemical oxidation processes, integrate electrochemical, photochemical and catalytic oxidation to achieve optimal results in the degradation of toxic and non-biodegradable organic substances. The objective of these combined electrochemical oxidation processes is the creation of hydroxyl radicals, the ultimate cause of oxidation of the organic matter present in the waste water. Identification of the most suitable electrode materials generally necessitates carrying out specific tests adapted to the nature of the waste water that has to be treated. The technique is reported to be applicable to treat waste water loaded with persistent organic pollutants such as pesticides and herbicides; polycyclic aromatic hydrocarbons (PAHs); volatile organic compounds (VOCs) and chelating agents. No efficiency data has been found for this technique.

Combined electrochemical oxidation has been applied to pharmaceutical waste waters, dye-stuff effluents and for disinfection and odour control in municipal waste water treatment plants. The CWW BREF mentions two municipal plants in Europe using the technique.

**Table 7** presents a list of advantages and disadvantages for these techniques together with some information on their commercial availability and potential treatment capacities. **Table 8** provides removal efficiencies and comments on their potential use in relation to overall treatment plants configurations.

***Table 7:*** Advantages and Disadvantages of Electrical/Electrochemical Techniques.

| Technique | Advantages | Disadvantages | Maturity/Applicability |
|---|---|---|---|
| Electrocoagulation/ Electroflotation | Energy efficiency | High capital and maintenance costs | |
| | Selectivity | Low rates of flow | |
| | Can be automated | Fouling of electrodes | |
| | No chemicals needed (apart from pH control) | | |
| | High removal efficiencies | | |
| | Short treatment time and less sludge production when compared with chemical coagulation | | |

| Technique | Advantages | Disadvantages | Maturity/Applicability |
|---|---|---|---|
|  | Claims of 88% less costly than chemical coagulation |  | Most information found comes from laboratory and pilot scale trials. However, commercial plants are being offered by a few companies in Europe and US. Examples of small scale plants used to treat run off from fracking, waters from decommissioning of chemical plant, produced water onshore wells One company in Europe claims treatment capacities of up to 24,000 m3/d. Another company in the US also claims it can be scaled up to 2,500 gpm (16,000 m$^3$/day) although no examples of operational cases were found. |
|  |  |  |  |
| Electrodialysis | High efficiency metal removal on single metal effluents | Less efficiency when combination of metals are present | Mature technology used in desalination. Many companies manufacture ED equipment. Not known application in a refinery context. |
|  | Simple to operate and maintain | Electrodialysis needs to be operated below the current density limit to be energy efficient |  |
|  | Longer membrane lifespan than RO |  |  |
|  | Better than RO on lower salinity (<5g/l) waters |  |  |
|  | Better water recovery |  |  |
|  | Better than RO in the presence of oil, and organic substances |  |  |
|  |  |  |  |
| Combined Electrochemical Oxidation | Increased biodegradability of organic compounds | Electrode fouling | It is being used in municipal treatment plants in Europe. Unknown capacity. Not known application in a refinery context. Potentially used ahead of biological treatment to increase the biodegradability of persistent substances. |
|  | Total mineralisation of organic compounds | Applied to low volume wastewaters |  |
|  | Safe operation (operates at low |  |  |

| Technique | Advantages | Disadvantages | Maturity/Applicability |
|---|---|---|---|
| | pressures and temperatures | | |
| | Low energy consumption | | |
| | Generally safe operation. Compared to techniques such as chemical oxidation, there is no transportation and storage of dangerous reactants (e.g. chlorine dioxide) | | |

*Table 8:* Electrical/Electrochemical Techniques Efficiencies and Point of Treatment

| Technique | Reported Efficiencies | Point of Treatment |
|---|---|---|
| Electrocoagulation/ Electroflotation | Reduces COD, O&G and heavy metals.<br>As reported by Nutechnology: As (97%), Cd (96.8%), Cr (99.9%), Co (82.7%), Cu (99.75%), Pb(99.96%), Mn(98.27%), Hg(98.45%), Ni (99.96%), Se (44%), V (99.24%).<br>The technology also claims Phosphate (99.3%), Toluene (99.9%),<br>xylenes (99.96%), Ethylbenzene (99.86%), free CN (99.99%). | Can be used on its own or in combination with other techniques.<br>End of pipe/post treatment polishing.<br>Also as pre-treatment to reduce COD prior to biological treatment and after primary treatment. |
| | | |
| Electrodialysis | Different efficiencies for different metals (75-99%). High efficiencies on single metal effluents. Less so in multiple metals effluents.<br>In single metal effluents:<br>Ni 90-95%<br>Cu>97%<br>Cr 79-99%<br>Cd max 86%<br>Pb 82-95% | Potentially end of pipe, polishing. |
| | | |
| Combined Electrochemical Oxidation | None found | Unknown in the context of refinery operations |

### 3.2.3. Membrane Techniques

This Section covers treatment techniques that are based on the presence of a membrane which acts as a barrier to separate two phases from each other, thereby restricting movement of components through it in a selective way. The techniques identified in this study include Membrane Distillation (MD), Membrane Bioreactors (MBR), micro and ultrafiltration (MF and UF) and nanofiltration (NF) and reverse osmosis (RO).

**Membrane distillation** was identified as an emerging technique in the CWW BREF 2016. Membrane Distillation (MD) is a hybrid thermal-membrane process driven by the vapor pressure differential across the hot and cold sides of a hydrophobic membrane resulting in the passage of water vapor through the membrane, followed by condensation to produce distilled water. The liquid feed to be treated by MD must be in direct contact with one side of the membrane and does not penetrate the dry pores of the membranes due to their hydrophobic nature. In MD, the membrane itself acts only as a barrier to hold the liquid/vapour interfaces at the entrance of the pores and it is not necessary to be selective as required in other membrane processes. The main requirements for the MD process are that the membrane must not be wetted and only vapour and non-condensable gases must be present within its pores. The pore size of the membranes used in MD lies between 10 nm and 1 µm. There are different MD configurations based on how the membrane is kept separate from the liquid feed, via an air gap, a colder aqueous solution, a cold inert gas or where vacuum is applied in the permeate side.

The advantage of the MD process in comparison to the conventional separation processes is that it relies on a lower operating temperature (much lower than boiling point) and near atmospheric pressures. In contrast to pressure-based membrane processes, MD in principle does not require additives like acids or anti-scalants because the membranes are a lot less sensitive to pollution.

**Membrane bioreactors (MBRs)** combine biological processes and membrane filtration to achieve better treated effluent quality by exploiting the dual benefits of membrane separation and activated sludge processes (ASPs). The MBR process is an alternative to conventional activated sludge processes for biological waste water treatment and is BAT in the CWW BREF. It consists of the combination of a membrane process (e.g. microfiltration or ultrafiltration) with a suspended growth bioreactor. In an MBR system for biological waste water treatment, the secondary clarifier and the tertiary filtration step of a traditional aerated sludge system is replaced by membrane filtration. Typical arrangements consist of vacuum-driven membrane units submerged in the aerated portion of the bioreactor or pressure-driven membrane systems located outside the bioreactor. Membranes are typically configured with hollow tube fibres or flat panels and have pore sizes ranging from 0.1 to 0.4 microns. MBRs are applied to a wide range of industrial and domestic waste waters with high organic loads to reduce COD, BOD and SS for which reported removal efficiencies are high.

**Microfiltration (MF) and ultrafiltration (UF)** are membrane processes that retain certain substances contained in waste waters on one side of the membrane. The liquid that permeates through the membrane is referred to as the permeate. The liquid that is retained is referred to as the concentrate. The driving force of the process is the pressure difference across the membrane. Membranes used for MF and UF are 'pore-type' membranes which operate like sieves. The solvent and particles of molecular size can pass through the pores, whereas suspended particles, colloidal particles, bacteria, viruses, and even larger macromolecules are held back. Microfiltration (MF) and ultrafiltration (UF) use hydrophobic membranes to remove particulate material and colloids to sizes up to 0.1 µm (MF) and 0.01 µm (UF). These membranes cannot remove dissolved salts and metals but produce a clarified effluent that can be used for certain uses (utility water of firefighting water in the refinery context). Membrane materials include glass fibre, polycarbonate, polyvinylidene fluoride, cellulose acetate and polyamide for microfiltration and polymers such as cellulose acetate, polyamide, polyimide, polycarbonate, polyvinylchloride, and others for ultrafiltration.

Hydrophobic membranes are susceptible to fouling in the presence of oil and hydrocarbons and for this reason granulated activated carbon filters are typically used to remove dissolved organic compounds prior to filtration. Ceramic membranes are now widely available and are more suitable for effluents containing oil. Microfiltration (MF) and/or ultrafiltration (UF) are typically used to remove suspended solids as pre-treatment for nanofiltration and reverse osmosis in tertiary treatment for the purposes of water reuse.

**Nanofiltration and reverse osmosis** are membrane processes where the permeation of a liquid through a membrane, is separated into a permeate that passes through the membrane and a concentrate that is retained, due to the pressure difference across the membrane. These membranes can hold particles down to the size of organic molecules and even ions. Reverse osmosis treatment systems are composed of polyamide membranes with pore sizes of less than 0.001 µm and they have a high salt rejection of 99%. They allow water to pass through and retain the solute (e.g. salts, metal ions and certain organics). They are more susceptible to fouling by the presence of hydrocarbons and therefore oil and grease concentrations limits are typically less than 1 mg/l, although concentrations in the ug/l range is known to have caused fouling problems.

Nanofiltration uses membranes of similar size as those in reverse osmosis and is used to remove selected organic compounds and for general softening. It has a lower salt rejection rate than reverse osmosis and therefore the operating pressure of nanofiltration is lower than reverse osmosis. NF membranes allow water, single valence ions (e.g. fluorides, sodium and potassium chloride) and nitrates to pass through, while retaining multiple valence ions (e.g. sulphate and phosphates). Provided that the feed is particle-free, these membranes are mainly used when complete recycling of permeate and/or concentrate is desired.

NF and RO are often used in combination with post-treatment techniques for the permeate, such as ion exchange or GAC adsorption.

The techniques described above are based on membrane technology but present quite different operational designs, are at different stages of development and are targeted at different types of industrial waste waters and at distillation of brackish water (desalination). Membrane distillation is still at a pilot (laboratory and field) stage and it is targeted primarily at desalination and treatment of metals, it is not operational at full scale yet and there are no known application to refinery effluents. MPPE is more advanced with small scale plants already in operations to treat a variety of effluents with oil and organic substances and have demonstrated high efficiencies with target substances BTEX and PAHs. Finally, MBR are well developed as an alternative to biological treatment in chemical and pharmaceutical industries and also in refineries

**Table 9** summarises the main advantages and disadvantages of these techniques, while **Table 10** presents reported removal efficiencies and role in wwt plants.

*Table 9:* Advantages and Disadvantages of Membrane-Based Techniques

| Technique | Advantages | Disadvantages | Maturity/Applicability |
|---|---|---|---|
| Membrane Distillation | Safe operation due to low pressure and temperature. | Relatively low permeate flux in comparison with pressure-based membrane processes such as RO. | Many laboratories and several small-scale pilots have been carried out. Focused on sea water desalination and metals treatment. Offers potential for water purification in the pharmaceutical, chemical and textile industries. Various MD vendors are at different stages of technology development with Aquastill, Scarab, Aquatech, KMX Technologies, and Memsift Innovations currently lead the commercial market. |
| | Do not require additives like acids or antiscalants as membranes are less sensitive to membrane pollution. | Membrane fouling and total or partial pore wetting.<br>High thermal energy consumption. | |
| | Lower capital and operational costs compared to pressure-driven membranes (UF, RO) | | |
| | | | |
| Membrane Bioreactor | Reduced amount of sludge (compared to conventional activated sludge system) | High running costs (energy) because of the high pressure drop and high air-flushing rate required for its operation | Several commercial plants in operation in Europe in the chemical and pharmaceutical industries with high treatment capacities in the thousands of $m^3$ per day.<br>Bioreactors are currently used in refineries (e.g. by Petrobras in Brazil). |
| | Good efficiency with inlet COD variations for medium to high COD loading (3 to 30 g/l) | Membranes are sensitive to abrasion | |
| | Contrary to a conventional clarifier, the MBR system may act as a physical barrier in upset conditions | Silicones in the influent can rapidly plug the membranes | |
| | Can operate at much higher solids concentrations (typically 8,000-12,000 mg/l) compared to the conventional | Pressure variations must be controlled as membranes are quite sensitive and can break | |

| Technique | Advantages | Disadvantages | Maturity/Applicability |
|---|---|---|---|
|  | activated sludge system (typically 3,000-6,000 mg/l) |  |  |
|  |  |  |  |
| Microfiltration and Ultrafiltration | High separation efficiency | Clogging and fouling of the membranes | Microfiltration and ultrafiltration are well developed techniques used in a variety of sectors such as the food industry (cheese, milk, juices, wine, beer), the metal industry, the textile industry, and the pharmaceutical industry. |
|  | Modular systems | High operating pressure and high pumping demand |  |
|  |  | No mechanical stability |  |
|  |  |  |  |
| Nanofiltration and Reverse Osmosis | High separation efficiency | Clogging and fouling of the membranes | Nanofiltration and reverse osmosis are well established technologies for desalination (RO) and in the chemical industry. |
|  | Modular system | High pressures required. |  |
|  | Recycling of permeate and concentrate is possible | Low permeate fluxes |  |
|  | Low operating temperatures |  |  |
|  | Possibility of fully automatic operation |  |  |

***Table 10:*** Membrane Based Techniques' Efficiencies and Point of Treatment

| Technique | Reported Efficiencies | Point of Treatment |
|---|---|---|
| Membrane Distillation | The technique has been reported to offer capability for the removal of metals from an effluent from a nano-electronics industry where it showed silicon, aluminium, and copper concentrations below their detection limits for the following influent concentrations: silicon (95.16 mg/L), aluminium (9.9 mg/L) and copper (3.5 mg/L). The removal of toxic metals was also reported although no specific information was found. | Unknown in relation to a refinery context. |
|  |  |  |

| Technique | Reported Efficiencies | Point of Treatment |
|---|---|---|
| Membrane Bioreactor | Reported efficiencies for:<br>TOC, COD, TP 95.2%<br>BOD 99.7%<br>TN 88.9%<br><br>Target metals: 33%-.99%<br>Benzene >90%<br>Toluene 65%- >99%<br>Xylene 98%->99%<br>PAH 95%->99%<br>See full list in Annex A | Alternative to activated sludge biological treatment. |
| | | |
| Microfiltration and Ultrafiltration | None reported | Microfiltration (MF) and/or ultrafiltration (UF) are typically used to remove suspended solids as pre-treatment for nanofiltration and reverse osmosis in tertiary treatment for the purposes of water reuse. |
| | | |
| Nanofiltration and Reverse osmosis | Cadmium and mercury >90% | NF and RO can be applied as tertiary treatment for reuse of the treated effluent. |

### 3.2.4. Adsorption Techniques

Adsorption refers to the transfer of gas or liquid molecules into a solid sorbent surface and holding them via physical and/or chemical intermolecular interactions. Adsorbent materials have high porosity and high surface area giving them high adsorption capacity. Adsorbents can be natural (e.g., charcoal, clays, minerals such as bentonite and vermiculite, zeolites, and ores) or synthetic (produced from agricultural products and wastes, industrial or urban wastes, sewage sludge, metal oxides, and polymeric adsorbents). Adsorption has been effective in removing dyes, organic pollutants and metals from various industrial wastewater effluents (Ahmed 2022). Biosorption involves concentrating pollutants, particularly heavy metals, with the help of biomass sources such as peanut and hazelnut shells, green algae, orange peel and maize cob or husk, or their chemical modification or thermal conversion to activated carbon.

The number of possible natural or synthetic adsorbents is too great to cover in this report and only a few are described here to provide an overall perspective of their functionality and potential for the treatment of refinery waste waters. The technique selected include Granulated Activated Carbon (GAC), as a benchmark given their wide use in many applications from polishing treated waste waters to remediation of contaminated groundwaters (GAC is considered a conventional technique). Mention is also made of some innovative techniques such as nano-adsorbents, hydrogels and graphene.

For some decades, **activated carbon (AC)** has been employed widely in the gas and water purification industries and extensively used in petroleum refineries and petrochemical processing. Removal of oils, greases, and suspended solids is implemented in the primary step treatment. Activated sludge can assist with the biodegradation of dissolved organic compounds in secondary treatment, while highly refractory substances may require additional tertiary treatment by a variety of techniques including adsorption by GAC. As an adsorbent, activated carbon serves also as a polishing step for biological treatment and pretreatment for membrane units such as RO. As a growth medium, it lends its solid surface to the oil-degrading microbes for growth purposes. By its versatile nature, AC can be easily integrated into other treatment processes, such as carbon-enhanced membrane bioreactors, biofilm reactors and fixed-film activated sludge process (Amakiri et al 2022).

AC can be used to remove organics such as pesticides, phenols, pharmaceuticals, organic halogens, non-biodegradable compounds, dyes, and metals such as $Hg^{2+}$, $Pb^{2+}$, Cd2+, $Cu^{2+}$, and $Ni^{2+}$ (Ahmed 2022). A high adsorption efficiency of 90% was reported for AOX substances.

Adsorption on natural materials such as **zeolites** has been gaining more interest. For example, Clinoptilolite, a type of zeolite, has shown high selectivity to $Pb^{2+}$, $Cd^{2+}$, $Zn^{2+}$, and $Cu^{2+}$. Natural **phosphates (NP)** constitute another category of raw adsorbents. NPs are abundant, cheap, and they are non-hazardous to the environment. Phosphates can be used for heavy metals removal. NPs have also been used to remove emerging and persistent organic contaminants.

**Industrial by-products** such as carbonaceous wastes, agricultural by-products, mineral-derived sources, etc. can be used as low-cost adsorbents for industrial wastewater treatment. For example, steelmaking slag has showed adsorption capacities of up to 99.1%. Other examples of low-cost industrial by-product adsorbents are fly ashes, waste Fe, hydrous $TiO_2$, and other waste products which can be fine-tuned chemically to enhance pollutant removal.

Large numbers of studies have been focussed to develop highly efficient **nano-adsorbents** to remove heavy metals from wastewater with high performance and lower cost. Graphene, activated carbon and carbon nanotubes have been the most common and commercially studied adsorbents.

**Hydrogels** are another innovative adsorption technique made up of a three-dimensional (3D) network of hydrophilic polymers that maintain their structure by the physical and chemical linking between the individual chains. Along with heavy metals removal, hydrogels have been used for medicine and biomedical engineering.

**Ion exchange** is the reversible interchange of ions between a solid (ion exchange resin) and a liquid. Ion exchange resins are made from insoluble polymers and are typically bead-shaped. Ion exchange removes undesired or hazardous ionic constituents of waste water and replace them by more acceptable ions from an ion exchange resin, where they are temporarily retained and afterwards released into a regeneration or backwashing liquid.

Along with absorption, ion exchange is a form of sorption. Ion exchange is a reversible process, and the ion exchanger can be regenerated or loaded with desirable ions by washing with an excess of these ions. Typical ion exchangers are ion-exchange resins, zeolites, montmorillonite, clay and soil humus. Ion exchangers are either cation exchangers, which exchange positively charged ions (cations), or anion exchangers, which exchange negatively charged ions (anions). Ion exchange equipment typically consists of a vertical cylindrical pressure vessel with a corrosion-resistant lining that contains the resin, usually as a packed column with several possible configurations. Control valves and a piping system direct the flow of waste water and regeneration solution to the proper locations. Finally, a system that regenerates the resin, consists of salt-dissolving and dilution control equipment.

**Table 11** provides advantages and disadvantages of the use of Activated Carbon as and ion exchange techniques. Innovative adsorption techniques reviewed as part of this report are mostly at research stage and not much information on the operation of these alternatives have been found. Table 12 includes removal efficiencies for the adsorption techniques discussed above. Further information is included in Annex A.

***Table 11:*** Advantages and Disadvantages of Activated Carbon (Adsorption Technique).

| Technique | Advantages | Disadvantages | Maturity/Applicability |
|---|---|---|---|
| | | | |
| Activated Carbon | High removal efficiency | Clogging and blockage due to solids in the waste water necessitating upstream filtration | Conventional adsorbent materials such as activated carbon, zeolites and silica have been used for a long time in the treatment of refinery waste water. Non-conventional adsorbents such as industrial, or agricultural by-products, nano-adsorbents and hydrogels are a continued subject of research. |
| | Enables the removal of refractory and/or toxic organic compounds | The efficiency of adsorption processes varies widely with waste water composition and feed concentration | |
| | Usually small footprint | Mixtures of organic compounds may cause significantly reduced adsorption capacity | |
| | Treatment can be automated | Spent adsorbent has to be regenerated (high energy consumption) or disposed of (causing waste to be incinerated) | |
| | Various applications for pre-treatment, supporting biological treatment and as polishing step. | Scouring effect in the activated sludge unit causing erosion (for PAC -Powdered Activated Carbon) | |
| | | | |
| Ion Exchange | In principle, all ions can be removed from aqueous liquids | Prefiltration is required | Ion exchange is widely used in a variety of sectors including the food and beverage industry, hydrometallurgy, |

| Technique | Advantages | Disadvantages | Maturity/Applicability |
|---|---|---|---|
| | Operates on demand and is insensitive to flow variations | Bacteria growth on the resin surface and fouling caused by precipitation or adsorption | metals finishing, chemical, petrochemical, pharmaceutical technology, potable-water treatment, industrial water treatment, and others.<br>The technology is commercially available and has been tried and tested in industrial applications. |
| | High efficiencies are possible | Interference of competing ions in the waste water | |
| | Possible recovery of valuable species and of water | Attrition of resin particles, due to regeneration or mechanical impacts | |
| | A large variety of specific resins are available | The brine and sludge resulting from regeneration has to be treated or disposed of | |

***Table 12:*** Adsorption Techniques' Efficiencies and Point of Treatment.

| Technique | Reported Efficiencies | Point of Treatment |
|---|---|---|
| Activated Carbon and other adsorbents | For GAC: Metals between 88% and 100% (Hg). COD has a reported efficiency of 50%-75%, Phenols 60%-80% and AOX >90%.<br>Bentonite: metals >99% for Cu, Co, Ni, Zn, and Pb ions.<br>Graphene: Ni 78%, Zn 100%. Most other metals show efficiencies of >90%.<br>Carbon nanotubes present a higher variation in efficiencies with Hg at 25% and Cd at 96%.<br>Rice husks (Cr at 78% and other metals at >96%)<br>Zeolite with average of >90% for most metals, Cd showing the lowest efficiency at 66%. | Adsorption can either be used before biological treatment for removing toxic compounds or be placed after the physico-chemical treatment steps for ensuring the complete removal of micropollutants. |
| | | |
| Ion Exchange | Metals: 80%-99%<br>Phosphate: 99% | The technology is commercially available and has been tried and tested in industrial applications. |

### 3.2.5. Extraction Techniques

**Extraction or solvent extraction** entails the transfer of a soluble substance from the waste water phase into a solvent. Preferably, solvents should have low solubility and miscibility with water such as light crude, toluene, pentane, hexane and should be easily separated from the waste water because of density difference. Also, low toxicity and flammability solvents are preferred. Extraction typically operates in columns where the water is brought into contact with the solvent using various configurations.

Downstream facilities include liquid/liquid separation and distillation of the solvent fraction. The remaining waste water phase normally has to get rid of the dissolved extraction solvent, e.g. by stripping or GAC adsorption. An extraction system also typically includes storage facilities for the extraction solvent and the residue.

Besides the recovery of phenols, extraction has been reported also for the recycling of metals such as zinc, phosphoric acid and esters and chloro-aromatics. Extraction is often used as a pretreatment to adsorption and/or biological treatment units and it is frequently used in the chemical industry, especially in the Large Volume Organic Chemicals and Organic Fine Chemicals sectors.

In the **Micro Porous Polymer Extraction (MPPE)** process, hydrocarbon-contaminated water is passed through a column packed with macro porous polymer particles. The particles are porous polymer beads, which contain a specific extraction liquid immobilized in the pores of the MPPE particle. The immobilized extraction liquid removes the hydrocarbons from the water. Only hydrocarbons that have affinity for the extraction liquid are removed. The purified water is recovered from a separate stream while the hydrocarbons phase is recovered for discharge. MPPE is a compact and robust technology that requires preliminary treatment to function at maximum capacity with no addition of chemicals required (Veolia 2019). Compared to other technologies, MPPE units are compact and have a small footprint. The unit is fully automated. Once installed, the unit can treat higher and lower flows and concentrations with minimum flow reduction. The units present no biological fouling because of periodic in situ regeneration by steam. The technique can be scaled up to treat thousands of $m^3$ per hour.

In **pertraction**, the pollutants are removed from the waste water by absorption into an organic extraction agent or extractant with membranes forming the interface between the waste water and the extractant. Therefore, the extractant is not added directly to the waste water, as in a conventional extraction process. This eliminates the separation phase needed in the solvent extraction technique which is often difficult and time consuming. The flows of waste water and extractant can be adjusted to maximise the contact between the waste water and the extractant.

A pertraction system consists of one or multiple membrane modules that include membranes in a hollow fibre configuration to gain maximum membrane surface per volume. The extraction liquid flows down one side of the membrane with its pores filled with the organic extractant, while the waste water is passed along the other side of the membrane. In this way, the pollutants diffuse from the waste water, through the membrane and to the extractant. The extractant can be regenerated using (amongst other things) a vacuum film vaporiser. It is also possible to reuse the extractant. The choice of extractant depends on the selectivity desired. However, normally this is not required to remove overall organic pollutants.

**Table 13** summarises the main advantages and disadvantages of these techniques, while **Table 14** presents reported removal efficiencies and role in waste water treatment plants.

***Table 13:*** Advantages and Disadvantages of Extraction Techniques.

| Technique | Advantages | Disadvantages | Maturity/Applicability |
|---|---|---|---|
| | | | |
| Extraction | Enables removal and recycling of refractory and or toxic organic compounds and some metals | Residues have to be disposed or incinerated | Extraction is a technique frequently used in the chemical industry, especially in the LVOC and OFC sectors. One example found of an extraction plant removing phenols from wastewaters from a resin manufacturing facility. |
| | | Limited application because of solvent characteristics | |
| | | | |
| Micro Porous Polymer Extraction | No chemicals required | May require pre-treatment to improve efficiency | Commercially used to treat produced water from upstream O&G. Operating plants on LNG and FLNG plants, gas plants, specialty chemicals, pharmaceuticals and groundwater pump and treat. Commercially available. Modular set up can be upscaled to treat thousands of $m^3/h$. |
| | Energy consumption much lower than steam stripping | High installation and maintenance costs reported | |
| | Compact equipment and small footprint | | |
| | No emissions to air | | |
| | No sludge generation | | |
| | | | |
| Pertraction | Use a much lower quantity of extractant. | The Membrane can become polluted if membrane polluting compounds are present | The process has been demonstrated at pilot scale at various installations. A full-scale installation of 15 $m^3/h$ has been operational at an industrial site in the Netherlands since 1998 for the treatment of aromatic compounds with an efficiency of >95%. Commercial plants are available. |
| | Avoids time consuming separation between waste water and extractant | | |
| | Compact design and relatively simple process | | |
| | Low energy consumption | | |

*Table 14:* Extraction Techniques' Efficiencies and Point of Treatment.

| Technique | Reported Efficiencies | Point of Treatment |
|---|---|---|
| Extraction | Phenols: 99% | Extraction is often used as a pretreatment to adsorption and/or biological treatment units. |
| | | |
| Micro Porous Polymer Extraction | PAH 90%<br>BTEX >90%<br>PAH 60%<br>Alkyl Phenols 30% | Unknown in the context of refinery |
| | | |
| Pertraction | >95% for general aromatic organic compounds. With further modules in series >99% is possible (as per pilot test) | Unknown |

### 3.2.6. Precipitation Techniques

**Chemical precipitation** is a chemical reaction that forms particulates (i.e. solid precipitate) that can be separated from the water portion by an additional process, such as sedimentation, air flotation or filtration. It removes colloidal precipitates such as insoluble heavy metal sulphides or hydroxides. The technique can also remove phosphorous. A chemical precipitation facility usually consists of one or two stirred mixing tanks, where the agent causing precipitation (i.e. precipitation chemicals) and possibly other chemicals (e.g. flocculants) are added, a sedimentation tank and storage tanks for the chemical agents.

Typical precipitation chemicals include lime, sodium hydroxide, sodium carbonate and dolomite to precipitate heavy metals; calcium salts (other than lime) to precipitate sulphate or fluoride; and sodium sulphide to precipitate heavy metals such as arsenic, mercury, chromium, cadmium, nickel. Polyorganosulphides are known to be used to precipitate mercury. The precipitation of metals as hydroxides is most commonly used.

The technique requires also the use of flocculants to assist further separation such as ferrous and ferric salts; aluminium sulphate; polymers (cationic, anionic or non-ionic); polyorganosulphides. Chemical precipitation as a pre-treatment technique in combination with coagulation and filtration is BAT in the LVOC BREF to treat copper from the oxychlorination process.

Chemical precipitation can be applied at different stages of the waste water stream, such as directly at the source to remove heavy metals most effectively, as the main technique for the removal of phosphates, sulphate and fluoride, and to remove phosphates after the biological stage in a central WWTP, where the sludge is collected in the final clarifier.

**Crystallisation** (known commercially as METCLEAN) is closely related to precipitation, but instead of a chemical reaction in the waste water a precipitate is produced on seed material such as sand or minerals, working in a fluidised-bed process (a pellet reactor system), and thus involves also an adsorption process. The pellets grow and move towards the reactor bottom. The driving force of the process is the reagent dosage and pH adjustment. The technique consists of the cylindrical reactor with a bottom influent and a top effluent; the seed material such as pellets of filter sand or minerals which are kept in a fluidised-bed condition; and the circulation system with a recirculation pump.

Supersaturation of the salts occur at the bottom of the reactor where with the large crystallisation surface of the fluidised reactor almost all the anion or metal content crystallises on the pellets. This ongoing process results in metal coating around the granules that grows continually, increasing their diameter until eventually they need to be replaced. Thus, the granules become a waste by-product of the process.

In most cases, crystallisation is applied to remove heavy metals from waste water streams and to recover them subsequently for further usage, but fluoride, phosphate and sulphate can also be treated.

**Table 15** summarises the main advantages and disadvantages of these techniques, while **Table 16** presents reported removal efficiencies and role in waste water treatment plants.

***Table 15:*** Advantages and Disadvantages of Precipitation Techniques.

| Technique | Advantages | Disadvantages | Maturity/Applicability |
|---|---|---|---|
| | | | |
| Chemical precipitation | Waste water over a large concentration range can be treated (from some g/l down to less than 1 mg/l) | Significant sludge formation that requires disposal | Chemical precipitation is a well-established technique in the chemical and metals industries with ready availability of equipment and chemicals. Its use has also been reported in the petrochemical industry. |
| | | Gas formation is common; with sulphide, the generation of hydrogen sulphide is possible | |
| | | | |
| Crystallisation | Compact (small footprint) and flexible units, thus enabling modular set-up and tailor-made material selection | Only applicable to ionic constituents forming in soluble or almost insoluble salts | The process has been used to treat waste waters resulting from flue gas desulphurisation (FGD) from coal power plants and solid waste incinerators. It has been tested at pilot scale and implemented at full scale in plants in Denmark, France and US for the removal of heavy metals from FGD wastewaters |
| | No sludge production (reported to produce up to 20 times less waste than in conventional chemical precipitation) | Reagents restricted to non-hazardous substances | |

| Technique | Advantages | Disadvantages | Maturity/Applicability |
|---|---|---|---|
| | Water-free pellets with high purity which enables recycling or further usage of the metal content in other sectors | Total salt content of waste water is not decreased | |

***Table 16:*** Precipitation Techniques' Efficiencies and Point of Treatment.

| Technique | Reported Efficiencies | Point of Treatment |
|---|---|---|
| Chemical Precipitation | Cd: 58% (inflow of 36 ug/l),<br>Cr: 87% (inflow of 390 ug/l),<br>Ni: 95% (inflow of 1070 ug/l) Hg: >87% (inflow 680 ug/l)<br>Cu, Pb and Zn: >87% (inflow over 5000 ug/l for zinc) | Chemical precipitation can be applied at different stages of the waste water stream: directly at the source to remove heavy metals most effectively, as the main technique for the removal of phosphates, sulphate and fluoride, and to remove phosphates after the biological stage. |
| | | |
| Crystallisation | Capability to treat several metals including: Cd, Cr, Hg, Mo, Ni, Se, Zn, Cu, V, Ba and Sr with reported efficiencies as high a 99%. | At source such as for the removal of metals from wastewater from FGD processes or before biological treatment to reduce metals concentrations. |

### 3.2.7. Other Techniques

The **Falling Film Contactor is** described in the LOVC BREF. A falling film contactor increases the mass transfer rate between immiscible liquids (typically a hydrocarbon in a water/aqueous solution) using a vertical cylinder containing metal fibres. When used for waste water treatment, pollutants in the water are transferred into the hydrocarbon phase. The aqueous phase adheres to (wets) the metal fibres and it flows down the length of the fibres by a combination of gravity and interfacial drag between the two immiscible phases. Hydrocarbons also flow through the cylinder concurrently and in between the aqueous-wetted fibres. The large surface area and tight packing of the metal fibres bring the ultra-thin falling films of the aqueous phase into close contact with the hydrocarbon phase. The interfacial surface area produced is an order of magnitude greater than in conventional extraction devices, allowing impurities to easily diffuse between phases. The use of a falling film can improve the efficiency of the subsequent phase separation process.

The main target of this techniques is the removal of volatile hydrocarbons and other organic substances. The technology is stated to have been commercially developed and was subsequently implemented in Petrotel Lukoil Refinery in Romania, although this seems to be associated to the removal of mercaptans from hydrocarbons. However, no further information was available on other examples of implementation or development by the environmental technology providers. There are not known applications to refinery effluents.

**Naturally improved microorganisms** is a technique identified as an emerging technique in the CWW BREF 2016. It consists of the use of naturally improved microorganisms (e.g. prokaryotic cells or bacteria, photosynthetic bacteria or eukaryotes such as yeasts, fungi and photosynthetic microalgae) to treat waste waters loaded with refractory TOC/COD. It requires the selection of naturally-occurring microorganisms; the generation of microbial variants with enhanced characteristics to treat the targeted pollutants in waste waters; and the introduction of the improved microorganisms into the water treatment process. Depending on the characteristics of the waste water being treated at the plant the abatement efficiency can vary from 60% to 98% and 70% to 97% for COD and TOC, respectively. A 92% BOD efficiency was reported for refinery/petrochemical waste waters. These abatement efficiencies are related to pharmaceutical and chemical effluents. The technique is generally applicable to new and existing installations in the industrial or municipal sectors This technique is reported as common practise in optimising the biotreatment step of the water treatment plants of the refinery sector. However, no actual examples have been found.

**Evaporation** of waste water is a distillation process where water is the volatile substance, leaving the concentrate as bottom residue to be disposed of. Its main aim is to reduce the volume of waste water or to concentrate mother liquors. The volatile steam is collected in a condenser and the condensed water is, if needed after subsequent treatment, recycled. As per distillation, operating under vacuum decreases the boiling temperature and enables the recycling of substances that would otherwise decompose. There are many types of evaporators. Their suitability depends on the individual requirements. Evaporators are usually operated in series, where the condensation heat of one stage heats the condensate (i.e. waste water) of the preceding stage. Operation under vacuum minimises energy demand. Evaporation is normally a waste water-free process, because the condensate will be recycled, with or without further treatment, and the concentrate will be recycled or disposed of as waste, e.g. by incineration.

**ABMet** is a waste water treatment that removes nitrate and nitrite to non-detect levels through a biological denitrification process within a biofilter, resulting in the formation and off-gassing of nitrogen gas. The ABMet process also removes selenium by biologically reducing selenate and selenite to particulate elemental selenium which is then removed as waste solids collected near the top of the biofilter from where it flows by gravity to a waste storage tank, pond, or solids handling system. The biofilter contains a seed culture product that consists of specialized bacteria strains selected for treatment of selenium laden waters that are seeded only once.

Waste is typically decanted and supernatant recycled to the head of the system for processing. The effluent tank stores effluent for periodic backwashing of the biofilter for degassing and for the removal of solids, including elemental selenium.

The advantage of the ABMet treatment process is that provides selenium removal in a single step while other biological systems require numerous unit operations to transform selenium from one form to another (selenate to elemental Se) and then rely on other unit operations to remove the elemental selenium along with TSS and organics. With ABMet, selenium is transformed, captured and removed all within the biofilter while keeping TSS and organics below most discharge limits.

**Table 17** summarises the main advantages and disadvantages of these techniques, while **Table 18 p**resents reported removal efficiencies and role in waste water treatment plants.

***Table 17:*** Advantages and Disadvantages of “other” Techniques.

| **Technique** | **Advantages** | **Disadvantages** | **Maturity/Applicability** |
|---|---|---|---|
| | | | |
| Falling Film Contactor | High efficiency in removing VOCs (>90%) | Liquid emissions with extracted VOCs need treatment in WWT | The technology is stated to have been commercially developed and was subsequently implemented in Petrotel Lukoil Refinery in Romania, although this seems to be associated to the removal of mercaptans from hydrocarbons. However, no further information was available on other examples of implementation or development by the environmental technology providers. |
| | Non-selective removal of VOCs. | The need to maintain high vacuum for the efficiency of the process | |
| | | Mass transfer resistance can occur for gaseous reactants or products that need to diffuse to and away from the solid catalyst deposited on the reactor wall. | |
| | | In some types of contactors the film flow becomes unstable at high throughputs, and it may break up into rivulets, fingers, or droplets. | |
| | | | |
| Naturally Improved Microorganisms | A reduction of TOC/COD levels in water effluents | None identified | The technique is generally applicable to new and existing installations in the industrial or municipal sectors This technique is applicable in optimising the biotreatment step of the water treatment plants of the refinery sector. |
| | | | |
| Evaporation | Material recovery is possible | Residues have to be disposed of, normally by incineration if not suitable for recycling | Evaporation is applied when concentrated waste water streams are wanted or recommended to concentrate mother liquors and liquors from waste gas scrubbing to recycle valuable substances.<br>One facility (detonators manufacturer) reported to be using evaporation. |
| | Enables the removal of refractory and/or toxic organic compounds from wastewater | Volatile contaminants pollute the condensate (needing subsequent treatment) or are emitted as waste gas | |

| Technique | Advantages | Disadvantages | Maturity/Applicability |
|---|---|---|---|
| | Reduces the amount of waste water produced | Vulnerable to fouling, corrosion and foaming | |
| | Reduces the amount and volume of hazardous waste | High energy consumption | |
| | | | |
| ABMET | Ability to produce an effluent with Selenium at less than 5 µg/l | The technology requires long retention times (6-24 h) | The ABMet system has been demonstrated in applications treating Flue-Gas Desulfurization (FGD) wastewaters, coal power plant ash landfill leachate, coal mine waters, phosphate mine waters, metal refinery wastewater, and agricultural runoff waters. Not known application in the chemical and petrochemical industries were found. Commercially available with several providers |
| | | Potential for plugging requiring periodical backwashed. | |
| | | The bacterial culture could be affected by variations in their environment (such as the occurrence of shock loads). | |
| | | The effluent requires post-treatment (aeration to increase DO level) before final discharge. | |

***Table 18:*** “Other” Techniques’ Efficiencies and Point of Treatment.

| Technique | Reported Efficiencies | Point of Treatment |
|---|---|---|
| Falling Film Contactor | No reported efficiencies for the target substances | No information available |
| | | |
| Naturally Improved Microorganisms | Efficiency can vary from 60% to 98% and 70% to 97% of the COD and TOC, respectively (data related to pharmaceutical and chemical effluents). 92% BOD reduction achieved in refinery/petrochemical waste waters. No information found for the target substances. | The technique is an improvement to the existing biological treatment |
| | | |
| Evaporation | No reported efficiencies for the target substances | No information available |
| | | |
| ABMET | A pilot study (19-38 L/min) performed by using ABMet® to reduce selenium levels from refinery wastewater demonstrated selenium reduction from 368 µg/L to 2.3-4.7 µg/L after 3 weeks. | As per nitrification / denitrification systems |

# 4. TECHNOLOGY READINESS LEVELS AND TECHNIQUES APPLICABILITY TO REFINERY EFFLUENTS

## 4.1. INTRODUCTION

As shown in Section 3, the literature search resulted in a large number of techniques that could potentially be applied to reduce the concentrations of the target substances in refinery effluents. As a means to further evaluate the actual applicability of these techniques in a refinery setting, a further screening of the technologies is carried out in this section. The screening is based primarily on the Technology Readiness Level (TRL) of each technology as set out by the BRIDGEHE H2020 Project, and on the applicability of the technique to the treatment of refinery effluents. This screening will result on the most relevant techniques for further assessment of their applicability, costs, level of environmental protection and their degree of environmental benefits as set out in the Sevilla process.

## 4.2. TECHNOLOGY READINESS LEVELS

The Technology Readiness Level (TRL) scale was used into the EU in 2014 as part of the Horizon 2020 framework program to support the funding of projects. The TRL scale was originally defined by NASA in the 1990's as a mean for measuring or indicating the maturity of a given technology, from initial conception to its commercialisation. In this context, TRLs describe the various stages new technologies go through during their life cycle. The scale TRL 1-7 is used for technology development and qualification (re: ISO 20815:2018, I.21.2 Table I.8). For example, when a technology is at TRL 1, scientific research has just started, and the first results are used to be translated into future research and development. This is followed by analytical and laboratory studies (TRL 2 and 3) before a laboratory prototype is available (TRL 4). In TRL 6, the prototype has to be demonstrated in a real environment, so to confirm the engineering is feasible, and at TRL 7 the technology requires that the working model or the prototype is demonstrated in an operational environment, under industrial conditions. Once ready for implementation, and proven during operations is at TRL 8, and when it is considered a commercial technology, it has reached TRL 9. A summary of TRL levels definition is included in **Table 19**.

***Table 19:*** Technology Readiness Levels Definitions (BRIDGE2HE project).

| **Technology Readiness Levels Definitions** | |
|---|---|
| **TRL Levels** | **Definitions** |
| TRL 1 | Basic principles observed |
| TRL 2 | Technology concept formulated |
| TRL 3 | Experimental proof of concept |
| TRL 4 | Technology validated in the lab |
| TRL 5 | Technology validated in relevant environment |
| TRL 6 | Technology demonstrated in a relevant environment |
| TRL 7 | System prototype demonstration in an operational environment |
| TRL 8 | System complete and qualified and demonstrated in continuous mode |
| TRL 9 | Commercial plant up and running for full range of operating conditions |

Based on the above definitions and the information found during the literature review and obtained from Concawe members and waste water treatment equipment vendors, a technology readiness level was assigned to each identified technique to help select those techniques that will be assessed further later in this report. TRLs for each technique are shown in **Table 20**. Further information on the justification for the selected TRLs is included in the Table in Annex B.

**Table 20** also shows the industrial sector where each technique is primarily applied and whether it is or has been used in the refinery sector. This is because high TRLs in one sector are not necessarily transfer to other sectors, without further research and testing given the very different nature of effluents between industrial sectors.

***Table 20:*** Assigned Technology Readiness Levels to Identified Techniques.

| Technique | Assigned TRL | Primary Industrial Sector | Technique | Assigned TRL | Primary Industrial Sector |
|---|---|---|---|---|---|
| Ultrasonic Reactors | TRL7 | Metal Industry | Nanofiltration and Reverse Osmosis | TRL 9 | Several industries, known in refineries for water reuse |
| Photocatalytic Oxidation with $TiO_2$ | TRL 4 or TRL 5 | Pharmaceutical, municipal, dye industry | Granulated Activated Carbon | TRL 9 | Several sectors including refineries |
| Supercritical Water Oxidation | TRL 9 | Municipal sludge, spent catalysts | Novel Adsorption Techniques | TRL 4 | Potential for several industries |
| Wet Air Oxidation | TRL 8 | Spent catalyst/caustics | Ion Exchange | TRL 9 | Various industries, not in refineries. |
| Wet Oxidation with $H_2O_2$ | TRL 8 | Chemical, petrochemical | Extraction | TRL 9 | Chemical industry |
| Photo-Fenton Method/ $H_2O_2$/UV | TRL 5 | Various, potential for refinery effluents | Micro Porous Polymer Extraction | TRL 9 | Produced water, potential use in refineries |
| Ozonation | TRL 9 | Municipal, general industry, refinery industry | Pertraction | TRL 6 | Several industries, not known use in refineries |
| Electrocoagulation/Electroflotation | TRL 9 | Chemical, oil and gas, potential for refinery effluent | Chemical Precipitation | TRL 9 | Several sectors including refineries |
| Electrodialysis | TRL 9 | Water Desalination | Crystallisation | TRL 9 | Chemical |
| Combined Electrochemical Oxidation | TRL 4 | Municipal | Evaporation | TRL 6 | Chemical |
| Membrane Distillation | TRL 4 or TRL 5 | Sea desalination, metals | Naturally Improved Microorganisms | TRL 6 | Applicable to refinery effluents |

| Technique | Assigned TRL | Primary Industrial Sector | Technique | Assigned TRL | Primary Industrial Sector |
|---|---|---|---|---|---|
| Membrane Bioreactor | TRL 9 | Chemical, pharmaceutical, potential for refinery effluents | Falling Film Contactor | TRL 5 | Fuel manufacturing for removal of mecaptans |
| Microfiltration and Ultrafiltration | TRL 9 | Several, known in refineries for water reuse | ABMET | TRL 9 | Several industries, not known use in refineries |

As indicated by INCITE (Innovation Centre for Industrial Transformation and Emissions), relevant techniques shall be at a level of technological maturity that has been demonstrated in a relevant environment or system prototype demonstration in an operational environment (i.e., at least Technology Readiness Level (TRL) 6-7). Therefore, techniques below this TRL were discarded for further assessment unless they qualified because of their applicability to refinery effluents (see below). Similarly, some techniques with high TRL were also not selected if that TRL originated from its use in an industry other than the petroleum refining industry.

## 4.3. TECHNIQUE APPLICABILITY

In addition to the techniques assigned TRLs, the techniques were also screened by their applicability to refinery effluents. In particular, the following criteria was also used to screen techniques for their selection and further analysis.

- Is the technique currently used at any refinery;
- Was the technique tested to treat refinery waste waters;
- Is the technique reported to be used in refineries, the petrochemical sector or upstream oil and gas operations (even if no specific sites identified)?

If the answer is yes to any of the above, the techniques were selected for further assessment. Some techniques, such as membrane filtration techniques (NF + RO and MF + UF) were not selected. Although some refineries may have used these, they are typically used in the context of further treating treated effluents with the intention of reusing the water (primarily the removal of salts) for other internal or external uses and not necessarily for the reduction of pollution prior to discharge to the environment. A reported test in a Concawe member refinery of UF+ RO for the removal of metals showed the techniques to be too expensive. A similar conclusion was obtained for Supercritical Water Oxidation based on tests in refinery effluents. Further information on the justification for the selected TRLs is included in the Table in Annex B.

## 4.4. SELECTED TECHNIQUES FOR FURTHER ASSESSMENT

Based on the above criteria and the previous assigned TRLs, the following techniques were selected for further assessment.

- Ozonation;
- Naturally Improved Microorganisms;
- Micro Porous Polymer Extraction;
- Membrane Bioreactors;
- Electrocoagulation/Electroflotation;
- Granulated Activated Carbon;
- Chemical Precipitation;
- Pretraction.

In the following Sections, the above selected techniques are further evaluated in terms of their environmental benefits, cross media effects, applicability to refinery effluents and costs.

# 5. FURTHER ASSESSMENT OF SELECTED IDENTIFIED TECHNOLOGIES

## 5.1. INTRODUCTION

The purpose of the project is to identify those innovative techniques, or techniques used in other industries, that can treat the list of substances listed in Table 1. Some of these substances have BAT AELs such as benzene, lead, cadmium, nickel and mercury. Others are included in the REF BREF BAT conclusions but have no assigned AELs such as toluene, ethylbenzene, xylenes, phenol index and vanadium. Finally, others are not included in the REF BREF BAT conclusions and include PAHs, AOX, total phosphorous, total cyanides, arsenic, chromium, cobalt, copper, manganese, selenium and zinc. **Table 21** provides a summary of the applicability of each selected technique to each of the target substances. A cross was assigned for a substance when evidence of efficiency for the specific substance was found in the literature. Some of the selected innovative techniques can treat several substances such as activated carbon or MPPE, while for others specific reference to the capability to treat the target substances was not found (such as Naturally Improved Microorganisms for use in biological treatment and membrane bioreactors). However, since these techniques can remove overall COD or TOC loads, they will also be capable of removing some of the organic substances targeted in this report.

***Table 21:*** Target Substances of Identified Innovative Techniques.

| Technique | Phenol Index | BTEX | PAH | AOX | Total Phosphorous | Total Cyanides | Metals |
|---|---|---|---|---|---|---|---|
| Ozonation | | x | | x | | | |
| Electrocoagulation | | x | | | x | x | x |
| Combined Electrochemical Oxidation | | | x | | | | |
| Membrane Bioreactor | | | | | | | |
| Micro Porous Polymer Membrane | x | x | x | | | | |
| Adsorption by Activated Carbon | x | x | x | x | | x | x |
| Other natural and synthetic adsorption techniques | | | | | | | x |
| Naturally Improved Microrganisms | | | | | | | |
| Chemical Precipitation | | | | | x | | x |
| Pertraction | x | | x | x | | | |

The following sections present an assessment of the selected techniques in terms of their environmental benefits and applicability. Capital and operational costs associated with these techniques are discussed in Section 6. The assessment follows guidance from INCITE, the European Innovation Centre for Industrial Transformation and Emissions, the EU's central point of reference for identifying and evaluating the environmental performance of innovative industrial techniques in terms of decarbonisation, depollution, or for increasing resource efficiency (e.g. water and energy efficiency) and circularity.

In general terms, the aim of the environmental performance analysis is to determine whether the technique either provides a higher level of environmental protection or an equal level of environmental protection at lower costs than the relevant alternative currently applied. For this to occur, data must be available for environmental performance parameters such as measured consumption of energy or water, emissions to air, water or soil, etc., efficiency and financial information of real-world applications where possible. As such, Section 5.2 provides a further assessment of the selected techniques' environmental benefits, applicability and cross media effects, while Section 5.3 provides information on their capital and operational costs.

## 5.2. ENVIRONMENTAL FOOTPRINT AND APPLICABILITY OF SELECTED TECHNIQUES

A qualitative assessment of the selected techniques is presented below to further assess their overall environmental footprint and their general applicability to refineries. To facilitate the assessment, a performance assessment ranking scheme was used loosely based on similar schemes proposed by others (Arthur et al 2005 and Amakiri et al 2022) for the assessment of technologies used in the treatment of oil and gas produced water. Their scheme was modified based on the findings of the literature review and considering the most relevant for their application to refinery effluents. The ranking used to assess these technologies is based on a scale from 1 to 5 where 1 means the technology performs badly or have a high environmental footprint, while a ranking of 5 represents the highest performance for the relevant criteria or lower environmental footprint. The criteria used in this report are described below.

Consumption of resources (**Table 22**) includes both the use of chemicals for the technique to function such as oxidants or flocculants and the energy consumption required. It includes a scale from 1 to 5 as shown below.

***Table 22:*** Consumption of resources ranking.

| Consumption of resources | Rank |
|---|---|
| Low | 5 |
| Moderately Low | 4 |
| Moderate | 3 |
| High | 2 |
| Very High | 1 |

Waste /emissions refer to primarily the generation of sludge material that requires management, either its treatment or disposal, and also other relevant emissions such as gaseous emissions or noise. A simplified scale with three levels only (1, 3 and 5) (**Table 23**) is used in this case to provide a general ranking given their general lack of quantification.

***Table 23:*** Waste/emissions ranking.

| Waste/Emissions | Rank |
|---|---|
| Low | 5 |
| Moderate | 3 |
| High | 1 |

The durability of the treatment technology (**Table 24**) is a measure of the susceptibility to failure or downtime. Some technologies rely on automated activation of pumps and valves to move fluid while other technologies feature simpler flow paths that are gravity driven. Simpler technologies are easier to maintain and cheaper to operate. Techniques operating at high temperatures and pressures can result in aggressive environments prone to corrosion. Also applies to fouling of membranes and electrodes.

*Table 24:* Durability ranking descriptions.

| Durability | Rank |
|---|---|
| Inlet water driven by gravity, no moving parts, facility not prone to fouling and scaling. Simple to operate and maintain. | 5 |
| Simple automated pumping cycles and few adjustments needed to complex automated cycles needing occasional adjustment and repair. Moderate fouling/scaling. Require moderate maintenance. | 3 |
| Significant scaling/fouling.<br>Operator needed frequently to make adjustments and repairs during process. Require regular maintenance | 1 |

Integration (**Table 25**) refers to the system's ability to be integrated to existing unit processes without major modifications. A simplified ranking is also used for this criterion.

*Table 25:* Integration ranking.

| Integration | Rank |
|---|---|
| High | 5 |
| Moderate | 3 |
| Low | 1 |

Footprint (**Table 26)** refers directly to the size of the technique and ancillary infrastructure needed as well as to the degree of onsite modifications required to install the technique in an average refinery configuration. Actual footprint depends on both the nature of the technique itself and also the capacity intended to treat resulting also in a simplified ranking for this criterion.

*Table 26:* Footprint ranking.

| Footprint | Rank |
|---|---|
| Small | 5 |
| Moderate | 3 |
| Large | 1 |

Finally, efficiency relates to the capacity to remove one of more of the substances targeted in this report (**Table 27**).

*Table 27:* Efficiency removal ranking.

| Removal Efficiency | Rank |
|---|---|
| >95% | 5 |
| 90%-95% | 4 |
| 75%-90% | 3 |
| 50%-75% | 2 |
| <50% | 1 |

The results of the assessment are included in **Table 28**. The table also shows the main treatment stage to which the technique is most applicable, although it is noted that some of these techniques can be applied to more than one stage, both as a pre-treatment to reduce COD and recalcitrant organic substances prior to the biological treatment and as a polishing step after biological treatment.

***Table 28:*** Qualitative Technology Assessment.

| Technique | Principal Treatment Stage | Chemical Demand | Energy Demand | Waste / Emissions | Durability | Integration | Footprint | Efficiency |
|---|---|---|---|---|---|---|---|---|
| **Electrocoagulation** | Primary | 5 | 3 | 2 | 3 | 5 | 5 | 5 |
| **Chemical Precipitation** | Primary/Secondary/ Tertiary | 1 | NI | 1 | 3 | 4 | 3 | 3 to 4 |
| **Pertraction** | Primary | 4 | 4 | 5 | 5 | 5 | 5 | 5 |
| **Membrane Bioreactor** | Secondary | 3 to 4 | 4 | 3 | 3 | 3 | 5 | >3 |
| **Naturally Improved Microrganisms** | Secondary | 5 | 5 | 5 | NI | 5 | 5 | NI |
| **Micro Porous Polymer Membrane** | Tertiary/Primary | 5 | 3 | 5 | 5 | NI | 5 | 1 to 5 |
| **Adsorption by Activated Carbon** | Tertiary/Primary | 5 | 3 | 1 to 3 | 3 | 5 | 5 | 2 to 4 |
| **Ozonation** | Tertiary | 2 | 2 | 5 | 5 | 5 | 5 | 4 |

Notes
NI- No information found

The above assessment provides a general overview of the environmental footprints associated with these techniques based on the information available, as discussed in the following sections.

## 5.2.1. Electrocoagulation

In the case of electrocoagulation, the technique is easy to install and operate. Compared to chemical coagulation the process doesn't require additional chemicals and the sludge produced is more stable, has larger flakes and is easier to dewater. In addition, the effluent generally contains fewer dissolved inorganic substances than chemical coagulation. The EC process contains few or no moving parts and is electronically controlled, which means that the maintenance costs (apart from cleaning and replacing the electrodes) are cheaper. Although a certain decrease in dissolved COD is observed in many cases, this technique is not ideally suited for the removal of dissolved organic molecules, but of heavy metals and emulsions and colloids. Removal efficiencies for metals, emulsions and colloids are in the same order of magnitude as for a classic physico-chemical treatment.

Although low in general, electrocoagulation uses more energy than chemical coagulation due to electricity needs (approximately 1 KWh/m$^3$).

The technology is commercially available in Europe and US and had been applied to oily waters associated with fracking operations, produced water and wastewaters from decommissioning operations of chemical plant. All of these applications are primarily small scale. However, treatment capacities of 15,000 and 24,000 m$^3$/d have been claimed by manufacturers in US and Europe respectively although no examples of operational cases were found.

## 5.2.2. Chemical Precipitation

Chemical Precipitation is a proven and relatively simple technique, and constitutes the baseline for precipitation in the petrochemical, chemical and metal industries. The technique has great selectivity in removing specific dissolved substances while others remain. However, the technique uses a large amount of reagents some of which can be expensive. This result in a large amount of sludge produced that needs further management. If it contains heavy metals, it may be considered a hazardous waste resulting in high processing costs.

In general, the efficiency of precipitation is high, particularly for single substances, although this efficiency can decrease for combinations of substances which also makes predicting final concentrations difficult in these circumstances.

Precipitation can be applied at different stages of the waste water stream, such as directly at the source; as the central treatment technique for the removal of phosphates; and to remove phosphates after the biological stage in a central WWTP, where the sludge is collected in the final clarifier.

Chemical precipitation is a well-established technique in the chemical and metals industries with ready availability of equipment and chemicals. Its use has also been reported in the petrochemical industry.

### 5.2.3. Pertraction

As with any extraction process, an extraction solvent is also used in this technique, however, the amount of extractant (solvent) is much lower than for other extractions techniques. Also, the extractant can be easily regenerated and reused and energy consumption is low. Pertraction can be used to remove a wide range of components, such as persistent organics with high removal efficiencies (typically >99%), even at low concentration levels. Furthermore, selectivity can be influenced by the choice of extraction solvent.

Pertraction installations tend to be small modular plants due to the high surface area and mass transfer of the pertraction membranes. Pertraction has been commercialised as a cheaper alternative to air stripping, and to a combination of air stripping and activated carbon.

Reportedly, pertraction is used in the chemical, pharmaceutical and petrochemical industries; in surface treatment using organic solvents; in the metal industry; for tank cleaning; in chemical laundries; and in wood conservation. However, no examples were found. The process has been demonstrated at pilot scale at various installations. A full-scale installation of 15 $m^3/h$ has been operational at an industrial site in the Netherlands since 1998 for the treatment of aromatic compounds to replace the use of an onsite incinerator. No known applications in refineries.

### 5.2.4. Membrane Bioreactor

The MBR combines a biological wastewater treatment system with a physical process, increasing the complexity of the process. Both steps require specific attention to process management and optimization of the control parameters. This results in a more compact footprint of up to a fifth of a conventional activated sludge system. While MBR systems can be highly automated, close follow-up is required for its proper operation.

Similar to conventional activated sludge systems, MBR technology aims to remove organic compounds (COD and BOD), suspended solids, nutrients (nitrogen and phosphorus) and bio-accumulable or bio-degradable micropollutants, where the biological conversion processes are the same as those of activated sludge systems. Because the bacteria are kept in the reactor for longer, there is a greater chance that components that are difficult to decompose or larger can be broken down. By removing suspended solids, a lower COD value of the effluent is almost always obtained compared to a conventional system. As a residual material, sludge must be removed from the installation at regular intervals, while cleaning fluids must be disposed of.

Membrane Bioreactors have generally higher energy consumption when compared with conventional activated sludge systems, with 2 to 18 KWh/m$^3$ (some 3.8 KWh/m$^3$ average) reported for operational MBRs in chemical plants, versus an average of 2 KWh/m$^3$ reported for conventional activated sludge treatment plants.

Several commercial plants in operation in Europe in the chemical and pharmaceutical industries with high treatment capacities in the thousands of m$^3$ per day. Bioreactors are currently used in refineries (e.g. by Petrobras in Brazil).

### 5.2.5. Naturally Improved Microorganisms

The technique is generally applicable to new and existing installations and consists of the use of naturally improved microorganisms (e.g. prokaryotic cells or bacteria, photosynthetic bacteria or eukaryotes such as yeasts, fungi and photosynthetic microalgae) to treat waste waters loaded with refractory TOC/COD. The process involves the selection of the naturally occurring microorganisms; the generation of the variants with enhanced characteristics to treat the target substances; and their introduction into the WWT process.

The technique is essentially a biological treatment and will present similar environmental footprint as other biological treatments. It is likely more applicable to chemical and petrochemical facilities facing issues with specific refractory substances instead of using chemical oxidation or incineration. Its use in refineries appears less practical.

Naturally improved organisms’ plants have been reported at laboratory to pilot scale tests at a few refineries in Europe.

### 5.2.6. Micro Porous Polymer Membrane

MPPE systems removes dissolved and dispersed hydrocarbons with high efficiencies >99%, down to below ppb level and can treat different types of hydrocarbons, including aliphatic, aromatic, polyaromatic and halogenated hydrocarbons. Reported efficiencies for gas/condensate and oil fields were >99% for BTEX and PAHs with influents of 300 to 3,000 ppm for BTEX and 0.2 to 2.1 ppm of PAHs.

As the process is based on affinity of hydrocarbons to an immobilised extraction liquid in a porous polymer bed, no chemicals other than the extraction liquid is required. The system produces no sludges, no emissions and have low noise levels. Durability is generally good as no fouling of the polymer bed occurs due to automatic regeneration.

MPPEs come in compact units with a small footprint and they are regularly used in offshore installations. In a refinery context it would be applied before biological treatment and after the API, as it requires primary treatment.

Manufacturers claimed low energy consumption due to the low energy required to release hydrocarbons from MPPE particles (in situ regeneration), with an energy consumption claimed to be 50 times lower than steam stripping. Additional environmental benefits claimed include the generation of practically pure hydrocarbons that can be reused (in the context of produced water) and low polymer waste given its long life.

A mature technique (first commercial MPPE unit in operation was in 1994). The technology is commercially available for the treatment of produced water from oil and gas production facilities and operating plants have been reported on LNG plants, gas plants, specialty chemicals, pharmaceuticals and groundwater pump and treat. The technology has been listed by OSPAR as Best Available Technology (BAT) for the treatment of produced water. Modular set ups can be upscaled to treat thousands of $m^3$/h. The technology is available in Europe.

### 5.2.7. Adsorption Using Activated Carbon

Activated carbon is a commonly used adsorbent, particularly suitable for the removal of low concentrations of non-degradable organic compounds from industrial waste waters, particularly non-polar compounds. In powder form, activated carbon is also added in aerobic and anaerobic wastewater treatment systems.

Activated carbon adsorption is a proven and widely used technique due to its low energy and maintenance costs and its simplicity and reliability. An activated carbon column requires limited supervision and maintenance. It is frequently used as a tertiary purification for the removal of organic micropollutants and COD, and to a lesser extent also metals in organic complexes.

The treatment process does not require added chemicals, and the process has a general low energy consumption. Higher energy is required though for the regeneration or incineration of the carbon. In the case of regeneration, approximately 10% of the carbon is lost.

Activated carbon as a treatment technique is extensively used in the textile industry, dry cleaning, the chemical industry, in groundwater remediation, and the pharmaceutical industry. GAC is used as part of WWTP in a refinery in China and it is widely available in Europe. Non-conventional adsorbents such as industrial, or agricultural by-products, nano-adsorbents and hydrogels are a continued subject of research.

### 5.2.8. Ozonation

Chemical oxidation is normally applied when the waste water contains contaminants that are not readily biodegradable, or not biodegradable at all (e.g. inorganic compounds), might disturb or overload the biological or physico-chemical process in a downstream WWTP or have properties too harmful to allow them to be released into a common sewer system. Overall, the efficiency of chemical oxidation is very good.

Ozone is an unstable compound which cannot be transported and therefore needs to be generated on site. Therefore, storage facilities may be required for oxygen bearing in mind the hazardous potential of these substances. After treatment, surplus ozone has to be eliminated, e.g. using a catalyst system based on manganese oxide.

Reported energy consumption varies from 6 to 15 KWh/kg of COD (for ozone generated from oxygen) to 12 to 30 KWh/kg of COD for ozone generated from air.

Widely available commercially as a polishing step in municipal and industrial treatment plants. An ozonation plant is part of a reuse water stream with capacity of 2500 $m^3$/h at a refinery in China. The technique is widely available in Europe.

## 5.3. ESTIMATED COSTS OF SELECTED TECHNIQUES

### 5.3.1. Introduction

This section presents estimated investment and operating costs of the selected techniques where available. Source of information are the scientific literature reviewed, EU BREFs, VITO (the Flemish knowledge Centre for Best Available Techniques), suppliers information and interviews with waste water suppliers. For older price/cost information, these are shown as reported at the time and where relevant (capital costs primarily) are also shown adjusted by inflation and converted into Euros. In reality, cost increase for industrial equipment and processes has been above general inflation, so I anticipate that some of the adjusted cost numbers to 2024 basis are a conservative approach. When available, operating costs were translated to costs /$m^3$ or per kg of COD for comparison purposes. Where possible, the costs of the selected techniques were compared with techniques commonly used in refineries/chemicals waste water treatment plants.

### 5.3.2. Estimated costs of Selected Techniques

**Electrocoagulation/Electroflotation**

The CWW BREF (referring to VITO) provides an estimated operational cost of €0.15 (2010 cost) per $m^3$ of effluent for large installations and for the removal of metals.

VITO also provides additional investment costs for electrocoagulation. For a 1 $m^3$ /hr effluent with some 200 mg/l of metals, it estimates an investment cost of just €150,000 (€204,000 corrected by inflation) with an energy consumption of 1 KWh/$m^3$. For a 4 $m^3$/hr effluent with 1,500 ppm of total phosphorous the investment costs was €100,000 (€136,000 in 2024) and operational costs of €15 per $m^3$, with a removal efficiency of 80% for total phosphorous. Another example refers to a metal company with a waste water effluent of 250 $m^3$/year and an energy consumption of 0.8 to 1 KW/$m^3$. The operating cost of electrocoagulation in this case was almost €19 per $m^3$.

While not providing a capital cost, nor an operating cost, a provider of waste water treatment plants claims that for a waste water effluent of 15,840 $m^3$/day, containing a variety of metals, operating savings of about €400,000 can be achieved when compared with chemical precipitation.

The general understanding is that electrocoagulation entails high operating cost which is a disadvantage or impractical for large industrial applications, but a few sources discuss electrocoagulation operating costs compared with conventional chemical coagulation.

Bayramoglu et al. (2007) did an economic analysis of operating costs for the treatment of textile wastewater by electrocoagulation including energy consumption, electrode material, labour, sludge handling, maintenance and depreciation costs for a chemical plant treating 1,000 $m^3$/day using different electrode materials, operating time, pH and current density. The most cost-effective configuration showed an operating cost of \$0.25/$m^3$. Treating the same waste water with chemical coagulation the authors found that chemical coagulation costs were 3.2 times higher than electrocoagulation.

Another study by Rodriguez et al 2007, for the treatment of metallurgic wastewater using electrocoagulation and chemical coagulation showed that for the same flowrate of wastewater (110 $m^3/y$) the energy cost of electrocoagulation was €220 (at todays' value) while chemical coagulation was €106, which is not surprising as electrocoagulation consumes electricity. On the other hand, the material cost for electrocoagulation was €440 compared to €1,100 for chemical coagulation which reflects the large quantities of chemicals required in chemical coagulation. Overall, the total treatment cost for electrocoagulation at €660, was less than that of chemical coagulation at €1,206.

Finally, Espinoza-Quinones et al. (2009) studied the effectiveness of electrocoagulation in the treatment of tannery wastewater. The experimental results showed that electrocoagulation is more cost effective than conventional methods while achieving the desired removal efficiencies. The cost of electrocoagulation was $1.7/$m^3$ of treated effluent compared to $3.5/$m^3$ using conventional methods.

The above studies appear to show that, at low flows, electrocoagulation can be more economic than chemical coagulation.

### Chemical Precipitation

The CWW BREF provides an investment cost of €0.03/$m^3$ (approximately €0.04 in 2024 values) although it does not specify a treatment volume, neither the number of operational years used in the calculation. For operating costs, the CWW BREF refers to sedimentation as having similar costs and a value of €2.5/$m^3$ is provided for the operation of a laminar or tube settler.

According to the ITRC Mining Waste Group (ITRC 2010), the capital cost of a zinc and cadmium plant, operating at a low 11 $m^3/h$ to a high of 34 $m^3/h$, had a capital cost of approximately $4.3 million in 2000 (€7.36 Mln at 2024 values).

Information on costs was provided by a CONCAWE member for co-precipitation with FeCl3 for the removal of metals. The targeted pH depends on the metal to be removed which in terms affects the chemicals required. If several metals are present the process may require two stages at two different pHs plus thickener and sludge treatment afterwards. A capital cost (total installed cost) or €30 Mln and €80 Mln were quoted for a 550 $m^3/h$ volume effluent (for one and two stages respectively) and corresponding to operating costs of between €3 Mln and €9 Mln per year. These costs were estimated based on bench tests with biological treatment waste water for the removal of selenium, vanadium and copper. This equated to operating costs of €0.62/ $m^3$ and €1.87/$m^3$ respectively.

Chemical precipitation is generally considered a high-cost treatment. Impacts to cost result primarily from the disposal of large quantities of sludge generated during the process and from the amount of reagents needed. In general, the cost of sludge disposal can amount to almost 50% of the overall operational costs, the cost of reagents some 32% and the remaining costs (19%) result from energy consumption (Chiavola A. et, 2020).

The overall cost of chemical precipitation depends on many variables, including the characteristics of the wastewater, the chemicals and dosages to be used, the volume of water to be treated, and the level of water purity desired. Moreover, chemical costs can vary widely depending on the form and quantity of material to be procured. It should be noted, however, that estimation of treatment cost cannot be determined solely on the price of the chemicals. For example, one study found that while it was less expensive to purchase alum than ferric sulfate, overall treatment costs were less using ferric sulfate (EPA 2000).

Generally speaking, lime is readily available and the least expensive of common treatment options. A completely enclosed lime chemical handling system costs between \$110,000 and \$130,000 (€193,000 to €220,000 at 2024 values), with the lower prices reflecting gravity versus pump systems.

Chemical precipitation is a widely used technique that can be considered the baseline for the treatment of metals and also phosphorous. A comparison of chemical precipitation with ion exchange by Chiavola A, et, 2020, for the removal of phosphorous from the same domestic sewage showed ion exchange performing as well as chemical precipitation and with lower costs. Furthermore, the ion exchange process offered also the opportunity to recover phosphorous from the exhausted ion exchange resin.

### Pertraction

The cost of pertraction is highly dependent on the amount and composition of the effluent to be treated and on the final concentrations to be achieved with the amount of the extractant playing a major role in process optimization. A larger amount of extraction solvent means a greater driving force and therefore a smaller membrane surface area. A small amount of extractant leads to a smaller regeneration unit.

Pertraction can remove organic substances effectively down to ppb level with the mass transfer coefficient being independent of the concentration of the substance to be removed between 100 mg/l and 0.1 ug/l (Jansen et al 1992). It is often compared in performance to air stripping and air stripping in combination with GAC. The CWW BREF, citing information from TNO (Dutch Organization for Applied Scientific Research) explores this by comparing costs of removing trichloroethylene using both pertraction and a combination of air stripping and GAC, to achieve a concentration of 10 ug/l from and influent with 10 mg/l, at an operational plant in the Netherlands. The operational cost of pertraction was €0.5/m$^3$ (2005 cost), while the cost using air stripping followed by GAC was €1.7/m$^3$ (€1.03/m$^3$ for the activated carbon and €0.67/m$^3$ for air stripping). This seems pertraction less expensive than air stripping followed by activated carbon filtration or only activated carbon filtration with a configuration of two filters in series.

No capital cost of pertraction plants were found.

### Membrane Bioreactors

CWW BREF, quoting VITO, provides a capital cost estimate of €16 Mln (cost of 2010 equivalent to some €21.8 Mln in 2024) for a membrane bioreactor treating 10,000 m$^3$/d of municipal waste water and an operating cost of some €0.3/m$^3$ which includes energy, chemical consumption, membrane cleaning and general maintenance.

Another example relates to a MBR used in a chemical industry with a flow rate of 2,000 m$^3$/d and an influent COD concentration of 3,000 mg/l. In this case, a capital investment cost of €3 Mln is quoted (approximately €4 Mln in 2024 value) and an operating cost of between €0.2 and €0.5 in 2010.

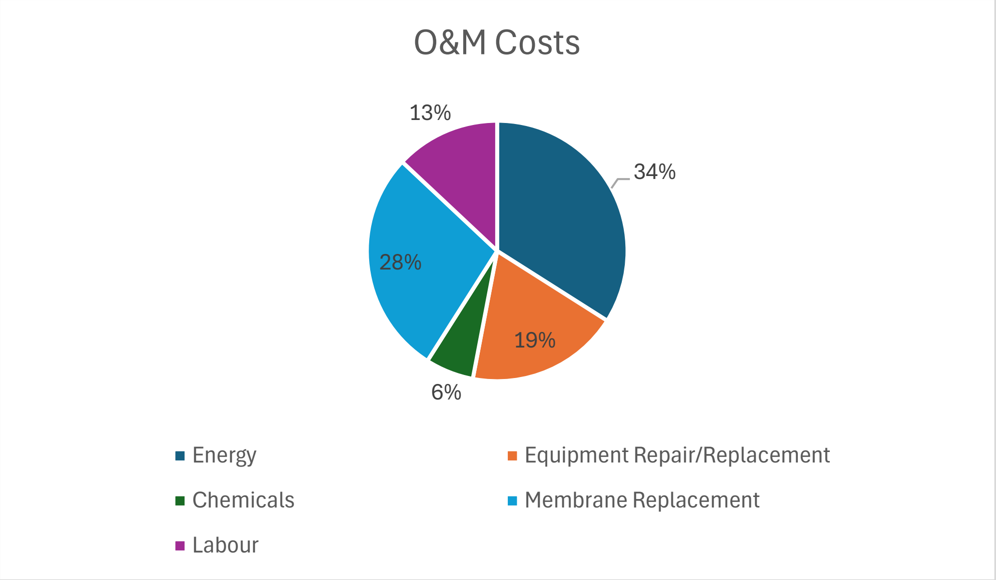
The REF BREF also provides information on the cost of MBRs. A 5,000 m$^3$ aeration tank biotreater, at a refinery in France, treating 450 m$^3$/h was built for €18 million (cost in 2009 equivalent to €24.5 Mln in 2024). This cost includes only building and installation of the basin. Another example quoted is a bioreactor with 1,000 m$^3$/h capacity and a capital cost of €5.5 mln in 2005 (€8.3 mln at 2024 values).

Dizayee et al 2023, undertook a cost benefit analysis of refinery effluent pretreatment upstream of a membrane bioreactor. He estimated a capital cost for a waste water volume of 1,800 $m^3$/d of approximately USD 12.3 Mln in 2023 (app. €11.6 Mln). This CAPEX information was restricted to the cost of the installed capital equipment, excluding costs specific to the locality of the installation (i.e., civil engineering costs). The operating costs where USD 0.191/$m^3$ (€0.18/$m^3$) of which USD 0.02/$m^3$ were related to the chemicals used and USD 0.171/$m^3$ where related to an energy consumption of 0.857 KWh/$m^3$. The study looked at the benefits of pre-treatment that demonstrated the API-DAF sequence to be extremely cost effective, with around 90% removal of TSS and O&G achieved by this sequence, with the O&G reliably removed to levels below 50 mg/L in the treated effluent, thereby affording a downstream MBR reasonable protection against membrane fouling. In terms of the COD, the removal is significantly lower (around 75% overall) compared with a projected >90% removal by the MBR. However, the API-DAF specific energy consumption in kWh per $m^3$ effluent treated is almost an order of magnitude lower than for the MBR. Therefore, investment in pretreatment steps to optimize COD removal is likely to provide a cost benefit since the energy demanded by aerobic COD removal by the biological process, such as the MBR, is directly proportional to the COD concentration.

Membrane bioreactors are alternatives to conventional biological treatment such as activated sludge. Capital costs for a 450 $m^3$/h activated sludge treatment plant was quoted in CWW BREF at €18 Mln in 2011 (representing a cost of €24.9 Mln at 2024 values). A yearly operating cost of 2% was quoted for this refinery. Another biological plant with a 1,600 $m^3$/d capacity had a capital cost of €950,000 (equivalent to €1.3 Mln at 2024 values).

Much work has been carried out to understand the costs of MBR applied to municipal treatment plants, in particular in the US. DeCarolis J et al 2007, developed costs estimates for full-scale (1 and 5 MGD, equivalent to app. 4,500$m^3$/d and 22,700 $m^3$/d respectively) MBR facilities designed to treat municipal wastewater. Their estimates included both capital and operational / maintenance (O&M) costs related to the headworks, MBR process (biological process and membrane system), chlorine disinfection and effluent storage. The costs associated with the membrane systems were developed from budgetary cost quotes provided by suppliers. For costing purposes, it was assumed that all MBR facilities were built on a clean plot of land and effluent quality was represented by BOD at 290 mg/l, COD at 630 mg/l, TDS at 1200 mg/l and total phosphorous at 2 mg/l. Total capital costs of the 4,500 $m^3$ ranged from $7.9Mln to $9.85 mln (€11.5 mln to €14.4 mln at 2024 values), while the amortized cost ranged from $520,000 to $640,000 per year (€761,000 to €938,000 at 2024 values). For the 22,700 $m^3$/d, the total capital cost was $32 Mln to $ 38 Mln (€46.8 to €55.6 Mln at 2024 values) and the amortized cost $2 Mln to $2.5 Mln/year (€2.9 Mln to 3.6 Mln at 2024 values). The range in capital costs directly reflects the range of membrane system costs from different MBR suppliers. The capital costs include headworks, basins construction, membrane system, blower and pump building, electrical, mechanical, plumbing, site works, land cost and contractor overhead and profit. The maintenance costs include: energy, equipment repair/replacement, chemicals, membrane replacement and labour. **Figure 4** shows an approximate break down of maintenance costs for the 4,500 $m^3$/d plant.

***Figure 4.*** Estimated Operation and Maintenance Costs for 4,500 m$^3$/d membrane bioreactor system (adapted from DeCarolis et al 2007)



The capital cost estimates of the newly developed MBR facilities were compared with previous cost estimates to gain an understanding of cost trends. The authors found that there had been a steady increase (~24%) in costs associated with MBR process components (excluding membrane system) between 2000-2006. Interestingly, the opposite trend was observed for membrane system costs, which actually have decreased by approximately 33% over the same time period. The rise in non-membrane costs associated with the MBR facilities was due to the increased cost of concrete and other raw materials used for plant construction. The drop in membrane system costs may be attributed to advancements in manufacturing and increased competition in the marketplace. These trends have resulted in the overall total cost for 4,500 m$^3$/d MBR systems to be fairly level (i.e. < 10% increase) between 2000 and 2006.

Another example is the municipal waste water treatment plan at La Center, in Washington State, USA. The wastewater treatment works at the town was originally constructed in 1967, based on a conventional activated sludge process, which was upgraded to a sequencing batch reactor (SBR) in 2004. Due to an anticipated 8.7% annual growth over a 20-year period a replacement with a membrane bioreactor was implemented.

Three phases were planned for the installation: two complete phases for the MBR and one to increase the capacity of the solid’s treatment and disposal. The total CAPEX for the plant was determined as being around $25 Mln in 2022 (€25.5 Mln at 2024 prices). The treatment plant had a capacity of 15,900 m$^3$/d. The MBR plant designed comprised two process trains with four membrane tanks (Phase 1) with two of the membrane tanks left empty as no membranes were initially required in all four tanks. In the event of an increase in flow the City can add membranes into the empty membrane tanks (Phase 2).

The switch from the SBR to the MBR produced a 92% reduction in the total suspended solids and 57% reduction in BOD loads discharged to the receiving stream. The MBR also reduced the amount of biosolids produced by 32%, reducing the cost of residuals management. An examination of the actual costs of operation of the SBR and MBR revealed the MBR to be 13% lower in operating costs than the SBR prior to optimisation, and 19% less following optimisation of both the solids handling and the membrane operation.

Finally, capital costs for MBR systems historically have tended to be higher than those for conventional systems with comparable throughput because of the initial costs of the membranes. In certain situations, however, including retrofits, MBR systems can have lower or competitive capital costs compared with alternatives because MBRs have lower land requirements and use smaller tanks, which can reduce the costs for concrete.

Fleischer et al. (2005) reported on a cost comparison of technologies for a 12-MGD (45,424 $m^3$/d) design in Loudoun County, Virginia. Because of a COD limit requirement, activated carbon adsorption was included with the MBR system. It was found that the capital cost for MBR plus granular activated carbon at $12/gallon (€400/$m^3$ or €18 Mln capital investment in 2024 values) was on the same order of magnitude as alternative processes, including multiple-point alum addition, high lime treatment, and post-secondary membrane filtration.

### Naturally Improved Microorganisms

- No costs were found associated with this technique. Costs are associated mainly with laboratory analysis and DNA sequencing, and with scaling up bioreactors to validate efficiency. A typical series of activities include:
- Waste water samples collection and analysis;
- Bacteria isolation, culture enrichment and maintenance;
- Morphological, biochemical and molecular characterisation of isolates;
- Development of tailored made bacterial consortium and assessing efficiency potential in lab tests; and
- Scaling up bioreactors (pilot scale).

### Micro Porous Polymer Extraction

The cost of microporous polymer extraction (MPPE) can vary significantly depending on factors like the specific application, scale of operation, and the type of polymer used, but generally falls within the range of €1 - €10 per litre of treated water, when considering the cost of the polymer beads and the associated extraction process.

Key factors influencing MPPE cost:

- Polymer type: Different polymers have varying manufacturing costs, with highly selective polymers potentially being more expensive;
- Particle size and morphology: Customized particle sizes and shapes can influence the cost of production;
- Extraction capacity: The amount of contaminant a single gram of MPPE can extract will impact the overall cost per litre of treated water;
- System Setup: The cost of the extraction column, pumps, and associated equipment can add to the overall cost.

The initial cost of purchasing the MPPE resin and setting up the extraction system can be substantial, especially for large-scale operations. The cost of the extraction column, pumps, and associated equipment can add to the overall cost.

At the Ormen Lange Project, a MPPE has been in operation since 2005 to remove dispersed oil (aliphatics), dissolved and dispersed aromatics (BTEX) and poly aromatics (PAHs). The plant has a capacity of 70 $m^3/h$. Reported capital and operating costs were €500,000 to €600,000 (€750,000 to €900,000 at 2024 values) and €130,000/year (€194,000 at 2024 values) respectively. As a comparison, treatment by activated carbon had a capital cost of €260,000 to €390,000 (€390,000 to €584,000 at 2024 values) and an operational cost of €39,000/year (€58,500 /year at 2024 values).

**Activated Granulated Carbon (GAC)**

Activated carbon adsorption is a proven and much used technique because of the low energy and maintenance costs, simplicity and reliability. An activated carbon column requires a limited amount of supervision and maintenance.

The CWW BREF provides some capital and operational costs for a 1000 $m^3/d$ effluent, although the nature of the effluent is not known. A capital costs of between €50,000 and €1,000,000 (2010 values) was reported, equivalent to €68,000 and €1.3 Mln when adjusted for inflation. Operating costs were in the range of €0.4 to €0.7 /$m^3$ (2024 values).

Investment costs are relatively high for small units treating less than 100 $m^3$ per day. Operating and maintenance costs are related to the replacement of the adsorbent bed. The regeneration or the destruction of the adsorbent are more expensive than the treatment itself. As regeneration is relatively expensive, the technique is generally unattractive for highly contaminated streams that consume large amounts of carbon.

Cost for treatment of produced water from oil and gas producing fields in Norway were already provided in the MPPE Technique costs.

The cost of adsorption with activated carbon varies greatly depending on the volume to be treated, and the loading and efficiencies required. The price of active carbon varies greatly between countries. For example, a ton of activated carbon in the US had an average approximate cost of €6000 per ton (€6 per kg), while in Belgium was approximately €3,600 per ton or €3.6 per kg. Average treatment costs can vary between €0.05 and €4 /$m^3$ (2008 cost equivalent to €0.07 and €5.5 per $m^3$ in 2024).

Cost information was also obtained from an operating waste water treatment at a former ethanol production facility located in the US (NewFields). The waste water is stored in surface lagoons and this needs to be treated and discharges in compliance with an NPDES limits. The treatment system consists of:

- Chemical addition and flocculator systems/tanks;
- Clarifier;
- Filtration (sand/bag/or multimedia filters needed to extend carbon life and reduce carbon backwash frequencies);
- Carbon Treatment;
- Bioreactor for BOD removal;

- Denitrification reactor;
- Ammonia stripper.

The effluent is characterised by suspended solids concentrations of between 50 and 5,000 mg/l, ammonia between 300 and 600 mg/l and BOD between 500 and 2000 mg/l. The cost for carbon treatment was estimated at €2.69 to €5.2 per $m^3$ of effluent; the range in costs depending on the different concentrations of the substances to be treated and on the degree of pre-treatment used. In this case, the overall cost of activated carbon represents approximately 15% of the overall treatment cost.

**Ozonation**

The cost of ozonation is determined by various factors, such as volume of wastewater, type and concentration of the pollutant, presence of disruptive components, desired yield, and the costs of producing ozone, including oxygen costs and energy consumption costs.

Typically, energy consumption for the production of ozone based from pure oxygen is 6 to 15 kWh/kg $O_3$. From air it is 17 to 30 kW/h/kg $O_3$. For an ozone concentration of 8 to 10%, 10 to 12 kg of O2 are required per kg of $O_3$. A MT of oxygen cost an average of €220.

The required dosage of ozone must be determined via experiments. A typical ozone dosage is 2 kg ozone/kg COD. The operational costs for energy and oxygen will depend on the required dosage. Considering its limited stability, ozone must be produced on-site. For an ozone generator with a capacity of 1.5 kg ozone/h, one should consider an investment cost of €100,000 (2008 data, €140.000 at 2024 values). The contact tank and piping must be able to resist oxidising conditions.

Mousset et al, 2021, reports that the cost efficiency of ozonation depends on the pH of the solution and taking account of the power consumption and chemical costs. Based on laboratory tests, he found that increasing the solution pH from 7 to 12 reduced the operating cost from approximately €1.08/g of TOC to €0.82/g of TOC.

The design of an ozone system for a particular project includes many variables that impact cost, such as ozone dose, feed gas system, redundancy, dissolution system, contactors, equipment, construction materials, controls, and instrumentation. These cost variables may vary from project to project depending on site-specific conditions.

While not directly applicable to the treatment of contaminants in waste water, the International Ozone Association (as reported by Mundi et al 2018) developed approximate capital costs of ozonation for disinfection of municipal treatment facilities (based on the inactivation of Crystoporidium) by gathering information from ozone equipment manufacturers and ozone water treatment systems across North America. Capital cost used included equipment (generators, ozone generator cooling system, feed system, piping, valves, appurtenances, and instrumentation, off-gas control units, ozone monitors, residual monitors), and construction costs (earthworks, contractors, building, E&I, oxygen supply, pipping, valves, etc). The information was used to create a relationship between capital cost and installed ozone system capacity in pounds per day (ppd) that can be used to determine costs for any flow and ozone concentration requirements. As an example, for a flow of 60 MGD (227,124 $m^3$/d) and an ozone concentration of 2 mg/l, capital costs were $5,582/pound/day (approximately €15,000/kg /d at 2024 values), resulting in a total capital cost of $8.37 Mln (€9.5 Mln at 2024 values).

Using a different example, the operational cost for a treatment plant with a 43.4 MGD (173,600 $m^3$/d) of treated water flow, about 1.16 mg/L ozone dose, about 420 lb/day (190 kg/d) ozone production, was $216,000 in 2012 (€280,000 in 2024) for the average annual ozone cost of energy and liquid oxygen. To this, an additional $97,000/year (€126,000 in 2024) for other ozone labour and O&M costs (about 45% of the $216,000 average annual ozone cost of energy and liquid oxygen).

As part of this project, costs of ozone generation equipment was requested from a vendor. An ozone generator system along with a power supply unit of 2 kg/hr was quoted at USD 34,500 (approx., €32,800). Excluding the compressor the cost would be USD 22,600 (€21,500).

# 6. CONCLUSIONS

This report presents the findings of the identification and assessment of innovative wastewater treatment techniques to reduce the concentrations of several organic and inorganic substances and heavy metals in fuel manufacturing sites' wastewater discharges. Some of these substances were selected because they have BAT-AELs in the REF BREF, while others are listed in the REF BREF but have no BAT-AELs in the current BAT conclusions; however, when in high concentrations they can affect the performance of the wastewater treatment and prevent it from attaining the discharge limits on other parameters that have BAT-AELs in the REF BREF. The selected substances are listed in **Table 29**.

***Table 29:*** List of Substances Targeted in this Report

| | | | |
|---|---|---|---|
| Organics | Phenol Index | Metals | Nickel |
| | BTEX | | Arsenic |
| | PAHs | | Chromium |
| | AOX | | Cobalt |
| Inorganics | Total Phosphorous | | Copper |
| | Cyanides (as Total CN) | | Manganese |
| Metals | Cadmium | | Selenium |
| | Lead | | Vanadium |
| | Mercury | | Zinc |

As part of this project, a comprehensive literature search of technologies capable of dealing with such parameters was conducted, including technologies applied to other industrial sectors other than the petrochemical sector. The technologies identified as applicable to each selected substance are listed in **Table 30**. As it is evident from this table, some technologies can be applied to more than one substance, depending on the mode of action of each technology.

***Table 30:*** Applicability of Techniques to Substances for refinery wastewater treatment

| **Substance** | **Technique** | | **Substance** | **Technique** |
|---|---|---|---|---|
| **Phenol Index** | Ultrasonic Reactors | | **AOX** | SCWO |
| | Photocatalytic Oxidation | | | Wet Oxidation w/$H^2O^2$ |
| | Photo-Fenton | | | Wet Air Oxidation |
| | SCWO | | | NF + RO |
| | Wet Oxidation | | **Total Phosphorous** | Ultrasonic reactors |
| | NF + RO | | | Electrocoagulation |
| | GAC and advanced adsorption materials | | | NF + RO |
| | Ion Exchange | | | Crystallisation |

| Substance | Technique | | Substance | Technique |
|---|---|---|---|---|
| | Extraction | | **Total Cyanides** | Electrocoagulation |
| | MPPE | | | Bio/Nano adsorbents |
| | Membrane distillation | | **Metals** | Ultrasonic Reactors |
| **BTEX** | SCWO | | | Electrodialysis |
| | Membrane Distillation | | | Electrocoagulation |
| | MPPE | | | Bio/nano-adsorbents |
| | Electrocoagulation | | | GAC |
| | Wet Air Oxidation | | | MBR |
| **PAH** | Combined Electrochemical Oxidation | | | NF + RO |
| | SCWO | | | Ion Exchange |
| | MPPE | | | Chemical precipitation |
| | MBR | | | Crystallisation |
| | Pertraction | | | ABMET (Se) |

The Technology Readiness Level (TRL) for each technology was also rated together with its applicability to refineries' wastewaters, since high TRLs in one sector are not necessarily transferable to other sectors without further research and testing given the very different nature of effluents between industrial sectors.

Technologies with a TRL over 6-7, and found to be potentially applicable to refinery effluents, were selected for further assessment. These included the eight technologies listed below (and their targeted substances):

- Ozonation: BTEX and AOX.
- Naturally Improved Microorganisms: no sufficient information.
- Micro Porous Polymer Extraction: phenol index, BTEX and PAH.
- Membrane Bioreactors: metals, PAH.
- Electrocoagulation/Electroflotation: BTEX, total phosphorous, total cyanides and metals.
- Granulated Activated Carbon: BTEX, phenol index, PAH, AOX, total cyanides, metals.
- Chemical Precipitation: total phosphorous and metals.
- Pertraction: Phenol index, PAH and AOX.

A qualitative assessment of the selected techniques was undertaken to further assess their overall environmental footprint and their general applicability to refineries. Finally, for each technology selected, estimated investment and operating costs are provided.

A main conclusion of this study is that high TRLs for techniques applied to a specific sector or to several sectors does not necessarily translate into a similar level of application to the fuel manufacturing sector in terms of their efficiencies, costs, and general applicability. Such techniques still need to be tested through pilot scale demonstrations in an operational environment to assess their applicability to fuel manufacturing sites' effluents.

Additionally, the techniques selected cannot treat refineries effluents on their own, as they will typically form part of a combination of techniques to achieve the desired effluent quality. Also, cross media impacts can often result from the application of new techniques, and these should be considered when assessing the applicability of a technique at a given location and in a specific industrial sector.

Finally, it is expected that this report can provide a useful reference on a variety of techniques that may be considered for further testing to gain a better understanding of their applicability to wastewaters from fuel manufacturing facilities.

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## ANNEX A: DESCRIPTION OF IDENTIFIED TECHNIQUES

# Advanced Oxidation Techniques

## Ultrasonic Reactors

### Description

This technique was identified as an emerging technique in the CWW BREF 2016, for the treatment of sulphate-rich waste waters that are treated with aluminium oxide under acidic conditions and the pH neutralise with lime slurry or liquid lime. The effluent is then passed through an ultrasonic reactor at a controlled rate where sulphate can precipitate as calcium aluminium sulphate oxide in a very fine precipitate, almost colloidal in nature. Flocculation is started with the addition of Epofloc L1-R (a heavy metal precipitant which is a carbamine), which precipitates aluminium and any other metals present. The process follows with clarification where the sludge is removed and treated in a filter press and can then be disposed of or reused/recycled. As stated in the CWW BREF 2016, this technique is also able to remove phosphates, heavy metals, and results in general COD reduction.

Ultrasound has gained popularity as a wastewater treatment technique in recent years. The intense conditions of acoustic cavitation cause water molecules and dissolved oxygen to split into • OH and O2– •. Thus, organic pollutants can break down and inorganic pollutants can oxidise in this reactive environment. Typical ultrasonic systems consist of a generator, one or more transducers, a booster, an emitter and the reactor vessel. The reactor’s configuration has an essential role regarding the cavitation activity and are designed to reduce dead zones and increase active cavitation zones (Amadou 2022).

### Target Substance and Technique Efficiencies

The technique is used to remove the following contaminants from waste waters as discussed in the CWW BREF 2016 and Elmobarak et al 2021:

- Sulphate (up to 99.7% abatement efficiency);
- COD (up to 55% abatement efficiency);
- phosphate (up to 99.9% abatement efficiency);
- heavy metals (up to 99.7% abatement efficiency);
- Phenols (99% abatement efficiency);
- MTBE (98% abatement efficiency).

### Applicability

The technique can be applied as an end-of-pipe technique or included within a waste water treatment plant. The technique can be applied to new or existing plants. If the technique is retrofitted, this often will involve adding some dosing pumps and the ultrasonic reactor. Assuming the settlement tank or clarifier is of a suitably size, the technique can be applied to large or small plants. In the case of large plants, several ultrasonic reactors may be required to handle the flow (normally only required for flow rates of > 40 m3/h). It should be mentioned that the refinery waste waters are rarely sulphate rich and therefore this technique may have low applicability in the refining sector.

### Technology Maturity

In addition to the removal of sulphate and associated precipitates mentioned above, ultrasonic reactors have been used to reduce fouling in ultrafiltration membranes, and to reduce the viscosity of heavy oils. It has been reported to be used commercially for the treatment of sewage sludge although no commercially available suppliers have been found. According to CWW BREF 2016, the technology is stated to have been implemented in Rimex Metals Ltd, UK. The ultrasonic reactor installed at Rimex is part of several treatment steps (pH adjustments and precipitation of heavy metals and phosphate), after which the ultrasonic reactor is used to removed biological phosphate. The process continues with flocculation, clarification and filtration. A capacity of 40 $m^3$/h reported.

One company found to offer small modular ultrasonic reactors but is unclear what their proposed application is. Not known application.

### Environmental Benefits

Ultrasonic reactors can remove a wide range of organic and inorganic substances from waste waters including metals.

The resultant filter cake produced has a lower moisture content and is often non-hazardous and can be disposed of in a suitable landfill site or reuse in several applications such as raw material in the cement industry; as a treatment material for paint wastes; in waste stabilisation/ solidification; in the treatment of contaminated soils.

### Cross Media Effects

A side effect of this technique is the fact that the precipitate produced is fine and extremely slow to settle requiring a settlement tank/clarifier designed for this purpose. The reactor can experience high dissipation rate reducing efficiency.

### References

CWW BREF 2016, Elmobarak et al 2021, Adamou, 2025, Lippert 2020.

## Photocatalytic Oxidation

### Description

This technique was identified as an emerging technique in the CWW BREF 2016. The technique is a low-temperature system based on photocatalysis that can degrade a range of organic compounds as well as destroy microorganisms in aqueous effluents.

The technique is simple to operate and with few moving parts. It is also highly reliable and robust. The system is capable of being scaled to a variety of throughput requirements, from litres to cubic metres per day, and can be operated either on a continuous flow or a batch basis, depending on the target material to be treated.

The basic configuration can use either a suspended photocatalyst that can be recovered for reapplication, or an immobilised photocatalyst coated on an inert substrate. The latter approach has, in general, a lower destruction efficiency than the former, but it reduces the need for a recovery plant and is therefore simpler to build and to use.

With a suspended catalyst, a mixture of the target material to be treated, the catalyst and water is passed as a thin slurry film over a series of plates and exposed to UVA light. If sufficient degradation of the target material occurs, then the treated mixture can be passed through a catalyst recovery system, after which the water and treated target material can be released into the environment by discharge through a conventional water treatment system; the catalyst can be recycled for further use in the process. If further processing is required before transferring the degraded pollutant stream into the water treatment plant, a continuous loop system can be operated or, if batch processing is required, then the process mixture can be put into a holding tank for further treatment prior to discharge.

With an immobilised catalyst, the process is clearly simpler, whether a batch or a continuous flow is used.

### Target Substance and Technique Efficiencies

The photocatalytic process can be applied to industrial waste waters for general organic pollutant destruction; specific pollutant degradation such as pharmaceutical- or pesticide-contaminated waters; toxicity reduction; biodegradability improvement; general BOD/COD removal; odour and colour improvement. No data on efficiency for the above elements was found. Removal efficiencies of 99% and 98% have been reported for Phenols and MTBE respectively.

### Applicability

This technique is probably only applicable to small-scale specialist treatment such as dye-stuff and pharmaceutical industry. The technique is likely less suitable for the fuel manufacturing sector.

### Technology Maturity

In 2009, there was no commercial application of this technique to the knowledge of the TWG for the review of the CWW BREF.

### Environmental Benefits

No chemicals are consumed with the implementation of this technique.

### Cross Media Effects

Energy consumption (by the UV lamps as well as pumps to circulate the water effluents) is a cross-media effect associated with this technique. Power consumption will be dependent on the reactor size and the energy requirement will depend on throughput. For a reactor suitable for treating ~ 2 200 l/d, or ~ 15 $m^3$/week, 200 lamps of 80 W each will be needed and with a treatment time of approximately 1.5 hours, the energy consumption will be about 24 kWh.

### References

CWW BREF 2016, Elmobarak et al 2021.

## Super Critical Water Oxidation

### Description

This technique was identified as an emerging technique in the CWW BREF 2016. Supercritical Water Oxidation (SCWO) is a special application of the high-pressure variant of wet air oxidation. The oxidation reaction takes place in the supercritical region of water, i.e. temperatures over 374°C and pressures above 22.1 MPa. Under these conditions water becomes a fluid with unique properties that can be used to advantage in the destruction of recalcitrant substances such as polychlorinated biphenyls (PCBs) or per-and polyfluoroalkyl substances (PFAS).

Waste water is brought to the supercritical pressure by a high-pressure pump before it enters the economiser, where the feed is preheated by the reactor effluent. At start-up, or if the organic concentration in the waste water is less than 4%, the feed has to be heated further to reach the supercritical temperature range. When oxygen is added to the feed, the temperature in the reactor will rise to about 600°C. The reactor effluent flows into the economiser, then through a heat recovery steam generator and through an effluent cooler. Finally, a control valve drops the effluent pressure to atmospheric conditions and the liquid and gas phases are separated. The organic waste water content is reduced to carbon dioxide, water and nitrogen. The process causes salts to precipitate out of solution, meaning they can be treated using conventional methods for solid-waste residuals. The process oxidises metals to their highest oxidation state and destroys all volatile solids.

### Target Substance and Technique Efficiencies

The technique is stated to exceed 99.9% of efficiency in abating pollutants such as Organic compounds, 1,2,4-Trichlorobenzene, 4,4-Dichlorobiphenyl, DDT, PCB 1234, PCB 1254 and dioxins. The nature of the technique means results in the complete mineralisation of organic substances. The technique is most efficient at COD influent concentrations of between 30 g/l and 200 g/l.

### Applicability

Several companies in the United States are working to commercialize supercritical reactors to treat hazardous wastes. Widespread commercial application of SCWO technology requires a reactor design capable of resisting fouling and corrosion under supercritical conditions.

In Japan a number of commercial SCWO applications exist, among them one unit for treatment of halogenated waste built by Organo. In Korea two commercial size units have been built by Hanwha.

In Europe, Chematur Engineering AB of Sweden commercialized the SCWO technology for treatment of spent chemical catalysts to recover the precious metal, the AquaCat process. The unit has been built for Johnson Matthey in the UK. It is the only commercial SCWO unit in Europe and with its capacity of 3000 l/h it is the largest SCWO unit in the world. Chematur's Super Critical Fluids technology was acquired by SCFI Group (Cork, Ireland) who are actively commercializing the Aqua Critox SCWO process for treatment of sludge. SCFI Group operate a 250 l/h Aqua Critox demonstration plant in Cork, Ireland.

AquaNova Technologies, Inc. https://aquanovatech.com is actively commercializing their 2nd-generation transpiring-wall SCWO reactor ("TWR") with a focus on waste treatment and renewable energy applications. AquaNova's patent-pending TWR-SCWO technology is projected to treat a broad variety of wastes, including PFAS, while generating electric power with improved system thermal efficiency. AquaNova is targeting larger-scale industrial applications.

AquaNova Technologies was founded by Tom McGuinness, the original inventor of the transpiring-wall reactor (TWR) under US patent 5,384,051.

Water Inc. is a company offering commercial SCWO systems that convert organic wastes to clean water, energy and minerals. It is spun out after more than seven years of research and development funded by the Bill & Melinda Gates Foundation to Prof. Deshusses laboratory based at Duke University. The founders of Water, Prof. Marc Deshusses and Kobe Nagar, possess the waste processing reactor patent relevant to SCWO. Water is actively commercializing its AirSCWO systems for the treatment of biosolids and wastewater sludges, organic chemical wastes, and PFAS wastes including unspent Aqueous Film Forming Foams (AFFFs), rinsates or spent resins and adsorption media. The first commercial sale was announced in February 2022.[15]

Aquarden Technologies (Skaevinge, Denmark) provides modular SCWO plants for the destruction of hazardous pollutants such as PFAS, pesticides, and other problematic hydrocarbons in industrial waste streams.[16] Aquarden is also providing remediation of hazardous energetic wastes and chemical warfare agents with SCWO, where a full-scale SCWO system has been operating for some years in France for the Defense Industry.

There is not known application in the fuel manufacturing sector. overall capacities seem to be small compared with refinery average effluents. Is it considered primarily a polishing technique to treat recalcitrant organic compounds. The application of this technique in the fuel manufacturing sector should be considered following a more in-depth evaluation of its applicability to its waste water streams, including the economics and cross-media impacts, such as energy use and greenhouse gas emissions.

## Technology Maturity

Several plants have operated and are currently in operation. Design issues means that research is still ongoing to develop more reliable reactors. Several of the reactors mentioned above were purposely built for a specific function and are not necessarily transferable to different effluents such as fuel manufacturing effluents.

## Environmental Benefits

SCWO has a high destruction efficiency due to the complete solubilisation of organic compounds. It also the oxidation of metals and potential for energy production. At influent COD concentrations above 100 g/l, SCWO has the capacity to generate electricity.

## Cross Media Effects

One of the main problems with this technology is the level of corrosion experienced due to the precipitation of salts. Indeed, several plants that started operation had been closed due to design issues. This results in high capital costs (though the development of more sophisticated reactors such as transpiring wall reactors and high maintenance costs may solve these issues). Finally, this technique can currently process low flows (max reported 306 t/d involving the treatment of sludge).

## References

CWW BREF 2016, VITO 2009, Vadillo 2018, Scheitin 2013, Svastrom 2003, Zhang 2016, SCFI Industries

# Wet Air Oxidation

## Description

Wet air oxidation is the reaction of oxygen in the aqueous phase under high pressure and temperature, used to increase the solubility of oxygen in water. The reaction often takes place in the presence of catalysts. Reaction products are dependent on the waste water content and can include:

- Carbon monoxide and carbon dioxide from organic content;
- Nitrogen from ammonia/ammonium and organics which contain nitrogen, if a catalyst is used;
- Nitrate from nitrite and organics which contain nitrogen;
- Hydrogen chloride from chlorinated organic compounds if present;
- Sulphate from sulphides;
- Phosphate from compounds which contain phosphorus.

There are two types of wet air oxidation processes, a low-pressure wet air oxidation one operating at between 0.5 and 2 MPa, and a high-pressure wet air oxidation that operates at >2 MPa. The high pressure type operates also at a higher temperature (up to 340°C). Typical equipment in wet air oxidation includes the reactor, which can have different configurations, high pressure pump, compressor for air/oxygen supply, gas/liquid separator, pressure reducing valves and heat exchanger. Given the high pressures and temperatures involved in the process the materials specifications are high, requiring enamelled materials or lined with PTFE. Metal parts to be operated at temperatures of up to 200°C must be manufactured from titanium or its alloys with palladium. The requirements for the high-pressure variant are special titanium alloys for heated areas.

## Target Substance and Technique Efficiencies

Wet air oxidation targets refractory substances and achieves reduction of COD and TOC. In low pressure reactors efficiencies reported include 60% to 90% for COD and 60% to >90% for AOX. For high pressure reactors efficiencies include 99% for COD (on an influent of 30 g/l), 95% for TOC and 80% for AOX. However, the performance of the technique is not assessed by looking just at the efficiency of the oxidation process, but also by taking into account the efficiency of the subsequent biological process.

Efficiencies vary according to the type of spent caustic being treated, the temperature used and the retention time of the process. The treatment of sulphidic spent caustic with a temperature of 200°C and 60 minutes retention time COD removal efficiency was 77.8% and TOC removal was 12.3%. For a Cresylic spent caustic treated at 260°C COD removal was 78% and TOC removal was 72%. Higher recoveries were observed for a naphthenic spent caustic and at similar temperature (Siemens).

## Applicability

Wet air oxidation is applied to waste water which contains contaminants that are either not readily biodegradable or might disturb the biological process in a downstream biological WWTP, or which have properties which are too harmful to allow them to be released into an ordinary sewer system such as phenol, naphthalene or chlorinated aromatics (in low pressure systems) and nitro, organo amino, sulphur, phosphorous and chlorinated compounds in high pressure versions. Wet air oxidation might also replace a central biological WWTP, if the amount of waste water is too small to warrant such a plant or if there is no biotreatment available.

Wet air oxidation is mainly applied to processes including the production of dyes and intermediates; the oxidation of aromatic sulphonates; the production of derivatives of phenol or naphthol and the production of aromatic hydrocarbons.

Commercial plants are being used for the treatment of spent caustic effluents from Petrochemical Ethylene Plants and PDH Plants, and from Refinery's Merox Units, Isomerization Unit, DHDT and Hydrocracker Units and Propylene Recovery Units. Operational units include the Vadodara refinery in India and the Indorama olefins plant in Louisiana, US. Both plants have a treatment capacity of 3 $m^3$/hr. Wet air oxidation is also used at Repsol Química in Tarragona, Spain.

### Technology Maturity

Mainly used for the treatment of spent caustics therefore small capacity (3 $m^3$/hr). Commercial plants operating in India, US, Spain.

### Environmental Benefits

Elimination of refractory organic content or inhibitors to subsequent biological treatment is the main environmental benefit.

### Cross Media Effects

Under adverse conditions, the generation or regeneration of dioxins can occur, so residues might need further treatment. The effluents from this process – aqueous and off-gas (carbon monoxide, lower hydrocarbons) – have to undergo downstream treatment, e.g. biological treatment, adsorption or the stripping of waste water, and gas scrubbing, biofiltration or thermal/catalytic oxidation of waste gas.

Wet air oxidation implies the consumption of air or oxygen and energy. The energy consumption depends on the TOC load. When the TOC content exceeds the autothermal range, the generated heat can be used by means of installed heat exchangers.

### References

CCW BREF 2016, VITO 2009, Linde Engineering India Pvt. Ltd.

## Fenton/Photo-Fenton

### Description

Fenton is a mixture of hydrogen peroxide (H2O2) and ferric ions. This mixture has great oxidising potency in an acid medium. The standard reaction of the Fenton process proposed by Haber and Weiss in 1934 includes an aqueous integration of hydrogen peroxide (H2O2) and ferrous ions (Fe2+) in an acidic medium, leading to H2O2 breaking into a hydroxyl ions and a hydroxyl radical, and the oxidation from Fe2+ to Fe3+. The standard pH in Fenton's reaction observed in several reports is 3 and, consequently, can be considered the suitable operational pH.

Elmobarak 2021, citing Wang et al. (2019) indicates a ratio of [Fe2+]/[H2O2] of 1:5 generates similar findings to a ratio of 1:2 but needs less reagents. In general, the reaction of the Fenton process alone is not able to degrade and fully mineralise organic substances effectively. The reaction of the Fenton method is efficient up to the instant where each Fe2+ that exists in the reaction is reacted to Fe3+, hence disrupting the production of hydroxyl. While the Fenton's reaction has been extensively reviewed and showed to give good results in the treatment of waste waters, its effectiveness increases when UV radiation is applied to the system. The UV irradiation greatly increases the organic contaminants degradation rate of Fenton, which is susceptible to UV emissions with wavelengths over 300 nm.

The removal of contaminants and the inhibition of toxic compounds are some of the major advantages of AOPs. For example, more conventional techniques such as filtration, adsorption, and flotation are not as effective in completely separating the organic pollutants (non-destructive physical separation procedures), which only eliminate the pollutants, transporting them to other stages, and thus producing intense residues (Elmobarak et al 2021).

## Target Substance and Technique Efficiencies

Fenton and Photo-Fenton techniques have shown promising results in treating COD and BOD with up to 92 and 90% abatement efficiency, respectively. The technology is however shown to be sensitive to the process conditions, particularly the pH of the environment, to operate effectively.

## Applicability

The AOP methods can be applied as a polishing step, or in an integrated setting, whereby the AOPs are applied in conjunction with the conventional techniques such as biological treatment and membrane technologies. This technique is more suitable for low volume waste water effluents, and hence its efficient application in the fuel manufacturing sector may be limited. There may be opportunities for small scale process water streams to use the AOP technique at the pre-treatment step.

## Technology Maturity

The Photo-Fenton method that has been tested at a pilot scale to treat municipal waste water treatments (Klamerth et al. 2010). However, the application of Photo-Fenton in treating waste water from petrochemical industry has been shown to be costly, especially due to the associated electric energy and reagent costs (Rubio-Clemente et al., 2015). Given the efforts, it however appears that the energy costs of this technique are still an ongoing prohibiting factor for the industrial implementation of the technique in the fuel manufacturing sector.

## Environmental Benefits

Small footprint and can be easily integrated with other treatment processes.

## Cross Media Effects

The cost of Fenton and Photo-Fenton methods are relatively higher than the traditional techniques such as filtration, adsorption, and flotation, as they require continuous input of expensive chemical reagents. The technique would also need to be used in conjunction with pre-treatment and/or established treatment techniques for increasing the treatment capacities. Other drawbacks include the creation of a strong acid environment, and large production of ferric sludge, which limits further application of the technique in the large-scale industrial applications.

Most effective catalysts are metals, which are toxic for the later biological step. Therefore, they need to be removed. Failure on this step, would cause a reduction of activity in the biological treatment and increase the final COD.

## References

Elmobarak et al 2021, Garrido-Cardenas 2020, Rubio-Clemente 2015, Adetunji 2021.

## Hydrogen Peroxide ($H_2O_2$)/UV

### Description

Hydrogen peroxide ($H_2O_2$) is a powerful oxidant with a standard reduction potential of 1.77 V that is used to reduce concentrations of organic compounds in waste waters. However, $H_2O_2$ is less effective in treating more persistent substances presenting a low reaction rate. The application of $H_2O_2$ to degrade organic compounds is more efficient when it is performed in combination with other components or sources of energy that are competent at producing hydroxyl radicals (•OH), which can increase their oxidation potential. Through UV radiation in wavelengths >300 nm, hydrogen peroxide ($H_2O_2$) can decompose and create these •OH. Degradation of organic compounds occurs when •OH and hydroperoxyl (HO2●) radicals are created. However, the hydroperoxyl radicals have a smaller reduction potential with a value of 1.7 V compared to the hydroxyl radicals with a value of 2.8 V; as a result, their production is less desired.

Photolysis of H2O2 is generally achieved using mercury vapor lights. However, it should be noted that almost 50% of the energy expended is wasted in heat or in emissions of wavelengths >185 nm. A cheaper and widely used alternative is the germicide lamp; though, the efficiency is smaller as it radiates in a range from 210 to 240 nm.

### Target Substance and Technique Efficiencies

The technique is used to degrade organic compounds in waste waters. Several studies have evaluated the application of $H_2O_2$ with and without UV radiation. Its application to refinery waste water after pre-treatment using different separation processes such as coagulation and flotation, looked at total petroleum hydrocarbons (TPH), 1,2-dichloroethane (DCE), dichloromethane (DCM), and MTBE. In this occasion, the study showed UV emission did not substantially impact the compounds degradation, except for DCM, which showed higher stability compared to others. Overall, an 83% removal rate was observed in the presence of UV. Other studies using $H_2O_2$ in combination with UV showed a reduction of phenol of 99% with an influent of 100 mg/l, a reduction of COD of 36% and 40% with influents of 350 mg/l and 9000 mg/l respectively, and a reduction of 98% for MTBE on an influent of 25 mg/l. When a catalyst TiO2 was used in combination with UV, COD saw a reduction of 93% on an influent of 970 mg/l.

### Applicability

See Fenton/Photo-Fenton Technique.

### Technology Maturity

Currently, many water reuse facilities rely on systems which treat municipal waste water effluent by a sequence of membranes (micro- or ultrafiltration and reverse osmosis (RO)) followed by an advanced oxidation process (most commonly UV/$H_2O_2$) A few water treatment companies were found to offer advance oxidation processes such as hydrogen peroxide/UV on a batch or continuous treatment mode. However, when applied to industrial waste water there is typically the need for a pilot before full implementation. No information of its full-scale use in refineries was found.

### Environmental Benefits

$H_2O_2$/UV typically has a small footprint and can be easily integrated with other treatment processes.

## Cross Media Effects

A few advantages in using this technique have been identified. The $H_2O_2$ reagent is completely soluble in water, there is no restriction of mass transfer, it is an active supply of •OH, and there is no necessity for a removal method after the treatment. The operating pH should be small (pH < 4) to void the impact of separating radical types, mainly ionic types such as bicarbonate and carbonate ions, which results in improving the degradation rate.

## References

VITO 2008, CWW BREF 2016, Elmobarak et al 2021, Garrido-Cardenas 2020, Rubio-Clemente 2015, Adetunji 2021

# Ozonation

## Description

The use of ozone (O3) has been extensively applied to eliminate undesirable organic pollutants in both purification of drinking water and wastewater treatment. Ozone (O3) is a selective oxidant that reacts with electron-rich organic compounds. Hydroxyl radicals (•OH) produced from the consumption of O3 is a nonselective oxidant, which quickly reacts with several organic composites at closely controlled rates of diffusion. The creation of radicals, for example the superoxide radical (O2-●) and hydroxyl radical (•OH), happens when ozone is combined with water, via a complicated series of reactions. The ozone oxidation rate in water is improved at a greater pH. The reaction integration of •OH and molecular ozone produces the oxidation of the organic compound. The ozone oxidation potential can be improved by adding hydrogen peroxide (H2O2). In fact, ozonation using H2O2/O3 systems was found to be the best AOP method for the disinfection of water. Similarly, the combination of ozone/catalyst was found to be more efficient for COD and TOC reduction, than ozone oxidation only.

The ozone process can also be improved through the decomposition of ozone with direct radiation ($\lambda = 254$ nm) which produces H2O2 as a transitional compound which then decomposes to •OH radicals. A study on the use of O3/UV on a wastewater sewage treatment plant showed that the major parameters affecting the efficiency of the UV/O3 process were the efficient distribution of O3, the monitoring of the comparative pressure in the reactor, the ratio of ozone added, and UV radiation intensity.

## Target Substance and Technique Efficiencies

Ozonation is primarily used for disinfection in Municipal waste water plants and increasingly for the degradation of organic compounds (primarily COD reduction). A study conducted on wastewater from a sewage treatment plant that uses a combination of O3/UV advanced oxidation process showed COD and BOD reductions of 43% and 32% respectively. The required dosage of ozone should be determined experimentally. A typical ozone dosage is 2 kg ozone/kg COD.

## Applicability

Ozone systems, as per other AOPs, can be used in a multi-injection point scheme for pretreatment, intermediate oxidation and polishing to improve efficiency, lower ozone doses, and reduce total ozone consumption and energy use. Ozone pretreatment increases the biodegradability of more recalcitrant substances for subsequent biological treatment.

### Technology Maturity

The usage of AOPs with ozone has more industrial uses in water treatment in comparison to all other AOPs. Ozonation has been applied in water treatment for several decades, first for disinfection, later for oxidation of inorganic and organic pollutants. In recent years, ozone has been increasingly applied for enhanced municipal wastewater treatment for ecosystem protection and for potable water reuse.

An example of ozonation in a refinery context is the PetroChina Sichan facility. With a volume of 2,500 m3/h, the system needed to treat two streams of effluents, one coming from the refinery's oil-based stream and the second one from the ethylene's salt-based stream. In addition, the system needed to comply with the following requirements:

- Reuse up to 70 percent of the wastewater effluent for cooling tower feedwater;
- Meet a maximum discharge flow rate of less than 430 m3/h;
- Comply with a chemical oxygen demand (COD) discharge standards of 60 mg/L.

The treatment sequence begins with a wastewater pretreatment process, including primary and secondary oil removal, nitrification and denitrification biological treatment, secondary clarification and lamellar clarification for polishing. Next, the effluents are combined and enter the reuse treatment line, which begins with a gravity sand filter followed by two water treatment processes: ozone oxidation and biological aerated flooded filters (BAFF), known as the SUEZ's Oxyblue process.

The reuse process is followed with ultrafiltration (UF) and reverse osmosis (RO). The RO reject is then fed to the brine treatment line where it undergoes hard COD removal using the Oxyblue process again and granular activated carbon (GAC) filtration.

### Environmental Benefits

Ozonation has typically a small footprint and can be easily integrated with other treatment processes.

### Cross Media Effects

Because ozone is an unstable compound, it cannot be stored or transported and has to be generated on site. After treatment, surplus ozone has to be eliminated, e.g. using a catalyst system based on manganese oxide. Safety requirements to handle ozone are strict.

### Reference

CWW BREF 2016, Veolia Ozonation Information, Elmobarak 2021.

# Electrical/Electrochemical Techniques

## Electrocoagulation

### Description

Electrocoagulation (EC) is a technology that involves the release of a coagulant by the electrolytic dissolution of metal ions from metal electrode following application of an electric current, resulting in simultaneous formation of hydroxyl ions and hydrogen gas production

(Cerqueira et al. 2014). The coagulants aggregate and precipitate suspended solids with a simultaneous adsorption of dissolved pollutants (Chaturvedi 2013). Electroflotation can be implemented after electrocoagulation where hydrogen gas bubbles ensure flotation. This approach is suited to small-scale systems, and when electricity is inexpensive. Small bibles of hydrogen and oxygen gas that are released from the electrodes collide with air bubbles causing pollutant particles to float. The process does not require any chemicals addition (except for pH control) and can tolerate a broad range of pollutants and fluctuation in influent quality. The process can be fully automated. It differs from other coagulation techniques in that it requires low operation costs, small land space requirement along with generation of uniform and finely dispersed gas bubbles (Ibrahim et al. 2001). The pollutant removal efficiency is dependent on solution pH, current density, temperature, etc. (Ibrahim et al. 2001).

### Target Substance and Technique Efficiencies

Electrocoagulation has been used to reduce organic and suspended solids from a variety of industrial waste waters. The technology reduces COD, O&G and suspended solids. Reported efficiencies for oily and industrial waste waters including refinery and oily bilge waters where 95% to >99% for oil/TPH, 81 to >97% for oil and grease, 93% for BOD, 87% to 99% for COD and 90% to 99% for suspended solids. One study reported a phenol removal rate of 97%.

Efficiencies reported by one manufacturer included phosphate (99.3%), toluene (99.9%), xylenes (99.96%), Ethylbenzene (99.86%) and free CN (99.99%).  The process can remove heavy metals as they adsorbed in the precipitated material. Removal efficiencies for metals reported by the same manufacturer include: As (97%), Cd (96.8%), Cr (99.9%), Co (82.7%), Cu (99.75%), Pb (99.96%), Mn (98.27%), Hg (98.45%), Ni (99.96%), Se (44%), V (99.24%).

Although electrocoagulation is a simple technique, potential reactions could be complex and difficult to predict. In general, the more complex the waste water matrix (the higher the amount and types of pollutants present), the more complex the reactions, the harder to predict the results. Laboratory tests are needed to verify the applicability of the technique.

### Applicability

The technique can be used as a standalone treatment process or in combination with other treatment processes. The literature shows several laboratory tests with an electrocoagulation configuration after the API and before the biological treatment. The technology can be scaled up to treat large volumes of wastewater.

### Technology Maturity

Most papers describe laboratory or small bench scale tests using effluents from a diverse range of industries. One company NuEnergy Technologies Corp in the US can scale up electrocoagulation plants of up to 2500 gpm or 15, 840 m3/day.

Another manufacturer offers a mobile multi-stage Electrocoagulation unit that has been deployed to treat Oil & Gas wastewaters including produced water from onshore drilling platforms; surface run-off from fracking activities for discharge to a local watercourse; treatment of waste waters from the decommissioning of oil refinery for safe discharge to site outfall. Volumes associated with these plants have been relatively low.

### Environmental Benefits

Electrocoagulation produces significantly less sludge and therefore much lower sludge handling costs.  Unlike chemically produced sludges, EC produces a broadly a neutral pH, easy to dewater and non-leaching, sludge.

### Cross Media Effects

Some authors claimed high capital costs while maintaining energy efficiency. The process can experience operating issues due to plugging of the electrodes requiring replacement. Manufacturers claim that compared with chemical coagulation, the operational cost is up to 88% less.

### References

Adetunji 2021, Mousazadeh 2021, Ibrahim 2022, Nuenergytech, Kolina, Dynameau, Ventilacqua, VITO 2008.

## Electrodialysis

### Description

Electrodialysis is a type of electro-membrane technology that separate ions by selective transport of a fluid through ion-exchange membranes under the influence of an electric field. In particular, electrodialysis produces two streams of different concentrations flowing in alternate compartments separated by cation and anion exchange membranes. In this way, when an electrical current is applied to the cell, positively charged cations the waste water migrates towards the cathode through the cation exchange membranes, and are rejected by the Anion exchange membranes, and vice versa. This results in the generation of diluted and concentrated solutions between the membranes.

Electrodialysis processes are different from distillation techniques and other membrane-based processes (such as reverse osmosis) in that dissolved species are moved away from the feed stream, whereas other processes move away the water from the remaining substances. Because the quantity of dissolved species in the feed stream is far less than that of the fluid, electrodialysis offers the practical advantage of much higher feed recovery in many applications. The process can be operated in a continuous batch mode. It can achieve treatment capacities of up to 20000 m3/day.

### Target Substance and Technique Efficiencies

Electrodialysis (ED) is mainly applicable for the removal of inorganic minerals, dissolved solids (TDS), and heavy metals.  ED can meet regulatory standards for some dissolved organics. Different efficiencies have been reported for different metals of between 75% and 99%. Higher efficiencies can be achieved for single metal effluents (Ni with 90%-95%, Cu with >97%, Cr with 79% to 99% and Cd with a maximum of 86%). A Concawe member tested electrodialysis at one of their refineries to remove metals (copper, nickel, zinc, iron and manganese). The test appeared to show electrodialysis to be less efficient than the usual physico-chemical treatment used.

### Applicability

On an industrial scale, electrodialysis is mainly applied to desalinate brackish water for drinking water production. In this application, electrodialysis tends to be more cost-effective than reverse osmosis for total dissolved solids feed concentrations of less than 3,000 ppm, or when high recoveries of the feed are required.

A large waste water treatment plant associated with a polymer manufacturing facility uses a combination of membrane bioreactor (MBR), electrodialysis reversal (EDR) and thermal vapor recompression (TVR). It has been reported that the combination of these technologies will enable the plant to reach near-zero liquid discharge (ZLD) and implement water reuse. The plant is planned to be commissioned in 2024 and will treat a total maximum flow of 600 $m^3$ each day.

### Technology Maturity

Several companies manufacture electrodialysis plants in several countries (Suez is one of main manufacturers). Electrodialysis represents some 4% of the desalination market after reverse osmosis and thermal distillation.

### Environmental Benefits

Removal of inorganic minerals, dissolved solids and metals.

### Cross Media Effects

Fouling and short membrane life due to precipitation of poor soluble salts can restrict the efficiency of ED. Electrodialysis produces reject water/brine with high concentration of salts/pollutants. Membranes need to be clean, through rinsing which produces waste and the membranes need to be disposed once their cycle life is finished. Considerable amount of energy is needed during treatment. Chemical usage during treatment is required for cleaning and the prevention of scales. Poor removal of non-charged substances such as organics, silica, boron, and microorganisms. Performs better than Reverse Osmosis in the presence of oil, and organic substances.

Mines et al. (2009) estimated an energy consumption of about 0.30–0.44 kWh/kg.

### References

Amakiri 2022, Shrestha 2021, Karim et al 2020, Veolia website, Mines et al 2009, CWW BREF 2016, VITO 2008.

## Combined Electrochemical Oxidation

### Description

This technique was identified as an emerging technique in the CWW BREF 2016. The electrochemical processes can be classified into two main groups: direct electrolysis and Indirect electrolysis. Direct electrolysis (also called ‘anodic oxidation’, ‘direct oxidation’ or ‘electrochemical incineration’) is where a pollutant reacts at the anode surface with adsorbed hydroxyl radicals. Indirect electrolysis is where the pollutant reacts in the solution with an electro generated reagent produced at the anode (e.g. O3, ClO-, Cl2, ClO2) or at the cathode (e.g. H2O2).

Combined electrochemical oxidation processes, integrate electrochemical, photochemical and catalytic oxidation to achieve optimal results in the degradation of toxic and non-biodegradable organic substances. Several configurations are possible:

- Anodic oxidation and cathodic generation of hydrogen peroxide (H2O2);
- Cathodic generation of hydrogen peroxide and UV irradiation;
- Catalytic electrochemical oxidation with in situ generation of hydrogen peroxide and a specific catalysts); and
- Electrochemical generation of oxidising agents (e.g. H2O2, O3), UV irradiation and varied catalysts.

The objective of these combined electrochemical oxidation processes is the creation of hydroxyl radicals, the ultimate cause of oxidation of the organic matter present in the waste water. Identification of the most suitable electrode materials generally necessitates carrying out specific tests adapted to the nature of the waste water that has to be treated.

### Target Substance and Technique Efficiencies

The technique is reported to be applicable to treat waste water loaded with persistent organic pollutants such as pesticides and herbicides; polycyclic aromatic hydrocarbons (PAHs); volatile organic compounds (VOCs); chelating agents. No efficiency data has been found.

### Applicability

Specialist discharges such as pharmaceutical, dye-stuff, landfill leachate and for disinfection and odour control in municipal waste water discharges.

### Technology Maturity

The use of this techniques has been reported to be used by the Lovö Waterworks in Stockholm, Sweden and by VTU Technology in the CoolOx water treatment plant in Graz, Austria. While EO technology has been applied in actual wastewater treatment to some extent, most investigations are still in the laboratory /pilot stage.

### Environmental Benefits

No reagents are used. Electrochemical methods are generally safe because of the mild conditions used (relatively low temperature and pressure) and the small amount and innocuous nature of the added chemicals.

Other advantages include:

- The treatment equipment is simple and requires little floor space;
- No secondary pollution is generated; and
- Treatment cycles are short.

### Cross Media Effects

Energy (to carry out electrolysis) is considered to be the most important cross-media effect. The techniques is reported to consume 9.2 kWh per m3 for waste water with an incoming EDTA concentration of 500 ppm.

### References

CWW BREF 201.

# Membrane-Based Techniques

## Membrane Distillation

### Description

This technique was identified as an emerging technique in the CWW BREF 2016. Membrane Distillation (MD) is a hybrid thermal-membrane process driven by the vapor pressure differential across the hot and cold sides of a hydrophobic membrane resulting in passage of water vapor through the membrane, followed by condensation to produce distilled water. The liquid feed to be treated by MD must be in direct contact with one side of the membrane and does not penetrate the dry pores of the membranes. The membrane materials most used in MD are polypropylene (PP), polyvinyl difluoride (PVDF), and polytetrafluorethylene (PTFE). The hydrophobic nature of the membrane prevents liquid solutions from entering its pores due to surface tension forces. As a result, liquid/vapour interfaces are formed at the entrances of the membrane pores. In MD, the membrane itself acts only as a barrier to hold the liquid/vapour interfaces at the entrance of the pores and it is not necessary to be selective as required in other membrane processes such as pervaporation. The main requirements for the MD process are that the membrane must not be wetted and only vapour and non-condensable gases must be present within its pores. The pore size of the membranes used in MD lies between 10 nm and 1 µm. Four main MD configurations exist:

- Direct Contact Membrane Distillation (DCMD), where an aqueous solution colder than the feed solution is maintained in direct contact with the permeate side of the membrane.
- Air Gap Membrane Distillation (AGMD), where a stagnant air gap is interposed between the membrane and a condensation surface.
- Sweeping Gas Membrane Distillation (SGMD), where a cold inert gas sweeps the permeate side of the membrane carrying the vapour molecules and condensation takes place outside the membrane module.
- Vacuum membrane Distillation (VMD), where vacuum is applied in the permeate side of the membrane module by means of a vacuum pump.

The advantage of the MD process in comparison to the conventional separation processes is that it relies on a lower operating temperature (much lower than boiling point) and near atmospheric pressures. In contrast to pressure-based membrane processes, MD in principle does not require additives like acids or anti-scalants because the membranes are a lot less sensitive to membrane pollution.

### Target Substance and Technique Efficiencies

The MD process has been successfully applied on laboratory scale for the separation of non-volatile compounds from water like ions, colloids, macromolecules; for the removal of trace volatile organic compounds from water such as benzene, chloroform, trichloroethylene; and for the extraction of other organic compounds such as alcohols from dilute aqueous solutions. No reported efficiencies for any of the targeted substances have been found.

### Applicability

The target application of MD is the desalination of saline waters such as seawater or brines. In addition to water desalination, MD has a wide range of industrial applications such as hydrogen sulfide removal, the treatment of wastewater from the pharmaceutical, metal finishing industries, direct sewer mining, oily wastewater, and water recovery from flue gas.

The technique has been reported to offer capability for the removal of metals from an effluent from a nano-electronics industry showed silicon, aluminium, and copper concentrations below their detection limits for the following influent concentrations: silicon (95.16 mg/L), aluminium (9.9 mg/L) and copper (3.5 mg/L) and has also been reported for the removal of toxic metals although no specific information was found.

### Technology Maturity

While significant research papers over the past decade focused on bench-scale testing and/or modelling of MD process, there were limited studies that addressed MD technology implementation at pilot and/or demonstration scale. Various MD vendors are at different stages of technology development with Aquastill, Scarab, Aquatech, KMX Technologies, and Memsift Innovations currently lead the commercial market. Most of the applications review tend to involve low volumes.

There are not known applications of this technique to fuel manufacturing effluents.

### Environmental Benefits

Separation/concentration of non-volatile compounds (e.g. ions, acids, colloids, macromolecules) from aqueous flows and the removal of trace amounts of VOCs like benzene, chloroform and trichloroethylene from water are the achieved environmental benefits of membrane distillation.

### Cross Media Effects

It is difficult to provide an overall assessment of this technology from laboratory and field scale tests since various designs exist for this technology with different membrane materials, module configurations, and energy efficiencies. This makes the results from these evaluations very specific to the vendors’ specifications rather than general technology assessment. Very limited studies were conducted where multiple MD designs were tested side-by-side to identify the pros and cons of each system based on a level playing field. However, results of research on this technique indicated that pre-treatment of the influent is important for stable operation of MD as the presence of chemicals in the feed can lead to MD membrane pore wetting. Although MD total energy consumption is high compared to RO, by using gas, with a much lower cost than electricity, the overall energy cost of MD can be comparable with RO.

### References

CWW BREF 2016, VITO 2009, Hussain A. et al, 2021

## Membrane Bioreactors

### Description

Membrane bioreactors (MBRs) combine biological processes and membrane filtration to achieve better treated effluent quality by exploiting the dual benefits of membrane separation and activated sludge processes (ASPs). The MBR process is an alternative to conventional activated sludge processes for biological waste water treatment and is BAT in the CWW BREF. It consists of the combination of a membrane process (e.g. microfiltration or ultrafiltration) with a suspended growth bioreactor. In an MBR system for biological waste water treatment, the secondary clarifier and the tertiary filtration step of a traditional aerated sludge system is replaced by membrane filtration (the separation of sludge and suspended solids). Typical arrangements consist of vacuum-driven membrane units submerged in the aerated portion of the bioreactor or pressure-driven membrane systems located outside the bioreactor. Membranes are typically configured hollow tube fibres or flat panels and have pore sizes ranging from 0.1 to 0.4 microns.

## Target Substance and Technique Efficiencies

MBRs are applied to a wide range of industrial and domestic waste waters with high organic loads to reduce COD, BOD and SS. Efficiencies from a MBR treating waste waters from a pharmaceutical manufacturing process showed removal rates of 95.2% for TOC, 99.7% for BOD, 95.2% for COD, 88.9% for TN and 95.2% to total phosphorous.

Experimental results from D. Bolzinella et, 2010 showed the following removal efficiencies:

Membrane Reactor Efficiencies for Target Substances

| Target Substance | Influent in ug/l | Efficiency in % |
|---|---|---|
| Arsenic | 8.7 | 31-43 |
| Cadmium | 0.9 | >99 |
| Cobalt | 2.6 | >99% |
| Chromium | 18 | >99 |
| Copper | 79 | 49-94 |
| Mercury | 1.3 | >99 |
| Manganese | 118 | 77-84 |
| Nickel | 71 | 48-65 |
| Lead | 51 | 16-43 |
| Selenium | 3.5 | 71 |
| Vanadium | 4.7 | 79 |
| Zinc | 306 | 77 |
| Benzene | 1 | >90 |
| Toluene | 2 | 65->95 |
| Xylene | 7 | 98->99 |
| PAHs | 2.2 | 95->99 |

## Applicability

MBR is an alternative to activated sludge biological treatment. The membrane bioreactor technique is applicable after highly efficient mechanical pre-treatment and for the removal of biodegradable compounds, suspended solids and microbial contaminants. It can be combined with nitrogen and phosphorus elimination. Membrane bioreactors can be applied when retrofitting existing plants or for new installations.

## Technology Maturity

Several commercial plants in operation in Europe in the chemical and pharmaceutical industries with high treatment capacities in the thousands of m3 per day.

## Environmental Benefits

MBRs achieves overall reduction of the load of suspended solids, COD, BOD, TOC, TP as well as reduction of the volume of sludge compared to conventional aerated sludge treatment. It has a smaller footprint compared with conventional aerated sludge treatment, especially if tertiary filtration and a UV disinfection unit would be necessary to achieve comparable output quality.

### Cross Media Effects

Cross-media effects include energy consumption (mainly for pumping and aeration), chemical consumption (for membrane cleaning) as well as membrane replacement. The energy requirements of MBR systems may be twice those of conventional activated sludge systems.

As with other membrane separation processes, membrane fouling is the most serious problem affecting the performance of MBR systems that can lead to significant increase in hydraulic resistance. Frequent membrane cleaning and replacement is therefore required, increasing the operating costs significantly. The primary method to address fouling is aeration along with periodic chemical cleaning. Membrane aeration to control fouling was reported to account for 35% to 40% of the total power consumption of an MBR.

### References

CWW BREF 2016, VITO 2008, EPA 2007, Cerqueira et al, 2013, Dizayee K.K. 2023.

## Micro and Ultrafiltration

### Description

Microfiltration (MF) and ultrafiltration (UF) are membrane processes that retain certain substances contained in waste waters on one side of the membrane. The liquid that permeates through the membrane is referred to as the permeate. The liquid that is retained is referred to as the concentrate. The driving force of the process is the pressure difference across the membrane.

Membranes used for MF and UF are 'pore-type' membranes which operate like sieves. The solvent and particles of molecular size can pass through the pores, whereas suspended particles, colloidal particles, bacteria, viruses, and even larger macromolecules are held back.

Microfiltration (MF) and ultrafiltration (UF) use hydrophobic membranes to remove particulate material and colloids to sizes up to 0.1 µm (MF) and 0.01 µm (UF). These membranes cannot remove dissolved salts and metals but produce a clarified effluent that can be used for certain uses (utility water or firefighting water in a refinery context). Membrane materials include glass fibre, polycarbonate, polyvinylidene fluoride, cellulose acetate and polyamide for microfiltration and polymers such as cellulose acetate, polyamide, polyimide, polycarbonate, polyvinylchloride, and copolymers of acrylonitrile and vinyl chloride among others. Hydrophobic membranes are susceptible to fouling in the presence of oil and hydrocarbons and for this reason granulated activated carbon filters are typically used to remove dissolved organic compounds prior to filtration. Ceramic membranes are now widely available and are more suitable for effluents containing oil.

### Target Substance and Technique Efficiencies

Targets of MF and UF are particulate material and colloids to sizes up to 0.1 µm (MF) and 0.01 µm (UF).

### Applicability

Membrane filtration (MF and UF) is applied when a solid-free waste water for downstream facilities, e.g. reverse osmosis or the complete removal of hazardous contaminants such as insoluble heavy metals, is desired. The choice between MF and UF depends on the particle size. Common MF applications include degreasing processes; metal particle recovery; metal plating waste water treatment; sludge separation after the activated sludge process in a central biological WWTP. Common UF applications include the removal of toxic non-degradable, segregation of oil/water emulsions; separation of heavy metals after complexation or precipitation; separation of compounds not readily degradable in sewerage treatment effluents. Microfiltration (MF) and/or ultrafiltration (UF) are typically used to remove suspended solids as pre-treatment for nanofiltration and reverse osmosis in tertiary treatment for the purposes of water reuse.

### Technical Maturity

Microfiltration and ultrafiltration are well developed techniques used in a variety of sectors such as the food industry (cheese, milk, juices, wine, beer), the metal industry, the textile industry, and the pharmaceutical industry.

### Environmental Benefits

The main environmental benefit is the treatment of waste water to achieve a quasi-solid-free effluent for further use or discharge.

### Cross Media Effects

Membrane treatment produces a residue (concentrate) of approximately 10% of the original feed volume, in which the target substances are present at levels approximately 10 times their concentration in the original feed that needs treatment or disposal. In both cases, the permeate water from a membrane process can potentially be reused or recycled in the industrial process, thus reducing water input and discharge.

Operating costs of MF ranged from €0,1 to €0.15 per m$^2$ of membrane.

### References

CWW BREF 2016, Concawe Report no 4/22, VITO 2008.

## Nanofiltration and Reverse Osmosis

### Description

Nanofiltration and reverse osmosis are membrane processes where the permeation of a liquid through a membrane, is separated into a permeate that passes through the membrane and a concentrate that is retained, due to the pressure difference across the membrane. These membranes can hold particles down to the size of organic molecules and even ions.

Reverse osmosis treatment systems are composed of polyamide membranes with pore sizes of less than 0.001 µm and they have a high salt rejection of 99%. They allow water to pass through and retain the solute (e.g. salts, metal ions and certain organics). They are more susceptible to fouling by the presence of hydrocarbons and therefore oil and grease concentrations limits are typically less than 1 mg/l, although concentrations in the ug/l range is known to have caused fouling problems.

Nanofiltration uses membranes of similar size as those in reverse osmosis and is used to remove selected organic compounds and for general softening. It has a lower salt rejection rate than reverse osmosis and therefore the operating pressure of nanofiltration is lower than reverse osmosis. NF membranes allow water, single valence ions (e.g. fluorides, sodium and potassium chloride) and nitrates to pass through, while retaining multiple valence ions (e.g. sulphate and phosphates).

Provided that the feed is particle-free, these membranes are mainly used when complete recycling of permeate and/or concentrate is desired.

## Target Substance and Technique Efficiencies

NF is applied to remove larger organic molecules and multivalent ions in order to recycle and reuse the waste water or reduce its volume and simultaneously increase the concentration of contaminants to such an extent that subsequent destruction processes are feasible.

RO separates water and the dissolved constituents down to ionic species. It is applied when a high grade of purity is required. Examples include desalination; removal of degradable compounds if biological treatment is not available, heavy metals, toxic compounds and the segregation of pollutants with the aim of concentrating or further processing them.

NF and RO are often used in combination with post-treatment techniques for the permeate, such as ion exchange or GAC adsorption.

In terms of the substances targeted in this report, these membranes can be used for the treatment of AOX, heavy metals, phosphates/phosphorous and phenols.

Efficiencies reported include cadmium and mercury at >90% (CWW),

## Applicability

Membrane units are arranged as modules either in parallel (to provide the necessary hydraulic capacity) or in series (to increase the degree of efficiency). NF and RO can be applied as tertiary treatment for reuse of the treated effluent.

## Technical Maturity

Nanofiltration and reverse osmosis are well established technologies for desalination (RO) and in the chemical industry. However, the use of membrane technology in fuel manufacturing sites to reuse treated effluents or to treat specific pollutants is not common.

## Environmental Benefits

The driving force for using NF and RO is the removal of toxic or inhibitory substances from waste waters and the reuse/recycle of the treated effluent in fuel manufacturing processes or external users.

## Cross Media Effects

Even under the best pretreatment regimes and programmes, membranes will foul and deteriorate in performance if cleaning is not ensured. So membrane systems should be designed in such a way that those modules can be taken offline and cleaned mechanically or chemically.

Membrane treatment produces a waste stream (concentrate) of approximately 10% of the original feed volume, in which the target substances are present at levels approximately 10 times their concentration in the waste water which may need further treatment prior to disposal or reuse.

Energy consumption has been reported at 1 to 3 KWh/m$^3$.

## References

CWW BREF 2016, Concawe Report no. 4/22, VITO 2008.

# Adsorption Techniques

## Granulated Activated Carbon and Innovative Adsorption Techniques

### Description

Adsorption refers to the transfer of gas or liquid molecules into a solid sorbent surface and holding them via physical and/or chemical intermolecular interactions. Adsorbents can be natural (e.g., charcoal, clays, minerals such as bentonite and vermiculite, zeolites, and ores) or synthetic (produced from agricultural products and wastes, industrial or urban wastes, sewage sludge, metal oxides, and polymeric adsorbents). Adsorption has been effective in removing dyes, and organic pollutants and metals from various industrial wastewater effluents.

Activated carbon (AC) for industrial wastewater treatment is usually applied in two forms powdered (PAC) and granular (GAC). AC can be used to remove organics such as pesticides, phenols, pharmaceuticals, organic halogens, non-biodegradable compounds, dyes, and metals such as Hg2+, Pb2+, Cd2+, Cu2+, and Ni2+. AC is also an efficient media for microbial growth, and biologically activated carbon (BAC) has been developed for the inactivation of biological pollutants within a short period. Attaching biomass to AC can remove contaminants by both adsorption and biodegradation. Cyanide, for instance, was found to be better removed by biologically activated GAC compared to virgin GAC.

Adsorption on natural materials such as zeolites has been gaining more interest. For example, Clinoptilolite, a type of zeolite, has shown high selectivity to Pb2+, Cd2+, Zn2+, and Cu2+ 10. Also, it was found that polymeric materials can be used to increase the efficiency of natural clay to remove heavy metals by modifying the natural clay into a composite named clay-polymer composite. For example, clay-poly(methoxyethyl) acrylamide (PMEA) composite has been synthesized to study its capacity to adsorb Pb2+ ions.

Natural phosphates (NP) constitute another category of raw adsorbents. NPs are abundant, cheap, and they are non-hazardous to the environment. Phosphates can be used for heavy metals removal. It was reported that NP has a monolayer adsorption capacity of 26 mg g-–1 for Cd2+ at a pH of 5.074. Another study reported a room temperature adsorption capacity of 200 mg Pb2+/g of rock phosphate (low-grade) when the initial aqueous Pb2+ concentration was 50 mg L–1. NPs have also been used to remove emerging and persistent organic contaminants such as Reactive Yellow (a reactive dye).

Industrial by-products such as carbonaceous wastes, agricultural by-products, mineral-derived sources, etc. can be used as low-cost adsorbents for industrial wastewater treatment. For example, steelmaking slag has showed adsorption capacities of up to 99.1%. Other examples of low-cost industrial by-product adsorbents are fly ashes, waste Fe, hydrous TiO2, and other waste products which can be fine-tuned chemically to enhance pollutant removal.

Biosorption involves concentrating pollutants, particularly heavy metals, by binding them with inactive microbial biomass mainly via adsorption and chelations. Examples include biomass sources such as peanut and hazelnut shells, green alga, orange peel, Rhizopus sp. Biomass, jackfruit, maize cob or husk, and their chemical modification or thermal conversion to AC have been used during biosorption.

Large numbers of studies have been focussed to develop highly efficient nano-adsorbents to remove heavy metals from wastewater with high performance and lower cost. Graphene, activated carbon and carbon nanotubes have been the most common and commercially studied adsorbents.

Hydrogels are another innovative adsorption technique made up of a three-dimensional (3D) network of hydrophilic polymers that maintain their structure by the physical and chemical linking between the individual chains. The important property of the hydrogel is that it can swell in water and hold a large amount of water while maintaining the structure. For a material to be considered a hydrogel, at least 10% of total weight (or volume) must constitute water. Along with heavy metals removal, hydrogels have been used for medicine and biomedical engineering.

### Target Substance and Technique Efficiencies

GAC is used for removing natural organic matter, synthetic organic compounds, and heavy metals. Adsorption efficiencies are typically high for most metals between 88% and 100% (Hg). COD has a reported efficiency of 50%-75%, Phenols 60%-80% and AOX >90%.

Bentonite, another type of clay has also exhibited high removal (>99%) of heavy metals removals like Cu2+, Co2+, Ni2+, Zn2+, and Pb2+ ions. The adsorption affinities of the metal species were as follows: Co2+>Cu2+>Ni2+ = Zn2+>Pb2+. Another study also reported the complete (100%) removal of Pb2+ from aqueous solutions using 20 g L-1 of bentonite.

Graphene has high removal efficiencies for between 78% (Ni) and 100% for Zn. Most other metals show efficiencies of >90%).

Carbon nanotubes present a higher variation in efficiencies with Hg at 25% and Cd at 96%. Overall high efficiencies were also observed for rice husks (Cr at 78% and other metals at >96%) and zeolite with average of >90% for most metals, Cd showing the lowest efficiency at 66%).

### Applicability

Adsorption has been primarily applied to metals and some organic compounds including general COD reduction. Adsorption can either be used before biological treatment for removing toxic compounds or be placed after the physio-chemical treatment steps for ensuring the complete removal of micropollutants.

### Technology Maturity

Conventional adsorbent materials such as activated carbon, zeolites and silica have been used for a long time in the treatment of fuel manufacturing waste water (Lawan). Non-conventional adsorbents such as industrial, or agricultural by-products such as rice husk and sawdust are a continued subject of research.

An example of application of GAC to fuel manufacturing and chemical effluents is its application at the PetroChina Sichuan refinery, where it is used to treat reject brine from the UF and RO treatment and after ozonation and biological treatment, as a polishing step.

### Environmental Benefits

High selectivity for specific contaminants. Some adsorbents are the waste of certain processes therefore contributing to the circular economy.

### Cross Media Effects

Although AC has a high adsorption capacity, it can maintain this capacity only until the adsorption material becomes exhausted with pollutants, requiring expensive thermal/chemical regeneration and the loss of a significant fraction of adsorbent during this regeneration. The regeneration process of GAC releases off-gases that contain the thermal and chemical decomposition products of the adsorbed compounds. With each regeneration, a proportion of about 10% will be lost and has to be replaced by fresh GAC.

The generation of off-gases with regeneration requires subsequent waste gas treatment, if not at the chemical site itself, then at the site of the regenerating company. If the GAC cannot be regenerated, it has to be disposed of as chemical waste and incinerated. This might be the case if the GAC is contaminated with persistent and toxic organics such as PCBs and heavy metals (CWW BREF). Other environmental impacts include the transport of spent GAC to and from regeneration, and the energy consumption of the regeneration process.

In addition, the adsorption mechanism of AC depends on various factors such as dispersive, electrostatic and chemical interactions and intrinsic properties of the solute and adsorbent, and hence the interaction between the pollutants and AC is difficult to predict.

The regeneration of zeolite adsorbent generates a concentrated stream of ammonia, which is sent to a conventional waste water treatment plant for biological treatment or, alternatively, which undergoes a treatment comprised of air stripping to recover ammonia, followed by adsorption in dilute acid to form a fertiliser which can be sold.

The comparative advantages of low-cost adsorbents described above such as steelmaking slag are their relatively low prices and abundance since they are natural materials or byproducts from agricultural and industrial activities. Required wastewater-pretreatment and fine-tuning the adsorbent materials are some limitations. Moreover, in some cases, the heavy metals in the slag may leach out and cause secondary contamination.

### References

Amakiri 2022, Shrestha 2021, Karim et al 2020, CWW BREF 2016.

## Ion Exchange

### Description

Ion exchange is the reversible interchange of ions between a solid (ion exchange resin) and a liquid. Ion exchange resins are made from insoluble polymers and are typically bead-shaped. Ion exchange removes undesired or hazardous ionic constituents of waste water and replace them by more acceptable ions from an ion exchange resin, where they are temporarily retained and afterwards released into a regeneration or backwashing liquid.

Along with absorption and adsorption ion exchange is a form of sorption. Ion exchange is a reversible process, and the ion exchanger can be regenerated or loaded with desirable ions by washing with an excess of these ions.

Typical ion exchangers are ion-exchange resins, zeolites, montmorillonite, clay and soil humus. Ion exchangers are either cation exchangers, which exchange positively charged ions (cations), or anion exchangers, which exchange negatively charged ions (anions).

Ion exchange equipment typically consists of a vertical cylindrical pressure vessel with a corrosion-resistant lining that contains the resin, usually as a packed column with several possible configurations. Control valves and a piping system direct the flow of waste water and regeneration solution to the proper locations. Finally, a system that regenerates the resin, consists of salt-dissolving and dilution control equipment.

Storage facilities for the regeneration chemicals are necessary.

## Target Substance and Technique Efficiencies

Ion exchange can be used to soften water by capturing multivalent cations, such as calcium and magnesium, for specific ion removal such as boron, or for full demineralization where all dissolved inorganic solids are removed from the water (WBCSD).

Ion exchange can remove heavy metal ions, cationic or anionic, such as Cr3+ or cadmium; soluble, ionic or ionisable organic compounds, such as carboxylic acids, sulphonic acids, some phenols, amines as acid salt, quaternary amines and alkyl sulphates.

Some ion exchangers are able to remove specific metals from the waste water. This selective ion exchange process is much more efficient in removing toxic metals from the effluent. Furthermore, the column is capable of a very high level of clean-up and is also able to operate efficiently with mixed content effluents.

Typical effluent ion concentrations that can be achieved are in the range of 0.1–10 mg/l with influent concentrations of 10–1 000 mg/l (80 to 99% efficiency). A 99% removal efficiency for phosphate has been reported.

Ion exchange is feasible as an end-of-pipe treatment, but its greatest value lies in its recovery potential. It is commonly used as an integrated operation in waste water treatment, e.g. to recover rinse water and process chemicals. Typical influent concentrations are between 10 mg/l and 1 000 mg/l. Suspended particles in the feed should be less than 50 mg/l to prevent plugging, thus gravity or membrane filtration are appropriate pretreatments.

## Applicability

Ion exchange is widely used in a variety of sectors including the food and beverage industry, hydrometallurgy, metals finishing, chemical, petrochemical, pharmaceutical technology, potable-water treatment, industrial water treatment, semiconductor, power, and others.

Chemical precipitation and ion exchange was reported for the removal of Hg from waste waters from the production of mercury salts.

## Technical Maturity

The technology is commercially available and has been tried and tested in industrial applications. No specific examples of their use in refineries were found.

## Environmental Benefits

The removal of undesired or hazardous ionic constituents from waste water streams.

## Cross Media Effects

The regeneration of ion exchange resins results in a small volume of concentrated acid or salt solution, which contains the removed ions originating from the resin. This enriched liquid has to be treated separately to remove these ions, e.g. heavy metals by precipitation.

The rinsing water from regeneration contains the same ions as the brine, but in relatively low concentrations. Whether this part can be discharged directly or has to undergo treatment depends on the actual concentrations. At a plant in Germany, the rinsing water from regeneration is reused in waste gas scrubbers.

Ion exchange implies the consumption of ion exchange resins, regeneration liquids, water for backwashing and rinsing, and energy for the pumps. The addition of other chemicals, e.g. to suppress microbiological fouling, may be necessary.

Sources of noise are the pumps, which can be enclosed.

No information on operating costs were found.

### References

CWW BREF 2016, Concawe Report no. 4/22, NFM BREF 2017.

# Extraction Techniques

## Extraction

### Description

Extraction or solvent extraction entails the transfer of a soluble substance from the waste water phase into a solvent. Preferably solvents should have low solubility and miscibility with water such as light crude, toluene, pentane, hexane and should be easily separated from the waste water because of density difference. Also, low toxicity and flammability solvents are preferred. Extraction typically operates in columns where the water brought into contact with the solvent using various configurations.

Downstream facilities include liquid/liquid separation and distillation of the solvent fraction. The remaining waste water phase normally has to get rid of the dissolved extraction solvent, e.g. by stripping or GAC adsorption. An extraction system also typically includes storage facilities for the extraction solvent and the residue.

### Target Substance and Technique Efficiencies

The use of extraction for the removal of phenols has been reported with abatement efficiencies of 99%.

### Applicability

Solvent extraction is used with a variety of organic contaminants and metal complexes, when a suitable solvent is available and if the contaminant concentration is not too low. At low concentrations, adsorption or biological treatment are preferable. Besides the recovery of phenols, extraction has been reported also for the recycling of metals such as zinc, phosphoric acid and esthers and chloro-aromatics.  Extraction is often used as a pretreatment to adsorption and/or biological treatment units.

### Technical Maturity

Extraction is a technique frequently used in the chemical industry, especially in the LVOC and OFC sectors. One example found of an extraction plant removing phenols from wastewaters from a resin manufacturing facility.

### Environmental Benefits

The removal of pollutants from waste waters and their recovery.

### Cross Media Effects

Potential loss of organic solvent during operation via emissions to air and residues in waste water. Potential pills/leakages of solvent into soils. After solvent recovery (distillation or rectification, the bottom residue that contains the extracted contaminants has to be disposed of as chemical waste, normally by incineration. Extraction involves the consumption of solvents and energy.

### References

CWW BREF 2016,

https://www.metso.com/globalassets/industry-pages/metals-refining/hydrometallurgy/solvent-extraction/brochure-solventextraction-4822-02-24-en-mng-web.pdf

https://kochmodular.com/past-project/phenol-recovery/

## Micro Porous Polymer Extraction (MPPE)

### Description

In the MPPE process, hydrocarbon-contaminated water is passed through a column packed with macro porous polymer particles. The particles are porous polymer beads, which contain a specific extraction liquid immobilized in the pores of the MPPE particle. The immobilized extraction liquid removes the hydrocarbons from the water. Only Hydrocarbons that have affinity for the extraction liquid are removed. The purified water is recovered from a separate stream while the hydrocarbons phase is recovered for discharge. MPPE is a compact and robust technology that requires preliminary treatment to function at maximum capacity with no addition of chemicals required (Veolia 2019).

Compared to other technologies, MPPE units are compact and have a small footprint. The unit is fully automated. Once installed, the unit can treat higher and lower flows and concentrations with minimum flow reduction. The units present no biological fouling because of periodic in situ regeneration by steam. The technique may be scaled up to treat thousands of m3 per hour.

### Target Substance and Technique Efficiencies

MPPE systems removes dissolved and dispersed hydrocarbons with efficiencies >99%, down to below ppb level and can treat different types of hydrocarbons, including aliphatic, aromatic, polyaromatic and halogenated hydrocarbons. Amakiri 2022, summarised previous authors reported efficiencies indicating removal of >90% BTEX and PAH from produced water including a 60% reduction in mercury and can also remove phenols. Reported efficiencies for gas/condensate and oil fields were >99% for BTEX and PAHs with influents of 300 to 3000 ppm for BTEX and 0.2 to 2.1 ppm of PAHs. The reduction for alkyl phenols was reported at approximately 30% with an influent of 14 ppm.

### Applicability

The technology is already used for treating produced water in offshore/onshore locations. Several examples found include: Ormen Lange Field in Norway, Prelude and Pluto in Australia, and examples in Rotterdam, Netherlands and in Germany. It has also been used for the treatment of contaminated groundwater in pump and treat systems and for the separation of surfactants in surfactant enhanced remediation projects, and for the treatment of groundwater with LNAPL and DNAPL. The technology is best suited for natural gas production/treatment facilities, LNG terminals/gas to liquid plants, chemical industries, specialty chemicals, pharmaceutical raw material producers and chemicals/oil storage distribution industry. The author could not find any known application of this technology in refineries although the REF BREF lists MPPE as an option for the treatment of fuel manufacturing waste water upstream of the biological treatment plant.

At the Kollsnes field in Norway, produced water treatment comes from 5 gas fields. The existing biological WWT failed when produced water from new fields was added to the feed. To remedy this, a MPPE (20 m3/h capacity) unit was placed upstream the biological WWT to removes toxic aromatics and PAHs. The Biological WWTP recovered within 3 months.

### Technology Maturity

The first commercial MPPE unit in operation was in 1994. As mentioned above, the technology is used for the treatment of produced water in offshore and onshore fields and for the treatment of contaminated groundwater. The technology has been listed by OSPAR as Best Available Technology (BAT) for the treatment of produced water and is commercialised primarily by Veolia.

### Environmental Benefits

Manufacturers claimed low energy consumption due to the low energy required to release hydrocarbons from MPPE particles (in situ regeneration), with an energy consumption claimed to be 50 times lower than steam stripping. Environmental benefits claimed include the generation of practically pure hydrocarbons that can be reused (in the context of produced water), low polymer waste given its long life, low noise, no addition of chemicals, no emissions to air and no sludge generation.

### Cross Media Effects

High cost of installation and maintenance have been reported by Amakiri 2022, however, others claimed cost competitiveness compared with air stripping and activated carbon, steam stripping and biotreatment systems.

### References

Amakiri 2022, Veolia, REF BREF 2014.

## Pertraction

### Description

In pertraction, the pollutants are removed from the waste water by absorption into an organic extraction agent or extractant with membranes forming the interface between the waste water and the extractant. Therefore, the extractant is not added directly to the waste water, as in a conventional extraction process. This eliminates the separation phase needed in the solvent extraction technique which is often difficult and time consuming. The flows of waste water and extractant can be adjusted to maximise the contact between the waste water and the extractant.

A pertraction system consists of one or multiple membrane modules that include membranes in a hollow fibre configuration to gain maximum membrane surface per volume. The extraction liquid flows down one side of the membrane with its pores filled with the organic extractant, while the waste water is passed along the other side of the membrane. In this way, the polluted substances diffuse from the waste water, through the membrane and to the extractant. The extractant can be regenerated using (amongst other things) a vacuum film vaporiser. It is also possible to reuse the extractant.

The choice of extractant depends on the selectivity desired. However, normally selective is not required to remove overall organic pollutants.

### Target Substance and Technique Efficiencies

Pertraction can be used to remove a broad spectrum of organic compounds (e.g. pesticides, monocyclic aromatic compounds, PAHs). The yield for removing hydrocarbons is generally high, also at low concentrations (ppb level). Values of more than 99.5% can be achieved. Is it particularly efficient for low pollution concentrations.

Lab scale experiments with industrial waste water show that pertraction can treat waste waters with a broad range of components including aromatic, halogenated and poly aromatic hydrocarbons. Removal of these components is possible down to ppb level. The performance of the pertraction process characterized by the mass transfer coefficient is proven to be independent of the concentration from the components to be removed between 100 mg/l and 0.1 ug/l (Jansen. A et al 1992).

### Applicability

Reportedly, pertraction is used the chemical, pharmaceutical and petrochemical industries; in surface treatment using organic solvents; in the metal industry; for tank cleaning; in chemical laundries; and in wood conservation.

The pertraction installation can be of very compact construction, thanks to the high specific surface area and good mass transfer of the pertraction membrane modules.

### Technical Maturity

The process has been demonstrated at pilot scale at various installations. A full-scale installation of 15 m3/h has been operational at an industrial site in the Netherlands since 1998 for the treatment of aromatic compounds with an efficiency of >95%. The installation of this system allowed the chemical installation to stop the operation of an onsite waste water incinerator saving 5 million m3 of gas annually. No other applications at industrial scale were found. Pertraction modules (incl. diaphragms) are now commercially available.

### Environmental Benefits

The technique was reported to have a low energy consumption and compared with extraction reduces the amount of extractant needed.

### Cross Media Effects

Spent extractant needs to be regenerated.

### References

CWW Bref, Janssen A., et al 1992, VITO.

# Precipitation Techniques

## Chemical Precipitation

### Description

This technique is a chemical reaction to form particulates (i.e. solid precipitate) that can be separated from the water portion by an additional process, such as sedimentation, air flotation or filtration. It is also a useful technique to remove colloidal precipitates such as insoluble heavy metal sulphides or hydroxides. The technique can also remove phosphorous. A chemical precipitation facility usually consists of one or two stirred mixing tanks, where the agent causing precipitation (i.e. precipitation chemicals) and possibly other chemicals (e.g. flocculants) are added, a sedimentation tank and storage tanks for the chemical agents.

Typical precipitation chemicals include lime, sodium hydroxide, sodium carbonate and dolomite to precipitate heavy metals; calcium salts (other than lime) to precipitate sulphate or fluoride; and sodium sulphide to precipitate heavy metals such as arsenic, mercury, chromium, cadmium, nickel. Polyorganosulphides are known to be used to precipitate mercury. The precipitation of metals as hydroxides is most commonly used.

The technique requires also the use of flocculants to assist further separation such as ferrous and ferric salts; aluminium sulphate; polymers (cationic, anionic or non-ionic); polyorganosulphides. Chemical precipitation as a pre-treatment technique in combination with coagulation and filtration is BAT in the LVOC BREF to treat copper from the oxychlorination process.

### Target Substance and Technique Efficiencies

Data from an operational chemical plant showed abatement efficiencies of 58% for cadmium (inflow of 36 ug/l), 87% for chromium (inflow of 390 ug/l), 95% for nickel (inflow of 1070 ug/l) and >87% for mercury, copper, lead, and zinc on inflows of between 680 ug/l (for mercury) to over 5000 ug/l for zinc (CWW).

### Applicability

Chemical precipitation can be applied at different stages of the waste water stream, such as directly at the source to remove heavy metals most effectively, as the main technique for the removal of phosphates, sulphate and fluoride, and to remove phosphates after the biological stage in a central WWTP, where the sludge is collected in the final clarifier.

### Technical Maturity

Chemical precipitation is a well-established technique in the chemical and metals industries with ready availability of equipment and chemicals. Its use has also been reported in the petrochemical industry.

### Environmental Benefits

Driving forces for its use is the removal of pollutants such as heavy metals and phosphorous from waste waters and the potential recovery of material.

### Cross Media Effects

The main cross media effect is the large production of sludge that needs further management. A chemical facility in Germany produces 700 kg of dry sludge per kg of heavy metals removed (3500 kg of wet sludge per kg of metals). The disposal of the sludge requires the consumption of chemicals and energy. Chemical precipitation of phosphorous often increases the production of sludge (by 26%), and results in poor settling dewatering sludge characteristics.

### References

LOV BREF 2017, ITRC 2010

## Crystallisation (METCLEAN)

### Description

Crystallisation is closely related to precipitation, but instead of a chemical reaction in the waste water a precipitate is produced on seed material such as sand or minerals, working in a fluidised-bed process (a pellet reactor system). The pellets grow and move towards the reactor bottom. The driving force of the process is the reagent dosage and pH adjustment. The technique consists of the cylindrical reactor with a bottom influent and a top effluent; the seed material such as pellets of filter sand or minerals which are kept in a fluidised-bed condition; and the circulation system with a recirculation pump.

Supersaturation of the salts occur at the bottom of the reactor where with the large crystallisation surface of the fluidised reactor almost all the anion or metal content crystallises on the pellets. Periodically (typically once a day), some of the pellets are discharged and replaced by new seed material.

### Target Substance and Technique Efficiencies

In most cases, crystallisation is applied to remove heavy metals from waste water streams and to recover them subsequently for further usage, but fluoride, phosphate and sulphate can also be treated. Abatement efficiencies unknown.

A commercial application offered by Veolia claims treatment efficiencies as high a 99% and the capability to treat several metals including: Cd, Cr, Hg, Mo, Ni, Se, Zn, Cu, V, Ba and Sr.

### Applicability

In principle, almost all heavy metals, metalloids and anions can be removed from all kinds of waste water by crystallisation. The formation of salt pellets is feasible when the solubility of the generated salt is low and the metal or anion crystallises quickly into a stable crystal lattice. Crystallisers can operate at flows of up to 10000 m3/h and treat pollutants' content of between 10 mg/l to 100 g/l. Crystallisers are compact and flexible allowing modular set ups. Reported uses of commercial applications include the treatment of:

Potable water contaminated by arsenic or nickel;

Groundwater contaminated with metals;

Industrial wastewater from metal treatment industries, wood preservation and tanning containing metals;

Flue gas desulphurisation metals-containing wastewater from power plants.

### Technical Maturity

Examples exist in the chemical industry for the recovery of zinc and nickel in the production of rubber additives, and of nickel in the production of elastomers. This technique should not be confused with evaporators/crystallisers offers by several waste water treatment contractors. These systems, such as the mechanical vapor recompression crystallization (MVRC) system is being used in recent years for the treatment of high salinity waste water.

A commercial application of crystallisation is offered by Veolia’s product MetClean, that utilises the adsorption process in a fluidised bed reactor to remove a range of metals from solutions.

Veolia Water Technologies' experience includes As and the following metals: Cd, Cr, Hg, Mo, Ni, Se, Zn, Cu, V, Ba and Sr.

Treatment efficiency is as high as 99% in a one process step.20 times less waste (by weight) is produced by using Met-Clean™.

The waste product resulting from the treatment is a granule with a dry solids content of 80-90%. The savings in waste disposal cost will normally be sufficient to finance the capital and operating costs for a MetClean™ plant.

The footprint of the MetClean™ process is relatively small, making it a very cost-effective solution for several applications.

### Environmental Benefits

The main benefit of crystallisation is the abatement or recovery of heavy metals.

### Cross Media Effects

To achieve good removal results, the reagents necessary to form the precipitates are normally added in an overdosage. Normally no waste or sludge arises, since the precipitated salts are attached to the pellets. They are almost free of impurities and their moisture content is only up to 5–10% after atmospheric drying. The pellets can be used to recover the abated pollutant substances. Sources of noise are the pumps, which may need to be housed for noise abatement.

### References

CWW BREF, Veolia METCLEAN information, VITO 2010.

# Other Techniques

## Evaporation

### Description

Evaporation of waste water is a distillation process where water is the volatile substance, leaving the concentrate as bottom residue to be disposed of. Its main aim is to reduce the volume of waste water or to concentrate mother liquors. The volatile steam is collected in a condenser and the condensed water is, if needed after subsequent treatment, recycled. As per distillation, operating under vacuum decreases the boiling temperature and enables the recycling of substances that would otherwise decompose. There are many types of evaporators. Their suitability depends on the individual requirements. Evaporators are usually operated in series, where the condensation heat of one stage heats the condensate (i.e. waste water) of the preceding stage. Operation under vacuum minimises energy demand. Evaporation is normally a waste water-free process, because the condensate will be recycled –with or without further treatment – and the concentrate will be recycled or disposed of as waste, e.g. by incineration.

### Target Substance and Technique Efficiencies

Depending on the influent and type of pollution, the effectiveness lies around 99%.

### Applicability

Evaporation is applied when concentrated waste water streams are wanted or recommended to concentrate mother liquors and liquors from waste gas scrubbing to recycle valuable substances; evaporate and crystallise solids, either to recover or remove them from the waste water effluent; pretreat the waste water stream by concentrating it before thermal exploitation, wastewater incineration or disposal as hazardous waste.

When material recovery is the main purpose, a pretreatment operation is required before evaporation can be started. This could include the addition of acids, bases, etc. to lower the volatility of molecular compounds; separation of insoluble, free liquid phases, e.g. oil; chemical/physical operations to separate heavy metals and/or other solids.

Further treatment, e.g. incineration, after evaporation is required if the concentrate is not recycled.

### Technical Maturity

One facility reported to be using evaporation.

### Environmental Benefits

The recovery of materials from waste water streams and the minimisation of the waste water volume sent to treatment.

Efficiency and simplicity: excellent quality of the distillate produced, suitable for factory multi-purpose reuse; high level of concentration of the polluting fraction for significant reduction of disposal costs.

Waste-to-energy water treatment by-product separation provides an effective alternative energy option to reduce energy costs, CO2 emissions and replace fossil fuels.

Reliability and cost-effectiveness: low maintenance requirements and energy consumption.

Versatility: can treat feed water with little or no pretreatment, including hazardous and difficult streams.

Zero liquid discharge (ZLD): distillate can be recovered and recycled as process water (when possible) or for other factory purposes, helping plants meet discharge obligations and providing a potential income or saving source.

Component recovery: valuable materials can be separated or recycled, including precious metals or Active Pharmaceutical Ingredients (API).

Eco-friendliness: low carbon footprint. This allows us to meet and exceed the discharge limits required by local environmental legislation.

### Cross Media Effects

Residues need disposal normally by incineration if not suitable for recycling. High energy consumption.

### References

CWW BREF 2016

https://www.veoliawatertech.com/en/solutions/technologies/hpd-evaporation-crystallization

## Naturally Improved Organisms

### Description

This technique was identified as an emerging technique in the CWW BREF 2016. The technique, as described in the CWW BREF 2016, consists of the use of naturally improved microorganisms (e.g. prokaryotic cells or bacteria, photosynthetic bacteria or eukaryotes such as yeasts, fungi and photosynthetic microalgae) to treat waste waters loaded with refractory TOC/COD. It requires the selection of natural microorganisms; the generation of microbial variants with enhanced characteristics to treat the targeted pollutants in waste waters; and the introduction of the improved microorganisms into the water treatment process. The technique is an alternative to other techniques such as chemical oxidation to treat waste waters which contain COD/TOC.

### Target Substance and Technique Efficiencies

A reduction of TOC/COD levels in water effluents is the environmental benefit of the technique. Depending on the characteristics of the waste water being treated at the plant the abatement efficiency can vary from 60% to 98% and 70% to 97% of the COD and TOC, respectively. These abatement efficiencies are related to pharmaceutical and chemical effluents.

A treatment study (Biswas T., 2023) was carried out to improve the removal of BOD from waste waters from a refinery and storage depot in India receiving and storing petroleum and petrochemical products. The wastewaters generated from the facility contained a mixture of complex hydrocarbons like BTEX, styrene monomers, acetone and methanol. The existing conventional physico-chemical treatment followed by an Activated Sludge (AS) system could remove approximately 67% BOD from wastewater, often not reaching discharge standard. The native microbes though present at the site could not perform to the levels required. Thirty-one indigenous bacterial strains were isolated from the wastewater, the majority of which exhibited metabolic ability to produce key enzymes linked to hydrocarbon degradation such as amylase, protease and lipase producers. Out of 31 isolates, 14 isolates showed growth in presence of toluene as the sole carbon source and most of these isolates were represented by the genus Bacillus. Upon scaling from a lab test (5 l per day) to a pilot (12 m3 per day) processing capacity, approximately 92% removal of biological oxygen demand could be achieved within 18 to 20 h at the ambient condition in two moving bed biofilm reactors combined in series.

### Applicability

The technique is generally applicable to new and existing installations in the industrial or municipal sectors This technique appears to be a common practise in optimising the biotreatment step of the water treatment plants of the fuel manufacturing sector. The biological make-up is constantly monitored with sludges being kept apart for dealing with feedstock changes or process mishaps.

### Environmental Benefits

A reduction of TOC/COD levels in water effluents is the environmental benefit of the technique.

### Cross Media Effects

None identified

### References

CWW BREF; Biswas T., et al, 2021.

## Falling Film Contactor

### Description

This technique is described in the LOVC BREF. A falling film contactor increases the mass transfer rate between immiscible liquids (typically a hydrocarbon in a water/aqueous solution) using a vertical cylinder containing metal fibres. When used for waste water treatment, pollutants in the water are transferred into the hydrocarbon phase. The aqueous phase adheres to (wets) the metal fibres and it flows down the length of the fibres by a combination of gravity and interfacial drag between the two immiscible phases. Hydrocarbons also flow through the cylinder concurrently and in between the aqueous-wetted fibres. The large surface area and tight packing of the metal fibres bring the ultra-thin falling films of the aqueous phase into close contact with the hydrocarbon phase. The interfacial surface area produced is an order of magnitude greater than in conventional extraction devices, allowing impurities to easily diffuse between phases. The use of a falling film also improves the efficiency of the subsequent phase separation process.

### Target Substance and Technique Efficiencies

The main target of this techniques is the removal of hydrocarbons and other organic substances.

### Applicability

The technology is stated to have been commercially developed and was subsequently implemented in Petrotel Lukoil Refinery in Romania, although this seems to be associated to the removal of mercaptans from hydrocarbons. However, no further information was available on other examples of implementation or development by the environmental technology providers.

### Technology Maturity

There are not known applications to fuel manufacturing effluents.

### Environmental Benefits

Reduction of hydrocarbon in the waste water stream is the main environmental benefit of this technique. No information was however available on the achievable concentration levels or abatement efficiency. The technology presents low operating costs and minimum consumption of chemicals.

### Cross Media Effects

None identified.

### References

LOV BREF 2017

https://merichemtech.com/mass-transfer-surface-area-with-fiber-film-contactor/

https://ir.exxonmobil.com/news-releases/news-release-details/petrotel-lukoil-romania-refinery-selects-exxonmobils-scanfining

https://condorchem.com/en/falling-film-vacuum-evaporators/

## ABMet

### Description

ABMet is a waste water treatment that removes nitrate and nitrite to non-detect levels through a biological denitrification process within a biofilter, resulting in the formation and off-gassing of nitrogen gas. The ABMet process also removes selenium by biologically reducing selenate and selenite to particulate elemental selenium which is then removed as waste solids collected near the top of the biofilter from where it flows by gravity to a waste storage tank, pond, or solids handling system. The biofilter contain a seed culture product that consists of specialized bacteria strains selected for treatment of selenium laden waters that are seeded only once.

Waste is typically decanted and supernatant recycled to the head of the system for processing. The effluent tank stores effluent for periodic backwashing of the biofilter for degassing and for the removal of solids, including elemental selenium.

The advantage of the ABMet treatment process is that provides selenium removal in a single step while other biological systems require numerous unit operations to transform selenium from one form to another (selenate to elemental Se) and then rely on other unit operations to remove the elemental selenium along with TSS and organics. With ABMet, selenium is transformed, captured and removed all within the biofilter while keeping TSS and organics below most discharge limits.

### Target Substance and Technique Efficiencies

The process can treat effluent total selenium concentration down to below 5 ppb-total selenium and BOD and TSS concentrations down to 30 and 35 ppm respectively (Vendors data).

A pilot study (19–38 L/min) performed by using ABMet® to reduce selenium levels from fuel manufacturing wastewater demonstrated selenium reduction from 368 µg/L to 2.3–4.7 µg/L after 3 weeks (Ali et al 2021).

### Applicability

ABMet removes nitrate and nitrite to non-detect levels through a biological denitrification process which is also capable of removing selenium. ABMet's can be deployed in a modular form scalable to treat any flow rate. Full scale systems have been designed to treat flows from 25 to 1400 gpm (6 to 318 $m^3$/h).

### Technical Maturity

The ABMet system has been demonstrated in applications treating Flue-Gas Desulfurization (FGD) wastewaters, coal power plant ash landfill leachate, coal mine waters, phosphate mine waters, metal refinery wastewater, and agricultural runoff waters. Not known application in the chemical and petrochemical industries were found. Commercially available with several providers.

## Environmental Benefits

The removal of selenium from waste waters resulting in an inert sludge. Low energy consumption and no use of chemicals.

## Cross Media Effects

No post-treatment required apart to oxygenation of the effluent. ABMet operates in an automatic mode requiring low labour input. The system uses a single nutrient that provides the source of carbon, nitrogen, phosphorus and micro-nutrients, therefore requiring one single injection point, no other consumables are used, and this results in low operating costs.

The system requires no to minimum downtime and has low energy requirements with typical power consumption of less than 0.2 kW per $m^3$ treated. Overall operating costs are typically <€0.5/$m^3$.

## References

Veolia brochure https://www.wateronline.com/doc/selenium-removal-technologies-a-review-0001, Ali I. et al, 2021.

# ANNEX B: TECHNOLOGY READINESS LEVELS

| Technology | Targeted Substances | Maturity Description | Technology Readiness Level (TRL) |
|---|---|---|---|
| Ultrasonic Reactors | Sulphates, COD, phosphates, heavy metals, phenols, MTBE | Information mainly obtained from laboratory/small pilot in simulated environment. According to CWW BREF 2016, the technology has been implemented in Rimex Metals Ltd, UK. The ultrasonic reactor is part of several treatment steps (pH adjustments and precipitation of heavy metals and phosphate), after which the ultrasonic reactor is used to removed biological phosphate. The process continues with flocculation, clarification and filtration. One company found to offer small modular ultrasonic reactors but is unclear what their proposed application is. Not known application in the fuel manufacturing sector. | TRL7 based on a successful demonstration of continuous operation |
| Photocatalytic Oxidation with TiO2 | General organic substances, BOD/COD removal, biodegradability improvement, specific pollutants (pharmaceutical, pesticides), toxicity reduction, phenol index. | This technique is probably only applicable to small-scale specialist treatment such as dye-stuff and pharmaceutical industry. The technique is likely less suitable for the fuel manufacturing sector. No known commercial application at industrial scale. | TRL 4 or TRL 5 based on laboratory scale tests in a simulated environment. |
| Combined electrochemical oxidation | Biodegradability improvement, TOC, COD reduction, pesticides and herbicides, VOCs, PFAS, PAH, BTEX | Its use has been reported in municipal treatment plants in Europe (Sweden and Austria) mainly for disinfection, odour control, and inactivation of viruses and bacteria. Unknown capacity. Unknown efficiency and applicability for the target substances (no efficiencies found). Not known application in a fuel manufacturing context. Not known commercial availability. | TRL 4 based on laboratory tests. |

| Technology | Targeted Substances | Maturity Description | Technology Readiness Level (TRL) |
|---|---|---|---|
| Supercritical water oxidation (SCWO) | Organic compounds, BTEX, Phenol index, recalcitrant substances such as PAH, PCBs, dioxins, etc | Commercial operating plants available for range of contaminants. It is considered primarily a polishing technique to treat recalcitrant organic compounds. Mostly low capacity plants with the largest known in the UK at around 3 $m^3$ per hour used to treat spent chemical catalyst to recover metals and 300 tons per day in a case treating sludges. No known use on fuel manufacturing effluents. Overall capacities seem to be small compared with fuel manufacturing sites average effluents. | TRL9 (commercial plants available for different operating conditions) |
| Wet Air Oxidation | COD, TOC, AOX | Mainly used for the treatment of spent caustics therefore small capacity (3 $m^3$/hr). Plants operating in India, US, Spain. | TRL 8 (difficult to assess given its main used for treating spent catalyst) Although commercial plants exist, they do not cover range of operating conditions for treating wastewater in refineries. |
| Membrane distillation | Ions, acids, colloids, VOCs, BTEX, metals | Many laboratory and several small-scale pilots have been carried out. Focused on sea water desalination and metals treatment. Offers potential for water purification in the pharmaceutical, chemical and textile industries. Various MD vendors are at different stages of technology development. | TRL 4 or TRL 5 |
| Naturally improved microorganisms | Refractory TOC/COD | Laboratory to pilot scale tests at a few refineries in Europe | TRL 6 |

| Technology | Targeted Substances | Maturity Description | Technology Readiness Level (TRL) |
|---|---|---|---|
| Falling film contactor | Hydrocarbons | The technology is stated to have been commercially developed and was subsequently implemented in Petrotel Lukoil Refinery in Romania, although this seems to be associated to the removal of mecaptans from hydrocarbons. No further information was available on other examples of implementation or development by the environmental technology providers. | TRL 5 Based on the need of successful demonstration in fuel manufacturing waste water treatment |
| Photo-Fenton method | COD, TOC, Phenol index, | Oxidation with hydrogen peroxide is used in various industrial sectors such as in the production of pesticides, in the pharmaceutical and chemical industries, the petrochemical industry, in waste management and others.<br>A few water treatment companies were found to offer advance oxidation processes such as hydrogen peroxide/UV on a batch or continuous treatment mode. However, when applied to industrial waste water there is typically the need for a pilot before full implementation. No installed, operating full scale plant was found in the literature search and no information of its full-scale use in refineries was found. One demonstration plant was found in Spain but did not focus on any of the targeted substances. | TRL 5 |
| Ozonation | COD, BTEX | Widely available commercially as a polishing step in municipal and industrial treatment plants including example in fuel manufacturing site with large capacity volumes (2500 m3/h) as part of site’s WWTP. | TRL 9 |

| Technology | Targeted Substances | Maturity Description | Technology Readiness Level (TRL) |
|---|---|---|---|
| Macro Porous Polymer Extraction | Dissolved/dispersed hydrocarbons, BTEX, PAH, | A mature technique (first commercial MPPE unit in operation was in 1994). The technology is commercially available for the treatment of produced water from oil and gas production facilities. The technology has been listed by OSPAR as Best Available Technology (BAT) for the treatment of produced water. | TRL 9 |
| Membrane Bioreactor | Metals, BTX, PAH, TOC, COD, TP, BOD, TN | Several commercial plants in operation in Europe in the chemical and pharmaceutical industries with high treatment capacities in the thousands of $m^3$ per day. | TRL 9 |
| Electrocoagulation/electroflotation | General COD, Suspended Solids, toxic and non-biodegradable substances, heavy metals, phosphates, Cyanides | Several manufacturers offer electrocoagulation plants for several sectors. Examples of small scale plants found to treat Oil & Gas wastewaters including produced water from onshore drilling platforms; surface run-off from fracking activities for discharge to a local watercourse; treatment of waste waters from the decommissioning of oil refinery/chemical plant. Treatment capacities of 15,000 m3/d and 24,000 m3/d have been claimed by companies in Europe and US although no operational examples were found. | TRL 9 |
| Electrodialysis | Inorganics, TDS, heavy metals, Oil & Grease. | Several companies manufacture electrodialysis plants in several countries. Electrodialysis represents some 4% of the desalination market after reverse osmosis and thermal distillation. | TRL 9 |

| Technology | Targeted Substances | Maturity Description | Technology Readiness Level (TRL) |
|---|---|---|---|
| Granulated Activated Carbon (GAC) | BTEX, Phenols, AOX, heavy metals | Extensively used in the textile industry, dry cleaning, the chemical industry, soil remediation, and the pharmaceutical industry. GAC is used as part of WWTP in a refinery in China. Widely commercially available | TRL 9 |
| Adsorption (hydrogels, nano adsorbents) | Heavy metals, Phenol, Cyanides | Non-conventional adsorbents such as industrial, or agricultural by-products such as rice husk and sawdust are a continued subject of research. | TRL 4 |
| Chemical Precipitation | Heavy metals, phosphates, sulphates | Chemical precipitation is a well-established technique in the chemical and metals industries with ready availability of equipment and chemicals. Its use has also been reported in the petrochemical industry. | TRL 9 |
| Crystallisation (also known commercially as METClean) | Heavy Metals, phosphate, Sulphates | Beyond its common use in the treatment of liquid discharges from Flue Gas Desulphurisation (FGD) processes, crystallisation has been used for the treatment of industrial waste waters, in particular in the chemical industry. Examples exist in the chemical industry for the recovery of zinc and nickel in the production of rubber additives, and of nickel in the production of elastomers. A commercial application of crystallisation is offered by Veolia's product MetClean, that utilises the adsorption process in a fluidised bed reactor to remove a range of metals from solutions. | TRL 9 |

| Technology | Targeted Substances | Maturity Description | Technology Readiness Level (TRL) |
|---|---|---|---|
| Pertraction | Organic compounds including PAHs. | Reportedly, pertraction is used the chemical, pharmaceutical and petrochemical industries; in surface treatment using organic solvents; in the metal industry; for tank cleaning; in chemical laundries; and in wood conservation. However, no examples were found. The process has been demonstrated at pilot scale at various installations. A full-scale installation of 15 $m^3/h$ has been operational at an industrial site in the Netherlands since 1998 for the treatment of aromatic compounds to replace the use of an onsite incinerator. No known applications in refineries. | TRL 6 (based on pilots at several installations and only one reported example at operational plant). |
| Extraction | Phenols, Metals (Zn), chloro-aromatics, esthers, phosphoric acid. | Extraction is a technique frequently used in the chemical industry, especially in the LVOC and OFC sectors for the recovery of phenols and other substances. One example found of phenol extraction from waste waters from a resin producer plant. No known applications in refineries. Manly used for recovery of solvents/substances rather than general reduction of pollutants in waste waters. Commercially available through several companies. | TRL 9 |
| Distillation | Refractory, toxic pollutants, phenols | Waste water distillation has limited applications such as recovering product from mother liquors in the chemical industry. When applied to waste waters it has been to recover the solvent after waste water extraction, to treat oil emulsions, to recover organics from scrubbing liquors. | TRL 8 |

| Technology | Targeted Substances | Maturity Description | Technology Readiness Level (TRL) |
|---|---|---|---|
| | | There is no known application in refineries and it is unlikely to be applied to reduction of pollutants in waste waters. Commercially available through several companies | |
| Evaporation | None identified | Evaporation is applied when concentrated waste water streams are wanted or recommended to concentrate mother liquors and liquors from waste gas scrubbing to recycle valuable substances.<br>One facility (detonators manufacturer) reported to be using evaporation. | TRL 6 |
| Ion Exchange | Heavy metals, phenols, Phosphates | Ion exchange is widely used in a variety of sectors including the food and beverage industry, hydrometallurgy, metals finishing, chemical, petrochemical, pharmaceutical technology, potable-water treatment, industrial water treatment, semiconductor, power, and others.<br>The technology is commercially available and has been tried and tested in industrial applications. No specific examples of their use in refineries were found. | TRL 9 |
| Nanofiltration and Reverse Osmosis | Heavy metals, AOX, phosphorous/phosphates, phenols | Nanofiltration and reverse osmosis are well established technologies for desalination (RO) and in the chemical industry. However, the use of membrane technology in refineries to reuse treated fuel manufacturing effluent or to treat specific pollutants is not common. | TRL 9 |

| Technology | Targeted Substances | Maturity Description | Technology Readiness Level (TRL) |
|---|---|---|---|
| Microfiltration and Ultrafiltration | Particulate material and colloids to sizes up to 0.1 µm (MF) and 0.01 µm (UF) | Microfiltration and ultrafiltration are well developed and commercially available techniques used in a variety of sectors such as the food industry (cheese, milk, juices, wine, beer), the metal industry, the textile industry, and the pharmaceutical industry. There used in the fuel manufacturing sector is not common and mainly used on water reuse schemes. | TRL 9 |
| ABMET | Nitrate, nitrite, selenium | The ABMet system has been demonstrated in applications treating Flue-Gas Desulfurization (FGD) wastewaters, coal power plant ash landfill leachate, coal mine waters, phosphate mine waters, metal refinery wastewater, and agricultural runoff waters. Not known application in the chemical and petrochemical industries were found. Commercially available through several providers. | TRL 9 |

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