REVIEW ARTICLE

A Brief Review on Working Fluid Wastewater Treatment: A Glance at the Disposal of Exhausted Fluids Used in the Organic Rankine Cycle

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Received: 05 April 2022
Revised: 01 May 2022
Accepted: 08 June 2022

Abstract

Background: Treating working fluid wastewater (WFW) by having several organic/inorganic pollutants is not an easy task. There are many hurdles to adopt an appropriate treatment strategy through biological, physical, chemical, and electrochemical approaches.

Methods: The treatment methods of WFW are reviewed in this work through a critical literature survey. Therefore, databases such as Google scholar, science direct, and PubMed were considered to find literature. Altogether, about 49 articles were finally found relevant to the topic to extract and interpret findings.

Results: The best solution to treat WFW could be an integrated approach by designing various AOPs for the pre-treatment and post-treatment of main units. For this reason, and to meet discharge standards, measuring intermediates and the toxicity of reaction solution and final effluent by bioassay could be a complementary tool. Additionally, if the used AOP is a photocatalytic one, applying catalysts with a low energy bandgap and designing reactors to utilize the highest amount of energy is crucial to make a process cost-effective. Furthermore, using aeration could increase the number of radicals by supplying oxygen and removing contaminants from the reaction medium. Finally, if AOPs are the pretreatment unit, removing halogens should be done to predict floc breakage in the next step.

Conclusion: Hybrid treatment approaches with at least 80% efficiency in degrading and removing micropollutants could be reliable methods to dispose of working fluid wastewater. However, further research on them in the future is essential because of discharging a considerable volume of them annually worldwide.

Please cite this article as: Golbini Mofrad MM, Sillanpää M, Parseh I, Ebrahimi A, Amin MM. A Brief Review on Working Fluid Wastewater Treatment: A Glance at the Disposal of Exhausted Fluids Used in the Organic Rankine Cycle. J Health Sci Surveillance Sys. 2022;10(3):266-275.

Keywords: Advanced oxidation process, Environmental pollutants, Fluid waste disposal, Industrial wastes, Rankine cycle

Introduction

Working fluid wastewater (WFW) is the water used in the sector of machinery industries for manufacturing. It contains mineral oils, surfactant mixtures, and various additives, which cause its high COD, typically 10000-100000 mg/l, TOC typically in the range of 3000-5000 mg/l, turbidity typically in the range of 13000-17000 NTU, and low biodegradability (BOD_5 to COD ratio) less than 0.4.[1-3] More than 2,000,000 m^3 metalworking fluids (MWFs) per year are globally used while WFW volume could be 10-fold higher owing to its prior dilution before use.[1, 3, 4] Among WFW, those produced by Organic Rankine Cycle (ORC) technologies are quite challenging to treat. The organic working fluid (WF) used for the ORC should comply with safety

requirements, be environmentally friendly, and be cheap. WFs in ORC processes are selected according to the design of the ORC system. They can be classified into three categories: (1) wet fluids, (2) dry fluids, and (3) isentropic fluids. Except for water, propane, ethanol, and some wet fluids, other fluids are dry and isentropic mostly. Dry and isentropic fluids can be simple (e.g., carbon dioxide and ammonia) or complex organics such as aliphatic (N-pentane, N-hexane, Propane, Neo-pentane, Isopentane, N-butane, Isobutane, Propylene) and aromatic or cyclic hydrocarbons (e.g., Toluene, Benzene, -Xylene, Cyclohexane, Alkylbenzenes), halogenated hydrocarbons (e.g., HFCs, HFE7100, N-perfluoropentane and other chlorofluorocarbons or refrigerants), ethers, and even oils containing these compounds to convert thermal energy into electrical one.[5-7] Therefore, most of these substances have complex chemical structures and even some of them are toxic to living organisms.[8] Finding the best-operating conditions, the efficiency of the processes, and an optimal amount of the used ingredients like catalysts and type of catalysts could be considered the state-of-the-art of this short review. Many investigations on WFW treatment have been done, but they did not suggest beneficial strategies for the currents contaminated with halogenated fluids and other fluids used in organic Rankine technologies (ORTs).

Methods

In this paper, the newest treatment approaches for WFW are reviewed based on the critical literature survey through databases like Google scholar, Science direct, and so on and by using keywords.

Results

Table 1 presents some photocatalytic oxidation and AOPs studies carried out in recent years on the pollutants of WFW. In addition, several research in this regard, summarized in Table 2, have pointed out process

Table 1: Advanced Oxidation Processes (AOPs) or photocatalytic oxidation-based treatment approaches are used for Working Fluid Wastewater (WFW).

The applied processes	The type of Pollutants or wastewater	Results
Ozone+Catalyst (Titanium oxide)[9]	Containing Oil & Grease, COD, total petroleum hydrocarbon TPH, BOD, BTEX.	Ozone efficiency for O&G and TPH were achieved at 86% and 82%, respectively at a dosage rate of 12 SCFH and 6 SCFH at the end of run time 120 min.
TiO2+UV[10]	Soluble and emulsified cutting fluids containing esters with cyclic alkane, aliphatic esters, Phthalic acid esters, and silicones.	70% of the organic load at pH 8 was decomposed for all fluids.
UV/H_2O_2/NiO[11]	4-chlorophenol	100% removal at 60 min under neutral pH, with 0.2 mol/L H_2O_2, and 0.05 g/L of nickel oxide.
Fenton as pretreatment[12]	Industrial wastewater containing Ethylbenzene, Dimethyl phthalate, 2,6-Bis(1,1-dimethyl ethyl)-4-ethyl-phenol, 1,2-Benzenedicarboxylic acid, butyl 2-methyl propyl ester, and some aliphatic.	47% COD removal efficiency under the optimum conditions: hydrogen peroxide of 90.0 mM, ferrous ions of 20 mM, pH value of 3.0, and reaction time of 120 min. The BOD_5/COD ratio of wastewater increased from 0.32 to 0.69,
Photo-Fenton[13]	Xylene	Under 15 mg/l of initial value, 5100 mg/l H_2O_2, 14.5 mg/l iron, pH 2.5-3, 94.5% xylene removal after 60 min, 100% TOC removal within 90 min was achieved.
TiO_2/light expanded clay aggregate granules (LECA).[14]	water synthetically polluted with ammonia	The ammonia removal was more than 85% within 300 min of the process with an optimum calcination temperature of 550° C and pH 11. The kinetics of photocatalytic reactions were well fitted with a pseudo-first-order model. By using floated TiO_2/LECA as a photocatalyst in the aqueous solution of NH_3, the ammonia was photodegraded into N_2 and H_2 gases, while NO^{2-} and NO^{3-} were formed at very low concentrations.
TiO_2 (suspended powder)/UV (Xe-lump)[15]	NH_3/NH_4^+	At a pH of 9.9 and with suspensions of 0.01% (w/v) TiO_2, a degradation yield of 44.1±4.4% was attained after 6 h, and less than 11.3% of the NH_3/NH^{4+}originally present was transformed into the unwanted reaction products NO_2^- and NO_3^-. After a longer period, all NO_2^- formed during the degradation of NH_3/NH_4^+surely would be oxidized to NO_3^-. A part of the NO_3^- is formed by the oxidation of solved N_2.
Graphene–manganese ferrite (rG–$MnFe_2O_4$)/ visible light irradiation as heterogeneous photo-Fenton[16]	Ammonia	92% degradation was achieved through visible light irradiation of 50.0 mg L^{-1} NH_3-N solution at pH 10.5 in the presence of 1.0 mmol/L H_2O_2 for 10 h. The product for the degradation of NH_3 was identified as N_2 but not NO_2^- or NO_3^-.
MW-CWPO by using graphite as a catalyst[17]	Cutting-oil in water emulsions (COWE) containing COD=14860 mg O_2/L, TOC=3320 mg/L, BOD_5=1065 mg O_2/L	Thorough demulsification and high mineralization (XTOC: 80%, XCOD: 85%) only after 10 min in optimum operating conditions as graphite: 10 g/L, H_2O_2: 15.7 g/L, pH_0: 9

Table 2: The hybrid treatment approaches are used for Working Fluid Wastewater (WFW).

The applied hybrid techniques	Type of pollutants or wastewater	Results
Biodegradation+UV/H_2O_2, UV/Fe^{2+}/H_2O_2, UV/TiO_2 [18]	Spent MWFs	The UV /TiO_2 system was the cheapest option to achieve an excellent COD removal (82% at 20 min retention time and 10 L min^{-1} aeration rate). The photo-Fenton system was found to be efficient in terms of degradation rate, 84% COD removal (1 M Fe^{2+}, 40 M H_2O_2, 20.7 J cm^{-2}, pH 3) and improving wastewater biodegradability. The UV/H_2O_2 system was the most effective in removing recalcitrant COD in the post-biological treatment stage.
CA-DAF+Photo-Fenton[1]	MWF wastewater containing TPH (e.g., phenol, aliphatic hydrocarbons, benzene dicarboxylic acid)	Removal efficiencies of 99.85% and 98.9% were obtained for COD and TPH at the optimized photo-Fenton as pH 3, FeSo4: 100 mg/l, and H_2O_2: 17.8 g/l. The optimized operating conditions for CA-DAF were found by trial and error as an aeration rate of 15-20 l/min, the pressure was set at 3 bars, and the saturation time of 30 min. Synergistic effect analysis at the optimal condition of photo-Fenton system constituents was obtained as H_2O_2/Fe^{2+}> UV/H_2O_2 > UV/Fe^{2+}. The reaction kinetic was a well-fitted pseudo-first-order kinetic model. The post-treatment cost was estimated at approximately $26 per 1 m^3 of DAF effluent, and this process with the obtained cost was economic rather than other post-treatment approaches.
Induced air floatation (IAF)+photo-Fenton[19]	The residual waters contaminated with xylene	Organic load degradation efficiency was 90.5% and 89% using 1mM of $Fe^{2+}$and 150 mM H_2O_2 and 0.26 mM of $Fe^{2+}$and 150 mM H_2O_2, respectively, after 20 min of the photo-Fenton reaction. The organic load mineralization of 100% can be attained at the end of the experiment (90 min) for all concentrations in the photo-Fenton process.
A biohybrid process as biofilter+bubble column bioreactor[20]	Petroleum and fine chemical industry wastewater containing benzene	Under 1 hr retention time, complete benzene removal was done.
Bioreactor+Fenton process[21]	Exhausted MWFs	Fenton pretreatment of the MWF effluent significantly improved the biodegradability index, so that BOD_5/COD increased from 0.1660 to 0.538. The developed two-step treatment method achieved an overall decrease of 92% and 86% in COD and TOC, respectively.
Electron beam irradiation (as pretreatment)+zero-valent nano iron AOPs+bioreactor[8]	MWF wastewater	The bioreactor had been inoculated with a five-membered bacterial consortium previously reported to be effective for the biological treatment of MWF streams.[22] Sequential hybrid electron beam irradiation, biological, nanoscale zero-valent iron and biological treatment lead to synergistic detoxification and degradation of both recalcitrant streams, As determined by complementary surrogates and led to overall improved COD removal of 92.8±1.4%, up from 85.9±3.4% for the pristine metalworking fluid. Electron beam pre-treatment enabled more effective biotreatment, achieving 69.5±8% (p=0.005) and 24.6±4.8% (p=0.044) COD reductions.
Ozone+bioreactor[23]	Waste MWF	The bacterial consortia consisted of Agrobacterium radiobacter, Comamonas testosteroni, Methylobacterium mesophilic, Microbacterium esteraromaticum, and Microbacterium saperdae. 72% COD reduction (26.9% and 44.9% reduction after ozonation and biological oxidation, respectively) was obtained. The complete degradation of three non-biodegradable (viz. benzotriazole, monoethanolamine, triethanolamine) (22).
Fenton+UASB (2 phase)+SBR[24]	acrylic fiber manufacturing wastewater containing organics, sulfates, and ammonia	The COD removal and effluent BOD to COD were 65.5% and 0.529%, respectively, with the optimal Fenton conditions as ferrous 300 mg/L; hydrogen peroxide 500 mg/L; pH 3.0; reaction time 2.0 h. Through a two-phase UASB reactor, mesophilic operation (35±0.5° C) was done with HRT 28-40 h. In HRT not less than 38 h, COD and sulfate reduction were respectively 65% and 75%. Sulfate-reducing bacteria (SRB) were estimated for 35% in the sulfate-reducing phase, while methane-producing archaea (MPA) were estimated for 72% in the methane-producing phase. During the SBR process, shortcut nitrification was obtained by temperature control of 30° C.
O_3/UV/TiO_2+biological treatment by macroalgae *Ulva spp.*[25]	produced waters of petroleum refineries	After 5 min of treatment, the O_3 /UV /TiO_2 combination was very effective, and phenol concentration decreased by 99.9%, sulfide by 53.0%, COD by 37.7%, O&G by 5.2%, and ammonia by 1.9%. In addition, the following reductions in contaminants were obtained after 60 min of oxidation treatment: phenols 99.9%, O&G 98.2%, sulfide 97.2%, COD 89.2%, and ammonia 15%. Wastewater depuration showed a significant toxicity reduction of EC_{50}=89.2% for bacteria and EC_{50}=85.7% for fish, which was due to the biosorption/transformation of metals and ammonia compounds during the biological treatment.
Nano zerovalent iron (nZVI)/O_2+aerobic biological treatment[26]	Waste MWFs	I78% reduction in (COD) by nZVI oxidation at pH 3.0 and 67% reduction in neutral pH (7.5), and 85% concurrent reduction in toxicity was observed. This hybrid approach achieved an overall COD reduction of 95.5%.

integration as the most efficient solution for treating WFW. The best solution technique to treat WFW could be an integrated approach by designing various AOPs. Because of this, and to meet wastewater discharge standards, measuring intermediates and the toxicity of reaction solution and final effluent by bioassay is a complementary tool. Moreover, if the used AOP is a photocatalytic process, applying catalysts with a low energy bandgap and designing reactors to use the highest energy will be a key point in making a cost-effective process. Furthermore, via aeration could increase the number of radicals by supplying oxygen and removing contaminants from the reaction medium. However, if AOPs are the pretreatment unit, removing halogens should be done to predict floc breakage in the next step.

Discussion

Disposal or Treatment Approaches
Biological Treatment

The microbial masses or flocs are responsible for the pollutants removal in suspended growth systems which are consisted of a wide range of microbial species. In attached growth systems, the treatment mechanism is the attachment of microorganisms to a surface, e.g., filter and biofilm, and the passing of wastewater current through biofilms and aggregations. Halogen-containing oxidants can destroy the formed biofilm and aggregations and speed up the dissolution of solid matter into solution as given in Figure 1.[27] This destructive phenomenon is famous as floc breakage. Extracellular polymeric substances (EPS) made of polysaccharides, proteins, humic substances, nucleic acids, and lipids are responsible for making bioflocs or aggregations. Bridging an aggregation with other aggregations is the main mechanism for making bioflocs.[28] Oxidizing organic contents of EPS by halogens (e.g., fluoride and chlorine) released after decomposing refrigerants and consequently degrading aggregations and biofilms lead to floc breakage in microbial growth. Therefore, control of these anions could be taken into account to prevent this phenomenon.

These processes are generally applied to treat wastewater with a desirable BOD_5/COD ratio>0.4 and a high concentration of low molecular weight organic compounds. Due to economic and environmental aspects, biological processes are commonly preferred to chemical processes.[29] However, WFW is characterized by BOD_5/COD ratio lower than 0.4, and even nutrient amount is very low that affects food to microorganism (F/M) ratio. Moreover, the presence of toxic pollutants in WFW, such as chlorofluorocarbons or refrigerants, inhibit bacterial metabolism and reduce biological processes' efficiency. Therefore, biological processes are typically applied along with other treatment methods such as chemical or physical processes as pre-treatment or post-treatment. Another limitation of WFW treatment by biological units is hydraulic retention time (HRT).[30] Singh et al. revealed that adding stimulants like NH_4Cl and KH_2PO_4 in limiting quantities stimulates microbial growth in each metalworking fluid biofilm bioreactor. It could be influential in solving the problem of WFW treatability and robusting microbial consortium. Also, they found that adding both chemicals in excess

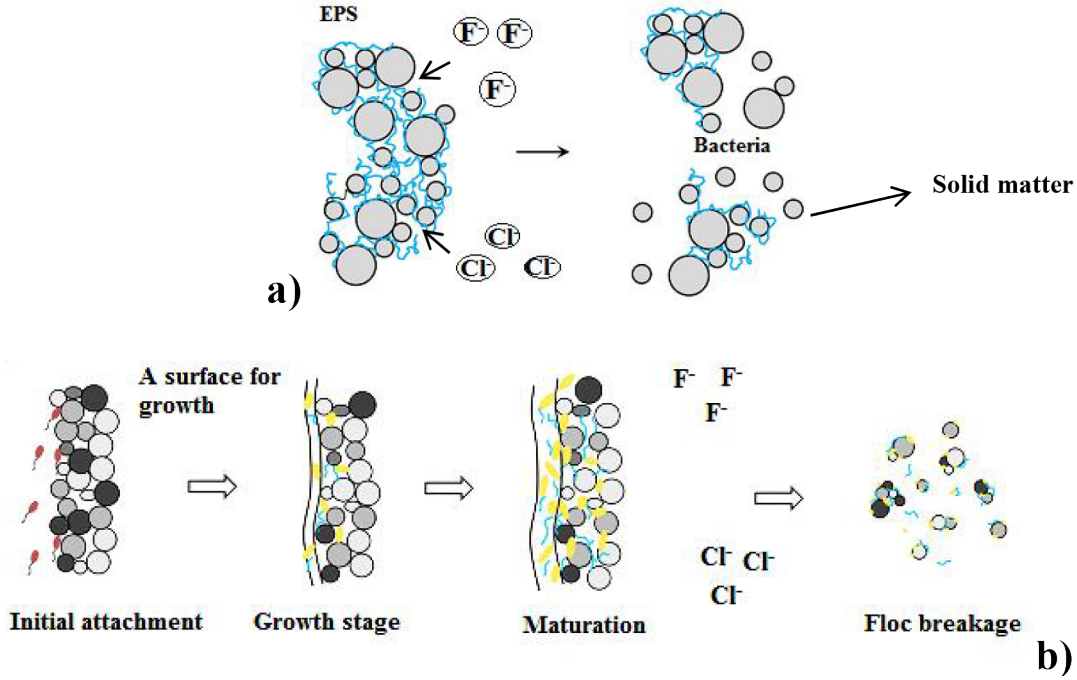

Figure 1: Oxidizing and degrading Extracellular polymeric substances (EPS) entangled with bacteria and solid matters initiated from Working fluids (WFs) as micropollutants, and floc breakage is caused by fluoride and chlorine ions after degradation of refrigerants. As a result, floc breakage in aggregations acts as a destructive factor on suspended and attached biological growth. a) Aggregation development in a suspended growth mechanism, b) Biofilm development in an attached growth mechanism

amounts to the bioreactor was prohibitive for biofilm yields. Although adding KH_2PO_4 led to a significant increase in total carbon removal performance, using NH_4Cl significantly decreased this performance. And, NH_4Cl stimulation improved saturated fatty amides and diethylene glycol butyl ether removals but curbed diisopropylamine removal. Additionally, the re-dispersion of recalcitrant organic matter resulted from restraining the oil/water separation carbon removal mechanism (a technique to separate and remove total carbon and oil) caused by NH_4Cl additions.[31]

Teli et al. investigated the role of biodegradation and physical-chemical mechanisms involved in the treatment of MWFs using a SAMBR. Among the detected physical/chemical removal mechanisms, bio-adhesion has been found to be the most critical one in MWF treatment with a reduced rate of 96% for TOC, while the membrane rejection mechanism is far insignificant by a TOC reduction rate of 0.2±0.18%. Bio-adhesion is an adherence mechanism of substances to biological surfaces like activated sludge flocs. Nonetheless, membrane separation will appear to be a severe removal rate after bio-adhesion has been saturated because the contribution from membrane separation is also poor, considering that bio-adhesion accounts for 96%. The deterrence of the hydrolytic/heteroacetogenic biomass was the most problematic sight in need for bioaugmentation of specific microorganisms to degrade MWFs. In the case of non-adoption during long-term operation, the bio-adhesive propensity of MWFs could be used as a potential method for removing MWFs from wastewater streams.[32] The membrane biological reactor (MBR) system effectively reduced COD by 90% for WFW, which is consistent with the results of other aerobic systems.[33] Gargouri conducted a study on reducing petroleum hydrocarbon content from engine oil refinery wastewater using a continuous stirred tank bioreactor (CSTR) monitored by spectrometry tools. The microbial consortium reduced the petroleum hydrocarbons (97%). After continuous aerobic treatment in the CSTR, the COD and BOD_5 average removals were as high as 97% and 78%, respectively. Also, C10-C35 n-alkanes (97.6%) was highly degraded after 200 days.[34]

Restricting nutrients for bacterial growth and preventing biodeterioration of MWFs within machinery works by immobilizing phosphorous using La_2O_3 to shape $LaPO_4$ instead of biocides could be influential in making MWFs safe for biological process treatment regarding the toxicity of biocides for any microbial growth. However, this alternative is applicable in producing eco-friendly MWFs before discharging the produced wastewater into the treatment unit.[35]

Bioaugmentation. Ławniczak and Marecik investigated the biodegradation potential of microbiota selected from miscellaneous environmental places towards different MWFs . The first experimental step was conducted to evaluate the biochemical oxygen demand reduction efficiency of the autochthonous and environmental microbial consortium. The following order explaining the biodegradation potential of consortium from the investigated places was found through the attained results:

Petroleum-contaminated soil>waste repository≥waste MWF tanks>pesticide-treated field>activated sludge>municipal sewage effluents.

For comparative goals, the most influential consortium isolated from petroleum-contaminated soil (PCS1) was considered for further analysis, along with the most influential consortium isolated from a waste MWF tank (WMT1). The evaluated consortiums obtained a complete biodegradation efficacy of decanoic and dodecanedioic acids as well as glycerin and polyethoxylated dodecanol. Notwithstanding, the PCS1 consortium was more versatile and revealed significantly higher biodegradation efficacy of mineral oil (80% compared to 50% in the case of WMT1). Analogously, tests using pristine and spent MWF solutions affirmed that the PCS1 consortium outperformed the WMT1 consortium within the biodegradation of MWF, including oil as the major constituent (COD removal of 80, 60, and 30%, respectively, in terms of semi-synthetic MWF, soluble oil, and spent MWF). Furthermore, findings of consortium dynamics evaluation applying quantitative real-time PCR after the biodegradation of various kinds of MWF confirmed that the PCS1 consortium was identified by high genetic stability.[36]

Physical, Chemical, and Physicochemical Treatment

The conventional physical treatment approaches for removing pollutants from aqueous solution include: adsorption by activated carbon, filtration (e.g., microfiltration, and nanofiltration) and membrane separation, sedimentation, centrifugation, dissolved air floatation (DAF), air or steam stripping, reverse osmosis, and other techniques based on separation.[10, 29, 37] The drawbacks/limitations of these approaches can be a long time for separation or precipitation, fouling via deposition, microbial growth, pore blocking, and macromolecular adsorption in filters and membranes,[38] the saturation of the activated carbon adsorption capacity, and the need for recovery, and secondary pollution by transfer of pollutant from the aqueous phase to the solid phase. Consequently, an expensive operation such as regeneration of the adsorbent materials and more processes of solid wastes are needed.[39] Chemical and physicochemical procedures are a practical option for the organic load removal from WFW, which can be coagulation and flocculation, chemical oxidation and hydrolysis, ammonia distillation (for the ammonia removal), open

evaporation ponds, electrocoagulation, AOPs, e.g., Fenton and photo-Fenton oxidation systems, etc.[37, 40] Disadvantages of chemical treatment procedures can be the consumption of chemicals, the safety of working with chemicals, the production of a large amount of sludge in chemical precipitation, especially coagulation and flocculation that need post-treatment for sludge, and long RT for precipitation.[39] However, chemical oxidation processes with strong oxidation agents such as hydroxyl radical (•OH), ozone, and other oxidants throughout AOPs are good strategies for removing non-biodegradable organic compounds from industrial wastewater.[41]

Coagulation. Chawaloesphonsiya et al. investigated chemical destabilization, coagulation, and flotation of emulsified MWF wastewater. For this reason, they selected a metal salt, aluminum sulfate ($Al_2(SO_4)_3 \cdot 14H_2O$), or alum as a coagulant. Effects of coagulant dosage and pH on destabilization performance were examined under the initial oil concentration in the range of 0.05–0.4% w/w (COD≈1700–15,000 mg/l) at the obtained suitable pH condition, and the optimal dosage of coagulant was evaluated concerning the terms of critical coagulation concentration (CCC) and zeta potential. The aggregation survey obtained the CCC at the Al^{3+}concentrations of 0.75 mM and 0.50 mM for emulsion (DE) and tap water emulsion (TE), respectively. Raising the coagulant dosage to 1.0 mM $Al^{3+}$for DE and 0.75 mM $Al^{3+}$for TE attained good separation behavior. Turbidities of 4–10 NTU can be attained in the pH range of 6.0–7.5 (95% efficiency). The same efficacy was achieved at a higher Al^{3+}dosage (1.25–2.5 mM). At this pH range (5–9), solid aluminum hydroxide ($AlOH_3$) was the dominant species apart from free Al^{3+}at pH < 5 and anionic $Al(OH)^{4-}$ at pH>9. This finding can describe the observed solid precipitates or flocs in the system, which is critical in the sweep flocculation mechanism. Properties of aggregates can influence the flotation behavior and even the operating condition.[42]

Electrocoagulation. Dias et al. studied the performance of a continuous electrocoagulation reactor along with an electrode polarity switch applied for treating an MWF from synthetic oily water. The influence of perforating the aluminum electrodes, altering the holes count, the distance between electrodes, and the flow rate were evaluated. Superior values of flow rate decreased final pH. Having 10 holes in aluminum plate electrodes, and by adjusting the flow rate and inter-electrode distance, 90.2±0.3% oil reduction was attained with an ultimate pH of 8.83, which was within restrictions permitted by legislation.[43]

AOPs

Photocatalytic Treatment-based Approaches

Photocatalytic oxidation processes are based on photoactivated metal oxides as semiconductors to remove contaminations in the aqueous medium. In photocatalytic systems, the UV irradiation of metal oxides upon diffusion of a photon with an energy higher than its bandgap results in the formation of electrons (e^-) in the conduction band and positive holes (h^+) in the valence band, as shown in Figure 1. The hole can either oxidize a compound directly or react with electron donors like water to form $OH^•$, which react with pollutants and mineralize them to CO_2 and H_2O.[11] Photocatalytic processes are divided into two types (1): homogeneous photocatalyst and (2) heterogeneous one.

In homogeneous photocatalysis, reactants and catalysts are in the same phase. By contrast, in heterogeneous ones, they are in different phases. The homogeneous photocatalysis systems include photo-Fenton ($UV/H_2O_2/Fe^{2+}$), UV/H_2O_2, and UV/O_3. $UV/H_2O_2/O_3$ have disadvantages such as sludge production, being uneconomical, especially UV/O_3 and UV/H_2O_2 as the process consumes large amounts of oxidant and has a high running cost. The heterogeneous photocatalytic systems with applying metal oxides such as UV/TiO_2, UV/ZnO, UV/NiO, $UV/H_2O_2/TiO_2$, UV/H_2O_2/ZnO, UV/TiO_2/US, UV/WO_3, UV/SnO_2, UV/Fe_2O_3, UV/Bi_2O_3, UV/ZrO_2, and other same processes. These processes have advantages, including faster reaction rates, low cost, and operating well at ambient temperature and pressure conditions.[11, 44-47] In addition, heterogeneous photocatalytic approaches can efficiently eliminate recalcitrant organic pollutants at low-cost energy. Figure 2 proposes the schematic of possible photocatalytic decomposition and mineralization for some working fluids (Benzene, Toluene, p-Xylene, Perfluoropentane, Neo-pentane). The photocatalytic degradation systems can be affected by parameters such as temperature effect, catalyst concentration, concentration of pollutants in the influent stream, initial pH, radiation intensity, oxidants concentration, reactor design, aeration, and the effect of ionic species (Table 1).

Hybrid Treatment Approaches

As shown in Table 2, air flotation-based treatment or pretreatment (e.g., DAF and IAF systems) indicates a good efficiency in COD, TOC, and TPH removal from wastewater containing high oil & TPH concentration.[1, 19] Oller et al., reviewed the combination of AOPs and biological treatment. They concluded that industrial wastewater treatment, either by AOP or by biological processes toxicity analysis is a decisive factor; so that, influents with high toxicity (>50%) necessarily require AOPs for the first step of treatment. On the other hand, non-toxic and partially toxic influents require biodegradability analysis during AOP treatment, and if the TOC amount of these currents is greater than

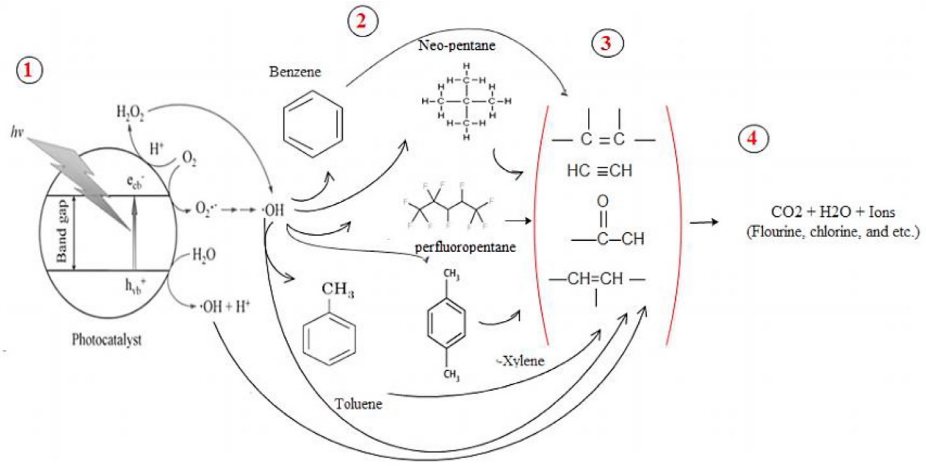

Figure 2: The probable photocatalytic degradation schematic of some Working fluids (WFs) used in Organic Rankine Cycle (ORC) technology: (1) Irradiation of photocatalyst by energy source (UV lamp or sun) for OH• production, (2) Attack of OH• to complex hydrocarbons or organic compounds (aromatic and aliphatic), (3) Producing of simple carbon-based substances, (4) OH•' attack to the produced simple substances, and mineralization (the CO_2, H_2O, Halogens, and formation of other ionic shapes).

500 mg/l, it is needed to dilute them to be imported into biological treatment. Also, AOP effluents can be discharged to the biological treatment unit if biodegradable.[48] Amin and et al. combined chemical addition- dissolved air floatation (CA-DAF) with the photo-Fenton process for treatment of MWFs. They found that this hybrid approach has removal rates higher than 98% for COD, TOC, and TPH, which can be a very effective strategy for achieving environmental discharge guidelines.[1]

Process Safety by Analyzing Intermediates and Bioassay

Thiruvenkatachari et al., observed the production of benzene and benzoquinone during treating wastewater contaminated with terephthalic acid.[49] Based on Gargouri's study, the simultaneous use of GC/MS and FTIR proved to be a useful complementary tool to assess the impact of treatment strategies on hydrocarbon-contaminated wastewater.[34] various papers observed Phenol as the photocatalytic degradation product of benzene.[50-53] Mofrad et al. investigated UV/H_2O_2/ZnO reactions as post-treatment for WFW. Within this study, Phthalic acids and compounds were detected as the main pollutants of influent and phenolic matters as intermediates of reaction.[2]

Bioassay can effectively assess the toxicity of AOP or chemical oxidation of effluent before discharge to the biological treatment step and even final effluent. Some studies have well revealed this issue. Corrêa's study showed a toxicity test with the *vibrio fischeri* (Lumistox) and the fish *Poecilia vivipora* as a proper option for bioassay of final treated effluent.[25] Rizzo investigated Bioassays as a tool for evaluating advanced oxidation processes in water and wastewater treatment. Later, it was found that proper application can be a really useful tool to evaluate the dangerousness of AOPs and set up the appropriate operative condition. The organism exposed to intermediates or toxic compounds should be chosen following the final application of the treated water matrix; for instance, inhibition tests with *D. Magna* may be appropriate to assess the toxicity of wastewater treatment plant effluent before its disposal to charge surface waters, also bioassay via plants may be appropriate to detect the toxicity of the treated effluent before its agricultural reuse. However, due to the low concentrations of micropollutants, acute toxicity tests cannot be the most appropriate to assess their ecotoxicological hazard, although they might have a chronic effect. Accordingly, research on chronic effects should be further expanded. A few notices should be considered in explaining the AOP's influence on industrial wastewater biodegradability. Toxicity analyses maybe not be appropriate for this purpose, so they can be applied just as screening experiments before applying more appropriate biodegradability tests (e.g., activated sludge bioassays, respirometry).[54]

Photocatalytic degradation and chemical destruction of WF and similar fluids can generate NO2- and NO3- from ammonia oxidation and organic intermediates as shown in Figure 1. For treating the WFW streams contaminated with ammonium, the degradation of NH_3/NH_4^+should not turn into producing NO_2^- and NO_3^-. To achieve higher degradation rates, doped or coated powdered catalysts could be applied to improve the adsorption of the NH_3^+at the photocatalyst surface, while the adsorption of N_2 should be avoided to decrease the formation of unpleasant NO_2^- and NO_3^-. Under optimized conditions, the pH required for a thorough degradation also might be lowered.[15, 16]

Conclusion

Treatment of WFW is complicated due to the presence of non-biodegradable and complex organics. Moreover,

toxic matters are bonded with halogens, ammonia, and other fluids used in machinery works and ORC technologies. Using stimulants effectively supports biofilms in biological treatment, but the prohibition of amine utilization and increasing emulsion stability are barriers for improving the microbial growth and WFW treatability. Another promising strategy to solve the problem of MWFs treatability in a biological process could be bioaugmentation, but there are not enough findings around reliable microbial species to make a decision. Therefore, according to the literature, it is suggested that AOPs-based-hybrid treatment approaches with optimized conditions have high efficiency and are the best option for their disposal. AOPs can be used as pretreatment for biological systems where making microbial flocs and growth is the case due to the release of halogens after biodegradation and being toxic for microbial consortium so that floc breakage is the result of oxidizing and degrading EPS by chlorine, fluoride, and other halogens. Moreover, they could be utilized as post-treatment for chemical, physical, and physicochemical units like DAF, IAF, and precipitation by coagulation and flocculation. Chlorine and fluorine ions must be controlled and removed when WF contains chlorofluorocarbons or refrigerants throughout aeration and adsorption. These ions harm photocatalytic degradation if they remain in the reaction solution. Additionally, tracing intermediates and final products in AOP is the case, and finding operational conditions is critical to operating that. However, due to the increasing use of new WFs in ORC technology concerning energy recovery worldwide, and consequently introducing new pollutants, doing and designing new treatment strategies and studies as well as toxicity assay is an insatiable need to tackle the challenge of their disposal in the future.

Conflicts of interest*:* None declared.

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