

# Supercritical water oxidation for the treatment of various organic wastes: A review

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**Abstract**— *The removal of complex organic and chemical industrial wastes is not accessible using conventional treatment methods. Incineration and hydrothermal oxidation under supercritical conditions are two options for dealing with a wide range of hazardous wastes. Incineration is an effective treatment for removing hazardous waste. The main disadvantages of incineration are a source of unwanted emissions and high operating costs. Supercritical water oxidation (SCWO) is considered a green technology for destroying organic waste with friendly environmental emissions. The removal efficiency reached 99.99% within a short residence time. In this review, the treatment of organic waste by SCWO is shown using co-fuel and catalysts to enhance the performance of SCWO.*

**Keywords**— *Co-fuel, hazardous wastes, industrial scales, supercritical water oxidation, treatment.*

## I. INTRODUCTION

The environment is facing the problem of the generation of hazardous and domestic waste. The amount of hazardous waste increases rapidly every year. The treatment of toxic and non-recyclable organic waste is not easy, and hazardous waste is difficult to remove using traditional methods. Environmental standards are moving in the direction of safe and complete removal of organic waste. Additionally, public health concerns are another constraint. The application of conventional treatment methods faces rejection because of the increase in legislation and guidelines that aim to protect the environment and human health [1–5].

Conventional treatment methods are used to treat organic hazardous waste, for example, biological treatment, chemical oxidation, incineration, and adsorption. These technologies have shortcomings that lead to a limited ability to remove organic waste. The emerging technology is supercritical water oxidation (SCWO), which has the power to destroy a wide range of non-recyclable waste. SCWO has gained attention in the last decade due to the advantages of this technology in the treatment of chemical weapons and complex industrial wastes. The main advantage is the destruction method

when compared with other methods, such as landfills, lagoons, and deep-well injections. Landfilling does not completely destroy hazardous components and contaminates air, groundwater, and soil. The systems of deep-well injection face the problem of plugging or fouling if the concentration of organic waste is 1% or more. Regulatory action and public concerns contribute to the restrictions on using land-based disposal of organic hazardous waste. Methods of destruction that depend on the oxidation of organic aqueous waste include incineration, wet air oxidation (WAO), biological treatment, activated carbon treatment, and SCWO. The treatment of diluted organic carbon content (less than 1%) is effective using biological treatment or activated carbon. In cases where the organic content is more than 1%, traditional technologies do not have a high probability of destroying waste. Additionally, the cost of these technologies is not economically suitable when the organic concentration is more than 1%. On the other hand, incineration is an effective method for dealing with a high concentration of organic waste of more than 30% [1,6]. The range of incineration temperature is 900–1100°C and excess air is 100%–200%. Incineration emissions must also be regulated to remove particulates, acids, gases, and NO<sub>x</sub> by expensive filters at the end of the incineration

process. The cost of these instruments is high when compared to the incinerator [1,7].

The range of organic content is from 1% to 20%. WAO or SCWO considers alternative treatment methods for incineration or activated carbon. WAO has the effectiveness for destroying wastewater and sludge. It converts organic waste into wanted by-products. WAO can be applied as an enclosed system. The capital cost of WAO is high compared to incineration, but its operating cost is less than incineration. In the WAO process, the energy of reaction and inorganic substances can be recovered. In addition, WAO has disadvantages that make this technology require enhancements; for example, the range of reaction time is from 15 min to 120 min, and the maximum removal efficiency reaches 75%–90% [8,9]. The conditions of WAO ranged 398–573 K as temperature and 0.5–20 MPa as pressure. These operating conditions are not suitable to destroy some organic waste, for example, m-xylene and acetic acid. Thus, the need to applying the environmental regulations and health standards is a motivation to use high temperatures and pressures that enhance the reaction medium. SCWO is used to deal with a wide range of organic waste with high removal [10,11].

## II. SUPERCRITICAL WATER OXIDATION (SCWO)

SCWO is powerful in treating industrial wastewater and sludge, with a removal efficiency of more than 99.99% [12,13]. The medium of supercritical water

takes place above 374°C and 22.1 MPa [14]. Water under these conditions will be converted to a non-polar solvent. The medium of supercritical water is a solvent for organics, and its properties increase the solubility of organics and gases. The supercritical water phase has advantages, including a single phase with free mass transfer limitations, an accelerated kinetics reaction, a high diffusion coefficient, and a short residence time [15–19].

SCWO could be considered an alternative treatment technology for mineralizing complex industrial wastes and hazardous military wastewater into wanted by-products and desired gaseous emissions [20]. Supercritical temperature positively influences the removal of organic waste when compared with pressure [21,22]. Thus, the range of operating temperature is 450–600°C, and pressure is 24–28 MPa [16]. This technology consists of several stages, including feed preparation and pressurization. Organic and oxidant streams are injected into the preheater separately to elevate the temperature of the streams to the required condition. Then, the organic stream and oxidant stream will be collected at the entrance of the reactor. The source of oxygen varies; for example, hydrogen peroxide is used on a laboratory scale, and oxygen or air is used on a large scale. The reactants leave via the reactor. After that, the products of the reaction pass through the heat exchanger to reduce the temperature of the reaction. Finally, the stream of liquid and gas passes via the back-pressure regulator to the separator phase with normal pressure and ambient temperature [22]. Figure 1 shows the main stages in the SCWO process [23].

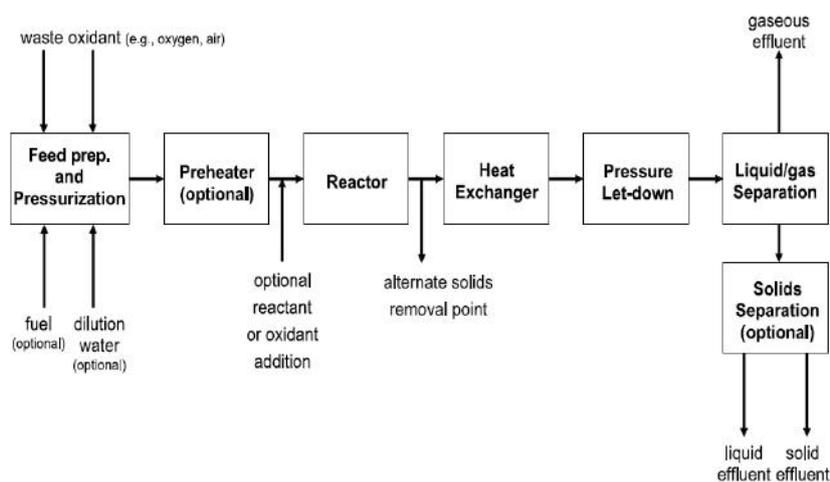


Fig.1: Stages of SCWO process

SCWO is an environmentally friendly treatment method. Gaseous emissions are CO<sub>2</sub> and N<sub>2</sub> if the waste comprises nitrogen-containing compounds. Air is used as a source of oxygen. Another gaseous emission is N<sub>2</sub>O, but this by-product can be removed by a catalyst. SCWO does

not generate NO<sub>x</sub> and SO<sub>x</sub>, while the same by-products are produced from combustion processes [24]. In addition, the operating temperature of SCWO is lower than the temperature of incineration. On the other hand, some waste contains heteroatoms that react to generate their

corresponding mineral acids. These acids are equalized with suitable bases to produce their salts. These salts are separated from the effluent. Finally, the main by-products of SCWO are desired water and wanted gaseous emissions[25–27].

*Feeding of solutions:* the first stage of SCWO system is injected organics and oxidant solution via two tubes separately to be heated and pressurized in two preheaters. The SCWO conditions must be achieved before mixing reactants at the inlet of reactor. Source of oxidant is various for example, hydrogen peroxide is employed for the laboratory scale, air or pure oxygen is used for large and pilot scales[1,22].

*Reaction:* the organics and oxidant solutions would be mixed at the entrance of the reactor. The reaction will start at the inlet of reactor. This reaction is exothermic under supercritical conditions. The released heat is contributed to enhancing the reaction rate[22].

*Cooling and depressurization:* the effluent of the reactor leaves with high temperature and high pressure. The temperature of stream at the output reactor is higher than the input temperature. The temperature of reaction stream will be reduced around the ambient temperature after leaving the heat exchanger, but the operating pressure of stream is still high. Then, this stream will pass through the back pressure regulator to reduce the operating pressure. The effluent leaves the back pressure system with ambient operating conditions to entering the separator phase. Gases pass via the top of the separator phase, while liquid and solid phases pass via the bottom of the separator phase. The main products of this technology are various gases (CO<sub>2</sub>, N<sub>2</sub>, other gases unreacted O<sub>2</sub> and N<sub>2</sub> O), water, salts, and metals. The products of SCWO are depending on the components of organics. The excess heat of the reaction could be applied for the generation of power and hot water for heating[22,28,29].

### **2.1 Operating Conditions of SCWO**

There are several operating conditions of SCWO such as temperature, pressure, residence time, oxidant ratio and initial concentration of organics.

Temperature and pressure are considered significant parameters to prepare the SCWO medium. Supercritical temperature has the positive influence the rate of reaction. The removal efficiency of wastes increases with increasing temperature. Numerous researchers have demonstrated the important effect of temperature on the destruction of hazardous wastes. The range of temperature is from 400 to 650 °C[30]. The by-products of SCWO will be non-harmful above 650°C[31]. Supercritical pressure is an essential parameter. Some researchers demonstrated the role of pressure is important

for preparing the supercritical phase, but the increase of pressure is not significant. The range of pressure was investigated from 24 to 50 MPa. According to literature survey, the influence of operating pressure above 22.1 MPa the oxidation rate is not essential [22,29].

Oxidant ratio considers an essential condition in the SCWO process. Various oxidants are used in the SCWO process such as, hydrogen peroxide, air and pure oxygen. The scale of SCWO system and the cost of oxidant are considered the main parameters for choosing the oxidant. Hydrogen peroxide is used for the experimental work. Pure oxygen and air are applied for the large scale. The efficient of oxidant is different; hydrogen peroxide is quickly decomposed to free radical if compared with pure oxygen and air[32]. Several published papers were demonstrated the positive influence of hydrogen peroxide and it is easy to be delivered through pump.

Residence time is another important operating parameter. Selection of the residence time depends on the volume of reactor and capacity of pump (volumetric rate) in the continuous system. The range of residence time is from second to several minutes in SCWO. The flow rate must be turbulent at different supercritical temperature [1].

Initial concentration of organics has a significant influence the rate of reaction. The range of organic content is from 1% to 20% under supercritical conditions. The high concentration >20% leads to increasing the exothermic reaction. Consequently, the released heat creates technical problems. Total organic carbon (TOC) and chemical oxygen demand (COD) are used to expressing the initial concentration of organic in SCWO process[1].

## **III. SCWO FOR TREATING ORGANIC HAZARDOUS WATES**

Researchers have carried out the SCWO process to deal with a wide range of sludge and dangerous organic wastes; the findings have demonstrated the effectiveness and viability of SCWO technology. There are many applications of SCWO on small and industrial scales that show the power of this technology. Various contaminants were treated by SCWO, such as biphenyl [33], polychlorinated biphenyls [34,35], 3-methylpyridine [36], pyridine [37], phenol [38], benzene [39], methyl tert-butyl ether [40], Thiodiglycol [41], o-creso [42], methanol [43], ethanol [44], urea [45], ammonia [46], and pesticide [47]. These examples were for models of chemical substances. Additionally, SCWO has the same power to destroy real waste. Studies will be reviewed in this paper.

### **3.1 SCWO of Nitrogen-Containing Hydrocarbons**

Numerous studies have been carried out on the destruction of nitrogen-containing hydrocarbons present in wastewater, such as ammonia, aniline, naphthalene, quinazoline, p-nitroaniline, N,N-Dimethylformamide, fenuron, and real waste (as leachate). The primary reasons to select this group are (1) the decomposition of nitrogen-containing hydrocarbons in water would produce ammonia, nitrate, and nitrite that would be considered toxic to aqueous life, such as fish or humans; (2) the chemistry of nitrogen is complex: the incomplete destruction of these wastes by incineration would generate unwanted substances, such as  $\text{NO}_x$ ; and (3) nitrogen-containing wastes are disposed of in various industries [48–54]. Most of these studies examined the effects of SCWO operating conditions on the removal efficiency of nitrogen-containing hydrocarbons and their intermediates, TOC removal %, and COD removal %. In addition, some studies have focused on the mechanisms of the reaction to determine the behavior of nitrogenous hydrocarbons under various operating conditions. The main investigated by-products of this group are molecular nitrogen, ammonia, nitrate, and nitrite. Other studies have determined kinetic parameters to study the rate of reaction [55–57].

### **3.2 SCWO of Non-Heteroatom Organic Compounds**

Many studies under supercritical conditions have been carried out on the removal of aliphatic or aromatic non-heteroatom compounds. These compounds are produced as wastewater by various industries. Wastewater effluents need to be investigated by SCWO to assess their treatability. Previous SCWO studies have concentrated on different organic compounds, including methane, acetic acid, and phenol.

Savage and his team oxidized methane in a tubular reactor under supercritical water conditions; the reaction temperature ranged from 525 to 587°C and the pressure was 250 atm. The main product at a low conversion was CO, while  $\text{CO}_2$  was the main product at a high conversion of methane [58]. Another team, Aki and Abraham, employed a catalyst, using  $\text{Cr}_2\text{O}_3$  and  $\text{MnO}_2$  to partially oxidize methane and produce methanol. All experiments were carried out in a tubular reactor under a supercritical environment; the operating temperature ranged from 400 to 475°C at a constant reaction time. The main products were methanol and formic acid. Other methane conversion products were acetic acid, acetone, and ethyl alcohol [26].

Another resistant organic compound, acetic acid, has been investigated by several researchers. Lee and his group examined the effect of hydrogen peroxide and oxygen on the conversion of acetic acid in a batch reactor;

the reaction temperatures were 400, 450, and 500°C. They found the acetic acid conversion to be significantly improved by using  $\text{H}_2\text{O}_2$  to reach 97.7% at 500°C and 10 min more than  $\text{O}_2$  to reach 64.3% at 500°C and 30 min. The oxidant ratio was also examined; the effect of an increased oxidant ratio was significant, and the TOC removal efficiency improved at 5 SR and 450°C to reach 97.8% in the presence of  $\text{H}_2\text{O}_2$  and 63.9% in the presence of  $\text{O}_2$  [59]. Another study investigated acetic acid at 250 bar and an initial reaction temperature of 400°C in an adiabatic tubular reactor, with residence times of 34.2, 26.4, and 24.6 s. The concentrations of acetic acid were 3.35%, 3.92%, and 4.9%, respectively. The flow rate of the oxidant was replaced by changing the residence time. The results of the conversion of acetic acid were 30.5%, 98.4%, and 96.6% at high temperatures of 438, 558, and 568°C, respectively. The increment in temperature resulted from the oxidation of acetic acid, and the major by-products of acetic acid were carbon dioxide and water [60].

Phenol wastewater is produced by various industries and is an intermediate used during the treatment of organic compounds. This compound has therefore been investigated by several research groups. Thornton and Savage (1990) examined phenol under sub-supercritical operating conditions. Various ranges of residence time, operating temperature, and pressure were performed. Their results demonstrated the influence of residence time on the removal of phenol; the removal efficiency of phenol was 46.2% at 15.75 s and 99.8% at 66.75 s. Operating pressure showed a significant influence on the enhancement of conversion efficiency; for example, the conversion efficiency improved from 2.2% at 188 atm to 72.9% at 278 atm and 32 s [61].

### **3.3 SCWO of Real Wastes**

Cardona and his group destroyed landfill leachate using a batch reactor under supercritical conditions, and they found that the removal efficiency of TOC was 99.5% at 400°C, 30 min, and 300% of oxygen excess. In addition, the maximum removal efficiency of total nitrogen was 92.2% at 500°C, 100% oxygen excess, and 30 min [62]. Landfill leachate was treated with SCWO in a batch reactor. The authors investigated the temperature, oxidant ratio, and time in the presence of a catalyst of  $\text{CeMnO}_x/\text{TiO}_2$ . The results were significant with increasing temperature, oxidant ratio, and time in the presence of the catalyst. The catalyst is stable and active under supercritical conditions [63]. In the same work, researchers used methanol to enhance the removal of landfill leachate, and the effect of methanol on the removal efficiency of total organic carbon was significant.

Sánchez-Oneto and his team investigated the SCWO of cutting fluid wastes under a constant pressure of 25 MPa using a continuous flow system. The SCWO process destroyed these wastes, and COD and TOC removal reached more than 95% at 500°C. The removal of real waste confirms the possibility of this technology in the treatment of complex wastes[64].

Wenbing et al. (2013) examined the SCWO of oily wastewater in the presence of ethanol. They found that the increase in co-fuel contributed to the rising removal of COD, and they demonstrated the positive effect of temperature and pressure on COD removal[20]. The SCWO of oily sludge was treated using a batch reactor. This work investigated the effects of reaction temperature, pressure, reaction time, and the initial concentration of COD. The results demonstrated the positive effect of temperature and reaction time on COD removal efficiency. Pressure and oxidant ratio do not have a significant influence on the removal of organic matter[65].

Xu and his team showed the treatment of pesticides using SCWO. Temperature, oxygen ratio, and reaction time were examined in this work. They demonstrated a positive effect of temperature on the removal efficiency of COD and total nitrogen removal [47]. Furthermore, the oxidant ratio and the reaction time have a significant influence on the removal of COD at a temperature > 500°C. Zhang and his team investigated the SCWO of textile sludge, and this work showed the influence of temperature and oxidant ratio on the removal efficiency of total organic carbon and chemical oxygen demand. High removal was achieved at 550°C, and the oxidant ratio improved the removal of organic matter[66]. Other researchers have used SCWO for treating the textile stream using a continuous flow system. They demonstrated the positive influence of SCWO on the removal of the chemical oxygen demand[67].

### **3.4 SCWO of Nuclear Waste**

Nuclear power plants have used organic ion exchange resins in water treatment systems to reduce corrosion, remove radioactive contaminants, and control system chemistry. Organic resins are employed in cleaning processes for removing radionuclides and regeneration system water. The volume of organic ion exchange resins is large, and spent organic resins are contaminated radioactive materials; thus, there is a need for effective technology to protect the environment. Incineration is used to reduce the volume and destroy this waste, but unwanted radioactive materials (radionuclides), as well as harmful emissions, such as nitric oxides or sulfuric acid, are released from an incinerator when the temperature is raised more than 800°C [68,69]. Leybros et al. (2010) oxidized

organic resins under supercritical conditions. All experiments were carried out in a continuous supercritical system. The effluent was analyzed by GC/MS, and it was found that around 50 species were classified as cationic and anionic resins. The results showed that the TOC degradation of organic-rate resins was more than 95%. However, this work did not refer to radionuclide contaminants in the effluent or their destiny. In addition, the nitrogen compounds present in the effluent of the reactor without decomposition and sulfur were converted to sulfur ions. Lastly, the findings of SCWO have promised the ability of this technology to destroy organic resins and reduce unwanted emissions.

### **3.5 SCWO of Heteroatom Organics**

Numerous researchers have demonstrated the ability of this technology to destroy organic compounds containing hydrogen, oxygen, and carbon. SCWO has converted organic compounds to carbon dioxide and water, but when the organic compound contains heteroatoms, such as chloride and sulfate, the destruction of these organic compounds will generate acids that attack the system at a temperature range of 250–350°C. The organic compound influences the performance of the SCWO process. To control this problem, the solution would be to neutralize the organic compound with alkaline to produce salt. This step may produce dissolved salt, but if this salt does not dissolve in water under supercritical conditions, salt precipitation will occur in the SCWO system because the SCWO medium is not a suitable solvent for some salts. Consequently, salt accumulates on the wall and plugs the tubing. Both domestic and industrial wastewater streams comprise these heteroatoms organic compounds that were treated by SCWO to assess the performance and capability of this technology at different conditions, to deal with corrosion and salt precipitation and to enhance the efficiency of SCWO. In addition, the products of the conversion of these compounds might be considered dangerous when compared to the products of other organic compounds and must be treated before disposal into the environment[1].

Lee et al. (1990) showed the effect of hydrogen peroxide and oxygen on the enhancement of the removal efficiency of 2,4-dichlorophenol at 450°C and 2 min. The removal efficiency in the presence of hydrogen peroxide increased to 99.99%, whereas the effect of oxygen occurred less than the effect of hydrogen peroxide; for example, the removal efficiency of 2,4-dichlorophenol was 87% at 500°C and 10 min. Additionally, at 400°C, they found the effect of water density at reaction conditions on the conversion of this compound to be low[59].

Marrone and his team studied the destruction of methylene chloride in a tubular reactor under sub- and supercritical conditions. The experimental pressure was 246 bar, the operating temperature ranged from 25 to 600°C, and the residence time ranged from 7 to 23 s. The major products of methylene chloride conversion were hydrochloric acid, formaldehyde, carbon monoxide, carbon dioxide, methanol, and hydrogen, while the minor products were a low concentration of methane, chloromethane, and chlorinated hydrocarbons. The major compounds under subcritical conditions were formaldehyde and hydrochloric acid. Formaldehyde was converted into carbon monoxide and hydrogen. While the oxidation of this compound could generate CO, hydrogen, methanol, and HCOH, CH<sub>2</sub>Cl<sub>2</sub> and chlorinated hydrocarbons were still not oxidized at 550°C. The oxidation of methylene chloride was high at 600°C, and the main products were CO<sub>2</sub> and HCl [70].

Hatakeda et al. (1999) studied the effects of hydrogen peroxide and oxygen under supercritical water oxidation on the conversion of 3-chlorobiphenyl, with operating temperatures ranging from 473 to 723 K in a batch reactor. They also studied the effects of temperature and oxidant concentration. The efficient hydrogen peroxide significantly enhanced the 3-chlorobiphenyl conversion to reach 99.99% at 30 min and 0.36 g/ml, while the oxygen effect at the same conditions increased the conversion to 14%. The researchers referred to the role of free radicals in improving the TOC conversion. In addition, they used a flow system to destroy polychlorinated biphenyls and kanechlor at 30 MPa and 673 K; residence times ranged from 10.7 to 101.7 s using hydrogen peroxide, and the findings showed the conversion to be 99% in all runs. Twenty-two intermediate compounds were produced at oxidant ratio 56%, organic concentration 21 mM, and conversion 63.5%, including m-chlorophenol, biphenyl, dibenzofuran, 3-chlorobiphenyl, dichlorobiphenyl, 2-monochlorodibenzofuran, and 4-monochlorodibenzofuran. The team observed that a low concentration of nickel, iron, molybdenum, chromium, and cobalt occurred in the results of the Hastelloy C-276 analysis[34].

Ma et al. (2014) treated o-chlorophenol in supercritical water and studied the effect of sodium hydroxide and potassium hydroxide on the removal efficiency, and the yield of Cl<sup>-</sup> with the temperature range of 380–420°C. Their results showed the effect of potassium hydroxide on removal efficiency to be better than that of sodium hydroxide, and the effect of potassium hydroxide on the yield of Cl<sup>-</sup> to be significantly more than that of sodium hydroxide, due to the fact that potassium

hydroxide would generate free ions in supercritical water more readily than sodium hydroxide[71].

#### IV. ENHANCEMENT OF THE SUPERCRITICAL WATER OXIDATION

Operating conditions are considered the main parameters to improve SCWO, such as temperature, initial concentration, the amount of oxidant, and residence time. Pressure has not had a significant influence on the performance of SCWO[48]. In this section, the influence of other operating conditions, such as co-fuel and catalysts is reviewed.

##### 4.1 Enhancement SCWO by Co-Oxidation

This section discusses the use of co-fuel in SCWO, focusing on the role of co-fuel in improving the destruction of resistant compounds. Numerous examples illustrate the role of co-oxidation in SCWO. For instance, ammonia has been oxidized by various co-fuels because it requires a high temperature, a long residence time, and/or the addition of a catalyst to complete the destruction. Various co-oxidation fuels have been used in SCWO to improve the conversion of organic compounds. In general, the reaction of co-fuel and oxidant is faster. Thus, this reaction accelerates the oxidation process of other compounds in the reactor [72,73]. Co-fuels could be considered a second-generation source of free radicals when the reaction takes place; then, the free radicals contribute to an increase in the conversion of organic waste [72,74,75]. The excess heat released from the oxidation of co-fuels could add heat to the reaction. Then, the conversion of organic waste increases [74,76]. Yang et al. (2018) demonstrated that the hydroxyl group in IPA, ethanol, and methanol was active under supercritical conditions, contributing to an acceleration in the decomposition rate. The activity of co-fuels is good. Some studies have demonstrated that methanol decomposes faster than IPA, but IPA enhances the removal of nitrogen more than methanol[74].

Many examples have demonstrated the use of different kinds of alcohol to improve SCWO performance. Most results are important; for example, methanol, ethanol, isopropyl alcohol, and propylene glycol are investigated. Several reasons show the positive influence of alcohol on the SCWO rate. The main mechanism of the reaction under supercritical water conditions is free radicals. Oxygen reacts with water to generate powerful free radicals, such as HO· and HO<sub>2</sub>·. Then, free radicals attack organic molecules and convert them into water and wanted gases[77].

Using alcohol as a co-fuel under supercritical water conditions contributes to the generation of extra free radicals. Several studies have investigated the effect of alcohol on the SCWO process. Free radicals are unstable intermediates that accelerate the rate of reaction in a short time. The pathways of the reaction are modified by the oxidation of alcohol. Many researchers have used co-fuel to improve oxidation conditions; for example, the removal efficiency of DBU and DMF was enhanced using IPA [55,78]. High concentrations of ethanol were used to improve the oxidation of methylphosphonic acid [79]. Cocero et al. (2000) co-oxidized acetonitrile, aniline, pyridine, and ammonia with isopropanol [80]. Zhang et al. (2013) showed the positive effect of methanol on the removal efficiency of acidic acid or phenol [81]. Ammonia was treated with IPA, ethanol, or methanol, and the results were interesting in the presence of IPA [73,75,76,82–86]. The influence of co-fuel is considered significant due to its ability in enhancing the removal efficiency of organic waste, and it accelerates the rate of reaction under SCWOs. In supercritical chemical organic compounds, ethanol enhanced the removal of MAP acid; the results were positive when the concentration of alcohol was increased. Al-Duri et al. (2016) showed the significant effect of adding isopropyl alcohol on the removal of the TOC of DBU. Others have worked on the destruction of ammonia under supercritical water conditions. Oe et al. (2007) found that the influence of methanol on ammonia was positive when the ratio of [(methanol)/(ammonia)] was increased by more than 2. Yang et al. (2018) found that the activity of a hydroxyl group in monohydric alcohol was active and that the removal of total nitrogen improved in the presence of isopropyl alcohol better than the influence of ethanol and methanol [74]. In SCWO, most studies of the influence of co-fuel on the performance of this technology depend on the use of monohydric alcohol, but Al-kaabi et al. (2021) carried out a laboratory scale to investigate the oxidation of 3-methylpyridine with dihydric alcohol and compared the effect of propylene glycol and isopropyl alcohol on the removal of TOC and total nitrogen. Their results are remarkable, and the number of hydroxyls has a high influence on the SCWO process; at 425°C, the removal efficiency was enhanced and reached 93% at 10 s with a ratio of 3[(propylene glycol)]/[3-methylpyridine]. Various remarkable results have confirmed the performance of SCWO enhanced in the presence of co-fuel [36].

#### 4.2 Enhancement of SCWO by Catalyst

Golmohammadi et al. (2018) investigated synthesized catalysts, such as  $\text{Cr}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{MnO}_2$  nanoparticles. The findings were that the removal of tributylphosphate increased in the presence of nano-

catalysts. The performance of catalysts rose in the order of  $\text{CeO}_2 > \text{Co}_3\text{O}_4 > \text{Cr}_2\text{O}_3 > \text{MnO}_2$  [87]. Angeles-Hernández et al. (2009) also used a mixed catalyst ( $\text{MnO}_2/\text{CuO}$ ) to improve the destruction of quinoline. The results confirmed that the activity of a catalyst depends on temperature and pressure. The removal of quinoline was improved at the critical point of the water. In addition, the values of organic removal and TOC were close. In other words, the intermediates were destroyed due to the presence of a catalyst [88]. Civan et al. (2015) studied the SCWO of landfill leachate in the presence of a catalyst of  $\text{Ni}/\text{Al}_2\text{O}_3$ . They examined the effect of operating conditions, such as temperature, residence time, catalyst, and oxidant ratio. The results showed a remarkable effect of operating conditions on the removal efficiency of TOC and total nitrogen removal with  $\text{Ni}/\text{Al}_2\text{O}_3$  [89]. Ding et al. (1998) studied the oxidation of ammonia under supercritical water conditions in the presence of  $\text{MnO}_2/\text{CeO}_2$  in supercritical water; a packed-bed reactor was used with a continuous flow system. The results demonstrated that the rate of conversion was enhanced with the catalyst [90].

## V. SCWO REACTOR CONFIGURATION

### 5.1 Batch Reactor

This reactor is various and is used to destroy a wide range of hazardous waste. The batch reactor consists of two parts: the upper part is a supercritical zoom for the reaction and the bottom part is a subcritical zoom for dissolving precipitated salt [57,91].

### 5.2 Continuous Flow Reactor

Various wastes are treated using continuous flow reactors due to the possibility of development, and they can be used with different scales. The basic kind is the tubular reactor, which was enhanced to the transpiring wall reactor [92].

### 5.3 Transpiring Wall Reactor

This reactor consists of dual plates. The outer vessel is outer pressure-resistant, and the inner vessel is porous. Supercritical water passes through the porous wall to form a protective layer against corrosion and salt precipitation [93]. Transpiring wall reactors are applied to deal with halogenated hydrocarbons. Figure 2 shows the schematic of a transpiring wall reactor.

### 5.4 Floating-type reactor

A floating-type reactor was developed to avoid the problem of corrosion. This reactor consists of two vessels: the outer vessel is pressure-resistant, and the inner vessel represents the nonporous vessel. The supercritical

reaction takes place in the inner nonporous vessel. The space between the two vessels is fed by a small water stream to protect the outer vessel. In Germany, researchers studied this reactor and found that the results were significant when compared to the transpiring wall reactor results. Figure 3 shows the floating-type reactor [94].

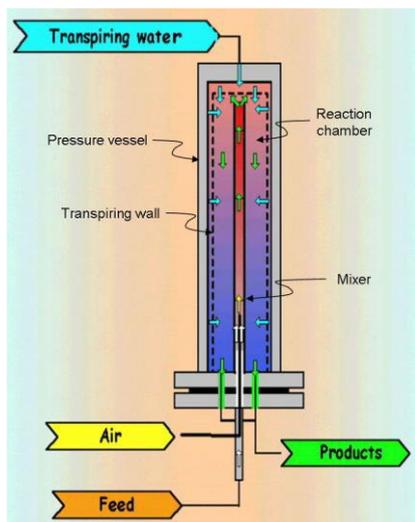


Fig. 2: schematic of a transpiring wall reactor[95]

## VI. INDUSTRIAL APPLICATIONS

Several researchers have summarized the current state of SCWO large-scale and pilot plants. The commercial spread of SCWO applications around the world faces obstacles, such as high pressure, salt precipitation, and corrosion. These problems lead to weak requests for this kind of application, although this technology has a high power to destroy organic waste. Thus, with the intensive study of problems of SCWO technology, a novel reactor will be developed to deal with various hazardous wastes, and SCWO will become an alternative process for incineration or landfill. Although the number of plants is limited, this method of treatment has high power for completely removing dangerous wastes compared to traditional methods[96–100].

Table 1 represents the list of SCWO plants. The first company was MODAR, which tried using SCWO technology commercially. The company started in 1980 and developed a novel reactor for dealing with a wide range of industrial organic wastes. In 1996, General Atomics acquired MODAR, and it employed this technology for destroying military waste. In 1998, the Organo Company in Japan, by depending on the MODAR system, built a large-scale SCWO plant[16,97]. In addition, the license for the MODEC process was given by Organo. The MODEC process was designed to avoid technical problems, such as salt precipitation and corrosion. Other Japanese companies, such as NGK

Insulator Ltd. and Hitachi Plant Engineering and Construction Co., have MODEC licenses. The MODEC process was developed by NGK and Hitachi for treating sewage sludge [22].

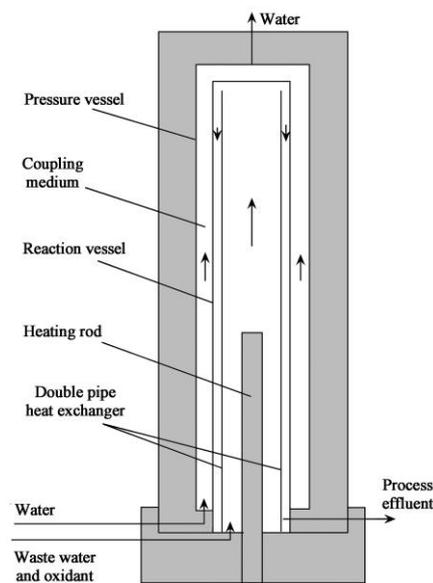


Fig. 3: Schematic of a floating reactor [94]

Two active companies in the United States, General Atomics (GA) and Foster Wheeler have carried out several projects for the treatment of military waste (USA forces). GA has achieved the treatment of chemical agents by SCWO. These agents include VX, HD, and GB. A full-scale system plant was built by Foster Wheeler. They used the transpiring wall reactor design in this SCWO plant in 1998 to deal with USA forces waste. This plant was managed by Sandia National Laboratories. In addition, Foster Wheeler has a pilot-scale plant for investigating the transpiring wall reactor. Photographic and halogenated solutions were tested by Foster Wheeler in 1999 [22,84,97].

Another company, EcoWaste Technologies, built and designed the first SCWO plant in the United States. This plant was used for the treatment of non-halogen organic wastes that were produced at Austin Research Laboratories. The stream of wastes consisted of alcohols, glycols, and amines with 10 wt% organic loading, and the rate was 1100 kg/h. The license of EcoWaste Technologies was given to Chematur Engineering in 1995 in Europe. In 1999, Chematur Engineering gained a license around the world. Chematur marketed the SCWO plant under the trade name Aqua Critox. Chematur designed and built a pilot-scale SCWO plant; the flow rate was 250 kg/h for investigating the destruction of amines, non-halogenated organic compounds, di-inking sludge, sewage sludge, and

spent-cutting fluid. The first SCWO plant was built by Chematur in the UK for Johnson Matthey [16,22].

SRI used the AHO process for treating hazardous wastes. AHO can be defined as a reactor filled with carbonate as a catalyst to enhance the oxidation process and for the adsorption of salt. The first license was gained

by Mitsubishi Heavy Industries (MHI) in 1999. SRI and MHI worked together to improve the AHO process and convert this system for commercial use. Two companies have planned to use the SCWO process (commercial large scale) for treating polychlorinated biphenyl (PCB) wastes [22,23,97].

*Table 1 : the SCWO plants in the world [97]*

<i>Companies</i>	<i>Periods</i>	<i>Licence</i>
<b><i>Innoveox</i></b>	<i>2008–present</i>	–
<b><i>SuperCritical Fluids International (SCFI)</i></b>	<i>2007–present</i>	<i>Parsons</i>
<b><i>SuperWater Solutions</i></b>	<i>2006–present</i>	-
<i>hydrothermale Oxydation Option (HOO)</i>	<i>2000–2008</i>	-
<b><i>Hanwha Chemical</i></b>	<i>1994–present</i>	-
<i>Chematur Engineering AB</i>	<i>1995–2007</i>	<i>Johnson Matthey, WS Atkins, Stora-Enso, Feralco AB</i>
<i>HydroProcessing, L.L.C.</i>	<i>1996–2003</i>	
<i>Foster Wheeler Development Corp.</i>	<i>1993–2004</i>	<i>Aerojet Gencorp Corp., Sandia National Laboratory</i>
<b><i>General Atomics (GA)</i></b>	<i>1990–present</i>	<i>Komatsu Ltd., Kurita Water Industries, Ltd.</i>
<b><i>SRI International</i></b>	<i>1990–present</i>	<i>Mitsubishi Heavy Industries, Ltd.</i>
<i>EcoWaste Technologies, Inc.</i>	<i>1990–1999</i>	<i>Chematur Engineering AB, Shinko Pantec (Kobelco)</i>
<i>MODAR, Inc.</i>	<i>1980–1996</i>	<i>Organo Corp.</i>
<b><i>MODEC (Modell Environmental Corp.)</i></b>	<i>1986–1995</i>	<i>Organo Corp., Hitachi Plant Engineering &amp; Construction, Ltd., NGK Insulators, Ltd., NORAM Engineering and Constructors, Ltd.</i>

The Hydro Processing Company has designed a SCWO plant to treat sewage sludge. Hydro-solids were recorded as their patented process, and they were used as an alternative for two units (sludge digestion unit, dewatering unit) in the traditional treatment method. They have designed and built pilot- and full-scale plants. The large-scale plant was built in Harlingen for wastewater treatment. Plant treatment was employed to deal with municipal and industrial wastewater sludge [23,101].

Other companies contributed to enhancing the SCWO process and to designing commercial pilot- and

large-scale plants. For example, Hanwha Chemical built a full-scale SCWO plant for destroying DNT/MNT wastewater; the flow rate was 2000 kg/h, and another plant was constructed for treating melamine wastewater with a flow rate of 35,000 kg/h [97,101].

**VII. PROBLEMS OF SCWO**

Corrosion is an essential problem that influences the spread of SCWO on a commercial scale. Corrosion contributes to reducing the life of the SCWO system. Thus,

the cost of treatment would be non-economical[101,102]. At supercritical temperatures, oxidized acids form and attack pipes and valves. In general, a corrosion phenomenon occurs in the hot components of a rig, such as a reactor preheater and heat exchanger. The influence of corrosion decreases at low concentrations and higher temperatures due to the lower density of the SCWO medium. The main reasons for corrosion in the SCWO system are high concentration of undissolved oxygen, high pH, decomposition of bases, acids and salts, high temperature and pressure, and high concentration of ion species at subcritical conditions[103]. In addition, this phenomenon in the SCWO process depends on the components of the waste stream, the material of alloy of the reactor, and other parts, as well as heat applications. The materials of the SCWO system are nickel alloy or stainless steel. Stainless steel can be used with waste streams that do not contain heteroatoms, such as sulfate, chloride, and phosphors [104]. Nickel alloy is suitable for hot parts and has high resistance to various operational conditions [22].

Salt precipitation is a second problem that occurs due to water being converted to a non-polar solvent under supercritical conditions. The solubility of inorganic substances is low. Then, these salts accumulate on the inner walls of the hot reaction parts. The continuity of salt precipitation on the inner walls of the SCWO system leads to plugging, decreasing heat transfer, and corrosion of the reactor [101,105]. Several studies have discussed salt precipitation. Various reactors were used to study this problem, such as transpiring wall, reverse flow, and tank reactors. Some techniques were applied to address salt precipitation, such as increasing the velocity of flow rate, mechanical cleaning, studying the low turbulence flow, density separation under high pressure, and adding chemicals. At present, there is no efficient and economical solution for salt precipitation. To avoid this problem, it is important to know the concentration of salt and to select a suitable reactor. Pretreatment of wastewater would be a significant step in controlling the problems of SCWO and give this technology the chance for comparison with commercial treatment methods [22,23,100].

### VIII. CONCLUSION

The SCWO process can be considered an alternative process for dealing with a wide range of hazardous and toxic organic wastes. SCWO has mineralized organic waste into water and wanted gaseous emissions. Various studies have demonstrated that different factors contribute to enhancing SCWO technology. Co-fuels have a remarkable influence on the

removal of hazardous waste. Methanol, ethanol, isopropanol alcohol, and propylene glycol have played important roles in the enhancement of the SCWO process. The influence of the catalyst is significant; the presence of catalysts has a positive impact on the removal efficiency of organic waste. Consequently, co-fuels or catalysts are used to enhance this process and reduce toxic gaseous emissions and by-products.

The main obstacles facing this technology are corrosion and salt precipitation. The intensive research and deep understanding of these two problems would contribute to the development of a new reactor design. If a suitable solution is found, SCWO technology will present significant competition to traditional technologies and incineration.

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