

APPLICATIONS OF WET AIR OXIDATION PROCESS IN WASTEWATER TREATMENT

SPECIAL TOPICS IN CHEMICAL ENGINEERING

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**1.0 ABSTRACT**

This project examines the application of wet air oxidation process in treating process wastewater with high organic content. The work focuses on investigating the efficiency of the Wet Air Oxidation (WAO) process as a pre-treatment step in an integrated chemical/biological water treatment process for industrial wastewater. Wet air oxidation is a process of oxidizing the organic compounds and inorganic components of wastewater at elevated operating conditions of temperature and pressure. High pressures of about 2-20 MPa are required for the process to keep the reactions in the liquid aqueous phase.

Literature from authors and researchers in process wastewater treatment are used in investigating the efficiency of the Wet Air Oxidation process in detoxifying highly organic wastewater. Reactor design, energy requirements and its effect on operating variables like temperature and pressure were also reviewed.Effects of oxygen and mass transfer limitations on the overall performance of the reactor was also discussed.

The increasing use of catalysts in making the Wet Air Oxidation process more efficient was also studied.Catalysts effect on the WAO efficiency process was investigated.Some other commercial WAO reactor configurations were reviewed with each having its advantages and limitations when compared with the conventional Zimmerman process.

Emerging and upcoming technologies in WAO were also reviewed with the obvious advantages pointed out.

**2.0 INTRODUCTION**

 Many process industries as part of their industrial processes/operations release aqueous organic and inorganic waste compounds as process waste-water.These industrial wastes have to be treated by processes involving biological, physical and chemical treatment methods before it is discharged to the environment to reduce the toxicity of the waste and also make them biodegradable compounds (Tungler et al,2015).

In selecting the best method for treating industrial wastes, some factors are considered.

The economics of the method is important as cost is critical in everyday’s business.The efficacy of the process also goes a long way in determining which treatment option to use as each available technology has its mechanisms of operation depending on the amount of wastewater produced and the contents and concentration of the pollutants (Kolaczkowskia et al,1999).

 Over the years, incineration has always been used to treat hazardous liquid wastes with high organic waste and inorganic waste contents.However, this method allows for gasoline consumption which is at a high cost and also the release of toxic substances like SO2 and Sulphides into the atmosphere.Also because these aqueous industrial wastes are non-biodegradable and toxic with high concentrations, it becomes much more difficult to treat them biologically (Tungler et al,2015).

 Wet air oxidation process over the years have been proven to overcome the limitations mentioned above and according to Tungler et al. (2015), it has proven to be an effective method for treating industrial aqueous non-biodegradable waste with high organic content and has successfully been used to treat the high organic content process-wastewater from chemical and pharmaceutical industries at elevated temperatures and pressures.

 Kolaczkowskia et al. (1999) defined Wet Air Oxidation as the oxidation of soluble or suspended organic/inorganic waste components in water using oxygen(O2) or air as the oxidizing agent at high operating conditions of temperature and pressure of about 398-573K and 0.5-20MPa either in the presence or absence of catalysts.

Wet air oxidation (WAO) is a technology used to treat the waste streams that are too dilute to incinerate and too concentrated for biological treatment (Kolaczkowskia et al,1999).

**4.0 LITERATURE REVIEW**

 Wet air oxidation can simply be defined as an aqueous phase oxidation process that involves the reaction between dissolved organics and a gaseous source of Oxygen(O2) which could be either oxygen or air at high temperatures of 150o to 320oC and pressures of 20 to 200bar (Arezoo,2013). According to Arezoo (2013), the liquid phase of the reaction is maintained by the high pressures which help to increase the concentration of oxygen and also hence increases the oxidation rate. The degree of oxidation in the WAO process is primarily dependent on the resident time, temperature and pressure of the process.

WAO technologies are efficient in treating wastewater that has a high fraction of toxic organic substances which are difficult to decompose biologically and inorganic compounds like hydrazines and sulphides(Arezoo,2013).

According to Heponiemi (2015), about 400 commercial WAO units are currently in operation all over the world treating wastewaters from pharmaceutical, chemical and petrochemical industries as well as urban sludge from biological treatment plants.

**4.1.0 History of wet air oxidation**

 The wet air oxidation process was originally developed by Zimmermann and its first industrial applications happened in the late 1950’s (Linda Y. Zou et al,2007).

Over 40 years ago, Zimmerman was on a quest of finding a new means of treating black liquors from papermills other than the Kraft process which was unsuitable. He resorted to combusting organic compounds that are dissolved or suspended in water using oxygen as an oxidizing agent at low temperatures. This method was similar to incineration as the organic fraction were combusted to produce CO2, compounds of N2, traces of CO and small amounts of volatile acetic acid (Debellefontaine & Foussard,2000). As the temperature was increased to about 3000C, he observed that the removal of the organic waste content exceeded 95% and a high pressure was needed to keep the reaction at this temperature.

 Debellefontaine &Foussard (2000) also noted that over time, WAO became an important phenomenon to consider and by the early 1970s it was being used to regenerate powdered activated carbon from wastewater treatment processes. As at 1960, it was already being used in sewage sludge treatment but the WAO process became very popular in the 1980s because it was capable of detoxifying liquids prohibited from land disposal by new regulations enforcing environmental protection (Debellefontaine & Foussard,2000).

**4.1.0 Process description**

The typical flow diagram of the Wet Air Oxidation process is shown in Figure 1 below.

 The WAO process consists mainly of an air compressor, a high-pressure pump, a heat exchanger as well as a reactor with a relief valve, and a downstream separator. The simplest reactor design is usually a con-current vertical bubble column with a height-to-diameter ratio in the range of 5–20 (Lawrence Wang et al,2007).

 They describe WAO as a continuous process that makes use of a rotary compressor and pumps to compress the air (or oxygen) and feed liquid waste stream to the required operating pressure for oxidation to occur. The raw waste is pumped to the bottom part of the reactor which is a bubble column through a series of pre-heaters. Heat exchangers help to recover energy from the reactor effluent and use it to preheat the feed/air mixture entering the reactor

The wastewater stays in the reactor for a sufficient period of time of about 15–120 mins to enable the desired chemical oxidation process to occur. Air or oxygen is compressed and can bubble at the lower part of the reactor (Lawrence Wang et al,2007).

****Top of FormBottom of FormFigure 1: Typical flow diagram of a Wet Air Oxidation Treatment Process. (Source: Heponiemi, 2015).

 According to Lawrence Wang et al. (2007), cryogenic oxygen may be used and pumped before vaporization to save shaft work during compression. They also noted that at the initial stage of the reaction, the reactor is usually run in adiabatic conditions and the temperature can be controlled by varying the total pressure while the heat is absorbed when water vaporizes in the gas stream and released when organic contaminants are oxidized in the liquid phase. The energy content of the liquid and gas outlet stream is usually sufficient to ensure the preheating of feed. According to Lawrence Wang et al. (2007), in some cases, WAO applies to very dilute feed (low COD feed) in which the heat released is too small to achieve the desired temperature, so additional heat is supplied. With higher concentration feed (high COD feed) some of the heat released must be removed by cooling or generating high-pressure steam. They also noted that the process can run with no additional energy if the oxygen up-take is greater than 15 g/L and the typical Carbon Oxygen Demand (COD) removal efficiency is always about 95% and the stream cannot be discharged into the environment because the final liquid effluent would contain a significant amount of low molecular weight organics, ammonia, inorganic acids and salts that need to be removed by treating them biologically. Hence, most of the WAO units are operated in connection with biological facilities in which a post-treatment is carried out before final release into the environment (Lawrence Wang et al,2007).

**4.2.0 WAO Reactions**.

 The Wet Air Oxidation process helps to convert hazardous organic waste compounds into CO2, water vapour, ammonia(NH3) for nitrogen-containing wastes, sulphates for sulphur containing compounds and halogen acids for halogenated wastes (Tungler et al,2015). The reactions involved are mainly oxidation and hydrolysis reactions in series and involve breaking down the complex organic compounds into simpler compound structures.

According to Tungler et al. (2015), the WAO process can take the form of any of the following reactions:

$Organics+O\_{2}\rightarrow CO\_{2}+H\_{2}O+RCOOH^{\*}$**(1)**

$Sulfur+O\_{2}\rightarrow SO\_{4}^{2-}$**(2)**

$Organics CL+O\_{2}\rightarrow CL^{-}+CO\_{2}+RCOOH^{\*}$**(3)**

$Organic N+O\_{2}\rightarrow NH\_{3}+CO\_{2}+RCOOH^{\*}$**(4)**

$Phosphorus+O\_{2}\rightarrow PO\_{4}^{3-}$**(5)**

In the reaction process, organic compounds are oxidized at high temperature and pressure and converted to CO2, water (H2O) and biodegradable short chain acids.

**4.3.0 Kinetic mechanism of wet air oxidation process**

 Considering the chemical equations expressed showing the different organic aqueous waste compounds being oxidized to form CO2, water vapour, sulphates etc, the general energy balance for the WAO process according to Debellefontaine & Foussard (2000) can be expressed as:

$C\_{m}H\_{n}O\_{K}CL\_{w}N\_{x}S\_{y}P\_{z}+\left(m+0.25\left(n-3x\right)-0.5k+2\left(y+z\right)\right)O\_{2}\rightarrow mCO\_{2}+0.5\left(n-3x\right)H\_{2}O+xNH\_{3}+wCL^{-}+ySO\_{4}^{2-}+zPO\_{4}^{3-}+Heat$**, (6)**

 where the heat value is about 435KJ/mol of O2 reacted)

 Some other chemical equations proposed by Debellefontaine and Foussard (2000) which explains further the complex mechanisms of WAO reactions are:

$O-O+R^{\*}\rightarrow ROO^{\*}$ **(7)**

$O\_{2}+RH\rightarrow R^{\*}+H\_{2}O\_{2}$ **(8)**

$ HO\_{2}^{\*}+RH\rightarrow R^{\*}+H\_{2}O\_{2}$ **(9)**

$H\_{2}O\_{2}+M\rightarrow 2HO^{\*}+M$ **(10)**

$ROO^{\*}+RH\rightarrow R^{\*}+ROOH$ **(11)**

The reaction is initiated by an organic radical R\* where it combines with molecular oxygen as seen in reaction (7) above, also reaction between the weakest C-H bonds and Oxygen shown in reaction (8) and also an attack by the HO2\* as shown in reaction (9) can produce this organic radical. According to Debellefontaine and Foussard (2000) hydrogen peroxide produced in reaction (9) due to temperature decomposes fast to hydroxyl ion radical HO\* as seen in reaction (10). Reaction (11) is a propagation step that produces oxidized species and hydroperoxides. For most of the molecules, the initiation step represented by reaction (8) is the limiting one and is dependent on temperature, with an activation energy above 100 or 200 kJ mol-1. This also explains why air oxidation becomes rapid at temperatures greater than 250 or 300oC and does not occur at room temperatures. On the other hand, the propagation step depicted by reaction (7) is usually rapid and the rate constants are about 107to 109 L/mol.s. (Debellefontaine&Foussard,2000).

 Luck (1999) stated the importance of understanding the mechanism of reaction kinetics as it would help in developing better models for the design of industrial reactors in wastewater treatment and other industrial processes.

 **(12) (12)**



Fig. 2. Simplified kinetic model for wet air oxidation (Source: Luck F, Catalysis Today 53 (1999) 81–91).

A generalized model of Wet Air Oxidation shown above for the Wet Air Oxidation process using Acetic acid as the rate-limiting intermediate and this model is used to represent the kinetic data of Wet Air Oxidation reactions. Group “A” includes all initial and relatively unstable intermediates (Organic Compounds and O2) and group “B” is represented by acetic acid. Both groups can lead to oxidation end products like CO2 and rate of reaction is determined by Eq (13). Equation (14) shows the evolution of the concentration of organic compounds over time in a batch reactor in which the concentration of dissolved oxygen remains constant over the reaction period. According to Debellefontaine and Foussard (2000), the kinetic model and mechanism developed for Wet Air Oxidation can be summarised into two:

1. The chemical reaction between the organic matter and oxygen dissolved in the liquid phase, producing CO2.This can be represented by the following equations:

 $r\_{c}=k\_{0}e^{^{-E}/\_{RT}}C(O\_{2})^{b}$ **(13)**

 $\frac{(A+B)}{(A+B)\_{O}}=\frac{K\_{2}}{K\_{1}+K\_{2}-K\_{3}}e^{-k\_{3}t}+\frac{K\_{1}-K\_{3}}{K\_{1}+K\_{2}-K\_{3}}e^{\left(K\_{1}+K\_{2}\right)t}$(**14**)

$K\_{1}=K\_{0,i}e^{^{-E\_{i}}/\_{RT}}(O\_{2})^{b\_{i}}$ **(15)**

The table below explains the meaning of the different parameters.

Table 1: Parameters influencing rate of reaction in liquid phase

|  |  |
| --- | --- |
| Symbol | Notation |
| b | Partial order of the reaction with respect to oxidation |
| C | The actual concentration of an organic compound(M) |
| E | Activation Energy(KJ/mol) |
| K0 | Pre-exponential factor coefficient(s-1) |
| (O2) | Concentration of O2 dissolved (mol/L |
| R | Gas Constant for ideal gases(J/molK) |
| T | Temperature(K) |
| t | Time(s) |
| *i* and o | The subscript for a specific compound at the inlet or initial condition, respectively. |
| (A+B) | A global indication of the actual value of the organic load such as COD or TOC value.  |
| *k*1, *k*2, and *k*3 | Constants for chemical reaction rates and are dependent on temperature and dissolved oxygen concentration.  |

1. The transfer of oxygen from the gas phase to the liquid phase and the transfer of CO2 to the gas from the liquid phase. The rate of transfer of a component between the two phases is expressed by

$r\_{t,i}=W\_{i}(Y\_{i}ϕ\_{i}\frac{P}{Y\_{i}}H\_{{i}/{w}}FP\_{i}-X\_{i})$ **(16)**

The table 2 below shows the information containing these parameters.

Table 2: Parameters influencing rate of reaction in gas phase

|  |  |
| --- | --- |
| Symbol | Notation |
| $$r\_{t,i}$$ | Rate of transfer of oxygen between 2 phases |
| **W*i*** | Overall Mass Transfer Coefficient |
| Yi | Mole fraction of component “*i*” in the gas phase |
| $$ϕ\_{i}$$ | fugacity coefficient for component “*i*”  |
| **P** | Total Pressure(Pa) |
| $$Y\_{i}$$ | Activity coefficient for component “*i*” in the solution. |
| **H*i*/*w*** | Henry’s law constant for the solubility of gas in water |
| **FP*i*** | Pointing factor for a specific component “*i*”;  |
| **X*i*** | Mole fraction of component “*i*” in the liquid phase |

**4.4.0 Modification to the WAO process by use of catalysts**

 To improve the efficiency of the WAO process, the use of catalysts was introduced. Catalyst help to improve the challenging operating conditions of the conventional WAO process (Lawrence Wang et al, 2007). According to Mantzavinos et al (1999), the conventional WAO process could be very expensive to operate due to the high capital and operating costs associated with the high temperatures and pressures and long residence times required for the process. Reduction in costs is made possible with the use of catalysts which help to promote milder operating conditions of reduced temperature and pressure and shorter residence times.

 Mantzavinos et al. (1999) also classified the different catalyst used in WAO process as the heterogenous catalysts and homogenous catalysts. However, the heterogenous catalysts are widely being used in most industrial applications because of the limitations associated with homogeneous catalysts which need to be separated by precipitation to remove the homogenous catalyst ions from final effluent (Mantzavinos et al,1999).

In summary, the catalytic wet air oxidation has cheaper energy requirements, higher oxidation rates and less intense reaction conditions to achieve same COD removal efficiency as with the non-catalytic process (Levec J and Pintar A,2007).

**5.0 DESIGN CONSIDERATIONS AND MASS TRANSFER THEORY IN WET AIR OXIDATION PROCESS**

 It is very interesting to note that although Wet Air Oxidation process depends on operating conditions like temperature, pressure and other variables earlier mentioned, the efficiency is very much dependent on the reactor design. According to Kolaczkowski et al. (1999), the required residence time and reactor volume would depend on the degree of oxidation, the rate of reaction and type of reactor used. Increasing the reaction rate would obviously reduce the reaction time and also equally reduce the size of reactor used.

 When designing a wet air oxidation reactor (bubble column reactor in this case), it is important to factor in the mass transfer processes occurring considering that the overall reaction rate of the WAO is governed by the mass transfer of oxygen from the gas to liquid phase, and the reaction between organic matter and dissolved oxygen occurring in the liquid phase (Debellefountaine &Foussard,2000). It is crucial to realise that in having an ideal reactor design, Kolaczkowski et al. (1999) says it is necessary to have a balance between the rising costs and safety implications and also the high temperature and pressure with increased mass transfer and reaction rates. At high temperatures used in Wet Air Oxidation processes, the only significant transfer resistance is located at the gas-liquid interface because gases diffuse very rapidly in the gas phase than in the liquid phase and this makes the gas phase resistance very negligible. The mass transfer is therefore limited by the liquid film resistance. (Debellefountaine &Foussard,2000; Kolaczkowski et al,1999)

 Wet air oxidation reactions take place at the bulk of the liquid and for such reactions, reactors with large liquid hold-up and high interfacial areas like bubble columns, jet column reactors and trickle bed reactors are required to overcome mass transfer limitations (Kolaczkowski et al,1999).

As stated above, gas transfer resistance is negligible and the mass transfer of oxygen in the liquid phase can be increased by raising the solubility of oxygen in the liquid phase or increasing the overall mass transfer coefficient (KLa). Kolawczkwosky et al. (1999) expresses this in equation 17 below as

 $r\_{m}=K\_{L}×a×\left(C\_{O2}^{\*}-C\_{02.L}\right)$ **(17)**

Where $r\_{m}$ is the rate of oxygen mass transfer

 $K\_{L}$ is the liquid side mass transfer coefficient

 $a$ is the gas liquid interfacial area and

 $C\_{O2}^{\*}$ is the concentration of saturated oxygen which increases with increase in temperature and partial pressure of oxygen.

In summary, Kolawczkwosky et al. (1999) described the overall mass transfer coefficient to be influenced by variables like pressure, temperature, gas flowrate, and the geometry of the reactor and their associated effects such as liquid hold-up, flow regime, bubble diameter, interfacial area and the mass transfer coefficient. They also emphasised the importance of monitoring the effects of these operating variables on bubble diameter, gas hold-up and

liquid mass transfer coefficient to ensure maximum mass transfer rate of oxygen to the liquid phase.

The following points by Kolawczkwosky et al. (1999) are worthy to note in wet air oxidation reactor design and fluid properties:

* The smaller the bubbles size in the reactor the larger, the area available for mass transfer.
* Gas hold-up increases as superficial gas velocity increase hereby leading to increased mass transfer. However, capital and operating costs go up due to the high working capacity of the gas compressor.
* The liquid side mass transfer coefficient (KL), depends on bubble size and liquid properties. The overall mass transfer coefficient (KLa) is, therefore, dependent on liquid properties, gas flowrate and bubble diameter.
* In bubble columns, the degree of liquid back mixing can be large, which leads to non-uniform residence times in the reactor which can affect conversion.
* The formation of carbon dioxide and consumption of oxygen would have effects on the oxygen partial pressure, resulting in a drop in the driving force for mass transfer
* If wet air oxidation processes are to operate at much lower temperatures and pressures, due to considerations of process safety and economics, there will be a significant reduction in saturated oxygen concentration which will result in a decrease in the concentration of oxygen in the liquid phase and drops the driving force for mass transfer.

 An increase in temperature increases not only the reaction rate and oxygen solubility but also the water vapour pressure. The reaction is known to be exothermic with the released energy increasing the reactor temperature and making water to vapourize. According to Kolawczkwosky et al. (1999), increasing pressure helps to increase the oxygen solubility and reduces the equilibrium quantity of water vaporized, which reduces the total latent heat of vaporization. Pressure can, therefore, be used to control the amount of water in the liquid state and maintain fluid temperature. In the design of wet air oxidation reactors, the overall oxidation rate is dependent on both mass transfer and reaction kinetics, and the rate controlling step depends on factors like reactor type, operating conditions and type of pollutant.

**6.0 COMMERCIAL WAO PLANTS IN USE**

Besides the Zimpro process unit described in the earlier part of this literature, there are other commercial units of the Wet Air Oxidation process that exist which differ in unit operations and process conditions. Some of these units include:

* Wetox Process: This process makes use of multiple series of CSTR’s which have like 4 to 6 different compartments as the reactor in use. According to Kolaczkowski et al. (1999), this process was invented by Fassell and Bridges in 1970 and is said to be effective at improving the oxygen mass transfer rate to the waste by increasing mass transfer area and decreasing the oxygen or air bubble size, increasing contact time for mass transfer by making use of eddy currents and lastly reducing the mass transfer resistance by reducing the thickness of the stagnant film around the bubble. The process flow diagram is shown below



. Fig. 3: Wetox process schematic (Kolawoscky et al,1999).

Kolawoscky et al. (1999) describe the Wetox reactor as having operating temperatures between 480K and 520K with a progressive temperature increase in each compartment as a result of the heat of oxidation of the waste. Liquid retention times vary from 30minutes to 1hr and pressure is around 4MPa.This reactor can be used for total organic content destruction if desired. As seen in Figure above, the liquid and vapour phases are being removed separately and this according to Kolawoscky et al. (1999) helps to improve the heat exchanger efficiency, reduce the volume of the liquid effluent and increase the liquid retention time.

They also highlighted the disadvantages of using mechanical stirrers in the Wetox process as they have high energy requirements and maintenance cost. Size constraint is also an issue as the horizontal reactor would take much space on a plant layout.

* Vertech Process

This aqueous phase oxidation (APO) process treats sludge using pure oxygen in a sealed

below-ground oxidation vessel consisting of two concentric tubes (downcomer and upcomer) and a heat exchange system (Luck,1999).

The Vertech process is represented in the figure below



Fig. 4. VerTech reaction vessel (Kolawoscky et al,1999).

As seen in the figure above, these concentric tubes (inner tube is the downcomer and the outer tube the upcomer) move downward in a shaft of depth 1200-1500m. The high depth of the vessel creates high pressure required for the wet air oxidation process (Kolawoscky et al,1999). They also compared the Vertech system with the conventional process (Zimpro process), with the Vertech system having less power requirements as the pumps are designed to overcome pressure drop losses. It is also interesting to note that the waste and oxygen pass in the reactor under plug flow conditions hereby leading to better reaction kinetics and conversion. According to Kolawoscky et al. (1999), the reactor is designed for turbulent conditions hereby leading to efficient mass transfer between the liquid and gas streams and also results in high heat transfer. This, however, has its own disadvantage as a longer reactor size would be required for keeping the streams at high velocity at a particular residence time. Some other limitations of the Vertech process as expressed by Kolawoscky et al. (1999), are environmental concerns related to drinking water contamination during processing of toxic materials and scale formation on the reactor walls.

* Kenox Process

The Kenox Wet Air Oxidation process was developed by the Kenox Corporation of Canada in 1986 at a drum re-conditioning plant in Mississauga, Ontario. According to Kolawoscky et al. (1999), the operating process conditions are at a temperature between 473K to 513K and pressures of about 4.1 to 4.7MPa with a residence time of about 40minutes. The Kenox reactor has 2 concentric shells with waste and air flowing through the inner cylinder and also through the space between the inner and outer cylinders.

The process is depicted in the figure below



Fig. 5. Kenox process schematic (Kolawoscky et al,1999).

The vanes of the pump help to circulate the waste and air mixture in the reactor. The Kenox system is designed such that it is modularized with more modules being added as the flowrate of the wastewater stream increases, and the effluent leaving the second reactor is cooled down, before it is separated into the liquid and gaseous phase. (Kolawoscky et al,1999). Significant cost reduction and a higher COD removal efficiency were identified by Kolawoscky et al. (1999) as some of the advantages of this process.

* Oxyjet Reactor System

This technology was developed by Researchers at the University de Sherbrooke in Canada and the Universidad Politecnica de Catalunya in Spain by combining tubular reactors and jet-mixers (Kolawoscky et al,1999). The process is represented by figure below



Fig. 6. Oxyjet process development unit (Kolawoscky et al,1999).

The main working principle of the Oxyjet System according to Kolawoscky et al. (1999) is that it provides a high interfacial area for flow which enhances the oxygen mass transfer rate to the liquid stream. In this system, the jet mixer helps to disperse the liquid into droplets causing a two-phase mist after which it then flows through a tubular reactor where oxidation of the organic compound occurs in a kinetic-controlled regime (Kolawoscky et al,1999). The Oxyjet system, when compared with the conventional bubble wet air process, has shorter residence times because the oxidation rate according to Kolawoscky et al. (1999) is totally dependent on reaction kinetics.

**7.0 EMERGING APPLICATIONS IN WET AIR OXIDATION**

A lot of research has gone into advanced oxidation of industrial wastewater and some methods have been identified as new emerging applications that improve the efficiency of waste removal in industrial water. This section would focus on the evolution of the WAO process and the techniques of operation.

* Super-critical Water Oxidation

This oxidation process is basically a modification to the traditional WAO process.

Linda et al. (2007) stated that if the operating temperature and pressure are higher than that of water at supercritical conditions, the oxidation potential is much greater and a better waste removal efficiency is realised. Hii et al. (2004) also observed that the reactions and kinetic mechanisms of the Supercritical Wet Air Oxidation process are different from the conventional WAO process because supercritical water differs in physical and chemical properties of subcritical water. To understand this concept better, the critical point of a fluid is defined as the highest temperature and pressure at which it can exist in liquid/vapor equilibrium, Linda et al. (2007) gives the critical temperature and pressure of water as 374°C and 221atm and above these process conditions, water is said to be supercritical water (SCW) and is an excellent solvent for organic compounds and gases.

 During supercritical wet air oxidation, wastewater is dissolved in oxygen or air which leads to rapid oxidation in a homogenous phase (Linda et al, 2007). This is proven where at temperatures of 400–450°C, 99–99.9% conversions (to carbon dioxide, carbon monoxide) can be achieved within 5 mins of reaction and if the operating temperatures are increased to 600–650°C, 99.999% conversion can be obtained in less than 1minute. An important property of water that changes as it approaches the critical point is the dielectric constant which influences the ability of water to act as an organic solvent (Linda et al,2007).

The flow diagram of the SCWO bench scale plant is shown in the figure below



Figure 7 Flow diagram of the SCWO bench scale apparatus (Linda et al,2007).

One of the key principles of this process is the interaction between the solute and solvent during extraction of organic compounds from wastewater (Linda et al,2007).

Some of the issues associated with the Supercritical wet air oxidation as highlighted by Linda et al,2007) include the corrosive ability of supercritical water and the high cost of materials used for fabrication.

* Photocatalytic Oxidation

This is a fast-growing field in the advanced oxidation process. The advanced oxidation process refers to the rapid and non-selective oxidation of organic pollutants by highly reactive species such as the hydroxyl radical. (Linda et al,2007). The Photocatalytic oxidation process makes use of Ultraviolet radiation in the solar system to energise the reactive species and make them capable of oxidizing the organic compounds in a wastewater stream. These organic compounds are thereafter converted to form CO2, H20 and mineral acids (Linda et al,2007).

They also noted that the photocatalytic oxidation process occurs when a semiconductor like Titanium Oxide(TiO2) functions as a catalyst by adsorbing photons. A lot of researches have been conducted on the use of TiO2 to remove toxic substances in wastewater with it being used to dechlorinate polychlorinated diphenyl.

 The rate of photocatalytic oxidation according to Linda et al. (2007) depends on

* Concentration of Oxygen
* Intensity of illumination
* Type of photocatalyst used
* Concentration of organic reactants
* Inorganic ions

Typical catalysts used in the photocatalytic oxidation process include fixed and the slurry types. Various types of photocatalytic reactors used in this process include the annular photoreactor, the packed bed photoreactor, photocatalytic Taylor vortex reactor, the TiO2 fluidized-bed reactor, the TiO2-coated fibre optic cable reactor, the falling film reactor, and some others (Linda et al,2007).

* Advanced Thermal Hydrolysis

This advanced process according to Hii et al. (2014) was developed by Abelleira et al in 2012. It is a modification to the thermal hydrolysis process which involves the combination of hydrogen peroxide addition and thermal hydrolysis. Hii et al. (2014) describes the combination of these two methods as working together to produce a great result in terms of achieving desirable sludge treatment effect. The high solubility of sludge solids and sludge dewaterability are advantages of this process are advantages of this process and according to Hii et al (2014), this process can also be used as a final sludge destruction method like the WAO. This process promises to be a very effective technology and operates under milder operating conditions than the WAO while still achieving comparable results.

**8.0 CONCLUSION**

The wet air oxidation process would continue to be very useful as a treatment technique in wastewater treatment. Despite the obvious challenges being faced by foremost industries, it has gone a long way in solving some of the basic water treatment challenges faced by chemical industries. In alleviating the limitations of the process that has been highlighted in this paper, modifications to the generic traditional process would continue to be an important factor in ensuring the efficiency of the Wet air oxidation process. Reactor design and operating conditions should be carefully thought through while safety and cost should not be ignored while choosing process variables.

# **7.0 References**

Antal Tungler, Erika Szabados and Arezoo M. Hosseini (2015). Wet Air Oxidation of Aqueous Wastes, Wastewater Treatment Engineering, Associate Prof. Mohamed Samer (Ed.), InTech, DOI: 10.5772/60935.Available from:<http://www.intechopen.com/books/wastewater-treatment-engineering/wet-air-oxidation-of-aqueous-wastes>.

Arezoo, M. H. (2013). Intensification of wet oxidation of industrial process wastewater.

Chen, G., Lei, L., Yue, P. L., & Cen, P. (2000). Treatment of desizing wastewater containing poly (vinyl alcohol) by wet air oxidation. *Industrial & engineering chemistry research*, *39*(5), 1193-1197.

Debellefontaine, H., & Foussard, J. N. (2000). Wet air oxidation for the treatment of industrial wastes. Chemical aspects, reactor design and industrial applications in Europe. *Waste management*, *20*(1), 15-25.

Heponiemi, A. (2015). *Catalytic Wet Air Oxidation of Industrial Wastewaters: Oxidation of Bisphenol A Over Cerium Supported Metal Catalysts* (Doctoral dissertation, A. Heponiemi).

Kolaczkowski, S. T., Plucinski, P., Beltran, F. J., Rivas, F. J., & McLurgh, D. B. (1999). Wet air oxidation: a review of process technologies and aspects in reactor design. *Chemical Engineering Journal*, *73*(2), 143-160.

Levec, J., & Pintar, A. (2007). Catalytic wet-air oxidation processes: a review. *Catalysis Today*, *124*(3), 172-184.

Lin, S. H., Ho, S. J., & Wu, C. L. (1996). Kinetic and performance characteristics of wet air oxidation of high-concentration wastewater. *Industrial & engineering chemistry research*, *35*(1), 307-314.

Luck, F. (1999). Wet air oxidation: past, present and future. *Catalysis today*, *53*(1), 81-91.

Mantzavinos, D., Sahibzada, M., Livingston, A. G., Metcalfe, I. S., & Hellgardt, K. (1999). Wastewater treatment: wet air oxidation as a precursor to biological treatment. *Catalysis Today*, *53*(1), 93-106.

Wang, L. K., Hung, Y. T., & Shammas, N. K. (Eds.). (2007). *Advanced physicochemical treatment technologies*. Humana Press.

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