1. Wet air oxidation

Wet Air Oxidation (WAO) is an aqueous phase oxidation process occurring, when a dissolved organic is mixed thoroughly with a gaseous source of oxygen at temperatures of 150 to 325°C and at pressures of 20 to 200 bar (Copa & Gitchel, 1998). The liquid phase is maintained by high pressure, which also increases oxygen concentration and thus, the oxidation rate. Water as an innocuous medium for oxidation has advantages of high density that allows using relatively small reactors, keeping salts dissolved in the solution, and due to quite constant heat capacity avoids pinch points caused by otherwise possible large changes in fluid densities. The process can be controlled by two steps; (i) transfer of oxygen to the liquid phase; and (ii) reaction between dissolved oxygen and organic matter.

The degree of oxidation principally depends on temperature, partial pressure, residence time and refractoriness of the substrate. Usually air (Willms et al., 1987) or oxygen (Baillod et al., 1985) is used as oxidants. According to Mishra et al. (1995) one can reduce the capital investment, when using oxygen instead of air, however the cost of oxygen is higher and has to be compared with savings in initial capital investment. WAO technologies are particularly suitable for the treatment of wastewater containing a high proportion of organic substances (including compounds chiefly toxic and biologically difficult to decompose), but also such inorganic compounds as hydrazine and sulphides. Industrial scale WAO can achieve easily up to 90-95% of conversion (Debellefontaine & Foussard, 2000). In most cases,
however, it is not enough to meet actual effluent discharge regulation. Thus, most of WAO units are followed by biological treatment.

2. Catalytic wet air oxidation

An alternative treatment technique to WAO is catalytic wet-air oxidation (CWAO). Soluble transition metal salts (such as copper and iron salts) have been found to give significant enhancement of the reaction rate. However, they require a post treatment to be separated and recycled. In this respect, heterogeneous catalysts, which can be easily set-up for continuous operation, are preferred. Mixtures of metal oxides of Cu, Zn, Co, Mn, and Bi are reported to exhibit good activity, but leaching of these catalysts was detected. On the other hand, heterogeneous catalysts based on precious metals deposited on stable supports are less prone to active ingredient leaching.

The information on catalytic oxidation of the multi-component mixtures of organic pollutants or complex industrial wastes are very limited. Experimental results of WAO of high-concentration chemical wastewater (chemical oxygen demand (COD) up to 42800 mg l\(^{-1}\)) containing various organic acids and inorganic compounds indicated that over 50% reduction of the chemical oxygen demand concentration could be easily achieved in about an hour at \(T=473\) K and total operating pressure of 3 MPa. Imamura et al. studied WAO of a domestic wastewater in the presence of Mn/Ce and Ru/Ce catalysts. At \(T=473\) K and oxygen partial pressure of 1.5 MPa, about 90% of initial organic carbon content (315 mg l\(^{-1}\)) was eliminated after a 3 h run. The removal efficiency of total organic carbon (TOC) from raw high-strength alcohol-distillery waste liquors (TOC up to 22500 mg l\(^{-1}\)) was investigated in a batch stirred autoclave over various catalysts. In the temperature and oxygen partial pressure ranges of 453–523 K and 0.5–2.5 MPa, respectively, TOC conversions did not exceed 60%. Zhang and Chuang showed that alkaline and acidic bleach plant effluents can be successfully treated by CWAO at 463 K under 1.5 MPa of oxygen partial pressure in the presence of Pd/Al\(_2\)O\(_3\) or Pd-Pt-Ce/Al\(_2\)O\(_3\) catalysts. 70% removal of TOC in the alkaline wastewater could be achieved. Leaching of the metal was strongly dependent on the pH and was significant at the low and high pH.
wet-air oxidation of acidic and alkaline Kraft bleach plant effluents was recently investigated in a batch slurry reactor in the presence of titanium or zirconium oxides, or ruthenium catalysts supported on these oxides. With the addition of ruthenium on these supports, over 99% TOC abatement could be achieved. The catalytic wet air oxidation of D0 and E1 (D0 and E1 effluents originated from the first ClO₂ treatment and washing and from the first alkaline extraction respectively) Kraft bleach plant effluents carried out in a trickle-bed reactor packed with a Ru/TiO₂ catalyst, demonstrated that ultimate destruction of parent organic compounds and their mineralization to CO₂ was achieved at 463 K and under 5.5 MPa total air pressure. Oxidation runs conducted in this reactor set-up proved long-term activity and chemical stability of the Ru/TiO₂ catalyst at hydrothermal operating conditions.

2.1. Supported metal oxides

Metal oxides can be classified according their physico-chemical properties. One of these properties is the stability of metal oxide. Metals with unstable high oxidation state oxides, such as Pt, Pd, Ru, Au, and Ag do not perform stable bulk oxides at moderate temperatures. Most of the commonly used metal oxide catalysts (Ti, V, Cr, Mn, Zn, and Al) have stable high oxidation state oxides. Fe, Co, Ni, and Pb belong to group with intermediate stability of high oxidation state oxides (Pirkanniemi & Sillanpaa, 2002). According to Kochetkova et al. (1992), the catalytic activity during phenol oxidation showed the following typical order:

\[
\text{CuO} > \text{CoO} > \text{Cr2O3} > \text{NiO} > \text{MnO2} > \text{Fe2O3} > \text{YO2} > \text{Cd2O3} > \text{ZnO} > \text{TiO2} > \text{Bi2O3}
\]

Mixtures of metal oxides frequently exhibit greater activity than the single oxide. Cobalt, copper, or nickel oxide in combination with the following oxides of iron (III), platinum, palladium, or ruthenium are reported as effective oxidation catalysts above 100°C (Levec & Pintar, 1995). In addition, combining two or more metal oxide catalysts may improve non-selectivity and catalytic activity.

Metal oxides usually are applied in form of fine particles or even powders. This form of catalyst gives maximum specific area, but the dispersion of particles can create unsteady state. To keep the stable state and in the same time not to lose active phase some porous support can be use. Also the residence time can be
shortened, because the organic to be oxidized can adsorb on the support increasing the concentration of organic in the surface. Commonly, alumina or zeolites are used as a support, but surface area of aluminum oxide is limited and the pore size of zeolites cannot be suitable for large organic compounds.

Recently activated carbon as support is of interest, as it has large surface area and broad range of pore size. Hu et al. (1999) investigated copper/activated carbon catalyst for wet air oxidation of dyeing and printing wastewater. They observed that catalyst supported by activated carbon is better than one supported on alumina in terms of COD and TOC (total organic carbon) removals.

3. Wet air oxidation as a precursor to biological treatment

Many industrial, domestic and natural activities collectively result in the production of vast quantities of hazardous wastes, of which wastewaters comprise about 90%. It was estimated that, in 1989, the US chemical industries alone generated nearly one billion metric tons of hazardous wastewaters which accounted for more than 99% of their annual waste production (including solid wastes and wastewaters). Given these large quantities of wastewater production, it is unsurprising that increasing environmental concerns have focused research on the development of efficient wastewater treatment technologies. The treatment and safe disposal of hazardous organic waste material in an environmentally acceptable manner and at a reasonable cost is a topic of great universal importance. There is little doubt that biological processes will continue to be employed as a baseline treatment process for most organic wastewaters, since they seem to fulfill the above two requirements. However, biological processes do not always give satisfactory results, especially applied to the treatment of industrial wastewaters, because many organic substances produced by the chemical and related industries are inhibitory, toxic or resistant to biological treatment. This is often due to the molecular structure of the substances, which may preclude biological attack due to the size or the shape
of the molecule and its associated functional groups. Therefore, alternative technologies such as physicochemical and thermal oxidation processes may be the only viable options for decontaminating a biologically recalcitrant wastewater. However, a chemical oxidation method aiming at complete mineralization might become extremely cost-intensive since the highly oxidized end-products which are formed during chemical oxidation tend to be refractory to further total oxidation by chemical means. Investment costs for biological processes may range from 5 to 20 times less than those of chemical processes such as ozonization or hydrogen peroxide oxidation, while treatment costs may range from 3 to 10 times less. A comparison of wastewater treatment costs using wet air oxidation, incineration or sewer discharge treatment has been recently reported by Wigston. To achieve 80% COD removal for a wastewater initially containing 50 g l\(^{-1}\) of COD, treatment costs would be as much as 100–120, 40–50 and 10.5 £ t\(^{-1}\) for incineration, wet air oxidation and sewer discharge respectively.

A potentially attractive alternative to complete oxidation through chemical means would be the use of a chemical oxidation pre-treatment step to convert initially bio recalcitrant organics to more readily biodegradable intermediates, followed by biological oxidation of these intermediates to biogas, biomass and water. A great deal of research into such integrated processes has been undertaken over the last 10–15 years. In several studies, aqueous solutions of various model organic compounds or actual wastewaters have been subjected to some form of chemical oxidation followed by biological oxidation and a review on this field has been recently published by Scott and Ollis. A variety of chemical and biological processes have been employed in these studies. The chemical pre-treatment include, among others, ozonization, UV irradiation, photo catalytic oxidation, hydrogen peroxide, electrochemical oxidation and wet air oxidation, while biological oxidation includes aerobic and anaerobic, pure and mixed, acclimatized and non-acclimatized cultures. Measures of biodegradability range from simple lumped parameters such as total organic carbon (TOC) (or DOC: dissolved organic carbon), chemical oxygen demand (COD) and biological oxygen demand (BOD) to specific toxicity and biodegradability tests and rates of substrate removal.
Wet air oxidation or wet oxidation (WAO) refers to the aqueous phase oxidation of organics and oxidizable inorganic components at elevated temperatures and pressures using a gaseous source of oxygen (either pure oxygen or air). Elevated temperatures are required to increase the oxidation rate and enhance the solubility of oxygen in the aqueous solution, while elevated pressures are required to keep water in the liquid state. Water provides an excellent heat transfer medium which enables the process to be thermally self-sustained with relatively low organic feed concentrations. As the concentration of oxidizable organic material increases to roughly 4%, the process becomes thermally self-sustained and further increases in concentration can lead to potential for energy recovery. From this point of view, WAO is ideally suited to wastewaters which are too dilute to incinerate and too toxic or concentrated for biological treatment. According to Debellefontaine et al., WAO would be suitable for wastewaters with COD loads from 10 to 100 g l⁻¹, while incineration would be suitable for effluents having a COD greater than about 100 g l⁻¹ and biological treatment would successfully treat non-toxic effluents with a COD of less than about 10 g l⁻¹.

An advantageous feature of the WAO process is that it creates minimal air pollution problems since contaminants tend to stay in the aqueous phase. The small amount of gas that is discharged consists mainly of spent air or oxygen and carbon dioxide. Since the degree of oxidation is primarily a function of temperature, oxygen partial pressure and residence time, actual operating conditions depend on the treatment objectives. Typical conditions for total destruction of organics would start from 200°C temperature and 4 MPa pressure, while milder conditions would be necessary or the partial oxidation of organics. The main application of WAO is still the conditioning and/or destruction of waste activated sludge with more than 50% of the total number of WAO plants built being used for this purpose. However, over the last several years, increased interest has been shown in the potential capability of WAO for treating wastewaters containing organic compounds which are not readily biodegradable, or which may be deleterious to biological treatment processes. WAO is usually an expensive process to install and operate because of the severe conditions required. High capital and operating costs are associated with the elevated pressures and temperatures employed, long residence times and use of
construction materials which should be resistant to the high corrosion rates occurring under severe operating conditions.

4. Experiment

   a. Autoclave reactor

   For our tests stainless steel autoclaves are used, which are equipped with magnetic stirrer, a hot plate and heating tape,. The thermometer is placed in a tube of sealed end which reaches the liquid phase within the autoclave. The autoclave could be purged with air, nitrogen and oxygen and the filled to the desired pressure. One tube is installed till the bottom of the vessel with a ventile on its outer end, for withdrawing liquid samples from the reaction mixture.
**Technical data**

The apparatus test pressure: 70 bar
The apparatus maximum working pressure: 50 bar
The apparatus highest working temperature: 250°C
The apparatus lowest working temperature: -10°C
Nominal volume of the reactor vessels: 70, 250, and 850 cm³

**Methods of operation**

Aqueous solutions, different industrial waste waters, in diluted form are oxidized in a 800 ml stainless steel high pressure autoclave capable of performing batch or continuous experiments at pressures up to 60 bar and temperatures up to 250°C. In a typical run, the aqueous solution of the waste water is loaded to the autoclave which is then pressurized with oxygen to the desired pressure and then heated up with electric heater to the set temperature. Whenever a catalyst is used, it is introduced to the solution before feeding it into the reactor.

Experiments are usually carried out at 230°C-250°C temperature and 50 bar pressure. In case of concentrated samples (COD>100000) samples are diluted and then oxidized.

**5.2. Determination of the chemical oxygen demand (COD)**

Chemical oxygen demand (COD) is an important test for assessing the quality of effluents and waste waters prior to discharge. The COD test predicts the oxygen requirement of the effluent and is used for the monitoring and control of discharges, and for assessing treatment plant performance. Chemical oxygen demand (COD) is used as a measure of oxygen requirement of a sample that is susceptible to oxidation by strong chemical oxidant. The dichromate reflux method is preferred over
procedures using other oxidants (e.g. potassium permanganate) because of its superior oxidizing ability, applicability to a wide variety of samples and ease of manipulation. COD value calculated from such oxidation for most organic compounds is 95-100% of the theoretical value.

In our experiment COD is determined by the dichromate method. The waste water to be measured has to be diluted with distilled water so that the diluted solution should have a COD value between 100 and 600 mg/L. The appropriate amount of sample is diluted to 100 ml in a calibrated flask and then 10 ml of the diluted sample is introduced into the container containing magnetic stirrer, stirring beads, 5 ml potassium dichromate and 10 ml sulphuric acid. After mixing during cooling the mixture is incubated for 120 minutes at 150°C temperature. After incubation samples are diluted with 45 ml distilled water and then cooled. Distilled water and potassium phthalate solution are also measured as the zero and calibration points respectively. Then the remaining dichromate is measured by titration using Iron (II) ammonium sulphate in the presence of three drops of a Ferroin indicator solution. Colour change is from blue to light-brown at the end-point. (Concentration of Iron (II) ammonium sulphate is checked at the beginning of each experiment before titration). The average value of two separate readings is taken, and then the COD concentrations are calculated from the following formula:

$$COD = \frac{(8000 \times C \times (V_1 - V_2))}{V_0} \times \text{(Dilution factor)}$$

$C$= Concentration of Iron (II) ammonium sulphate

$V_1$=Volume of Iron (II) ammonium sulphate solution consumed by the distilled water sample

$V_2$=Volume of Iron (II) ammonium sulphate solution consumed by the waste water sample

$V_0$= The initial volume of the sample before dilution

**5.3. Determination of the total organic carbon (TOC)**

The degree of oxidation to carbon dioxide which is occurring during WAO is assessed by measuring the liquid phase total organic carbon content. TOC is measured with a Shimadzu TOC analyzer whose operation is based on catalytic
combustion and non dispersive infrared (NDIR) gas analysis. Similarly to the COD measurement, the samples have to be diluted to that extent that their TOC values should range between 50 and 500 mg/L.

Total carbon (TC) is measured first, followed by inorganic carbon (IC). The TOC is determined by subtracting IC from TC. The uncertainty in this assay, quoted as the relative standard deviation of three or five separate measurements should not be larger than 1% for the range of TOC concentrations measured.

5.3.1. Working principle of TOC analyzer.

In the TOC-V, carrier gas is controlled using a pressure regulator and mass flow controller. Carrier gas at 150 ml/min is introduced into the combustion tube, which has been filled with an oxidation catalyst and heated to 680°C. The TC of a sample, which was burned in the combustion tube all forms carbon dioxide. The carrier gas, containing the carbon dioxide and other combustion products flows from the combustion tube to a dehumidifier (electric dehumidifier), where it is cooled and
dehydrated. Then it passes through a halogen scrubber before it reaches the cell of a non-dispersive infrared NDIR gas analyzer, where the carbon dioxide is detected. The analog detection signal of the NDIR forms a peak, and the area of this peak is measured by a data processor.

The peak area is proportional to the TC concentration of the sample. Therefore, when a TC standard solution has been analyzed to create a calibration curve equation expressing the relationship between TC concentration and peak area, the TC concentration in the sample can be calculated.

There are two methods available for measuring IC with this TOC-V, analysis within the injection syringe and using the optional IC reactor. In either case, the IC comprises the carbon within carbonates, hydrogen carbonates and in dissolved carbon dioxide.

In analysis using the IC reaction vessel (H type and N type with optional IC reactor kit) the TOC-V IC reactor kit allows sparging the IC reaction solution (reaction liquid acidified with HCl) with carrier gas. Only the IC of the sample, injected into the IC reaction vessel, is converted to carbon dioxide and detected by the NDIR.

In N type analysis which is in the syringe the sample is acidified to pH lower than 3 or with HCl inside the syringe. The sample is sparged with carrier gas and only the IC in the sample is converted to carbon dioxide, and detected by the NDIR.

6. Catalysts

-Either heterogeneous or homogenous catalysts are used.

-Mesh (Titanium with a Ruthenium Mixed Metal Oxide coating)
Applications of Mesh:

In highly acidic environments, such as
- Electro galvanizing
- Anodizing of Aluminum
- Recovery of metals
- Electro synthesis and membrane processes
- Precious metal plating
- Reverse pulse Copper plating
- Tinplating

7. Lab Exercise

Sample preparation and oxidation

1- Measure the pH of the sample with the help of pH paper

2- If the pH of the sample is in acidic range then basify with 20% NaOH solution.

3- Measure the TOC and COD of the sample waste water. In case the COD of the sample is more than 100000 mg/L then you have to dilute the sample.

4- Place 500 g of the sample in a 850 cm³ stainless steel autoclave including one magnetic stirrer.

5- In case of CWAO, measure the necessary amount of catalyst or a roll of mesh and added to the solution.
6- Assemble the autoclave and then pressurize it with 10 bar Oxygen.

7- Check if there is any leaking. In case of leaking, you have to empty the pressure and then tighten the screws and pressurize it again!

8- Rap the autoclave with heating strip and place it on the heating and magnetic stirrer.

9- Place the thermometer in the sealed thermometer tube.

10- Start with turning on the magnetic stirrer, if the magnetic stirrer is working properly (700rpm) then you can turn on the heater.

11- Start the oxidation (3-5 hours), when you have reached to the desired temperature then feel the reactor with Oxygen up to 50 bar.

12- During and after oxidation, measure the TOC and COD of the oxidized samples and calculate the percentage decrease of them.

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Budapest, 2012