

# OZOMAX LTD

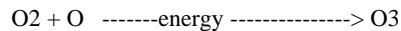
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## ADVANCED OXYDATION PROCESS AOP

### CHAPTER I

### INTRODUCTION

Discovered in the 19 Th. century Ozone a natural form of activated oxygen (allotropy) generally produced during lightning storms and continuously occurring in the stratosphere due to action of ultraviolet (UV) is being rediscovered for the 21 Th. century. It can be artificially produced by the action of high voltage discharge in air or oxygen.



This unstable form of oxygen breaks down to oxygen molecules and oxygen atoms which have high oxidation potential. If we examine the oxidation power of Ozone by measuring the REDOX potential will find out that O<sub>3</sub> is about 5 times more oxidising than oxygen & about twice as much as Chlorine. These high potentials increase its reactivity with other elements and compounds. This reactivity is about 20 to 50 times more reactive than chlorine and Permanganates as it is well documented in the case of the high kill rate of micro-organisms (Funguses, Bacteria & Viruses). This high kill rate means smaller retention times, storage tanks, are required to do the same disinfecting as other oxidants. In other words the capital cost for building these tanks and treatment plants are reduced considerably.

Ozone is a God given gift to all developing nations which most of them lack adequate chemical handling, storage, transportation infrastructure and production facilities. Ozone requires only electricity which is readily available from hydro, solar, wind or fuel electric generators. For the developed countries O<sub>3</sub> will allow decentralisation of services which will provide better flexibility and better cost management.

Here is non exhaustive list of Ozone applications where data & references are available:

#### Ozone chemical free treatments and applications

<u>Waste water effluents</u>	<u>Industrial /Agriculture</u>	<u>Food Industry</u>	<u>Others</u>
Domestic/Municipal	Cooling towers treatment	Drinking & water bottling	Smoke & odour treatment
Pulp & paper	Boiler water treatment	Grain silo disinfecting	Semiconductor wafers clean
Mining (Cyanide, Arsenic)	Chilled water treatment	Fruit & vegetable storage	Laundry water recycling
Pharmaceutical (Phenol)	Cutting fluids recycling	Meat storage	Med. instrument sterilisation
Textile	Barn disinfecting (air/water)	Slaughter house disinfecting	Hospital air sterilisation
Leather	Hydroponics	Fruits & vegetable wash	Aqua-culture
Petroleum/Petrochemicals	Animal waste treatment	Food containers sterilisation	Paper pulp bleach
Electroplating	Water dripping treatment	Wine/Beer SO <sub>2</sub> replacement	Sour gas desulfurisation
Heavy metal precipitation	Animal drinking water	Chicken egg wash	Zebra mussels treatment
Landfill leachates	Irrigation water disinfecting	Ozonated meat grinders	Rubber recycling,.....etc.

The question we should ask is if O<sub>3</sub> is so good why O<sub>3</sub> is not widely spread? The answer is simple which is up to recent times Ozone generators (mid-range) were very expensive with an average of cost of \$ 7000 US/Lb/day with advent of new materials, power supplies, high frequency generators prices are starting to go down around \$ 4000

US/Lb/day with an outlook in the near future around \$ 2000/Lb/day or even lower at this level of prices Ozone will compete with the other oxidising alternatives such as Chlorine, Hydrogen peroxides,.....etc.  
The time has come where this chemical free technology is an affordable reality.

### Design Considerations for Ozone Treatment

This article examines the different design considerations which must be made when designing an ozone treatment system. The following topics are discussed:

- 1) Organic and inorganic load
- 2) Ozone dissolution
- 3) Ozone injection alternatives
- 4) Post ozonation requirements

#### \* Organic and Inorganic Load

The reaction of ozone with most organic compounds may be modeled using a first order kinetic equation:

$$\ln (C/C_o) = -kt \quad (1)$$

where k is the reaction rate constant. The value of k is found by carrying out laboratory experiments. Typical values range from  $4 \times 10^{-3} \text{ sec}^{-1}$  to  $4 \times 10^{-4} \text{ sec}^{-1}$ . The value of k measured under ambient conditions and neutral pH may be adjusted to account for the effects of pressure, temperature and pH as follows:

$$k' = k'(b P/P_a)(c T/T_a)(d \text{ pH}/7) \quad (2)$$

where the subscript (a) represents ambient conditions.

Although Eq.2 implies that the reaction rate increases with increasing temperature, as is generally the case, it must be kept in mind that ozone solubility is adversely affected by increasing temperature. The effect of pH is illustrated in Figure 1.

The effects of these variables are captured in OZOCAL, a software developed by Ozomax Ltd. OZOCAL estimates the ozone dosage required to treat a given effluent based on its analysis. Typically, for organic contaminants 0.1 to 1.6 g O<sub>3</sub>/g COD is needed. The oxidation of heavy metals such as iron and manganese generally occurs in stoichiometric proportions.

#### \*Ozone Dissolution

For the diffusion of ozone from a gas bubble to an aqueous fluid the boundary conditions are such that the Fick's law simplifies to,

$$N_A = d_L * C \quad (6)$$

where C is the ozone concentration within the bubble and  $d_L$  is the mass-transfer coefficient as defined in Eq. 7,

$$d_L = 2D_{AB}/D_p + N \quad (7)$$

where  $D_p$  is the bubble diameter and N is a function of the Schmidt Number.

Equations 6 and 7 reveal two very important characteristics of ozone dissolution.

- 1) O<sub>3</sub> dissolution increases with the gaseous ozone concentration
- 2) O<sub>3</sub> dissolution increases with decreasing bubble diameter.

To take advantage of these two points the ozonator must be designed to efficiently dissipate heat which would otherwise cause the premature conversion of the ozone to oxygen thus lowering its concentration. Also, an oxygen feed may be used to yield higher ozone concentrations than those obtained from air. (See Figure 2) Secondly, the ozone/water contact should be made under pressure in order to produce small bubbles. (See Figure 3)

The maximum number of moles of O<sub>3</sub> transferred to the solution may be calculated from,

$$M_{O_3} = N_A * S * t \quad (8)$$

where S=total bubble surface area

t = contact time

This reveals a third important ozone dissolution characteristic:

3) O<sub>3</sub> dissolution increases with increasing retention time

Equation 8 also confirms point (2) above.

#### \* Ozone Injection

The principle methods currently used to introduce ozone into water and wastewater are:

- 1) contact column
- 2) venture injection
- 3) centrifugal injection

#### \*Post-Ozonation Requirements

The ozonation treatment step is usually followed by :

1)**Clarification:** to precipitate oxidized organic and inorganic matter

#### 2)**Filtration**

(nano, sand, charcoal): to remove precipitants. The use of activated carbon filters has the added advantage of adsorbing the excess unreacted, unrecycled ozone and allows it to convert back to oxygen.

3)**O<sub>3</sub> destruct in air vents:** may be accomplished using thermal, catalytic or ultraviolet destruction

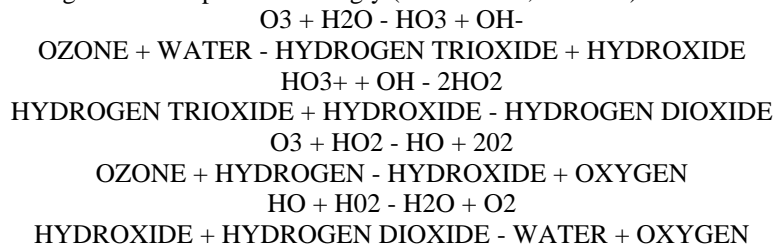
This increased understanding of ozone oxidation has led to the broadening of its applications making it the one of the fastest growing market segments within the drinking water and waste water treatment industry. Other industries employing ozone treatment include the agricultural, food, pharmaceutical, and electronic industries. Lower ozone production costs have allowed this material from the past to have modern applications.

## CHAPTER II

### THEORY OF AOP AND MECHANISMS OF OXIDATION

Ozone (O<sub>3</sub>) is an allotrope of oxygen (O<sub>2</sub>). It is 1.5 times as dense as oxygen and 12.5 times more soluble in water and leaves no residuals or byproducts except oxygen and a minimal amount of carbon dioxide and water. It can be manufactured from dry air or from oxygen by passing these gases through an electric field of high potential sufficient to generate a "corona" discharge between the electrodes. Ultraviolet light and shorter wavelength radiation also causes oxygen to undergo conversion to ozone, which may be used for industrial wastewaters (Belew 1969).

Ozone is highly unstable and must be generated on site. Its oxidation potential (-2.07V) is greater than that of hypochlorite acid (-1.49V) or chlorine (-1.36V), The latter agents being widely used in water treatment practice. Ozone is thought to decompose accordingly (Miller 1978, 167-168):



The free radicals (HO<sub>2</sub> and HO) react with a variety of impurities such as metal salts, organic matter including microorganisms, hydrogen and hydroxide ions. They are more potent germicides than hypochlorite acid by factors of 10 to 100 fold and disinfect 3125 times faster than chlorine (Nobel 1980). Experimental evidence indicates gram-negative bacteria to be on the order of 10-fold more susceptible than viruses to ozone (Miller 1978)

The measure of an oxidizer and its ability to oxidize organic and inorganic material is its oxidation potential (measured in volts of electrical energy). Oxidation potential indicates the degree of chemical transformation to be expected when using various oxidants. It gauges the ease with which a substance loses electrons and is converted to a higher state of oxidation (EPA 1990). Theoretically the substance with the lower oxidation potential will be oxidized by the substance with the higher oxidation potential. A substance can only be oxidized by an oxidizer with a higher potential (EPA 1978). The oxidation potentials of common oxidants and disinfectants associated with water and wastewater treatment are all of a lower oxidation potential than ozone. There is only one element with a higher oxidation potential than ozone and that is fluorine.

Oxidation potential does not indicate the relative speed of oxidation nor how complete the oxidation reactions will be. Complete oxidation converts a specific organic compound to carbon dioxide and water. Oxidation reactions that take place during water treatment are rarely complete, due to the large quantity of contaminants and relatively short durations of time in which to oxidize the water pollutants.

Therefore, partially oxidized organic compounds, such as aldehydes, ketones, organic acids, and alcohols, normally are produced during the relatively short reaction periods.

Although the relative position of an oxidant is indicative of its ability to oxidize other materials, it does not indicate how fast one material will be oxidized by another, nor how far toward completion (to carbon dioxide and water) the oxidation reaction will proceed.

Organic compounds treated with a powerful oxidant as ozone will not always be converted totally to carbon dioxide and water, especially under abnormal industrial wastewater conditions.

Therefore, no other commonly employed and less powerful water treatment oxidant (i.e. chlorine, bromine, chlorine dioxide, etc.), all of which have lower oxidation potentials than ozone, will oxidize an organic material completely to carbon dioxide and water if ozone will not.

There are three fundamental mechanisms which apply to the oxidation of organic compounds reacting with an oxidizer. Each mechanism is unique as to how organic compounds react with an oxidizer. But, in some cases, oxidants will react with organic compounds by all three mechanisms, although in sequential steps.

First. The addition mechanism which occurs with organic compounds containing aliphatic unsaturates, such as olefin. Ozone can add across a double bond to form an ozonide (EPA 1978):

This reaction occurs readily in nonaqueous solvents, but as soon as water is added, the ozone hydrolyzes to other products, with cleavage of the former double bond (EPA 1978):

Second. The substitution mechanism involves replacement of one atom or functional group with another.

For example, chlorine can react with phenol to produce o-chlorophenol. In this reaction the ortho-hydrogen atom is replaced by chlorine (EPA 1978):

Oxidation involves the introduction of oxygen into the organic molecule, with or without degradation of the organic compound. For example oxidation of phenol with either chlorine, chlorine dioxide or ozone can produce catechol (Pyrocatechol) as a first oxidation product (EPA 1978):

This specific reaction also can be viewed as an insertion reaction, whereby oxygen is inserted between the ring carbon and hydrogen to form the hydrogen group on the ring (EPA 1978)

Oxidation also can involve cleavage of carbon-carbon bonds to produce fragmented organic compounds.

For example, ozonation of styrene produces formaldehyde, benzaldehyde, and benzoic acid (EPA 1978):

At the last stage in treatment of organic compounds with oxidants, involve the production of carbon dioxide and water (EPA 1978):

There are many variables to consider when applying ozone to the industrial process. There are a variety of contaminants which can enter a waste stream at any given point in time. Also the chemicals used in the process can vary by surfacing type, bleach vs. hydrogen peroxide for oxidation and various soaps and mildewcides.

## **EXAMPLES OF AOP EFFECTIVENESS**

### **PHENOLS**

Phenols are a class of organic compounds which contain an aromatic ring upon which is substituted at least one hydroxyl group. The simplest phenol is phenol itself (EPA 1980):

Other phenols include those in which more than one hydroxyl group is substituted onto the single aromatic ring, or multiple and/or fused aromatic rings which contain one or more hydroxyl groups (EPA 1980):

Phenols as a class are present in the wastewaters from a number of industrial categories, in particular: \*

Soaps and detergents \* Textiles \* Organic chemicals \* Plastics and synthetics \* Petroleum refineries \* Iron and steel plants \* Photo processing \* Pulp and paper \*

The phenols present in these particular industries will at some point exist in the effluent of industrial water. The soaps and detergents and dyes from textiles are obviously contained in the effluent.

When treated with chlorine, phenol first forms Chloro-substituted phenols, which are known to impart disagreeable medicinal tastes and odors to drinking waters (EPA 1980). As a class, however, these compounds generally are rather easily oxidized by strong oxidants, such as ozone. Even continued additions of chlorine itself eventually will destroy the aromatic ring moiety.

It must be borne in mind, however, that even though phenols as a class are readily oxidizable, this does not necessarily mean that they will be easily oxidized completely to CO<sub>2</sub> and water. Phenol oxidation under water and wastewater treatment conditions can stop at some stage after rupture of the aromatic ring, far short of all of the organic carbon being converted to CO<sub>2</sub>, particularly if insufficient oxidant is used.

#### **NON CONVENTIONAL POLLUTANTS**

The first test is one conducted by Gregersen, which studies color reduction by ozonation of 4 unidentified chemical plant wastewater streams which included:

- (1) a combined wastewater,
- (2) a process wastewater,
- (3) an arsenic wastewater and
- (4) a low pH (acidic) nitrification process wastewater containing primarily a salicylic acid derivative. In addition, a number of nitro-aromatic compounds in water were oxidized.

The first two wastewaters lost considerable color after 10 minutes of ozonation, but the last two wastewaters seemed to be unaffected. Some organic carbon was eliminated. Activated carbon was recommended for treating these wastewaters, primarily because the technology needed to design treatment systems already existed. Ozonation followed by biological treatment was selected second, but it was not known to what degree the ozonic organic compounds were truly biodegradable (EPA 1980). The higher acid content of these last two wastewaters could have been adjusted with sodium hydroxide and possibly changed the outcome.

The following is a general listing of most of the reactive contaminants that respond to Ozone treatment:

Ozone is also effective in treating: Acetic Acid, Butoxyethanol, Isopropyl Alcohol, Methyl-Ethyl Ketone, Benzene, n-Butyl Phthalate Camphor, Para-Phenylenediamine, Styrene, Xylene, Acetone, Cetyl Alcohol, Glycerol, Propylene Glycol, Benzyl Alcohol, n-Butyl Acetate, Formaldehyde, Methacrylic Acid, Resorcinol, Tricresyl Phosphate, Toluene, Isobutane, Liquefied Petroleum Gas, Mineral Spirits, Propane, Methylene Chloride, Methyl Chloroform, Perchloroethylene, Trichloroethylene, Hydrogen Cyanide, Amino Phenol, Ammonia, Ammonium Persulfate, Phenacetin, Ethylene Tetracetic Acid (EDTA), Ethanolamine, Alkylated Silicates, Non-Ionic Detergents

Some of the compounds listed here react slowly when treated with Ozone alone, however when combined with one or the other - Ultraviolet or UltraSound the reaction and reaction time becomes extremely rapid. Both of these technologies are available in the unit and more details will be covered in their individual sections. It should also be noted at this point that in some cases in the primary Ozonation if the process is stopped too soon or if insufficient Ozone is used some compounds will be left in the stream in their more toxic form. To avoid this occurrence we have located just downstream of the primary Ozone treatment unit a Residual Dissolved Ozone Monitor. This way we can assure that if there is residual Ozone after primary treatment, we have supplied sufficient Ozone to carry all reactions to completion.

The unit is equipped with our own patent Ozone Generator with all needed controls for flow direction and quantity of flow to each input point. There are five Ozone input points and mixing with the treatment stream is accomplished using the Mazzie Venturi Injector which is laboratory proven to be 99+% effective. The prime Ozone treatment Unit is a SS tank sized to give up to 10 minutes residual treatment time based on the particular units maximum flow rate. This tank is closed at the top leaving an Off gas chamber at top

of the tank. The Off gas Ozone is reinjected at one point. This is in the Ozone Treatment Tank recirculation system. The Ozone Treatment Tank has two methods or points of Ozone injection here. The first is in the principal input flow line where the major injection occurs, then as a secondary reinforcement treatment we have our own developed method of recirculation within the tank with Ozone (some from the Off gas at the top of the tank reinforced with a small flow from the main Ozone system) being reblended into the contents of the tank. This should keep the waste stream saturated with Ozone.

Compounds normally refractory or slow reacting to Ozone or UV alone but which react to the combination of UV/Ozone:

Cyanide complexes of Iron - rapidly decompose cyanide to non-detect (N/D): Copper & Nickel complexed Cyanides, Other Metals complexed Cyanides, Cyanide containing waste water, Pesticides and insecticides, Organic and Amino Acids, Organic Nitrogen, Sulphur & Phosphorus compounds.

Chlorinated Organic compounds: Acetic Acid, Oxalic Acid, PCB's , DDT, Alcohols, Phenolic compounds, Methyl ethylketone, Propane, Chloroform.

N,N - Diethyl - Meta - Toluamide (DEET), Ferrocyanide, TNT (Pink Water), Polmitic Acid, Ferricyanide, Glycine, Cresols, o-Toluidine, Diethyl ether, Ethanol, Glycerol.

Several investigators have shown that N-dealkylated (deethylatrazine and deisopropylatrazine) and acetamido-s-triazines are the primary oxidation by-products of atrazine by O<sub>3</sub> and by O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> (table 1; fig. 1a). Under conditions which favored the production of hydroxyl radicals (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>), trace amounts of hydroxyatrazine may also be formed. These primary by-products are subsequently degraded to give complete N-dealkylated, deaminated, dehalogenated and hydroxylated s-triazines (deethyldeisopropylatrazine, ammelide ammeline, cyanuric acid,...) (table 1). For example, oxidation of deethylatrazine by O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> yields deethyldeisopropylatrazine as the major by-product (fig. 1b).

Identical by-products are produced by photochemical oxidation (O<sub>3</sub>/UV, H<sub>2</sub>O<sub>2</sub>/UV and TiO<sub>2</sub>/UV) (table 2; fig. 4 and 5). UV photolysis of atrazine at 253.7 nm (monochromatic radiation) yields hydroxyatrazine as the major product (= 0.95 -1.0 mole of hydroxyatrazine formed / mole of atrazine photolysed (fig. 4a) whereas N and N,N'-dealkylated, deaminated and hydroxyderivatives are produced by UV irradiation in the presence of ozone, hydrogen peroxide (fig. 4b) or photosensitisers.

The s-triazine ring is found to be resistant to chemical and photochemical oxidation. Pathways for the degradation of atrazine by molecular ozone (fig. 2) and by hydroxyl radical (fig. 3) are proposed.

#### *Kinetic rate constants:*

The second-order kinetic rate constants for the reaction of molecular ozone and of hydroxyl radical with atrazine have been determined by several authors from competitive experiments or from kinetic models. The rate constants for the reaction of ozone which have been measured (~ 6 l mol<sup>-1</sup> s<sup>-1</sup> at ~ 20°C) indicate that molecular ozone is not very reactive towards atrazine. The rate constants which have been determined for the reaction of hydroxyl radical with atrazine by using different modes of generation of hydroxyl radicals (O<sub>3</sub> + OH<sup>-</sup>; O<sub>3</sub> + H<sub>2</sub>O<sub>2</sub>; PhotoFenton; H<sub>2</sub>O<sub>2</sub> + UV) are in the order of 2 × 10<sup>9</sup> - 2.5 × 10<sup>9</sup> l mol<sup>-1</sup> s<sup>-1</sup> at ~ 20°C (table 3).

Rate constants for the reaction of hydroxyl radical with other s-triazines have been determined from competitive kinetic experiments. The relative rate constants show that methylthio s-triazines are far more reactive than methoxy s-triazines, which in turn are more reactive than chloro and hydroxy s-triazines (table 4). The kinetic data also confirm that deethyldeisopropylatrazine and cyanuric acid are very refractory to the oxidation by hydroxyl radical.

## **PHOTOXIDATION OF PHENOL IN AQUEOUS SOLUTION**

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### **ABSTRACT**

This paper presents the results of the oxidation of Phenol in aqueous solution in a semi-batch reactor. The advanced oxidation processes studied were UV, ozone, hydrogen peroxide and its combinations. The pH dependence and the influence of the initial concentration of hydrogen peroxide were studied to find the optimal conditions for a complete and fast oxidation of this organic compound.

Experimental results indicated that phenol is destroyed more rapidly by ozone at higher pH (9-12), while ozonation combined with hydrogen peroxide or/and UV is considerably faster at low pH (3-7).

### **KEYWORDS**

Wastewater, phenol, ozone, UV, hydrogen peroxide, hydroxyl radical.

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**INTRODUCTION:**

The oxidation processes involving hydroxyl radical have shown their potential to destroy toxic organic compounds in waste-water. The main interesting characteristics of hydroxyl radical are its very high oxidation potential (bigger than ozone and only smaller than fluorine) and the possibility of its generation by different ways. This radical may be produced by combining ozone with ultraviolet light (Glaze et al.,1982; Mirat et al.,1987; Esplugas et al.,1994; Prado et al.,1994), ozone with hydrogen peroxide (Paillard et al.,1986; Trancart, 1990; Duguet et al.,1990), hydrogen peroxide with ultraviolet light, hydrogen peroxide with ferrous or ferric ion (David et al.,1991; Joseph J.,1992) and by photocatalysis, which uses a semi conductor in combination with visible and UV radiation and molecular oxygen (Weir et al.,1990; Brezova et al.,1991).

Ozonation is a simultaneous mass-transfer/reaction-kinetics phenomenon. Kinetic modeling of the ozonation of phenol in water has been studied by Roth et al. (1982), using a semi-empirical model which incorporate the mass transfer, resulting from the diffusional resistance of ozone, and kinetics encountered during ozonation with operating parameters for scale-up for wastewater treatment. The combination of ozone and hydrogen peroxide is used essentially for the contaminants which oxidation is difficult and consumes large amounts of oxidant. Because of the high cost of ozone generation, this combination makes the process economically feasible. The photolytic ozonation (uv/ozone) was also used for the oxidation of phenolic compounds; Gurol et al. (1987) studied the photolytic ozonation of mixtures of phenols, TOC removal by UV light alone was negligible, by ozone 30% has been removed and more than 95% by UV/ozone.

In order to compare the different advanced oxidation processes phenol has been chosen because it is a very simple organic compound, easily soluble in water at different condition of acidity. In addition phenol constitutes one of the main pollutants to be removed from wastewater.

**EXPERIMENTAL**

All experiments were performed in the experimental installation shown in figure 1. The reactor is tubular with a spherical vessel with 4.54 L capacity upper. The design of this reactor possibilities the cocurrent circulation of gas (oxygen and generated ozone) and liquid (aqueous

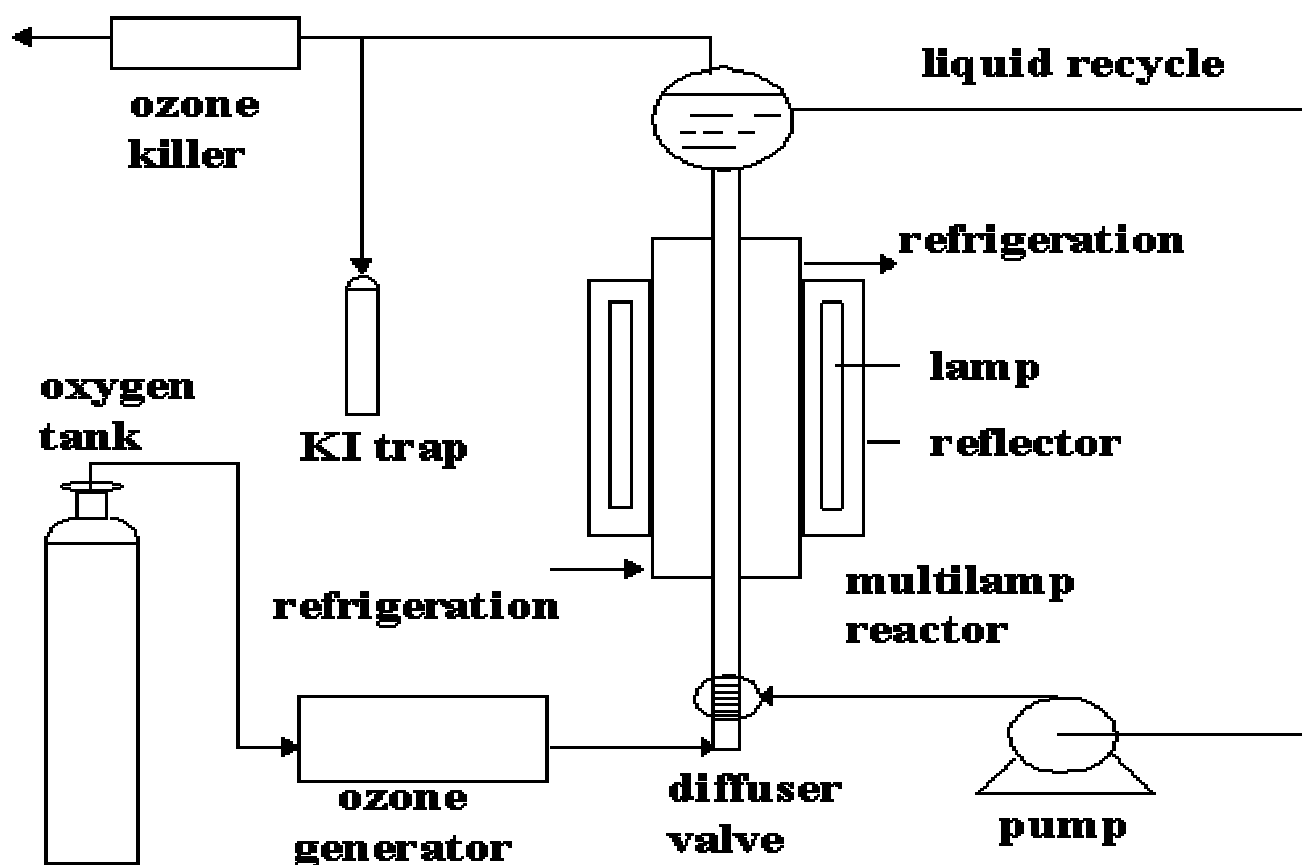


solutions of the compounds studied) which are mixed with a diffuser valve in the bottom of the reaction tube.

Oxygen gas was supplied in standard cylindrical tanks and fed to an ozone generator model TDZ 11-20 TODOZONO. The saturation concentration of ozone was determined to be 1.5-2 mg/L depending on the flow rate of gas through the system. The reactor is surrounded by four low mercury lamp (15 Watts each lamp) which emit radiation at 253.7 nm.

For every experiment, the reactor was filled with 2500 cm<sup>3</sup> of aqueous solutions of analytical grade phenol (from PROBUS), buffered with 0.01M Na<sub>2</sub>HPO<sub>4</sub>/0.01M KH<sub>2</sub>PO<sub>4</sub> to adjust the pH at 6.9. A 0.05M borax buffer was used to adjust the pH of phenol solutions at 9.3.

The samples were taken at appropriate time intervals and analyzed immediately by high pressure liquid chromatography (HPLC) using a Waters chromatograph. The analyses were made in reverse phase with an ODS<sub>2</sub> SPHERISORB column eluting the injected sample (20 μL) with a mixture of acetonitril-water (50:50 v/v) in the case of phenol, with a flow rate of 1 cm<sup>3</sup>.min<sup>-1</sup>.



*Figure 1. Experimental installation.*

For all experiments done with ozone, the ozone gas excess was passed out through the top of the reactor into a bottle containing 2% KI solution for the later iodometric determination of ozone production (Birdsall, 1952). The concentration of residual dissolved ozone was followed by the Indigo procedure (Hoigné and Bader, 1983). A spectrophotometer SHIMADZU model UV-1203 was used to measure the change in absorbance of the indigo.

In addition, samples were also analyzed to determine the total organic carbon (TOC), using a Dohrman DC-190 high level TOC analyzer.

The operating conditions in the experimental series were:

ozone production =  $0.2 - 0.3 \text{ g.h}^{-1}$

radiation intensity =  $7.22 \text{ } \mu\text{einstein.s}^{-1}$

gas flow rate =  $60 \pm 4 \text{ L.h}^{-1}$

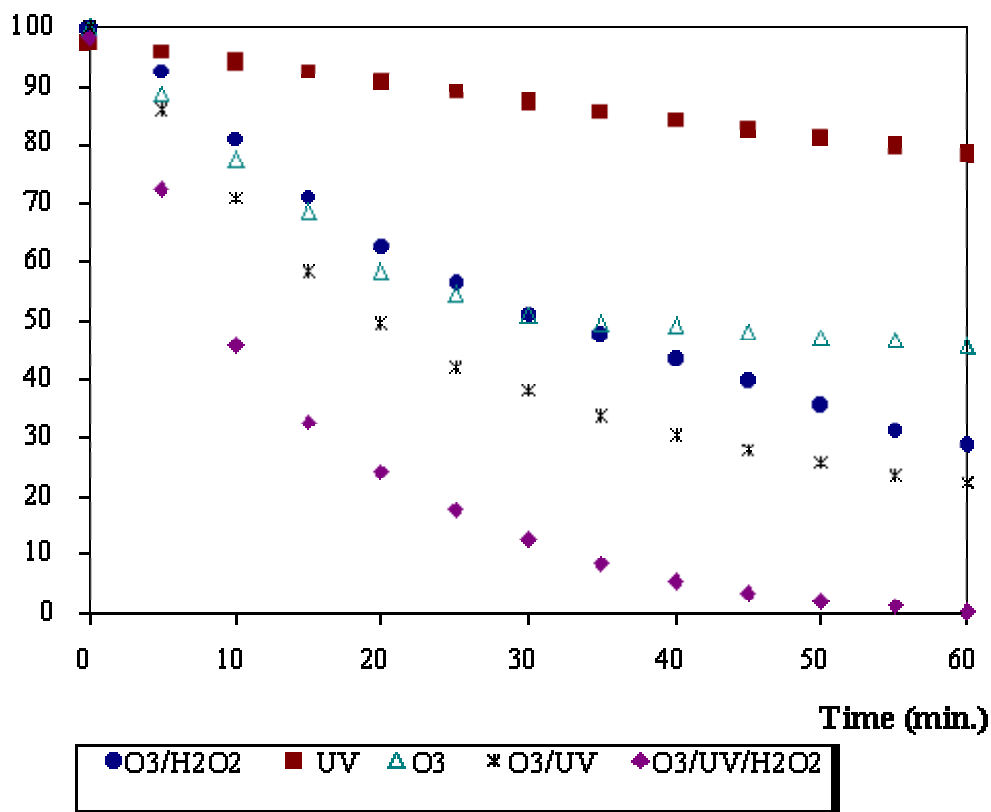
liquid recirculation rate =  $100 \pm 5 \text{ L.h}^{-1}$

reaction volume = 2.5 L

temperature = 18 - 25 °C

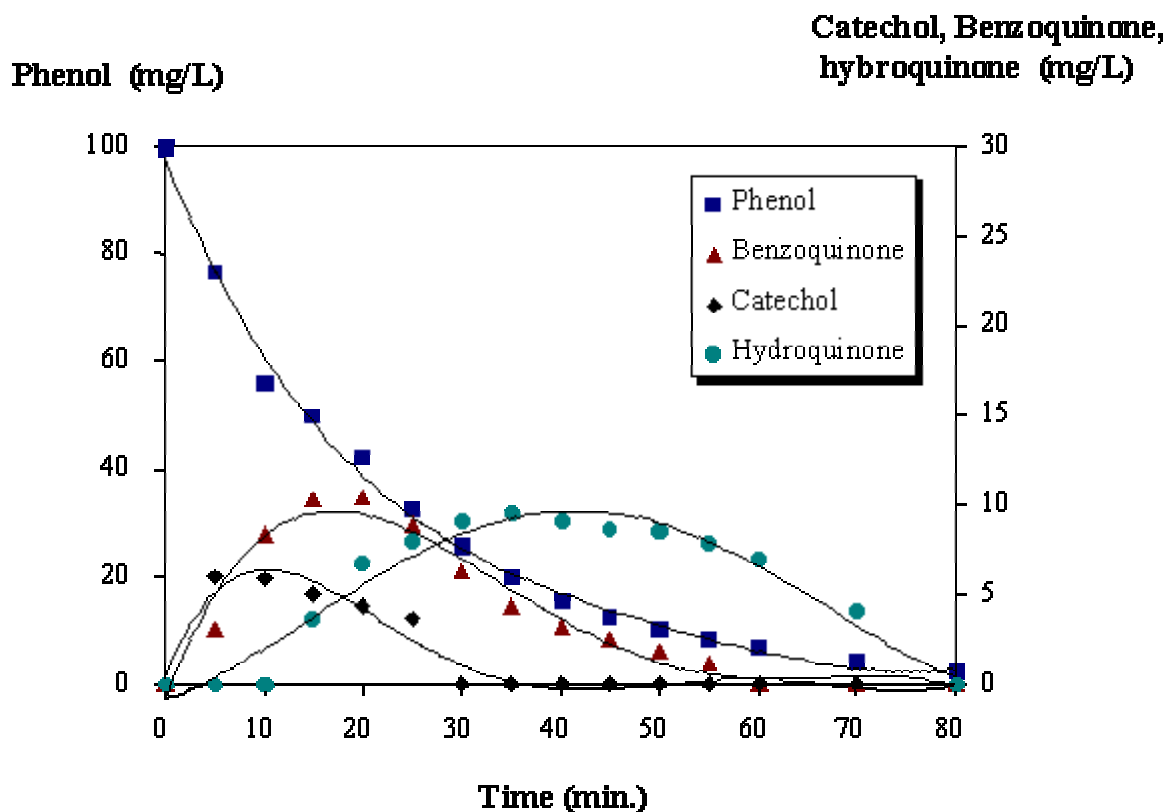
## RESULTS AND DISCUSSION

Figure 2 shows the rate of disappearance of phenol at non buffered acid pH (4.9) using different AOP. It can be observed that the combination of UV/Ozone/Hydrogen Peroxide leads to a better degradation of the phenol. In this unbuffered experiment, the pH dropped (3.2) due to the formation of acidic intermediates and products.

**Phenol (mg/L)**

**Figure 2. Profiles of phenol with different AOP.  $pH=4.9$ ,  $[H_2O_2]_0=3.19 \cdot 10^{-3} \text{ mol.L}^{-1}$**

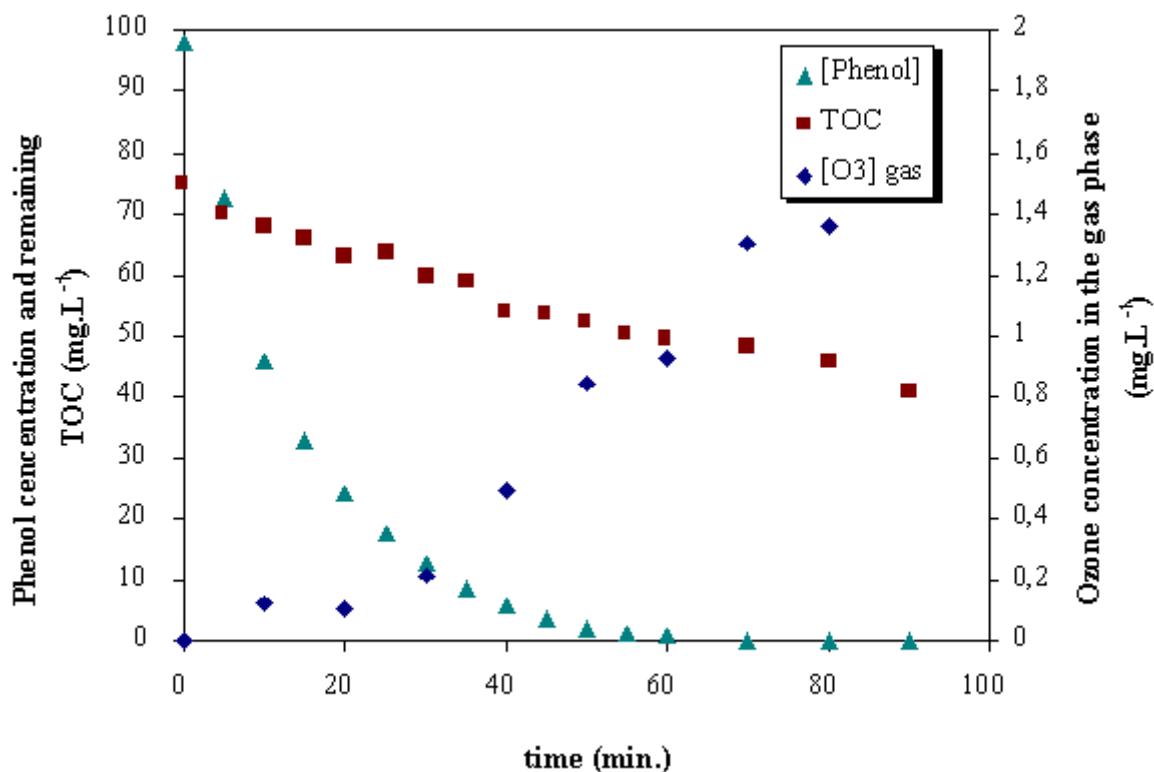
The photolysis with 253.7 nm radiation practically does not degrade phenol. But the combination UV/ozone gave better results than the using only ozone. In the degradation of phenol using ozone there are two main reactions: the direct reaction of ozone with phenol and its products and the reaction of the hydroxyl radical generated. Some intermediate products as benzoquinone, catechol and hydroquinone were detected during the degradation of phenol (figure 3).



**Figure 3. Profiles of phenol, benzoquinone, catechol and hydroquinone.**

**AOP: O<sub>3</sub>/UV/H<sub>2</sub>O<sub>2</sub>. pH=4.9, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub>=1.59.10<sup>-1</sup> mol.L<sup>-1</sup>.**

Additionally, it must be taken into account the low rate of ozone decomposition at acid pH (Gurol and Singer, 1982) and the predominant direct reaction with molecular ozone. Ozone in the exit gas appeared few minutes after the beginning of all experiments with ozone (figure 4).



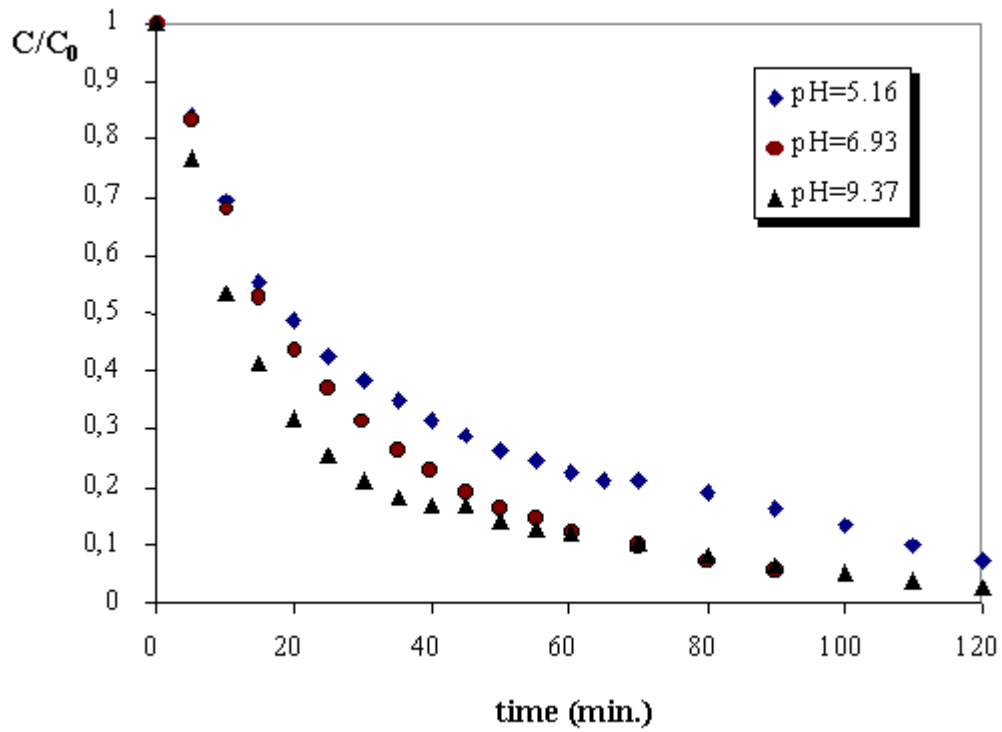
**Figure 4. Profiles of phenol, TOC remaining and ozone in gas phase.**

***O<sub>3</sub>/UV/H<sub>2</sub>O<sub>2</sub> , pH=4.9, [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub>=6.37.10<sup>-2</sup> mol.L***

The influence of initial hydrogen peroxide concentration have been studied in the case of phenol, several experiments were carried out with different initial concentrations of hydrogen peroxide. It was observed that the oxidation rate of phenol first increases when hydrogen peroxide concentration increases, the opposite effect was observed at high concentrations. 63.7 mmol/L was found to be the optimal concentration and it corresponds to the removal of all phenol and 40% TOC after 70 min. reaction time.

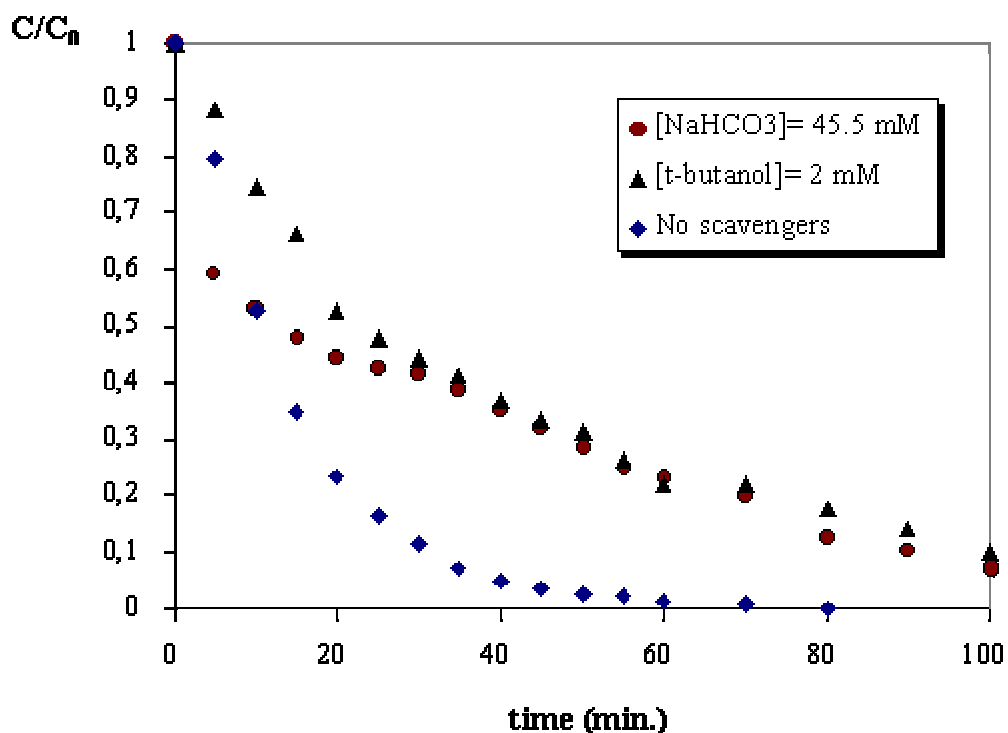
The pH is certainly the most important variable in advanced oxidation processes. In the experiments performed with the system UV/ozone, as it is shown in figure 5, when the pH increases the degradation rate also increases. The pH influence has been studied for the other oxidation processes, with the pH range used (4.8-5.2 for acidic pH, 6.8-7.1 for neutral pH

and 9-9.5 for basic pH) the experimental results obtained show that ozonation, UV/ozono and ozone/hydrogen peroxide are faster at basic pH, while photolysis and UV/ozone/ hydrogen peroxide have a faster reaction rate at low pH values.



**Figure 5. Influence of pH in the uv/ozone process.**

More interesting is the influence of the presence of radical scavengers in the aqueous medium in the degradation rate. As it is shown in figure 6 the presence of t-butanol and the anion hydrocarbonate decreases drastically the degradation rate. After one hour reaction time the conversion is nearly 100% in the case of ozonation and only 75% adding radical scavengers. This result confirms that the free radical pathway is significant at higher pH values.



**Figure 6. Ozonation at basic pH. Influence of the presence of scavengers.**

## CONCLUSIONS

All the Advanced Oxidation Processes used in this work leads to the removal of the compounds studied, but with different degradation rates. It is possible to mineralize the organic compounds.

The pH is an important variable to take into account. At acid pH, the direct attack by molecular ozone is predominant and any source of radicals ( $H_2O_2$  or/and UV) improve the efficiency of ozonation, while at neutral and basic pH there is a major contribution of the free-radical pathway and the addition of hydrogen peroxide and/or UV can promote or inhibit the reaction of ozonation.

The presence of scavengers of hydroxyl radicals as t-butanol and sodium bicarbonate

decreases the rate of phenol oxidation at higher pH values..

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## **CHAPTER III**

### **AUXILLARY PROCESSES TO AOP**

#### **3.1 ELECTROCHEMICAL FLOCCULATION UNIT:**

There is still a lack of a complete analytical study of all ramifications and applications of Electrochemical Flocculation. We do know that Electrochemical Flocculation is the process of applying a direct or alternating electrical current and voltage of varying strength to electrodes contacting water or waste water which results in the formation of Floc which can be filtered to remove suspended and flocced dissolved substances. The mechanism by which this flocculating occurs are complicated and involve the interconversion of electrical and chemical energies reacting with and on substances in the water or waste water.

Compounds which are Non-Reactive to Ozone but show excellent reaction with the Electrochemical method: Calcium Oxide, Phosphoric Acid, Silicas, Sodium Persulfate, Hydrogen Peroxide, Potassium Persulfate, Sodium Bromate, Strontium Peroxide, Tetrasodium Purophosphate, Titanium Dioxide.

At this point we would call to your attention that through out this documentation as we list contaminants treated by each technology there are a great many if not in total at least duplication of treatment. Therein lies the primary reason for the ability of this unit to do such a thorough job of contamination elimination. The unit makes use of at least two and often three different treatments technologies which are effective against each contaminant within the waste stream. The percentage of effectiveness varies, however the total effect is as indicated by the lab results. The Electrochemical Flocculation Unit is a unit of our design and patent pending. Just in front of this there is located another Ozone Venturi Injector to assure the oxidation (Ozonization) is still active as the waste stream passes through the Floc unit. The synergistic effect of the these methods improve the efficiency of the Electrochemical Flocculation System.

## 3.2 Activated Carbon

Activated carbon is a carbon which have been subjected to a chemical or physical activation. These two processes presents some advantages and disadvantages.

### Physical Activation

#### Advantages

The main advantages of physical activation are to make “clean” activated carbons, without incorporation any mineral impurities and produce essentially microporous carbon. The microporosity is useful for gaseous effluent applications.

The raw materials often used is coconut shell. The physical chemistry of this activated carbon : pH=9, very hard, apparent density 0.5.

### Physical Activation processes & Disadvantages

- 1- First step carbonization process of the precursor to eliminate volatile materials such as hydrogen and oxygen by mild temperature heating .

#### Disadvantage :

The carbonization “combustion” process is responsible for low yield of the A.Carbon because there is formation of tar and hydrocarbons such as CH<sub>4</sub>, CH<sub>3</sub>OH which contribute in removing a high percentage of the available carbon.

- 2- Second step higher temperature activation (900C-1000C). The activation processes takes place by partial combustion of carbon under flow of oxidant gas such as carbon dioxide and steam or mixture of them.

#### Disadvantage:

- Long activation time (several hours);
- weak yield of activated carbon (15 %) to get surface area BET 1100m<sup>2</sup>/g;
- Narrow pore distribution (essentially microporous chars).

### Chemical Activation

The chemical activation of wood by phosphoric acid, KOH or ZnCl appears to be an interesting process to produce activated carbons with a good yield at low temperatures (< 500°C) and wide pore size distribution .

Acidic character are usually obtained with chemical activation process. Among the activation reagents, phosphoric acid is preferred because it has a minor environmental impact as compared to zinc chloride process . Another advantage to use Phosphoric acid is that it can be recycled/recovered from the washing step after carbonization.

#### Advantages:

The advantage of chemical activation with phosphoric acid is that it is a one-step carbonization and activation stage; an interesting yield (~ 40%); a lower temperature of activation (<500°C); a short activation time (3-5 hours); a higher BET surface area (1800-2200 m<sup>2</sup>/g) .

The activation atmosphere appears to influence the porosity and the chemical properties of chemically activated carbon. The steam decrease volatile materials and phosphorus content in

activated carbon. Nitrogen and air increase micropores volume of activated carbon whereas steam increases mesoporosity volume and microporosity. In industrial process, the activation is usually carried out under various atmospheres, such as air (nitrogen and oxygen) and carbon. This gaseous atmospheres produce acidic properties for such carbons.

The raw materials often used with phosphoric acid is soft wood and the yield of activated carbon from wood is close 44%. The physical chemistry of this activated carbon : pH=3, medium hard, apparent density 0.4.

**Disadvantages:**

Chemical activation will introduce impurities such as Zn and P, depending on the chemical agent used. The impurities could affect the chemical surface properties of the carbon .

Both pore size distribution and surface chemistry play an important part on the adsorption phenomenon of the gas, the liquids and the solids. Before using activated carbon or buying an activated carbon be sure that what your are buying is adequate for your application.

**Ozone and Activated carbon**

It was found that activated carbon with the proper activation process catalyse the effect of Ozone By allowing higher rate of reactivity. This is due to that Carbon is fixing the organic molecules which allow the active radicals to oxidize them . It can be explained by the high probability of collision between the molecules as the organic molecules are now present at few angstrom layers at the surface of the carbon and much higher concentration instead of being diluted

In a much larger volume.

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**Other referneces from several pollution magazines and articles from the internet too numerous to mention in this general audience & non -technical paper**

