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On the possible treatment procedures for organic contaminants

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1. Introduction

A compound that is repellent, unacceptable or involving in the metabolism in order to make harmful effects to the human being or other living systems is called a pollutant. Most of the organic compounds are a part of day-to-day life either as solvents or as polymeric compounds and insecticides. Above certain percentages, in any states of matter, they will show their adverse effects that will affect life directly or indirectly. Once they enter into the lifecycle, they cannot undergo decomposition by its own. Removal of these compounds from the environment is difficult [1, 2, 3]. For example, DDT (Dichloro diphenyl trichloroethane) is a widely

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Correspondence/Reprint request: Dr. B. Viswanathan, National Centre for Catalysis Research, Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India. E-mail: bviswanathan@hotmail.com used pesticide, more than that it is a dangerous pollutant, which cannot be easily removed from the environment. This type of difficult-to-remove compounds is called as persisting organic pollutants (POPs). It is necessary to evolve specific and suitable abatement technologies for the pollutants. A realization of the existing technologies can give a pavement to more efficient future techniques. This review focuses on the various available and emerging technologies in this regard. One way of broad classification of organic compounds is as volatile organic compounds and non-volatile organic compounds.

1.1 Volatile organic compounds (VOCs)

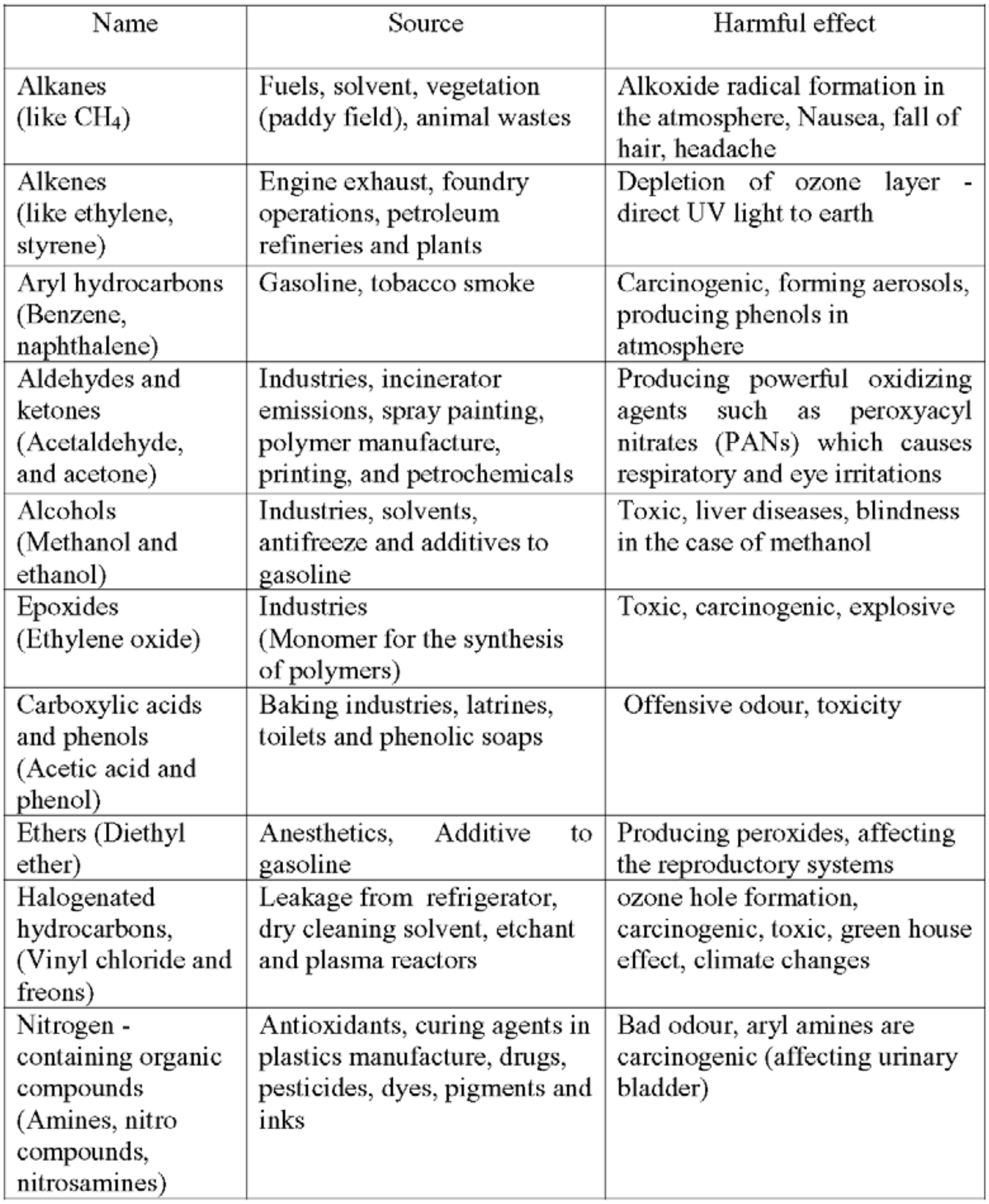
The term VOC refers to a wide-ranging class of compounds. Any compound of carbon excluding carbon monoxide, carbon dioxide, carbonic acid, metal carbides or carbonates and ammonium carbonates that participates in atmospheric photochemical reactions is called as a VOC. Any organic compound with vapour pressure exceeding 0.1 mmHg under standard conditions (25 °C and 760 mm Hg) may be regarded as a VOC. VOCs are commonly found in industrial effluents as by-products or as unused reactants and their release has widespread environmental implications. These VOCs mainly possess low molecular weight, high vapour pressure and hydrophobic nature. The solubility of these compounds is based on polarity. The volatility is mainly due to weak intermolecular forces like vander Wall's forces that exist in these compounds. VOCs mostly exist as gases (CH_4) or liquids (CH_3OH) and rarely as solids (naphthalene). Owing the volatility, these VOCs easily pollute the air (atmosphere) and less likely to pollute the liquid (water) and least pollute the solid (soil). They are transported from one place to another very easily through the air [4]. Various VOCs, their main sources and the harmful effects are tabulated in Table 1.

VOCs, in general, directly cause the following problems. They are eye irritation or watering, nose and throat irritation, headaches, nausea or vomiting, dizziness, asthma exacerbation, chronic disease like cancer, liver damage, kidney damage and central nervous system damage [5, 6]. They affect the living systems indirectly by the formation of ozone-hole and photochemical smog.

1.2 Non-volatile organic compounds (Non-VOCs)

Non–VOCs mainly are the high molecular weight compounds with strong inter molecular forces like hydrogen bonding. They mostly exist as solids or high boiling liquids and have low vapour pressure. Examples are polyols, carboxylic acids and POPs.

Table 1. Different type of VOCs, their main sources and the harmful effects.



Name	Source	Harmful effect
Alkanes (like CH_4)	Fuels, solvent, vegetation (paddy field), animal wastes	Alkoxide radical formation in the atmosphere, Nausea, fall of hair, headache
Alkenes (like ethylene, styrene)	Engine exhaust, foundry operations, petroleum refineries and plants	Depletion of ozone layer - direct UV light to earth
Aryl hydrocarbons (Benzene, naphthalene)	Gasoline, tobacco smoke	Carcinogenic, forming aerosols, producing phenols in atmosphere
Aldehydes and ketones (Acetaldehyde, and acetone)	Industries, incinerator emissions, spray painting, polymer manufacture, printing, and petrochemicals	Producing powerful oxidizing agents such as peroxyacyl nitrates (PANs) which causes respiratory and eye irritations
Alcohols (Methanol and ethanol)	Industries, solvents, antifreeze and additives to gasoline	Toxic, liver diseases, blindness in the case of methanol
Epoxides (Ethylene oxide)	Industries (Monomer for the synthesis of polymers)	Toxic, carcinogenic, explosive
Carboxylic acids and phenols (Acetic acid and phenol)	Baking industries, latrines, toilets and phenolic soaps	Offensive odour, toxicity
Ethers (Diethyl ether)	Anesthetics, Additive to gasoline	Producing peroxides, affecting the reproductory systems
Halogenated hydrocarbons, (Vinyl chloride and freons)	Leakage from refrigerator, dry cleaning solvent, etchant and plasma reactors	ozone hole formation, carcinogenic, toxic, green house effect, climate changes
Nitrogen - containing organic compounds (Amines, nitro compounds, nitrosamines)	Antioxidants, curing agents in plastics manufacture, drugs, pesticides, dyes, pigments and inks	Bad odour, aryl amines are carcinogenic (affecting urinary bladder)

These non-VOCs pollute the environment by the dissolution in precipitates, dry deposition, photochemical reactions, incorporation in particulate matter and uptake by plants. Forest trees have a large surface area exposed to the atmosphere and remove a large quantity of organic materials from air. The cuticle layer of plants is lipophilic (affinity for organic matter), so that the deposition of organic matter is facile and stable. Persistent organic pollutants (POPs) are the major pollutants that fall into the non-VOCs category. The POPs are carbon-based products and by-products of human industry. As the name suggests, they are persistent in the environment, resisting degradation through natural processes. They have the ability to accumulate through the food cycle and to be transported long distances. For instance, Toxins as pesticides are able to kill or alter an organism directly. All common pesticides share the property of blocking a vital metabolic process of the organism to which they are toxic. The most hazardous of these 12 pollutants are called as the "Dirty Dozen" [7]. These POPs are given in Table 2.

Table 2. POPs, their applications and remarks.

POP	Application	Remark
Aldrin (1)	Pesticide used to kill termites and grasshoppers in soils	The estimated fatal dose for an adult male is about five grams
Chlordane (1)	To control termites in soil and used as a broad-spectrum of insecticide	It can kill organisms like mallard ducks and pink shrimps
Dichloro diphenyl-trichloroethane (DDT) (1)	To control malaria-carrying mosquitoes (Extensively used in world war II)	It can still be found in food all over the world.
Dieldrin (1)	To control termites and textile pests. Also to control insect-born diseases and insects living in agricultural soils	It is highly toxic to water-living animals. The residues of dieldrin have been found in air, water, soil, living organisms, pasteurized milk and even in humans. Dieldrin is a toxic pesticide.
Dioxins (3)	Produced unintentionally due to incomplete combustion. They are also produced during the manufacture of pesticides and other chlorinated substances	Although fish die shortly after the intake of dioxins, humans are mostly affected by changes in the systems of human body. Humans are exposed to dioxins mainly through meat
Furans (3)	Occur during the burning of different toxic wastes, can also be manufactured during the production of PCBs	135 different types of furans are structurally similar to dioxins and their toxicity varies. Furans come from burning garbage and it is almost impossible for the economy to ban or restrict the burning
Endrin (1)	An insecticide used to control rodents, it is sprayed on the leaves of cotton and grain crops	The primary exposure to humans is through food, although its dietary intake estimates are below the limits.
Hexa chloro benzene (HCB) (1, 2 and 3)	To kill fungi that affect food crops, it was widely used to control wheat bunt from 1954 to 1959	HCBs can be passed to an infant through the placenta and breast milk. They are highly toxic to humans and can cause death, metabolic disorders, colic and debilitation.

Table 2. Continued

Heptachlor (1)	To kill soil insects such as grasshoppers and malaria-carrying mosquitoes	Responsible for the decline of several US wild bird populations, causes behavioral changes and reduced reproductive success in rats and rabbits
Mirex (1)	An insecticide that is mainly used to combat different types of ants and termites, a fire retardant in plastics, rubber and electrical goods	A possible carcinogen to human, harmful to a number of plant species, fish and crustaceans. Mirex is considered as one of the most constant and persistent of POPs because it has a half-life of 10 years
Poly chlorinated biphenyls (PCBs) (2 and 3)	Used in industry as heat exchange fluids, in electrical transformers and capacitors and as additives in paint, carbonless copy paper and plastics	Although only 13 out of the 209 different types of PCBs have a dioxin-like toxicity, they are generally highly toxic
Toxaphene (1)	An insecticide that is used on cotton, cereal grains, fruits, nuts and vegetables to control ticks and mites in livestock	The exposure to humans mainly occurs through food

These POPs are mainly classified as insecticides (1), industrial chemicals (2) and by-products (3) of various manufacturing or combustive processes. These classifications are indicated with the respective numbers in Table 2.

In general, POPs are a possible carcinogen to human and they damage lungs, kidneys, stomach and immune systems. Other health impacts include skin rashes, diminished intelligence, spontaneous abortions, severe deformities and increased mortality in embryos. They also affect the development of immune, nervous, endocrine and reproductive systems in infants [8]. The POPs are mainly spread over by humans through consumption of contaminated food especially fatty foods such as meat, fish and dairy products. POPs spread also by contact with the skin or eyes or passed from mother to infants through milk. POPs enter the atmosphere by adhering to airborne particles and can therefore, travel long distances in air and then get accumulated in colder regions of the planet.

1.3 Need for the treatment of organic contaminants

In order to avoid these hazardous effects of organic pollutants in the environment, governments had put legislation on the production and usage of these hazardous materials. International convention called as Stockholm

Convention implemented on May 17, 2004 bans or eliminates 12 of the most toxic chemicals. The Stockholm convention aims to reduce and, eventually, eliminate global POPs [9].

Because of these legislations, industries have to remove these hazardous compounds by treating with suitable methods prior to the emission. These organic pollutants may affect the living systems directly or indirectly. For instance, cancer caused by the exposure to vinyl chloride is a direct effect whereas the formation of photochemical smog is an indirect effect. However, the impact of a VOC on the environment depends on the concentration and properties of the individual compounds. Even though, human being is not intentionally synthesizing some pollutants, they are formed as by-products in some cases. So one has to look upon the ways for removing those using suitable strategies. Depending upon the medium where the pollution occurs, the nature and the concentration of the pollutants, one has to select the appropriate technique. Those techniques not only should be effective but also be economically viable. There are two ways of escaping from these compounds. One is trapping those compounds and removes and another is converting them chemically into harmless compounds. Based on this, treatment technologies for organic contaminants can be classified into two types, non-destructive methods and destructive methods.

2. Non- destructive methods

In these methods, contaminants are not chemically altered but they are separated from the medium contaminated by them. One advantage of non-destructive method is that the solvents can be recovered and reused. The following are the non-destructive methods.

2.1 Absorption

Absorption mainly based on the dissolution of a pollutant in a liquid. In absorbers (or scrubbers), the vapor stream is introduced into an absorption chamber where it is mixed with the liquid. Similar to adsorption, which involves adsorbent regeneration, the VOCs are transferred from a gas stream to liquid absorbent, and the liquid must be treated to recover the pollutant and reuse the liquid. If the absorbent cannot be regenerated, the liquid will be disposed off. The series traps containing water and organic low volatile solvents can be used to treat the out stream organic gases. Mainly the regeneration can be done by the distillation or column chromatography [10].

2.2 Adsorption

Adsorption process mainly based on the removal of organic contaminates present in the air stream. The VOC containing air stream is passed through the solid (adsorbent) column, so that the VOCs can be adsorbed on the adsorbent [10]. The adsorbed VOCs will be removed by using inert gas or steam and therefore the adsorbent can be regenerated. The schematic diagram is shown in the Fig. 1. In the set up, adsorbent column (down) is regenerated when another adsorbent column is in use. In the regeneration process, the steam is passed through the adsorbent column and the exhaust is condensed. The mixture from the condenser is bubbled through the water where the water- miscible VOCs can be trapped.

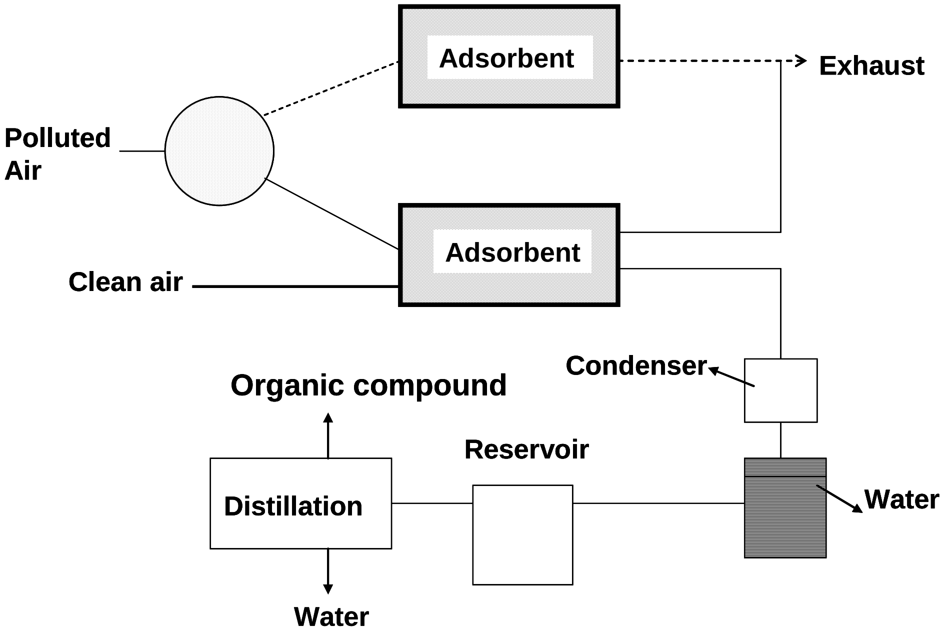


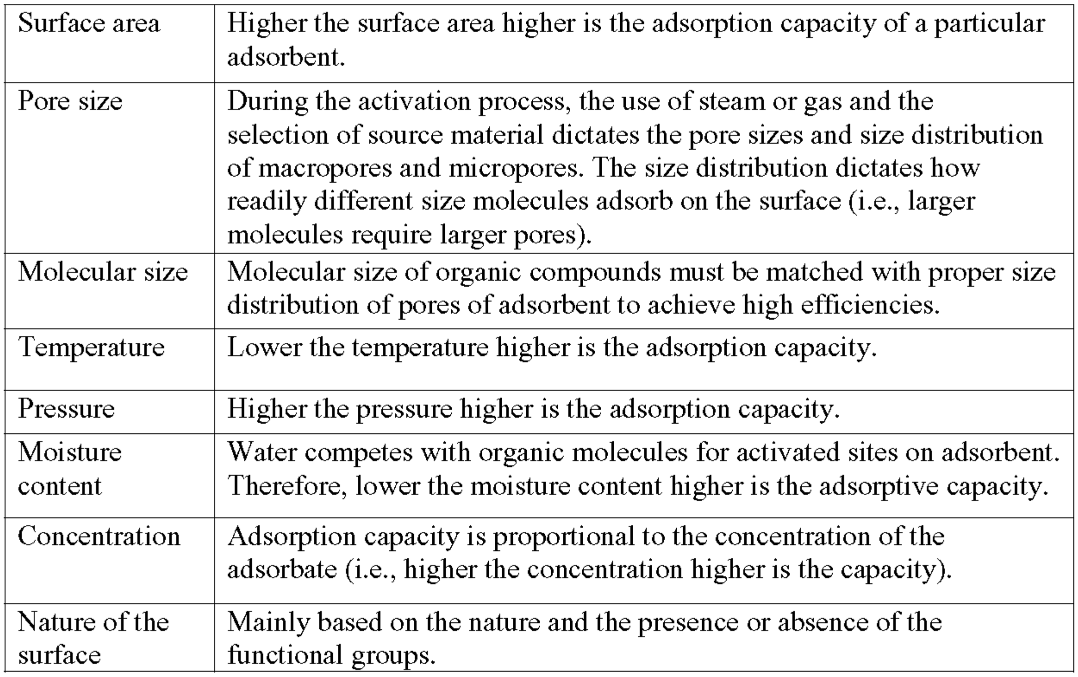
Figure 1. Schematic diagram of adsorption process.

The water immiscible mixture will be distilled, so that water can be separated from VOCs. High boiling VOCs may not be suitable for this process due to the difficulty in regeneration. By this method, the air stream containing the VOCs of concentration less than 100 ppm by volume is treated, where the condensation and combustion are not feasible [11].

The nature of the VOCs also affects the adsorbent capacity. Various modifications are known in this basic set up. In order to avoid the external unit used for the distillation to remove the water, inert gas can be used instead of steam. This method is known as Rankine method. In this method, the more solvent is supplied to the adsorbent bed to make the condensation feasible. Another method known is Brayton method, where the adiabatic expansion and compression is used to generate the cold and hot gas streams. These cold and hot gas streams are used to condense and regenerate the adsorbent bed respectively. When one needs to condense the recovered VOCs from the adsorbent at low temperatures (< 73 °C), the Brayton method is cheaper than the Rankine method.

The materials mainly known for this technique are activated carbons, activated carbon fiber cloths (ACFCs), hydrophobized zeolites, MCM-41, silica gel, polymer resins, papers and ceramers [12, 13]. The properties such as surface area, pore size distribution, adsorbate molecular size, temperature, pressure, moisture content, and concentration of adsorbate are important criteria for good adsorption. High acidity may lead to chemisorption. However, hydrophobicity may not be important for some VOCs that are hydrophilic, for instance, acetone.

Table 3. Important factors for the good absorption capacity.



Surface area	Higher the surface area higher is the adsorption capacity of a particular adsorbent.
Pore size	During the activation process, the use of steam or gas and the selection of source material dictates the pore sizes and size distribution of macropores and micropores. The size distribution dictates how readily different size molecules adsorb on the surface (i.e., larger molecules require larger pores).
Molecular size	Molecular size of organic compounds must be matched with proper size distribution of pores of adsorbent to achieve high efficiencies.
Temperature	Lower the temperature higher is the adsorption capacity.
Pressure	Higher the pressure higher is the adsorption capacity.
Moisture content	Water competes with organic molecules for activated sites on adsorbent. Therefore, lower the moisture content higher is the adsorptive capacity.
Concentration	Adsorption capacity is proportional to the concentration of the adsorbate (i.e., higher the concentration higher is the capacity).
Nature of the surface	Mainly based on the nature and the presence or absence of the functional groups.

Among the materials used, activated carbon was found to be more efficient for the following reasons [14, 15].

1. Good surface area and porosity due to the high surface to mass ratio
2. Alterable surface functionalities and porosities
3. Cheaply available
4. High lifetime - this can be used for 3-5 years with regeneration cycles.

2.3 Condensation

Condensation is the process by which a vapor is converted into a liquid either through the reduction in temperature or by an increase in pressure.

Typical condensation systems for pollution control applications use temperature reduction as the impetus for condensation [16].

Simple condensation set up is shown in Fig. 2. Condensation efficiencies are dictated by the ability to cool the gas temperature. As the temperature of the VOC-containing gas stream is reduced, weak electrostatic forces causing them to condense mutually attract the organic molecules. The temperature at which condensation begins is referred to as the dew point. In order to achieve higher efficiencies and additional condensation, the temperature must be reduced below the dew point so that the vapor pressure will be lowered and hence reduce the amount of organic molecules remaining in vapor form. Typical efficiencies for condensation are 70 – 90 %. This technology is mainly applied in smaller streams with very high concentrations [17]. VOCs with higher boiling point are considered as good candidates for the condensation, because they can be easily condensed. Condensation systems may operate in the range of 5 °C using chilled water or brine solutions and are used for either lower efficiency applications or those operating on high boiling components. Refrigeration condensation systems use compressed coolants and can operate at temperatures as low as -101°C [18]. At these temperatures, a defrosting cycle is implemented which typically requires a redundant condensation unit to provide uninterrupted operation. Condensation technologies have advantages and disadvantages over other pollution control technologies, which can make the selection process as confusing. The condensation temperature is directly proportional to the concentration of the VOCs in the air stream [19, 20].

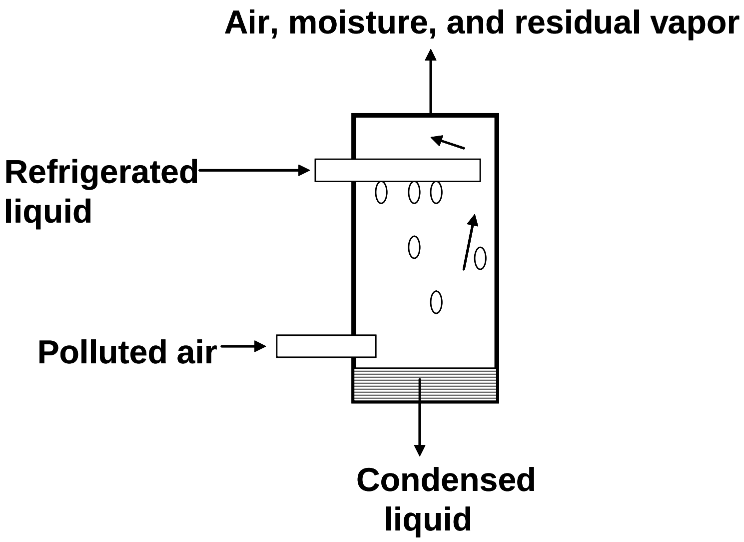


Figure 2. Schematic diagram of condensation technique.

2.3.1 Reverse Rankine cycle condensation

The Rankine cycle heat pump can recover VOCs from the airstreams without degrading the solvents. The typical Rankine reverse condensation set up is shown in Fig. 3. Usually a closed cycle Rankine heat pump with a separate working fluid is used to condense VOCs. This makes condensing and evaporating temperature of the working fluid fixed and dictates the temperature range over which the VOCs must condense. At low temperature, the Rankine cycle is slow to achieve operating temperature. Typical condensing temperature for the reverse Rankine heat pump is -29 °C to -35 °C. However, it can reach temperatures down to - 73 °C.

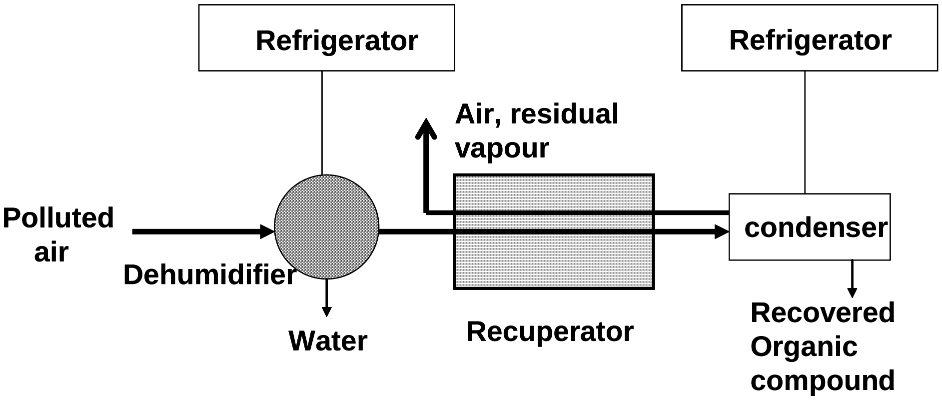


Figure 3. Schematic diagram of Rankine cycle condensation.

2.3.2 Reverse Brayton condensation

Reverse Brayton cycle uses the cooling caused by the expansion to produce the low temperature for the condensation of VOCs. The set up for the Reverse Brayton condensation is given in Fig. 4. Theoretically, the only limit on the condensation temperatures, the reverse Brayton cycle can reach, is the temperature at which oxygen liquefies (-183 °C). But process limitations restrict the lowest condensation temperature to be approximately -101 °C. The reverse Brayton cycle heat pump has several advantages over the Rankine heat pump.

(1) It can operate efficiently at temperatures below -73 °C
(2) It handles fluctuation in temperature, composition or flow rate in the VOC contaminant air stream.
(3) It achieves the low condensation temperature rapidly, thus making start-ups and shutdowns less of problem.
(4) It can produce the lower effluent VOC concentrations (because it can reach lower condensation temperature.

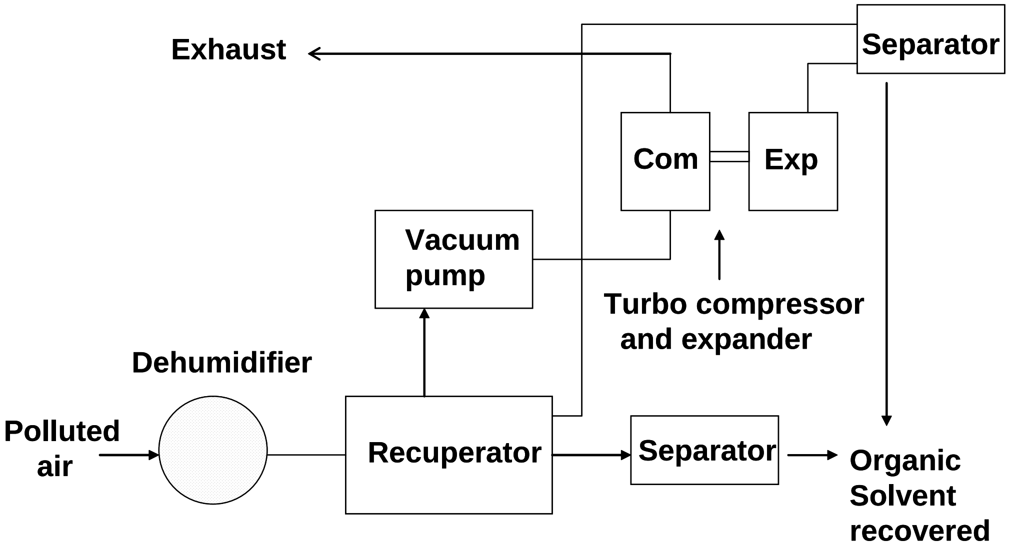


Figure 4. Schematic diagram of reverse Brayton condensation.

2.3.3 Cryogenic condensation

Cryogenic condensation is a process used as an effective method for VOC emissions control. Cryogenic condensation technology is based on lowering the vapor pressure of a component by reducing the temperature of the process stream and thus increasing the recovery of the components in the liquid phase [21]. Nitrogen gas is widely used in the chemical process industry as inert gas and it can be transported and stored in its liquid state at low temperatures and high pressures. Liquid state is a convenient state to use. The low temperature capability of liquid nitrogen allows for the design of highly efficient condensation systems. At temperatures below – 84 °C, the vapor pressure of most organic compounds is depressed sufficiently to condense 95 to 99 % of the compounds from a typical emissions stream. In addition, the outlet nitrogen can be recycled for reuse within the plant [22, 23].

Cryogenic condensation is well suited for VOC emission control because of its ability to respond instantly to changes in VOC flow rate and solvent loading. It can recover virtually any VOC species even under varying conditions. This method can deal with all VOCs (even in the presence of water) and can function when the concentration and composition are changing over time [24]. This flexibility makes it particularly suitable for VOC control in multi-product and multi-purpose plants where batch or continuous processes are employed. Because of the cost of the liquid nitrogen, to make this method economical the minimum concentration of VOCs (3 - 5%) should be there in air stream. Typically, the only constraint on the VOC itself is that its freezing point should be below -30 °C. Otherwise, freezing is likely to occur.

Cryogenic condensation systems generally consist of one or a series of plate-fin or shell-and-tube heat exchangers. The VOC stream and the liquid nitrogen stream flow through the heat exchanger in opposite directions to maximize heat transfer as shown in Fig. 5. The VOC condenses on the shell side of the exchanger and then drains into a collection tank, from which it can be recycled or recovered. During condensation, the presence of water vapor or VOCs with a high melting point can cause freezing on the external surface of the tubes inside a condenser [24]. A solid buildup will blanket the heat transfer area and thus reduce the efficiency of the process, unless suitable precautions are taken. One method of preventing buildup due to freezing is to periodically flush the pipes with the condensed phase. Another method is to use two condensers in parallel (continuous operation) so that one condenser is in operation while the other is out of service being cleaned or defrosted. Another option when excessive moisture is a concern is to arrange two condensers in series. In the first or pre-cooling stage, the VOC stream is cooled to about 0 °C in order to trap the water. Air sweeps can sometimes be replaced with nitrogen sweeps to enhance the recovery of VOCs from the vent gas. The amount of VOC recovered is proportional to the fraction of VOC in the vapor (expressed as the partial pressure of the component). Recovery rates are increased at higher vapor concentrations. For example, if a 5 % concentration of VOC in a gas stream is technically feasible, the vent stream concentration is controlled at 0.5% in air to eliminate the risk of explosion. In other words, the concentration is controlled below the lower explosion limit (LEL), and then the addition of nitrogen can render the atmosphere inert and at the same time allow a VOC concentration of 5%, without which the mixture would be explosive. Thus,

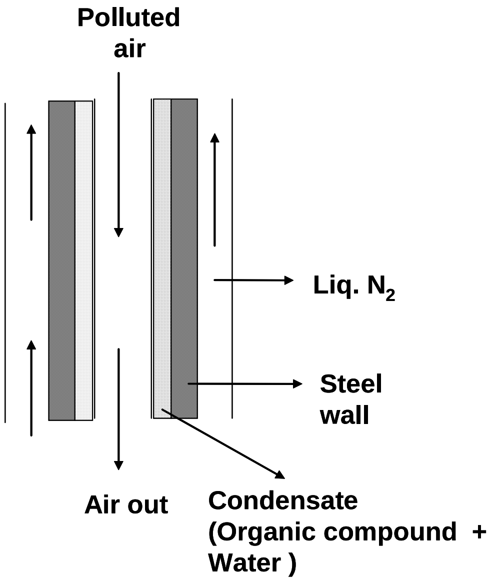


Figure 5. Cryogenic condensation process.

VOC recovery is increased while maintaining safe operating conditions. In general, heat exchanger materials must be made out of stainless steel (316). Because, it must be compatible with both the streams and the low temperature operation. However, carbon steel or cast iron is not allowed. Thus, this method is safer technique than the other techniques like incineration. Disadvantages of this method is VOCs are often released or captured as mixtures in large volume gas streams, then the condensed mixtures are not easily separated. To maximize the purity and minimize the cross-contamination, batches may have to be separated by purging and flushing of the system [25, 26].

2.4 Air stripping

Air stripping is used mainly for purifying the ground water contaminated by VOCs. This may not be useful for non-VOCs. In general, air stripping takes place in a packed tower (known as an air stripper) or an aeration tank. In air strippers, the (VOCs) are transferred from water to air. Typically, air stripping takes place in a packed tower (known as an air stripper) or an aeration tank. Types of aeration methods include packed towers, diffused -bubble aeration, tray aeration, and spray aeration [27, 28, 29].

2.4.1 Packed tower aeration (PTA)

The air stripper includes a spray nozzle at the top of the tower as shown in Fig. 6. It sprays groundwater that has been pumped to the surface over the packing in the column. The water trickles down through the spaces between the packing materials toward the bottom of the tank. Packing or baffles within the tower increase the surface area of the contaminated water that is exposed to air, thus maximizing the amount of volatilization. Packing material is made of plastic, steel or ceramic. A sump at the bottom of the tower collects decontaminated water. The air carries VOCs to the top of the tank where they are collected and cleaned. If VOCs are still present, the process can be repeated.

2.4.2 Diffused-bubble aeration

Diffuser systems inject air (usually as bubbles) into water. The VOCs are transferred from the water to the bubbles as they rise through the liquid. Smaller bubbles provide a greater surface area per unit volume over which mass transfer can occur. In the most common systems, the water passes through a series of tanks (0.5–6 m deep), simulating a plug-flow reactor. The VOCs-contaminated air leaves the water when the bubbles reach the surface and is vented out of the unit. Shallow-tray (20–30 cm deep) aeration is a variant of this technology in which a thin layer of water passes across a series of plates perforated with holes. Air coming up through the holes causes the water to froth, and the mass transfer occurs [31].

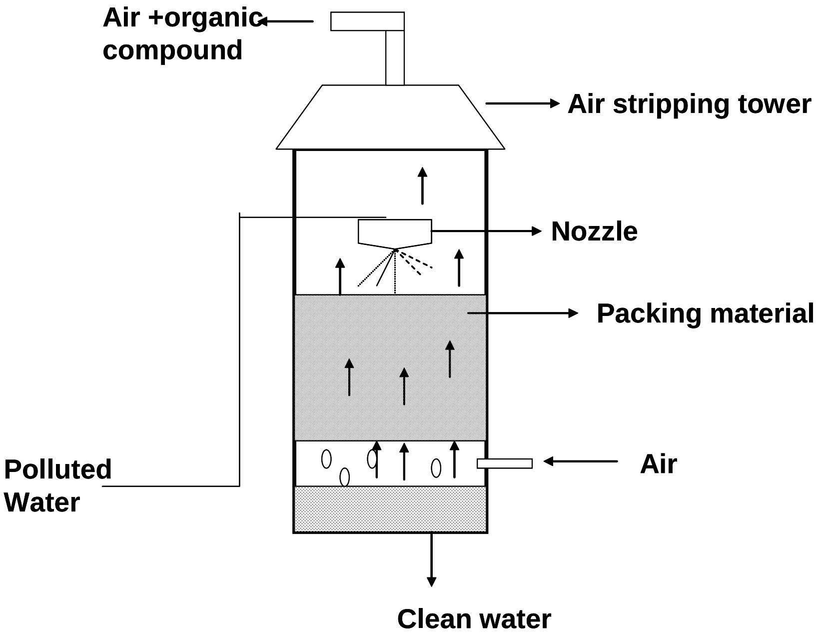


Figure 6. Schematic diagram of packed tower aeration (PTA).

2.4.3 Tray aeration

Tray-aeration systems are similar to countercurrent PTA except that the tower contains a series of slats (for example, made of redwood) or trays with perforated bottoms (for example, made of wire mesh). In some cases, a solid medium (such as stone, ceramic spheres) is placed in the trays to promote transfer of VOCs to the air. Water entering the top of the aerator is distributed over the trays or slats. Natural, forced, or induced draft causes air to flow past the thin film of water formed [31, 32].

2.4.4 Spray aeration

In this technique, water is formed into droplets (with a high ratio of surface area to volume) when it is forced through a nozzle. The droplets are sprayed upward, downward, or at an inclined angle into a large volume of air that is often flowing in a countercurrent direction. The simplicity of spray-aeration systems is that they can easily be retrofitted onto the inlet of an existing atmospheric storage tank to enhance the efficiency of removal of VOCs from water. Their VOC-removal efficiency is mainly a function of the size of the water droplets and the ratio of air to water (A:W ratio) [33].

The advantages offered by aeration tanks are considerably lower profiles (less than 2 m or 6 feet high) than packed towers (5 to 12 m or 15 to 40 feet high) where height may be a problem, and the ability to modify performance or adapt to changing feed composition by adding or removing trays or chambers. Modifying packing configurations greatly increase removal efficiency. This unit packs a number of trays in a very small chamber to maximize air-water contact while minimizing space. Because of the significant vertical and horizontal space savings, these units are increasingly being used for ground water treatment [31]. Air strippers can be operated continuously or in a batch mode where the air stripper is intermittently fed from a collection tank. The batch mode ensures consistent air stripper performance and greater energy efficiency than continuously operated units, because the mixing in the storage tanks eliminates any inconsistencies in feed water composition.

Air stripping is effective only for water contaminated with VOC or semi-volatile concentrations with a Henry's constant greater than 0.01. (The higher the Henry's law constant, the more likely substances will volatilize rather than remaining in water). Compounds with low volatility at ambient temperature may require preheating of the groundwater. Algae, fungi, bacteria and fine particles may foul the equipment and therefore the pretreatment or periodic column cleaning is required.

2.5 Membrane technology

These membrane-based methods are used for many purposes like separating the one component from the mixture, no matter whether it is organic or inorganic and consists of vapour or liquid [34]. Since the removal of organic compounds is our topic of interest, pervaporation and gas permeation are two processes dealt with the membrane-based separation. In the pervaporation process, liquid is treated with the membrane to separate the components whereas in the gas permeation the separable components will be in gas phase. The dehydration of solvents and separation of organics from waste water are the examples for pervaporation and the removal of condensable solvent from the air is example for gas permeation [35, 36, 37].

2.5.1 Pervaporation

Pervaporation means the combined words of **per**meation and e**vaporation** and is often an attractive alternative to other separation methods. Pervaporation (PV) is a typical membrane process to transport small amounts of a neutral organic compounds (e.g. low volatile aromatics) from a liquid across the membrane to the permeate to vacuum side. An example is the removal of phenol from water. The feed water-phenol mixture with more than 1000 ppm phenol passes a membrane unit with a high phenol permeable membrane. The contents of phenol in the retentate decreases to ~100 ppm [38, 39]. Pervaporation involves the separation of two or more components across a membrane by differing rates of diffusion through a thin polymer and an evaporative phase change comparable to a simple flash step. Pervaporation is typically suited for separating a minor component of a liquid mixture, thus high selectivity through the membrane is essential.

The mass transport takes place in three consecutive steps:

1. Sorption of components from the feed onto the membrane at the upstream side
2. Diffusion of the sorbed components through the membrane
3. Desorption of the permeant from the membrane at the permeate side.
4. The other driving force for separation is the difference in partial pressures across the membrane. By reducing the pressure on the permeate side of the membrane, a driving force is created. Another method of inducing a partial pressure gradient is to sweep an inert gas over the permeate side of the membrane. These methods are described as vacuum and sweep gas pervaporation respectively [40, 41, 42].

Fig. 7 shows a typical pervaporation system [43]. In this system, the feed stream is compressed and sent to a condenser where the liquid solvent is recovered. The condenser bleed stream, which contains approximately 5,000 ppm of the VOC, is then sent to the membrane module. The feed is allowed to flow along one side of the membrane and a fraction of the feed (permeate) passes through the membrane and leaves in the vapor phase on the opposite side of the membrane. The "vapor phase" side of the membrane is either kept under a vacuum or it is purged with a stream of inert carrier gas. The permeate is finally collected in the liquid state after condensation. The liquid product is rich in more rapidly permeating component of feed mixture. The retentate is made up of the feed materials that cannot pass through the membrane module. In the membrane module the stream is further concentrated to 3 % VOC. The concentrated stream is then returned to the compressor for further recovery in the condenser. Its main use in organic synthesis is the removal of water during reaction (equilibrium shift), but other separation applications are possible. Other applications include removal of organics from aqueous streams, separation of heat sensitive products and dehydration of organic solvents [44, 45].

2.5.2 Types of membranes

The membranes used in pervaporation processes are classified according to the nature of the separation being performed.

2.5.2.1 Hydrophilic membranes

Hydrophilic membranes are used to remove water from organic solutions. These types of membranes are made of polymers with glass transition temperatures above the room temperature. The polyvinyl alcohol, polyethylene glycol, polyallylamine chloride are example of a hydrophilic membrane material [46, 47].

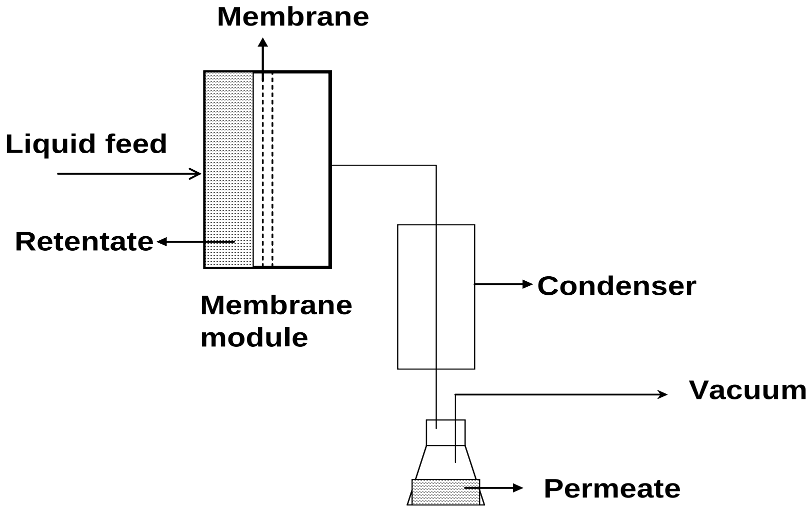


Figure 7. Schematic diagram of pervaporation of contaminated air stream.

2.5.2.2 Organophilic membranes

Organophilic membranes show good permeation rates for organic molecules but at the expense of low selectivity. Such membranes are used on a technical scale to remove pollutants or recover final products (e.g. of fermentation) from water [48, 49]. These membranes are typically made up of elastomer materials (polymers with glass transition temperatures below room temperature). The flexible nature of these polymers makes them ideal for allowing organics to pass through. Examples include nitrile, butadiene rubber, and styrene butadiene rubber, polytetrafluoroethylene (PTFE) and polypropylene polyvinylidene fluoride (PVDF). Only little industrial use has been observed despite the high apparent potential of this technology. In the area of organophilic pervaporation membranes, mostly three types of fillers have been used. They are zeolites [50], silicates [51] and carbon sieves [52].

The basic forms in which a membrane has been cast or molded are

1. Flat sheet
2. Hollow fibre (Fine tubes, less than 3 mm in diameter)
3. Tubular

The stability of the membrane is also an important factor. The stability is not quantitatively defined, but, generally, it is said to be instable when there is a change or loss in the separation properties, and decomposition or degradation of the membrane occurs. The membrane can lose its stability by thermal, chemical or mechanical causes.

2.5.3 Configuration based membrane modules

Membrane modules are of four types based on the configuration.

2.5.3.1 Flat sheet tangential flow (TF) module

This module uses flat sheet element. Its structure is simple and replacement is easy. This is similar to filtering and its density is about 100 to 400 m^2/m^3. Membrane is placed in a sandwich style with the feed side facing each other. The feed flows from its side and permeate comes out from the top and bottom of the frame. The membrane is held apart by the corrugated spacer. The flow is laminar-turbulent.

2.5.3.2 Tubular membrane module

This module has several tubes used in parallel. The density is not more than 300 m^2/m^3. Ceramic membranes are usually monoliths of tubular capillaries. Channels are in the millimetre range. It becomes module by attaching end fitting and acts as a means for permeate collection. Many monoliths are usually incorporated into one modular housing and not self-supporting. Normally modules are inserted in other material tube with the diameter more than 10 mm. It can operate with simple pre-treatment feed liquid. Membrane replacement and washing is easy. The flow of the stream is turbulent.

2.5.3.3 Hollow fibre membrane module

This module uses the hundreds or thousands of fibre bundles together. The capillary has very small diameter (<1mm). This consists of large number of membranes in a module and self-supporting. The density is about 600 to 1200 m^2/m^3 (for capillary membranes) up to 3000 m^2/m^3 (hollow fiber). The size is smaller than the other module for given performance capacity. Hollow fiber is a flexible membrane. It can carry out the filtration by two ways, either “inside-out or outside-in". In the process of “inside–out”, the permeate is collected out of membrane. However, in the process of “outside-in” the permeate passes into membrane bore. The flow is laminar-turbulent.

2.5.3.4 Spiral wound membrane module

This module uses the flat sheet element. Flat sheet sealed like an envelop and wound in a spiral. It formed from a plate and sheet wrapped around a centre collection tube. Its density is about 300 -1000 m^2/m^3 and diameter can vary up to 40 cm. Feed flows axially on cylindrical module and permeate flow in to the centre pipe. The flow is laminar flow. Features are high pressure durability, compactness, low permeate pressure drops, membrane contamination and minimum concentration polarization.

The system will process the off-gas, producing a concentrated liquid VOC stream and a purified gas containing less than 10 ppm VOC that can be discharged or recycled to the gas-generating process.

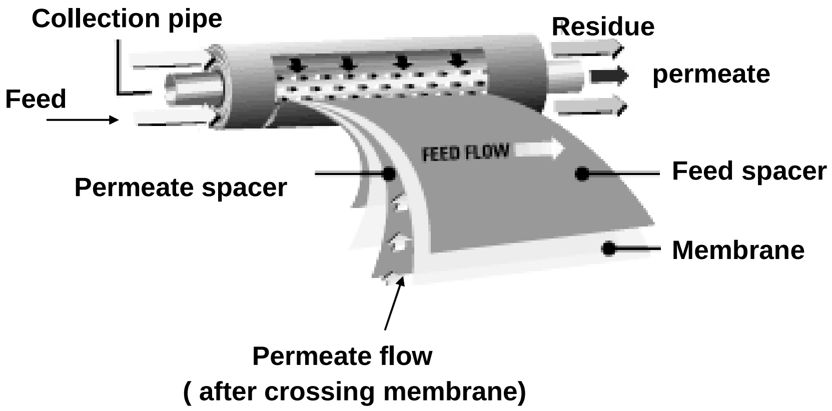


Figure 8. Schematic of a spiral-wound membrane module [53].

To achieve high selectivity or high flux for specific compounds the modifications of membranes such as filling, grafting or coating have been performed [50]. The most common is adding fillers, especially high aspect ratio fillers. It improves physical properties such as increased stiffness or reduced creep and a variety of other purposes. It improves thermal stability, high voltage resistance, electrical conductivity, radiation shielding and optical as well as aesthetic effects [51]. In many cases, filled polymeric membranes show permeability lower than the conventional unfilled membranes, and hence can serve as barriers for oxygen, water and other solutes. The selection of polymer membrane is an important task to achieve good separation. Depending upon the nature of the mixture to be separated, one has to choose the membrane. Polydimethoxy siloxane (PDMS) composite membranes, PDMS and polyether-block-polyamide (PEBA) membranes filled with carbon black are used for the removal of VOCs [51, 52].

3. Destructive methods

In the destructive methods all the VOCs has to be chemically altered to the non-pollutant state. When one need not recover the solvents or VOCs from the air-contaminated stream, one has to completely convert them into other compounds like CO_2 and H_2O. This process is known as complete oxidation or incineration. The following are the destructive methods.

3.1 Thermal oxidation

The thermal oxidation is the process of oxidizing combustible organic compounds by raising the temperature of the material above its auto-ignition point in the presence of oxygen. But the complete oxidation needs higher temperatures of the order of 700-1000 °C. This thermal energy can be supplied by using flame or by the using heating coils. During incineration, the heat will be generated due to the exothermic nature and hence heat should be dissipated [53]. In order to make use of the heat generated, heat exchangers are used which in turn can be used as the pre-heaters. There should be enough air supply in the combustion chamber so that generation of partially oxidized CO like harmful gases can be avoided. Generally, halogenated VOCs require higher temperatures. There are three types of thermal oxidizers known [54, 55]. They are

1. Direct thermal oxidizers
2. Regenerative thermal oxidizers and
3. **3.** Recuperative thermal oxidizers

3.1.1 Direct thermal oxidizer

The direct-fired thermal oxidizers use the highest quantities of natural gas as the fuel because they do not employ any type of heat recovery. The set up for the direct thermal oxidation is shown in Fig. 9. This high heat requirement generally dictates that these units are only employed where the concentration of organic compounds is above 50 % of the Lower Explosive Limit (LEL). The LEL is the lowest organic concentration at which an air stream can be combustible. This level is different for each organic compound and must be calculated for mixtures. This method requires the greatest amount of auxiliary fuel to maintain the oxidation temperature, thus needs the highest operating cost. Flares are useful for destruction of intermittent streams [56]. Instead of flame if heating coils are used, then it is called fameless thermal oxidation. This gives low CO in exhaust. Treating the air stream containing below 400 ppm is economically questionable.

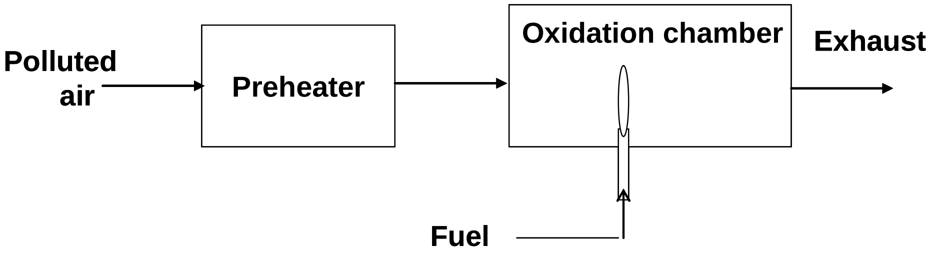


Figure 9. Schematic diagram of direct thermal oxidizer.

3.1.2 Regenerative thermal oxidizers

Regenerative thermal oxidizers implement heat recovery to lower operating costs. They use ceramic heat exchanger to achieve heat recovery efficiencies of 85 % to 95 %. The set up for the regenerative thermal oxidizers is shown in Fig. 10. Regenerative thermal oxidizers use three beds of ceramic media for heat recovery. The ceramic bed (A) is used as the outlet bed where

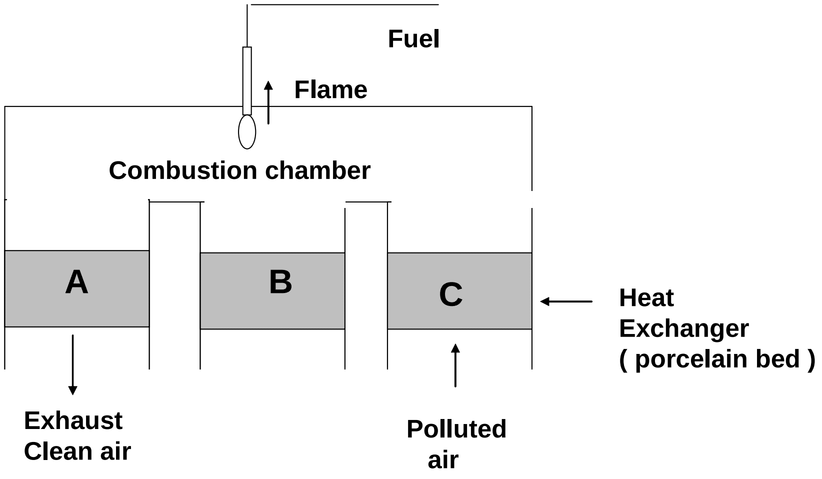


Figure 10. Schematic diagram of regenerative thermal oxidizer (RTA).

heat will be transferred from oxidized gas stream prior to being exhausted to atmosphere. After 1 to 2 minutes, the system flow will switch direction and enter through the preheated ceramic bed (A) that was previously used as the outlet and B is used as inlet. In this manner, the incoming gas stream is preheated minimizing or possibly eliminating any need for natural gas. This cycle will occur continuously to achieve the high levels of heat recovery. The third bed (B) is used for the regeneration of the combustion chamber by passing air. This set up costs higher than the thermal oxidizers, but greatly reduces the requirement of the fuel [57, 58, 59].

3.1.3 Recuperative thermal oxidizers

Recuperative thermal oxidizers implement heat recovery to lower the heat requirement and thus reducing the operating costs. Recuperative thermal oxidizers typically use shell and tube heat exchangers made of metal to exchange heat between the exhaust of the oxidizer and the incoming inlet stream for preheating as shown in Fig. 11. This design typically achieves a heat recovery efficiency of 50 % to 70 %. This technology is typically implemented in applications where the inlet stream is at 25 % of the LEL [59].

3.2 Catalytic oxidation

Thermal oxidations require high temperature and hence cost for heat generation is high. It is not economical. However, the cost of heat generation can be reduced considerably by making use of the catalytic oxidation. The catalytic oxidation is the process where the oxidation is taking place with assistance of catalysts. One more advantage of this method is that it enhances the complete oxidation of VOCs. The diagram of typical catalytic set up for the VOC oxidation is given in Fig. 12. The air stream comes through the preheater followed by the catalytic bed and heat exchanger.

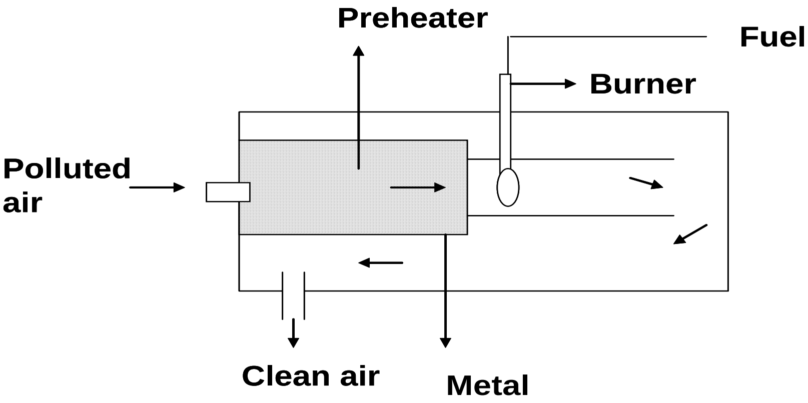


Figure 11. Schematic diagram of recuperative thermal oxidizer.

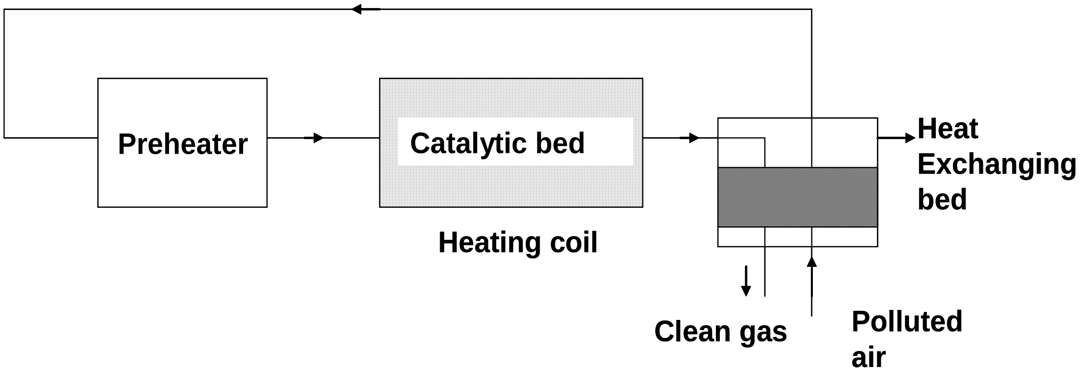
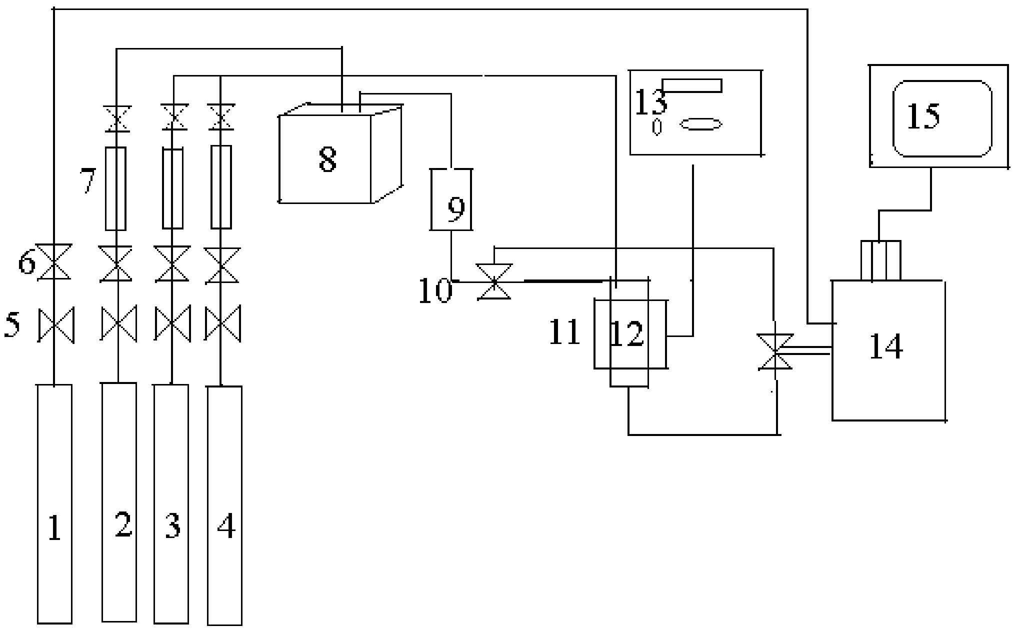


Figure 12. Schematic diagram of catalytic thermal oxidizer.

The catalytic set up for VOC oxidation for research purpose is shown in Fig. 13. In this set up the VOCs is kept in the constant temperature bath. The air and the diluter gas pass through this so that VOC also is taken in the stream. By adjusting the temperature of bath, one can control the concentration of the VOC. This stream containing VOC will be passing through the dilute chamber, followed by the catalyst in the reactor where the oxidation is taking place. Then, the product stream is connected to GC-mass spectrometer for the analysis. H_2 is used for reduction of the catalyst if needed. The preheating is preferable for better results. At different reactions catalyst test is carried out to understand temperature needed for the complete oxidation. Optimizing the space velocities also is important. The temperature of complete oxidation may vary with the nature of the VOCs. Because it depends upon the reactivity of each compound, the reactivity of the VOCs will be in the following order with Pt/Pd bi-metallic catalyst [60]. Alcohols > aldehydes > aromatics > ketones > acetates > alkanes > chlorinated hydrocarbons.



1. Helium cylinder
2. Air cylinder
3. Nitrogen cylinder
4. Hydrogen cylinder
5. Filter
6. Mass flow controller
7. Check valve
8. Constant temperature bath
9. Dilution camper
10. Three way cock
11. Furnace
12. Reactor
13. Temperature controller
14. Gas chromatograph
15. Data processor analyzer

Figure 13. Schematic diagram of catalytic oxidation set up (research purpose).

In practical approach, the exhaust gas may contain more than one VOC. In that case, in catalytic oxidation of one VOC may be affected by the other VOC due to the competitive adsorption on the catalyst. As a result, one of the VOCs may be left out of oxidation. In such cases, one has to choose the suitable catalytic systems. The following are the features of the catalyst important for the better catalytic activities.

1) Hydrophobic nature

Since water is one of the products in oxidation, the adsorption of H_2O is possible on the catalyst if it is hydrophilic in nature, which leads to the deactivation of catalyst or need high temperatures. Adsorption of organic compound is more favorable on a hydrophobic support.

2) Thermal stability

Thermal stability of the catalyst is quite important, because loss of the catalyst or catalytic activity is important in the view of cost. As a result, though the carbon is good catalytic support, it is not in practice for VOC abatement to use carbon as a support due to its poor thermal stability.

3) Oxygen storage capacity

This assists the oxidation process. Examples are CeO_2 and V_2O_5. Oxygen storage capacity arises due to their variable oxidation states of the metal in the metal oxides.

4) High surface area

More the surface area more will be the amount of VOC that can be oxidized. Hence, the cost of the process depends on the surface area of the catalyst.

5) Resistance to poisoning

Catalyst should not undergo poisoning by the coke formation and strong adsorption of some specific compounds during the run. Particle size also affects the catalytic activity. Smaller the size of the metal catalyst higher will be the number of active sites. Since the oxidation process is exothermic, the possibility of sintering will be high. Due to sintering, the catalytic activity will be decreased.

3.2.1 Catalysts

Though various catalysts are available in literature, the possible and viable systems only can be implemented in practice. The catalysts known are based on the supported metals and the transition metal oxides. Mainly, the metal oxides based on the p and s block elements are used as the supports for the noble metals or non- noble metals. Examples are MgO, SiO_2 and Al_2O_3. The transition metal oxides are used as catalysts with some exceptions like TiO_2. Metals except the noble metals may be in the form of oxides during oxidation reactions. Catalysts can be classified into two types i.e., noble metal catalysts and non-noble metal oxide catalysts.

3.2.1.1 Noble metal catalysts

The noble metals commonly used as components of combustion catalysts are platinum and palladium, singly or as a bi-metallic catalyst and Au. Other noble metals like Ru and Rh can be active, but tend to have lower activity for combustion, and undergo sintering more easily and are more susceptible to loose metal component as volatile material. Generally, noble metal supported on hydrophobic supports is more active for the following reasons [61]. The addition of water to the feed gas did not affect the conversion of benzene, toluene and xylene on the hydrophobic catalyst of Pt, as there was no significant loss in conversion as the proportion of water vapour increased. A further advantage of the hydrophobic catalyst is that the combustion of VOC mixtures containing two and three components did not decrease the conversion when compared to the single components. An opposite trend has been observed in the case of hydrophilic catalysts [62]. It can be seen that there is a significant decrease in the temperature required for combustion to occur in the case of hydrophobic catalysts.

Table 4. Noble metal catalysts and their catalytic activity for complete oxidation.

Catalyst	VOC	Surface area (m^2/g)	T_{100} * (°C)	Reference
Pt/Al_2O_3	Propene Propane MIBK Methanol	260 260 149 84	180 350 232 202	[71] [71] [73] [86]
Pt/HBEA (Si/Al = 50)	*o*-xylene	> 500	230	[83]
Pt/HFAU	MIBK	134	180	[76]
Pt/TiO_2	Formaldehyde	55	RT	[75]
Pt/SDB Styrene divinyl copolymer	Toluene	497	143	[86]
Pt/ Activated carbon	benzene Toluene	530	137 160	[87]
Pd/HBEA	Toluene Propene	590	195 202	[65]
Pd /CsFAU	Propene	414	180	[65]
Pd/TiO_2 Pd/ZrO_2 $Pd/ZrO\text{-}TiO_2$ (Mesoporous)	Toluene	174 142 440	190 270 278	[69]
$0.5\%Pd3\%TiO_2$	Benzene	39	350	[72]
Pd/SBA-15	Benzene	750	185	[76]
Pd/Zr pillared Liponite	Benzene	434	210	[77]
$Pd/10\%V_2O_5/Al_2O_3$	Benzene	NA*	280	[78]
Au/CoO_x	Propene Methane ethane	79	180 348 243	[68]

* NA – Not available
* T_{100} – Complete oxidation temperature

The comparison of the catalytic activity of various noble metal catalysts with different VOCs is given in Table 4. However, one cannot compare the activities as such because it depends upon other factors like particles size of the catalyst, dispersion, surface area, nature of the VOCs, flow rate variation, method of preparation, and ratio of O_2 to VOC. Since the activity toward oxidation reactions is high, the low temperature oxidations are observed. However, for the same catalyst when the support is changed activity vary drastically. One more advantage of the metal-based catalyst is, it can be regenerated easily whereas the one based on the metal oxide alone may need high temperature.

3.2.1.2 Non-noble metal oxide catalysts

If one looks at the catalyst cost wise, non-noble metal catalysts will be preferred. Much attention is given on evolution of the metal oxide systems. Recently, so many transition metal oxide catalysts have been known for the better performance as shown in table 5. CoO_x and MnO_x based catalyst are known for the better performance than the other metal oxides. Some of the mixed metal oxides are also known for a decade. The major draw back is poor surface area. Since they are forming only in the high temperature, synthesis of those materials with high surface area is tedious due to the agglomeration. The synthesis of advanced materials of active catalyst (like aerogel) has to come up, so that the catalysts will be efficiently exploited since the surface to volume ratio increases.

Table 5. Transition metal oxide catalysts and their catalytic activity.

Catalyst	VOC	Surface area (m^2/g)	T_{100} ($^\circ C$)	Reference
$Co/Zr_{95}Y_5O_x$	Toluene	75	272	[64]
CrOOH aerogel	Ethyl acetate	611	315	[79]
CuO	Methanol	81	255	[80]
NiO	Methanol	154	280	[80]
Cu/ZrO_2	Propene	52	> 500	[82]
γ-MnO_2	n-hexane	103	172	[66]
CoO_x	Propane	69	205	[67]
MnO_x	Propane	76	342	[67]
CuO	Propane	385	385	[67]
Cr-ZSM-5	Ethyl acetate benzene	366	280 480	[81]
20%LaCoO3/$Ce_{0.9}Zr_{0.1}O_2$	Benzene	22.7	452	[63]
$La_{0.6}Ca_{0.4}FeO_3$	Propane Ethanol	16.7	432 255	[70]
$La_{0.8}Sr_{0.2}MnO_{3+x}$	Propene Benzene Hexane Toluene	22	225 320 277 235	[84]
$LaMnO_3$	Isopropanol benzene	22	235 > 400	[85]

3.2.1.3 Catalysts for halogenated VOCs (H-VOCs)

The catalytic destruction of H-VOC to CO_2, H_2O and HCl / Cl_2 appears very promising in the current stage. The destruction of halogenated VOCs, particularly those of short chain length, is of great industrial and environmental importance [65]. Even though the noble metal catalysts are more active, they are deactivated quickly [87]. In order to avoid this problem, the attention was mainly focused on the metal oxide based catalysts. Since the activation of carbon–halogen bond is difficult, the catalytic oxidation also required high temperatures. Comparing to non-halogenated VOCs the halogenated VOCs require high temperatures for the oxidation. The catalytic oxidation of a range of CFCs including CFC-113 ($CF_2ClCFCl_2$), CFC-114 (CF_2ClCF_2Cl) and CFC-115 (CF_3CF_2Cl) in the presence of hydrocarbons were carried out by a series of acidic metal oxides and supported metal oxides and the relative order for CFCs destruction was CFC-113 > CFC-114 > CFC-115. This shows that more number of Cl atoms in the CFC favors the oxidation [88].

Supported transition metal oxides of chromium, manganese, nickel, copper and cobalt and other acidic oxide materials such as zeolites and TiO_2/SiO_2 [89] have been extensively studied, but generally, they have low activity and are often subject to deactivation when used for H-VOCs oxidation. The oxidation of trichloroethylene with a wide range of metal oxides has been studied [90] and the order of their activities is $Cr_2O_3 > Mn_2O_3 > Co_3O_4 > CuO > La_2O_3 > CeO_2 > NiO > MgO\text{-}CaO > MgO > CaO > ZnO > SiO_2\text{-}Al_2O_3 > V_2O_5 > SiO_2\text{-}TiO_2$.

Though Cr_2O_3 and Mn_2O_3 are active, they have poor stability. The VO_x/TiO_2 systems were known as active as well as stable. CrO_x and $MnOx/TiO_2$ are also found to be less active than the VO_x/TiO_2. Further, the metal oxides such as CrO_x, SnO_x, WO_x, NbO_x, TaO_x, MoO_x, ZrO_x and BiO_x were impregnated on TiO_2 with VO_x. The WO_x and MoO_x are the two systems performing well. It is important to know that $V_2O_5–WO_3$ / TiO_2 is the state-of-the-art catalyst for the selective catalytic reduction (SCR) of NO_x emissions by NH_3. Currently, this is the good catalyst for H-VOCs. The marked activity is mainly due to the formation of Bronsted acid sites due to the addition of MoO_x or WO_x onto VO_x/TiO_2 [91, 92].

4. Photo-assisted methods

Abatement of organic contaminants with light assisted chemical and catalytic methods provides pollution less, easy, environmentally benign and economical method. The clean air act of 1990 calls for a 90 % reduction in the emission of 189 toxic chemicals over the next decade, 70 % of these being VOCs [93]. Therefore, there is a great deal of interest in developing processes that can destroy these compounds. Since a large number of VOCs is oxidizable, photochemical oxidation processes can be looked upon as a viable method. Recent progress in chemical water treatment has led to the development of advance oxidation processes (AOPs) [94]. Theses processes have been defined as those, which involve in the generation of hydroxyl radicals (OH.) in sufficient quantity to carry out the destruction of toxic pollutants [95]. Two ways to produce OH radicals are photocatalysis and electrolysis. In photocatalysis, these radicals are generated upon illumination of aqueous suspensions of a semiconductor with the light of sufficient energy [96]. Electron-hole pairs are then photo-generated in the semiconductor, which can migrate to the interface where they react with suitable adsorbed redox species. In aerated aqueous suspensions, the photo-generated electrons promote the reduction of dissolved oxygen

$$O_2 + e- \rightarrow O_2.- \qquad (1)$$

whereas the photo generated holes oxidize adsorbed water molecules to give hydroxyl radicals [97, 98].

$$H_2O + h^+ \rightarrow OH. + H^+ \qquad (2)$$

The $O_2.-$ formed from reaction (1) can lead to the generation of H_2O_2 after several steps [99, 100, 101].

$$O_2 .- + H^+ + 2 e^- \rightarrow HO_2. \text{ --------------- } \qquad (3)$$

$$HO_2. + e^- \rightarrow HO_2^- \text{ ------------- } \qquad (4)$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \text{ -------------- } \qquad (5)$$

Most of the researchers have proved that there are different degradation pathways in direct photolysis and photocatalysis. The direct photolysis of 2, 4, 6-trinitrotoluene (TNT) [102, 103] and pentachlorophenol (PCP) [97] generates complex organic products which resist mineralization to CO_2. In contrast, addition of TiO_2 to the photolysis solution resulted in disappearance of these primary products and a decrease in total organic content (TOC). Hence, it is necessary to have a medium, which can absorb light and transfer to the organics to be oxidized. Several simple oxide and sulfide semiconductors have band-gap energies sufficient for promoting or catalyzing a wide range of chemical reactions of environmental interest. They include TiO_2 (E_g = 3.2 eV), WO_3 (E_g = 2.8 eV>, $SrTiO_3$ (E_g = 3.2 eV), α-Fe_2O_3 (E_g = 3.1 eV for $O^{2-} \rightarrow Fe^{3+}$ transitions), ZnO (E_g = 3.2 eV) and ZnS (E_g = 3.6 eV). However, among these semiconductors TiO_2 has proven to be the most suitable for widespread environmental applications. TiO_2 is biologically and chemically inert. It is stable with respect to photocorrosion and chemical corrosion. It operates at ambient temperatures and pressures. TiO_2 shows efficient destruction of toxic contaminants and it is inexpensive and the reaction products are usually CO_2 and H_2O, or HCl, in the case of chlorinated compounds. The primary criteria for good semiconductor photocatalysts for the degradation of organic compounds are that the redox potential of the H_2O / OH. (OH- = OH. + e^- ; E = -2.8 V) couple lies within the band gap domain of the material and that they are stable over prolonged periods. The metal sulfide semiconductors are unsuitable based on the stability requirements in that they readily undergo photoanodic corrosion while the iron oxide polymorphs (α-Fe_2O_3, α-FeOOH, β-FeOOH, δ-FeOOH and γ-FeOOH) are not suitable semiconductors, even though they are inexpensive and have nominally high band gap energies, because they readily undergo photocathodic corrosion. ZnO appears to be a suitable alternative to TiO_2. However, ZnO is unstable with respect to incongruous dissolution to yield $Zn(OH)_2$ on the ZnO particle surfaces and thus leading to catalyst deactivation over time. It has been observed that the mineralization of nitrogen-containing compounds is relatively slow when compared to compounds containing heteroatoms of phosphorus, sulfur and chlorine [104]. The choice of the phase in which a photocatalytic decontamination is performed depends on the cost of the process. A schematic representation of the photocatalytic reactor set up for the degradation of organic contaminants is given in Fig. 14. Recently it was reported that the cost of detoxifying trichloroethylene (TCE) in ground water stream by a combination of air stripping and photocatalytic oxidation is significantly less than the cost of direct treatment of the water by any advanced oxidation method [105]. The following Table 6. provides a list of the organics oxidation activities with the assistance of light and TiO_2 catalyst. Preparation conditions, calcination temperature, doping and loading will affect the reactivities towards different substrates.

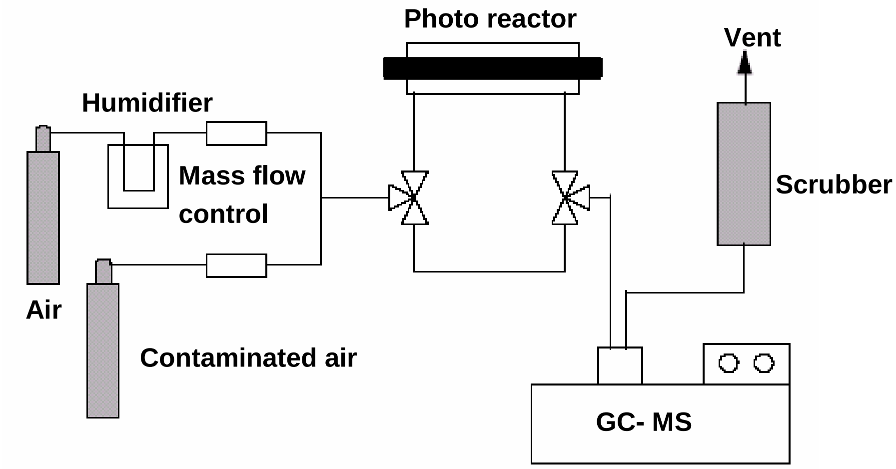
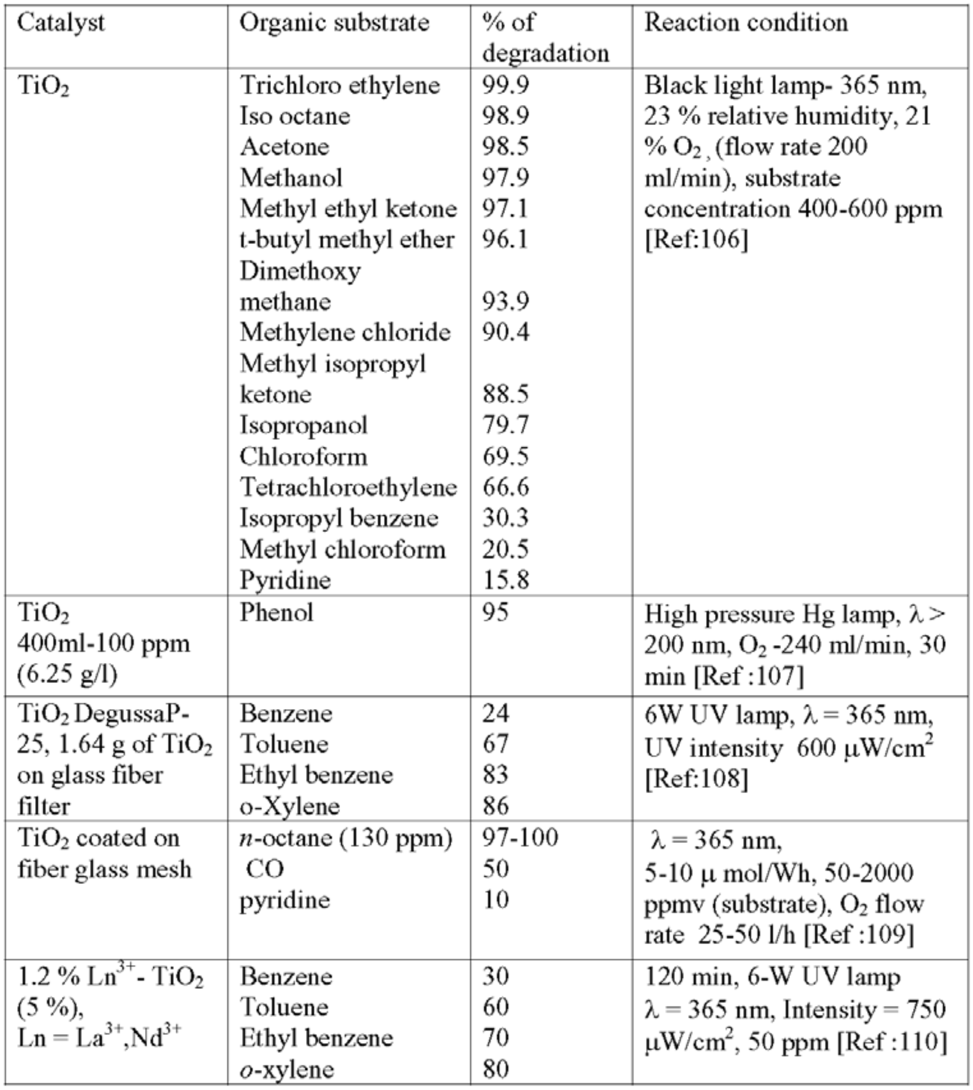


Figure 14. Experimental setup used in the photocatalytic destruction of VOCs.

Table 6. Observed degradation of some of the priority organic contaminants by TiO_2 photocatalysis.



Catalyst	Organic substrate	% of degradation	Reaction condition
TiO_2	Trichloro ethylene	99.9	Black light lamp- 365 nm, 23 % relative humidity, 21 % O_2, (flow rate 200 ml/min), substrate concentration 400-600 ppm [Ref:106]
	Iso octane	98.9	
	Acetone	98.5	
	Methanol	97.9	
	Methyl ethyl ketone	97.1	
	t-butyl methyl ether	96.1	
	Dimethoxy methane	93.9	
	Methylene chloride	90.4	
	Methyl isopropyl ketone	88.5	
	Isopropanol	79.7	
	Chloroform	69.5	
	Tetrachloroethylene	66.6	
	Isopropyl benzene	30.3	
	Methyl chloroform	20.5	
	Pyridine	15.8	
TiO_2 400ml-100 ppm (6.25 g/l)	Phenol	95	High pressure Hg lamp, $\lambda >$ 200 nm, O_2 -240 ml/min, 30 min [Ref :107]
TiO_2 DegussaP-25, 1.64 g of TiO_2 on glass fiber filter	Benzene	24	6W UV lamp, $\lambda = 365$ nm, UV intensity 600 $\mu W/cm^2$ [Ref:108]
	Toluene	67	
	Ethyl benzene	83	
	o-Xylene	86	
TiO_2 coated on fiber glass mesh	*n*-octane (130 ppm)	97-100	$\lambda = 365$ nm, 5-10 μ mol/Wh, 50-2000 ppmv (substrate), O_2 flow rate 25-50 l/h [Ref :109]
	CO	50	
	pyridine	10	
1.2 % Ln^{3+}- TiO_2 (5 %), Ln = La^{3+},Nd^{3+}	Benzene	30	120 min, 6-W UV lamp $\lambda = 365$ nm, Intensity = 750 $\mu W/cm^2$, 50 ppm [Ref :110]
	Toluene	60	
	Ethyl benzene	70	
	o-xylene	80	

Studies have shown that enhanced photo activities were seen for Fe(III), Mo(V), Ru(III), Os(III), Re(V), V(IV) and Rh(III) substitution for Ti(IV) at the 0.5 atomic percentage level in the TiO_2 matrix. The maximum enhancements were 18-fold (CCl_4 reduction) and 15- fold ($CHC1_3$ oxidation) increase in quantum efficiency for Fe (III)-doped nano sized TiO_2 [111-113]. The general c1asses [94, 114-118] of compounds that have been degraded, although not necessarily completely mineralized by semiconductor photocatalysis include alkanes, haloalkanes, aliphatic alcohols, carboxylic acids, alkenes, aromatics, halo aromatics, polymers, surfactants, herbicides, pesticides and dyes. A partial tabulation of organics degradation catalyzed by illuminated semiconductors is provided in Table

7. In addition to organic compounds, a wide variety of inorganic compounds is sensitive to photochemical transformation on semiconductor surfaces. Few examples are ammonia, azide, chromium and mercury. The suspended semiconductor particulates have been shown to generate H_2O_2 upon irradiation, which can further strengthen the organic demineralization.

However, its technological application seems limited by several factors, among which the most restrictive one is the need of using an ultraviolet (UV) excitation source [160]. The efficient use of solar light or, in other words, of the visible region of the spectrum, may then appear as an appealing challenge for developing the future generation photocatalytic materials [161,162]. One new approach to produce visible light activated TiO_2 photo catalysts is by doping with anions such as N^{3-}, C^{4-}, S^{4-} or halides (F^-, Cl^-, Br^-, I^- [163]. When used in combination with other degradation methods efficiency as well as the rate of degradation can be enhanced. One major concern in the application of TiO_2 photocatalytic process is the lower efficiency due to the high-speed recombination of photo-generated electron and hole. Photoelectrocatalysis is considered to be an ideal approach because the high degree charge recombination could be successfully solved by using an anodic bias [164–167]. But the main purpose of photoelectrocatalysis was just to represent a proof-of-concept that anodic bias on TiO_2 electrode could drive away the photo generated electron and hole in different directions and reduce their recombination.TiO_2 immobilized on a conducting substrate can be used as the electrode.

Table 7. Semiconductor photocatalytic degradation of organics.

Main classification of the substrate	Representative substrates	References
Chlorinated aromatics	Chloro phenols, chlorobenzenes, 2,4-D, PCBs, DDT, chlorinated surfactants	[119-129]
Chlorinated aliphatic and olefinic compounds	Chlorinated ethanes, ethylene, propane, chloroform, chloroether, chloranil, chloroacetic acid	[121, 23,130-135]
Nitrogenous compounds	Nitro phenols, nitro benzene, DMF nitro toluene, EDTA, methylene blue, methyl orange, N- heterocycles such as pyridine, piperidene	[131,136-148]
Hydrocarbons, alcohols carboxylic acids, hetero atom compounds halo carbons and	Butadiene, acetone, ethanol, bromo, fluoro phenols, HCHO, cresols, sucrose, cyclohexane, naphthalene, adipic, oxalic acids,	[131,137, 149-159]

5. Electrocatalytic methods

Rapid generation of hydroxyl radicals by means of electro catalysis makes it an attractive alternative for the organics treatment. By suitably selecting the electrode material, depending upon the nature of the substrate to be mineralized, the efficiency can be varied in orders of magnitude. Extensive use of electrocatalysis was for the hazardous chloro organics, since the selective removal of chlorine atoms from their structure allows reducing the toxicity of chloroaromatics, which makes it possible to dispose the dechlorinated compounds by more convenient and economic manner. Few representative examples for the electro catalytic degradation of chloro aromatics have been given in Table 8. along with the electrocatalyst used. As it is essential to have hydroxyl radicals, it is always desirable to couple both Fenton reaction and electrocatalysis [168]. A schematic set up for electrocatalytic process is given in Fig. 15.

Table 8. Electrocatalysis of chloro aromatics.

Catalyst and condition	Organic substrate	Conversion (%)	Reference
5 % Pd / C felt, 4 h ,111 mA /cm^2	2, 4 -D 3, 4 -D 2, 4, 5-T 2, 4, 6-T	97 94 97 100	[169]
5 % Pd / C cloth, -1.2 V	2, 4 –D	84-96	[170]
Pd (10 min), Pd/ Fe (3 min), 200 mA, ultra sound 20 kHz	2, 4 –D 2, 4- DCP	65 70	[171]
Fe^{3+}/ Fe^{2+}, 50 mg/l, pH = 3, 300 mA	Chlorophene	99	[172]
Fe^{3+}/ Fe^{2+}, 10 min, pH = 3, 100 mA	Diuron	93	[173]
0.048 % Pd/Fe	*o , m, p-* chlorophenol	80	[174]

6. Sonochemical methods

A well known advanced oxidation technique for wastewater treatment is ultrasound irradiation [171,175,176]. Its chemical effects are due to acoustic cavitation, whereupon estimated temperatures of 5000 °C and pressures of 1000 bar can be reached inside the cavitation bubbles, leading to the thermal decomposition of water molecules into HO. and H. [177]. Under these conditions, organic compounds may be either pyrolysed inside the bubbles or hydroxylated at the interface and in the bulk of the liquid phase. In heterogeneous processes, the primary effects of sonication are the elimination of oxide impurity layers at the catalyst surface and the increase of its active surface by pitting. Moreover, ultrasound irradiation can decrease the transit

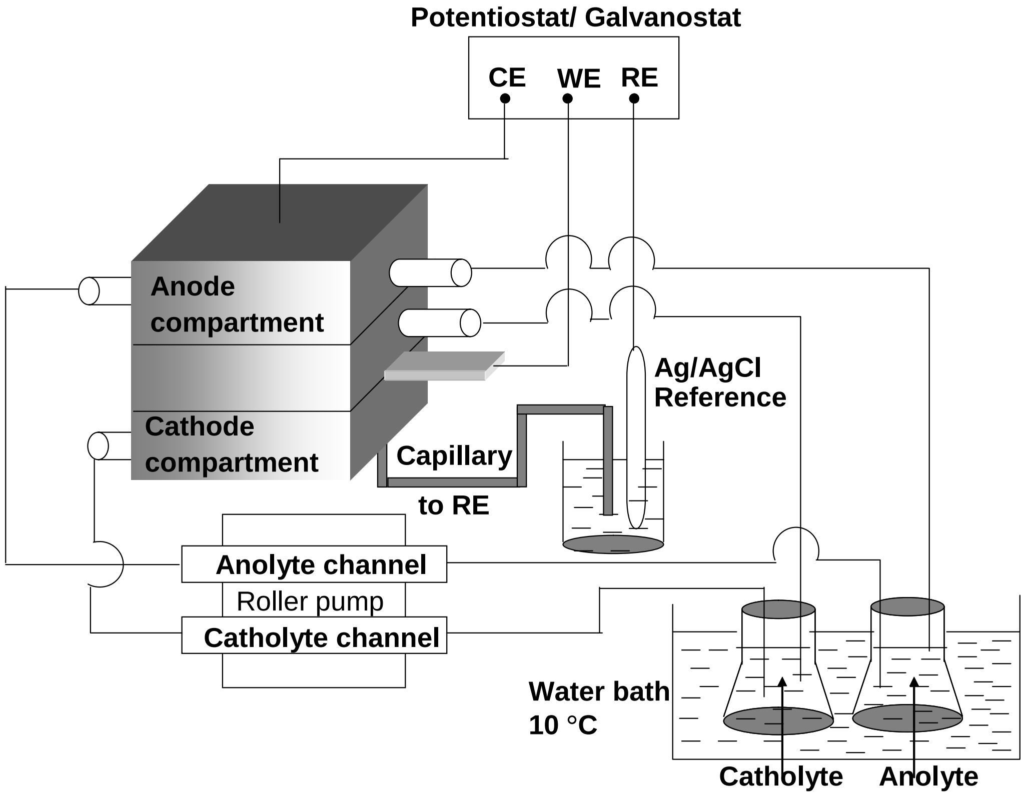


Figure 15. A schematic set up for electro catalysis.

time of intermediates and products through the boundary layer at the metal–liquid interface, increasing the reaction rates for mass transfer limited reactions [178,179]. Hung and Hoffman [180] reported that sonication increased the degradation rate of CCl_4 by a factor of 40 in their comparative study of FeO catalyzed dechlorination of CCl_4 in the presence and in the absence of ultrasound. Advanced oxidation processes such as photo/electro/O_3/Fenton/ ultra sound, if coupled and used not only the degradation rate is enhanced but also the draw backs of the individual techniques could be eliminated. Gogate et. al. have given a detailed description of the hybrid technologies and the chemistry of the AOPs [181].

7. Biochemical methods

Bioremediation is a treatment process that uses naturally occurring microorganisms such as yeast, fungi, or bacteria to break down, or degrade, hazardous substances into less toxic or nontoxic substances. Certain microorganisms can digest organic substances such as fuels or solvents that are hazardous to humans. The lower cost and the reduced environmental risk offer it to be a better choice for the decontamination. Even though biodegradation lacks its widespread usage due to the specific reaction conditions, selectivity of the micro organism and the reduced rates. Biochemical purification is one means of treating low level contamination. The biodegradation is done by microorganisms, which are either supported on media or maintained in suspension. Supported microorganisms are immobilized on organic media or inorganic structures while suspended microorganisms are maintained in a liquid phase such as activated sludge. In all instances, the microorganisms biodegrade organic contaminants into carbon dioxide and water. These compounds provide the food supply, which allows the microorganism to function and multiply. A list of biodegradable substrates is given in Table 9.

Table 9. Substrates and their biodegradability.

Biodegradable in certain circumstances	Biodegradable
Timber treatments, PCBs, PAHs, tars chlorinated solvents, explosives, pesticides, herbicides, cyanides,	Diesel, jet fuel, paraffin, ammonia, crude oil, lube oil, petrol, fuel oils, phenols, chlorophenols, creosote, glycols, alcohols, acids, ketones aldehydes, surfactants

Critical factors affecting microbial activity, which can be controlled to enhance biodegradation, include:

1. **Temperature:** Bioremediation can usually work between 5 – 50 °C, but the optimum temperature is in the range of 15 – 30 °C.
2. **pH**: Commonly, the optimum is between 5 and 9.
3. **Concentration of oxygen:** For successful aerobic biodegradation, oxygen should be present at >2 mg/l. But the presence of oxygen can be toxic where anaerobic bioremediation is the principal biodegradative process.
4. **The presence of nutrients:** (E.g. Nitrogen, potassium, phosphorus and trace elements): Typically, values of ~1 – 5 % nitrogen by weight of oil have been used with the ratio of nitrogen: phosphorus of 5 – 10:1).
5. **Moisture content:** 30 – 80 % by weight of the water-holding capacity. There are at least three main biological technologies for the degradation. The systems differ in their complexity, process design, equipment dimensions, and working parameters [182].

7.1 Biofilters

It is a packed bed reactor with compost, peat, soil or other bio-active media and external humidification (Fig. 16). The contaminated air passes through a bed of naturally occurring microorganism immobilized on the bio-active media. The bed and the air stream are kept moist to encourage microbial activity. The bio-active media provide the necessary nutrient salts for the micro organism. The bioactive support structure is kept in such a way to minimize the pressure drop across the biofilter. It provides a buffer to neutralize the possible acids from the degradation of chlorinated VOCs. The size of the biofilter depends on the concentration of the VOC, the biodegradability of the VOC and the flow rate [183]. Of course, there are some basic constraints using a biofilter system. Two of them are, first; the exhaust air must be free of caustic chemicals. For example, acids may kill the biological community. Second; the biofilter system is the VOC abatement technology with the largest footprint requirements.

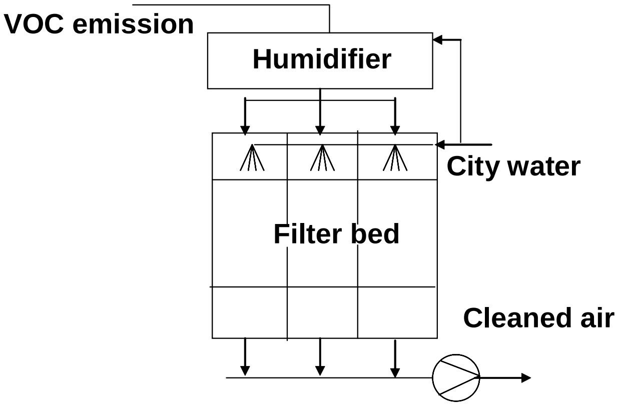


Figure 16. Schematic of biofilter.

7.2 Bioscrubbers

It is a two-stage system with a packed column for absorption and a separate liquid phase bioreactor for the degradation (Fig. 17). The VOCs are first scrubbed in an absorber with water. In a subsequent bioreactor with an activated sludge the absorbed constituents are degraded by microorganisms. The scrubbing liquid provides the nutrients for the microorganisms.

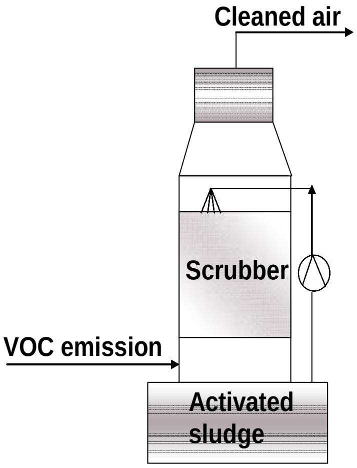


Figure 17. Schematic of a bioscrubber.

7.3 Biotrickling filter

It is a packed bed reactor with moving liquid phase and inert media (Fig. 18). The VOC-laden air stream is passed over the microorganisms immobilized as a biofilm on synthetic material with high surface area. The microorganisms are kept moist by the recirculating water, to which the nutrients are added. The VOCs dissolve in the aqueous phase and are destroyed by the growing microorganisms. Table 10. provides a few cases where the biodegradation has been achieved using different bioreactors.

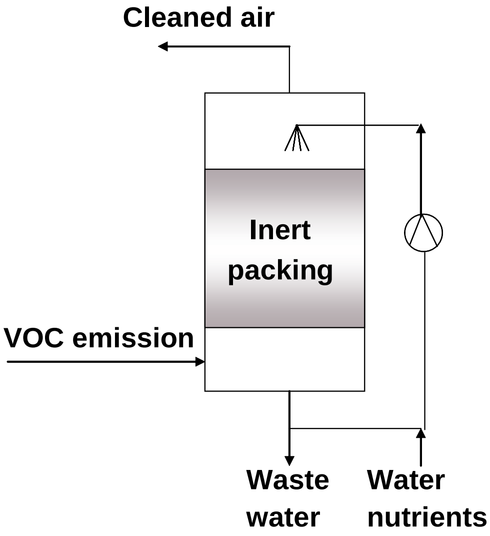


Figure 18. Schematic of a biotrickling filter.

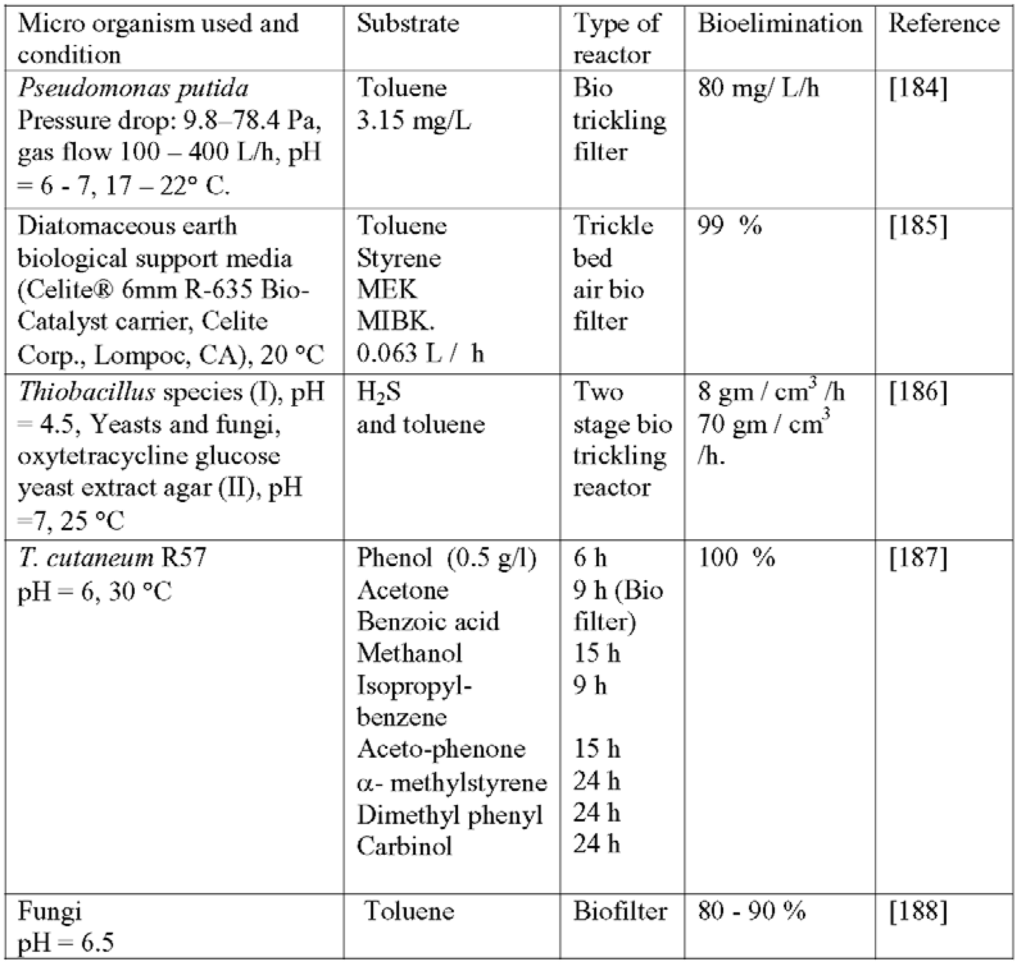
7.4 Bioreactors

Bioreactors which can mineralize pollutants can be grouped under two broad design types. In the first type, capture and destruction of pollutants occur in one unit operation (e.g., a column with a packed bed). In the second type, capture and destruction of pollutants occur in separate unit operations. A bioreactor system will include other units such as a particulate filter and a heating unit in addition to units needed for capture and destruction of pollutants. The term bioreactor is used to refer to the unit in which biooxidation (degradation) of the pollutants occurs. The column can be fluidized bed or a stirred tank.

7.4.1 Packed-bed bioreactor (Biofilter)

Capture and destruction of air pollutants occur together in the same unit operation. This commonly occurs in a packed bed. The open design bioreactors (biofilters) are mainly used for odor control (less than 50 ppm). Some were of

Table 10. Mineralization of organic contaminants through bioremediation.



Micro organism used and condition	Substrate	Type of reactor	Bioelimination	Reference
Pseudomonas putida Pressure drop: 9.8–78.4 Pa, gas flow 100 – 400 L/h, pH = 6 - 7, 17 – 22° C.	Toluene 3.15 mg/L	Bio trickling filter	80 mg/ L/h	[184]
Diatomaceous earth biological support media (Celite® 6mm R-635 Bio-Catalyst carrier, Celite Corp., Lompoc, CA), 20 °C	Toluene Styrene MEK MIBK. 0.063 L / h	Trickle bed air bio filter	99 %	[185]
Thiobacillus species (I), pH = 4.5, Yeasts and fungi, oxytetracycline glucose yeast extract agar (II), pH =7, 25 °C	H_2S and toluene	Two stage bio trickling reactor	8 gm / cm^3 /h 70 gm / cm^3 /h.	[186]
T. cutaneum R57 pH = 6, 30 °C	Phenol (0.5 g/l) Acetone Benzoic acid Methanol Isopropyl-benzene Aceto-phenone α- methylstyrene Dimethyl phenyl Carbinol	6 h 9 h (Bio filter) 15 h 9 h 15 h 24 h 24 h 24 h	100 %	[187]
Fungi pH = 6.5	Toluene	Biofilter	80 - 90 %	[188]

the size of a foot ball field [189]. The bioreactor units designed today are closed systems and have a much smaller footprint [190–192]. A system may include a separate pretreatment or humidification unit followed by one or more bioreactor beds. These beds may be one on top of the other or a series of separate columns. Packed beds usually contain a natural source of nutrients composed of compounds with nitrogen and phosphorous.

7.4.2 Water Trickling bioreactor (Biotrickling filter)

This system is similar to a conventional packed-bed bioreactor, in that capture and destruction of air pollutants occur in the same unit. The main advantage of this design of bioreactor system is its ability to handle large amounts of air pollutants containing halogens or sulphur. A secondary tank containing a neutralizing agent (and to which nutrients are added) is attached to the unit containing the micro-organisms and the pollutants. Hence, an additional set of parameters would need to be adjusted and monitored.

7.4.3 Activated carbon bioreactor

The operation is composed of two stages. Air pollutants in the air stream are first adsorbed by the activated carbon that is housed in a rotating wheel and then leached into a bath of oxygenated water as the wheel rotates. A moist film of micro-organisms is attached onto the rotating carbon surface. Hydrocarbons dissolved in the water serve as food to the micro-organisms. Oxygen is provided to the water by blowing air through two immersed perforated pipes. The nutrients are added to the water bath.

7.4.4 Scrubber bioreactor (Bioscrubber)

Capture and destruction occur in two separate units. The air flow containing the air pollutants are entered into a non-clogging tray tower in which biomass is pumped countercurrent to the air flow. The biomass flow containing the absorbed pollutants is then returned to another unit, referred to as the bioreactor, where the nutrients are added and most of the pollutants are decomposed. A given volume of fluid containing dissolved pollutants is returned to the bioreactor tank and the same volume of sludge is pumped from the bioreactor as blow down. The bioreactor is aerated by blowing ambient air which is then mixed with the input pollutant laden air stream going to the scrubber tower. Nutrients are fed directly to the bioreactor tank.

7.4.5 Membrane bioreactor

Capture and destruction of the pollutants occur in two separate units. Particulate prefiltered air is first passed into a membrane ‘separation/concentration’ unit made up of bundles of micro porous, hydrophobic hollow fibers. The air stream flow is inside the hollow fibers and the extracting fluid is on the shell side of the bundle. The stripping fluid helps to concentrate the pollutants and should have a low volatility and a high fluid / air partition coefficient. The pollutant laden stripping fluid is then directed into another membrane unit where the micro organisms are located. The pollutants diffuse across one side of the membrane pores and are destroyed by the bacteria on the other side where the aqueous nutrient stream flows. The separation in that membrane unit is governed by the partition coefficient in the stripping fluid/air and stripping fluid/aqueous system containing the micro-organism.

8. Other methods

8.1 Electron beam technique

There are many conventional methods for VOC removal including carbon adsorption and carbon absorption mainly developed for the industrial off gases. Electron beam irradiation (EBI) is a feasible technique for treating a large amount of flue gas, especially when its effluent temperature is relatively low [193-195]. Depending on the power of the accelerators, more than several hundred metric tons of gas per day (10^5–10^6 m^3) could be treated [196]. But when used in combination with other technologies, it can eliminate the short comings such as low removal efficiency of high concentration of VOC and the by-product formation [197]. Some of the results of degradation processes using electron beam technology are given in Table 11. Schematic of an electron beam-catalyst bed hybrid reactor is given in Fig. 19.

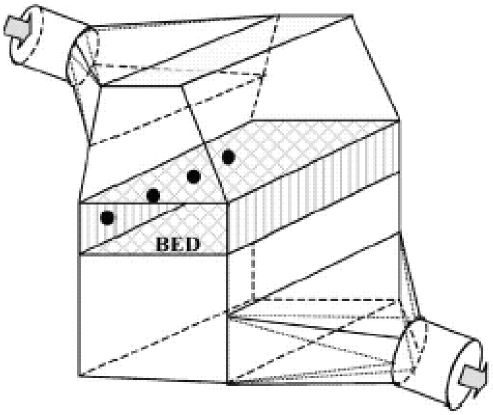
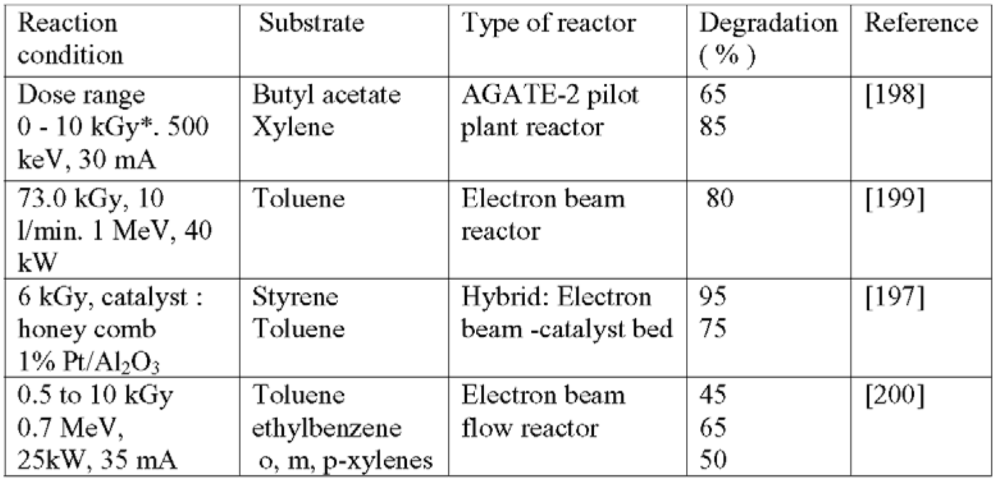


Figure 19. Schematic of electron beam and catalyst-bed hybrid reactor.

Table 11. Degradation processes using electron beam technology.



Reaction condition	Substrate	Type of reactor	Degradation (%)	Reference
Dose range 0 - 10 kGy*. 500 keV, 30 mA	Butyl acetate Xylene	AGATE-2 pilot plant reactor	65 85	[198]
73.0 kGy, 10 l/min. 1 MeV, 40 kW	Toluene	Electron beam reactor	80	[199]
6 kGy, catalyst : honey comb 1% Pt/Al_2O_3	Styrene Toluene	Hybrid: Electron beam -catalyst bed	95 75	[197]
0.5 to 10 kGy 0.7 MeV, 25kW, 35 mA	Toluene ethylbenzene o, m, p-xylenes	Electron beam flow reactor	45 65 50	[200]

*1 Gy = 1 J/kg = 1 $m^2 \cdot s^{-2}$ (Unit of absorbed dose)

8.2 Flaring technology

Flaring is the combustion process which has been the traditional method for the safe disposal of large quantities of unwanted flammable gases and vapors in the oil industry [201]. It can be considered as degradation by thermal oxidation. This is mainly applicable for VOCs with the exception of halogenated compounds. A properly operated flare can achieve a destruction efficiency of 98 % or more. Flaring is a VOC combustion control process in which the VOCs are piped to a remote, usually elevated location and burned in an open flame in the open air using a specially designed burner tip, auxiliary fuel, and steam or air to promote mixing for nearly complete destruction of VOCs.

Flares are generally categorized into two ways; (1) by the height of the flare tip (ground or elevated) (2) By the method of enhancing the mixing at the flare tip (steam assisted, air assisted, pressure assisted or non-assisted). Elevating the flare can prevent potentially dangerous conditions at ground level where the open flame or the ignition source is located near a process unit. Elevating the flare also allows the products of combustion to be dispersed above the working areas to reduce the effects of noise, heat, smoke and objectionable odors [202,203].

Steam-assisted flares are single burner tips, elevated above ground level for safety reasons that burn the vented gas in a diffusion flame. They are the predominant flare type found in refineries and chemical plants. The non-assisted flare consists of a flare tip without any auxiliary provision for enhancing the mixing of air into its flame. Its use is limited to gas streams that have low heat content and low C/H ratio that burn readily without producing smoke. This stream requires less air for complete combustion and has lower combustion temperature which will minimize the cracking reactions.

Pressure-assisted flares use the vent stream pressure to promote mixing at the burner tip. This will have the burner arrangement at ground level and must be located in a remote area of the plant where there is a plenty of space available. They have multiple burner heads that are to be operated based on the quantity of the gas being released. An enclosed flares burner heads are inside a shell that is internally insulated. The shell reduces noise, luminosity, heat radiation and provides wind protection. The advantages of flaring technology are

1. It can be an economical way to dispose of sudden releases of large amounts of gas.
2. In many cases it does not require auxiliary fuels to support combustion.
3. It can be used to control fluctuating waste streams.

8.3 Non-thermal plasma processes

The oxidation ability of plasma is stronger than that of ozone itself. Hence, non-thermal plasma processes have high potential to remove toxic contaminants in the air stream. Key points for practical usage of the process are reliability of the process, energy efficiency of the plasma (economy) and post-processed gas treatments after the plasma processing. A laser induced fluorescence (LIF) technology is used as a diagnosis of the plasma reaction [204]. Non-thermal plasma is found to be very effective in CFC decomposition as well as $DeNO_x$ reactions. In non-thermal plasma an electrical discharge generates the plasma. Typical non-thermal plasma discharge is glow or streamer modes. In the non-thermal plasma, rather high-energy free electrons are generated and activate various radicals [205]. Three different types of non-thermal plasma reactors are

1. A coil type reactor (surface discharge mode)
2. A rod type reactor (barrier discharge mode)
3. A bolt type reactor (barrier discharge mode)

Almost 95 % of the CFC removal is achieved in surface discharge plasma reactor [206].

8.4 Corona discharge processes

Corona discharge processes use a high voltage / low current electrical discharge to destroy a wide range of molecules in a gas stream containing organic contaminants. It is of two types, silent corona which uses radio frequency and the direct current corona. Both require too large energy input. Two recent developments to overcome this limitation are the dielectric packed-bed reactor and nanosecond pulse corona. The contaminated gas stream simply flows through a bed of dielectric beads (such as $BaTiO_3$). At both the entrance and exit of the bed an electrode is connected to a high voltage AC power supply. The beads act as small capacitors and they charge and discharge out of phase with the applied field. The intra-bead discharge generates electrons that react with the organic compounds to destroy it. The nanosecond pulse corona uses a wire centered in an unfilled tube through which the VOC-containing gas flows. A novel power supply discharges a capacitor through a spark gap to generate a high voltage pulse. The advantage of such a configuration is thought to be the generation of free electrons without excessive generation of ions. Though high destructive efficiencies are possible, generation of ozone, NO_x, and partial reaction products is possible (about 500 ppm ozone was generated at a voltage corresponding to near 100 % destruction efficiency). Improvements in the technology will be focusing on reducing power consumption and by-product formation and on scaling up to commercial application.

8.5 Wet air oxidation

Wet air oxidation (WAO) is the process of oxidizing organic contaminants in the presence of water. Any substance that is capable of burning can be wet air oxidized in water. This method is effective mainly for water-miscible contaminants. WAO is typically employed as a waste treatment technology when the waste is non-conductive to incineration or biological treatment. It is an ideal process for the pretreatment of wastes that are toxic to conventional biological facilities. The WAO process is uniquely suited to the oxidation of concentrated waste liqueurs, slurries and sludges where the oxygen demanding organic matter is about a few percent of the water stream [207].

The wet oxidation reactions take place between 100 and 372 °C at elevated pressures of the order of 2 MPa to 15 MPa, so as to maintain water in the liquid phase. This temperature range can be further subdivided into low (100-200 °C), medium (200-260 °C) and high temperature (260- 320 °C) operation. Industrial applications of low temperature oxidation (100-200 °C) include the thermal conditioning of sludge (TSC) and low strength sulfidic spent caustic ethylene spent caustics as well as for auto thermal TSC and for some industrial wastes. High temperature (260-320 °C) oxidation is used for refinery spent caustic, sludge destruction and most WAO treated industrial wastewaters. In

Table 12. Summary of reported heterogeneous catalytic WAO research.

Catalyst		Substrate	Reference
Active phase	Support		
Cu Cu-Zn Cu-Mg-La Cu-Cr-V Cu-Ce-Cd	Al_2O_3, SiO_2 Zn aluminate, MCM-41	Phenol, p-cresol chloro phenols, acetic acid, aniline, waste water	[214-223]
Mn Mn-Ce Mn-Zn-Cr Mn-Ce-O Mn	Al_2O_3, SR115, MCM-41	Phenol, chlorophenol, poly ethylene glycols, industrial wastes, aromatic compounds.	[214,217] [224-227]
Co Co-Bi Co-Ce Co-Cu-Ti-Al	Cement	Alcohols, amines acetic acid, ammonia phenol	[228-231]
Fe Fe Fe	SiO_2, Carbon, Al-pillared, clay	Chloro phenols, phenols	[11] [232][233]
Ru Ru-Rh	CeO_2, TiO_2 –ZrO_2, Al_2O_3	Alcohols, phenols, industrial wastes, acetic acid	[234-237]
Pt Pt-Pd Pt-Pd-Ce Pt-Au	TiO_2, TiO_2 –ZrO_2, Al_2O_3, CeO_2	Phenol, industrial wastes, black liquor, *p*-coumaric acid	[238-243]

wet oxidation, reactions take place in the aqueous environment where the water behaves like a catalyst and is an integral part of the reaction. It is well established that the chemistry of wet oxidation involves free radical formation with the oxygen derived radicals attacking the organic compounds and encouraging the formation of organic radicals [208]. The use of catalysts, such as homogeneous Cu^{2+} and Fe^{3+} or their heterogeneous counterparts or even noble metal catalysts, enhance the reactivity and the performance of the system [209-213]. Present research is to develop high durability and low cost catalysts. A characteristic of wet oxidation chemistry is the formation of carboxylic acids in addition to the primary end-products, CO_2 and H_2O, which can be removed easily by bio-degradation. A brief summary of the heterogeneous catalytic systems used for the wet air oxidation of different substrates are given in Table 12.

Implementation of any new technology at an industry requires its environmental friendliness more than its technical and economical feasibility [244]. The issues to be overcome include the inertia of past practices, overall systemic thinking and developing new technologies while the targeted processes, products and related environmental regulations keep changing.

9. Conclusion

Though various possible treatment procedures have been evolved, the adoption of any of these procedures for a chosen system still appears to be empirical and some systematics at the conceptual level are outlined in this presentation.

10. References

1. Rife, R., Thomas, T. W., Norberg, D. W., Fournier, R. L., Rinker, F. G., Bonomo, M. 1989, Environ. Prog., 8, 167.
2. www.epa.gov/oppfead1/international/pops.htm, (Accessed in January 2007).
3. http://www.chem.unep.ch/pops/POPs_Inc/proceedings/Iguazu/STONE.html, (Accessed in January 2007).
4. Tsezos, M., and Bell, J. P., 1989, Water Research, 23, 5, 561.
5. http://health_info.nmh.org/HealthNews/rueters?NewsStory1002200221.htm, (Accessed in January 2007).
6. Woodruff, T.J., Caldwell, J., Cogliano, V.J., and Axelrad, D.A., 2000, Environ. Research, 82, 3, 194.
7. Piispanen, W., Cooke, W. M., and Allen, J. M., 1984, The Science of The Total Environment, 36, 1, 159.
8. Singh, H.B., Salas, L.J., Smith, A.J., and Shioeishi, H., 1981, Atm. Environ., 15, 4, 601.
9. www.pops.int/ (Accessed January 2007).
10. www.p2pays.org/ref/10/09883.pdf (Accessed January 2007).

11. Wilhelm, M., Soltmann, C., Koch, D., Grathwohl, G., J., 2005, Europ. Ceramic Soc., 25, 271.
12. Zhao, X. S., Ma, Q., and Lu, G. Q., 1998, Energy & Fuels, 12, 1051.
13. Beck, J. S., Vartuli, J. C., 1996, Curr. Opin. Solid State Mater. Sci., 1, 76.
14. Zhao. X.S, Ma, Q., Lu. G.Q.M., 1998, Energy and fuels, 12, 1049.
15. Davis, W.T., Kim, G.D., and Perry, T.C., 2001, Separation and Technology, 36, 931.
16. Englemann V.S., 2005, Met.Finish.Guide –Dir., 102, 11A, 428.
17. www.ucc.ie/research/hmrc/SWERF/proceedings/Schlumberger/frankganzevles.pdf, (Accessed in January 2007)
18. Lines, J.R., and Smith, A.E., 2000, Chem. Processing, 1.
19. www.membrane.unsw.edu.au/imstec03/content/papers/NOV/imstec145.pdf5, (Accessed in January 2007)
20. Ozturk, B., Yilmaz, D., 2006, Process safety and Environental protection, 84, 391.
21. Robert, J. D., and Robert, F.Z., 2002, Environ. Progress, 21,111.
22. Vineeth, G., and Nishith, V. V., 2002, Chem. Eng. sci., 57, 2679.
23. Rood, M.J., and Larson, S.M., 1996, Gas.Sep.Purif., 10, 2, 123.
24. Dwivedi, P., Gaur, V., Sharma, A., and Verma, N., 2004, Sep. Puri. Technol., 39, 23.
25. Colburn, A.P., Drew, T.B., 1937, Trans. Am. Inst. Chem. Eng., 33, 197.
26. Zesis, B., 1997, Poll. Eng., 97, 1.
27. Parker, W.J., Moneith, H. D., Bell. J.P., and Melcer, H., 1996, Water. Environ. Res., 68, 1132.
28. Risk assessment of Radon in drinking water, 1999, the national academy Press, Washington, 219.
29. Juang, R.S., Lin, S.H., Yang, M.C., 2005, J. Memb. Sci., 255, 79.
30. Roizard, D., Teplyakov, V., Favre, E., Fefilatiev, L., Lagunstsov, N., Khotimsky, V., 2004, Desalination, 162, 41.
31. http://www.frtr.gov/matrix2/section4/4_50.html, (Accessed in January 2007).
32. http://www.epa.gov/tio/download/citizens/airstripping.pdf , (Accessed in January 2007).
33. http://enviro.nfesc.navy.mil/erb/restoration/technologies/remed/phys_chem/phc-02.asp. (Accessed in January 2007)
34. Paul, D., and Sikdar, S.K., 1998, Clean Products and Processes, 1, 39.
35. Dutta, B.K., Sikdar, S.K., and Ji, W., 1997, J. Sep. Purification, 1.
36. Zhang, L., Weng, H.X., Chen, H.L., and Gao, C.J., 2002, J. Environ. Sci., 14, 2,181.
37. Smart, J., Schucker, R.C., and Lloyd, D.R., 1998, J. Membr. Sci., 143, 137.
38. Villaluenga, J.P.G., and Tabe-Mohammadi., A., 2000, J. Membr. Sci., 169, 159.
39. Hickey, M. J., and Gooding, C. H., 1994, J. membr. Sci., 88, 1, 47.
40. Peng, M., Vane, L.M., and Liu, S,X., 2003, J.Hazard Mater., 98, 1-3, 69.
41. Boeddeker, K.W., Bengtson, G., and Bode, E., 1990, J. Memb. Sci., 53, 143.
42. Xianshe, F., and Huang, R.Y.M., 1997, Ind. Eng. Chem. Res., 36, 1048.
43. Shao, and Huang, R.Y.M., 2007, J. Memb. Sci., 287, 2,162.
44. Kumar, J.N., Shah, S.B., Sawant, J.B., Joshi, V.G., Pangarkar, 1997, J. Membr. Sci., 134, 225.
45. Smitha, B., Suhanya, D., Sridhar, S., and Ramakrishna, M., 2004, J. Memb.Sci., 241, 1,15,1.

46. Chandak, M.V., Lin, Y.S., Ji, W., and Higgins, R.J., 1997, J. Membr. Sci., 133, 231.
47. Moulin, P., Allouane, T., Latapie, L., Raufast, C., and Charbit, F., 2002, J. Membr. Sci., 197, 103.
48. Sampranpiboon, P., Jiraratananon, R., Uttapap, D., Feng, X., and Huang, R.Y.M., 2000, J. Membr. Sci., 174, 55.
49. Boom, J.P., Punt, I.G.M., Zwijnenberg, H., De Boer, R., Bargeman, D., Smolders C.A., and Strathmann, H., 1998, J. Membr. Sci., 138, 237.
50. Chandak, M.V., Lin, Y.S., Ji, W., and Higgins, R.J., 1997, J. Membr. Sci., 133, 231.
51. Li, L., Xiao, Z., Zhang, Z., and Tan, S., 2004, Chem. Eng. J., 97, 83.
52. Gabelman, A., and Hwang, S.T., 1999, J. Membr. Sci., 156, 61.
53. http://www.icac.com/i4a/pages/index.cfm?pageid=3400, (Accessed in January 2007)
54. http://www.fusionenvironmental.com/664661.html, (Accessed in January 2007)
55. Drysys, H., 1997, Filtration and separation, 22, 329.
56. Chou, M. S., Cheng, W.H., and Huang, B.J., 2000, J. Environ. Eng., 76, 912.
57. Choi, B. S., and Yi, J., 2000, Chem. Eng. J., 76, 2, 103.
58. Abanto, J., Reggio, M., and Ouellet, S.P., 2006, Appl. Ther. Eng., 26, 17-18, 2327.
59. Salvador, S., Commandre J.M., and Kara, Y., 2006, Appl.Ther. Eng., 26, 17-18, 2355.
60. Tichenor, B.A., and Palazzolo, M.A., 1987, Environ. Prog., 6, 3, 174.
61. Chuang, K.T., Cheng, S., and Tong, S., 1992, Ind. Eng. Chem. Res., 31, 2466.
62. Heneghan, C.S., Hutchings, G.J., and Taylor, S. H., 2004, Catalysis, 17, 105.
63. Mihai, A., Mihaela, F., and Vasile, P., 2007, Appl. Catal. B: Environ., 70, 1-4, 400.
64. Wyrwalski, F., Lamonier, J.F., Siffert, S., Aboukais, A., 2007, Appl. Catal. B: Environ., 70, 1-4, 393.
65. Tidahy, H. L., Siffert, S., Lamonier, J.F., Cousin, R., Zhilinskaya, E. A., Aboukais, A., Su, B.L., Canet, X., De Weireld, G., Frere, M., Giraudon, J.M., and Leclercq, G., 2007, Appl. Catal. B: Environ., 70, 1-4, 377.
66. Caroline, C., Valerie, R., Christophe, L., Paul, G., and Eric, M.G., 2006, Catal. Today, 117, 1-3, 350.
67. Benjamin, E.S., Tomas, G., Christopher, J., Stuart, H.T., Albert, F.C., and Graham, J.H., 2006, Appl. Catal. A: General, 67, 312.
68. Tidahy, H. L., Siffert, S., Lamonier, J.F., Zhilinskaya, E. A., Aboukais, A., Yuan, Z.Y., Vantomme, A., Su, B.L., Canet, X., De Weireld, G., Frere, M., NGuyen, T. B., Giraudon, J.M., and Leclercq, G., 2006, Appl. Catal. A: General, 61-69, 310.
69. Bibiana, P.B, Julio, A.J., and Luis, E.C., 2006, Appl. Catal. B: Environ.,65, 1-2, 21.
70. Andreea, C.G., Nina, B., Bernard, E. N., 2006, Catal. Today, 113, 3-4, 178.
71. Tomas, G., Benjamin, S., Amoros, D.C., Angel, L.S., and Stuart. H.T., 2006, Appl. Catal. B: Environ., 62, 1-2, 66.
72. Tseng, T.K., Chu, H., Ko, T. H., Chung, L. K., 2005, J. Hazard. Mater., 122, 1-2, 155.
73. Tsou, J., Magnoux, P., Guisnet, M., Orfao, J. J. M., and Figueiredo, J. L., 2005, Appl. Catal. B: Environ., 57, 2, 117.

74. Zhang, C., He, H., and Tanaka, K., 2005, Catal. Comm., 6, 3, 211.
75. Li, J. J., Xu, X.Y., Jiang, Z., Hao, Z. P., and Hu, C., 2005, Environ. Sci. Techol., 39, 5, 1319.
76. Li, J., Zheng, J., Hao, Z., Xu, X., and Zhuang, Y., 2005, J. Molec. Catal. A: Chemical, 225, 2, 173.
77. Ferreira, R. S. G., de Oliveira, P. G. P., and Noronha, F. B., 2004, Appl. Catal. B: Environ., 50, 4, 243.
78. Rotter, H., Landau, M. V., Carrera, M., Goldfarb, D., and Herskowitz, M., 2004, Appl. Catal. B: Environ., 47, 2, 111.
79. Gu, Z., and Hohn, K.L., 2004, Ind. Eng. Chem. Res., 43, 1, 30.
80. Abdullah, A.Z., 2003, Catal. Comm., 4, 11, 555.
81. Labaki, M., Lamonier, J.F., Siffert, S., and Zhilinskaya, E. A., Aboukais, A.,2003, Colloids and Surfaces, A: Physicochemical and Engineering Aspects, 227, 1-3, 63.
82. Tsou, J., Pinard, L., Magnoux, P., Figueiredo, J. L., Guisnet, M., 2003, Appl. Catal. B: Environ., 46, 2, 371.
83. lasin-Aube, V., Belkouch, J., Monceaux, L., 2003, Appl. Catal. B: Environ., 43, 2, 175.
84. Spinicci, R., Faticanti, M., Marini, P., De Rossi, S., and Porta, P., 2003, J. Molec. Catal. A: Chemical, 197, 1-2, 147.
85. Jeffrey, C.W., and Chang, T. Y., 1998, Catal. Today, 44, 1-4, 111.
86. Wu, J.C., Lin, Z. A., Tsai, F. M., and Pan, J. W., 2000, Catal. Today, 63, 419.
87. Everaert, K., and Baeyens , J., 2004, J. Hazard. Mater., 109, 113.
88. Nagata, H., Takakura, T., Tashiro, S., Kishida, M., Mizuno, K., Tamori, I., Wakabayashi, K., 1994, Appl. Catal. B, 5, 23.
89. Barresi, A.A., and Baldi, G., 1994, Ind. Eng. Chem. Res., 33, 2964.
90. Isupova, L.A., Sadykov, V.A., Tikhov, S.F., Kimkhai, O.N., Kovalenko, O.N., Kustova, G.N., Ovsyannikova, I.A., Doubii, Z.A., Kryukova, G.N., Rozouskii, A.Y., 1996, Catal. Today, 27, 249.
91. Bertinchamps, F., Gregoire, C., and Gaigneaux, E.M., 2006, Appl. Catal, B, Environ., 66, 10.
92. Bertinchamps, F., Attianese, A., Mestdagh, M.M., and Gaigneaux, E.M., 2006, Catal. Today, 112, 1-4, 165.
93. Armor, J.N., 1992, Appl. Catal. B: Environ., 1, 221.
94. Oliveros, L. E., and Braun, A.M., 1993, Chem. Rev., 93, 671.
95. Glaze, W.H., Kang, J.W., and Chapin, D.H., 1987, Ozone Sci. Eng., 9, 335.
96. Hermann, J.M., Guillard, C., and Pichat, P., 1993, Catal. Today, 17, 7.
97. Hoffmann, M., Martin, S., Choi, W., and Bahnemann, D., 1995, Chem. Rev. 95, 69.
98. Mills, A., Davies, R., and Worsley, D., 1993, Chem. Soc. Rev., 417.
99. Harbour, J.R., Tromp, J., and Hair, H.L., 1985, Can. J. Chem., 63, 204.
100. Bielski, B., Cabelli, D., Arudi, R., and Ross, A., 1985, J.Phys.Chem, 14, 1041.
101. Brillas, E., Mur, E., Sauleda, R., Sanchez, L., Peral, J., Domenech, X., and Casado, J., 1998, Appl. Catal. B: Environ., 16, 31.
102. Wang, Z.K., and Kutal, C., 1995, Chemosphere, 30, 1125.
103. Chun, H., Yizhong, W., and Hongxiao, T., 2000, Chemosphere, 41, 1205.
104. Waki, K., Wang, L., Nohara, K., and Hidaka, H., 1995, J. Mol. Catal., A: Chem. 95, 53.

105. Lichtin, N., and Avudaithai, M., 1994, Proceedings of Tenth International Conference on Photochemical Conversion and Storage of Solar Energy (IPS-lo).
106. Alberici, R.M., and Jardim, W.F., 1997, Appl. Catal. B: Environ., 14, 5548.
107. Ao, C.H., Lee, S.C., Mak, C.L., and Chan, L.Y., 2003, Appl. Catal. B: Environ., 42, 119.
108. Pichat, P., Disdier, J., Hoang-Van, C., Mas, D., Goutailler, G. and Gaysse, C., 2000, Catal.Today, 63, 363.
109. Li, F.B., Li, X.Z., Ao, C.H., Lee, S.C., and Hou, M.F., 2005, Chemosphere, 59, 787.
110. Choi, W., Termin, A., and Hofhann, M. R., 1994, J. Phvs. Chem., 98, 13669.
111. Choi, W. Y., Termin, A., and Hoffmann, M. R., 1994, Angew. Chem., 106, 1148.
112. Choi, W., Termin, A., and Hoffmann, M. R., 1994, Angew. Chem., 33, 1091.
113. Ollis, D. F., and Al-Ekabi, H., Eds., 1993, Photocatalytic Purification and Treatment of Water and Air, Elsevier: Amsterdam, 1993.
114. Blake, D. M., 1994, Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air. National Renewal Energy Laboratory.
115. Mills, A., Davies, R. H., and Worsley, D., 1993, Chem. SOC. Rev., 22.
116. Bahnemann, D., Cunningham, J., Fox, M. A., Pelizzetti, E., and Seruone, N., In Aquatic and Surface Photochemistrv, Helz. G. R., kepp, R. G., Brosby, D. G., Eds., 1994, Lewis Publiskers: goca Raton, FL, 261.
117. Pelizzetti, E., and Minero, C., 1993, Electrochim. Acta, 38, 47.
118. D’Oliveira, J. C., Minero, C., Pelizzetti, E., and Pichat, P., 1993, J. Photo-chem. Photobiol. A: Chem., 72, 261.
119. D’Oliveira, J. C., Al-Sayyed, G., and Pichat, P., Environ. Sci. Technol., 1990, 24, 990.
120. Ollis, D. F., Hsiao, C. Y., Budiman, L., and Lee, C. L., 1984, J. Catal., 88, 89.
121. Lepore, G., and Langford, C. H., 1989, Water Pollut. Res. J. Can., 24, 537.
122. Sabin, F., Turk, T., and Vogler, A., 1992, J. Photochem. Photobiol. A: Chem., 63, 99.
123. Anderson, M. A., Tunesi, S., and Xu, Q., 1991, In US. Patent Office: US. Patent.
124. Hidaka, H., Nohara, K., Zhao, J. C., Takashima, K, Pelizzetti, E., and Semone, N., 1994, New J. Chem., 18, 541.
125. Huang, D.G., Liao, S.J., Liu, J.M., Dang, Z., and Petrik, L., 2006, J. Photochem. Photobiol. A: Chemistry, 2006, 184, 3, 282.
126. Lin, C., and Lin, K.S., 2007, Chemosphere, 66, 10, 1872.
127. Huang, Q.D., and Hong, C.S., 2000, Chemosphere, 41, 6, 871.
128. Guo, Y., Wang, Y., Hu, C., Wang, Y., Wang, E., Zhou, Y., and Feng, S., 2000, Chem. Mater., 12, 11, 3501.
129. Mao, Y., Schoneich, C., and Asmus, K. D., 1991, J. Phys. Chem., 95, 80.
130. Lichtin, N. N., Dong, J., and Vijayakumar, K. M., 1992, Water Pollut. Res. J. Can., 27, 203.
131. Hsiao, C. Y., Lee, C. L., and Ollis, D. F., 1983, J. Catal., 82, 418.
132. Hong, A. P., Bahnemann, D. W., and Hoffann, M. R., 1987, J. Phys. Chem., 91, 6245.
133. Mills, G., and Hoffmann, M. R., 1993, Environ. Sci. Technol., 27, 1681.
134. Borisch, J., Pilkenton, S., Miller, M. L., Raftery, D., and Francisco, J. S., 2004, J. Phys. Chem. B., 108, 18, 5640.

135. Dieckmann, M. **S.,** Gray, K. A., and Kamat, P. V., 1993, Water Sci. Technol., 25, 277.
136. Matthews, R. W., Abdullah, M., and Low, G., 1990, Anal. Chim. Acta, 233, 171.
137. D'Oliveira, J. C., Guillard, C., Maillard, C., and Pichat, P., 1993, J. Environ. Sci. Health Part A: Environ. Sci. Eng., 28, 941.
138. Prairie, M. R., Evans, L. R., Stange, B. M., and Martinez, S. L., 1993, Environ. Sci. Technol., 27, 1776.
139. Reeves, P., Ohlhausen, R., Sloan, D., Pamplin, K., Scoggins, T., Clark, C., Hutchinson, B., and Green, D., 1992, Solar Energy, 48, 413.
140. Matthews, R.W., 1991, Water Res., 25, 1169.
141. Pramauro, E., Vincenti, M., Augugliaro, V., and Palmisano, L., 1993, Environ. Sci. Technol., 27, 1790.
142. Low, G. K. C., McEvoy, S. R., and Matthews, R. W., 1991, Environ. Sci. Technol., 25, 460.
143. Low, G. K. C., McEvoy, S. R., and Matthews, R. W., 1989, Chemosphere, 19, 1611.
144. Kormann, C., Bahnemann, D. W., and Hoffmann, M. R., 1991, Environ. Sci. Technol., 25, 3, 494.
145. Kopf, P., Gilbert, E., and Eberle**,** S.H., 2000, J.Photochem. Photobiol. A: Chemistry, 136, 3, 163.
146. Sampath, S., Uchida H., and Yoneyama, H., 1994, J.Catal. 149, 1, 189.
147. Tayade, R. J., Kulkarni, R. G., and Jasra, R. V., 2006, Ind. Eng. Chem. Res., 45, 3, 922.
148. Anpo, M., Aikawa, N., and Kubokawa, Y., 1984, J. Phys. Chem., 88, 3998.
149. Herrmann, J. M., Mu, W., Pichat, P., 1991, Heterog. Catal. Fine Chem., 2, 405, Stud. Surf. Sci. Catal., 59.
150. Peral, J., and Ollis, D. F., 1992, J. Catal., 136, 554.
151. Brezova, V., Brandsteterova, E., Ceppan, M., and Pies, J., 1993, Collect. Czech. Chem. Commun., 58, 1285.
152. Matthews, R. W., 1987, J. Phys. Chem., 91, 3328.
153. Izumi, I., Fan, F. F., and Bard, A. J., 1981, J. Phys. Chem., 1981,85, 218.
154. Harada, H., 1991, Chem. Exp., 6, 961.
155. Minero, C., Aliberti, C., Pelizzetti, E., Terzian, R., and Serpone, N., 1991, Langmuir, 7, 928.
156. Sun, B., Alexandre, V., Vorontsov, and Panagiotis, G., and Smirniotis, 2003, Langmuir, 19, 3151.
157. Iliev, V., Tomova, D., Todorovska, R., Oliver, D., Petrov, L., Todorovsky, D., and Uzunova-Bujnova, M., 2006, Appl. Catal. A: General, 313, 2, 4,115.
158. Vamathevan, V., Amal, R., Beydoun, D., Low, G., and McEvoy, S., 2002, J. Photochem. Photobiol. A: Chemistry, 148, 1-3, 233.
159. Belver, C., Bellod, R., Fuerte, A., and Fernández-García, M., 2006, Appl. Catal. B: Environ., 65, 3-4, 301.
160. Belver, C., Colon, G., Fernandez-Garcia, M., 2006, Synthesis, Properties and Application of Oxide nanoparticles, Fernandez-Garcia, M., Rodriguez, J.A., (Eds.), Wiley, USA (Chapter 17).
161. Thu, H., Karkmaz, M., Puzenat, E., Guillard, C., and Herrmann, J.M., 2005, Res. Chem. Intermed., 31, 449.

162. Zhao, J., Chen, C., and Ma, W., 2005, Top. Catal., 35, 267.
163. Ana, T., Lia, G., Zhub, X., Fua, J., Shenga, G., and Kunc, Z., 2005, Appl. Catal. A: General, 279, 247.
164. Pelegrini, R., Peralta-Zamora, P., Andrade, A.R., Reyes, J., and Duran, N., 1999, Appl. Catal. B: Environ., 22, 83.
165. Rodriguez, J., Gomez, M., and Lindquist, S.E., 2000, Thin Solid Films, 360, 250.
166. Vinodgopal, K., and Kamat, P.V., 1996, Chemtech., 26, 18.
167. An, T.C., Xiong, Y., Li, G.Y., Zha, C.H., and Zhu, X.H., 2002, J. Photochem. Photobiol. A: Chem., 152, 155.
168. Andreozzi, R., Caprio, V., Insola, A., Marotta, R., 1999, Catal. Today, 53, 51.
169. Tsyganok, A.I., and Otsuka, K., 1999, Appl. Catal. B: Environ., 22, 15.
170. Tsyganok, A.I., Otsuka, K., 1998, Electrochim. Acta, 43, 2589.
171. Yasman, Y., Bulatov, V., Rabin, I., Binetti, M., Schechter, I., 2006, Ultrasonics Sonochemistry, 13,271.
172. Sires, I., Garrido, J.A., Rodriguez, R.M., Brillas, E., Oturan, N., Oturan, M.A., 2007, Appl. Catal. B: Environ., 72, 382.
173. Edelahi, M.C., Oturan, N., Oturan, M.A., Padellec, Y., Bermond, A., and Kacemi, E., 2004, Environ. Chem. Lett., 1, 233.
174. Liu, Y., Yang, F., Yue, P., and Chen, G., 2001, Wat. Res., 35, 8, 1887.
175. Cheung, H.M., Bhatnagar, A., and Jansen, G., 1991, Environ. Sci. Technol., 25, 1510.
176. Hua, I., and Hoffmann, M.R., 1996, Environ. Sci. Technol., 30, 864.
177. Suslick, K.S., Hammerton, D.A., and Cline, R.E., 1986, J. Am. Chem. Soc., 108, 5641.
178. Mason, T.J., and Lorimer, J.P., 1988, Sonochemistry: Theory, Application and Uses of Ultrasound in Chemistry, John Wiley & Sons, New York.
179. Mason, T.J., 1991, Practical sonochemistry: a user’s guide to application in chemistry and chemical engineering, Ellis Horwood.
180. Hung, M., and Hoffman, M.R., 1998, Environ. Sci. Technol., 32, 3011.
181. Gogate, P.R., and Pandit, A.B., 2004, Adv. Environ. Res., 8, 3-4, 553.
182. Jantschak, A., Daniels, M., and Paschold, R., 2004, IEEE Trans. Semicond. Manufact., 17, 3.
183. Kim, D., Cai, Z., and Sorial, G.A., 2005, Chem. Eng. J., 113, 2-3, 153.
184. Peishi, S., Xianwan, Y., Ruohua, H., Bing, H., and Ping, Y., 2004, J. Cleaner Production, 12, 95.
185. Jeong, E., Hirai, M., and Shoda, M., 2006, J. Biosci. Bioeng., 102, 4, 281.
186. Cox, H.J., and Deshusses, M.A., 2002, Chem. Eng., 87,101.
187. Godjevargova, T., Ivanova, D., Alexieva, Z., and Dimova, N., 2003, Process Biochem., 38, 915.
188. Maestre, J.P., Gamisans, X., Gabriel, D., and Lafuente, J., 2007, Chemosphere, 67, 684.
189. Bohn, H., 1992, Chem. Eng.Progress, 34 -40.
190. http://www.epa.gov/ttn/atw/bio/bio_rsch.html (Accessed January 2007).
191. http://www.epa.gov/ttn/atw/bio/bio_rsch.html (Accessed January 2007).
192. Acuna, M.E., Revah, S., 1998, Proceedings of the Air & Waste Management Association 91stAnnual Meeting and Exhibit, San Diego, California.
193. Farooq, S., Kurucz, C., Waite, T.D., Cooper, W.J., Mane, S.R., and Greenfield, J.H., 1992, Water Sci. Technol., 26, 1265.

194. Hakoda, T., Hashimoto, S., Fujiyama, Y., and Mizuno, A., 2000, J. Phys. Chem., 104, 59.
195. Paur, H.R., and Matzing, H., 1993, Rad. Phys. Chem. 42, 719.
196. Sampa, M.H.O., Duarte, C.L., Rela, P.R., Somessari, E.S.R., Silveira, C.G., and Azevedo, A.L., 1998, Radiat. Phys. Chem. 52, 365.
197. Kima, J., Han, B., Kim, Y., Lee, J.H., Park, C.R., Kim, J.C., and Kim, K.J., 2004, Rad.Phys. Chem., 71, 427.
198. Tzing, H. M, Hirota, K., Woletz, K., and Paur, H.R., 1994, J. Aerosol. Sci., 25, I, 325.
199. Kim, J.C., 2002, Rad. Phys. Chem., 65, 429.
200. Han, D.H., Stuchinskay, T., Wonc, Y.S., Parkc, W.S., and Lim, J.K., 2003, Rad. Phys.Chem., 67, 51.
201. Brzustowski, T. A., 1976, Prog. Energy Combust. Sci., 2, 129.
202. www.p2pays.org/ref/10/09856.pdf (Accessed January 2007).
203. Lombardia, L., and Carnevalea, E., Cortib, a., 2006, Energy, 31, 3208.
204. Oda, T., 2003, J. Electrostat., 57, 293.
205. Oda, T., Takahashi, t., and Yamaji, k., 2004, IEEE Trans. Ind. Appl, 40, 5, 1249.
206. Masuda, S., Akutsu, K., Kuroda, M., Awatsu, y., and Shibuya, y., 1998, IEEE Trans. Ind. Appl., 24, 2, 223.
207. Fortuny, A., 1999, Catal. Today, 53, 107.
208. Luck, F., 1999, Catal. Today, 53, 81.
209. Hsieha, C.C., Leeb, J.F., Liuc, Y.R., and Changc, J.R., 2002, Waste Management, 22, 739.
210. Imamura, S., 1999, Ind. Eng. Chem. Res., 38, 1743.
211. Massa, P., Ivorra, F., Haure, P., Cabello, F.M., and Fenoglio, R., 2007, Catal. Comm., 8, 3, 424.
212. Li, N., Descorme, C., and Besson, M., 2007, Appl. Catal. B: Environ., 71, 3-4, 262.
213. Milone, C., Fazio, M., Pistone, A., and Galvagno, S., 2006, Appl. Catal. B: Environ., 68, 1-2, 28.
214. Sadana, A., and Katzer, J.R., 1974, Ind. Eng. Chem. Fundam., 13, 127.
215. Kim, S., Shah, Y.T., Cerro, R.L., and Abraham, M.A., 1991, Proc. Aiche Ann. Meet., Pittsburgh, 46.
216. V.S. Mishra, J.B. Joshi, V.V. Mahajani, Ind. Chem. Eng. 34 (1993) 211.
217. Sanger, A.R., Lee, T.T.K., Chuang, K.T., 1992, Progress in Catalysis, Smith, K.J., Sanford, E.C., (Eds.), Elsevier, 197.
218. Pintar, A., and Levec, J., 1992, Chem. Eng. Sci., 47, 2395.
219. E.O. Box, Jr., F. Fahra, US Patent 3 823 088 (1974).
220. Levec, J., Herskowitz, M., and Smith, J.M., 1976, Aiche. J., 22, 919.
221. Chen, I.P., Lin, S.S., Wang, C.H., and Chang, S.H., 2007, Chemosphere, 66, 1,172.
222. Gomes, H.T., Selvam, P., Dapurkar, S.E., Figueiredo, J.L., and Faria, J.L., 2005, Microporous and Mesoporous Materials, 86, 1-3, 2005, 287.
223. Zhu, W., Bin, Y., Li, Z., Jiang, Z., and Yin, T., 2002, Water Research, 36, 8, 1947.
224. Imamura, S., Nakamura, M., Kawabata, N., Yoshida, J., Ishida, S., 1986, Ind. Eng. Chem. Prod. Res. Dev., 25, 34.
225. Moses, D.V., and Smith, E.A., 1954, US Patent, 2, 690, 425.

226. Rodrigo, J.G., Adrian, L., Silva, M.T., Quinta-Ferreira, R.M., 2006, Appl. Catal. B: Environ., 71, 310.
227. Caps, V., and Tsang, S. C., 2000, Catal. Today, 61, 1-4, 10, 19.
228. Shmidt, F.K., Kochetkova, R.P., Babikov, A.F., Shiverskaia, I.P., Shpilevskaia, L.I., and Eppel, C.A., 1990, Proceedings of the 8th French–Soviet Meeting on Catalysis, Novossibirsk, 140.
229. Ito, M.M., Akita, K., and Inoue, H., 1989, Ind. Eng. Chem. Res., 28, 894.
230. Imamura, S., Hirano, A., and Kawabata, N., 1982, Ind. Eng. Chem. Prod. Res. Dev., 21, 570.
231. Imamura, S., Doi, A., and Ishida, S., 1985, Ind. Eng. Chem. Prod. Res. Dev., 24, 75.
232. Quintanilla, A., Casas, J.A., Mohedano, A.F., and Rodriguez, J.J., 2006, Appl. Catal. B: Environ., 67, 3-4, 206.
233. Guo, J., and Al-Dahhan, M., 2006, Appl. Catal. A: General, 299, 175.
234. Imamura, S., Fukuda, I., and Ishida, S., 1988, Ind. Eng. Chem. Res., 27, 718.
235. Barbier, J., Delanoe, F., Jabouille, F., Blanchard, G., and Duprez, D., 1998, J. Catal., 177, 378.
236. Harada, Y., and Yamasaki, K., 1993, Proceedings of IDA/WRPC World conference on Desalin Water Treatment, Yokohama, 231.
237. Takahashi, Y., Takeda, N., Aoyagi, T., and Tanaka, K., 1991, Proc. 4th Eur. Symp. Space Environ. Control Syst., Florence, ESA SP-324, 2, 643.
238. Massa, P., Ivorra, P., Haure, P., Cabello, F.M., and Fenoglio, R., 2007, Catal. Comm., 8, 3, 424.
239. Maugans, C.A., Akgerman, A., 1997, Wat. Res., 31, 3116.
240. Ishii, T., Mitsui, K., Sano, K., and Inoue, A., 1991, Eur. Patent, 431, 932.
241. Zhang, Q., Chuang, K.T., 1998, Appl. Cat. B: Environ., 17, 321.
242. Perkas, N., Minh, D.P., Gallezot, P., Gedanken, A., and Besson, M., 2005, Appl. Catal. B: Environ., 59, 1-2, 121.
243. Milone, M., Pistone, F.A., and Galvagno, S., 2006, Appl. Catal. B: Environ., 68, 1-2, 26, 28.
244. Kim B. R., Kalis, E. M., and Adams, J. A., 2001, Pure Appl. Chem., 73, 8, 1277.