Techniques of Wastewater Treatment

1. Introduction to Effluent Treatment and Industrial Methods

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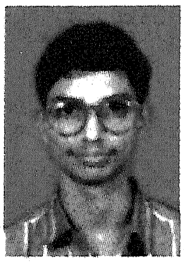

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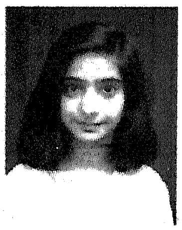

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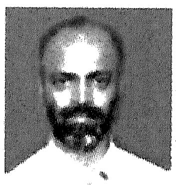

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What is an Effluent?

Liquid, solid and gaseous waste materials are often generated during the manufacturing of almost all the chemical and other industrial products. As a result of rapid industrial growth following World War II, the amount of waste material generated by industries has increased manifold and the treatment/removal of these contaminants from the natural resources such as air and water in which they are released has progressed into a special science, involving chemical, mechanical and biological processes. The word 'effluent' refers to the impure water containing inorganic salts, organic compounds, microbial contamination and turbidity disturbing the natural hydrologic cycle (water cycle). The hydrologic cycle can be maintained by the removal of toxic chemicals by many scientifically simple yet sometimes technologically very complex methods. The contaminants observed in an industrial effluent must meet certain standards of purity before they can be discharged into waterways. The most significantly observed impurities are listed in *Box* 1. The removal of these impurities from waste water is termed as 'waste water treatment' and the engineering aspects of employing it on large scale as 'waste-water engineering'.

Need for Effluent Treatment

Our environment is delicately balanced. It is a system of complex global chemical cycles working in harmony using the limited natural resources. Hydrologic cycle which is one of the most important and yet highly unevenly distributed use of water with subsequent addition of contaminants has been disturbing the environmental balance. To prevent this, the techniques

Box 1. Normally Identified Impurities in an Effluent.

1.**Dissolved mineral matter:** Calcium, magnesium hardness (soluble Ca, Mg salts), carbonates, bicarbonate alkalinity, mineral acidity and metal salts i.e. Ni, Cr, Hg, etc.
2. **Dissolved gases:** CO_2, O_2, N_2, H_2S (sulfur wastes) and CH_4 (only in ground water).
3. **Turbidity:** Inorganic or organic particles, which reduce the clarity of the water.
4. **Colour and Organic Matter:** Colour in water may exist in the form of colloidal suspension or non-colloidal matters.
5. **Micro-organisms:** These are small plants as well as animals and they are some of the most difficult contaminants to remove from water.

available for decontamination of wastewater are many, and the aim of these techniques is waste minimisation and toxicity reduction. Thus, if these methods are implemented correctly, the development and growth can be sustained without destabilising the hydrologic cycle. Preventing an effluent from entering into a large natural water source is the best option to control or limit its impact followed by minimisation of the contaminants in it. Typically, the chemical industries or to be more precise, the organic chemicals industries and the nuclear industry generate some of the most hazardous and toxic effluents. The toxicity varies from parts per billion (ppb, mg/m^3) to few thousands of parts per million (ppm, mg/L) levels in the water depending upon the product and its manufacturing process. *Table* 1 gives the information about some toxic contaminants and their maximum discharge levels in the effluent as noted by the Indian Pollution Control Board.

The purpose of these two articles is to make readers aware of the advances made in the treatment technique, with reference to the techniques of handling and treatment of liquid effluent. The most logical way of decontamination of an effluent containing organic compounds is oxidation to less hazardous compounds. Heavy metallic inorganic compounds are removed from effluents by extraction or reduction to form stable coagulates. The oxidation of contaminants is the key to successful operation of each technique and for most of the techniques, maximum levels of oxidation attainable with minimum cost involved in the

Table 1. Discharge levels of toxic contaminants in the industrial effluent (Water Pollution Control Act, 1974)

No.	Parameters	Discharge level not to exceed
1	Mercury	0.01 mg/l
2	pH	5.5 – 9
3	Suspended solids	250 mg/l
4	Biochemical oxygen demand	150 mg/l
5	Temperature	Shall not exceed 5°C above the ambient temperature of the receiving body.
6	Free available chlorine	0.5 mg/l
7	Oil and grease	10 mg/l
8	Copper	3 mg/l
9	Iron	3 mg/l
10	Zinc	5 mg/l
11	Chromium	2 mg/l
12	Phosphate	5 mg/l
13	Sulphide	2 mg/l
14	Phenolic compounds	5 mg/l
15	Hexavalent Chromium	0.1 mg/l
16	Nickel	3 mg/l
17	Cadmium	2 mg/l
18	Chloride	9000 mg/l
19	Sulphate	1000 mg/l
20	Cyanides	0.2 mg/l
21	Ammonical nitrogen	50 mg/l
22	Lead	0.01 mg/l
23	Total metal	10 mg/l

operation is the deciding factor for its large-scale implementation.

Techniques for Waste Water Treatment

Depending upon the size or the volume of wastewater from an industry, the technique to be employed changes. These techniques can be classified as chemical, physical and biological depending upon the method of implementation and the principle of operation and also the nature of the effluent. The contamination is generally given in terms of chemical oxygen

Box 2. Important Terms in the Analysis of an Effluent.

1. **Chemical Oxygen Demand (COD):** It is the amount of oxygen required to oxidise the polluting chemicals to CO_2 and H_2O. Normally, the discharge effluent should contain a maximum COD of 90 ppm.

2. **Biological Oxygen Demand (BOD):** It is the amount of oxygen required by the biological microbial mass during the effluent treatment to oxidise the biologically oxidizable pollutants and for their own sustenance. It is measured by the oxygen consumption of a pre-inoculated sample at 20-25^{0}C in darkness over an incubation period of five days.

3. **Dissolved Oxygen (DO):** It is the observed amount of O_2 dissolved in the water. DO in a treated effluent is always more than that in a fresh effluent.

4. **Suspended Solids:** As a result of surface charge on small particles in the effluent, larger solid particulate remains in a suspended manner in it. This is also termed as MLSS (Mixed Liquor Suspended Solids).

5. **Total Dissolved Solids:** Many inorganic salts, which are soluble in water are difficult to remove since they are totally dissolved and show high solubility in water.

demand (COD), biological oxygen demand (BOD) and dissolved oxygen (DO), etc., which are described in *Box* 2. It is necessary to know these terms as they are used to define the nature of toxicity associated with waste water.

The classification of techniques for the removal or the reduction of the contaminants based on the need and the available technology is as follows:

*1. **Biological treatment:*** Aerobic digestion (oxidation) of the effluent and anaerobic waste minimisation.

*2. **Chemical treatment:*** Direct chemical oxidation, photo-oxidation of the effluent, photo-catalytic oxidation and destruction of organic compounds by *sonication*.

*3. **Physical (thermal) treatment:*** Wet air oxidation (WAO), supercritical fluid oxidation of toxic contaminant and incineration (complete combustion).

Generally, on an industrial level a combination of two or three techniques is employed to get better results mainly due to the

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presence of multiple contaminants. The rate at which new chemical entities are discovered and synthetically made is far higher than the rate of bioadaptability, (usually in decades). As a result, conventional treatment schemes are facing difficulties in recent times. We start the discussion in the order of the maturity of the technology and its success on an industrial scale. The first section of the article discusses the conventional biological method of effluent treatment and wet air oxidation, which is a method of oxidising the higher molecular weight organic compounds not amenable to biological treatment. In the second section, emerging and advanced techniques of oxidation of the effluent are discussed in detail.

Biological Waste Water Treatment

Biological operations play an important role in the treatment of wastewater. The classification of these biochemical operations can be done on the basis of three parameters viz. biological environment, nature of biological transformation and reactor configuration. Biological environment decides whether the operation is anaerobic or aerobic while nature of transformation decides the way to transform the contaminants depending upon their nature i.e. organic, inorganic, etc. It includes destabilisation, flocculation and adsorption on biomass. Reactor configuration includes the different physical systems designed for carrying out the biological treatment based on different principles.

Basic Principles: The removal of oxidizable organic compounds and the coagulation of non-settlable colloidal solids using micro-organisms is the basic principle of biological treatment. The exact role of micro-organism varies with the physical system where they are used. In the process, the micro-organisms use the existing digestible (oxidizable) compounds and nutrients for their growth. The general source of energy is organic matter, carbon dioxide and nutrients. Thus depending upon the mechanism of energy assimilation by the micro-organisms and the environment, the method of treatment can be taken as aerobic (in presence of oxygen), anaerobic (in absence of oxygen) and

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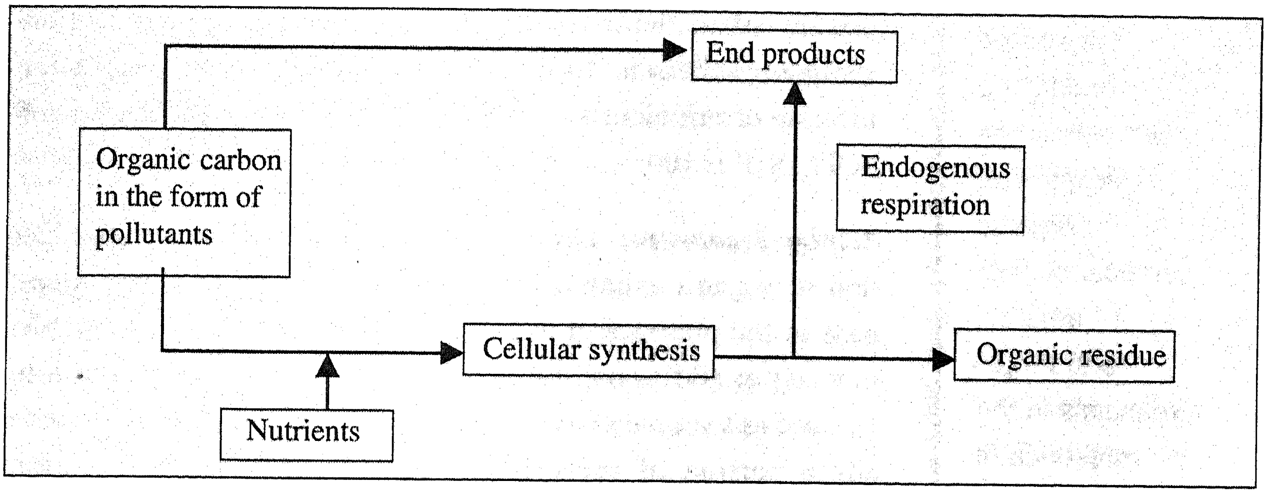

Figure 1. Schematics of aerobic bacterial metabolism in the organic carbon biological oxidation.

facultative (independent of oxygen) treatment. A general scheme of bacterial metabolism is shown in *Figure* 1, which indicates the path of oxidation of contaminants, growth of micro-organisms and decontamination. For complete degradation of contaminants, adequate oxygen has to be dissolved into the wastewater. The higher the partial pressure of oxygen at the gas-water interface, the more the oxygen that can be dissolved in the solution. For the same pressure and temperature conditions, the saturation limit for pure oxygen is about 5 times that of atmospheric oxygen. The amount of technical effort and the energy that is required for introduction of oxygen is determined from the difference between the saturation value and the desirable oxygen content. In the presence of dissolved oxygen (DO), biological metabolism of certain micro-organisms that are present in a body of water, proceeds in an aerobic fashion. Organic wastewater components may be oxidised all the way to CO_2 (mineralization) or some other metabolic by-product, whereas ammonium ion is transformed into nitrate (nitrification). In the case of excessive contamination with oxidizable substances, all the available dissolved oxygen gets consumed. If no additional oxygen is provided, only aerobic processes occur. Anaerobic wastewater treatment has an efficiency of less than 85%, and it is essentially used only for pre-treating wastewater characterised by a high organic load (>5000 mg/L or ppm) and insofar as possible, a constant quality. Some of the most important terms in analysing an effluent are given in the *Box* 2. Further, enough amounts of nutrients are required to have optimum degradation of organic substrate. Industrial waste water is treated only after addition of sufficient amounts of nutrients to it. Optimal ratio of BOD_5:N:P is 100:5:1 and C:N:P is 100:12:3.

Aerobic Treatment: The basic underlying principle is the oxidation of organic compounds with aerobic, heterotropic organisms in the presence of oxygen. The dissolved oxygen available in water or additionally supplied using some means of aeration is used as a source of oxygen for the growth of microbes. Generally a portion of the organic waste is used by aerobic and facultative bacteria to obtain energy for the synthesis of the remaining organic material into new cells. Only a portion of the original waste is oxidised to low energy compounds and the remainder is synthesised into cellular material known as endogenous respiration. A general reaction scheme of such oxidation process is

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Oxidation and synthesis

$$\underset{\text{(organic compound)}}{COHNS} + O_2 + \text{nutrients} \xrightarrow{\text{bacteria}} CO_2 + NH_3 + \underset{\text{(new bacterial cell)}}{C_5H_7NO_2} + \text{Other end products}$$

Endogenous respiration

$$\underset{\text{cells}}{C_5H_7NO_2} + 5O_2 \xrightarrow{\text{bacteria}} 5CO_2 + 2H_2O + NH_3 + \text{energy}$$

Micro-organisms can be in the form of activated sludge floc, fixed bio-film, floating bulking sludge and fast peeling bio-film. Amongst these, activated sludge floc has the highest potential for bio-degradation of organic substances. It consists of bacteria, fungi, protozoans and metazoans. In aerobic degradation of such organic substrates viz. fats, carbohydrates, materials are converted either to other organic substances or inorganic compounds such as water, CO_2, NH_3, etc. with the consumption of oxygen. When the organisms considered are present in large numbers in the system, almost complete degradation of carbon to CO_2 is possible. If the amount is less, a part of the intermediates remain in the treated wastewater in the form of non-separable organic substances.

Biological effluent treatment is generally carried out in a continuous mode of operation, since large amount of effluent is also generated continuously from all the processes.

Biological Oxidation Reactors for Effluent Treatment: Biological effluent treatment is generally carried out in a continuous mode of operation, since large amount of effluent is also generated continuously from all the processes. They are five types of treatments based on individual principles of operation.

I. Tank reactors: Micro-organisms are kept suspended in the effluent. They are of three types.

(a) Open lagoons: Open lagoon provides habitat for micro-organisms. Mechanical agitation is often used to increase the ability to handle higher BOD and COD content. They are long term retention basins, shallow in depth and their process efficiency depends upon surface area and wave action to transfer oxygen from the atmosphere. Here, due to limited solubility of O_2 in water, efficiency of the process depends upon the absorption of oxygen from the atmosphere. The process can be aerobic or anaerobic.

(b) Aerated lagoons: When BOD load in the effluent increases, naturally occurring surface oxidation becomes insufficient to sustain aerobic bacteria and hence supplementary oxygen is supplied to the lagoon. Turbulence induced on mechanical agitation of the water surface entraps oxygen and helps the micro-organisms to grow fast and consume the organic pollutants at a higher rate. *Figure* 2 shows one such mechanically agitated activated sludge system. Many times, the air is provided through the impellers, propellers and spargers at the bottom of the tank.

(c) Facultative lagoons: Facultative lagoons contain micro-organisms, which have the ability to survive with or without oxygen. They are slightly deeper than un-aerated lagoons.

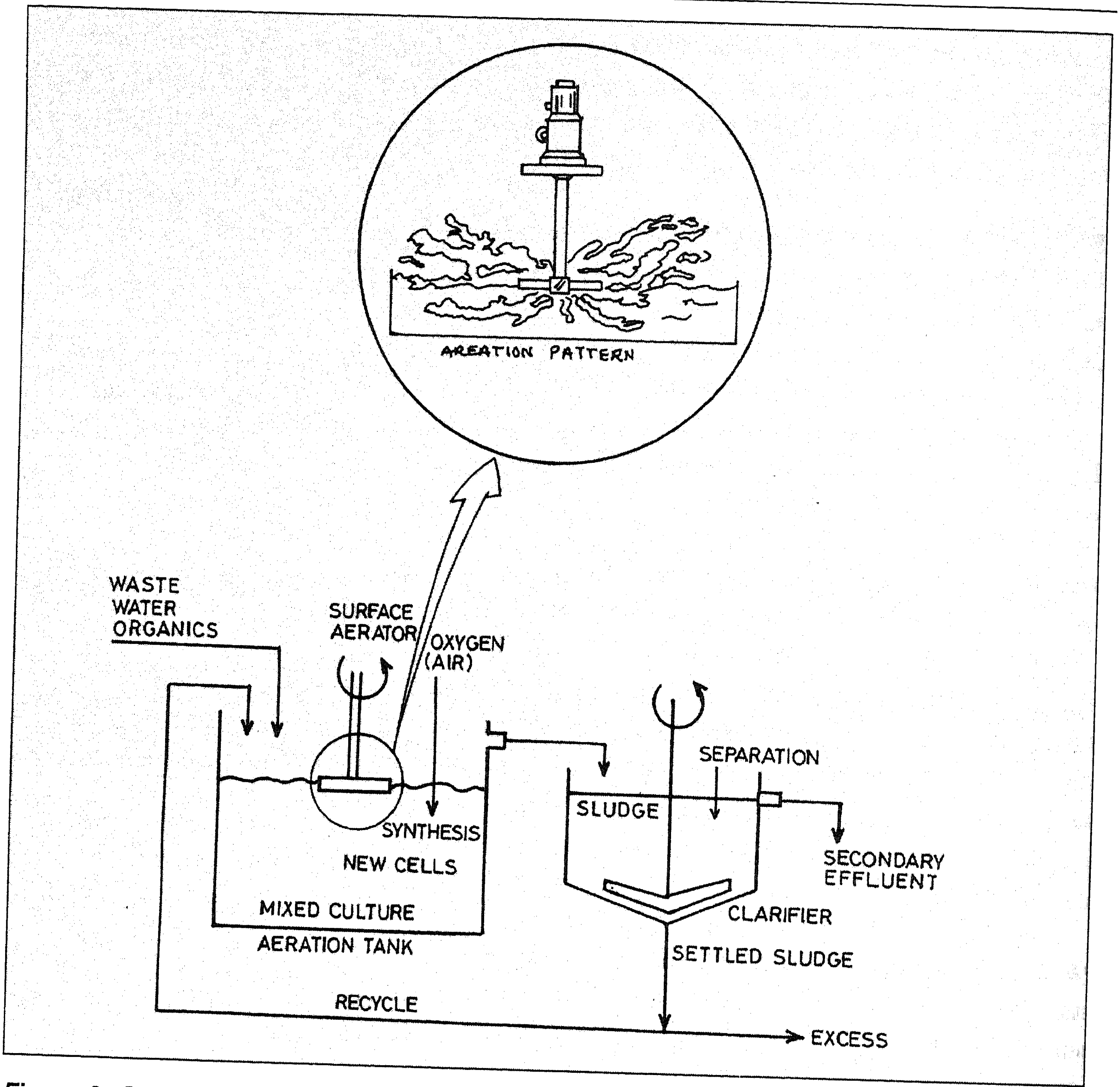

Figure 2. Schematic diagram of activated sludge process unit.

II. Fixed media reactors: Micro-organisms can be used as biomass in a fixed or immobilised state and effluent is passed over the fixed biomass. A biological slime layer is grown on a substrate continually exposed to raw effluent. As the slime layer grows in thickness, oxygen transfer to the innermost layers is impeded.

III. Tower type of reactors: In this reactor, a grid like structure is used to grow micro-organisms. Since the structure is highly porous, oxygen transfer is not a problem and oxygen contact

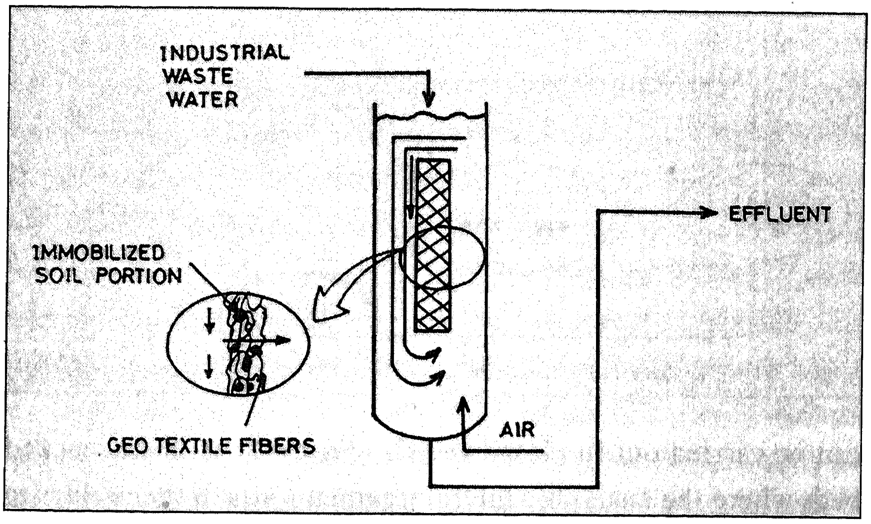

Figure 3. Immobilized soil bioreactor.

time is also more which reduces BOD to a significantly low value and that too with higher rates. Schematic diagram of this is shown in *Figure* 3.

Anaerobic Treatment: Anaerobic treatment or digestion is a two step process. Organic substances are first converted to carboxylic acids (acidification step) and then disproportionated to carbonic acid, methane and H_2 (which is termed as 'methanogenesis' or fermentation) in the second step. This is ideally suited for high BOD containing effluent but as usually the biodegradation is incomplete and the effluent from the anaerobic treatment needs further processing. Under anoxic/anaerobic conditions, oxygen required for aerobic metabolism is acquired through the biological reduction of some oxygen donor (NO_3, SO_4, PO_4) since free oxygen as such is not present. Anaerobic treatment

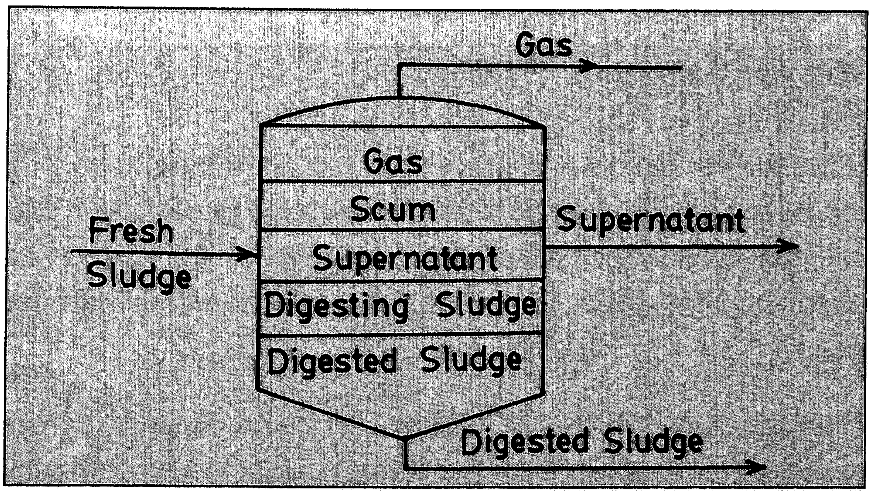

Figure 4. Anaerobic digestion.

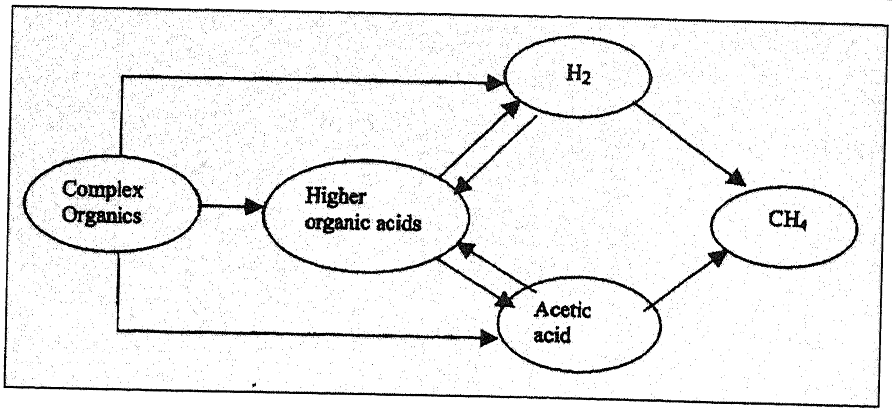

Figure 5. Steps in anaerobic digestion process.

can be carried out in closed vessels (*Figure* 4) or in the packed beds where the anaerobic micro-organisms attach themselves to the surface of the packings. A typical anaerobic digestion process is shown in *Figure* 5. This type of treatment has been used for processing the distillery spent wash which is among the highest volume of concentrated effluents generated in India.

Biological treatment is highly effective for the removal of most of the small molecular size contaminants. Despite their success and cost effectiveness, biodegradation processes are inherently slow, do not allow high degrees of removal, and are not suitable for compounds that are toxic to the micro-organisms. The sludge formed during the biological treatment has to be disposed of either by burning or using it for land filling. Sludge disposal may pose additional environmental problems. Evidently, the biological treatment of industrial waste water is of limited use only, and additional treatment by other methods is frequently required.

Wet Air Oxidation (WAO)

It has become necessary to innovate advanced techniques, which can make the large organic molecules undergo oxidation. WAO is a well-established technique of importance for wastewater treatment, particularly for toxic and hazardous waste containing water.

Fundamentals of WAO: WAO involves liquid phase oxidation of organic or oxidisable inorganic compounds at elevated temperatures (125-320 °C) and pressures (0.5-20 MPa) using a gaseous source of oxygen (air). It is also referred to as flameless combustion. Enhanced solubility of oxygen in aqueous solutions at these conditions provides a strong driving force for oxidation. Purpose of the elevated pressures is to keep water in liquid state at high temperatures. WAO results in the oxidation of organic compounds to CO_2 and H_2O and into other less hazardous products like acids. Higher the temperature, higher is the extent of oxidation achieved. Often the treated effluent contains mainly low molecular weight oxygenated compounds predominantly carboxylic acids, which are then amenable to further biological treatment. The degree and rate of oxidation is a function of temperature, oxygen partial pressure, residence time (the time for which the effluent remains in the reactor) and the oxidisability of the pollutant under consideration. The process flow diagram of a typical WAO unit is shown in *Figure 6*.

Mechanical Operation: In a continuous mode of operation required O_2 partial pressure is maintained by employing a compressor adding air to the reactor. Liquid feed to the plant is preheated. The WAO process becomes thermally self sustaining when the COD of the feed exceeds 20g/L and for sufficiently concentrated wastes (higher COD) it can be a net energy producer. WAO can be catalytic as well as non-catalytic. Non-catalytic aqueous phase oxidation requires long residence times (1 hr) and relatively severe temperatures (200-450 °C) and pressures (0.7-17 MPa). The conditions employed in catalytic WAO

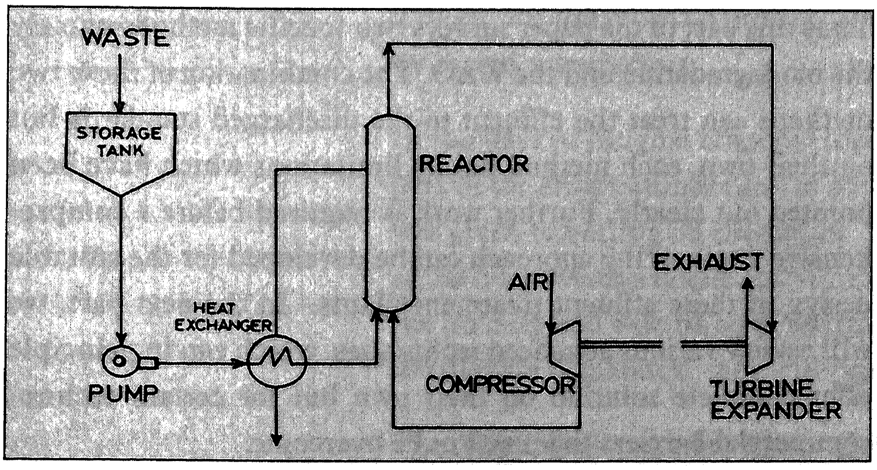

Figure 6. Basic flow sheet of wet air oxidation.

are less severe. In catalytic process, the catalyst acts to suppress the activation energy of the reactions and thus helps in lowering the severity of process conditions. The catalysts used for WAO are mainly Mn, Mn-Ce, Ni, Ni-Ce, Co-Bi, etc. During WAO, larger molecules are oxidised to various intermediate products mainly low molecular weight organic acids. Most of the intermediates are unstable and lead to complete oxidation to end products, such as CO_2 and H_2O. It has been observed that the oxidation rate increases with an increase in the molecular weight of the pollutant for both catalytic and noncatalytic systems. The mechanism of the process is the common electron transfer and can be easily understood by the scheme proposed for a compound such as acetic acid.

$$CH_3COOH + X \longrightarrow CH_3COOH.X$$
$$0.5\,O_2 + X \longrightarrow OX$$
$$CH_3COOH + OX \longrightarrow [HCHO] + [CO] + H_2O + X$$
$$[HCHO] + OX \longrightarrow [HCOOH] + X$$
$$[HCOOH] + OX \longrightarrow CO_2 + H_2O + X$$
$$CO + OX \longrightarrow CO_2 + X$$

where X indicates a vacant site developed on the surface of catalyst during its activation and OX an oxidised site capable of acting as catalyst for the reaction. Generally, acids viz. acetic acid, propionic acid, butyric acid and phenolic compounds like chlorophenols and nitrophenols are removed from the effluent by WAO.

Thus this part of the paper surveys two specific methods namely the biodegradation and the WAO. The combination of these two methods can treat the effluent to the discharged standards but on their own, each method has its limitations which have been pointed out clearly. Further work is required before a comprehensive engineering approach can be developed for the suitable design of these effluent treatment plants. In the next part, we will review various advanced techniques, which can in principle offer complete solution on their own but for certain techno-commercial barriers that need to be overcome.

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