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Chapter 11

Treatment Technologies for Organic Wastewater

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Additional information is available at the end of the chapter

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1. Introduction

1.1. Resources of organic wastewater

There are several contaminants in wastewater, with organic pollutants playing the major role. Many kinds of organic compounds, such as PCBs, pesticides, herbicides, phenols, polycylic aromatic hydrocarbons (PAHs), aliphatic and hetercyclic compounds are included in the wastewater, and industrial and agricultural production as well as the people living could be the source of organic wastewater endangering the safety of the water resource [1]. The wastewater of the farmland may contain high concentration of pesticides or herbicides; the wastewater of the coke plant may contain various PAHs; the wastewater of the chemical industry may contain various heterogeneity compounds, such as PCB, PBDE; the wastewater discharged by the food industry contains complex organic pollutants with high concentration of SS and BOD; and the municipal sewage contains different type of organic pollutants, such as oil, food, some dissolved organics and some surfactants. These organic pollutants in water can harm the environment and also pose health risks for humans.

1.2. Common poisonous substances in organic wastewater

The organic pollutants in the wastewater could be divided into two groups according to their biological degradation abilities. The organic pollutants with simple structures and good hydrophilicity are easy to be degraded in the environment. These organic pollutants, such as polysaccharide, methanol could be degraded by the bacteria, fungus and algae. However, some of them, such as acetone and methanol, could cause acute toxicity when existed in wastewater at a high concentration. On the other hand, the persistent organic pollutants, such as PAHs, PCBs, and DDT, are very slowly metabolized or otherwise degraded. Some of them, for example, the pesticides were widely used for several years. Although their concentration as well as the cute toxicity in the wastewater is lower than the soluble organic pollutant, they can be sequestered in sediment and exist for decades, and

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transport into the wastewater and then the food chain. The POPs are lipid soluble, and many of them mentioned above are carcinogenic, teratogenic, and neurotoxic. Since they are persistent, long way transported and toxic, these organic pollutants draw more attentions.

The classic poisonous substances in organic wastewater are as follow:

1. Water organic matter

Water organic matter is the genetic name of the organic compounds in the sediment and wastewater. Generated from the residues of the animal, plants and microorganisms, the water organic matters could be divided into two categories: one is non - humic, which is composed of the various organic compounds of organisms, such as protein, carbohydrate, organic acids, etc., the other is a special organic compounds named humus. Water organic matter could affect the physical and chemical properties of the water, and could also influence the self-purification, degradation, migration and transformation process in the water.

2. Formaldehyde

Formaldehyde is an organic compound with the formula CH_2O. The main sources of formaldehyde are organic synthesis, chemical industry, synthetic fiber, dyestuff, wood processing and the paint industry emissions of wastewater. With a strong reducibility, formaldehyde could easily combine with a variety of material, and is easy to be together. Formaldehy is a stimulus to skin and mucous membrane. It could enter the central nervous of human body and cause retinal damage

3. Phenols

Phenols are a class of chemical compounds consisting of a hydroxyl group (-OH) bonded directly to an aromatic hydrocarbon group. The phenol in the wastewater mainly comes from the coking plant, refining, insulation material manufacturing, paper making and phenolic chemical plant. Phenol is known human carcinogen and is of considerable health concern, even at low concentration. Phenol also has potential to decrease the growth and the reproductive capacity of the aquatic organisms.

4. Nitrobenzene

Nitrobenzene is an organic compound with the chemical formula $C_6H_5NO_2$. It is produced on a large scale as a precursor to aniline. In the laboratory, it is occasionally used as a solvent, especially for electrophilic reagents. Prolonged exposure may cause serious damage to the central nervous system, impair vision, cause liver or kidney damage, anemia and lung irritation[2]. Recent research also found nitrobenzene as a potential carcinogenic substance.

5. PCBs

PCBs are biphenyl combined with 2 to 10 chlorine atoms. PCBs are widely used as dielectric and coolant fluids, for example in transformers, capacitors, and electric motors, and various kinds of PCBs could be found the wastewater of this factories[3]. PCBs are carcinogenic, and could accumulate in adipose tissue, causing brain, skin and the internal organs disease, and

influence nerve, reproductive and immune system. PCBs also have shown toxic and mutagenic effects by interfering with hormones in the body. PCBs, depending on the specific congener, have been shown to both inhibit and imitate estradiol.

6. PAHs

PAHs are recalcitrant organic pollutants consisting of two or more fused benzene rings in linear, angular, or cluster arrangements. PAHs occur in oil, coal, and tar deposits, and PAHs in the aquatic system could come from accidently leaking, atmosphere deposition and contaminated sediment release. The concentration of PAHs, especially the PAHs with high molecular weight, in the water is usually low in the water owing to their hydrophobia property, but they are still among the most problematic substances as they could accumulate in the environment and threaten the development of living organisms because of their acute toxicity, mutagenicity or carcinogenity [4].

7. Organophosphorus pesticide

The wastewater of organophosphorus pesticide manufacturers often contains a high concentration of organophosphorus pesticide, intermedia productions and degradation productions, and the wastewater from the farmland could contain some of this pesticide since this substance could exist in the environment for a period of time. The discharge of water contained organophosphorus pesticide could cause serious environmental pollution. Some organophosphorus pesticides have acute poison on the people and livestock. In spite of the severe toxicity of the organophosphorus pesticide, it is easy to be degraded in the environment [5].

8. Petroleum hydrocarbons

The petroleum hydrocarbons in the water system mainly come from the industrial wastewater and municipal sewage. The industry, such as oil exploration, oil manufacture, transportation and refining could produce the wastewater with a mixture of various petroleum hydrocarbons. The petroleum hydrocarbons are toxic towards aquatic living things, and they could also aggravate the water quality by forming a layer of oil film, which could decrease the oxygen exchange of the air and water body.

9. Atrazine

Atrazine is the most widely used herbicide in conservation tillage systems, which are designed to prevent soil erosion. This chemical herbicide could stop pre- and post-emergence broadleaf and grassy weeds in dry farmland, and increase the production of the major crops [6]. The wastewater contained atrazine mainly comes from the chemical industry manufacturing this product and the farmlands which are over loaded. This substance could remain in the environment for a period of time, and it has been detected in the surface water and groundwater of many countries and regions. Atrazine could volatilize at high temperature and release poisonous gas such as carbon monoxide, nitrogen oxides, which could irritate people's skin, eyes and respiratory tract. Besides, atrazine also has a potential cause of birth defects, low birth weights and menstrual problems when consumed at concentrations below federal standards.

1.3. Environmental hazards of organic wastewater

High mount of hydrophilic organic pollutants, such as organic matters, oil could consume a large amount of soluble oxygen. The acute toxicity and high quantity of oxygen demand could worsen the water quality and lead to great damage to the aquatic ecological system. However, their bad influence towards the environment will not last long, since they could easily be degraded by microorganisms.

The situation is different for the POPs, which have low water solubility, high accumulation capacity and potential carcinogenic, teratogenic, and neurotoxic properties. For example, many of the organochlorine pesticides cited above are carcinogenic, teratogenic, and neurotoxic. The dioxins and benzofurans are highly toxic and are extremely persistent in the human body as well as the environment. Several of the POPs, including DDT and its metabolites, PCBs, dioxins, and some chlorobenzene, can be detected in human body fat and serum years after any known exposures. Lindane (hexachlorocyclohexane), which was used for the treatment of body lice and as a broad-spectrum insecticide, could cause very high tissue levels, and could cause acute deaths when improperly used.

Many factors, such as the characters of the pollutants, the environmental factors (PH value, temperature etc.), aging process could affect the toxicity of the organic wastewater, and their long-term influence to the ecosystem deserve further investigation.

1.4. Monitoring analysis method of poisonous substances

1. Gross analysis

The amount of organic compounds in wastewater is generally evaluated by chemical oxygen demand (COD) test, biological oxygen demand (BOD) test, and (TOC) test.

The basis for the COD test is that nearly all organic compounds can be fully oxidized to carbon dioxide with a strong oxidizing agent under acidic conditions. The COD value is always measured by the acidic potassium permanganate method and potessium dichromate method, and could reflect the pollution degree of reducing matter in water, including ammonia and reducing sulfide, so in wastewater with high quantity of reducing matter, the COD value will overestimate the organic pollutants in the water.

BOD value is the amount of dissolved oxygen needed by aerobic biological organisms in a body of water to break down organic material present in a given water sample at certain temperature over a specific time period. The BOD value is most commonly expressed in milligrams of oxygen consumed per liter of sample during 5 days of incubation at 20 °C and is often used as a robust surrogate of the degree of organic pollution of water. This is not a precise quantitative test, although it is widely used as an indication of the organic quality of water.

TOC value is the mount of total carbon (water soluble and suspended in water) in the water. Using combustion during the assessment, this method could oxidize all the organic pollutants, and value reflects the amount of organic matter more directly than BOD_5 or COD.

The COD, BOD and TOC test could quickly reflect the organic pollution in the wastewater, however, they can't reflect the kinds of organic matter and composition of the water, and therefore cannot reflect the total amount of the same total organic carbon pollution caused by different consequences.

2. Chromatography-mass spectrometry method

Chromatography-mass spectrometry method is an advanced method to separate and define the organic pollutants in the waste water. Spectrometry is the collective term for a set of laboratory techniques for the separation of mixtures. The separation is based on differential partitioning between the mobile and stationary phases. The structure diversity of different components in the wastewater results in a different retention on the stationary phase and thus changing the separation. The mobile phase of the chromatography can be gas or liquid, so the chromatography can be divided into gas chromatography (GC) and liquid chromatography (LC).

The mass spectrometer could ionize the organism and shoot it through an electric field. Since the electric field could bend the path (trajectory) of lighter molecules more than that of heavy molecules, the organic matter of different mass would strike at different position (the position is fixed for each organic matter) in the detector. This method could identify and quantify organic pollutants. The combination of chromatography and mass spectrometry could offer complete information on the type of organic pollutants in a sample and the concentration of each pollutant in the sample.

2. Biological treatment technology of organic wastewater

2.1. Principle of the biodegradation

Biodegradation is a process using microorganisms, fungi, green plants and their enzymes to remove the pollutants from natural environment or transform them harmless. Biodegradation could happen in nature world and is used in wastewater treatment in recent years since humanity strives to find sustainable ways to clean up contaminated water economically and safely.

2.2. Biodegradation of organic compounds

Chemical, physical and biological methods have been used to remove the organic compounds from the wastewater, and biological method has been paid much attention owing to its economic and ecologic superiority. The biodegradation rate and biodegradation degree of the organic substance partly depended on the characters of the substance. Some of the organic pollutants like organic matters, organophosphorus pesticide, which have relativity high water solubility and low acute toxicity, are bioavailable and easy to be degraded [7]. However, for some POPs and xenobiotic organic pollutants, such as polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), heterocyclic compounds, pharmaceutical substances, which possess a higher bioaccumulation,

biomagnification and biotoxicity properties, are reluctant to biodegradation in the nature condition. Organic material can be degraded aerobically with oxygen, or anaerobically, without oxygen [8].

2.3. Aerobic biodegradation

The principle of the aerobic biodegradation is as follow: oxygen is needed by degradable organisms in their degradation at two metabolic sites, at the initial attack of the substrate and at the end of respiratory chain [9]. Bacteria and fungi could produce oxygenases and peroxidases they could help with the pollutant oxidization and get benefits from observing the energy, carbon and nutrient elements released during this process. A huge number of bacterial and fungal general possess the capability to release non-special oxidase and degrade organic pollutants. There are generally two types of relationships between the microorganism and organic pollutants: one is that the microorganisms use organic pollutant as sole source of carbon and energy; the other is that the microorganisms use a growth substrate as carbon and energy source, while another organic compound in the organic substrate which could not provide carbon and energy resource is also degraded, namely cometabolism.

The classic aerobic biodegradation reactors include activated sludge reactor and membrane bioreactor.

2.3.1. Activated sludge reactor

Activated sludge is a process for treating sewage and industrial wastewaters using air and a biological floc composed of bacteria and protozoans. This technique was invented by Ardern and Lockett at the beginning of last century and was considered as a wastewater treatment technique for larger cities as it required a more sophisticated mode of operation (Fig. 1) [10].

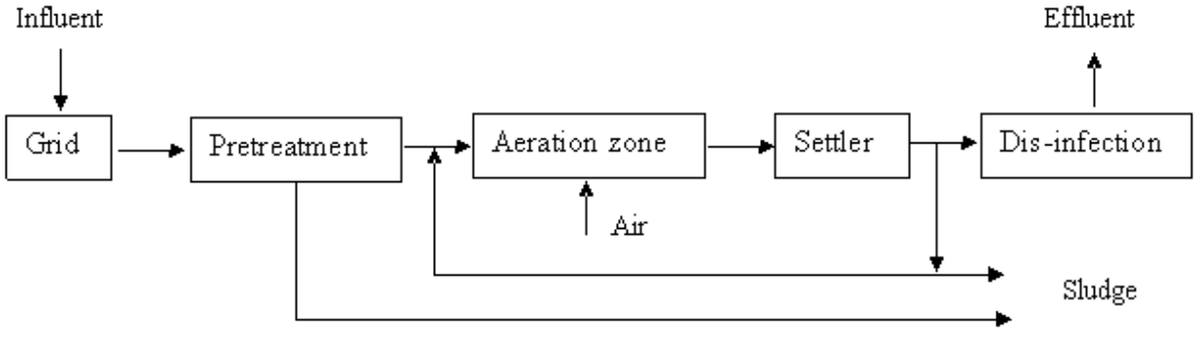


Figure 1. The scheme of the activated sludge reactor [1]

This process introduced air or oxygen into a mixture of primary treated or screened wastewater combined with organisms to develop a biological floc which reduces the organic content of the sewage, which is largely composed of microorganisms such as saprotrophic bacteria, nitrobacteria and denitrifying bacteria. With this biological floc, we could degrade

the organic pollutant and bio-transform the ammonia in wastewater. Generally speaking, the process contained two steps: adsorption followed by biological oxidation.

The technique could effectively remove the organic matters, nitrogeneous matters, phosphate in the wastewater, when there is enough oxygen and hydraulic retention time. However, the contaminated water is always short of oxygen, which could cause sludge bulking, a great problem decrease the water quality of the effluent. The oxygen concentration could be increased by including aeration devices in the system, but research need to be done to find out the optimal value since aeration would cause an increase of the costs of the wastewater treatment plants. Researches are also required to deal with the excess activated sludge, the by-product of this process, with a relatively low cost.

2.3.2. Membrane bioreactor

Membrane bioreactor (MBR) is the combination of a membrane process like microfiltration or ultrafiltration with a suspended growth bioreactor, and is now widely used for municipal and industrial wastewater treatment. The scheme of the reactor is showed in Fig. 2 [11].

The Principle of this technique is nearly the same as activated sludge process, except that instead of separation the water and sludge through settlement, the MBR method uses the membrane which is more efficient and less dependent on oxygen concentration of the water.

The MBR has a higher organic pollutant and ammonia removal efficiency in comparison with the activated sludge process. Besides, the MBR processes is capable to treat waste water with higher mixed liquor suspended solids (MLSS) concentrations compared to activated sludge process, thus reducing the reactor volume to achieve the same loading rate.

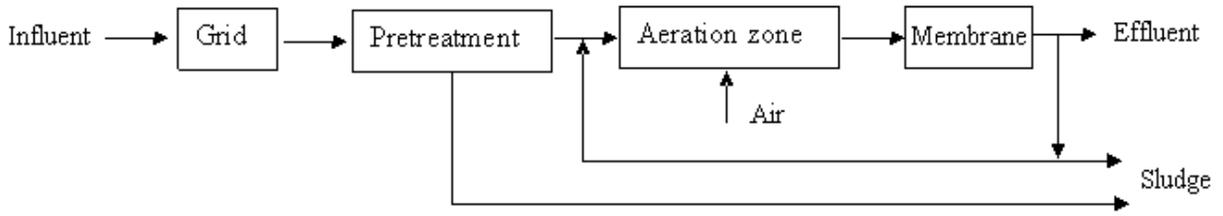


Figure 2. The scheme of the MBR reactor

However, membrane fouling greatly affects the performance of this technique, since fouling leads to significantly increase trans-membrane pressure, which increased the hydraulic resistance time as well as the energy requirement of this reactor. Alternatively frequent membrane cleaning and replacement is therefore necessary, but it significantly increases the operating cost.

2.4. Anaerobic biodegradation

Anaerobic degradation is a series of processes in which microorganisms break down biodegradable material in the absence of oxygen. The principle of the anaerobic degradation is as follow: first, the insoluble organic pollutant brakes down the into soluble substance,

making them available for other bacteria; second, the acidogenic bacteria convert the sugars and amino acid into carbon dioxide, hydrogen, ammonia and organic acid; third, the organic acids convert into acetic acid, ammonia, hydrogen and carbon dioxide; finally, the methanogens convert the acetic acid into hydrogen, carbon dioxide and methane, a kind of gaseous fuel [9].

Anaerobic degradation processes have always been considered to be slow and inefficient, in comparison to aerobic degradation. However, the anaerobic degradation not only decreases the COD and BOD in the waste water, but also produces renewable energy. Moreover, the anaerobic bacteria could break down some persistent organic pollutants, such as lignin and high molecular weight PAH, which show little or no reaction to aerobic degradation. Besides, anaerobic processes could treat the wastewater with high loads of easy-to-degrade organic materials (wastewaters of the sugar industry, slaughter houses, food industry, paper industry, etc.) efficiently and costly. These advantages make investigation and application of anaerobic microbial mineralization in organic polluted water important.

Generally speaking, anaerobic reactor could be divided into anaerobic activated sludge process and anaerobic biological membrane process. The anaerobic activated sludge process includes conventional stirred anaerobic reactor, upflow anaerobic sludge blanket reactor, and anaerobic contact tank. The anaerobic biological membrane process includes fluidized bed reactor, anaerobic rotating biological contactor, anaerobic filter reactor. Upflow anaerobic sludge blanket reactor and anaerobic filter reactor are selected as the representative of the two kinds of reactors mentioned above.

2.4.1. Upflow anaerobic sludge blanket reactor (UASB)

The UASB system was developed in 1970s. No carrier is used to in the UASB system, and liquid waste moves upward through a thick blanket of anaerobic granular sludge suspended in the system. As shown in Fig. 3, mixing of sludge and wastewater is achieved by the generation of methane within the blanket as well as by hydraulic flow. And the triphase separator (gas, liquid, sludge biomass) could prevent the biomass loss of the sludge through the gas emission and water discharge. The advantage of this system are that 1) it contains a high concentration of naturally immobilized bacteria with excellent settling properties, and could remove the organic pollutants from wastewater efficiently; 2) a high concentrations of biomass can be achieved without support materials which reduces the cost of construction. These advantages would increase the efficient and stable performance of this system [12].

2.4.2. Anaerobic biofilter

Anaerobic biofilter, so called anaerobic fixed film reactors, is a kind of high efficient anaerobic treatment equipment developed in 1960 s. These reactors use inert support materials to provide a surface for the growth of anaerobic bacteria and to reduce turbulence to allow unattached populations to be retained in the system (Fig 4). The organic matter of wastewater is degraded in the system, and produce methane gas, which will be released from the pool from the top [13].

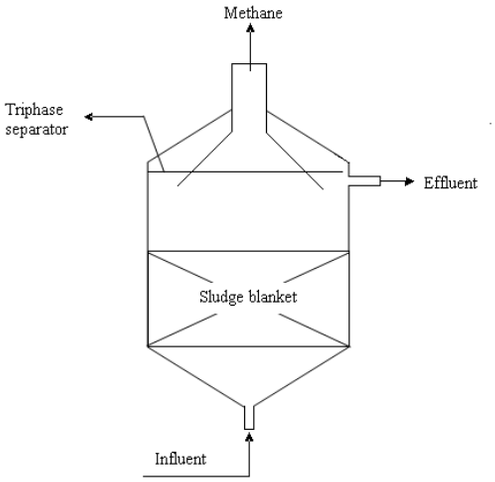


Figure 3. The scheme of upflow anaerobic sludge blanket reactor [1]

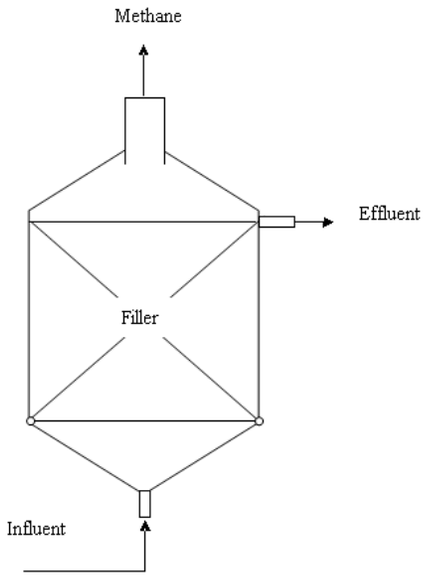


Figure 4. The scheme of the anaerobic biofilter [1]

The advantages of this system are as follow: 1) the filler provides a large surface area for the growth of the microorganisms, and the filler also increases hydraulic retention time of the wastewater; 2) the system provides a large surface area for the interaction between the wastewater and film; 3) the fact that microorganisms grow on the filler reduces the run of the degraders. These advantages could increase the efficiency of this treatment, and guarantee the water quality of the effluent. The backward of this system is that the system could be blocked when dealing with high concentration organic water, especially in the water inlet parts. And no simple and effective way for filter washing has been developed yet.

2.5. Combination of the aerobic and anaerobic biodegradation

Compared with the single anaerobic and aerobic reactors, the combination of the anaerobic and aerobic reactor is more efficient in organic pollutants degradation. The advantages of

the combined system are as follow: 1) the anaerobic process could get rid of the organic matters and suspended solid from the wastewater, reduce the organic load of the aerobic degradation as well as the production of aerobic sludge, and finally reduce the volume of the reactors; 2) wastewater pretreated by anaerobic technology is more stable, indicating that anaerobic process could reduce the load fluctuation of the wastewater, and therefore decrease the oxygen requirement of the aerobic degradation; 3) the anaerobic process could modify the biochemical property of the wastewater, making the following aerobic process more efficient. Investigation showed that the wastewater from aerobic-anaerobic combined reactor are more stable and ready for degradation, indicating that this technical have a huge potential for application. The classic aerobic-anaerobic reactors include A/O reactor, A2/O reactor, oxidation ditch, constructed wetland.

Two classic aerobic biodegradation reactors, oxidation ditch and constructed wetland are introduced.

2.5.1. Oxidation ditch

The oxidation ditch is a circular basin through which the wastewater flows. Activated sludge is added to the oxidation ditch so that the microorganisms will digest the organic pollutants in the water. This mixture of raw wastewater and returned sludge is known as mixed liquor. The rotating biological contactors could add oxygen into the flowing mixed liquor, and they could also increase surface area and create waves and movement within the ditches. Once the organic pollutant has been removed from the wastewater, the mixed liquor flows out of the oxidation ditch. Sludge is removed in the secondary settling tank, and part of the sludge is pumped to a sludge pumping room where the sludge is thickened with the help of aerator pumps [14]. Some of the sludge is returned to the oxidation ditch while the rest of the sludge is sent to waste.

The oxidation ditch is characterized by simple process, low maintain consumption, steady operation, and strong shock resistance. The effluent of the system has high water quality effluent with low concentration of organic pollutants, nitrogen and phosphorus. However, the problems of this reactor, such as sludge expansion, rising sludge and foam, are important factors which confines the development of this technique.

2.5.2. Constructed wetland

A constructed wetland is an artificial wetland which could wetlands act as a biofilter, removing sediments and pollutants such as heavy metals and organic pollutants from the water. Constructed wetland is a combination of water, media, plants, microorganisms and other animals. Constructed wetlands are of two basic types: subsurface-flow and surface-flow wetlands [15].

Physical, chemical, and biological processes combine in wetlands to remove contaminants from wastewater. Besides absorbing heavy metals and organic pollutants (especially POPs)

on the filler of the constructed wetland, plants can supply carbon and other nutrients such as nitrogen through their roots to for the growth and reproduction of the microorganisms. Plants could also pump oxygen to form an aerobic and anaerobic area in the deep level of constructed wetland to assist the breaking down of organic materials. The major reactor in constructed wetland was supposed to be microorganisms, and microorganisms and natural chemical processes are responsible for approximately 90 percent of pollutant removal, while, the plants remove about 7-10 percent of pollutants. In addition to organic pollutants, this device could remove the nitrogen and phosphorous in the wastewater and prevent eutrophication.

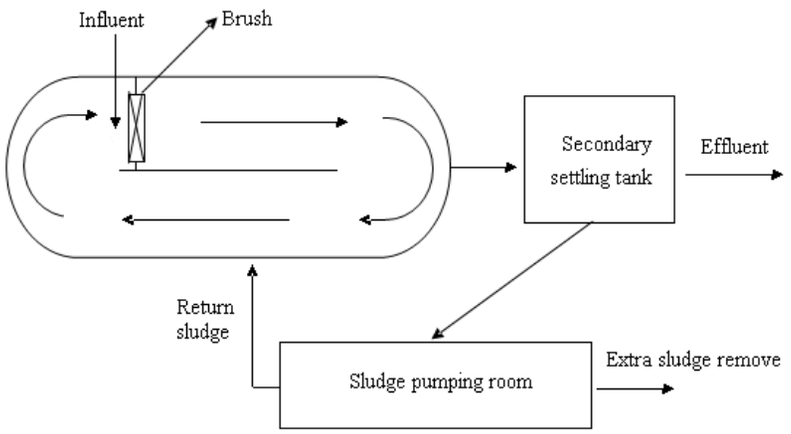


Figure 5. The scheme of the oxidation ditch [1]

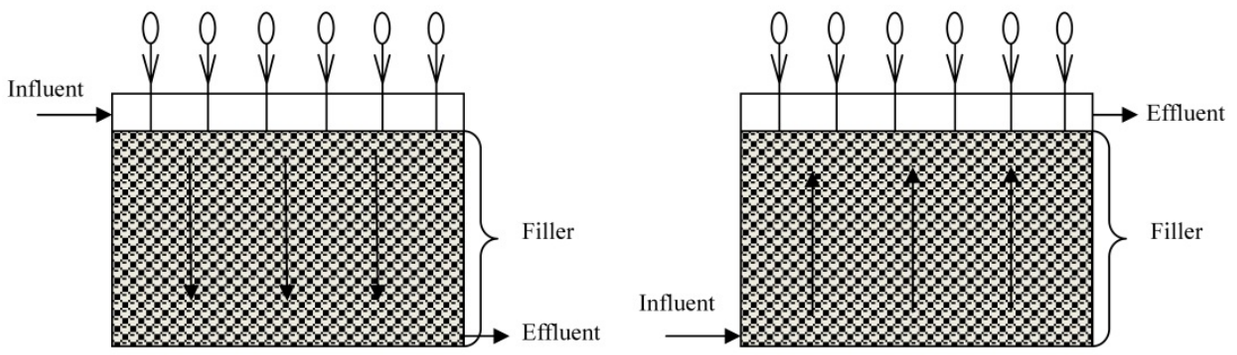


Figure 6. The scheme of the subsurface flow constructed wetland of different feeding pattern

As an economical, easy management and ecological friendly reactor, constructed wetland is supposed to be a promising technique to treat the wastewater in developing country. However, this technique was not widely used up to now for 1) the plants couldn't adapt to heavy contaminated wastewater, which strikes its application scope; 2) the device of this technique demands large area of land; 3) the efficiency of this device relativity lower than other biological device such as activated sludge process and membrane bioreactor. Thus, efforts should be made in plants selection, device structure modification and multiple devices combination to enhance the adaption and efficiency of this technique.

3. Chemical oxidation technologies

Nowadays, due to the increasing presence of molecules, refractory to the microorganisms in the wastewater streams, the conventional biological methods cannot be used for complete treatment of the effluent and hence, introduction of newer technologies to convert it into less harmful or lower chain compounds which can be then treated biologically, has become imperative. Chemical oxidation technology is one of these newer technologies which use chemical oxidant (H_2O_2, O_3, ClO_2, K_2MnO_4, K_2FeO_4 and so on) oxide pollutant to slightly toxic, harmless substances or transform it into manageable form. However, Chemical oxidation technologies constitute the use of oxidizing agents such as ozone and hydrogen peroxide, exhibit lower rates of degradation. Therefore, advanced oxidation processes (AOPs) with the capability of exploiting the high reactivity of hydroxyl radicals in driving oxidation have emerged a promising technology for the treatment of wastewaters containing refractory organic compounds. Several technologies like Fenton, photo-Fenton, wet oxidation, ozonation, photocatalysis, etc. are included in the AOPs and their main difference is the source of radicals.

3.1. Chemical oxidation technologies under normal temperature and pressure

This part aims at highlighting three different oxidation processes operating at ambient conditions viz. Fenton's chemistry (belonging to the class of AOPs) and ozonation, use of hydrogen peroxide (belonging to the class of chemical oxidation technologies).

3.1.1. Classification and principle

3.1.1.1. Hydrogen peroxide

Hydrogen peroxide (H_2O_2) is an environment friendly oxide which could oxidate organic pollutants efficiently and economically. The standard reduction potentials (1.77V, 0.88v) of hydrogen peroxide imply that it is a strong oxidant in both acidic and basic solutions [16]. It can oxidize many kinds of organic contaminants in wastewater directly. The very slow decomposition rate of hydrogen peroxide in the drinking water treatment, with mild operation conditions, can ensure a longer disinfection. Also, it can be utilized as a dechlorination agent (reductant) without organic halogen compounds production. Therefore, the hydrogen peroxide is the ideal drinking water pre-oxidant and disinfectant.

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad E^\circ = 1.77V$

$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \quad E^\circ = 0.87V$

However, considering for the removal of organic compounds in wastewater, the reactivity of hydrogen peroxide is generally low and largely incomplete due to kinetics, in particular in acidic media. It can be enhanced by homogeneous and/or heterogeneous catalysts, the progress named wet hydrogen peroxide catalytic oxidation (WHPCO). WHPCO operates at temperatures in the 20-80◎ range and atmospheric pressure.

3.1.1.2. Fenton

The Fenton's process has its origin in the discovery reported in 1894 that ferrous ion strongly promotes the hydrogen peroxide oxidation of tartaric acid. The mechanism of the Fenton's process is quite complex, and some papers can be found in the literature where tens of equations are used for its description. Nevertheless, it can be summarized by the following steps: first, a mixture of H_2O_2 and ferrous iron in acidic solution generates the hydroxyl radicals which will subsequently attack the organic compounds present in the solution [17].

$Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+HO^{-}+HO\bullet$

As iron (II) acts as a catalyst, it has to be regenerated, which seems to occur through the following scheme:

$Fe^{3+}+H_2O_2 \leftrightarrow Fe\text{-}OOH_2^{+}+H^{+}$

$Fe\text{-}OOH_2^{+} \rightarrow Fe^{2+}+HO_2\cdot$

The important mechanistic feature of the Fenton reaction is that in the outer-sphere single electron transfer from Fe^{2+} to H_2O_2 and generates hydroxyl radicals and hydroxide anions. Hydroxyl radicals are after fluorine atoms the most oxidizing chemical species. They are extremely powerful species to abstract one electron from an electron rich organic substrate or any other species present in the medium to form hydroxide anion. The oxidation potential of hydroxyl radicals has been estimated as +2.8 and +2.0V at pH 0 and 14, respectively. The high reactivity of HO• ensures that it will attack a wide range of organic compounds. Fenton reaction gives rise to CO_2 and the heteroatoms also form the corresponding oxygenated species such as NOx, SOx and POx, meaning that the carbons and heteroatoms of the organic substrate are converted to inorganic species. Equations illustrate the cyclic processes occurring in Fenton chemistry under aerobic conditions leading to the formation of CO_2.

$RH+HO\bullet \rightarrow R\bullet + H_2O$

$R\bullet + Fe^{3+} \rightarrow R^{+} + Fe^{2+}$

$R^{+} + H_2O \rightarrow ROH + H^{+}$

$R\bullet + Fe^{2+} \rightarrow \text{products} + Fe^{3+}$

$R\bullet + O_2 \rightarrow ROO\bullet$

$R\bullet + \bullet OOH \rightarrow RO\bullet + \bullet OH$

$ROO\bullet + RH \rightarrow ROOH + R\bullet$

$ROO\bullet + Fe^{2+} \rightarrow \text{products} + Fe^{3+}$

$ROO\bullet + Fe^{3+} \rightarrow \text{products} + Fe^{2+}$

The performance of Fenton oxidation application to wastewater treatment was based on the following parameters: operating pH, amount of ferrous ions, concentration of hydrogen

peroxide, initial concentration of the pollutant, type of buffer used for pH adjustment, operating temperature and chemical coagulation. The optimum pH has been observed to be 3 in the majority of the cases. The pollutant removal efficiency increases with an increase in the dosage of ferrous ions and hydrogen peroxide. However, care should be taken while selecting the dosage, for high dosage leasing environmental question and high treatment cost. The optimum dosage is available in the open literature or required to establish in laboratory scale studies under similar conditions.

The conventional Fenton reaction that hydrogen peroxide in conjunction with an iron(II) salt to produce high fluxes of hydroxyl radicals is homogeneous catalytic reaction. Therefore, the application of conventional Fenton reaction is complicated by the problems typical of homogeneous catalysis, such as catalyst separation, regeneration, etc. It is necessary to control pH carefully to prevent precipitation of iron hydroxide. Thus, heterogeneous catalysts Fenton reaction, i.e., solids containing transition metal cations (mostly iron ions) have been developed and tested [18].

3.1.1.3. Ozonation

Ozone is one of the most powerful oxidants with an oxidation potential of 2.07 V. In acidic conditions, ozone undergoes selective electrophilic attack which occurs at particular parts of complexing agent with high electronic density. Under alkaline environment, ozone is catalyzed by OH^- in basic conditions to intermediate compounds such as superoxide, HO radicals and HO_2 radicals which are highly reactive. Apart from pH, the degradation of target compounds in the liquid phase corresponds to the amount and form (species) of oxidants present in a reactor [19].

$$O_3+OH^-\rightarrow HO_2^-+O_2$$

$$O_3+OH^-\rightarrow HO\bullet+O_3^-$$

$$O_3+HO_2^-\rightarrow HO_2\bullet+O_3\bullet$$

The applications of ozonation for water treatment offer various advantages. Due to its short half-life of less than 10 min, the oxidant degrades most of pollutants rapidly. However, at pH 10, the half-life of ozone in solutions is less than 1 min. As a result, ozonation extensively consumes energy, thus reducing its treatment efficiency. Due to the improvement in ozone production from pure oxygen and the increase of its concentration in the feeding gas, an ozone generation with less cost may be economically attractive.

The performance of ozonation application to wastewater treatment was based on the following parameters: operating pH, ozone partial pressure, contact time and interfacial area, presence of radical scavengers, operating temperature, presence of catalyst, combination with other oxidation processes.

Very low reaction rates have been observed for the degradation of complex compounds or mixture of contaminants by ozonation alone. Catalyst such as BST catalyst TiO_2 fixed on alumina beads, Fe (II), Mn (II) can be used to increase the degradation efficiency. Heterogeneous catalytic ozonation has received increasing attention in recent years due to

its potentially higher effectiveness in the degradation and the mineralization of refractory organic pollutants and a lower negative effect on water quality. The major advantage of a heterogeneous over a homogeneous catalytic system is the ease of catalytic retrieval from the reaction media. Results suggest that catalytic ozonation with MnOx/MZ, CoOx/MZ and $CuOx/Al_2O_3$ is a promising technique for the mineralization of refractory organic compounds in water [20].

3.1.2. Reactors

3.1.2.1 Typical reactor used for Hydrogen peroxide

Introduction of hydrogen peroxide into the waste stream is critical due to lower stability of hydrogen peroxide. An addition point should give large residence time of H_2O_2 in the pollutant stream, but due to the practical constraints and poor mixing conditions, it is not always possible to inject H_2O_2 in line and an additional holding tank is required. The simplest, faster and cheapest method for injection of hydrogen peroxide is gravity feed system. Pump feed systems can also be used, but it requires regular attention.

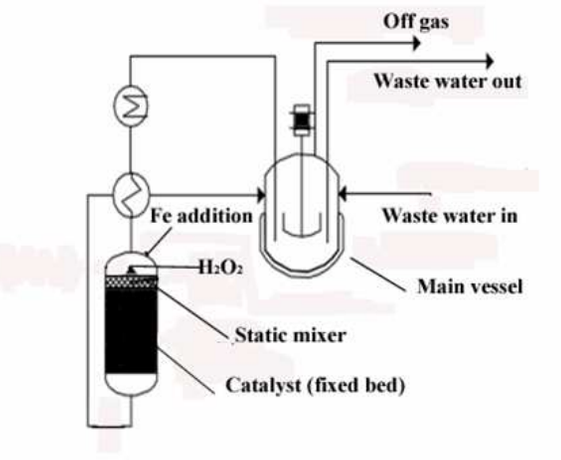


Figure 7. Typical reactor used for WHPCO technology.

Figure 7 reports a simplified flow diagram of the WHPCO technology for the treatment of olive oil milling waste water using Fe-ZSM-5 solid catalysts. H_2O_2 is added progressively at the top of a fixed bed catalytic reactor (before a static mixer), in order to maximize its local concentration. An iron solution is added on the top of the reactor to maintain catalyst activity constant. The feed solution is recirculated to and from a tank in order to have good turbulence in the catalyst bed, but also to guarantee the necessary total residence time to obtain the required level of removal of phytotoxic chemicals.

3.1.2.2. Typical reactor used for fenton oxidation

A batch Fenton reactor essentially consists of a nonpressurized stirred reactor with metering pumps for the addition of acid, base, a ferrous sulfate catalyst solution and industrial strength (35-50%) hydrogen peroxide. The reactor vessel should be coated with an acid-

resistant material, because the Fenton reagent is very aggressive and corrosion can be a serious problem. pH of the solution must be adjusted at 6, usually iron hydroxide is formed. For many organic pollutants, the ideal pH for the Fenton reaction is between 3 and 4, and the optimum catalyst to peroxide ratio is usually 1:5 wt/wt. Addition of reactants are done in the following sequence: dilute sulfuric acid catalyst in acidic solutions, pH adjusting agent (adjustment of pH at 3-4) and lastly added hydrogen peroxide slowly. Effluent of the Fenton reactor (Oxidation tank) is fed into a neutralizing tank for adjusting the pH (adjustment of pH at 9), then the stream followed by a flocculation tank and a solid-liquid separation tank for removing the precipitate. A schematic representation of the Fenton oxidation treatment has been shown in Figure 8 [21].

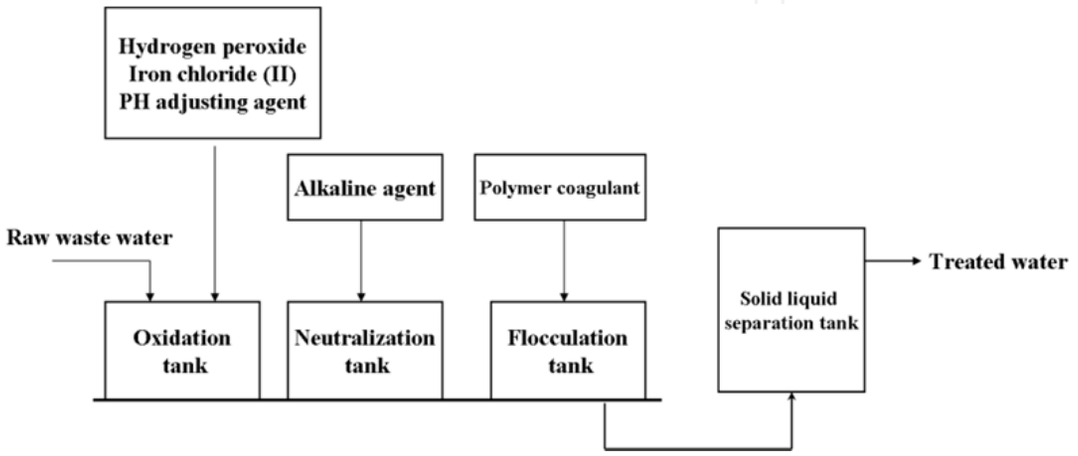


Figure 8. Typical reactor used for fenton oxidation.

3.1.2.3. Typical reactor used for ozonation

Ozone transfer efficiency should be maximized by increasing the interfacial area of contact (reducing the bubble size by using small size ozone diffusers such as porous disks, porous glass diffusers, ceramic membranes) and increasing the contact time between the gas and the water (increase the depths in the contactor, optimum being 3.7 to 5.5 m) [21].

3.1.3 .Application

3.1.3.1. Hydrogen peroxide

Hydrogen peroxide has been used in the industrial effluent treatment for detoxification of cyanide, nitrite and hypochlorite, for the destruction of phenol aromatics, formaldehyde, removal of sulfite, thiosulfate and sulfide compounds.

However, the application of hydrogen peroxide alone for wastewater treatment applications present major problems such as very low rates for applications involving complex materials, stability of H_2O_2 and mass transfer limitations. Hence, use of hydrogen peroxide alone does not seem to be a recommendable option for industrial wastewater treatment.

WHPCO process has been proposed for a variety of agro-food and industrial effluents: removal of dyestuffs from textile, treat sewage sludge, purify wastewater from

pharmaceutical and chemical production, dumping site, or from cellulose production and pre-treat water streams from food-processing industries (olive oil mills, distilleries, sugar refineries, coffee production, tanneries, etc.) [22].

3.1.3.2. Fenton

Fenton process can significantly remove recalcitrant and toxic organic compounds, and increase the biodegradability of organic compounds. Leachate quality in terms of organic content, odor, and color can be greatly improved following Fenton treatment. Fenton's reagent has been used quite effectively for the treatment and pre-treatment of leachate from composting of different wastes. Reported COD removal efficiencies range from 45% to 85%, and reported final BOD_5/COD ratio can be increased from less than 0.10 initially to values ranging from 0.14 to more than 0.60, depending on leachate characteristic and dosages of Fenton reagents. Color and odor in leachate can also be reduced considerably. The decolorization efficiency is as high as 92% in Fenton treatment of a mature leachate[23]. The optimal conditions for Fenton reaction were found at a ratio $[Fe^{2+}]$/[COD] equal to 0.1. Both leachates were significantly oxidized under these conditions in terms of COD removal 77-75% and BOD_5 removal 90-98%. Fenton's reagent was found to oxidize preferably biodegradable organic matter of leachate [24]. Pirkanniemi et al. (2007) [25] tested the Fenton's oxidation to degrade complexing agents such as N-bis[2-(1,2-dicarboxyethoxy) ethyl)] glysine (BCA5), N-bis[2-(1,2-dicarboxyethoxy)ethyl]aspartic acid (BCA6) and EDTA from bleaching wastewater. It was reported that an almost complete removal of EDTA was attained at its concentration of 76 mM.

3.1.3.3. Ozonation

Ozone can be used for treatment of effluents from various industries relating to pulp and paper production (bleaching and secondary effluents), Shale oil processing, production and usage of pesticides, dye manufacture, textile dyeing, production of antioxidants for rubber, pharmaceutical production etc.

Beltrán et al. (2006) [26] reported that ozonation alone improved the removal of succinic acid up to 65% at pH 7 with an initial concentration of 339 mM. Decolorization of dye Methylene Blue can be achieved by ozonation. The COD of basic dyestuff wastewater was reduced to 64.96% and decolorization was observed under basic conditions (pH 12), complete Methylene Blue degradation occurring in 12 min. The decolorization time decrease linearly with the increase in ozone concentration. For example, increasing ozone concentration from 4.21 g/m^3 to 24.03 g/m^3 in the gas phase reduces the decolorization time of 400 mg/L dye concentration by about 88.43% [27].

3.2. Chemical oxidation technologies under high temperature and pressure

3.2.1. Classification and principle

3.2.1.1. Wet air oxidation (WAO)

WAO is based on the oxidizing properties of air's oxygen. Typical conditions for wet oxidation range from 180 °C and 2 MPa to 315 °C and 15 MPa. Residence times may range

from 15 to 120 min, and the chemical oxygen demand (COD) and total organic carbon (TOC) removal may typically be about 75-90%. Insoluble organic matter is converted to simpler soluble organic compounds without emissions of NOx, SO_2, HCl, dioxins, furans, fly ash, etc.

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E^\circ = +1.23V$

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad E^\circ = +0.40V$

3.2.1.2. Catalytic wet air oxidation (CWAO)

Organic pollutant is impossible to obtain a complete mineralization of the waste stream by WAO, since some low molecular weight oxygenated compounds (especially acetic and propionic acids, methanol, ethanol, and acetaldehyde) are resistant to oxidation. Organic nitrogen compounds are easily transformed into ammonia, which is also very stable in WAO conditions. Therefore, WAO is a pre-treatment of liquid wastes which requires additional treatment. The use of catalysts (WACO) allows to use milder reaction conditions but especially to promote conversion of the reaction intermediates (for example, acetic acid and ammonia) which are very difficult to convert in the absence of catalysts, as mentioned above.

Though it varies with type of wastewater, the operating cost of CWAO is about half that of non-catalytic WAO due to milder operating conditions and shorter residence time. Although the homogenous catalysts, e.g. dissolved copper salts, are effective, an additional separation step is required to remove or recover the metal ions from the treated effluent due to their toxicity, and accordingly increases operational costs. Thus, the development of active heterogeneous catalysts has received a great attention because a separation step is not necessary. Various solid catalysts including noble metals, metal oxides, and mixed oxides have been widely studied for the CWAO of aqueous pollutants. To further decrease the reaction temperature and pressure, intensive oxidants are added and form Wet Peroxide Oxidation (WPO), WHPCO is belonging to WPO.

3.2.2. Reactors

3.2.2.1. WAO reactors

The experimental set up consisted mainly of a reactor and a condenser. It was equipped with suitable measuring devices, such as thermocouple, rotameter and pressure gauge. The material of construction for reactor is titanium. The top of the reactor is connected to a reflux condenser with a stainless steel flange. The reactor was equipped with a heating jacket and a gas sparger. The gas (air or oxygen) entered the reactor through the titanium sparger. Air or oxygen bubbled out through the sparger at high speed and thus ensured proper agitation [28].

3.2.2.2. CWAO reactors

Homogeneous catalysts for CWAO are usually transition metal cations, such as Cu and Fe ions. Industrial homogenous CWAO processes have been developed such as the Ciba-

Geigy/Garnit process working at high temperature (300 ◦C), and the LOPROX Bayer process working with oxygen below 200 ◦C in the presence of iron ions. Common two-phase reactor types used in homogeneous CWO include bubble columns, jet-agitated reactors, and mechanically stirred reactor vessels.

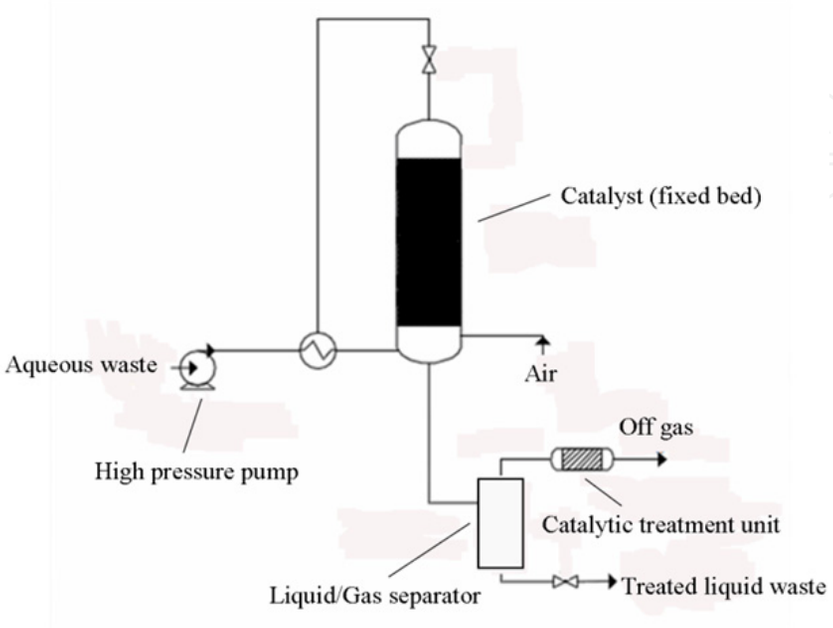


Figure 9. Typical reactor used for WACO process.

Figure 9 reports a simplified flow diagram of a WACO process which consists mainly of a high-pressure pump, an air or oxygen compressor, a heat-exchanger, a high-pressure (fixed bed) reactor and a downstream separator. The simplest reactor design is usually a cocurrent vertical bubble column with a height-todiameter ratio in the range of 5-20. A catalytic unit for the treatment of the off-gas is also typically necessary [25].

3.2.3. Application

WAO is not used as a complete treatment method, but only as a pretreatment step where the wastewater is rendered to nontoxic materials and the COD is reduced for the final treatment. For integrated WAO-biological treatment process, more detailed studies concerning the WAO pretreatment step are necessary for the design of a rational and efficient integrated process. The WAO process has been subjected to numerous investigations by researchers in the past decades as a pretreatment step before the biological treatment [29-32].

Pretreatment of Afyon (Turkey) alcaloide factory wastewater, a typical high strength industrial wastewater (COD= 26.65 kg/m^3; BOD_5= 3.95 kg/m^3) was carried out by WAO process. Experimental results indicated that over 26% COD removal of the wastewater could be achieved in 2.0 h of reaction time at 150°C; 0.65 MPa and with an airflow rate of 1.57×10^5 m^3/s. BOD_5/COD ratio is increased from 0.15 to 0.4. The experimental data also revealed that

the pressure and temperature effects on the COD removal were important. The COD removal was observed to increase with an increase in both pressure and temperature. Maximum COD removal was obtained at around pH 7.0 [28].

As considering for using the CWAO process to treat Afyon (Turkey) alcaloide factory wastewater, results indicate that the presence of catalyst increases the COD removal. The COD removal for 2.0 h reaction time increased from 25.7% without catalyst to 33.2% with 0.25 kg/m^3 catalyst. While the BOD_5/COD ratio is increased to over 0.4 [28].

CWAO makes a promising technology for the treatment of refractory organic pollutants (phenolic compounds, carboxylic acids, N-containing compounds) in industrial wastewaters, such as Olive oil mill wastewater, Kraft bleaching plant effluents, Coke plant wastewater, Textile wastewater, Alcohol-distillery wastewater, Landfill leachate, Pulp and paper bleaching liquor, Heavily organic halogen polluted industrial wastewater and so on [33].

4. Adsorption technology

4.1. Principle of adsorption technology

Adsorption offers a cleaner technology, free from sludge handling problems and produces a high quality effluent. Over the last few decades, adsorption has gained importance as an effective purification and separation technique used in water and wastewater treatment. Adsorption is the process by which a solid adsorbent can attach a component dissolved in water to its surface and form an attachment via physical or chemical bonds, thus removing the component from the fluid phase. Adsorption is used extensively in industrial processes for many purposes of separation and purification. The removal of metals, coloured and colourless organic pollutants from industrial wastewater are considered an important application of adsorption processes using suitable adsorbents.

Adsorption is nearly always an exothermic process. We can distinguish between 2 types of adsorption process depending on which of these two force types plays the bigger role in the process. Adsorption processes can be classified as either physical adsorption (van der Waals adsorption) or chemisorption (activated adsorption) depending on the type of forces between the adsorbate and the adsorbent.

Physical adsorption occurs quickly and may be mono-molecular (unimolecular) layer or monolayer, or 2, 3 or more layers thick (multi-molecular). As physical adsorption takes place, it begins as a monolayer. It can then become multi-layer, and then, if the pores are close to the size of the molecules, more adsorption occurs until the pores are filled with adsorbate. Accordingly, the maximum capacity of a porous adsorbent can be more related to the pore volume than to the surface area.

Chemisorption involves the formation of chemical bonds between the adsorbate and adsorbent is a monolayer, often with a release of heat much larger than the heat of condensation. Chemisorption from a gas generally takes place only at temperatures greater

than 300 °C, and may be slow and irreversible. Most commercial adsorbents rely on physical adsorption; while catalysis relies on chemisorption.

4.2. Development of adsorption materials

4.2.1. Activated carbon

Activated carbon is by far the most common adsorbent used in wastewater treatment. Since, during adsorption, the pollutant is removed by accumulation at the interface between the activated carbon (absorbent) and the wastewater (liquid phase) the adsorbing capacity of activated carbon is always associated with very high surface area per unit volume. Activated carbon can be manufactured from carbonaceous material, including coal (bituminous, subbituminous, and lignite), peat, wood, or nutshells (i.e., coconut). The manufacturing process consists of two phases, carbonization and activation. The carbonization process includes drying and then heating to separate by-products, including tars and other hydrocarbons, from the raw material, as well as to drive off any gases generated. The carbonization process is completed by heating the material at 400–600°C in an oxygen-deficient atmosphere that cannot support combustion. Powdered activated carbon is made up of crushed or ground carbon particles, 95–100% of which will pass through a designated mesh sieve or sieves. Granular activated carbon can be either in the granular form or extruded. It is designated by sizes such as 8×20, 20×40, or 8×30 for liquid phase applications and 4×6, 4×8 or 4×10 for vapor phase applications.

4.2.2 .Activated alumina

Activated alumina had been used in the treatment of wastewater and its adsorption capability for the removal of both organic and inorganic compounds was found to be favoured by a specific surface area, pore structure, ionic strength and chemical inertness. It can be produced from the mixtures of amorphous and gamma alumina prepared by the dehydration of $Al(OH)_3$ under low-temperatures of 300-600°C, with surface areas in the range of 250-350 m^2/g.

Research conducted on the use of microporous alumina pillared montmorillonite (clay) and mesoporous alumina aluminium phosphate as adsorbents had shown successful removal of fluoride, arsenic, selenium, beryllium, 2,4-chlorophenol, 2,4,6- trichlorophenol, pentachlorophenol, and also pesticides such as: molinate, propazine and atrazine from waster water. The removal efficiency of the pillared clay material for the herbicide was found to be higher than that of the mesoporous aluminium phosphate due to the substitution of the alkyl lateral chains of the aluminium phosphate during the sorption of s-triazines and the increase of P/Al ratio during the adsorption of propachlor.

4.2.3. Zeolites

The drawback suffered by activated carbon due to its high regeneration cost and production cost has lead to the application of zeolites as an alternative adsorbent. Zeolites are a group of

natural or synthetic hydrated aluminosilicate minerals which contain both alkaline and alkali-earth metals. It has been used as an adsorbent, molecular sieve, ion-exchangers and catalysts in the past decades, because their chemical properties and large effective surface area gives them superior adsorptive qualities. There are several types of zeolites such as MCM-22, ZSM-5, ZSM-22, BETA, and Y. Their adsorption equilibrium had been studied and showed that the synthetic zeolites have higher adsorption capacity than the natural zeolites for the removal of ink, dyes and polluted wastewater.

4.2.4. Peat

Peat and other biomass materials have been used previously in the treatment of wastewater containing heavy metals and organic compounds. Peat is a yellow to dark brown residue, which occurs during the first stage of coal formation. It is composed of partly carbonizing materials such as decayed trees and peats bogs that have accumulated in water–saturated environments and swamps. The main constituents of peat moss are lignin, humic acid and cellulose. In addition, the surface functional groups of peat include aldehydes, carboxylic acids, ketones, alcohols, ethers and phenolic hydroxides, which are all involved in the adsorption of pollutants. In addition, its polar nature is responsible for its specific adsorption potential for dissolved metals and polar organic compounds.

4.2.5. Natural materials

Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive adsorbents. The abundance, availability, and low cost of agricultural byproducts make them good adsorbents for the removal of various pollutants from wastewaters. Agricultural waste biomass currently is gaining importance. In this perspective rice husk, which is an agro-based waste, has emerged as an invaluable source for the utilization in the wastewater treatment. Rice husk contains ~20% silica, and it has been reported as a good adsorbent for the removal of heavy metals, phenols, pesticides, and dyes. The adsorptive capacity of rice husk silica had been evaluated by Grisdanurak et al. [34] and its adsorption capacity for chlorinated volatile organic compounds was found to be higher than that of commercial mordenite and activated carbons. It has been utilized for solving disposal problems and also as an adsorbent in treating organic wastewaters. The adsorption potential of this biomass for adsorbing phenol from aqueous solution was found to be depended on the pH, contact time and the initial phenol concentration. This result shows that phenol was adsorbed to a lesser extent at higher pH values. Phenol forms salts, which readily ionize leaving negative charge on the phenolic group while, its present on the adsorbent prevents the removal of phenolateions. In addition, the percentage adsorption of phenol for this test also decreases as the initial phenol concentration increases. The adsorption capacity determined for this test was 0.886 mg/g for phenol and the equilibrium data was fitted successfully by the Freundlich model [35].

4.2.6. Polymeric

Polymeric adsorbents are non-functionalized organic polymers which are capable of removing organics from water. The principle is quite simple. Wastewater is passed through a column containing the polymeric adsorbent. The organic materials are retained on the resin while water and some simple salts pass through. When the resin is fully loaded, the organics are stripped from the resin with solvents or caustic. The organic material may be concentrated by orders of magnitude in some cases. The following recommendations are those being used at the present time. The regenerants used are not the only ones possible. The choice of regenerant (solvent) usually depends on the availability at the particular location.

4.3. Adsorption equipment and their applications

Granular activated carbon systems are generally composed of carbon contactors, virgin and spent carbon storage, carbon transport systems, and carbon regeneration systems. The carbon contactor consists of a lined steel column or a steel or concrete rectangular tank in which the carbon is placed to form a "filter" bed. A fixed bed downflow column contactor is often used to contact wastewater with granular activated carbon. Wastewater is applied at the top of the column, flows downward through the carbon bed, and is withdrawn at the bottom of the column. The carbon is held in place with an underdrain system at the bottom of the contactor. Provisions for backwash and surface wash of the carbon bed are required to prevent buildup of excessive headloss due to accumulation of solids and to prevent the bed surface from clogging.

There are two basic types of water filters: particulate filters and adsorptive/reactive filters. Particulate filters exclude particles by size, and adsorptive/reactive filters contain a material (medium) that either adsorbs or reacts with a contaminant in water. The principles of adsorptive activated carbon filtration are the same as those of any other adsorption material. The contaminant is attracted to and held (adsorbed) on the surface of the carbon particles. The characteristics of the carbon material (particle and pore size, surface area, surface chemistry, etc.) influence the efficiency of adsorption [36].

The characteristics of the chemical contaminant are also important. Compounds that are less water-soluble are more likely to be adsorbed to a solid. A second characteristic is the affinity that a given contaminant has with the carbon surface. This affinity depends on the charge and is higher for molecules possessing less charge. If several compounds are present in the water, strong adsorbers will attach to the carbon in greater quantity than those with weak adsorbing ability.

5. Other technologies

5.1. Solvent extraction

Solvent extraction is a common form of chemical extraction using organic solvent as the extractant. It is commonly used in combination with other technologies, such as

solidification/stabilization, incineration, or soil washing, depending upon site-specific conditions. Solvent extraction also can be used as a stand alone technology in some instances. Organically bound metals can be extracted along with the target organic contaminants, thereby creating residuals with special handling requirements. Traces of solvent may remain within the treated soil matrix, so the toxicity of the solvent is an important consideration.

Solvent extraction method has many advantages, such as less investment in equipment, easy to operate and lower consumption. Moreover, the major pollutants can be effectively recycled by solvent extraction method. The extraction method is widely used in a variety of organic waste, such as phenol, organic carboxylation acids, organic phosphorus nitrogen, organic sulfonic acid, organic amine, etc. Solvent extraction has been shown to be effective in treating sediments, sludges, and soils containing primarily organic contaminants such as PCBs, VOCs, halogenated solvents, and petroleum wastes. The process has been shown to be applicable for the separation of the organic contaminants in paint wastes, synthetic rubber process wastes, coal tar wastes, drilling muds, wood-treating wastes, separation sludges, pesticide/insecticide wastes, and petroleum refinery oily wastes.

Adopting solvent extraction treatment technology for organic wastewater, the most important thing is to choose the right process flow specifically for specially appointed pollution. For the general flow, most difficult degradation of the pollutants are removed after the process of solvent extraction. Crafts residue mainly contain some pollutants which are not extractive and dissolved, and they would meet the emissions standards through the secondary treatment regeneration (such as biochemistry, chemical oxidation, etc.).

5.2. Incineration

Incineration involves the combustion of the organic (carbon-containing) solids present in wastewater solids and biosolids to form carbon dioxide and water. The temperature in the combustion zone of furnaces is typically 1023K to 1143K. The solids that remain at the end of the process are an inert material commonly known as ash. Either undigested wastewater solids or biosolids may be incinerated. The terms thermal oxidation and combustion may be used interchangeably with incineration.

Incineration takes advantage of the fuel value of wastewater treatment residual solids (referred to as sludge) and biosolids. In some cases, the energy recovered from this process has been used in heat exchangers and waste heat boilers to save on energy use at

the wastewater treatment plant. For example, in Montreal, a portion of the biosolids generated at the facility are incinerated, while the remaining portion is pelletized. Waste heat from the biosolids that are incinerated is used in the thermal dryers that produce fertilizer pellets. In Europe, there is a trend to use biosolids as a fuel source in dedicated power generation facilities. In addition, incineration results in a large reduction in volume and mass in comparison to other alternatives and options. The mass of solids in the ash that

results from the inceration process is approximately 10% of that of the biosolids fed into the incinerator. This reduces the mass and volume requiring disposal.

There are two common incineration technologies for wastewater solids and biosolids: fluidized bed incinerators and multiple hearth incinerators. Fluidized bed incinerators are steel cylinders lined with refractory bricks to withstand the high operating temperatures of the unit. Multiple hearth incinerators consist of a series of refractory brick hearths, stacked vertically. A rotating shaft through the centre of the hearths supports rake arms for each hearth, thereby facilitating drying and incineration. Solids are usually fed through at the top hearth and are directed to successive inner or outer dropholes as they move down through the hearths. Most of the ash is discharged from the bottom hearth.

Over the years, incineration technologies have evolved considerably and regulations and procedures have continually been enhanced to protect human and animal health and the environment. A considerable amount of scientific study has been undertaken to support the development of the regulations, and ongoing research contributes to the continuous improvement of this practice. However, some segments of the public still have concerns that incineration may be unsafe because of perceptions related to outdated technology and to experiences with incineration of other materials such as hazardous waste, municipal solid waste and medical waste.

5.3. Photocatalysis

To date, the most widely applied photocatalyst in the research of water treatment is the Degussa P-25 TiO_2 catalyst. This catalyst is used as a standard reference for comparisons of photoactivity under different treatment conditions. The fine particles of the Degussa P-25 TiO_2 have always been applied in a slurry form. This is usually associated with a high volumetric generation rate of reactive oxygen species as proportional to the amount of surface active sites when the TiO_2 catalyst in suspension. On the contrary, the fixation of catalysts into a large inert substrate reduces the amount of catalyst active sites and also enlarges the mass transfer limitations. Immobilization of the catalysts results in increasing the operation difficulty as the photon penetration might not reach every single surface site for photonic activation. Thus, the slurry type of TiO_2 catalyst application is usually preferred. With the slurry TiO_2 system, an additional process step would need to be entailed for post-separation of the catalysts. This separation process is crucial to avoid the loss of catalyst particles and introduction of the new pollutant of contami-nation of TiO_2 in the treated water [37]. The catalyst recovery can be achieved through process hybridization with conventional sedimentation [38], cross-flow filtration [39] or various membrane filtrations [40].

Natural clays have been used intensively as the support for TiO_2 owing to their high adsorption capacity and cost-effectiveness. The use of the photocatalytic membranes has been targeted owing to the photocatalytic reaction can take place on the membrane surface and the treated water could be continuously discharged without the loss of photocatalyst particles. To broaden the photoresponse of TiO_2 catalyst for solar spectrum, various material

engineering solutions have been devised, including composite photocatalysts with carbon nanotubes [41], dyed sensitizers [42], noble metals or metal ions incorporation [43], transition metals and non-metals doping [44].

5.4. Ultrasonic

High-frequency ultrasound is a mechanical wave, with a shorter wavelength, the energy concentration characteristics, its application mainly on the basis of energy major, along a straight line features of these two started. The 20th century, the early 90s, some scholars have begun to study abroad, such as the ultrasonic degradation of organic pollutants in water. Ultrasound technology is simple, efficient, non-polluting or less polluting characteristics, in recent years the development of a new type of water treatment technology. It combines advanced oxidation, pyrolysis, supercritical oxidation technology in one, and the degradation of speed, be able to water of harmful organic compounds into CO_2, H_2O, inorganic ions or organic toxic than the original readily biodegradable organic matter, and therefore in dealing with difficult Bio-degradation of organic contaminants has significant advantages.

6. Treatment processes of various industrial organic wastewaters

6.1. Coking plant

Coke, produced by the pyrolysis of natural coals, is an indispensable material for most of the metallurgical facilities. During coking, coal decomposes into gases, liquid and solid organic compounds. Coke wastewater contains high concentration of ammonia, phenols, thiocyanate, cyanide and lower amounts of other toxic compounds, such as polyaromatic hydrocarbons (PAHs), e.g. naphthalene, and heterocyclic nitrogenous compounds, e.g. quinoline. The individual concentration of the contaminants depends on the quality of coal and the properties of the coking process.

Coke wastewater handling usually consists of a series of physico-chemical treatments reducing the concentration of ammonia, cyanide, solids and other substances, followed by different biological treatments, mainly activated sludge process. The application of two or three consecutive activated sludge systems is particularly favored as readily biodegradable substrates like phenol can be removed in the first step. Phenols, which contribute to the greatest extent to the total COD in coke wastewater, are not only highly toxic and carcinogenic compounds, but also inhibit advantageous biological processes like nitrification. Under optimal circumstances, thiocyanate degradation can also be achieved in the first activated sludge step.

The influent concentrations of NH_4^+-N, phenols, COD and thiocyanate (SCN^-) in the wastewater ranged between 504 and 2340, 110 and 350, 807 and 3275 and 185 and 370 mg/L, respectively. A laboratory-scale activated sludge plant composed of a 20 L volume aerobic reactor followed by a 12 L volume settling tank and operating at 35 ◎ was used to study the biodegradation of coke wastewater. Maximum removal efficiencies of 75%, 98% and 90%

were obtained for COD, phenols and thyocianates, respectively, without the addition of bicarbonate. The concentration of ammonia increased in the effluent due to both the formation of NH_4^+ as a result of SCN^- biodegradation and to organic nitrogen oxidation. A maximum nitrification efficiency of 71% was achieved when bicarbonate was added, the removals of COD and phenols being almost similar to those obtained in the absence of nitrification [45]. An anaerobic-anoxic-aerobic (A(1)-A(2)-O) and an anoxic-aerobic (A/O) biofilm system were used to treat coke-plant wastewater. At same or similar levels of HRT, the two systems had almost identical COD and NH_3 removals, but a different organic-N removal. Set-up of an acidogenic stage benefited for the removal of organic-N and the A(1)-A(2)-O system was more useful for total nitrogen removal than the A-O system [46].

Newly studies for treatment of coking wastewaters are listed. Chu et al. investigated coking wastewater treatment by an advanced Fenton oxidation process using iron powder and hydrogen peroxide. The results showed that higher COD and total phenol removal rates were achieved with a decrease in initial pH and an increase in H_2O_2 dosage. At an initial pH of less than 6.5 and H_2O_2 concentration of 0.3 M, COD removal reached 44-50% and approximately 95% of total phenol removal was achieved at a reaction time of 1 h. The oxygen uptake rate of the effluent measured at a reaction time of 1 h increased by approximately 65% compared to that of the raw coking wastewater. This indicated that biodegradation of the coking wastewater was significantly improved. Several organic compounds, including bifuran, quinoline, resorcinol and benzofuranol were removed completely as determined by GC-MS analysis. The advanced Fenton oxidation process is an effective pretreatment method for the removal of organic pollutants from coking wastewater. This process increases biodegradation, and may be combined with a classical biological process to achieve effluent of high quality [47].

Bioaugmented zeolite-biological aerated filters (Z-BAFs) were designed to treat coking wastewater containing high concentrations of pyridine and quinoline and to explore the bacterial community of biofilm on the zeolite surface. The investigation was carried out for 91 days of column operation and the treatment of pyridine, quinoline, total organic carbon (TOC), and ammonium was shown to be highly efficient by bioaugmentation and adsorption. This bioaugmented Z-BAF method was shown to be an alternative technology for the treatment of wastewater containing pyridine and quinoline or other N-heterocyclic aromatic compounds [48].

6.2. Textile wastewater

Dyes and pigments have been utilized for coloring in the textile industry for many years. Several types of textile dyes are available for use with various types of textile materials. Textile wastewater contains dyes damages the esthetic nature of water and reduces light penetration through the water's surface, and also the photosynthetic activity of aquatic organisms. It also contains toxic and potential carcinogenic substances. Therefore it must be adequately treated before they can discharge into receiving water bodies. There are several applied treatment methods for textile effluents, involving biological, physical or chemical

methods and combinations of these. Among the different technologies that can be applied for the treatment of textile wastewaters, Coagulation-flocculation (CF) and Activated Sludge Process (ASP) are widely used as they are efficient and simple to operate. Generally, these processes can be applied alone to remove suspended colloidal particles or as pre-treatment prior to Ultrafiltration (UF), Nanofiltration (NF) or Reverse Osmosis (RO) respectively for dissolved organic substances removal, decolorization and desalination.

Biological treatment resulted in a high percent reduction in chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), and total phosphorus (TP), and in a moderate decrease in color. The process was found to be independent of the variations in the anoxic time period studied; however, an increase in solids retention time (SRT) improved COD and color removal, although it reduced the nutrient (TKN and TP) removal efficiency. Furthermore, combined treatment (biological treatment and Fenton oxidation) resulted in enhanced color reduction [49].

The treatability of textile wastewaters in a bench-scale experimental system, comprising an anaerobic biofilter, an anoxic reactor and an aerobic membrane bioreactor (MBR) was evaluated by S. Grilli et al. The MBR effluent was thereafter treated by a nanofiltration (NF) membrane. The proposed system was demonstrated to be effective in the treatment of the textile wastewater. The MBR system achieved a good COD (90-95%) removal; due to the presence of the anaerobic biofilter, also effective color removal was obtained (70%). The addition of the NF membrane allowed the further improvement in COD (50-80%), color (70-90%) and salt removal (60-70% as conductivity). In particular the NF treatment allowed the almost complete removal of the residual color and a reduction of the conductivity such as to achieve water quality suitable for reuse [50].

Typical contaminants of wool textile effluents are heavy metal complexes with azo-dyes. One of the most representative heavy metals is chromium. In aquatic environments chromium can be present as Cr(III) and/or Cr(VI), mainly depending on pH and redox conditions; the two forms behave quite differently, since Cr(III) is much less soluble and therefore less mobile than Cr(VI). The heavy metal can not be removed by activated sludge effectively. The constructed wetlands (CWs) in full-scale systems and in pilot plants evidenced good performances for several elements, including chromium. Donatella et al investigated the fate of Cr(III) and Cr(VI) in a full-scale subsurface horizontal flow constructed wetland planted. The reed bed operated as post-treatment of the effluent wastewater from an activated sludge plant serving the textile industrial district. Removals of Cr(III) and Cr(VI) was 72% and 26%, respectively. The mean Cr(VI) outlet concentration was 1.6±0.9 g/l and complied with the Italian legal limits for water reuse [51].

6.3. Food and fermentation wastewater

Food processing and fermentation industries have being experiencing a significant growth in China. Wastewater streams discharged from these industries are generally characterized with high strength organic and nutrient contents, e.g., COD 10000 mg/L, TN 600 mg/L, and

tend to bring serious water environment contamination if discharged without proper treatment. The conventional treatment of this kind of high strength wastewater is anaerobic/aerobic activated sludge processes.

Recent years, considerable concern has been focused on the development of the anaerobic membrane bioreactor (AMBR), which is an anaerobic reactor coupled with a membrane filtration unit. The viability of the AMBR treating high-concentration food wastewater depended upon feedwater organic concentration, loading rate, HRT, SRT, hydraulic shearing effect and membrane properties. The HRT kept at 60 h, SRT was designed for 50 days. The effluent COD removal achieved above 90% at loading rate of 2.0 kg/m^3/d and above 80% at a loading of 2.0-4.5 kg/m^3/d. The membranes all exhibited high efficiency in removal of SS, color, COD and bacteria, reaching 499.9%, 98%, 90%, and 5 logs, respectively [52].

Wang et al. [53] applied an anoxic/aerobic membrane bioreactor (MBR) to simultaneous removals of nitrogen and carbon from food processing wastewater. The system is proposed to be applied jointly with anaerobic pre-treatment. In order to simulate the quality from anaerobic pre-treatment, raw wastewater taken from a food processing factory was fed to the system after dilution. By continuous runs under appropriate operational conditions, COD, NH_4^+-N and TN removal was over 94, 91 and 74%, respectively. The anoxic reactor and aerobic MBR contributed 40-63 and 29-46% to COD removal, and 31-43 and 47-64% to NH_4^+-N removal, respectively. The maximum volumetric COD and TN loadings as high as 3.4 kg COD/m^3/day and 1.26 kg N/m^3/day were achieved.

Food processing and fermentation wastewaters can be characterized as nontoxic because they contain few hazardous compounds, have high BOD_5 and much of the organic matter in them consists of simple sugars and starch. Hence, this high-carbohydrate wastewater is the most useful for industrial production of hydrogen. Food Wastewaters obtained from four different food-processing industries had COD of 9 g/L (apple processing), 21 g/L (potato processing), and 0.6 and 20 g/L (confectioners A and B). Biogas produced from all four food processing wastewaters consistently contained 60% hydrogen, with the balance as carbon dioxide. COD removals as a result of hydrogen gas production were generally in the range of 5-11%. Overall hydrogen gas conversions were 0.7-0.9 L H_2/L-wastewater for the apple wastewater, 0.1 L/L for Confectioner-A, 0.4-2.0 L/L for Confectioner B, and 2.1-2.8 L/L for the potato wastewater [54].

Hydrogen yields were 0.61-0.79 mol/mol for the food processing wastewater (Cereal), ranged from 1 to 2.52 mol/mol for the other samples. A maximum power density of 8177mW/m^2 (normalized to the anode surface area) was produced using the two-chambered MFC and the Cereal wastewater (diluted 10 times to 595 mg COD/L), while at the same time the final COD was reduced to lower 30 mg/L (95% removal). Although more studies are needed to improve hydrogen yields, these results suggest that it is possible to link a MFC to biohydrogen to recover energy from food processing wastewaters, providing a new method to offset wastewater treatment plant operating costs [55].

6.4. Pharmaceutical wastewater

The pharmaceutical manufacturing industry produces a wide range of products to be used as human and animal medications. Treatment of pharmaceutical wastewater is troublesome to reach the desired effluent standards due to the wide variety of the products produced in a drug manufacturing plant, thus, variable wastewater composition and fluctuations in pollutant concentrations. The substances synthesized in a pharmaceutical industry are structurally complex organic chemical that are resistant to biological degradation. Soluble COD removal efficiency is about 62% at 30◎. Therefore, there is a need for advanced oxidation methods. As the process costs may be considered the main obstacle to their commercial application. Cost-cutting approaches have been proposed, such as combining AOP and biological treatment.

Fenton's oxidation is very effective method in the removal of many hazardous organic pollutants from wastewaters. Fenton's oxidation can also be an effective pretreatment step by transforming constituents to by-products that are more readily biodegradable and reducing overall toxicity to microorganisms in the downstream biological treatment processes.

Optimum pH was determined as 3.5 and 7.0 for the first (oxidation 30 min) and second stage (coagulation 30 min) of the Fenton process, respectively. For all chemicals, COD removal efficiency was highest when the molar ratio of H_2O_2/Fe^{2+} was 150-250. At H_2O_2/Fe^{2+} ratio of 155, 0.3M H_2O_2 and 0.002M Fe^{2+}, Fenton process provided 45-65% COD removal (influent COD 35000-40000 mg/L) [56].

Real pharmaceutical wastewater containing 775 mg dissolved organic carbon (3324 mg COD) per liter was treated by a solar photo-Fenton/biotreatment. The photo-Fenton treatment time (190 min) and H_2O_2 dose (66 mM) necessary for adequate biodegradability of the wastewater. And biological treatment was able to reduce the remaining dissolved organic carbon to less than 35 mg/L. Overall dissolved organic carbon degradation efficiency of the combined photo-Fenton and biological treatment was over 95%, of which 33% correspond to the solar photochemical process and 62% to the biological treatment [57]. Due to the high COD concentration in pharmaceutical wastewaters, anaerobic processes have been made to utilize, such as upflow anaerobic sludge blanket (UASB) reactor, anaerobic filter (AF), anaerobic continuous stirred tank reactor (CSTR) and a hybrid reactor combining UASB and AF. The COD reduction of anaerobic process treating pharmaceutical wastewater containing macrolide antibiotics was 70-75%, at a total HRT of 4 d and OLR of 1.86 kg COD/m^3/d [58].

The two-phase anaerobic digestion (TPAD) system comprised a CSTR and a UASBAF reactor, working as the acidogenic and methanogenic phases, respectively. The wastewater was high in COD, varying daily between 5789 and 58,792mg/L, with a wide range of pH from 4.3 to 7.2. Almost all the COD was removed by the TPAD-MBR system, leaving a COD of around 40mg/L in the MBR effluent, at respective HRTs of 12, 55 and 5 h. The pH of the MBR effluent was found in a narrow range of 6.8-7.6, indicating that the MBR effluent can be directly discharged into natural waters. As demonstrated by an overall COD removal efficiency of more than 99% [59].

6.5. Sugar refinery wastewater

Sugar refineries generate a highly coloured effluent resulting from the regeneration of anion-exchange resins (used to decolourize sugar liquor). This effluent represents an environmental problem due to its high organic load, intense colouration and presence of phenolic compounds. The colored nature of the effluent is mainly due to (1) the presence of melanoidins, that are brown polymers formed by the Maillard amino-carbonyl reaction and (2) the presence of thermal and alkaline degradation products of sugars (e.g. caramels). Most of the organic matter present in the effluent can be reduced by conventional biological treatments but the colour is hardly removed by these treatments.

The remaining colour can lead to a reduction of sunlight penetration in rivers and streams which in turn decreases both photosynthetic activity and dissolved oxygen concentrations causing harm to aquatic life. *P. chrysosporium* can remove color and total phenols from the sugar refinery effluent. A rotating biological contactor (RBC) containing *P. chrysosporium* immobilized on polyurethane foam (PUF) disks was operated with optimized decolourization medium, in continuous mode with a retention time of 3 days. During the course of operation the color, total phenols and chemical oxygen demand were reduced by 55, 63 and 48%, respectively. Addition of glucose was obligatory and the minimum glucose concentration was found to be 5 g/L [60].

Wastewater obtained from Guangxi Nanning sugar refinery (COD 86.02 g/L) is first diluted by 100 times, then treated by adding amphiphilic flocculants (CMTMC) mg/L at pH 6.6, COD removal to reached to 95%. The wastewater color changed from fuscous brown to buff yellow. After flocculation and purification, the treated water could reach the national first level discharge standards. (GB8978-88, China) [61].

Sugar refinery wastewater containing high organic load can be used as carbon sources for hydrogen production by microorganisms. As reported pretreated sugar refinery wastewater was used for the production of hydrogen by *Rhodobacter sphaeroides* O.U.001. Hydrogen was produced at a rate of 0.001 L hydrogen/h/L culture in 20% dilution of the wastewater. To adjust the carbon concentration to 70 mM and nitrogen concentration to 2 mM, sucrose or L-malic acid was added as carbon source and sodium glutamate was added as nitrogen source to the 20% dilution of SRWW. By these adjustments, hydrogen production rate was increased to 0.005 L hydrogen/h/L culture [62].

7. The cost accounting of different organic wastewater treatment

The cost of organic wastewater treatment includes two parts: the capital expenditure and the operation expenditure. The total cost relates to the characters of the influent, the technique we selected, the characters of the effluent, the time cost during the treatment etc. In this section, the pollutants are divided into degradable and reluctant ones. Some typical wastewater was selected in each group, and the feasible methods to treat it and their cost were discussed.

7.1. The degradable organic pollutants

Wastewater with degradable organic pollutants usually comes from domestic sewage, food processing, breeding industry etc. This wastewater has high BOD, and could break down in the nature condition, given enough time. Most of the techniques could be used to treat the degradable organic pollutants, and biological methods are favorite because of their efficiency and economic properties.

Sewage is one of the most important sources of degradable organic pollutants, which contributes to 37.5% of total COD in China in 2011. Therefore, sewages are treated before discharge in order to reduce the impact of the pollutants to the environment. Several biological methods, including aerobic biodegradation, activated sludge reactor, membrane bioreactor, constructed wetland etc., have been used in the sewages treatment, and their efficiency and cost have been compared. Taking the research of Song as an example[63], in response to the characteristics of decentralized domestic sewage, several treatment technologies including biogas purification tank, constructed wetland, viewing earthworm ecological, high rate algal pond, membrane bioreactor and integrated treatment equipment were applied to the domestic sewage, and their efficiency and cost were calculated and showed in table 1.

Treatment	**Load (m^3/d)**	**Capital expenditure (10^4Yuan/m^3)**	**Operation expenditure (10^4Yuan/m^3)**	**Quality of the effluent (GB18919-2002)**
Biogas purification tank	20-200	0.06-0.08	0.02-0.05	2nd grade
Constructed wetland	30-3100	0.06-0.2	0.05-0.2	1st grade B
Viewing earthworm ecological	2-12	0.7-2.0	0.5-1.2	1st grade B
High rate algal pond	-	-	-	1st grade B
Membrane bioreactor	5-100000	0.19-1.0	0.25-1.05	1st grade B
Integrated treatment equipment	20-	1.0-1.5	0.27-0.8	1st grade A

Table 1. The load, cost accounting and effluent of different treatments

According to the technologies, the biogas purification tank, constructed wetland, viewing earthworm ecological and high rate algal pond were characterized by low investment, operating cost, and convenient management. The membrane bioreactor and integrated treatment equipment had the higher operating cost, and the need for professional management, which could be used in the area with higher economic development and stricter effluent qualities.

The industrial waste water from agricultural and sideline food processing industry contain high concentration of organics and suspended substance. Food wastewater is composited of natural organic matters (such as protein, fat, sugar, starch), so they are of low toxicity and high BOD/COD value (up to 0.84). Physical (such as adsorption, air flotation), chemical

(flocculation) and biological methods (aerobic biodegradation, activated sludge reactor, sequencing batch reactor, oxidation pond) could be used to remove the pollutants. Most of the physical and chemical techniques are costly and need secondary treatment, therefore, food wastewater was mainly treated by biological methods. The cost varied greatly with the characters of the influent. Longda food industry compared the load and cost of oxidation pond and sequencing batch reactor, results were shown in the table 2 [64].

Treatment	Design capacity (m^3/d)	Wastewater quantity (m^3/a)	Total cost (Yuan/m^3)	Electricity consumption (kwh/m^3)
Oxidation pond	6500	1985300	0.56	0.335
Sequencing batch reactor	4500	1114200	0.455	0.25

Table 2. The load, cost accounting of oxidation pond and sequencing batch reactor

7.2. The reluctant organic pollutants

The reluctant organic pollutants, including benzene series, pharmaceutical intermediates, pesticide etc., mainly come from paper making industry, chemical industry, printing and dyeing wastewater, mechanical manufacturing industry, and agriculture [65]. This kind of wastewater is reluctant to biodegradation either owed to its toxicity or stable structure, therefore, their disposal usually costs higher than degradable ones.

The paper making wastewater reaches 10% of total industrial water. This kind of wastewater contained high concentration and complex structure pollutants, such as lignin, cellulose, hemicellulose, monosaccharide, and could cause serious pollution. The traditional two-stage biochemical treatment has relativity low cost, but the effluent could hardly meet the discharge standard of China owing to its high COD and chroma. The advanced oxidation technique could remove the pollutants from paper making wastewater efficiently, without any secondary pollution. However, the H_2O_2 used in this method is very expensive, which affects the application and extension of this technology [66]. Flocculation is another efficient method for paper making wastewater treatment, and its COD remove rate could reach 95% at the optimal condition, and the flocculants could be reused after treatment. The cost of this technique is in the middle of the two methods mentioned above (around 1.5-2 Yuan/m^3).

The printing and dyeing wastewater contains of much refractory bio-degradable organism with extremely high chrome, therefore, it is hard to be efficiently treated with biological technique [67]. Advanced oxidation could degrade the organisms and reduce the toxicity of this wastewater, but it is too expensive to be used to deal with a great amount of dyeing wastewater. The membrane separation technique could also obtain high pollutants remove rate, but the high cost of the membrane and the energy also hinder the technique from widely application. The flocculation is the most common used technique owing to its moderate price and basically satisfactory results. Partial related with the character of the wastewater, the cost of the flocculation treatment ranges from 3 yuan/m^3 to 5 yuan/m^3. Some

researchers suggested that the combination of the flocculation technique with other techniques, such as Fenton, biological technique could reduce the cost without affecting the effluent quality.

Generally speaking, among all the techniques, biological technique costs the lowest if the pollutants are degradable. The flocculation and adsorption techniques could dispose of the wastewater at a moderate price, but the flocculant and adsorbent need secondary treatment for reuse. Membrane separation and the advanced oxidation could remove pollutants efficiently, but they are costly.

8. Conclusion

The treatment technologies for organic wastewater at present were reviewed. That a variety of technologies such as biological treatment, chemical oxidation technologies, adsorption technology and the others were introduced. At last, the cost accounting of different organic wastewater treatments was discussed.

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