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Photo Oxidation and Biological Treatment of Waste Water

This work is
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Abstract

The various currently used advanced oxidation processes (AOPs) for pesticide elimination from waste water of VAPCO factory in Jordan.

This paper presents the results of the oxidation of pesticides in aqueous solution in a semi-batch reactor which we designed in The Faculty of Engineering.

The advanced oxidation processes, photo-Fenton's reagent studied and it is combinations with various analytical approaches for pesticide degradation by AOPs are discussed and analyzed by HPLC.

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Introduction:

It has been known for some time, that ultraviolet (UV) radiation will kill microorganisms. This technique has only recently been applied to the treatment of water. An ultraviolet radiation disinfections system typically has a stainless steel tube with a mercury vapor lamp inside running the length of the tube. The water inlet and outlet are at the ends of the tube. The water must be in contact with the UV radiation for sufficient time to kill microorganisms.

We made many studies according to these objectives involve using UV tube experiments in our collages' labs.

This study was firstly applied on using UV radiation alone (without any catalyst as the results shown below.

These process adapt the production of (OH) radicals by many means of oxidation processes which convert the toxic and complex compounds into another type of chemical

compounds which can be removed from waste water by another simple and traditional methods such as:

Chlorination, coagulation, and filtration.

The addition of the hydroxyl radicals is made by the hydrogen abstraction or any electrophilic addition to the double bond.

Free radicals + O_2 $\longrightarrow$ OH radicals .... (1)
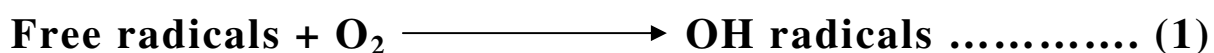
The reaction starts by a continuous oxidation removal, which is probably, can complete the mineralization process to the pollutants.

Also, there is a probability of connection between the free radicals with the aromatic compounds and forming phenols, which can be treated finally by a simple methods.

Other alkanic compounds contain chlorine will react slowly with the hydroxyl radicals.

The major sources of water pollution can be classified as municipal, industrial, and agricultural pollutants. Some of these pollutants are considered as toxic substances such as pesticides. Pesticide pollution of environmental waters is considered as a pervasive problem because

it has a direct adverse effect on the living organisms. The major sources of pesticide pollution are wastewater effluents from agricultural industries and pesticide formulating or manufacturing plants. At present, the strict environmental regulations in Jordan require the removal of pesticide loads from industrial wastewater effluents.

The chemical methods for treating waste water containing pesticides include oxidative process technologies. This method can be applied when the wastewater contains non-biodegradable or toxic contaminates for microorganisms. However, normal oxidative chemical processes cannot treat or transform the pollutants to biodegradable or nontoxic compounds. For this reason, a procedure based on the generation of reactive intermediates that initiate a sequence of reactions in which destruction and removal of organic pollutants generally referred to as advanced oxidation processes (AOPs) is more promising. These methods include photochemical oxidation processes.

Advanced oxidation processes (AOPs) are based mainly on hydroxyl radical chemistry. These processes are characterized by the

fact that no more toxic compound can be produced during the reaction. In addition, AOPs give a complete mineralization of the contaminant .

In addition, hydroxyl radical may attack aromatic rings of positions occupied by a halogen; generating a phenol homologue. Although hydroxyl radicals are among the most reactive radicals known, they react slowly with chlorinated alkane compounds. The variety on AOPs comes from the fact that there are many ways to produce hydroxyl radicals. This permits the performance for the requirements of any treatment. However, it should be taken into account that these AOPs are made by using some expensive reactants such as H_2O_2 and O_3 in the presence of ultra violet radiation, UV.

The principle of the photochemical reaction is the addition of energy to the chemical reaction in the form of radiation. This radiation is absorbed by certain functional group in the target molecule and it transfers the molecule to an excited state. The solar energy could be used as the source of such radiation for the degradation of some compounds. The principle of the photochemical reaction is the addition of energy for the chemical compound in form of radiation, which absorbed by the group of molecules to reach an excited state.

The solar energy can be used as the source of such radiation energy for the degradation of some compounds. Pesticide degradation is possible through different photochemical processes that require artificial light source (Generally, a UV lamp) or solar energy. Most of these methods require long treatment periods of high energy photons and rarely achieve a complete degradation of the pollutant.

❖ **Classifying water pollution:**

The major sources of water pollution can be classified as municipal, industrial, and agricultural. Municipal water pollution consists of wastewater from homes and commercial establishment .for many years, the main goal of treating municipal wastewater was simply to reduce its content of suspended solids, oxygen-demanding material, dissolved inorganic compounds, and harmful bacteria. In recent years, however, more stress has been placed on improving means of disposal of the solids residue from the municipal treatment processes .The basic method of treating municipal wastewater fall into three stages: primary treatment, including grit removal, screening, grinding, and sedimentation; secondary treatment, which entails oxidation of dissolved organic matter by means of using biologically active sludge,

which is then filtered off; and tertiary treatment, in which advanced biological method of nitrogen removal and chemical and physical method such as granular filtration and activated carbon absorption are employed . The handling and disposal of solid residues can account for 25 to 50percent of the capital and operational costs of a treatment plant .The characteristics of industrial water can differ considerably both within and among industries. The impact of industrial discharges depend not only on their collective characteristics, such as biochemical oxygen demand and the amount of suspended solids, but also on their content of specific inorganic and organic substances. Three option are available in controlling industrial wastewater can be pretreated for discharge to municipal treatment sources; or wastewater can be treated completely at the plant and either reused directly into receiving water.

❖ **Contaminants of concern in wastewater treatment**

The important contaminants of concern in wastewater treatment are suspended solids, biodegradable organic, pathogens, nutrients, priority, pollutants, refractory organic, heavy metals and dissolved inorganic.

Secondary treatment standards for wastewater are concerned with the removal of biodegradable organic, suspended solids, and pathogens.

Many of the more stringent standards that have been developed recently deal with the removal of nutrients and priority pollutants. Recently the European Union made out a list of dangerous compounds such as chloride hydrocarbons, chlorophenol, chloroanilines and nitrobenzene's , policuclic aromatic hydrocarbon ate, Inorganic substances, solvents, pesticides. considered as contaminants, to which constantly new substances are added.

❖ **Chemical characteristics**

Chemical characteristics of wastewater are included in four parts.

 Organic matter:

In wastewater of medium strength, about 75% of the suspended solids and 40% of the filterable solids are organic matters. These solid are derived from animals, plant Kingdome and the activities of man in the synthesis of organic .

The principle groups of organic substances found in wastewater are proteins (40 – 60 percent) carbohydrate (25 - 50 percent) fats and oil (10 percent and wastewater contains small quantity of large number of different synthetic organic molecules ranging from simple to extremely complex in structure.

Measurements of organic matter:

A number of different test have been developed to determine the organic contents of wastewater. In general, the test may be divided into those used to measure gross concentration in the range of 10^{-2} to 10^{-3} mg.L^{-1}.

Laboratory methods commonly used today to measure gross amount of organic matter (greater than 1 mg.L^{-1}) in wastewater include ,

(1) biological oxygen demand BOD

(2) chemical oxygen demand COD

(3) total organic compound TOC, complementing these laboratory tests is the theoretical oxygen demand (THOD),which is determined from the chemical formula of the organic matters .

Trace organic in the range of 10^{-12} to 10^{-3} mg.L^{-1} is determined using instrumental methods including gas chromatography and

spectroscopy. Within the years the sensitivity of the method has improved significantly.

❖ Biological oxygen demand (BOD):

The most widely used parameters of organic pollution applied to both wastewater and surface water is the 5- day BOD (BOD_5). This determination involves the measurement of the dissolved oxygen used by microorganisms in the biochemical oxidation of organic matter. Then if the test suffers from serious limitation, is further space devoted to it in this field? The reason is that BOD test result are now used :

1) to determine the approximate quantity of oxygen that will be required to biologically stabilize the organic matters present .

2) to determine the size of wastewater treatment facilities .

3) to measure the efficiency of some treatment processes

4) to determine compliance with wastewater discharge permits.

To insure that meaningful results are obtained, the sample must be suitably diluted with specially prepared dilution water ,so that adequate nutrients and oxygen will be available during the incubation period . Full discussion of BOD measurements will be given in experimental part.

Biochemical oxidation is slow process and theoretically takes at infinite time to go to completion. Within a 20-day period, the oxidation of the carbonate organic matter is about 95-99 percent complete, and in the 5-day period used for the BOD test. Oxidation is from 60 to 70 percent complete. The 20ºC used are an average value for slow –moving streams in temperature dependent.

The kinetics of the BOD reaction is for practical purpose. Formulated in accordance with first order reaction kinetics and may be expressed as

$$\frac{dL_t}{dt} = -kt$$

………………..2

where Lt is the amount of the first stage BOD remaining in the water at time t and k is the first reaction rate constant . This equation can be integrated as

$$LnL_t \Big|_0^t = -kt$$

…………3

$$\frac{L_t}{L} = \exp(-kt) = 10^{-kt}$$

………4

Where L or the BODL is the BOD remaining at time = 0 (i.e.the total or ultimate first-stage BOD initially present):

A typical value of k (base exp , at 20°C) is 0.23 day. The value of reaction –rate constant varies significantly however , with the type of waste.

Other type of BOD is nitrogenous biochemical oxygen demand (NBOD) and carbonaceous biochemical oxygen demands (CBOD) are well known .

Limitations of the BOD test:

A highly concentration of active , acclimated seed bacteria is required.

Pre-treatment is needed when dealing with toxic waste , and effects of nitrifying organisms must be reduced only the biodegradable organic is measured.

The test does not have stoichiometric validity after the soluble organic matter present in solution has been used.

An arbitrary , long period of time is required to obtain result.

Over the above the most serious limitation is that the 5- day period may or may not correspond to the point where soluble organic matter

that present has been used .The lakes of stoichiometric validity at all time reduced the usefulness of the test results.

❖ **Chemical oxygen demand (COD):**

The test is used to measure the content of organic matter of both wastewater and natural water . The oxygen equivalent of the organic matter that can be oxidized is measured by a strong chemical oxidizing agent in an acidic medium . Potassium dichromate has been found to be excellent for these purpose . The test must be performed at an elevated temperature .A catalyst (silver sulfite) is required to aid the oxidation of certain classes of organic compounds in general way by unbalanced equation.

$$\text{Organic matter} \left(C_a H_b O_c\right) + Cr_2O_7^{-2} + H^+ \xrightarrow{\text{CATALYST}} Cr^{+3} + Co_2 + H_2O$$
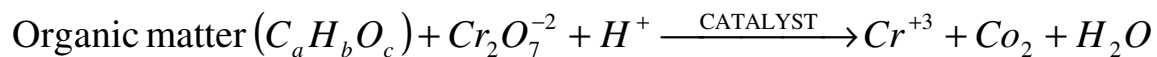
The COD test used to measure organic matter in the wastes that contain compound , which are toxic to biological life .

The COD of a waste is , in general , higher than the BOD because the more compound can be chemically oxidized than can be biologically oxidized . For many types of wastes , it is possible to correlate COD

with BOD . This can be vary useful because the COD can determine in three hours , compared with five day for BOD.

❖ **Total organic carbon (TOC):**

Another means for measuring the organic matters present in the water is the TOC test , which is especially applicable to small concentration of organic matter .This test is performed by injecting a known quantity of sample in to a high – temperature furnace or chemically – oxidizing environment . The organic carbon is oxidized to carbon dioxide in the presence of a catalyst. The carbon dioxide in that is produced is quantitatively measured by means of an infrared analyzer. Acidification and aeration of the sample prior to analysis eliminate error due to the presence of organic compound may be oxidized , and the measured TOC value will be slightly less than the actual amount present in the sample.

❖ **Inorganic matter:**

Several inorganic components of wastewater and natural waters are important in the establishing and controlling water quality. The concentration of inorganic substances in water are increased both by the geologic formation with which the water comes in contact and by

the wastewater , treated or unrelated , that are discharge to it. An example of such inorganic compound, sulfur , heavy metals (nickel(Ni) , manganese(Mn) , lead (Pb) , chromium (Cr) , cadmium(Cd) , zinc(Zn) , copper(Cu) ,iron(Fe), and mercury (Hg).

❖ **Gases:**

Gases commonly found in untreated wastewater include nitrogen (N_2), oxygen(O_2),carbon dioxide (CO_2),hydrogen sulfide (H_2S), ammonia(NH_3).

❖ **Biological treatment**

With proper analysis and environmental control, almost all the wastewater can be treated biologically. Therefore, it is essential to understand the characteristics of each biological process to ensure that the proper environment is produced and controlled effectively.

Objective of biological treatment

The general objectives of the biological treatment of wastewater are to coagulate, remove the nonsettleable colloidal solids and to stabilize the contained organic matter. For domestic wastewater, the objective is simply reduce the organic content, and in many cases, the nutrients

such as nitrogen and phosphorous. However, sometimes the removal of trace organic compound that may be toxic is also an important treatment objective. In agricultural wastewater treatment, the objective is to remove the nutrients, specifically the nitrogen and phosphorous, that are capable to stimulating the growth of aquatic plants. Beside all of that, in industrial wastewater, the objective is to remove and reduce concentration of organic and inorganic compound.

Role of microorganisms:

The removal of carbonaceous BOD, the coagulation of nonsettlrable colloidal solid, and the stabilization of organic matter are accomplished biologically using of microorganisms, principally bacteria. The microorganisms are used to convert the colloidal and dissolved carbonaceous organic matter into various gases and into cell tissue. Because cell tissue has specific gravity slightly greater that of water the resulting cell can be removed easily from treated liquid by gravity settling

Introduction to microbial metabolism:

Understanding of the biochemical activities of the important microorganisms is the basic information to design a biological treatment process .the two major topics considered here are

(1) the general nutritional requirements of the microorganisms

(2) the nature of microbial metabolism based on the need for molecular oxygen.

In order the microorganisms to reproduce and function properly an organisms must have

1) A sours of energy

2) Carbon for synthesis of new cellular material

3) Inorganic elements or nutrients

Organic nutrients (growth factor) may also be required for cell synthesis Carbon and energy source usually referred to as substrate.

Tow of the most common sources of cell carbon for microorganisms are organic matter and carbon dioxide. Organisms that use organic carbon for the formation of cell tissue are called heterotrophs. Organisms that derive cell carbon from carbon dioxide are called autotrophy.

The conversion of carbon dioxide to cell tissue is a reductive process that need net input of energy. The energy needed for cell synthesis may be supplied by light or by chemical oxidation reaction.

The principal inorganic nutrients needed by microorganisms are nitrogen, sulfur, potassium, magnesium, and calcium…. etc. In addition to these inorganic nutrients needed, organic nutrients may also be needed by some organisms.

Bacterial growth

Effective environmental control in biological waste treatment is based on understand of the basic principle governing the growth of microorganisms. Bacteria can reproduce by binary fission, by a sexual mode or by budding. Generally, they reproduce by binary fission (i.e.by dividing, the original cell becomes two new organisms) .the time required for each fission, which is termed the generation time, can vary from days to less than 20 min. For example, if the generation time is 30 min, one bacteria would 16 777 216 bacteria after period of 12 h.

This computed value is a hypothetical figure , for bacteria would not continue divide indefinitely because of various environmental

limitations such as substrate concentration nutrient concentration or even system size different growth rate can be used for bacteria growth like , growth in term of bacterial mass and growth and growth in mixed cultures.

To ensure that the microorganisms will grow , they must be allowed to remain in the system long enough to reproduce.

This period depend on their growth rate , which is related directly to the rate at metabolize or utilize the waste. Assuming that the environmental condition are controlled properly. Controlling the growth rate of the microorganisms can ensure effective wastewater stabilization.

In both batch and continuous culture systems the rate of growth of bacteria cell can be define by the following relationship.

$$r_g = \mu X$$ ………………………5

Where rg = rate of bacteria growth , Gtvss.L-1.S-1

μ = specific growth rate , s-1

X = concentration of microorganisms gTVSS

Because dX/dt =rg for both culture the following relationship is also valid for batch reactor

$$\frac{dX}{dt} = \mu X \qquad \dots\dots\dots\dots\dots\dots\dots\dots..6$$

In batch culture , if one of the essential requirements (substrate and nutrients) for growth were present in only limited amount it would be depleted first and growth would cease in continuous culture , growth is limited. Experimentally it gas been found that the effect of a limiting substrate or nutrient can often be defined adequately using the following expression proposed by monod(1949).

$$\mu = \mu_m \frac{s}{k_s + s} \qquad \dots\dots\dots\dots\dots\dots\dots.7$$

Where

μ = specific growth rate , s-1

μm = maximum specific growth rate , s-1

s = concentration of growth limiting substrate in solution , g.L-1

ks = half velocity constant , substrate concentration at one – half the maximum growth rate g.L-1

ks = half velocity constant substrate at one – half the maximum growth rate g.L-1

If the value of μ is substituted in the last equation the resulting expression for the rate growth rate is

$$r_g = \frac{\mu_{mXs}}{k_s + s}$$ ………………..8

In both batch and continuous – growth culture system , a portion of substrate is converted to new cell and a portion is oxidized to inorganic and organic en products. Because the quantity of the new cell produced has been observed to be reproducible for given substrate , the following relationship gas been developed the rate of substrate utilization and the rate of growth.

$$r_g = Yr_{su}$$ ………………..9

Where

Y= maximum yield coefficient , g/g(defined as the ratio of the mass of cell formed to the mass of substrate consumed)

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rsu = substrate utilization rate , g.L-1 .s-1

On the bases of laboratory study , it has been concluded on:

1.   The oxidation state of the carbon source and nutrient elements

2.   The degree of polymerization of the substrate .

3.   Pathways of the metabolisms.

4.   The growth rate

5.   The various physical parameter of cultivation.

If the we take r_g from the a above equations the rate of substrate utilization can be defined as follow:

$$r_{su} = \frac{\mu_m xs}{y(ks + s)}$$ …………………..10

In the last equation the term μm /y is often replaced by the term k , defined as the maximum rate of substrate utilization per unit mass of microorganisms:

$$k = \frac{\mu_m}{y}$$ ………………………11

If the term k is substituted for the term μm /y the resulting expression is:

$$r_{su} = \frac{kxs}{(k_s + s)}$$ ………………….12

In bacteria system used for wastewater treatment , the distribution of cell age is such that not all the cell in the system are in the log – growth phase. Consequently , the expression for the rate of growth must be corrected to account for the energy required for cell maintenance. Other factors , such as death and perdition , must also be considered. Usually these factors are lumped together , and it is assumed that decrease in cell mass caused by them is proportional to the concentration of organisms present. This decrease is often identified in the literature as the endogenous. The endogenous decay term can be formulated as follow:

$$r_d (\text{Endogenous decay}) = -k_d x$$ ……………13

Where kd = endogenous decay coefficient s-1

When equation 13 is combined with equation 7 the following expression are obtained for the net rate of growth :

$$r'_g = \frac{\mu_m xs}{k_s + s} - k_d x$$

$$r'_g = -yr_{su} - k_d x \qquad \ldots\ldots\ldots\ldots\ldots\ldots.14$$

Where rg = net rate of bacteria growth rate is given by equation 15 which is same as the expression by van U (1967)

$$\mu' = \mu_m \frac{s}{k_s + s} - k_d \qquad \ldots\ldots\ldots\ldots\ldots\ldots.15$$

Where μ = net rate of bacteria growth rate , s-1

The effect of endogenous respiration on the net bacteria yield are

accounted for by defining an observed yield as follow:

$$y_{OB} = \frac{r'_g}{r_{su}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots.16$$

so another way to write is

$$\mu' = Y_{OB}\,\mu_m \frac{S}{K_s + S} - K_d \qquad \ldots\ldots\ldots\ldots..17$$

The temperature effect of the biological reaction-rate constant is very important in assessing the overall efficiency of a biological treatment

process. Temperature not only influences the metabolism activities of the microbial population but also gas and thoughtful effect on such factors as gas-transfer rates and settling characteristics of the biological solids. The effect of temperature on the reaction rate of a biological process is usually expressed in the form expressed by the equation

$$r_T = r{20}\,\theta^{(T-20)} \quad \ldots\ldots\ldots\ldots..18$$

rT = reaction rate at T°

r20 =reaction rate at 20°

θ =temperature activity coefficient

T=temperature in °C

❖ **Basic types of bioreactors**

There are two basic types of biological and chemical reactor:

• Continuous stirred tank reactor (CSTR)

• Plug flow reactors.

CSTR are easily visualized as vessels or tank that are to achieve uniformity throughout the tank. A very important characteristic of the

CSTR is that the concentration of the reactants in the outlet is equal to the concentration of the reactant in the vessel regardless of the concentration of the reactants in the inlet.

Plug flow reactors can be modeled as a pipe where the reactants move as a plug along the pipe. The concentration of the reactants will vary along the pipe and there is no mixing between the beginning and the end of the system. In bio-application different reactors configuration systems are available such as fluidized bed bioreactor system, packed bed bioreactor, air spared fixed bed bioreactor and rotating media bioreactor.

❖ **Bioreactor can be operated in three ways:**

Batch reactor:

Is simplest type of reactor operation. In this mode, the reactor is filled with medium and the reaction is allowed to proceed. When the reaction has finished the contents are emptied for downstream processing. The

reactor is then cleaned, re-filled, re-inoculated and the process starts again.

Continuous reactor:

Fresh media is continuously added and bioreactor fluid is continuously removed. As a result, cells continuously receive fresh medium and products and waste products and cell are continuously removed for processing. The reactor can thus be operated for long period of time without having to be shut down. Continuous reactor can be many times more productive than batch reactors. This is partly due to the fact that the reactor does not have to be shut down as regularly and also the growth rate of the bacteria in the reactor that can be more easily controlled and optimized. In addition, cell can be immobilized in continuous reactors.

The fed batch reactor

Is the most common type of reactor used in industry. In this reactor, fresh media is continuous or sometimes periodically added to the bioreactor but unlike a continuous reactor, there is no continuous removal. The reactant is emptied or partially emptied when reactor is

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full or fermentation is finished. As with the continuous reactor, it is possible to achieve high productivities due to the fact that the growth rate of the feed entering the reactor.

Sequencing batch reactor

The SPR process has widespread application where mechanical treatment of small wastewater flows is desired. Because it provides batch treatment, it is ideally suited for wide variation in flow rates. Furthermore ,operation in the″ fill and draw″ mode prevents the ″washout ″ of biological solids that often occurs with extend aeration systems. Another advantage of SBR system is that they require less operator attention and produce a very high quality effluent.

The SBR process operates on a fill and draw batch system wherein the reactor acts as a biological reactor and settling tank at various stage of the treatment cycle. Wastewater may be accumulated in a batch and then delivered to a reaction tank (s) which contain activated sludge. The batch is subject to biological treatment for a prescribed period of time with both anoxic and aerobic cycles possible. At the end of the reaction period, the batch is allowed to settle, after which the clarified treated effluent is decanted from the top of the tank. The sludge

remains in the tank to provide the biological population for the subsequent cycle. Excess biomass is pumped on a regular basis to a sludge holding tank for digestion and disposal.

The various stages in the SBR sequence are:

Stage 1: Filling

During this stage the SBR tank is filled with the influent wastewater .in order to maintain suitable F/M (food to microorganism) ratio, the wastewater should be admitted in to the tank in a rapid, controlled manner . this method function similarly to a selector, which encourages the growth of certain microorganisms with better settling characteristics

Stage 2:Reaction

This stage involves the utilization of biochemical oxygen demand (BOD) and ammonia nitrogen, Where applicable, by microorganisms. The length of the aeration period depends on the strength of the wastewater and the degree of nitrification (conversion of the ammonia to a less toxic form of nitrate or nitrite) provided for in the treatment.

Stage 3:settling

During this stage, aeration is stopped and the sludge settle leaving clear, treated effluent above the sludge blankets. During for settling varies from 45 to 60 minutes depending on the number of the cycle per day.

Stage 4: Decanting

At this stage of the process effluent is removed from the tank through the decanter, without disturbing the settled sludge.

Stage 5: Idle

The SBR tank waits idle until a batch accumulates and it is time to start a new cycle with the filling stage.

Stage 6: Sludge wasting

Excess activated sludge is wasted periodically during the SBR operation. As with any activated sludge treatment process, sludge wasting is the main control of the effluent quality and microorganisms population size. This is how the operator exerts control over the effluent Quality by adjusting the mixed liquor suspended solids (MLSS) concentration and the mean cell residence time (MCRT).

In the process, the SBR tank acts as the equivalent of several components in the conventional activated sludge treatment process, as follows:

1.Aeration tank: the SBR tank acts as an aeration tank during the reaction stage where the activated sludge is mixed with the influent under aerated conditions.

2.Secondary clarifier: the SBR tank acts as a secondary clarifier during the settling and decanting stages where the mixed liquor is allowed to settle under quiescent conditions, and the overflow is discharged to the next stage of treatment.

3.Sludge return system: the activated sludge, following settling in the SBR tank, is mixed with the influent similar to the sludge return system, except that the feed is transferred to the sludge rather than the sludge being transferred to the front end of the plant.

❖   **Methods for treatment waste water:**

1.   **physical Entrainment:**

a.   Activated carbon filtration.

b.   Membrane technology.

2. **Biodegradation**

3. **Chemical Reactions.**

Entrainment is losing acceptance as a final solution for waste disposal because of its law efficiency when dealing with a high concentration of pollutants. More ever, entrained pollutants must be further treated for complete destruction.

Biological process is more efficient than physical entrainment since it is well- established and it is cheap, but acting a partial treatment of toxic waste by oxidation technology is a useful step for producing intermediates that are readily biodegrable.

Oxidation processes include:

1. photo chemical degradation process (UV/O_3 , UV/ H_2O_2)

2. photo catalysis (TiO_2/UV)

3. photo fenton reagent

4. chemical oxidation process(O_3 , O_3/ H_2O_2, H_2O_2/ Fe^{+2})

Oxidation detoxification is still used in some experimental plants

To achieve these technologies an optimization and modeling of the reactor used is a necessary step . Also making assessment of the efficiency of oxidation technology by a chemical engineering skills and pre collection step of information on the degree of mineralization on kinatics of disappearance of the parent compound and by- products may be assist workers involved in pesticides degradation by :

1.   knowing the advantages and limitations of the chemical oxidation processes for pesticide removal from waste water.

2.   comparing between the different process by calculating the degree of mineralization achieved through different processes.

Oxidation processes are made upon finding intermediates result from degradation and destruction of organic compounds by using advanced oxidation processes (AOPs)

Such as :

1.   photo chemical processes

2.   ozonation

3.   new technique based on the situation of free hydroxyl radicals (wet air oxidation process , electro chemical treatment,…etc).

❖   **Photo chemical process:**

To treat water from pesticides is possible by using an artificial light sources (high pressure mercury or a xenon arc lamp) or natural sun light.

Disadvantages of photo chemical process:

1.	require long treatment period

2.	require a high energy photon

3.	Doesn't achieve a complete degradation of pollutants

Most of its reaction (when pollutants irradiated with the UV light) is dechlorination .

Chlorination : substituting of CL_2 with OH and forming a radical species, enhance using a homogenous or heterogeneous photo catalysis

Heterogeneous catalyst include:

Semi conductor slurries (TiO_2/UV) (ZnO/UV)

Homogenous photo chemistry include :

Single phase systems(H_2O_2/UV) (Fe^{+3}/ UV)

Titanium dioxide (TiO_2) is the most widely accepted photo catalyst for pesticides destruction in water .

TiO_2 is a semi conductor that absorbs light at $\lambda < 385$ nm with the corresponding promotion of an electron from the valance band to the conduction band.

Relative importance of reductive and oxidative path ways appears to be PH dependent .

Heterogeneous photo catalyst s are generally used as suspend slurries that can be fixed on a glass support (beads, fibers or simply the reactor walls).

Process using fixed catalyst are much less effective than those using freely suspend catalyst.

- To use adsorbent materials such as activated carbon with TiO_2 enhance the rate of mineralization of propy zamide, and reduse the concentration (COD) of solute phase intermediate .

- Homogenous photo catalysis for detoxifying waste waters polluted with pesticides has hardly been used because:

1. The rate of photolysis of aqueous H_2O_2 into hydroxyl radicals is optimum over irradiation wave length s of 210-230 nm .

2. The hydroxyl radical generation rate is reduced in the UV-C spectrum region   because of the competition of photon absorber amount in this region .

3. Other difficulties in homogenous processes can arise from fluctuation in the H_2O_2 concentration (COD) .

❖   **Fenton's Reagent:**

A mixture of hydrogen peroxide and ferrous or ferric ions , provides another source of hydroxyl radicals .under acid conditions (PH 3-5) this reagent is a powerful oxidant of organic compounds .

To achieve more power degradation source of UV/visible irradiation introduced.

The efficiency of any photochemical process depend on the quantum number , but to measure the quantum number to the (AOP's) is very hard because of the complexity of the reaction mixture , which is usually heterogeneous.

The reactions of degradation usually being a surface limiting reaction , therefore the observed constant rate of TiO_2 reaction for an organic substrate usually lows the saturated behavior .

It is important to start the process using TiO_2photocatalyst with the dilution , because of the competition between the intermediate and the substrate on the semiconductors' active sites.

Reaching to point at which the yield become constant , giving you an indicator that the concentration (COD) of the catalyst is optimum.

Many large experiments are made to remove atrazine by using TiO_2/UV where TiO_2 as coated fibers are used instead of TiO_2 powder. The disadvantage of using that catalyst is the necessary of filtration process after treatment to remove catalyst particles from treated water ,but it is difficult and expensive because sub micron filters are required .so, sedimentation process could be used as alternative one .

The reaction in Fenton's reagent is in two stages:

1.   the hydroxyl radical stage .

2.   redox recycling of Fe^{+3}- Fe^{+2} producing a Fenton catalyst in the reaction medium .

Fenton's reagent reactions depend on :

- the concentration (COD) of Fe^{+3} _ Fe^{+2}.

- the concentration (COD) of H_2O_2.

- the intensity of the used light .

- the concentration (COD) of Fe^{+3} _ Fe^{+2} should be ranged from 5mg/l To 15mg/l . and become as : $FeSO_4$ or $Fe(ClO_4)_{3.}$ or $FeCl_3.H_2O_2$

- the wave length needed here ⋋ (300-400)nm.

- The efficiency of the process is better in the acidic medium (PH=5) , where the PH value can be adjusting during the process by chelating reagent.

- Fenton reagent is sufficient for degradation of triazine herbicides and chloro acetanilide.

The iron salts may constitute a pollution source and its removal is recommended by neutralization to precipitate the dissolved iron as $Fe(OH)_{3.}$

A flate photo reactor could be used combined with (TiO_2/UV) , with $(1*0.3)m^2$ surface area ,UV light of six 36W- black light .

TiO_2 powder P25 with BET surface area 50+/- 15 m^2/g, average primary particle size 21 nm , purity > 99.5% and content of 83.9% anatase and 16.1% rutile was used as a photocatalyst.

Operating parameters for (TiO_2/UV)process are:

1.dosage of photo catalyst.

2. the structure of the reactor

3. flow rates through the flat –plate reactor

4.UV radiation intensity

5. titled angle of the reactor.

Most of the reactions of photo catalyst process is first order reaction and the rate of photo reaction is determinened by the film thickness of the fluid inside the reactor and the dosage of photo catalyst.

Optimum operating:

o Film thickness=1.4 mm

o TiO_2 dosage =1g/l.

o As the intensity of UV light increased the efficiency of the process will   increase.

- TiO_2 is the most often used photo catalyst due to its considerable photo catalytic activity , high stability , non- environmental impact and low cost.

- to over come the common difficulty of separating the used TiO_2 suspension after treatment precipitation followed with the filtration was used to determine the separation efficiencies.

- TiO_2 photo catalyst wasn't dissolved in water and very easy to be separated from solution , enabling it to be reused many times.

- TiO_2 in a small pillar pellet was made in Germany ranging from 2.5 to 5.3 mm long and with a diameter of 3.7 mm, and it is almost pure TiO_2 (83.2% anatase and 16.8% rutile), with a S – content of< 20ppm , and a Cl content of the order of 0.1 wt %.

- TiO_2 pellet performance is preferable in water treatment process than TiO_2 powder.

- TiO_2 catalysts (in powder form) are used directly as slurry in water or fixed (coated) on a carrier material.

- In fixation coating make the slurry –reactor system a preferable option with respect to photo catalytic degradation efficiency .

- Using TiO_2 pellet (2-4nm) is better than using TiO_2 powder because it is very easy to separate from the treated water since it doesent dissolve in water.

- A solar photo reactor , with flat plate structure was chosen , since it could use both direct and diffuse components of solar UV radiation , and has the potential for low cost development .

❖ **Experimental section:**

Chemical and instrument

The pesticide used in this study are Alpha – cyper methrin 10% , Hexa conazole 5% , Aver mectin 2.5 % , Triadimenol 10% , Lambda – cyhalothrin 5% and delta methrin 2.5% .

They are kindly supplied from, **VAPCO** factory (Jordan), and these are the same of wastewater which produced from this factory,

The equipments were used in this investigation involved a 5 liter liquid reservoir an ultraviolet radiation device typically has a stainless steel tube with a mercury vapor lamp inside the running the length of the tube , an ultraviolet light type **AQOAPRO** (USA) , the lamp power is 14 W and emit radiation basically at 253 nm. The pump was used **AMSTAR** type (USA), with a maximum flow rate 300 ml/min. Ozonator type ZPI(USA) , production power (0.17 g O_3 /h) . High – performance liquid chromatography HPLC .

❖ Procedure:

Different solution was prepared from each of the six pesticides with a concentration of 20ml of pesticides per liter distilled water is stored in a tank of 5 dm^3 capacity. These concentrations are similarly of those of wastewater which are produced from the factory .The solution was delivered from the tank by a pump through a soft plastic pipe of 5mm diameter the solution enters the UV source. The solution was circulated by gravity to the tank as shown in Fig. 1. For each solution was added 10 ml H_2O_2, H_2O_2 / UV. Three sets of experiments using the same solution of the same concentration : Fe(II) 10 mg/L then 10 ml H_2O_2, Fe(II) 10 mg/L, H_2O_2 //Fe^{+2}/UV and then ozone O_3/UV were conducted .

❖ Result and Discussion:

Figure 2 shows the effect of Fe^{+2}/UV on the degradation of different pesticides. It is evident from Fig. 2 that the concentration of all pesticides decreases during the first two hours from there exposure to the effect of Fe^{+2}/UV. However the extent of degradation differs from pesticide to another. For example the concentration of alpha-cyper methrin after two hours equals 25% of the initial concentration, and that of avramactin equal 33% of its initial concentration. This behavior could be attributed to the structure of these pesticides. Some pesticides are easily degradable compared to others due to there relatively meta-stable structure.

Figure 3 shows the effect of homogeneous system of H2O2/UV on the degradation of different pesticides. The behavior of degradation in this system is similar to that shown in figure 2. However, the concentration of all pesticides decreases to lower values under the effect of H_2O_2 /UV in the case of Fe^{+2}/UV and the degradation process occurs in a faster rate. For example, triadimentol concentration

decreases sharply 2 g/l to 0.05 g/l during the first two hours. This behavior indicates that pesticides are more sensitive to H_2O_2 than Fe^{+2} under the same conditions.

Figure 4 depicts the combined effect of Fe^{+2} / H_2O_2 /UV on the degradation of the same pesticides with the same concentration ranges. It is evident that the effect of Fe^{+2} /H_2O_2 /UV is more significant and the concentration of some pesticides like avramectin and deltamethrin after two hours of exposure approaches zero. In addition, the rate of degradation under the effect of Fe^{+2} H_2O_2 /UV increases compared to that in the case of Fe^{+2} /UV or H_2O_2 /UV.

Figure 5 shows the effect of O_3 /UV on the degradation of the same pesticides of the same concentration. It is clear the degradation power of O_3 /UV system is larger than that of Fe^{+2} /UV, H_2O_2 /UV and that of Fe^{+2} / H_2O_2 /UV .This indicates that ozone is stronger than the other agents as an oxidizing agent. For example the concentration of alpha-cyper methrin decreases from 2 to 1.25 in the first 30 minutes and to 0.21 g / l after two hours.

Conclusion:

Pesticides are among the most significant pollutants in wastewater. This wastewater plays important roles in the pollution of surface water and ground water. Recently, in Jordan, an attention starts to be paid to the studies of pesticides in water. One of the most interesting is started in the **VABCO** Company. Based on that, the main objectives of this proposal are concentrated on the **VABCO** wastewater and divided into four folds:

1-To reduce the pesticides pollutants from wastewater to reach a point where the regulations of Jordan in the environments can be applied.

2-To remove the effective compounds from wastewater.

3-To use the most efficient and economic method to treat the wastewater.

4-Reuse the wastewater treatment (either for the process of the **VABCO** company or for other applications)

Fig.(1):Photo Oxidation and Biological Treatment of Waste Water Device
1. Ozonator   2. UV Lamp
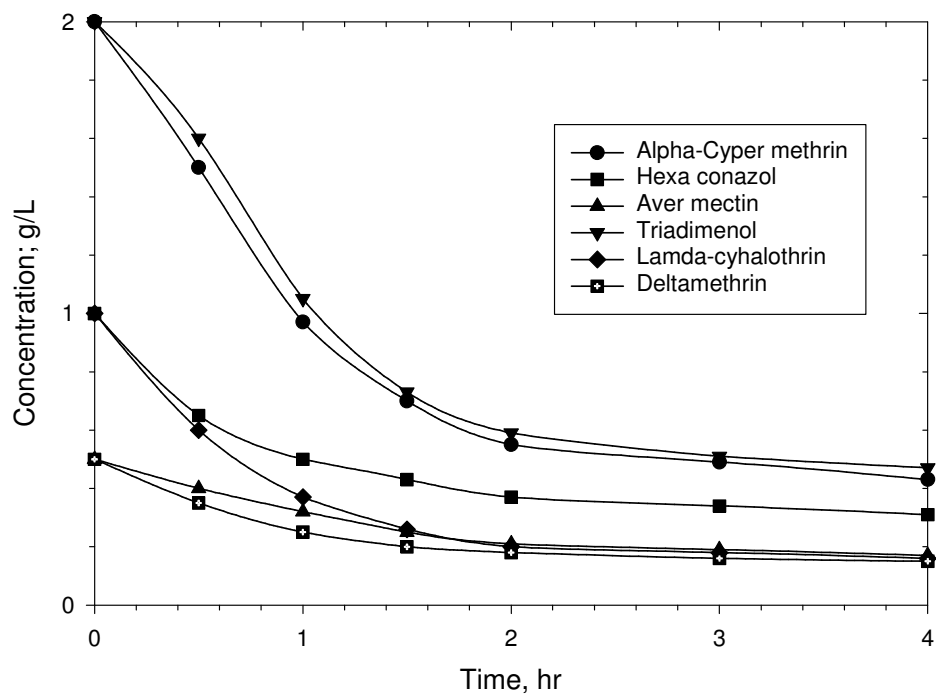   4. Reservover   3. Pump

Figure 2: Effect of Fe(II)/UV on the removal of on different
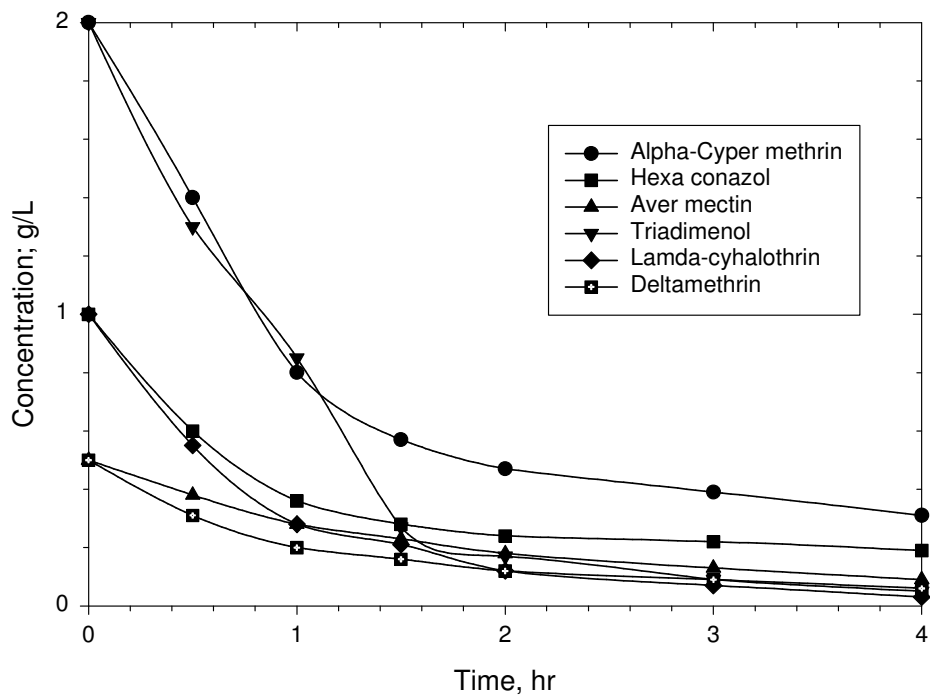
pesticides.

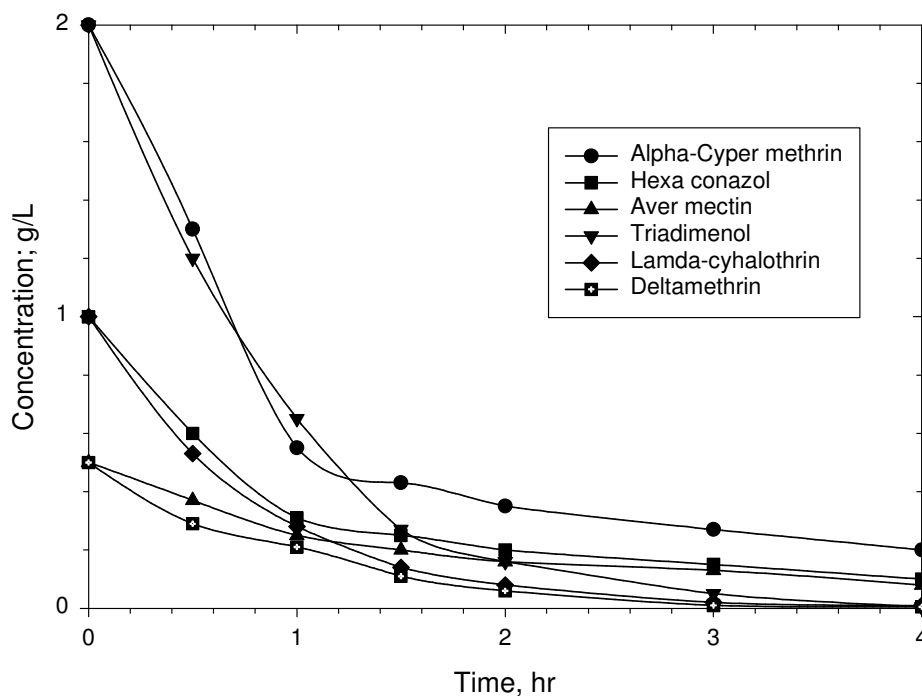Figure 3: Effect of H_2O_2/UV on the removal of on different pesticides.

Figure 4: Effect of Fe(II)/H$_2$O$_2$/UV on the removal of on different
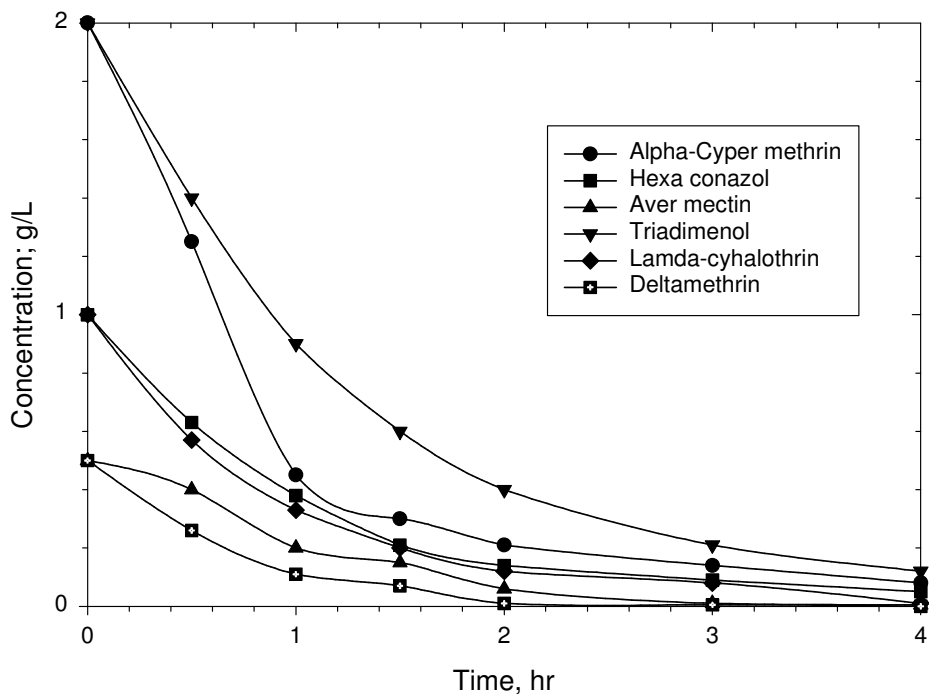
pesticides.

Figure 5: Effect of O$_3$/UV on the removal of on different pesticides.

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