Solar Photocatalytic Treatment of Pharmaceutical Wastewater

By

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FINAL PROJECT REPORT

Submitted to the Civil Engineering Programme
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CERTIFICATION OF APPROVAL

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Amir bin Ahmad Astor

A project dissertation submitted to the
Civil Engineering Programme
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Approved:

Malay Chaudhari

Prof. Malay Chaudhari
Project Supervisor

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK

June 2008

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

Amir Bin Ahmad Astor

ABSTRACT

The objective of the final year project is to provide an alternative for treating pharmaceutical wastewater using solar photocatalytic treatment. It has been demonstrated that the solar photocatalytic method can be an alternative to conventional methods of waste treatment which are much more complex and costly. The fact that the semiconductor can be activated by sunlight greatly reduces the use of electric power and hence the operating cost and time. Furthermore, the catalyst has the potential for reuse and the catalyst use is safe and nontoxic. There were two batches of sample taken from a pharmaceutical industry with initial chemical oxygen demand (COD) of 446 and 2052 mg/L. In the experiment, various dosage of zinc oxide was used, from 1g/L to 5g/L. The use of 3g/L zinc oxide resulted in around 70% and 24% of COD reduction when exposed to sunlight (0.75-0.1 kW/m^2) for 150 minutes, respectively. However, the results achieved was not as expected and did not meet the requirement the Malaysian discharge standard A and B. Several alternatives and improvements are listed to improve and achieve the objective of the project.

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CHAPTER 1

INTRODUCTION

1.1. Background of the Study

The pharmaceutical industry generates process wastewaters containing various pollutants, which depend on the nature of the processes by which the products are produced. Human and veterinary pharmaceutical compounds are a source of increasing environmental concern because they are used in large quantities and their physical and chemical properties make them likely to be transported into hydrologic systems.

The pharmaceutical wastewater is known to have high chemical oxygen demand (COD) and variable concentration of salts. Most pharmaceutical substances are manufactured utilizing batch processes where at the end of a manufacturing batch another pharmaceutical intermediate or substance is made, thus generating different waste streams. Furthermore, the environmental and health impacts on ecosystems and humans are uncertain because of lack of research and lack of evidence showing certain and visible impact to human health and environment.

Over the last decade, the Malaysian pharmaceutical market has grown at between 8 to 10% annually, with so little treatment option; the need of effective economic alternatives to treat the pharmaceutical wastewater is increasing. Conventional wastewater treatment approaches, for example, on-site conventional activated sludge (CAS) treatment combined with liquor clarification can successfully achieve the required contaminant reductions. However, the reliability of successful treatment using conventional approaches can be problematic. Industrial processes at pharmaceutical installations and the batch processing of wastewater give rise to specific challenges to wastewater treatment systems.

Levels of many pharmaceutically active compounds (PhACs) are barely reduced and they are, therefore, detected in wastewater treatment plant effluents. The presence of PhACs in surface, drinking, and wastewaters is well documented in the literature (Halling-Sørensen *at el.*, 1998; Kolpin *at el.*, 2002; Joss *at el.*, 2005; Metcalfe *at el.*, 2003; Castiglioni *at el.*, 2006; and Heberer, 2002). Although present at low concentrations in the environment, drugs can have adverse effects on aquatic organisms. These effects are chronic rather than acutely toxic, and depend on exposure (bioavailability), susceptibility to the compound in question, and the degradability of the compound (Jjemba, 2006).

1.2. Problem Statement

1.2.1. Problem Identification

The conventional approach for treating the wastewater can be used to successfully reduce the pollutants. For example, aerobic biodegradation processes with long hydraulic retention times has proven to be efficient for the treatment of pharmaceutical effluents; however, it can be difficult to use conventional activated sludge processes due to the unreliable operation of secondary clarifiers.

Another problem that arises with the treatment of pharmaceutical effluents is that the residual sludge is often considered a hazardous waste and is difficult and expensive to dispose of. With conventional treatment approaches, the high rate of sludge production can result in limited success in final clarification stages and subsequent problems with effluent solids loading.

In pharmaceutical wastewater treatment systems, batch processing can lead to sludge bulking and variations in dissolved solids content. This can result in destabilization of bacterial flocs and the subsequent loss of biomass into the final effluent, compromising the efficiency of COD removal in the process. Alternative treatment solutions for pharmaceutical wastewater clearly need to be considered (Noble, 2006).

1.2.2. Significance of the Project

This project may give an alternative method to treat the pharmaceutical wastewater in order to solve the problem with normal method. Additionally, the photocatalytic process has mild operating conditions and the fact that the semiconductor can be activated by sunlight can reduce significantly the electric power requirement and hence the operating cost.

1.3. Objective and Scope of the Study

1.3.1. The Relevancy of the Project

The objective of this project is to determine the effectiveness and suitable dosage of the catalyst used for solar photocatalytic treatment for pharmaceutical wastewater. The results of this project may show the reduction of chemical oxygen demand and the potential of repetitive use of the catalyst.

1.3.2. Feasibility of the Project within the Scope and Time Frame

The feasibility of the project within the scope and time frame is to get the best possible way to manage and complete the task given. Scope includes gathering all the information and theory on solar photocatalytic method, and work on the experiment using sample of wastewater taken from a pharmaceutical industry.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1. Solar Photocatalytic Treatment

Solar photocatalytic detoxification methods have recently shown great promise in the treatment of industrial wastewater, groundwater and contaminated air. Additionally, the semiconductor mediated photocatalytic process has also shown great potential for disinfection of air and water, thus making possible a number of applications (Peral *et al.*, 1997; Alfano *et al.*, 2000 and Malato *et al.*, 2003).

For certain semiconductors, especially the ZnO and TiO_2, by irradiation of with light energy level greater then the band gap energy level, conduction band electrons and valence band holes are produced. Part of the photogenerated carriers; recombine in the bulk of semiconductor, while the rest reach the surface, the valence band holes will act as powerful oxidant and the conduction band electrons act as reductant (Kositza *at el.*, 2004).

The valance band holes can either oxidize directly the organic molecules or react with water or hydroxyl ions (OH^-) which are adsorbed at catalyst surface to generate hydroxyl radicals (Malato *at el.*, 2004; Kositza *at el.*, 2004 and Saha and Chaudhari, 2003). These radicals with other highly oxidant species are reported to be responsible for the primary oxidizing step in photocatalytic detoxification. The hydroxyl radicals easily attack the adsorbed organic molecules or those located close to the surface of the catalyst, thus leading to their complete mineralization (Kositza *at el.*, 2004).

The photogenerated electron in the conduction band may react with oxygen by adsorbing the oxygen molecular to form superoxide ions. These ions can react with water and generate hydrogen peroxide and hydroxyl ions. Clearage of hydrogen peroxide by the conduction band electrons yields further hydroxyl radicals and hydroxyl ions. The hydroxyl ions can react with the valence band holes to form additional hydroxyl radical (Saha and Chaudhari, 2003). With the increase in the irradiation time, the number of absorbed photons is higher. Thus this will produce more amount of hydroxyl radicals (Parida and Parija, 2006), meaning more organic molecule will be mineralized.

There is also one reagent known as ferrioxalate reagent or fenton reagent, a mixture of Fe^{+2} salts and H_2O_2, which can easily oxidize organic compounds. It has been applied for water and soil treatment recently (Chamarro *et al.*, 2001; Bidga, 1995 and Lee and Hosomi, 2001). This reagent can produce hydroxyl radicals in a very simple way.

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

It is also possible to enhance the reaction with artificial or natural light (UV or VIS light) and also produce additional hydroxyl radicals, leading to regeneration of catalyst (Oliveros *et al.*, 1997; Fallmann *et al.*, 1999 and Arana *et al.*, 2001).

$$Fe^{+2} + H_2O_2 + hv \rightarrow Fe^{+2} + H^+ + OH^\bullet$$

These reaction are known to be the primary forces in photochemical self-cleaning of atmospheric and aquatic environment (Faust and Zepp, 1993).

2.2. Zinc Oxide

Zinc oxide occurs naturally as the mineral zincite. It has molar mass of 81.4 g/mol, density of 5.61 g/cm^3 and appears in white powder, Zinc oxide is for the most part insoluble in water; however, it is soluble in acids and alkalis. The zinc oxide used in many dye stuff today, from simple white pigments in paints to medical applications, and recently the zinc oxide also been used in researching new technology for treating many kind of wastewater.

Among the semiconductor-assisted photocatalysts, ZnO plays vital roles due to its high activity toward photocatalytic degradation and mineralization of environmental organic and inorganic pollutants (Li and Haneda, 2003 and Dindar and Icli, 2001). ZnO is a well known semiconductor oxide under and its photodegradation mechanism has been proven to be similar to that of TiO_2 although it shows less vigorous oxidation states (Dindar and Icli, 2001).

It is observed that higher quantum yield of hydrogen peroxide (H_2O_2) formation of zinc Oxide (ZnO) then by titanium dioxide (TiO_2) and lower steady state concentration of peroxide for titanium dioxide arises from a decreased quantum yield of peroxide formation combined with an enhanced degradation quantum yield (Kormann *et al.*, 1988 and Hoffman *at el.*, 1964).

Irradiation of three semiconductors (TiO_2, ZnO and Fe_2O_3) under concentrated sunlight have shown a vigorous photodegradation of phenol for all of the concentrations between 1×10^{-4} and 2×10^{-5}M. Phenol was completely degraded in less than 10 minuntes by TiO_2 and ZnO, and 12–27% phenol was left after 15 minutes of irradiation in presence of Fe_2O_3. A striking observation that can be seen in Figure 1- the photoreactivity of ZnO is higher than Fe_2O_3, and as reactive as TiO_2 under concentrated sunlight. A complete loss of the phenol fluorescence emission band is seen in irradiation with concentrated sunlight in presence of the ZnO photocatalyst (Dindar and Icli, 2001).

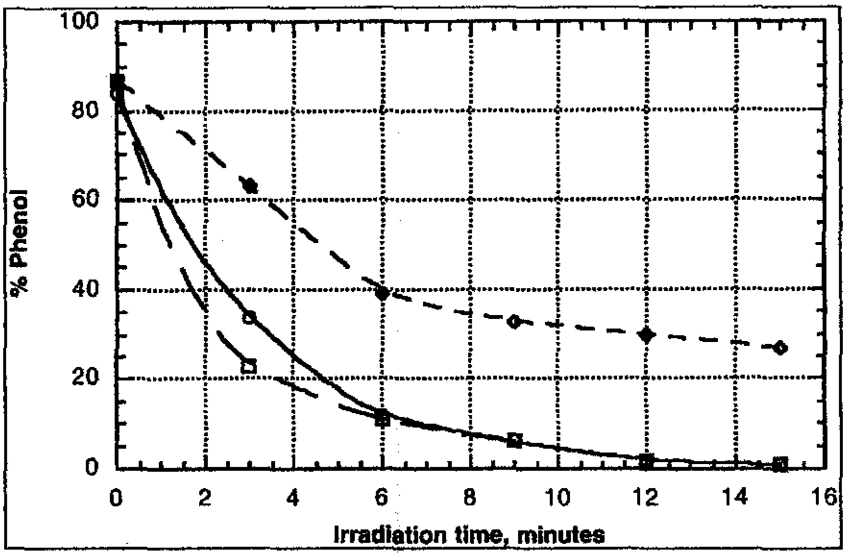

Figure 1. Degradation of phenol at an initial concentration of 1 x 10–4 M with TiO_2 (O); ZnO (□); Fe_2O_3 (◊) under concentrated sunlight

The ZnO fluorescence emission at 370 nm (λexc = 355 nm) at elevated temperatures (310–630 K), provided evidence for the potential photocatalytic capacity of ZnO even at very high temperature (Schubnell *at el.*, 1996). Combining these facts, one may infer that low-cost, polydisperse ZnO can replace TiO_2 as the main photoactive metal oxide used for solar purification of contaminated waters under concentrated sunlight. The employment of simple parabolic mirror to concentrate direct sunlight will prove to be an efficient and economical method for the removal of organic pollutants with aqueous ZnO suspensions (Dindar and Icli, 2001).

2.3. Pharmacuetical Wastewater

Pharmaceutical wastewaters are high in chemical oxygen demand (COD) and variable concentration of salts. Most pharmaceutical substances are, by nature, biologically active and hydrophilic in order that the human body can take them up easily, and persistent to avoid degradation before they have a curing effect. Depending on the pharmacology of a medical substance it will be excreted as a mixture of metabolites, as unchanged substance, or conjugated with an inactivating compound attached to the molecule (Halling-Sørensen *at el.*, 1998).

The pharmaceutical are manufactured in variety of processes; fermentation, chemical synthesis, extraction and other complex methods. Moreover, the pharmaceutical industry produces many products using different kind of raw material as well as processes; hence it is difficult to generalize its classification. Table 1. shows the classes of pharmaceutical product and typical examples (Wang *et al.*, 2004).

Table 1. Classes of Pharmaceutical Products and Typical examples

Classes	Subclasses with typical examples
Medicinal	Antibiotic (penicillins, tetracyclines)
	Vitamins (A, D, E, B, C)
	Anti-infective agent (sulphonamides)
	Central depression and stimulant
	Gastro-intestinal agent and therapeutic nutrients
	Hormones and substitutes
	Autonomic drug
	Antihistamines
	Dermatological agents-local anesthetics (salicylic acid)
	Expectorant and mucolytic agent
	Renal acting and endema reducing agent
Biologicals	Serums, vaccines, toxoids and antigens
Botanicals	Morphine, reserpine, quinine, curare, various alkaloids, codeine, and caffeine.

Based on the process involved in manufacturing, pharmaceutical industries can be subdivided into several major subcategories:

- Fermentation.
- Extractions.
- Chemical synthesis.

Wastewater generated from fermentations process discharge from reactor cleaning and sterilizations, off-gas scrubber effluents and off-specifications batches (Stephenson and Blackburn, 1998). These waste generated in this process called spent fermentation broth. One commercial ketone solvent has been reported as having a BOD of approximately 2kg/L or some 9000 times stronger then untreated domestic sewage. One thousand gallons of this solvent were calculated as equivalent in BOD to the sewage coming from a city of 77,000 people. The nature and composition of a typical spent fermentation broth is depicted in Table 2 (Wang *et al.*, 2004).

Table 2. Characteristic of a Typical Spent Fermentation broth

Composition	
Total solids	1-5 %
The total solids comprise	
Protein	15-40 %
Fat	1-2 %
Fibers	1-6 %
Ash	5-35 %
Carbohydrate	5-27 %
Steroids, antibiotics	Present
Vitamin content of the solids	Thiamine, Riboflavin, Pyridoxin, HCl, Folic acid at 4-2,000 µg/g
Ammonia, N	100-250 mg/L
BOD	5,000-20,000 mg/L
pH	3-7

Wastewater generated from extraction process may come from spent raw material, solvent used in extraction and spills and equipment wash waters. Meanwhile, in chemical synthesis process generated highly variable as are the processes which they are generated. Such as, process solutions, vessel wash waters, filtrates, concentrates, spent solvent and scrubber effluents. Additionally, from pump seal water, spills and cleaning wash water, this may contain significant concentration of volatile organics (Stephenson and Blackburn, 1998). A typical example of untreated synthetic organic chemical waste for a pharmaceutical plant located in India is given in Table 3. (Wang *et al.*, 2004).

Table 3. Characteristic if Untreated Synthetic Drug Waste

Parameter	Concentration range (mg/L)
p-amino phenol, *p*-nitrophenolate, *p*-nitrochlorobenzene	150-200
Amino-nitrozo, amino-benzene, antipyrene sulfate	170-200
Chlorinated solvents	600-700
Various alcohols	2,500-3,000
Benzene, toluene	400-700
Sulfanilic acid	800-1,000
Sulfa drugs	400-700
Analogous substances	150-200
Calcium chloride	600-700
Sodium chloride	1,500-2,500
Ammonium sulfate	15,000-20,000
Calcium sulfate	800-21,000
Sodium sulfate	800-10,000

Although wastewater stream from all process have the potential to contain high organic loading, fermentation and synthesis usually generate larger volume of wastewater and the wastewater generated usually contain higher organic loading. An estimated 84% of the organic compounds are recycled and 16% are waste organics. Approximately 2.7 % of the waste organics are discharged to sewer (Stephenson and Blackburn, 1998).

The pharmaceutical wastewater components may consist of prescription drugs, medications, and hormonal substances, over-the-counter medications, human antibiotics and last but not the least veterinary antibiotics (Lewis and Zaugg, 2003). A number of common pharmaceuticals are regulated as hazardous chemical waste. Table 4. shows the common pharmaceutical regulated as hazardous chemical waste

Pharmaceutical waste that exhibit one or more of the EPA characteristics of a hazardous chemical waste are also regulated as a hazardous chemical waste. These characteristics are:

- Corrosivity
- Ignitability
- Reactivity
- Toxicity

Table 4. Common pharmaceuticals are regulated as hazardous chemical waste

Arsenic Trioxide	Epinesphrine	Nitroglycerine	Selenium sulfide
Chloroform	Formaldehyde	Phenacetine	Streptozotcin
Chorambucil	Hexachlorophene	Phenol	Uracil Mustard
Cyclophosphamide	Lindane	Physostigimine	Warfin >0.3%
Dauomycin	Mephalan	Reserpine	
Dicholodifluoromethene	Mitomycin C	resorcinol	
Diethylstilbestrol	Nicotine	Saccharin	

Environmental, Health and Safety, Univercity of California-Irvine (www.ehs.uci.edu)

2.4. Treatment of Pharmaceutical Wastewater

2.4.1. Activated Sludge

Biological treatment removed on the average 90% of influent COD. Removal of phenol was 47% with average effluent phenol concentration of 36 mg/L for the oxidation ditch operated at two COD removal rates of 0.19 and 0.21/day. This shows that only half of the phenol could be removed during biological oxidation.

An estimate of bacteria yield coefficient for treatment of pharmaceutical wastewater was 0.75 mg VSS/mg COD. This value of yield coefficient is much higher than normally encountered in activated sludge treatment of domestic wastes. It is suspected that the higher value of yield coefficient could be because of prolific growth of bacteria at higher

F/M ratios. This suggests that the wastewater was rich in all nutrients required for the proper growth of bacteria and there was no inhibition by phenol (Mayabhate *at el.*, 1988).

2.4.1. Membrane Bioreactor (MBR)

The performance this type of treatment for long-term operational stability of the system and possible effects of solids retention time on the efficiency of removal of target compounds. Pharmaceuticals were, in general, removed to a greater extent by the MBR integrated system than during the conventional activated sludge (CAS) process. For most of the compounds investigated the performance of MBR treatment was better (removal rates >80%) and effluent concentrations of, examples diclofenac, ketoprofen, ranitidine, gemfibrozil, bezafibrate, pravastatin, and ofloxacin were steadier than for the conventional system. Occasionally removal efficiency was very similar, and high, for both treatments (Radjenovic *at el.,* 2007).

2.4.2. ZeeWeed Membrane Bioreactor

Advanced wastewater treatment technologies such as ZeeWeed membrane bioreactor (MBR) systems offer a highly efficient, compact, and reliable alternative to CAS systems. ZeeWeed MBR, manufactured by Zenon Membrane Solutions, a part of GE Water and Process Technologies, eliminates multiple process steps of CAS systems, combining clarification, aeration, and filtration into a single process step.

Durable reinforced hollow fibre membranes are specifically designed to operate in a high solids environment and produce near drinking-water quality effluent in a fraction of the space and time of CAS systems (Noble, 2006).

2.4.3. Photocatalytic Treatment Using Titanium Dioxide

Figure 2- a 3-D representation of the polynomial obtained from the experimental data in heterogeneous photocatalytic degradation of pharmaceutical agent salbutamol in aqueous titanium dioxide suspensions. The coordinates of the graph show the TiO_2 concentration

and pH level. The vertical axis represents the salbutamol degradation (%) after 30 min of light irradiation during the photocatalytic process.

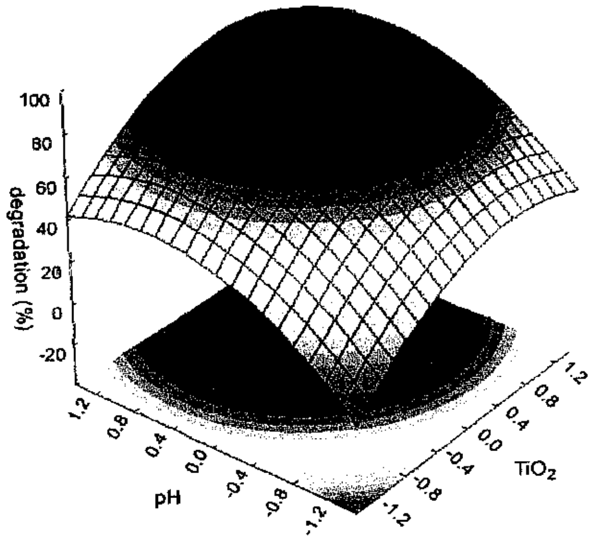

Figure 2. Response surface showing the effect of TiO2 concentration and pH on the degradation rate expressed as salbutamol (%) after 30 minutes irradiation

It is observed that the degradation rate increases proportionally to TiO_2 concentration (up to 600 mg/L), as expected, confirming the positive influence of the increased number of TiO_2 active sites on the process kinetics. At higher catalyst loading (higher than 600 mg/L), a slight decrease of salbutamol degradation (%) was observed, irrespective of the initial pH value. The availability of active sites increases with catalyst loading, but the light penetration, and hence, the photoactivated volume of the suspension shrinks. Similar observations have been also reported in other studies on various organic substances. This phenomenon may also be attributed to the aggregation of titania particles at high concentrations, causing a decrease in the number of surface active sites. In addition, the decrease on the degradation rate at higher catalyst loading may be due to deactivation of activated molecules by collision with ground state molecules (Sakkas, *at el.*, 2007).

CHAPTER 3

METHODOLOGY AND HAZARD ANALYSIS

3.1. Experimentation

The experimentation will consist of preliminary experiment and detailed experiment. Allow familiarization of the project and assessment of the feasibility of treatment. It will also help in gaining the skill to run the experiment and tackling down problems that may arise.

The preliminary experiment will be done by following method:

1. The quality of the pharmaceutical wastewater sample was measured using the COD test.
2. 200 mL of the sample was taken in a 500 mL beaker.
3. 1 g/L of ZnO was added and kept in suspension by constantly stirring using a magnetic stirrer and exposed to sunlight.
4. A 20 mL aliquot was taken out at interval of 30 minutes, and COD was measured.
5. The sunlight intensity was recorded.

The detailed experimentation will be done by following method:

1. Water quality of sample taken from the pharmaceutical wastewater was measured using chemical oxygen demand (COD) test.
2. 200 mL of the sample was taken in a 500 mL Borosil glass beaker, one control sample was used (without ZnO added into the sample)

3. 1 g/L of Zinc oxide was added and kept it in suspension by constantly stirring and exposed to the sunlight.
4. A 20 mL of the sample was taken at specific intervals and measure the COD. Record the result obtained. (before measuring the COD sample will be filtered with 0.45 µm filter paper) COD measurement for the second batch sample had to be diluted to 1:10 before running the measurement process.
5. The experiment then repeated with other dosage of ZnO: 2 g/L, 3 g/L and 4 g/L.
6. The sunlight intensity was recorded.

3.2. Tools and Material

Tools:

- Environment laboratory apparatus.
- Solarimeter.
- Magnetic stirrer.

Materials that may be use are:

- Pharmaceutical wastewater collected from Pharmaniaga Manufacturing Berhad.(Bangi).
- Zinc oxide.
- 0.45 µm filter paper.

3.3. Hazard Analysis

The result of a hazard analysis is the identification of potential risks and the selection of means of controlling or removing them. In this particular project, the used of pharmaceutical wastewater and chemical substance or semiconductor, ZnO, hazard analysis also include the knowing the effects, behaviors, chemical and physical properties.

3.3.1. Pharmaceutical Wastewater Hazard Information

There are many chemical and pharmaceutical compounds used in research or in the treatment of diseases that are also considered by the EPA to be hazardous wastes when disposed of. Pharmaceutical substances are designed to affect human metabolism at very low concentrations, this potency does not necessarily change when a chemical enters the waste stream where an active ingredient in a discarded drug could act on an unintended target. The toxicity of pharmaceutical formulations can present both occupational and environmental hazards.

1. Antineoplastic agents (the type of drug most often used in chemotherapy) are extremely toxic designed to kill dividing cells.
2. Some radioactive compounds are used for the same purpose or are used as tracers or markers.
3. Nitroglycerin causes blood vessels to dilate and can be used to treat chest pain, but it is also well known for its explosive properties.
4. Flammability hazards are common for drugs that use alcohol-water mixture for solubility so the drug can be administered in liquid form. These and other solvents can pose a fire hazard (ignitability).
5. Preservatives and other ingredients can pose a toxicity hazard over and above the effect of the main active ingredient.

3.3.2. Handling the Pharmaceutical Wastewater

1. Use glove and additional cautious in handling the sample to avoid direct contact.
2. If sample contacts the skin, flush the affected areas with water, followed by washing with soap and water.

3. Clothing contaminated with zinc oxide should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing. Persons laundering the clothes should be informed of the hazardous properties of zinc oxide.

3.3.3. Zinc Oxide Hazard Information

The National Institute for Occupational Safety and Health (NIOSH) has established recommended exposure limits (RELs) for zinc oxide of 5 mg/m^3 for total dust as a time weighted average (TWA) for up to a 10-hour workday and a 40-hour workweek and a 15 minute ceiling of 15 mg/m^3 (NIOSH 1992). Exposure to zinc oxide can occur through inhalation, ingestion, and eye or skin contact.

Even though ZnO just a nuisance dust, exposed to high concentrations of ZnO can result in respiratory system effects in humans. Inhalation of zinc oxide fume can result in metal fume fever. This is a self limiting condition characterized by flu-like symptoms which resolve within 24 to 48 hours. Repeated exposures to zinc oxide by skin contact have resulted in papular-pustular skin eruptions in the axilla, inner thigh, inner arm, scrotum and pubic areas. Epidemiologic studies of zinc refinery workers found no correlation between industrial zinc exposures and lung or other types of cancer. (ACGIH 1991)
There are several symptoms and sign of expose toward ZnO.

Acute exposure	-Resulting in coughing, substernal pain, upper respiratory tract irritation, rales, chills, fever, nausea, and vomiting.
Chronic exposure	-Resulting in papular-pustular skin eruptions in the axilla, inner thigh, inner arm, scrotum and pubic areas.

3.3.4. Handling the Zinc Oxide

1. If zinc oxide contacts the skin, flush the affected areas with water, followed by washing with soap and water.
2. Clothing contaminated with zinc oxide should be removed immediately, and provisions should be made for the safe removal of the chemical from the clothing.

Persons laundering the clothes should be informed of the hazardous properties of zinc oxide.

3. Person who handles zinc oxide should thoroughly wash hands, forearms, and face with soap and water before eating, using tobacco products, using toilet facilities, applying cosmetics, or taking medication.
4. Do not eat, drink, use tobacco products, apply cosmetics, or take medication in areas where zinc oxide or a solution containing zinc oxide is handled, processed, or stored.

CHAPTER 4

RESULTS AND DISCUSSION

Table 5. Characteristic of pharmaceutical wastewater

Parameter	Concentration
BOD5 (mg/L)	273
COD (mg/L)	446 - 2052
Soluble COD (mg/L)	454
TSS (mg/L)	24
TVSS (mg/L)	22
NO_3-N (mg/L)	3.18
NH_3-N (mg/L)	2.73
Total Phosphorous (mg/L)	7.33
Turbidity (NTU)	30
pH	2.89 - 4

4.1. Preliminary Experiment

The preliminary experiment was done using a zinc oxide dose of 1.0 g/L and exposed to the sunlight with intensity from 0.2 to 0.4 kW/m^2 for 120 minutes. In Figure 3. shows that about 50% COD reduction occurred in 30 minutes. The final COD was 218 mg/L, showing that this treatment has great potential for treating the pharmaceutical wastewater. Presumably, partial mineralization of the wastewater and other chemicals occurred.

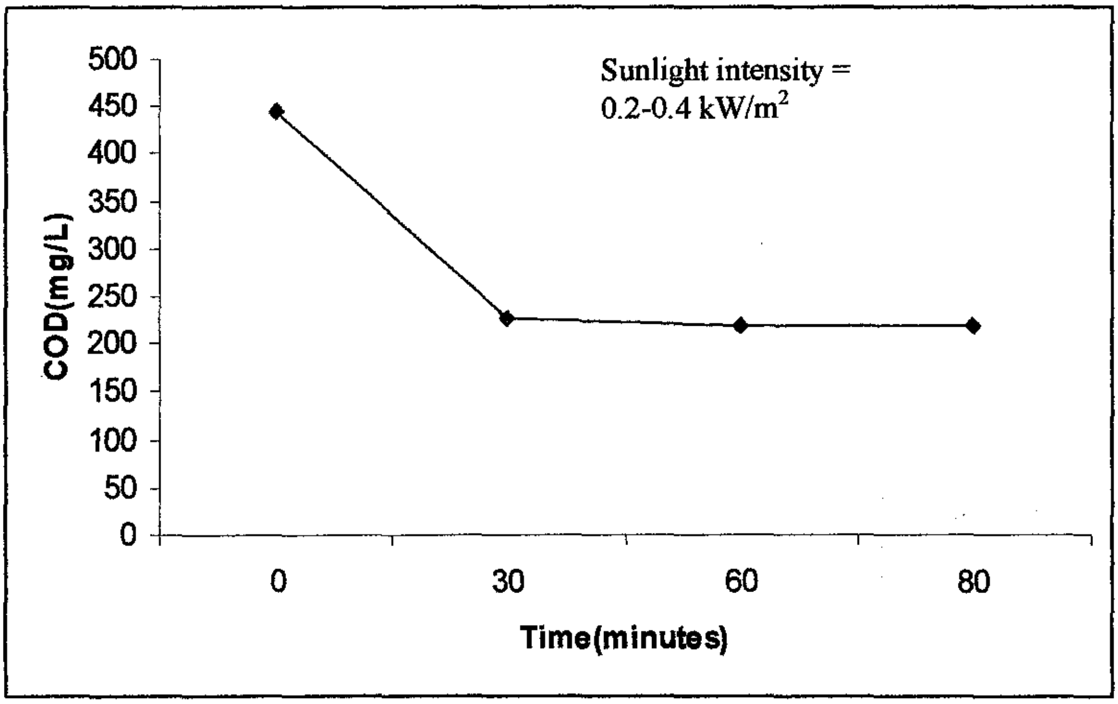

Figure 3. Preliminary experiment of Solar photocatalytic treatment

4.2. Detailed Experiment

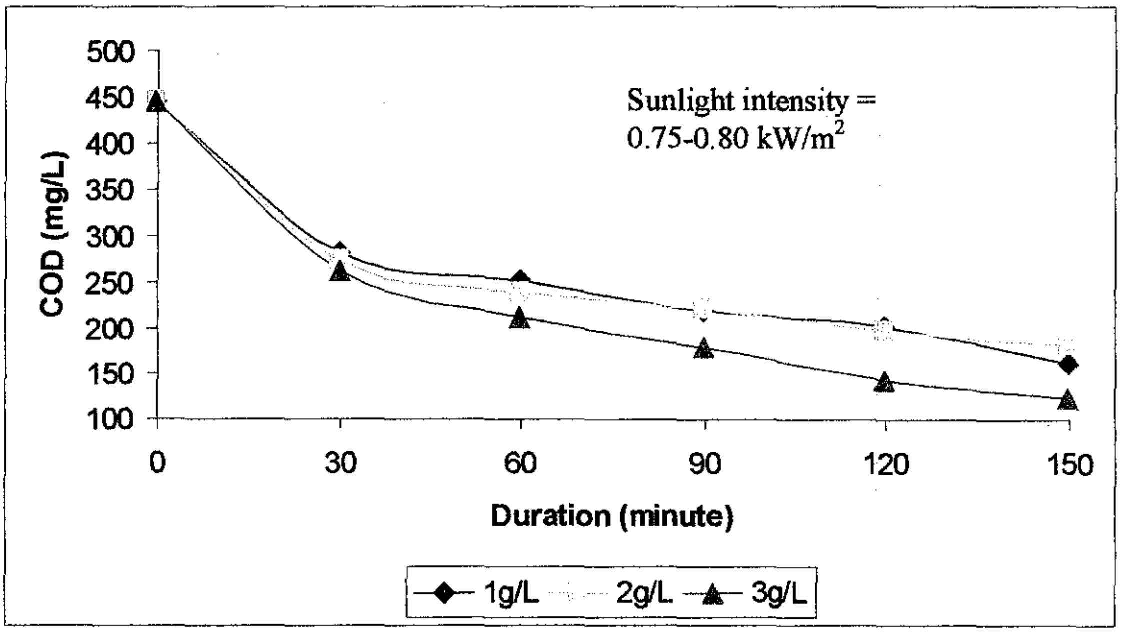

Figure 4. Detail experiment of solar photocatalytic treatment with ZnO, dosage of 1g/L, 2g/L and 3g/L

In Figure 4. showing the result for the detailed experiment. The result was obtained by exposing the sample under the sunlight (0.75-0.80 kW/m^2) for 150 minutes using varies of zinc oxide dosage. The COD reduction for 1g/L dosage was about 60% reduction and same goes with 2g/L dosage. Mean while, for 3g/L it was around 72% of reduction. Comparing the result of the preliminary experiment with the detailed experiment, the reduction of COD is increasing by 10% in using 1g/L dosage of zinc oxide. The different may cause for higher sunlight intensity.

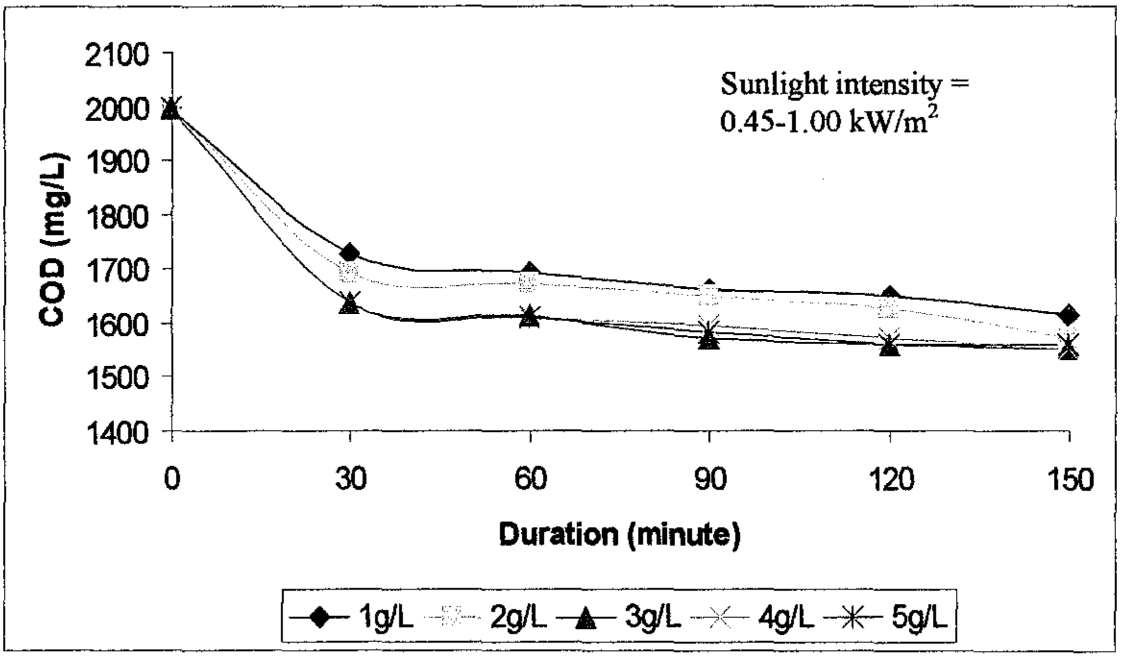

Figure 5. Detail experiment of solar photocatalytic treatment with ZnO using second batch sample taken from the pharmaceutical factory, dosage from 1g/L to 5g/L

The concentration of COD reduction using second batch sample taken from the factory is shown in Figure 5. In 30 minute the COD reduction was around 18 – 20% under the sunlight intensity 0.45-1.00 kW/m^2. Prior to the experiment the sample was diluted with ratio of 1:10. Comparing the 3g/L with 5g/L of ZnO, shown that the COD reduction at 5g/L slightly lower then 3g/L. However, from the observation using 5g/L dosage the sample were in very milky like and probably there some ZnO not fully utilized where the sunlight was unable to penetrate deep in the sample.

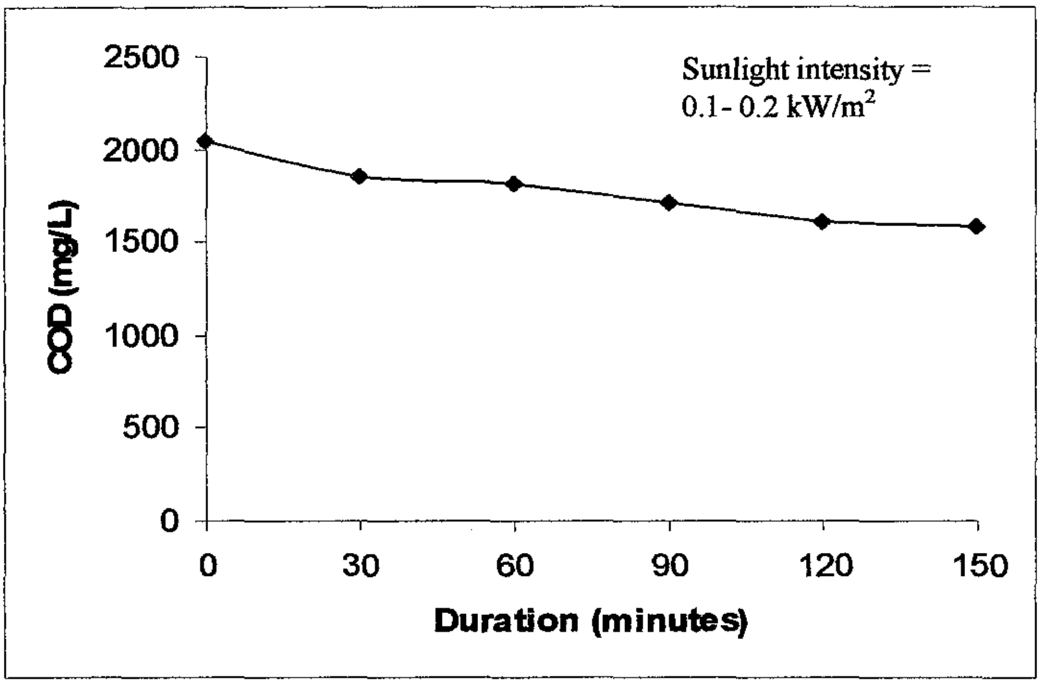

Figure 6. Results of solar photocatalytic treatment of second batch sample using 3g/L of ZnO and 1mL of H_2O_2

Due to unpromising result from the second batch sample, the detailed experiment has been modified by adding 1mL of hydrogen peroxide. The result of the detailed experiment modified by adding 1mL is shown in Figure 6. After 150 minutes of exposing, the experiment reduces about 23% of the COD. However, the experiment where run under sunlight intensity of 0.1-0.2 kW/m^2, which is low comparing with the others, detailed experiment.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The solar photocatalytic treatment of pharmaceutical wastewater was divided into preliminary experiment and detailed experiment. There were two batch samples taken from the same pharmaceutical industry. The first batch sample had an initial COD of 446 mg/L. In 30 minute the COD reduction was around 72% under a sunlight intensity 0.45-1.00 kW/m^2. The second batch sample had an initial COD of 2052 mg/L. In 30 minute the COD reduction was around 18 – 20% under a sunlight intensity 0.75-0.8 kW/m^2.

5.2. Recommendations

The results of this project was not as expected and did not meet the requirement of Malaysian discharge standard A and B, which are COD 50 mg/L and 100 mg/L, respectively. Below are the lists of possible alternatives that will improve the solar photocatalytic treatment for the pharmaceutical wastwater.

1. Instead of using ZnO, the experiment also can be done using titanium dioxide or Fenton reagent. Both of these semiconductors are know to successfully treat other type of wastewater.

2. Throughout the project it clearly shown that the sunlight intensity was inconsistent. Thus it is suitable to use an artificial solar light or using UV-reactor. The suitable irradiation intensity would be around 075-0.8 kW/m^2.

3. The wastewater sample can be pretreated with alum coagulation and flocculation process prior to the detailed experiment.

In industry the waste produced are in batches that may have different concentration of pollutant for each batch. Thus the solar photocatalytic treatment can be used as pretreatment for biodegradability treatment. This type of process for treating pharmaceutical wastewater using semiconductor oxidation prior to the degradability treatment has been done, where the applicability of Fenton's oxidation for the pretreatment of pharmaceutical effluent originating from medium scale drug manufacturing plant producing various antiseptics and disinfectant solutions, followed by aerobic sequencing batch reactor (SBR) (Tekin *at el.*, 2006)

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APPENDICES

Table A- 1. Results of first batch sample.

Dosage (g/L)	Duration (minutes)	Chemical Oxygen Demand (COD) (mg/L)
1	0	446
	30	283
	60	252
	90	219
	120	202
	150	162
2	0	446
	30	274
	60	240
	90	221
	120	198
	150	182
3	0	446
	30	263
	60	214
	90	180
	120	143
	150	124

Table A- 2. Results of second batch sample.

Dosage (g/L)	Duration (minutes)	Chemical Oxygen Demand (COD) (mg/L)
1	0	2052
	30	1727
	60	1694
	90	1661
	120	1650
	150	1617
2	0	2052
	30	1694
	60	1672
	90	1650
	120	1628
	150	1573
3	0	2052
	30	1639
	60	1617
	90	1573
	120	1562
	150	1551
4	0	2052
	30	1639
	60	1612
	90	1595
	120	1573
	150	1551
5	0	2052
	30	1639
	60	1612
	90	1584
	120	1562
	150	1562

Table A- 3. Result of second batch sample using 3g/L of ZnO and 1mL H_2O_2

Dosage (g/L)	Duration (minutes)	Chemical Oxygen Demand (COD) (mg/L)
3	0	2052
	30	1848
	60	1815
	90	1705
	120	1606
	150	1584

Table A- 4. Malaysia discharge standard A and B

Parameters	Units	Standard	
		A	B
Temperature	°C	40	40
pH	-	6.0 - 9.0	5.5 - 9.0
BOD5 @ 20°C	mg/l	20	50
COD	mg/l	50	100
Suspended Solids	mg/l	50	100
Mercury	mg/l	0.005	0.05
Cadmium	mg/l	0.01	0.02
Chromium, Hexalent	mg/l	0.05	0.05
Arsenic	mg/l	0.05	0.10
Cyanide	mg/l	0.05	0.10
Lead	mg/l	0.10	0.50
Chromium, Trivalent	mg/l	0.20	1.0
Copper	mg/l	0.20	1.0
Manganese	mg/l	0.20	1.0
Nickel	mg/l	0.20	1.0
Tin	mg/l	0.20	1.0
Zinc	mg/l	1.0	1.0
Boron	mg/l	1.0	4.0
Iron (Fe)	mg/l	1.0	5.0
Phenol	mg/l	0.001	1.0
Free Chlorine	mg/l	1.0	2.0
Sulphide	mg/l	0.50	0.50
Oil and Grease	mg/l	Not Detectable	10.0

Figure A- 1. Solarimeter

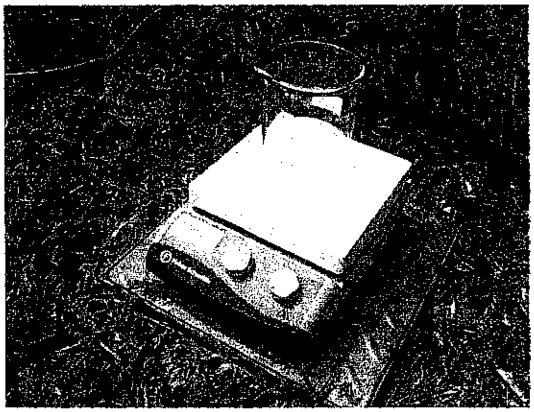

Figure A- 2. Experimental setup