Design of Solar Parabolic Collector for the Treatment of Textile Wastewater by Solar Photo-Fenton Process

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ABSTRACT

Design of Solar Parabolic Collector for the Treatment of Textile Wastewater by Solar Photo-Fenton Process

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This project presents a simple bench scale design of one of solar collectors a tubular parabolic type. This collector is designed for the collection of ultraviolet radiation from sun light to be used for the field of photocatalytic oxidation processes for water and wastewater treatment. Homogeneous and heterogeneous photocatalytic oxidation processes consider promising techniques for treatment of wastewater containing very toxic and recalcitrant pollutants which are not being able to be degraded or oxidized with the classic and traditional water treatment processes. The basis of these processes depend on the generation and production of free hydroxyl radicals the powerful oxidizing agents which are able to oxidize these strong pollutants with a high efficiency and low costs and convert them to friendly by-products. In our study an aqueous solution of dye was selected as an example of industrial wastewater generated from the textile industry which is famous with its toxic characterization since the dyes consider very refractory and permanent matters.

Several parameters were studied such as the type of the photocatalyst, the effect of initial dye concentration, the dose of the photocatalyst, pH values of the aqueous solution, addition of oxidant and irradiation time. Trials also were carried out to enhance the behaviour of the photocatalyst by addition of Bentonite.

The experimental results proved the high efficiency with this technology. The experimental results show high percentage of both colour and COD removal which it means that the treated water not only reached the limit values of its discharge according to the environmental laws and legislations but also it means that the treated water can be reused in industrial and irrigation purposes. This technology considers an economic technique, since the electrical UV lamps are replaced with natural sunlight and consequently the costs of electrical and power consumption are much reduced.
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الملخص بالعربي

تصميم لمجمع شمسي لمعالجة مخلفات مصانع النسيج

(بفترة الفنتون الضوئي المحفزة)

يعرض هذا المشروع تصميم بسيط على نطاق مقعد واحد لجمع الطاقة الشمسية من نوع مكافئ أنبوبي.

تم تصميم هذا المجمع لجمع الأشعة فوق البنفسجية من ضوء الشمس لاستخدامها في مجال عمليات الأكسدة ب (فوتوكاتاليت). للمياه و معالجة مياه الصرف الصحي.

لعمليات الأكسدة ب (فوتوكاتاليت) المتجانسة وغير المتجانسة نظرًا في التقنيات الواعدة لمعالجة مياه الصرف الصحي التي تحتوي على ملوثات سامة جداً وعديدة والتي لا تكون قادرة على أن تتحلل أو تتأكسد مع عمليات معالجة المياه الكلاسيكية والتقليدية.

أساس هذه العملية تعتمد على توليد و إنتاج جذور (الهيدروكسيل) الحرة المؤكسدة القوية لحمض الأمين، و تكوين كفاءة عالية و تكاليف منخفضة و تحويلها إلى صديقة من المنتجات.

في دراستنا تم اختيار محلول مائي مصبغ كمثال المياه العادية الصناعية الناتجة عن صناعة الغزل والنسيج.

تمت دراسة العديد من المفاعلات مثل نوع الحفاز الضوئي ، وتأثير تركيز الصباغ الأولية، وجرعة من الحفاز الضوئي ، وقطر اليدروجيني للحلول المائية، إضافةً إلى فحص وقت التشبع وأجريت تجارب أيضاً لتعزيز سلوك الحفاز الضوئي عن طريق إضافة (البنتونيت).

وتكون هذه التكنولوجيا تقنية اقتصادية، حيث يتم استبدال مصابيح الأشعة فوق البنفسجية الكهربائية مع ضوء الشمس الطبيعي، وبالتالي تكاليف استهلاك الطاقة الكهربائية و يتم تخفيف بكثير.
CHAPTER (1)

INTRODUCTION

One of the characteristics that best define today’s society in what is understood as developed countries is the production of waste products. There is practically no human activity that does not produce waste products and in addition there is a direct relationship between the standard of living in a society or country and the amount of waste products produced. Approximately 23% of the world’s populations live in developed countries, consume 78% of the resources and produce 82% of the waste products [1]. In addition, it has to be pointed out that the volume of residual waste increases in an exceptional way with regards to a country’s level of industrialization. At present, there are some five million known substances registered, of which approximately 70,000 are widely used worldwide, and it is estimated that 1,000 new chemical substances are added to the list each year.

The need for sustainable growth is countered by the reality of demographic growth. Many countries are experiencing a period of non-sustainable growth, with very variable macroeconomic achievements in the various countries. Even in the case where some countries have achieved a beneficial macroeconomic progress, these achievements are not reflected in the standard of living and quality of life of large sections of the population. These large contrasts are reflected in the problems related to the rational management of water, which cannot be dealt with in a unilateral way, but by many different procedures. A recent publication [2] describes in a generic form the problems that societies have had to face regarding water use as the society evolved. The countries with sustainable development have, one by one, confronted the problems related to biological contamination, with the
levels of heavy metals, with the intensive use of nutrients, and with organic contaminants at very low levels. Water disinfections, the treatment of effluents before being discharged into water systems, the limitation and substitution of nitrates and phosphates in products that are used on a massive scale, and the development in analytical chemistry and in ecotoxicology are examples of some of the “tools” used to combat these problems.

Up until relatively recently, the discharging of waste in the environment was the way of eliminating them, until the auto-purifying capacity of the environment was not sufficient. The permitted levels have been vastly exceeded; causing such environmental contamination that our natural resources cannot be used for certain uses and their characteristics have been altered. The main problem stems from waste coming from industry and agriculture, despite the fact that the population also plays an important role in environmental contamination. Phenols, pesticides, fertilizers, detergents, and other chemical products are disposed of directly into the environment, without being treated, via discharging, controlled or uncontrolled and without a treatment strategy.

In this general context, is very clear that the strategy to continue in the search of solutions to this problem that every day presents a sensitive growth, mainly in the developing countries, it will be guided to two fundamental aspects:

- The development of appropriate methods for contaminated drinking, ground, and surfaces waters, and mainly
- The development of appropriate methods for wastewaters containing toxic or non-biodegradable compounds.

Textile processing is one of the most important industries in the world and it
employs a variety of chemicals, depending on the nature of the raw material and product. Some of these chemicals are different types of enzymes, detergents, dyes, acids, sodas and salts. The discharge of wastewaters that contains high concentration of reactive dyes is a well-known problem associated with dyestuff activities [3]. Wastewaters from textile and dye industries are highly colored with significant amount of auxiliary chemicals. The discharge of these wastewater introduced intensive color and toxicity to aquatic environment causing serious environmental problem [3]. Reactive dyes are widely used in the textile industries because of its simple dyeing procedure and good stability during washing process [4]. Due to the complex aromatic structure and stability of these dyes, conventional biological treatment methods are ineffective for degradation [5]. Hence, the concentration remains constant in the environment.

A number of physical and chemical techniques had been reported for the treatment of dye effluents. Among these, the advanced oxidation processes are more efficient as they are capable of mineralizing a wide range of organic pollutants. All existing water treatment processes, currently in use, have limitations of their own and none is cost-effective.

In recent years, heterogeneous photocatalysis [6,7] that couples low energy ultraviolet light with semiconductors acting as photocatalysts has emerged as a viable alternative for the traditional and conventional water treatment methods for the removal of organic pollutants in water and air [8]. The appeal of this process technology is the prospect of complete mineralization of the pollutants into a harmless compound [9].

The artificial generation of photons required for the detoxification of polluted water is the most important source of costs during the operating of
photocatalytic waste water treatment plants. This suggests using the sun as an economically and ecologically sensible light source. With a typical UV-flux near the surface of the earth from 20 to 30 W/m² the sun puts 0.2 to 0.3 mol photons/m²h in the 300 to 400 nm range at the process disposal [10]. The treatments processes of different types of effluents to be used must guarantee the elimination or recuperation of the pollutant in order to reach the strict authorized levels for the discharge of these effluents. The levels of pollutants allowed in discharge waters, are directly related with the type of present pollutant in the effluent.

In general, the elimination of organic pollutants in aqueous solution need one or various basic treatment techniques [11]: chemical oxidation, air desorption, liquid-liquid extraction, adsorption, inverse osmosis, ultra-filtration and biological treatment. Depending on the present compound in solution the methods to use can be destructive as for example, chemical oxidation, incineration or degradation, which only allow the efficient elimination of the pollutant from an aqueous form; and the non-destructive methods, among which is liquid-liquid extraction and absorption, that allow the recuperation of the pollutant. On the other hand, the application of one or other of the methods depends on the concentration of the effluent. It is necessary to choose the most adequate method according to the characteristic of the concentration.

Once again, it has to be chosen between those techniques, which are useful for high concentrations of pollutants, like incineration or some chemical oxidation methods, and those techniques for low concentrations of pollutants, for example adsorption, membrane techniques, and some chemical oxidation methods as well. The choice of one or other of the
methods basically depends on the cost of the process and other factors like the concentration and volume flow of the effluent to be treated.

In recent years advanced oxidation processes (AOPs) have been developed to meet the increasing need of an effective wastewater treatment. AOP generates powerful oxidizing agent hydroxyl radicals which completely destroy major classes of organic pollutants at ambient conditions. The combination of UV irradiation with photocatalysts is one of such methods which has attracted considerable attention in recent years, due to its effectiveness in mineralization (i.e. conversion to inorganic species) of organic compounds [17,18]. This has included removal of dye pollutants from residual textile treatment waters [19–21]. Heterogeneous photocatalysis through illumination of UV (or) solar light on a semiconductor surface such as TiO$_2$ is an attractive advanced oxidation process [22]. Such an UVTiO$_2$-based solar catalytic oxidation system exhibits some attractive characteristics. First, TiO$_2$ is stable, insoluble, nontoxic and environmentally acceptable by being fairly inert biologically and chemically. Second, TiO$_2$ is inexpensive reusable. Third, the photocatalyst titanium dioxide (TiO$_2$) is a wide band gap semiconductor (3.2 eV), has high photoactivity and is successfully used as a photocatalyst for the treatment of organic [23,24] and dye pollutants [25–28]. A further important advantage is the fact that the process can be powered by natural sunlight.

Photodegradation of pollutants using TiO$_2$ with solar light can make it an economically viable process since solar energy is an abundant natural energy source. This solar energy can be used instead of artificial light sources. The artificial light sources need high electrical power which is costly and hazardous. Solar energy has been successfully used for photocatalytic degradation of pollutants [29,30]. Solar photocatalytic oxidation also
appears to be a better treatment method for dyes-containing wastes than conventional biological processes [31,32]. While these compounds are highly recalcitrant to biodegradation [33], they can be destroyed by solar catalytic oxidation within hours [34]. Furthermore, during the anaerobic digestion stage of the conventional biological treatment process, the dyes can be readily transformed to other intermediates which are usually more toxic than the parental dyes. Solar catalytic oxidation, on the contrary, can oxidize these dyes efficiently to CO\(_2\) and mineral ions [35].

1.1. Literature Review

1.1.1. Chemical oxidation

In the last 20 years, a rather fast evolution of the research activities devoted to environment protection has been recorded as the consequence of the special attention paid to the environment by social, political and legislative international authorities leading in some cases to the delivery of very severe regulations [36,37].

The fulfillment of severe quality standards is especially claimed for those substances exerting toxic effects on the biological sphere preventing the activation of biological degradation processes. The destruction of toxic pollutants as also that of the simple biologically recalcitrant compounds must be therefore demanded to other, non biological technologies. These technologies consist mainly of conventional phase separation techniques (adsorption processes, stripping techniques) and methods which destroy the contaminants (chemical oxidation/reduction).

Chemical oxidation aims at the mineralization of the contaminants to carbon dioxide, water and inorganic compounds or, at least, at their transformation
into harmless products. Obviously the methods based on chemical destruction, when properly developed, give complete solution to the problem of pollutant abatement differently from those in which only a phase separation is realized with the consequent problem of the final disposal. It has been frequently observed [38,39] that pollutants not amenable to biological treatments may also be characterized by high chemical stability and/or by strong difficulty to be completely mineralized. In these cases, it is necessary to adopt reactive systems much more effective than those adopted in conventional purification processes.

A lot of researches have been addressed to this aim in the last decade pointing out the prominent role of a special class of oxidation techniques defined as advanced oxidation processes (AOP) which usually operate at or near ambient temperature and pressure [40]. This discussion points to a synoptic presentation of these oxidation techniques with special attention given to fundamental chemical aspects.

1.1.2. Photochemical processes

For the oxidation of organic pollutants, a series of researchers have proposed direct photooxidation with ultraviolet light [41]. However, there are a number of limitations for its use. The first one being that the organic compound to be eliminated must absorb light in competition with other compounds of the effluent to be treated. The second one is that the organic compounds generate a wide variety of photochemical reactions that can produce products more complex for degradation. In addition, not all the radiation emitted by the source of radiation is fully exploited, only the radiation absorbed and only a part of this produces chemical changes which means that some reactions of photodegradation have very slow kinetics.
The addition of energy as radiation to a chemical compound is the principle of the photochemical processes. The molecules absorb this energy and reach excited states the enough time to be able to carry out chemical reactions. A large amount of studies [42] dealt with the degradation of chemicals in water using the Hg emission at 253.7 nm produced by low-pressure mercury lamps. However, results showed that 253.7 nm irradiation alone could not be used as an effective procedure for the removal of organics from water: it may be useful for the degradation of substituted aromatic, however it is totally inefficient for effective removal of chlorinated aliphatics. It should, however, be noted that low-pressure Hg lamps are quite efficient for water disinfections purposes. Medium and high-pressure lamps, with a broader emission spectrum, have been more frequently used for the degradation of contaminants. Medium-pressure Hg lamps emit particularly strongly in the spectral region between 254 and 400 nm and are not only effective in generating hydroxyl radicals from e.g. hydrogen peroxide or ozone, but also by causing electronic transitions in a large number of organic molecules.

In the photochemical reactions, hydroxyl radicals may be generated by water photolysis (Cervera and Esplugas, 1983):

\[
\text{H}_2\text{O} \stackrel{\text{hv}}{\rightarrow} \text{H}^\bullet + \text{OH}^\bullet
\]  

(1)

Photolysis involves the interaction of light with molecules to bring about their dissociation into fragments. This reaction is a poor source of radicals, and in the reaction medium large quantity of reaction intermediates that absorb part of the radiation are generated, which decreases considerably the photooxidation kinetics of the contaminants. That fact makes the process valid only for effluents with low concentration of pollutants. The photochemical treatment, although partially solving the problem of the
refractory compounds, has some negative aspects in its practical application, as the high cost of UV radiation production. Furthermore, not all the emitted radiation is used, only the absorbed radiation, and only a fraction of this radiation produces chemical changes. This fact makes that some photodegradation reactions have a very low yields and slow kinetics. To accelerate the process, other oxidants like hydrogen peroxide and/or ozone, metallic salts or semiconductors like TiO2 can be added, giving rise to the so-called Advanced Oxidation Processes. Instead of UV lamps, solar light could be used as radiation energy to degrade some compounds.

1.1.3. Advanced Oxidation Processes (AOPs)
Advanced oxidation processes although making use of different reacting systems, are all characterized by the same chemical feature: production of OH radicals. OH radicals are extraordinarily reactive species, they attack the most part of organic molecules with rate constants usually in the order of $10^6$–$10^9$ M$^{-1}$ s$^{-1}$ [41,42] (Table 1.1). They are also characterized by a little selectivity of attack which is a useful attribute for an oxidant used in wastewater treatment and for solving pollution problems. The versatility of AOP is also enhanced by the fact that they offer different possible ways for OH radicals production thus allowing a better compliance with the specific treatment requirements.

A suitable application of AOP to waste water treatments must consider that they make use of expensive reactants as H$_2$O$_2$, and/or O$_3$ and therefore it is obvious that their application should not replace, whenever possible, the more economic treatments as the biological degradation. A list of the different possibilities offered by AOP is given in the Figure 1.1.
The potentialities offered by AOP can be exploited to integrate biological treatments by an oxidative degradation of toxic or refractory substances entering or leaving the biological stage.

Table 1.1
Second order rate constants for ozone and hydroxyl radical for a variety of compounds

<table>
<thead>
<tr>
<th>Organic compound</th>
<th>Rate constant (M(^{-1})s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(O_3^a)</td>
</tr>
<tr>
<td>Benzene</td>
<td>2</td>
</tr>
<tr>
<td>Toluene</td>
<td>14</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>0.75</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>17</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>(n)-Butanol</td>
<td>0.6</td>
</tr>
<tr>
<td>(t)-Butanol</td>
<td>0.03</td>
</tr>
</tbody>
</table>

\(^a\)From [9].

\(^b\)From [8].

- \(H_2O_2 / Fe^{2+}\) (Fenton)
- \(H_2O_2 / Fe^{3+}\) (Fenton-like)
- \(H_2O_2 / Fe^{2+} (Fe^{3+}) / UV\) (Photo assisted Fenton)
- \(H_2O_2 / Fe^{3+} - Oxalate\)
- \(Mn^{2+}/Oxalic acid/Ozone\)
- \(TiO_2 / hv/ O_2\) (Photocatalysis)
- \(O_3 / H_2O_2\)
- \(O_3 / UV\)
- \(H_2O_2 / UV\)

Figure 1.1. Advanced oxidation processes.
Another aspect concerning the opportunity of AOP application is that referring to the polluting load of wastes normally expressed as COD. Only wastes with relatively small COD contents (≤5.0 g/L) can be suitably treated by means of these techniques since higher COD contents would require the consumption of too large amounts of expensive reactants. Wastes with more massive pollutants contents can be more conveniently treated by means of wet oxidation or incineration [43] (Figure 1.2).

Wet oxidation makes use of oxygen or air to achieve pollutant oxidation at high temperatures (130–300°C) and pressure (0.5–20 Mpa). Since oxidation is an exothermic process, simple thermal balance shows that wastes with COD contents higher than approximately 20 g/L undergo autothermic wet oxidation, whereas fuel consumption should be taken into account to achieve combustion temperatures for leaner wastewaters. For these wastes, the cost evaluation of fuel consumption will give the selection criteria for the application of AOP or wet oxidation treatment.

Figure 1.2. Suitability of water treatment technologies according to COD contents.
1.1.4. Solar chemistry

The dramatic increases in the cost of oil beginning focused attention on the need to develop alternative sources of energy. It has long been recognized that the sunlight falling on the earth’s surface is more than adequate to supply all the energy that human activity requires. The challenge is to collect and convert this dilute and intermittent energy to forms that are convenient and economical or to use solar photons in place of those from lamps. It must be kept in mind that today there is a clear world-wide consensus regarding the need for long-term replacement of fossil fuels, which were produced million of years ago and today are merely consumed, by other inexhaustible or renewable energies. Under these circumstances, the growth and development of Solar Chemical Applications can be of special relevance.

These technologies can be divided in two main groups:

1. Thermo-chemical processes: the solar radiation is converted into thermal energy that causes a chemical reaction. Such a chemical reaction is produced by thermal energy obtained from the sun for the general purpose of substituting fossil fuels.

2. Photochemical processes: solar photons are directly absorbed by reactants and/or a catalyst causing a reaction. This path leads to a chemical reaction produced by the energy of the sun’s photons, for the general purpose of carrying out new processes.

It should be emphasized, as a general principle, that the first case is associated with processes that are feasible with conventional sources of energy. The second is related only to completely new processes or reactions that are presently carried out with electric arc lamps, fluorescent lamps or lasers.
From the outset, it was recognized that direct conversion of light to chemical energy held promise for the production of fuels, chemical feedstock, and the storage of solar energy. Production of chemicals by reactions that are thermodynamically ‘uphill’ can transform solar energy and store it in forms that can be used in a variety of ways. Wide ranges of such chemical transformations have been proposed.

These processes generally start with substances in low-energy, highly-oxidized forms. The essential feature is that these reactions increase the energy content of the chemicals using solar energy. For such processes to be viable, they must fulfill the following requirements:

• The thermo-chemical reaction must be endothermic.
• The process must be cyclic and with no side reactions that could degrade the photochemical reactants.
• The reaction should use as much of the solar spectrum as possible.
• The back reaction should be very slow to allow storage of the products, but rapid when triggered to recover the energy content.
• The products of the photochemical reaction should be easy to store and transport.

The other pathway for the use of sunlight in photochemistry is to use solar photons as replacements for those from artificial sources. The goal in this case is to provide a cost-effective and energy-saving source of light to drive photochemical reactions with useful products. Photochemical reactions can be used to carry out a wide range of chemical syntheses ranging from the simple to the complex. Processes of this type may start with more complex compounds than fuel-producing or energy-storage reactions and convert them to substances to which the photochemical step provides additional value or destroy harmful products. Therefore, the problem becomes one of
identifying applications in which the use of solar photons is possible and economically feasible. The processes of interest here are photochemical; hence, some component of the reacting system must be capable of absorbing photons in the solar spectrum. Because photons can be treated like any other chemical reagent in the process, their number is a critical element in solar photochemistry.

Because they are very technologically and environmentally attractive, solar chemical processes have seen spectacular development in recent years. In the beginning, research in solar chemistry was centered only on converting the solar energy into chemical energy, which could then be stored and transferred over long distances. Together with this important application, other environmental uses have been developed, so that today the entire range of solar chemical applications has a promising future. In principle, any reaction or process requiring an energy source can be supplied by solar energy.

1.1.5. Solar radiation as source of light

Solar radiation and in particular its ultraviolet component, is considered of interest being the existence of ultraviolet radiation the key of some heterogeneous and homogeneous photocatalytic processes, such as TiO$_2$/UV and H$_2$O$_2$/Fe$^{2+}$/UV-vis or H$_2$O$_2$/Fe$^{3+}$/UV-vis system (photo-Fenton). The use of solar light as source of radiation in the photo-Fenton and Fe$^{3+}$/UV-vis system has been studied, taking as reference the recent development of solar technology in water detoxification by means of heterogeneous photocalysis (TiO$_2$/UV) [44,45]. In this sense, this section describes the power of sunlight as source of energy, as well as the basic factors related to the photocatalytic technology and its application. In addition, it outlines the basic principles
related to the solar spectrum and especially to the solar UV radiation since this part of the solar spectrum is the most important one for driving chemical processes and the main features of the collectors used for wastewater detoxification.

All the energy coming from that huge reactor, the Sun, from which the earth receives $1.7 \times 10^{14}$ kW, means $1.5 \times 10^{18}$ kWh per year, approximately 28000 times the consumption of all the world in that period [47].

The radiation in the exterior of the atmosphere has a wavelength between $0.2 \mu m$ and $50 \mu m$, which is reduced in an interval between $0.3 \mu m$ and $3 \mu m$ when reaching the surface, due to the absorption of part of it by different atmospheric components (ozone, oxygen, carbon dioxide, aerosols, steam, and clouds). The solar radiation that reaches the ground level without being absorbed or scattered, is called direct radiation; the radiation, which has been dispersed but reaches the ground level is called diffuse radiation and the addition of both is called global radiation. In general, the direct component of global radiation in cloudy days is minimum and the diffuse component is maximum, producing the opposite situation in clear days.

### 1.1.6. Water contaminants

Environmental pollution is a pervasive problem with widespread ecological consequences. Recent decades have witnessed increased contamination of the Earth’s drinking water reserves. In any case, a consensus exists that the environmental impact of a given contaminant depends on the degree of exposure (its dispersion and the resulting concentration in the environment) and on its toxicological properties. The assessment of exposure involves comprehension of the dispersion of a chemical in the environment and estimation of the predicted concentration to which organisms will be
exposed. Assessment of the contaminant’s effect involves summarizing data on the effects of the chemical on selected representative organisms and using these data to predict a no-effect concentration on a specific niche. Organisms may consume chemicals through ingestion of food and water, respiration and through contact with skin. When a chemical crosses the various barriers of the body, it reaches the metabolic tissue or a storage depot. Toxicity of a chemical is usually expressed as the effective concentration or dose of the material that would produce a specific effect in 50% of a large population of test species.

Decontamination of drinking water is mainly by procedures that combine flocculation, filtration, sterilization and conservation, to which a limited number of chemicals are added. Normal human sewage water can be efficiently treated in conventional biological processing plants. But very often, these methods are unable to reduce the power of the contaminant. In these cases, some form of advanced biological processing is usually preferred in the treatment of effluents containing organic substances. Biological treatment techniques are well established and relatively cheap. However, these methods are susceptible to toxic compounds that inactivate the waste degrading microorganisms. To solve this problem, apart from reducing emissions, two main water treatment strategies are followed: (i) chemical treatment of drinking water, contaminated surface and groundwater and (ii) chemical treatment of waste waters containing biocides or non-biodegradable compounds.

Chemical treatment of polluted surface and groundwater or wastewater, is part of a long-term strategy to improve the quality of water by eliminating toxic compounds of human origin before returning the water to its natural cycles. This type of treatment is suitable when a biological processing plant
cannot be adapted to certain types of pollutants that did not exist when it was designed. In such cases, a potentially useful approach is to partially pre-treat the toxic waste by oxidation technologies to produce intermediates that are more readily biodegradable. Light can be used, under certain conditions, to encourage chemicals to break down the pollutants to harmless by-products. Light can have a dramatic effect on a molecule or solid, because, when it absorbs light, its ability to lose or gain electrons is often altered. This electronically excited state is both a better oxidizing and a better reducing agent than its counterpart in the ground. Electron transfer processes involving excited-state electrons and the contact medium (for example water) can therefore generate highly reactive species like hydroxide (‘OH) and superoxide (O$_2^-$) radicals (see Table 1.2).

### Table 1.2

**Oxidation potentials of common substances and agents for pollution abatement.** The more positive the potential, the better the species is an oxidizing agent.

<table>
<thead>
<tr>
<th>Oxidizing reagent</th>
<th>Oxidation Potential, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>3.06</td>
</tr>
<tr>
<td>Hydroxide radical (‘OH)</td>
<td>2.80</td>
</tr>
<tr>
<td>Ozone</td>
<td>2.07</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>1.77</td>
</tr>
<tr>
<td>Chlorine dioxide</td>
<td>1.57</td>
</tr>
<tr>
<td>Chlorine gas</td>
<td>1.36</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1.23</td>
</tr>
<tr>
<td>Hypochlorite</td>
<td>0.94</td>
</tr>
<tr>
<td>Iodine</td>
<td>0.54</td>
</tr>
<tr>
<td>Superoxide radical (O$_2^-$)</td>
<td>-0.33</td>
</tr>
</tbody>
</table>

These can then be used to chemically decompose a pollutant into harmless end-products. Alternatively, light can be used directly to break up pollutant
molecule bonds photolytically. These processes are called Advanced Oxidation Processes (abbreviated as AOPs). Many oxidation processes, such as TiO$_2$/UV, H$_2$O$_2$/UV, Photo-Fenton [48,49] and ozone processes (O$_3$, O$_3$/UV, O$_3$/H$_2$O$_2$) are currently employed for this purpose.

1.1.6. Photodegradation principals
For the benefit of those who may have a limited background in photochemistry, a brief outline of some basic concepts of photochemistry is presented here. In order for photochemistry to take place, photons of light must be absorbed. The energy of a photon is given by

$$U = \frac{hc}{\lambda}$$  \hspace{1cm} (1.1)

where $h$ is Planck’s constant (6.626 $10^{-34}$ J s), $c$ is the speed of light and $\lambda$ is the wavelength. For a molecule’s bond to be broken, $U$ must be greater than the energy of that bond [50].

When a given wavelength $\lambda$ of light enters a medium, its spectral irradiance $E^i_\lambda$ (W m$^{-2}$ nm$^{-1}$) is attenuated according to the Lambert-Beer law, which is expressed in two ways, one for gas phase and the other for liquid phase:

$$\ln\left(\frac{E^o_\lambda}{E^l_\lambda}\right) = \alpha_\lambda p_i l \quad \text{gas phase}$$  \hspace{1cm} (1.2)

$$\log\left(\frac{E^o_\lambda}{E^l_\lambda}\right) = \varepsilon_\lambda c_i l \quad \text{liquid phase}$$  \hspace{1cm} (1.3)

$E^o_\lambda$ and $E^l_\lambda$ are the incident spectral irradiances and at a distance $l$ into the medium, $\alpha_\lambda$ is the absorption coefficient (cm$^{-1}$ atm$^{-1}$), $p_i$ is the partial pressure (atm) of component $i$, $\varepsilon_\lambda$ is the extinction coefficient (M$^{-1}$ cm$^{-1}$), and $c_i$ is the concentration (M) of component $i$. The absorbence $A_\lambda$ at wavelength $\lambda$ is the product $\varepsilon_\lambda c_i l$. The photochemical quantum yield ($\phi$) is defined as the
number of molecules of target compound that reacts divided by the number of photons of light absorbed by the compound, as determined in a fixed period of time. Normally, the unit is the maximum quantum yield attainable. The term photocatalysis implies the combination of photochemistry with catalysis. Both light and catalyst are necessary to achieve or to accelerate a chemical reaction. Photocatalysis may be defined as the “acceleration of a photoreaction by the presence of a catalyst”. Heterogeneous processes employ semiconductor slurries for catalysis, whereas homogeneous photochemistry is used in a single-phase system. Any mechanistic description of a photoreaction begins with the absorption of a photon, being sunlight the source of photons in solar photocatalysis. In the case of homogeneous photocatalytic processes, the interaction of a photon-absorbing species (transition metal complexes, organic dyes or metalloporphyrines), a substrate (e.g. the contaminant) and light can lead to a chemical modification of the substrate. The photon-absorbing species (C) is activated and accelerates the process by interacting through a state of excitation (C*). In the case of heterogeneous photocatalysis, the interaction of a photon produces the appearance of electron/hole (e⁻ and h⁺) pairs, the catalyst being a semiconductor (e.g. TiO₂, ZnO, etc). In this case, the excited electrons are transferred to the reducible specimen (Ox₁) at the same time that the catalyst accepts electrons from the oxidizable specimen (Red₂) which occupies the holes. In both directions, the net flow of electrons is null and the catalyst remains unaltered.

\[
C \xrightarrow{hv} C^* \quad (1.4)
\]

\[
C^* + R \rightarrow R^* + C^* \quad (1.5)
\]
1.1.7. Heterogeneous photocatalysis

The concept of heterogeneous photocatalytic degradation is simple: the use under irradiation of a stable solid semiconductor for stimulating a reaction at the solid/solution interface. By definition, the solid can be recovered unchanged after many turnovers of the redox system. When a semiconductor is in contact with a liquid electrolyte solution containing a redox couple, charge transfer occurs across the interface to balance the potentials of the two phases. An electric field is formed at the surface of the semiconductor and the bands bend as the field forms from the bulk of the semiconductor towards the interface. During photoexcitation (a photon with appropriate energy is absorbed), band bending provides the conditions for carrier separation. In the case of semiconductor particles, there is no ohmic contact to extract the majority carriers and to transfer them by an external conductor to a second electrode. This means that the two charge carriers should react at the semiconductor/electrolyte interface with the species in solution. Under steady state conditions the amount of charge transferred to the electrolyte must be equal and opposite for the two types of carriers. The semiconductor-mediated redox processes involve electron transfer across the interface. When electron/hole pairs are generated in a semiconductor particle, the electron moves away from the surface to the bulk of the semiconductor as the hole migrates towards the surface (see Figure 1.3). If these charge
carriers are separated fast enough they can be used for chemical reactions at the surface of the photocatalyst, i.e., for the oxidation or reduction of pollutants [51,52]. Metal oxides and sulphides represent a large class of semiconductor materials suitable for photocatalytic purposes. Table 1.3 lists some selected semiconductor materials, which have been used for photocatalytic reactions, together with band gap energy required to activate the catalyst [53].

![Figure 1.3. Fate of electrons and holes within a particle of illuminated semiconductor in contact with an electrolyte.](image)

The final column in the table indicates the wavelength of radiation required to activate the catalysts. According to Plank’s equation, the radiation able to produce this gap must be of a wavelength (λ) equal or lower than that calculated by Equation 2.10.

$$\lambda = \frac{hc}{E_G}$$  \hspace{1cm} (1.10)

where $E_G$ is the semiconductor band-gap energy, $h$ is Planck’s constant and $c$ is the speed of light.

Summarizing, a semiconductor particle is an ideal photocatalyst for a specific reaction if:
• The products formed are highly specific.
• The catalyst remains unaltered during the process.
• The formation of electron/hole pairs is required (generated by the absorption of photons with energy greater than that necessary to move an electron from the valence band to the conduction band)
• Photon energy is not stored in the final products, being an exothermic reaction and only kinetically retarded.

| Table 1.3
Selected properties of several semiconductors |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Band gap (eV)</td>
<td>Wavelength corresponding to band gap (nm)</td>
</tr>
<tr>
<td>BaTiO₃</td>
<td>3.3</td>
<td>375</td>
</tr>
<tr>
<td>CdO</td>
<td>2.1</td>
<td>590</td>
</tr>
<tr>
<td>CdS</td>
<td>2.5</td>
<td>497</td>
</tr>
<tr>
<td>CdSe</td>
<td>1.7</td>
<td>730</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.2</td>
<td>565</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.4</td>
<td>887</td>
</tr>
<tr>
<td>GaP</td>
<td>2.3</td>
<td>540</td>
</tr>
<tr>
<td>SnO₂</td>
<td>3.9</td>
<td>318</td>
</tr>
<tr>
<td>SrTiO₃</td>
<td>3.4</td>
<td>365</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3.0</td>
<td>390</td>
</tr>
<tr>
<td>WO₃</td>
<td>2.8</td>
<td>443</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.2</td>
<td>390</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.7</td>
<td>336</td>
</tr>
</tbody>
</table>

1.1.8. Homogeneous photodegradation

The use of homogeneous photodegradation (single-phase system) to treat contaminated waters dates back to the early 1970s. The first applications concerned the use of UV/ozone and UV/H₂O₂. The use of UV light for photodegradation of pollutants can be classified into two principal areas [54-56]:
• Photooxidation. Light-driven oxidative processes principally initiated by hydroxyl radicals.
• Direct photodegradation. Light-driven processes where degradation proceeds following direct excitation of the pollutant by UV light. Photooxidation involves the use of UV light plus an oxidant to generate radicals. The hydroxyl radicals then attack the organic pollutants to initiate oxidation. Three major oxidants are used: hydrogen peroxide (H$_2$O$_2$), ozone and Photo-Fenton reaction. H$_2$O$_2$ absorbs fairly weakly in the UV region with increasing absorption as the wavelength decreases. At 254 nm, $\varepsilon_\lambda$ is 18 M$^{-1}$ cm$^{-1}$, whereas at 200 nm is 190 M$^{-1}$ cm$^{-1}$. The primary process for absorption of light below 365 nm is dissociation to yield two hydroxyl radicals:

$$H_2O_2 \xrightarrow{hv} 2\cdot OH$$

(1.11)

The use of hydrogen peroxide is now very common for the treatment of contaminated water due to several practical advantages: (i) the H$_2$O$_2$ is available as an easily handled solution that can be diluted in water to give a wide range of concentrations; (ii) there are no air emissions; (iii) a high-quantum yield of hydroxyl radicals is generated (0.5). The major drawback is the low molar extinction coefficient, which means that in water with high UV absorption the fraction of light absorbed by H$_2$O$_2$ may be low unless very large concentrations are used. Furthermore, especially as concerns the focus of this text, H$_2$O$_2$ absorption is very low in the Solar UV range (up 300 nm).

Ozone is generated as a gas in air or oxygen in concentrations generally ranging from 1 to 8% (v/v). It has a strong absorption band centered at 260 nm with $\varepsilon_\lambda = 3000$ M$^{-1}$ cm$^{-1}$. Absorption of light at this wavelength leads to formation of H$_2$O$_2$:

$$O_3 \xrightarrow{hv} O(^1D) + O_2$$

(1.12)
Hydroxyl radicals are then formed by reaction of ozone with the conjugate base of hydrogen peroxide:

\[
O(1D) + H_2O \rightarrow H_2O_2 \quad (1.13)
\]

Since the net result of ozone photolysis is the conversion of ozone into hydrogen peroxide, UV-ozone would appear to be only a rather expensive method of making hydrogen peroxide. However, there are other oxidation-related processes occurring in solution, such as the direct reaction of ozone with a pollutant (Table 1.3). Ozone may have advantages in water with high inherent UV absorbence, but it involves the same problem as hydrogen peroxide for use in solar energy processes.

The essential step of the Fenton reaction is the same as for all AOPs. Highly reactive radicals (like HO\(^-\) and HO\(_2\)-\(^-\)) oxidize nearly all organic substances to yield CO\(_2\), water and inorganic salts. In the case of Photo-Fenton, Fe\(^{2+}\) ions are oxidized by H\(_2\)O\(_2\) while one \(^1\)OH is produced (1.18), and the Fe\(^{3+}\) or complexes obtained then act as the light absorbing species that produce another radical while the initial Fe\(^{2+}\) is recovered (1.19 and 1.20).

\[
Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^* \quad (1.18)
\]

\[
Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + H^+ + OH^* \quad (1.19)
\]

\[
[Fe(OOC – R)]^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R^* \quad (1.20)
\]

Note that in equation (1.20) the ligand R-COO– can be replaced by other organic groups (ROH, RNH\(_2\) etc.). Compared to other homogeneous...
photooxidation processes, the advantages of Photo-Fenton are the improved light sensitivity (up to a wavelength of 600 nm, corresponding to 35% of the solar radiation). On the other hand, disadvantages, such as the low pH values required (usually below pH 4) and the necessity of removing iron after the reaction, remain.

Some pollutants are able to dissociate only in the presence of UV light. For this to happen, the pollutant must absorb light emitted by a lamp (or the sun) and have a reasonable quantum yield of photodissociation. Organic pollutants absorb light over a wide range of wavelengths, but generally absorb more strongly at lower wavelengths, especially below 250 nm (Figure 1.4). In addition, the quantum yield of photodissociation tends to increase at lower wavelengths, since the photon energy is increasing (Equation 1.1). The net chemical result of photodissociation is usually oxidation, since the free radicals generated can react with dissolved oxygen in the water. In practice, the range of waste waters that can be successfully treated by UV alone is very limited.

1.1.9. Applications to water treatment

As mentioned above, UV light can be used in several ways. But direct photolysis can occur only when the contaminant to be destroyed absorbs incident light efficiently. In the case of UV/ozone and UV/hydrogen peroxide this does not happen. But here too, absorption by some sensitizers must initiate the reaction, and limited absorption by the solute or the additive restricts efficiency. Furthermore, these mixtures often still require large quantities of added oxidant. By contrast, in heterogeneous photocatalysis, dispersed solid particles absorb larger fractions of the UV spectrum efficiently and generate chemical oxidants in situ from dissolved oxygen or
water (see Figure 1.4). These advantages make heterogeneous photocatalysis a particularly attractive method for environmental detoxification. The most important features of this process making it applicable to the treatment of contaminated aqueous effluents are [57,58):

- The process takes place at ambient temperature.
- Oxidation of the substances into CO$_2$ is complete.
- The oxygen necessary for the reaction is obtained from the atmosphere.
- The catalyst is cheap, innocuous and can be reused.
- The catalyst can be attached to different types of inert matrices.

1.1.10. Solar collector technology generalities

Traditionally, different solar collector systems have been classified depending on the level of concentration attained by them [59]. The concentration ratio (CR) can be defined as the ratio of the collector aperture area to the absorber or reactor area. The aperture area is the area intercepting radiation and the absorber area is the area of the component (either fully illuminated or not) receiving concentrated solar radiation. This CR is directly related to the working system temperature and, according to this criterion; there are three types of collectors:

- Non-concentrating or low-temperature, up to 150º C
- Medium concentrating or medium temperature, from 150º C to 400º C
- High concentrating or high temperature, over 400º C.

This traditional classification considers only the thermal efficiency of the solar collectors. Non-concentrating solar collectors (Figure 1.5) are static and non-solar-tracking. Usually, they are flat plates, often aimed at the sun at a specific tilt, depending on the geographic location. Their main advantage is their simplicity and low cost. An example is domestic hot-water technology.
Medium concentrating solar collectors concentrate sunlight between 5 and 50 times, so continuous tracking of the sun is required. Parabolic Trough Collectors (PTC) and holographic collectors (Fresnel lenses) are in this group. The first have a parabolic reflecting surface which concentrates the radiation on a tubular receiver located in the focus of the parabola. They may be one-axis tracking, either azimuth (east-west movement around a north-south-oriented axis) or elevation (north-south movement around an east-west-oriented axis), or two-axis tracking (azimuth + elevation). Fresnel lens collectors consist of refracting surfaces (similar to convex lenses) which deviate the radiation at the same time they concentrate it onto a focus.

![Image of non-concentrating solar collectors for domestic heat water application]

**Figure 1.5.** Non-concentrating solar collectors for domestic heat water application

![Image of medium-concentrating solar collectors. PTC type]

**Figure 1.6.** Medium-concentrating solar collectors. PTC type
High concentrating collectors (Figure 1.7) have a focal point instead of a linear focus and are based on a paraboloid with solar tracking. Typical concentration ratios are in the range of 100 to 10000 and precision optical elements are required. They include parabolic dishes and solar furnaces.

Figure 1.7. High concentration solar collector.

Up to now, the solar collectors used for photocatalysis have been in the two first categories. Direct radiation is the radiation which has no interference from the atmosphere and, consequently, a known direction, and can therefore be concentrated. Global radiation is composed of direct and diffuse radiation.

1.1.11. Specific features of solar UV light utilization

The specific hardware needed for solar photocatalytic applications have much in common with those used for thermal applications. As a result, both photocatalytic systems and reactors have followed conventional solar thermal collector designs, such as parabolic troughs and non-concentrating collectors. At this point, their designs begin to diverge, since [60]:

- the fluid must be exposed to ultraviolet solar radiation, and, therefore, the absorber must be UV-transparent, and
- temperature does not play a significant role in the photocatalytic process, so no insulation is required.

The first engineering-scale outdoor reactor for solar detoxification was developed by Sandia National Laboratories (USA) at the end of the eighties (see Figure 1.8) where a parabolic trough solar thermal collector was modified simply by replacing the absorber/glazing-tube combination with a Pyrex tube through which contaminated water could flow. Since then, many different concepts with a wide variety of designs have been proposed and developed all over the world, in a continuous effort to improve performance and reduce the cost of solar detoxification systems. Among these different concepts, several of the most important with regard to the definition of the overall system are those related to whether or not radiation must be concentrated, the type of reflective surface to be used, the way the water circulates through the reactor (tube, falling film or stirred vessel) and the way in which the catalyst is employed.

![First engineering scale outdoor solar detoxification reactor using one-axis parabolic trough collector. Part of the 465 m2 parabolic trough system at Sandia National Laboratory. Courtesy of National Renewable Energy Laboratory (USA)](image-url)
One of the most important reactor design issues is the decision between concentrating or non-concentrating collector systems. Concentrating systems have the advantage of a much smaller reactor-tube area, which could mean a shorter circuit in which to confine, control and handle the contaminated water to be treated. The alternative of using high-quality ultraviolet-light transmitting reactors and supported-catalyst devices also seems more logical, both economically and from an engineering point of view, if concentrating collector systems are to be used.

Nevertheless, concentrating reactors have two important disadvantages compared to nonconcentrating ones. The first is that they cannot concentrate (i.e., use) diffuse solar radiation, which is unimportant for solar thermal applications, because diffuse radiation is a small fraction of the total solar radiation. However, solar photocatalytic detoxification with TiO$_2$ as a catalyst uses only the UV fraction of the solar spectrum and, since this radiation is not absorbed by water vapour, as much as 50 percent of this, or more in very humid locations or during cloudy or partly cloudy periods, can be diffuse. As non-concentrating solar collectors can make use of both direct and diffuse UV radiation, their efficiency can be noticeably higher. The second disadvantage of concentrating collectors is their complexity, cost and maintenance requirements. The consequence of these disadvantages is that present state-of the-art favours the use of non-concentrating reactors for solar photocatalytic applications. An additional disadvantage of concentrating reactors is that the quantum efficiency is low, due to a square root rather than linear dependence of rate on light flux.

For many of the solar detoxification system components, the equipment is identical to that used for other types of water treatment and construction materials are commercially available. Most piping may be made of
polyvinylidene fluoride (PVDF), chlorinated polyvinyl chloride (CPVC), or simply polyethylene. In any case, piping, as well as the rest of the materials, must be resistant to corrosion by the original contaminants and their possible by-products in the destruction process. Neither must materials be reactive, interfering with the photocatalytic process. All materials used must be inert to degradation by UV solar light in order to be compatible with the minimum required lifetime of the system.

Optical material requirements are similar to other closed solar systems, but photocatalytic reactors must transmit UV light efficiently because of the process requirements. In some cases, when a steam pressure of contaminants in water is sufficiently low, a closed system could not be required and then a transmissive UV containment material could be avoided.

All pipes, reactor and connection devices must be strong enough to withstand the necessary water-flow pressure. Typical parameters are 2 to 4 bar for nominal system pressure drop and a maximum of 5 to 7 bar. Concentrating system materials must also be able to withstand possible high temperatures that could result from absorption of concentrated visible and infrared light in the reactor.

With regard to the reflecting/concentrating materials, aluminium is the best option due to its low cost and high reflectivity in the solar terrestrial UV spectrum. Commercially available film products incorporate a thin aluminium foil with an acrylic coating. The last peculiarity of solar photocatalytic systems is the requirement of a catalyst; in the case of TiO$_2$ it can be deployed in several ways, such as slurry or as a fixed catalyst (like a fiberglass matrix inserted in the reactor tube).
1.2. Problem Statement Objective
Taking the above-mentioned concept into account, the present study focused on oxidation of Methylene dye by solar photocatalysis. This dyestuff was provided from Germany, and was used throughout the present investigation as received and without further purification. The selection of textile wastewater was due to its recalcitrant and even toxic nature in conventional biotreatment. The dye is highly water-soluble and can be used for dyeing and printing acrylic fibers. For the practical application of dye wastewater by the Solar Photo-Fenton process, there is a need to determine the optimal conditions of experimental parameters.

The effects of various physicochemical conditions on the degradation of the dye by solar photocatalytic oxidation were studied to find out the optimum conditions for removal of color and aromatic part of the dye.

1.3. Problem Justification and Outcomes
The work was divided in different sections with the following objectives:

- To study the effect of the photocatalytic oxidation process on the degradation rate of the selected dye as a model substances of dyes used in the sector of textile industries. The objective of this part was, after studying a wide range of experimental conditions to understand the mechanisms to propose a general empirical kinetic equation for the degradation of this compound as a function of photocatalyst, its initial concentration and H$_2$O$_2$.

- To study the possibility and benefits of using natural sunlight as a source of ultraviolet radiation using own design of tubular parabolic solar collector to carry out the different experiments for the photocatalytic oxidation processes.
The development of a strategy to be applied in wastewater treatment, using as example waters produced in textile activities to evaluate a general strategy for the treatment of the different generated wastewaters in Saudi Arabian Kingdom. The aim of this study was to explore the possibility of using the heterogeneous photocatalytic oxidation processes pre- or post-treatment to enhance the global removal performance. This study was performed at Department of Chemical Engineering, Faculty of Engineering, Jazan University in Saudi Arabian Kingdom.

To achieve the experimental objectives and to reach the optimum operating conditions, the following variables were chosen to be followed throughout the treatment:

- Concentration of target compounds
- pH
- Dose of Fe(II) as a catalyst used in the study
- Hydrogen peroxide concentration
- Chemical Oxygen Demand (COD)
- Colour removal

Finally to study the possibility to recycle or to reuse the treated water for the industry purposes as cooling water or for the agricultural purposes for irrigation through knowing the final organic load for the water after treatment and comparing it with the limit value for discharge this water in the local canals and streams according to the national environmental laws and legislations.
1.4. Problem Constraints

The textile industry needs large quantities of water of good quality in its fundamental processing steps, which generally imply the utilization of a large number of chemicals such as organic dyestuffs, surfactants, chelating agents, pH regulators, etc. These processes generate very toxic wastewater, whose treatment is often difficult due to the presence of some not biodegradable species with complex structure. Hence there is considerable current interest in developing alternative and more cost-effective methods.
CHAPTER (2)
DESIGN APPROACH AND METHODOLOGY

All photocatalytic experiments carried out in this work have been done in Chemical Engineering Department, Faculty of Engineering at Jazan University, Saudi Arabian Kingdom during Fall season (Mars/April 2014) using natural light irradiation from 11 am to 16 pm.

2.1. Design approach

2.1.1. Model substrate and materials

Methylene Blue dye of Merck. This dye is in current use at the dyeing sector of textile industries for Spinning and Weaving. It was chosen as a model substrate because of its toxicity and it is widely used in textile industry in SA. This dyestuff was used throughout the present investigation as received and without further purification.

Ferrous sulphate hepta hydrated is known as Fenton reagent powder and is used as sources of photocatalyst to study the effect of catalyst is supplied from Merck Hydrogen peroxide solution (35% w/w) in stable form was provided by Merck. Water used throughout this study was tap water. All reagents employed were not subjected to any further purification.

2.1.2. Experimental set-up

A laboratory unit was used for the batch experiments by using a photo-solar reactor. The schematic diagram of the experimental set-up used in this study is shown in Figure (2.1).
The system consists of a tubular solar reactor, a holding tank and a recirculating pump in a total recirculation loop with a feed tank by a peristaltic pump.

2.2. Design Methodology

Synthetic solutions from the dye taken under study were prepared by dissolving definite amounts of the dye in water in the holding tank and were mixed vigorously until constant concentration is achieved through the system. High concentration of dye (80 ppm) was selected to simulate high-loaded reactive dye containing industrial wastewater. Latter the catalyst is added at different amounts, dispersed by strongly mechanically mixing with the dye solution for 5 minutes. The initial pH value of the dye solution was constant in all the experiments. Constant amount of hydrogen peroxide (1 ml/L) is injected one batch time at the beginning of each experiment to enhance the degradation efficiency of the dye.

The degradation experiments were started by pumping the suspension of the catalyst and dye at a fixed flow rate of 60 L/h for three hours. The total reaction volume was 8 L and is separated in two parts: 2 L as the irradiated volume in the tubular solar reactor and 6 L the dead volume of the connecting tubes and the holding tank.

At the start of every experiment the reactor was well rinsed with water, the reactor was then filled with the dye solution and it was ensured that no other traces of dye or catalyst from the last experiment remained in the system. Clean connecting tubes and new fresh catalyst were used for every new experiment. Several experiments are done to study the effect of the different investigated photo-catalysts and their amounts on the degradation efficiency
of the dye. The effect of each parameter was studied by fixing the values of other parameters.

Samples were taken at regular time intervals from the collector and first were centrifuged to get ride off the residual catalyst and then were analyzed immediately to avoid further reaction. For COD determination, the reaction was stopped instantly by adding NaOH to the reaction samples to decompose any residual hydrogen peroxide and prevent hydrogen peroxide from reacting with dye during the analysis, since hydrogen peroxide cannot proceed at pH >10.

The percent of color removal of the dye in the reaction mixture at different times was obtained by measuring absorbance at maximum wavelength (\(\lambda_{\text{max}} = 420\) nm) and computing the concentration from calibration curve. A PD-303 UV spectrophotometer (APEL Type), from Japan was employed for absorbance measurements. Chemical oxygen demand (COD) was carried using dichromate solution as the oxidant in strong acid media, colorimetric method.

![Schematic Diagram of Solar Catalytic Oxidation Unit.](image)

**Figure 2.1.a. Schematic Diagram of Solar Catalytic Oxidation Unit.**
Figure 2.1.b. Solar parabolic collector used in the study.

Figure 2.1. Experimental set-up.
CHAPTER (3)
THEORETICAL BACKGROUND

3.1. Design specifications and assumptions
The absorber tube develops 2.5 m * 40 mm ID and is placed in the focus of parabolic collector (1.5 m * 1.15 m) and mounted on a fixed platform titled 30°05’ (local latitude). The nominal aperture area of the parabolic collector is 2 m², which reduces to an effective aperture of 1.5 m² as a result of the separation between the mirrors and the dead space inevitably lost in joints. Solar rays are reflected by the parabolic mirrors on contaminated water to be treated circulates. The reflecting surface is made of an aluminized polymeric film yielding 85% reflectivity among 295 and 385 nm. As compound parabolic collector does not concentrate light inside the photoreactor, the system is outdoors and is not thermally insulated; the maximum temperature achieved inside the reactor during the experiment is 45°C.
Mixing was accomplished by means of a closed external circulating loop through the illuminated part of the photoreactor by the use of a peristaltic pump. The flow system was assembled with polytetrafluorethylene (PTFE) connectors.

3.2. Mathematical design model
Compound parabolic concentrators (CPCs) are concentrators utilizing non-imaging optics. Other reflecting systems tested in previous studies [52,54] have a varying concentration during the day because they are essentially image forming systems and depend on the angle of incidence of the sun on the reflector. A major advantage of CPC systems is that the concentration
factor remains constant for all values of sun zenith angle within the acceptance angle limit.

When non-imaging optics is used to design a mirror for a cylindrical absorber, the result obtained is a compound parabolic concentrator (CPC). CPC mirrors have been widely used and tested in the field of photocatalysis to enhance the UV radiation reaching the photocatalyst and it has been proven that the CPC is the best optic to use to concentrate the solar UV spectrum [52,54].

This work reports results on the evaluation of the use of one of tubular CPC mirrors to enhance the oxidation efficiency under real solar radiation conditions in cloudy and clear days.

We define: aperture area = A; absorber area = A_{abs}; Sun zenith angle on the concentrator = \( \Theta \); acceptance angle of the CPC = \( \Theta_c \); concentration factor = \( C = A/A_{abs} \). The fundamental problem of radiation concentration is how can radiation which is incident on A and uniformly distributed over a range of angles (\( \Theta \leq \Theta_c \)) be concentrated onto the smaller absorber area \( A_{abs} \) without the need for repositioning the system as the value of \( \Theta \) varies. For a cylindrically shaped reactor the concentrating system is two dimensional.

In this case, the second law of thermodynamics states that the maximum possible concentration or ideal concentration is \( C_{\text{ideal}} = 1/\sin \Theta_c \).

In this case, given the diffuse nature of the UV-A spectrum, only a homogeneous distribution of light on the absorber tube is required, not a high concentration. Hence, a system with a concentration factor of 1 (\( C = 1 \)) sun was designed. Then, \( \Theta_c = 90^\circ \) and the shape of the mirror is defined by an involute to the absorber. The aperture of the system is 15.7 cm and is numerically equal to the perimeter of the absorber. Due to the non-imaging
nature of the reflectors, the entire absorber is homogeneously illuminated at all times, even on cloudy days.

The CPC mirrors were built with highly reflective aluminum sheets type 320 G ALANOD anodized aluminum of 0.5 mm thickness.

Figure 3.1., illustrates the individual components of the tubular solar parabolic concentrator used in this study.
Figure 3.1. Components of solar parabolic collector. (a) Glass tube configuration. (b) Design of CPC for the glass tube experiments. (c) Experimental tube fitted in CPC mirror inclined 37° with respect to horizontal facing south.
Chapter (4)
DESIGN PROCEDURE AND IMPLEMENTATION

4.1. Design procedure
In our study several parameters are investigated such as the initial concentration of the selected dye in the aqueous solution, irradiation time, catalyst loading (dose of the catalyst), pH values, the addition of an oxidant such as hydrogen peroxide as an electron acceptor and the addition of the absorber like Bentonite. The optimal objective was to find out the optimum operating conditions affecting the colour and COD removal of the dye solution selected in this study. The reaction kinetics was also examined. The study investigated all the mentioned parameters or these operating conditions on the % colour removal of the dye solution. Finally the % COD removal was also measured and estimated at the optimum operating conditions.

4.2. Design implementation
4.2.1. Effect of solar radiation
The efficiency of color removal of the dye in the supernatant as determined from the spectrophotometric measurements is determined. Figure 4.1 show the efficiency of color removal of the dye against different types of photo chemical oxidation processes used in this study. The experiments were carried out using a constant dye concentration of 30 mg/L, a constant reaction time of 1 hour, constant dose of catalyst 0.2 g/L and constant pH (equals 5).
Using solar light only, a very low of colour removal was observed comparing with UV/H\textsubscript{2}O\textsubscript{2} using solar light and solar photo-Fenton process.
This can be attributed by the free hydroxyl radicals produced in UV/H₂O₂ using solar light and solar photo-Fenton process [63].

![Graph showing the effect of type of photochemical processes on % colour removal of the dye.](image)

Figure 4.1. Effect of type of photochemical processes on the % colour removal of the dye. [pH=5, reaction time 1 hour, catalyst dose 0.2 g/L and initial dye concentration 30 mg/L].

### 4.2.2. Comparison between dark Fenton Process and Photo-Fenton Process

Figure 4.2 shows Comparison between dark Fenton Process and Photo-Fenton Process. As be noticed from Figure 4.2 that dark Fenton process was enhanced using solar light due to more free hydroxyl radicals are produced by this process.
4.2.3. Effect of initial dye concentration

At a fixed weight of Fe(II) (0.2 g/L), H₂O₂ (1 ml) irradiation time (1 hour) and pH = 5, the effect of initial dye concentrations ranging from 30 to 70 mg/L on the photocatalytic was investigated under solar irradiation. Figure (4.3) illustrates the % colour removal of the dye versus initial dye concentration. As depicted from the Figure, a decrease in the % colour removal was observed upon the increase of initial dye concentration. Similar observations have also been reported for the photocatalytic oxidation of other dyes and organic compounds [64-66]. One possible cause for such results is the solar radiation screening effect of the dye itself. At a high dye concentration, a significant amount of solar radiation may be absorbed by the dye molecules rather than the photocatalyst particles, consequently, by
increasing the initial dye concentration, the photon flow reaching the catalyst particles decreased due to the fact that increasing numbers of photons were absorbed by the dye molecules present in the solution and/or on the catalyst surface, and thus reduces the efficiency of the catalytic reaction [67].

Another possible cause is the interference from intermediates formed upon solar photocatalytic of the parental dye. These intermediates may include aromatics, aldehydes, ketones and organic acids as shown by previous studies with various aromatic compounds [68]. They may compete with the dye molecules for the limited adsorption and catalytic sites on photocatalyst particles [69] and thus inhibit decolorization.

Such suppression would be even more pronounced in the presence of an elevated level of degradation intermediates formed upon an increased initial dye concentration.

Figure 4.3. Effect of initial dye concentration on the % colour removal of the dye. [pH=5, catalyst dose 0.2 g/L and irradiation time 1 hour].
4.2.4. Effect of catalyst dose

The % colour removal of the dye using the photocatalytic oxidation process against the concentration of Fe(II) was determined and shown in Figure (4.4) over the catalyst range from 0.1 to 0.5 g/L, initial dye concentration of 30 mg/L, pH value of 5 and within irradiation time of 1 hour. Iron in its ferrous form acts as photo-catalyst and requires a working pH below 5. To further elucidate the role of Fe(II) concentration on the mineralization of the effluent, a series of experiments varying the concentration of iron and keeping fixed the other parameters, were carried out. Figure (4.4) shows a plot the efficiency of colour removal as a function of initial Fe(II) concentrations for a reaction time 60 min. The Figure shows that the addition of Fe(II) enhances the efficiency of colour removal. The results indicate that increasing initial quantities of iron in solution produce increasing rates of colour removal. The best colour removal (99.7 %) was obtained with initial Fe(II) concentration 0.2 g/L. Lower initial concentrations of Fe(II) would cause fewer OH• free radicals to be available for oxidation. When further increase of initial Fe(II) concentration H$_2$O$_2$ ratio (Fe(II) > 2 g/L), it can also be observed that the efficiency of the colour removal actually decreases attains a plateau. This may be due to: (a) the increase of formation of a brown turbidity in the solutions during the photo-treatment, which hinders the absorption of the UV light required for the photo-Fenton process and promoted the recombination of hydroxyl radicals (Reaction 3)[40-42]; (b) the redox reactions since OH radicals may be scavenged by the reaction with another Fe(II) molecule as indicated below (Reaction 4) [41, 42, 44]; (c) the Fe(III) formed can react with H$_2$O$_2$ (Reaction 5) as well as with hydroperoxy radicals with regeneration of Fe(II) in the solution resulting in decrease in degradation rate [41, 42]. It is
desirable that the ratio of H$_2$O$_2$ to Fe(II) should be as small as possible, so that the recombination can be avoided and the sludge production from iron complex is also reduced.

![Graph](image.png)

**Figure (4.4). Effect of catalyst dose (g/L) on the % colour removal of the dye.** [pH=5, initial dye concentration of 30 mg/L and solar irradiation time 1 hour].

### 4.2.5. Effect of addition of hydrogen peroxide as an electron acceptor

To elucidate the role of H$_2$O$_2$ concentration on the photodegradation of the dye in the Solar Photo-Fenton system, some experiments are carried out by varying the initial H$_2$O$_2$ concentrations at constant COD and initial Fe(II). As shown in Figure (4.5), the degradation efficiency represented by % colour removal is demonstrated when H$_2$O$_2$ concentration increases from 0.5 to 1 ml/L, which is explained by the effect of the additionally produced OH• radicals [40-42]. However, above this H$_2$O$_2$ concentration, the reaction rate levels off and sometimes is negatively affected, by the progressive
increase of the hydrogen peroxide. This may be due to auto-decomposition of H₂O₂ to oxygen and water and recombination of OH• radicals. Excess of H₂O₂ will react with OH• competing with organic pollutants and consequently reducing the efficiency of the treatment, the H₂O₂ itself contributes to the OH• radicals scavenging capacity according to the reactions below. It is found that, the optimal H₂O₂ concentration is 1 ml/L mol/L for the degradation of dye with 99.7% colour removal after 60 min solar irradiation time as shown in Figure (4.?). Therefore, H₂O₂ should be added at an optimal concentration to achieve the best degradation. This optimal H₂O₂ concentration depends on the nature and concentration of the compound to treat and on the iron concentration.

\[
\begin{align*}
H_2O_2 + O_2^- & \rightarrow OH\cdot + OH^- + O_2^- & \text{Reaction (1)} \\
H_2O_2 + hv & \rightarrow 2OH\cdot & \text{Reaction (2)} \\
H_2O_2 + e^- & \rightarrow OH^- + OH\cdot & \text{Reaction (3)} \\
H_2O_2 + 2e^- & \rightarrow 2OH^- & \text{Reaction (4)} \\
H_2O_2 + 2h^+ & \rightarrow O_2 + 2H^+ & \text{Reaction (5)} \\
OH\cdot + H^+ + e^- & \rightarrow H_2O & \text{Reaction (6)} \\
H_2O_2 + OH\cdot & \rightarrow HO_2\cdot + H_2O & \text{Reaction (7)} \\
HO_2\cdot + OH\cdot & \rightarrow H_2O + O_2 & \text{Reaction (8)}
\end{align*}
\]
4.2.6. Effect of pH values

The most important parameter that influences the photocatalytic degradation is solution pH. Previous studies indicate that pH may affect photocatalytic oxidation in a number of ways. First, the pH changes can influence the adsorption of dye molecules onto the catalyst surfaces, an important step for photocatalytic oxidation to take place. Second, as indicated in Reaction (9), OH· can be formed by the reaction between hydroxide ion and positive hole. An acidic condition would thus favor OH· formation and enhance degradation [78]. Figure (4.6) shows the effect of pH on the decolorization of the dye in the presence of 0.2 g/L of Fe(II), dye concentration of 30 mg/L within irradiation time of 60 minutes. As seen in Figure (4.6), the highest
decolorization rate was observed at pH 3 with 100% comparing with 99.7% colour removal at pH equals 5.

![Graph showing color removal vs solar irradiation time for different pH values]

**Figure 4.6. Effect of pH values on the % colour removal of the dye.** [catalyst dose 0.2 g/L, initial dye concentration 30 mg/L and irradiation time 1 hour].

\[
\text{HO}_2 + h^+_\text{VB} \rightarrow \text{OH}^- + \text{H}^+ \quad \text{Reaction (9)}
\]

**4.2.7. Enhancement the behaviour of Fe(II) by addition of Bentonite**

Homogeneous photocatalysis employing Solar Photo-Fenton Process has demonstrated its efficiency in degrading a wide range of ambiguous refractory organics into readily biodegradable compounds, and eventually mineralized them to innocuous carbon dioxide and water.

A way to increase the photocatalytic activity way was the use of materials such as silica, alumina, zeolites, glass, porous nickel or clays, but no
improvement of photoefficiency was observed. Activated carbon (AC) is another type of co-adsorbent that has been used in photodegradation of organic pollutants in aqueous phase and according to our knowledge, using AC support has been reported up to now the more promising results, which is attributed to the synergistic effect between the AC and the Fe(II). In our work, the solar photocatalytic oxidation of the dye was examined the effect of addition of Bentonite impregnated with Fe(II). FE(II)/Bentonite Catalyst were tested in the photocatalytic decolourization of aqueous solution of the dye with solar radiation.

Figure 4.7 shows the effect of addition of Bentonite on FE(II) of the solar photocatalytic oxidation of the dye against the % removal of colour of the dye comparing with using Fe(II) with solar light only. The operating conditions were Fe(II): Bentonite mass ratio 1:1, pH value equals 5, irradiation time 45 minutes, dye concentration = 30 mg/L, Fe(II) = 0.2 g/L. As shown in Figure (4.7), the solar photocatalytic activities for the decolourization of the dye with both Fe(II)/Bentonite is higher (100%), compared with the corresponding FE(II) only (96%), because Fe(II)/Bentonite consists of fine powder exhibited higher dispersion in the aqueous solution in comparison with the Fe(II) photocatalysts alone, which were supposed to be one of the reasons for faster decoularization for the dye. These better results could be due to the combined effect of adsorption and photodecolourization. Bentonite acts as an adsorbent in adsorbing the dye molecules from the solution. The adsorbed molecules on the surface of the Bentonite then come in contact with Fe(II) which causes photodecolourization. Fe(II)/Bentonite acts as semiconductor as well as adsorbent to give dual effect to the dye removal regardless the characteristics of the dye. In the present case, the Bentonite adsorption worked well in
combination with Fe(II) photodegradation for removal of the colour of the dye. The dual effect was capable of increasing the efficiency or performance of the whole degradation system.

**Figure 4.7.** Enhancement the behaviour of Fe(II) by addition of Bentonite on the % colour removal of the dye. [pH=5, catalyst dose 0.2 g/L, initial dye concentration 30 mg/L, Fe(II): Bentonite mass ratio 1:1 and solar irradiation time 45 minutes].

**4.2.8. Kinetic registration**

The relationship between % colour removal of the dye and the irradiation time during the solar photocatalytic oxidation is described by a pseudo first order, which is rationalized in terms of the Langmuir-Hinselwood mood, modified to accommodate reactions occurring at a solid-liquid interface [98] according to Equation (9).

\[
\ln \frac{C_t}{C_0} = -k_t K_t = -k_0 t 
\]

(Equation 9)
where \( r \) is the rate of decolourization of X dye, \( C_0 \) and \( C_t \) are the concentration (mg/L) of the dye at irradiation times 0 and \( t \) (min), \( K \) represents the equilibrium constant for adsorption of the organic substrate onto photo-catalyst, \( k_r \) reflects the limiting rate of reaction at maximum overage for the experimental conditions and \( k_0 \) is the overall pseudo first-order reaction rate constant (in min\(^{-1}\)) and \( t \) is the irradiation time (in min).

The % colour removal of the dye by solar photo-Fenton process at different types of catalysts (Fe(II) and Fe(II)/Bentonite) was observed as a function of irradiation time and data were fitted to be a pseudo first-order rate model as shown in Figure (4.8). The operating conditions were catalyst dose 0.2 g/L, pH=5, initial dye concentration of 30 mg/L, solar irradiation time of 45 minutes and Fe(II):Bentonite mass ratio 1:1.

The rate constants were determined using a first-order rate model (Equation 9) and their values were evaluated as the slopes of the linear lines shown in Figure (4.8) and are calculated to be 0.036 and 0.084 min\(^{-1}\) for the solar photocatalytic oxidation of the dye with Fe(II) and Fe(II)/Bentonite respectively. The experimental data in the Figure show that % colour removal of the dye by using Fe(II) and Fe(II)/Bentonite photocatalysts have good results.
4.2.9. Degradation of the dye under optimal conditions

Based on the results obtained in the characterization experiments, the optimal conditions for the solar photocatalytic oxidation of the dye with solar photo-Fenton process were found to be 0.2 g/L Fe(II), pH=5 and initial dye concentration 30 mg/L. One experimental run was carried out to follow the degradation of the dye with time. Both % colour removal and % COD (Chemical Oxygen Demand) removal were investigated along the irradiation time for the solar catalytic oxidation of the dye. Figure (4.9) shows the % of color and COD removal in the reaction solution during the solar photo-Fenton photocatalytic oxidation process of the dye at optimum operating conditions. As indicated, the dye was decolorized by about 73.3% within the first 30 min and reached 96% within 45 min and reached 99.3% within 60
min then remained almost unchanged till 120 min of reaction time. COD removal reached 60.1, 69.4 and 73% within 30, 45 and 60 min irradiation time respectively, indicating the formation of organic intermediates derived from the dye. The % COD removal then increased with time but very slowly till a constant level of 80.7% within 120 min and 81.5% within 210 min of solar irradiation. These results indicate that the fast decolorization of the dye was followed by much slower mineralization of intermediates formed subsequently. On the other hand, the persistence of a low but constant COD removal in solution suggests the accumulation of dead-end product(s) which is(are) resistant to degradation by the solar photocatalytic oxidation reaction. Therefore, it should be readily removed by biological treatment systems and is unlikely to pose a problem to the environment.

![Graph showing % Colour removal and % COD removal with Solar irradiation time (min)](image)

Figure 4.9. Decolourization and Degradation of the dye under the solar photocatalytic oxidation using solar photo-Fenton process. [pH=6.7, catalyst dose 0.5 g/L and initial dye concentration 80 mg/L].
CHAPTER (5)
FEASIBILITY STUDIES AND MARKET NEEDS

Homogeneous solar photocatalytic oxidation processes consider very economic processes for the following reasons:

- These processes utilize the natural sunlight, the natural source of ultraviolet radiation (UV) instead of using the electrical UV lamps which are very expensive and have also limited life time. It is known that UV lamps consume energy which are also very expensive, since we have to use many numbers of electrical UV lamps, but when we use solar parabolic collectors that means that we will save money consuming in purchasing such these electrical UV lamps. On other hand electrical UV lamps are very difficult in handling, since they could be easier broken.

- These methods depend on the generation and production of free hydroxyl radicals, the strong powerful oxidation agents with high oxidation efficiency which are able to oxidize and degrade the very toxic and strong pollutants in a very short time comparing with the other famous oxidizing agents such as atomic oxygen, ozone,…etc. Thus, these processes save time, and consequently save the money are going in costs of using equipments for a long time.

- The raw materials consumed in these processes are the photocatalyst which it is used in a very low amount and also a low amount of oxidant when it is needed. The prices of such these materials are very cheap especially when they are bought in commercial grades or when they are present in the locally market. More save in money can be achieved when the photocatalysts are easy to be regenerated and recycled to be used for several times.
The fixed costs are represented in the construction of solar collectors are considered one time only. They are stayed and can be worked for long time without damage. They have very long life time. Moreover, the materials are needed for the construction are not imported and easily found in the local market in very cheap prices. The configurations and design of such these collectors are easy and not complicated and they are easy to be worked and handled.
CHAPTER (6)
CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions
This study presents presented herein aimed to evaluate the application of the solar homogeneous photocatalytic oxidative degradation of dyestuffs in synthetic dyehouse effluents under using Solar Photo-Fenton Process. Methylene Blue dye was selected as model substance and it is a biorecalcitrant compound used in textile processing and found in the dyehouse effluents. In a recent project study, it was concluded that hydroxyl radicals were the main reactive species. It was also pointed out that Solar Photo-Fenton process remove the colour of the selected dye and degraded it efficiently.

The addition of 1 ml/L H$_2$O$_2$ as an electron acceptor and 0.5 g/L Fe(II) as photocatalyst showed an enhancing effect on color removal during the oxidation of the dye by solar radiation and leads to complete decolourisation. The kinetic study shows that the degradation of the dye by solar catalytic oxidation was found to be pseudo first-order. The results clearly delineate the important role of the selection of the most appropriate amount and type of photocatalysts in achieving highest color removal efficiency. It can also be concluded that presence of hydrogen peroxide as an oxidant accelerate the degradation of the dye.

Optimal physicochemical conditions for the degradation a 30 mg/L dye solution, under solar photocatalytic oxidation, were determined to be: Fe(II) loading of 0.2 g/L; initial H$_2$O$_2$ concentration of 1 ml/L; initial pH 0f 5. Under these conditions, the dye can be decolorized by 99.6% mineralized with a COD removal of 85% within 180 min.
The increase in the photocatalytic activity of Fe(II) by the addition of Bentonite was observed. Bentonite was loaded into Fe(II) with mass ratio Fe(II)/Bentonite of 1:1. The experiments revealed that colour removal by the photocatalytic oxidation of the dye aqueous solution is more effective in Fe(II)/Bentonite than Fe(II) only. About 100% colour removal of the dye was observed with Fe(II)/Bentonite in comparison to 96% with Fe(II) only under the same operating conditions of pH, irradiation time, initial dye concentration and Fe(II)/Bentonite of 1:1 mass ratio. This can be attributed to synergistic effect of Bentonite. The separation of the catalysts from solutions, one of the most important drawbacks of photocatalysis, was overcome by simple sedimentation and decantation. In particular, the typical features of the photocatalyst would make it very suitable for configurations and efficient photoreactor for purification of polluted water. The results show also reduction of COD values after the solar photo-Fenton oxidation of the dye in the presence of Fe(II), which means that the dye is degraded, mineralized and converted to biodegradable compound or intermediates and/or end products, which can be more readily biodegradable. The efficient decolorization and degradation respectively indicate that solar photo-Fenton photocatalytic oxidation can be used as a simple, efficient and economic treatment of wastewater containing very toxic dyes. Degradation, however, was not complete probably due to presence of intermediates compounds resistance to degradation by solar photo-Fenton catalytic oxidation process.

**B. Recommendation**

The study proved that the fact that the industrial effluents can be treated with solar irradiation instead of the artificial UV-light driven solar simulators
would eliminate major operational costs and makes this approach an attractive alternative treatment process worthwhile to explore further. Further study may be done to investigate possibility of following the solar-catalytic oxidation by biological treatment to obtain maximum color and COD removal of the wastewater generated from textile industry.

The presence of the powerful sunlight along the year in Saudi Arabian kingdom and all Gulf Countries encourage and recommend the use of solar photocatalytic processes as very economic techniques for the wastewater. The results assured that Advanced Oxidation Processes (AOPs), especially the homogeneous and heterogeneous photocatalytic oxidation processes are promising techniques and they are recommended for the treatment of the industrial wastewater containing very toxic and recalcitrant pollutants that can not be able to be degraded with the classic and traditional treatment processes. This is attributed with the production of the free hydroxyl radicals generated by these processes. So, these techniques can be used for the treatment wastewater coming from different fields of industries like petroleum, pharmaceutical, textile and other industrial sectors which produce wastewater with very high load of organic and inorganic pollutants.

Homogeneous photocatalytic oxidation using solar photo-Fenton process can be used also for the surface, ground and sewage wastewater.

The economic of these processes can be also reduced very much and using immobilized photocatalyts to avoid using photocatalyts as slurry is recommended. The photocatalyts also can be used again also by their regeneration.

Applicability of these advanced techniques are recommended not only for the treatment of the wastewater containing high polluted contaminants and reaching with their concentrations in the final stream to be compatible with
the environmental rules and legislations concerning the disposal of such wastewater, but also to recycle and reuse these treated wastewater for the industrial and irrigation purposes.


[56] De Laat, J., Gallard, H. and Legube, B. “Comparative study of the oxidation of atrazine and acetone by H$_2$O$_2$/UV, Fe(III)/UV, Fe(III)/H$_2$O$_2$/UV and Fe(II) or Fe(III)/H$_2$O$_2$”, Chemosphere, 39(1999) 2693-2706.


Project Submission
and
ABET Criterion 3 a-k Assessment Report

Project Title:  Design of Solar Parabolic Collector for the Treatment of Textile Wastewater by Solar Photo-Fenton Process

DATE:  3 / 7 / 1435
PROJECT ADVISOR:  Prof. Dr. Montaser Youssry Ghaly

Team Leader:  Mohammad Abdu Othman
Team Members:
Ahmad Jurishy Harissi  Mohammad Abdu Othman
Faiz Ahmad Almalki  Majed Jubran Almalki
Nouh Mohammad Oreabi  Yagoub Abdu Hakami

Design Project Information
Percentage of project Content- Engineering Science  50%
Percentage of project Content- Engineering Design  50%
Other content  0%

All fields must be added  100%

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70
Fill in how you fulfill the ABET Engineering Criteria Program Educational Outcomes listed below

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<tr>
<th>Outcome (a), An ability to apply knowledge of mathematics, science, and engineering fundamentals.</th>
<th>Please list here all subjects (math, science, engineering) that have been applied in your project. Engineering design, Environmental Engineering, Reaction kinetics, Water treatment, Unit operation, Chemical oxidation</th>
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<td>Outcome (b), An ability to design and conduct experiments, and to critically analyze and interpret data.</td>
<td>In this part, if the project included experimental work for validation and/or verification purposes, please indicate that. The experimental part includes the removal of colour, organic load and COD from wastewater containing dyes. So analysis to determine the colour and COD are carried out and the data obtained are interpreted to be taken into consideration in the design of the treatment unit.</td>
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<tr>
<td>Outcome (c), An ability to design a system, component or process to meet desired needs within realistic constraints such as economic, Environmental, Social, political, ethical, health and safety, manufacturability, and sustainability.</td>
<td>All projects should include a design component. By design we mean both physical and non physical systems. The solar parabolic reactor was designed in this study to powerful collect solar energy to be used as a source of UV radiation to apply the solar photocatalytic oxidation technique for the treatment of wastewater containing toxic dyes and convert it to environmentally friendly products to meet with international laws and legislation concerning the discharge of wastewater treatment. The techniques used in this study is economic and save money since it use the natural solar energy. Treated water can be reused to be used in irrigation or cooling water purposes.</td>
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<td>Outcome (d), An ability to function in multi-disciplinary teams.</td>
<td>This outcome is achieved automatically by the fact that all projects composed of at least 3 students. However, if the project involved students from other departments, that would be a plus that is worth to be highlighted. The project includes 6 student from Chemical Engineering Department and No multidisciplinary team.</td>
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<td>Outcome (e), An ability to identify, formulate and solve engineering problems.</td>
<td>In order to meet this specific outcome, it would help if you have a Problem Statement section in your project report. If not, then briefly highlight how the “students” were able identify, formulate and solve the project’s problem. The students can practice the technical design considerations and applications. They can use this design to solve an important issue such as wastewater treatment. The can be able to optimize the operating conditions to maximize the benefits of their design.</td>
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<td>Outcome (f), An understanding of professional and ethical responsibility.</td>
<td>Here professional and ethical responsibility depends on the project context. The most ethical in the project must take in design consideration is to obtain water with good quality to human uses.</td>
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<td>Outcome (g), An ability for effective oral and written communication.</td>
<td>Good report and good presentation will fulfill this outcome. The students introduce good report.</td>
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<td>Outcome (h), The broad education necessary to understand the impact of engineering solutions in a global economics, environmental and societal context.</td>
<td>This outcome is usually fulfilled by highlighting the economic feasibility of the project, and emphasizing that the project would not harm the environment and does not negatively affect human subjects. The undertaken work proved the efficiency of using the techniques in this study for the treatment of different types of wastewater containing very toxic pollutants successfully. The project introduce very economic and easy practicable techniques. Scaling up of this design will be very helpful in the industrial scales. This project gives a practical solutions for the very important environmental issue, the water pollution and the lackage of water.</td>
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<td>Outcome (i), A recognition of the need for, and an ability to engage in life-long learning.</td>
<td>This outcome is fulfilled by suggesting a plan for future studies and what else could be done based on the outcome of the current project. The futural plan for this work is to examine the real industrial wastewater from different industrial sectors which are characterized with their containing of toxic and refractory organic pollutants aiming to reuse this treated water for irrigation and industrial purposes and pollution prevention.</td>
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<td>Outcome (j), A knowledge of contemporary issues</td>
<td>Extensive literature review by the “students” for the current state of the art will fulfill this outcome. There are more references in this work.</td>
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<tr>
<td>Outcome (k), An ability to use the techniques, skills, and modern engineering tools necessary for engineering practice.</td>
<td>List all technologies included in the project (hardware and software) Excel program used in the interpreting of the data.</td>
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By signing below certify that this work is your own and fulfills the criteria described above

Student Team Signatures

_________________________  __________________________

_________________________  __________________________

_________________________  __________________________

Project Advisor Signature  __________________________

Date  __________________________

College Coordinator of Capstone Projects  __________________________

Approved By  __________________________
B-Project Budget and Expenses to data

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