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Performance of advanced photocatalytic detoxification of municipal wastewater under solar radiation - A mini review

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Abstract
During the last few years, there has been a plethora of research and development in the area of solar photocatalysis. The aim is to understand the fundamental processes and enhance photocatalytic efficiencies especially for air, soil and water pollution control. Municipal waste water is limited by continual organic water pollutants and micro-organisms that are not removed by conventional mechanical and biological treatment. In this overview of the most recent paper, studies focused on the treatment of municipal wastewater (containing organic compounds) by photocatalysis and the effects of various parameters such as pH, light intensity, Advance oxidation method etc. have been studied It can be concluded that the photocatalysis process is suitable for the treatment of drinking water, municipal and industrial wastewater. Some studies on the economic analysis of photocatalytic systems are also included.

Keywords: Solar photocatalysis, Photocatalytic reactors, Municipal wastewater treatment, Solar radiation, Photo-Fenton.

1. Introduction

In recent years, it has been found that solar photocatalytic detoxification is one of the promising methods for the disinfection and treatment (colour, odour, COD etc.) of the municipal wastewater. The combination of light and catalysts has proven very effective for water purification [1]. Conventional water and wastewater treatment processes have been long established in removing many chemical and microbial contaminants of concern to public health and the environment. However, the effectiveness of these processes has been increasingly challenged with the identification of more and more contaminants, rapid growth of population and industrial activities and diminishing availability of water resources [2].
Solar heterogeneous or homogeneous photocatalytic method is suitable for the municipal wastewater of small communities and villages, where there is a wide variation of the population between winter and summer seasons. This variation leads, during the year, to wastewater effluents with very different hydraulic and organic load, thus causing problems to the biological treatment plants and leading therefore to effluents of low quality [2]. The treatment technology, including advance oxidation process (AOPs), and solar irradiation, the emphasis was placed on their basic principles, applications, and new technology developments. Advantages and disadvantages of these technologies are compared to highlight their current limitations and future research needs [3].

The major applications investigated for this technology are colour removal; [4-9] reduction of COD (chemical oxygen demand); [10,11] mineralization of hazardous organics;[12-15] destruction of hazardous inorganic such as cyanides; [16] treatment of heavy metals; [17,18] degradation of harmful fungicides, herbicides, and pesticides; [19-21] purification and disinfection of water; [22,23] destruction of malodorous compounds; [24] decontamination of soil; [25] decontamination of indoor air; [26,27] and destruction of cancer cells; [28,71]. The efficiency of TiO_2, photo-fenton and the modified photo-fenton (ferrioxalate) reagent in the presence of solar irradiation was evaluated by the organic content reduction (dissolved organic carbon, DOC) of a municipal wastewater [2].

The present review aims are to develop a method which takes care of energy saving & water recycle/reuse together. Photocatalytic detoxification will be investigated through laboratory experiments as an alternative to conventional secondary treatment. It is very important to develop processes for the clean-up of polluted water [1]. This study was to utilize different chemical oxidation method for reducing refractory organic matter in municipal wastewater [29]. Moreover, to the best of our knowledge the application of solar detoxification for the zero effluent discharge at household level has not yet been investigated [1]. In conventional treatment methods, lot of energy is wasted and also they generate harmful by-products. Instead of these, photo catalytic oxidation method can be used as

(i) It is eco-friendly, very less sludge generation, energy efficient and sustainable method.
(ii) It does not create any harmful by-products

1.1 Solar ultraviolet radiation potential in India

Earth receives $1.7x10^{14}$ kWh, meaning $1.5x10^{18}$ kWh per year of solar radiation, which is approximately; 28000 time the world energy consumption per year [30]. In a tropical country like India ((8º4”-37º6” N latitude), highest level of global solar UV radiation is received. Adequate amount of Solar UV radiation is received for almost 10 months a year. Average mean peak irradiance of Solar UV- A is 47 W/m^2 - 66 W/m^2 and average mean peak irradiance of Solar UV- B is 0.195 W/m^2 - 0.3384 W/m^2 [31]. Nearly, 95-98% of the sun ultraviolet radiation reaching the earth’s surface is UV- A. Only 2-5% of UV light at the earth surface is solar UV - B. Practically all of UV - C and much of UV- B is absorbed by the ozone and the atmosphere.

According to Blanco et al. [32] the UV radiation represents between 3.5% and 8% of the solar spectrum, fluctuating with the presence of clouds and increasing with altitude. The percentage of global UV radiation (direct + diffuse), with regard to the global, generally increases when the atmospheric transitivity decreases, mainly due to clouds, but also to aerosols and dust [33]. In fact, the average percentage of UV with respect to total radiation on cloudy days is upto 2% higher than values on clear days. Since the UV radiation is not absorbed by water vapor, as much as 50% of this, or more in very humid locations or during cloudy or partly cloudy periods, can be diffused. The diffuse component can make up to 50% of the total available UV light even on a clear day because the shorter wavelengths UV photons are more readily scattered within the atmosphere. Solar energy available in various regions is typically 8.3% ultra-violet (200-400 nm), 38.2% visible (400-700 nm), 28.1% near infra-red (700-1100 nm) and 25.4% infrared/far-infrared portion. Figure 1 shows the ultraviolet spectrum on the earth surface.

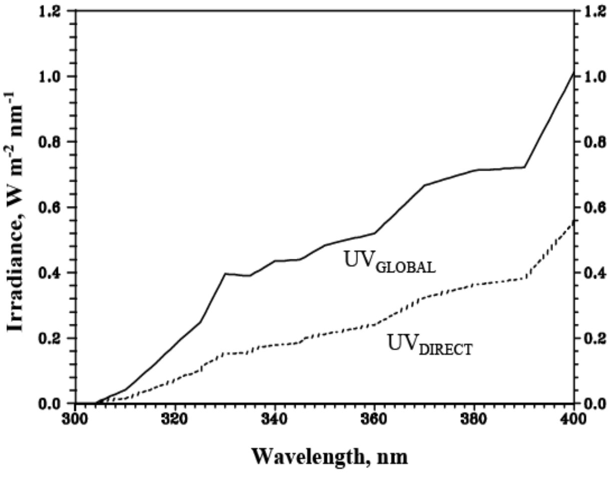

Figure 1. Ultraviolet spectrum on the earth surface [34]

2. Photocatalytic reactors

Photocatalysis has been a subject of increasing interest during the last twenty year. It has various potential applications such as metal recovery, abatement of NOx, synthesis of ammonia but the recent development have been induced mainly by the application to the abatement of organic pollution both in the aqueous and the gaseous phase. This development participates to the general concern about the environment and the increasing constraints on the toxicity of wastes [35].

As the compound parabolic concentrators (CPCs) do not concentrate light inside the photoreactor, the system is outdoors and is not thermally insulated; the maximum temperature achieved inside the reactor during the experiments is 45°C. Solar ultraviolet radiation UV was measured by a global UV radiometer (KIPP & ZONEN, model CUV3), mounted on a platform tilted 37° (the same angle as the CPCs), which provides data in terms of incident $W_{UV}m^2$. This gives an idea of the energy reaching any surface in the same position with regard to the sun. With equation (1) combining of the data from the experiments of several days and their comparison with other photocatalytic experiments is possible [36].

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n UV_{G,n} \frac{A_{CPC}}{V_{TOT}} \qquad (1)$$

where, tn is the experimental time for each sample, $UV_{G,n}$ is the average UV_G during Δ_{tn}, A_{CPC} is the collector surface, V_{TOT} is the total plant volume and $Q_{UV,n}$ is the accumulated energy (per unit of volume in kJL^{-1}) incident on the reactor for each sample taken during the experiment.

2.1 Type of photocatalytic reactors

In recent year several reactors for the solar photocatalytic treatment have been developed and tested. Both type of solar reactors exhibit specific advantages and disadvantages, which are summarized in Table 1.

Table 1. Comparison between non-concentrating and concentration system used in solar photocatalytic application [45- 48]

Non-concentrating Collector		Concentrating Collector	
Advantages	Disadvantage	Advantages	Disadvantage
+ Direct and diffuse radiation	- Laminar flow (low mass transfer)	+ Turbulent flow	- Only direct radiation
+ No heating	- Vaporization of reactants	+ No vaporization of compounds	- High cost (sun tracking)
+ Low cost and fewer maintenance requirements	- Reactant contamination and mass transfer problems in photocatalysis	+ More practical use of a supported catalyst as less is needed per unit collector surface	- Low optical efficiency and usually expensive
+ High optical efficiency	- Weather resistance, chemical inertness and ultraviolet transmission	+ More practical use of a supported catalyst	- Low optical efficiency
+ Hight quantum efficiency (r = k I with TiO2)	- Water overheating	+ Smaller reactor tube area	- Low quantum efficiency (r = k $I^{<1}$ with TiO2
+ Since recombination of e^-/h^+ is lower than in a concentrating system because the photonic density is lower, they have both high optical efficiency and high quantum efficiency	- Reactant contamination	+ There is no evaporation of volatile compounds	- Lower optical efficiency and quantion of e^-/h^+ than in non-concentration systems Possible water overheating

2.1.1 Parabolic trough reactor (PTR)

A PTR concentrates the parallel (Direct) rays of the photocatalytically active ultraviolet part of the solar spectrum by a factor of 30 to 50 and can be characterized as a typical plug flow reactor. In the wavelength range which can be used for the excitation of TiO_2 (UV-A, 300-400nm) the diffuse [$E_{dif\,(300\text{-}400)}$ =24.3 W/m^2] and direct [$E_{dir\,(300\text{-}400)}$ =25.0 W/m^2] portion of the solar radiation (AM 1.5) reaching the surface of the earth are almost equal [37-39].

2.1.2 Thin-film-fixed-bed reactor (TFFBR)

Solar photons can also be used without further concentration in a fixed bed reactor system. The TFFBR employs both the diffuse portion of the solar radiation. Coating of the plate was achieved using P25 TiO_2 from Degussa followed a patented method [38-41].

2.1.3 Double skin sheet reactor (DSSR)

A new kind of non concentrating reactor is DSSR [42-44]. This type of reactor employs both the direct and diffuse portion of the solar radiation, but after the degradation process the photocatalysis has to be removed from the liquid.

3. Solar photocatalytic degradation of contaminants

Finally Photocatalysis mineralizing the contaminants into carbon dioxide, water, and inorganic, practical applications of solar technologies have been studied and developed most intensively for heterogeneous TiO_2 photocatalysis and homogeneous photo-Fenton. There is no general rule at all, each case being completely different [46, 47].

In general, the types of compounds that have been degraded include alkanes, haloalkanes, aliphatic alcohols, carboxylic acids, alkenes, aromatics, haloaromatics, polymers, surfactants, herbicides, pesticides, and dyes. Equation 1generally holds true for a general organic compound equation (2) of $C_nH_mO_p$ [48].

$$C_nH_MO_p + \left[\frac{(m-2p)}{4} + n\right] O_2 \rightarrow nCO_2 + \frac{m}{2} H_2O \tag{2}$$

Apart from developments on increasing photocatalytic reaction rate, the most important progress in solar photocatalysis, in recent years has been related to combination with biological treatment and the application of toxicological analytical methods. Contaminant treatment, in its strictest meaning, is the complete mineralisation (TOC=0) of the contaminants, but photocatalytic processes only make sense for hazardous non-biodegradable pollutants. [47] Therefore, biologically recalcitrant compounds could be treated with photocatalytic technologies until biodegradability is achieved. Subsequently, the water can be transferred to a conventional biological plant. Such a combination reduced treatment time and optimised the overall economics, since the solar detoxification system can be significantly smaller [49, 50]. As shown in Figure 2, the active component disappears after several minutes of irradiation, but TOC remains after several hours. Therefore, the use of AOPs as a pre-treatment can be justified if the intermediates resulting from the reaction (more oxidized compounds, such as carboxylic acids, alcohols, etc.) are readily degraded by micro-organisms [51, 52]. The treatment, based on the photo-Fenton reaction [53-56], mineralizes 80% of the TOC in the rinse water in a batch process.

4. Effects of operating parameters

The rate of photo mineralization of an organic compound depends on the nature of the photocatalyst, catalyst loading, reactor configuration, concentration of the compound, wavelength, radiant flux, pH and advance oxidation processes in presence of interfering adsorbing species and mass transfer (especially for immobilized TiO2).

4.1 Effect of pH

pH of the aqueous solution significantly affects TiO_2 including the charge of the particle and the size of the aggregates it forms. The pH at which the surface of an oxide is uncharged is defined as the Zero Point Charge (pH_{zpc}), which for TiO_2 is around pH 7 [57]. K. Okamoto et al. [58] suggested a pH of 3.5 as optimal for the degradation of phenol (with reduced anatase) in contrast to another study on alkaline pH conditions, which concluded that alkaline conditions are necessary for the elimination of phenols and COD [59]. Mean particle-size measurements (presented in Figure 3) have been found to be constant at pH 7. 3 increase to 2-4 µm when dispersion reaches pHzpc. In contrast, these variations in particle size could be an advantage for separating the catalyst from water (by sedimentation and/or filtration) at completion of photocatalytic treatments [57].

The pH of an aqueous solution significantly affects all metal oxide semiconductors, including the surface charge on the semiconductor particles, the size of the aggregates formed and the energies of the conduction and valence bands. The adsorption of the contaminants and thus the rates of degradation will be maximum near the zero point charge of the catalyst**.** The pH value of zero point charge for P25 has been measured as 6.25 [58]. The pH of a solution is an important parameter in the photocatalytic degradation of organic compounds due to the fact that pH influences the surface change of the semiconductor, the photoredox process. The decolourization rates under UV/H_2O_2 decreased with increasing pH [59, 60]. In alkaline condition, H_2O_2 will decompose into water and oxygen rather than hydroxyl radicals [60, 61]. This causes the lower decolourization rates of azo dyes at higher pH values because the concentration of OH^- is reduced under these conditions**.** The decolourization rate was increasingly less effective at pH values higher than 8. While acidic conditions achieve a more effective decolourization, the effect of pH values in the range of 8 to 11 is still relatively limited, but the reaction rate and efficiency is certainly dramatically reduced at a pH of 12 [62]. The interfacial energetic at acidic and alkaline pH were also compared Figure 4.

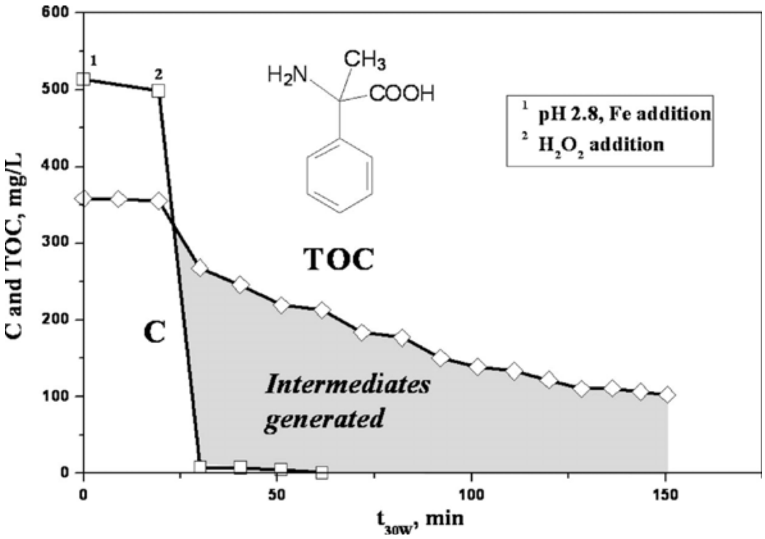

Figure 2. Degradation of a model contaminant (2-amino-2-phenyl-propionic acid, C_0=500 mg/L) dissolved in water by photo-Fenton at Fe=20 mg/L [45]

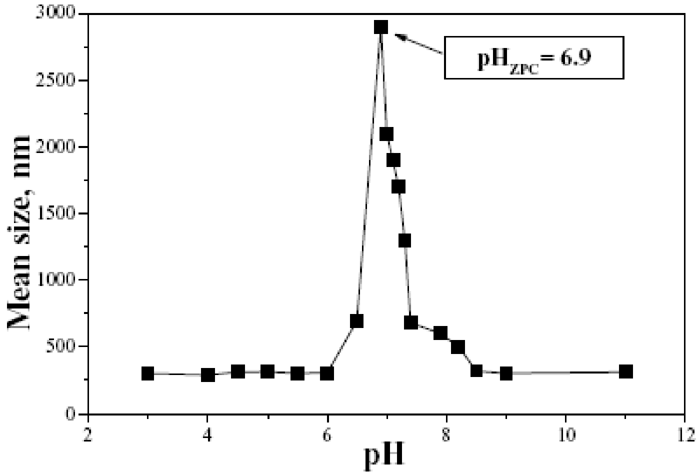

Figure 3. Mean particle size of TiO2 (P-25) suspended in water versus pH. [TiO2]=0.2 g/L [57]

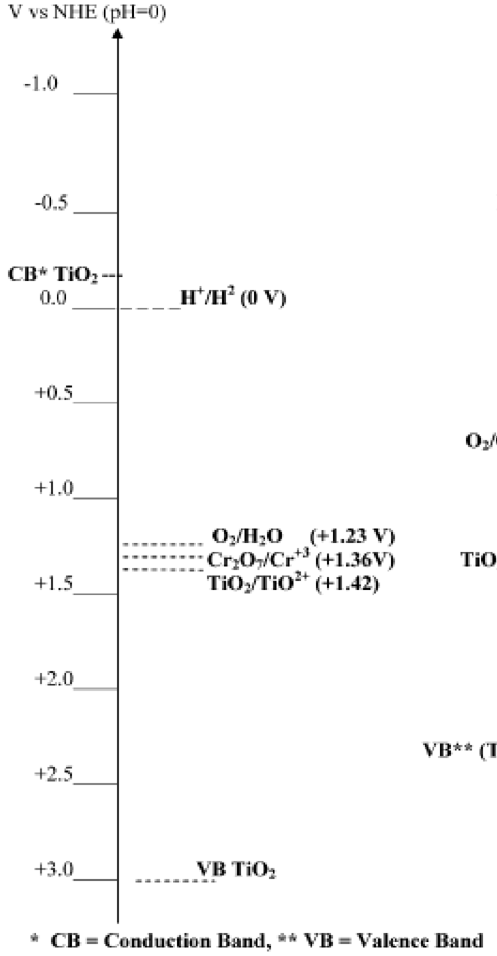

Figure 4. Surface-band energetics at TiO_2 and solution redox levels for pH 0 and 10 cases [63]

4.2 Effect of light intensity and wavelength

Considering the unidirectional solar irradiation, the collection of radiation in solar reactors is carried out in two ways [64]**.** Use of a fixed reactor where a large surface of the solution or suspension is exposed to the sun: trickling on a flat plate supporting a catalyst mesh, flowing a sinuous path [65]**,** flowing through an array of pipes so as to increase the residence time, or through a flat fixed-bed [66], or exposure within a tank such as those designed for water stations, which can be equipped with impellers designed to ensure a good mixing and aerating of the slurry**.** More elaborate system (Fresnel lenses, holographic collector) can be used on a reactor of small dimension. When using a focusing system, the volume of fluid is reduced, this makes it easier to build. It is also a necessity as the whole system (collector + reactor) must be placed on a motorised support so as to track the sun. However, it leads to a high irradiation flux, which may reduce the quantum yield of degradation. In addition, depending on the weather, an important fraction of the sunlight can be diffuse instead of direct, which reduces the efficiency of the focusing system [67].

Some studies have also reported increased efficiency with UV-C radiation than UV-A for the degradation of certain organic materials [68, 69]. Direct photolysis and the higher probability of trapping of electron-hole pairs with shorter wavelength excitation were thought to be the possible reasons for such an effect. It is estimated that only 5% of the incident solar irradiation is of use for the TiO_2 band gap photocatalytic reaction. This significantly limits its practical application. Therefore, modification of TiO_2 photocatalyst to enhance light absorption and photocatalytic activity under visible light irradiation is the subject of recent research [70]. One such parameter is the effect of ultraviolet light intensity on the observed rate of pollutant destruction.

At low light intensity and correspondingly low carrier concentrations, the rate of oxidation of a particular compound is proportional to light intensity, while at higher light intensity the rate is dominated by second-order charge carrier recombination and has a square-root dependence on light intensity [71-75]**.**

The transition from one regime to the other depends on the photocatalyst material, but is typically above 1 sun equivalent (7x10-5 Einstein's m^{-2} s^{-1}). This transition depends on the (immobilized) catalyst configuration and on the flow regime in the photoreactor, and varies with each application [76]. The optimal light power utilization corresponds to the domain where the destruction rate is proportional to light intensity.

Several studies in the literature deal with the optimal concentration of TiO_2 slurries, with can from 0.01to 2 g/L. almost all of them well known titanium Degussa P25, recognized as the most efficient from of titanium dioxide. Obviously the optimal catalyst concentration depends on a number of additional parameter, mainly on the design of the photoreaction and light intensity Table 2.

Table 2. Optimal concentration of TiO_2 for disinfection under different experimental conditions

Process Description	Photocatalysis Used	Source of Light	Reference
Cr (VI) reduction	TiO2 Degussa P-25	365 nm black blue fluorescent UV lamp	[88]
Cr (VI) reduction	TiO2 Degussa P-25	150 W Medium pressure mercury lamp	[89]
Photoreduction of Cu (II)	TiO2 Degussa p-25	Fluorescent black light bulbs	[90]
Microorganism inactivation	TiO2 Degussa 0.1 (g/l)	UV sunlight: 20 W/m2	[91]
aqueous organic contaminant	TiO2 Degussa 0.05 (g/l)	UV solar light collected by a CPC type collector: 30 W/m2	[92]
Microorganism inactivation	TiO2 Degussa 0.5 (g/l)	Lamp: 1000 W/m2 (0.5% UV-C, 7% UV-A.B)	[93]
Microorganism inactivation	TiO2 Degussa p-25 1.0 (g/l)	UV Solar Light: 35 W/m2	[94]
Microorganism inactivation	TiO2 Degussa p-25 1.0 (g/l)	Black light lamp: 45 W/m2	[95]
Microorganism inactivation	TiO2 Degussa p-25 1.0 (g/l)	UV lamp: 67.9 µE/sm2	[96]
ZnO	TiO2 Degussa p-25	-	[97]

4.3 Effect of H_2O_2 dosage

UV/H_2O_2 process is efficient in mineralizing organic pollutants. A disadvantage of this process is that it cannot utilize solar light as the source of UV light due to the fact that the required UV energy for the photolysis of the oxidizer is not available in the solar spectrum [77]. Different concentrations of H2O2 (100, to 3000mg/l) were added to study the effect of H_2O_2 concentration on the decolourization rate. The removal rate increased with increasing initial concentration of H_2O_2. However, as the initial concentration of H_2O_2 reached a certain value, the increase in decomposition rate became less. The decolourization rate was slow at low H_2O_2 concentration, as the formation of hydroxyl radicals was insufficient. At higher H_2O_2 concentration, more OH^- was produced leading to a faster oxidation rate. However, these free radicals preferred to react with the excess of H_2O_2 rather than with the dye [78, 79]. Hydroperoxyl radicals ($HO_2^{\cdot}$) equation (3, 4, 5) as the competitive reaction product are much less reactive than OH^- and do not seem to contribute to the decolourization of RR195A.

$$H_2O_2 \xrightarrow{hv} 2HO\cdot \tag{3}$$

$$H_2O_2 + HO\cdot \rightarrow H_2O_2 + HO_2^- \tag{4}$$

$$HO_2^- + HO\cdot \rightarrow H_2O + O_2 \tag{5}$$

H_2O_2 with the initial concentration of 300 to 900 mg/L is suitable for the decolourization of RR195A using UV/H_2O_2 system as it gave a high decolourization rate. By adding 300 to 900 mg H_2O_2/L, the decolourization was about 99-100% at 30 minutes of irradiation. The most favorable initial H_2O_2 concentration that was observed for the optimum decolourization of RR195A was 300 mg H_2O_2/L.

4.4 Effect of photo-fenton's dosage

The presence of oxalate in equation (6) the Fe^{3+}/H_2O_2 system leads to an additional improvement of the photocatalytic efficiency [80]. Although it is well known for some time that Fenton reagent, a mixture of Fe^{2+} salts with equation (7) hydrogen peroxide (H_2O_2), can easily oxidize organic compounds, it has been applied for water and soil treatment only during the last years [81-83]. The addition of other powerful oxidizing species, such as equations (8) and (9) H_2O_2 or sodium peroxydisulfate ($Na_2S_2O_8$) to TiO_2 suspensions, is a well-known procedure and in many cases lead to an increase in the rate of photo-oxidation [84-86].

$$Fe^{2+}H_2O_2 \rightarrow Fe^{3+}OH + OH^{\cdot} \tag{6}$$

$$Fe^{3+}H_2O + hv \rightarrow Fe^{2+}Fe^{2+}H + OH^{\cdot} \tag{7}$$

$$H_2O_2 + O_2^- \rightarrow OH^{\cdot} + OH^- + O_2 \tag{8}$$

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + S_4^- \tag{9}$$

The investigation on COD removal from oil recovery wastewater using fenton process, [87] reported that 86% reduction of COD was achieved for H_2O_2 to Fe^{2+} mass ratio equal to 8.7 (w/w).

5. Economic analysis of solar photocatalysis system

Although the process of solar detoxification was very effective, the economic viability is not yet favorable for some application [98, 99]. The cost of wastewater treatment using solar detoxification systems depends on several parameters, i.e. rate constant, reactor type, catalyst and pre & post–treatment costs [100]. The authors reported an economic analysis of this technology for future application not only to solar photocatalytic disinfection, but also to decontamination of organic pollutants [45].

5.1 Energy consumption

AOPs based on artificial light may be associated with increased operating cost, a major fraction of which is related to energy consumption see equation (10). J.R. Bolton et al. [101] introduced the concept of specific electric energy consumption per unit mass of pollutant (e.g. COD) degradation (E_{EM}):

$$E_{EM} = \frac{Pt}{V(COD_o - COD)} \tag{10}$$

where V is the effluent Volume in liters in liters, t is the treatment time in hours, P is the lamp power in kW, COD_o and COD is the concentration in g/l before treatment and after treatment time t, respectively.

6. Conclusion

To the summarize this review, the following conclusions can be made:

(i) This technique can be used effectively for the purification and disinfection of municipal wastewater.
(ii) Various designs of photocatalytic reactors, using both solar and artificial light, have been proposed. The solar–based reactors should be chosen according to the climatic conditions of the location and economic feasibility of the reactor.
(iii) The photo-Fenton experiments were considerably faster than those with TiO_2, but a detailed experimental analysis has to be made in order to arrive at a conclusion concerning the most appropriate method for application.

The use of solar light, combined with the simple technology required for this method, can offer economically reasonable and practical solutions to the processing of municipal water were solar intensity is easily available.

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