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SOLAR PHOTOCATALYTIC TREATMENT OF PHENOLIC WASTEWATER- POTENTIAL, CHALLENGES AND OPPORTUNITIES

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ABSTRACT

Quantity of water use in Indian industries is very high compared to other countries water usage. Inefficient water use by industry in India creates lot of problems. This quantity could be reduced to a minimal by recycling the water after sufficient treatment. The available treatment processes do not aim at sufficient treatment required for recycling of water but it concentrates more on achieving the standards, hence complicating the process. Complicated Effluent Treatment process neither helps in recycling of water nor getting standards achieved but results in higher energy consumption for Effluent Treatment Plant. This work aims at sufficient in-situ treatment of wastewater and recycling of water for low-grade applications in the industry. Complete destruction of the contaminant is possible using inexhaustible, free source of energy from sunlight thus consuming very less primary energy for its operation. Photocatalytic experiments were carried out using laboratory photo reactor for degradation of phenol wastewater. The experiments were carried out with 0.2 g/l of TiO_2 catalyst for different concentration of phenol wastewater ranging from 20, 50,100,200,300,400 and 600 ppm. It is found that complete degradation of phenol is possible in a reasonable time (i.e. less than 5 hrs) when concentration of phenol is ≤100 ppm. The paper also reviews the potential, opportunities and challenges of solar photocatalytic wastewater treatment for Indian environmental conditions.

Keywords: wastewater, phenol, solar, photocatalytic treatment, potential, challenges.

INTRODUCTION

The world's ever increasing population and progressive adoption of an industrial based lifestyle led to an increased anthropogenic impact to the environment. (Asamudo *et al.*, 2005). The enigma for the public, scientists and academicians is how to tackle the contaminants that jeopardize the environment. The advancement in science and technology, since industrial revolution, has enabled humans to exploit natural resources (P. Gunasekaran, 2003). Also industrial wastes, sewage and a wide array of synthetic chemicals, pollute considerable parts of water resources. The menace of water-borne diseases and epidemics still threatens the well being of population. Thus, the quality as well as the quantity of clean water supply is of vital significance for the welfare of mankind (S.S. Dara, 2001).

Industry requires good quality water for its use, and for this it uses cleaner upstream water. However, the water discharge is always of lower quality than the feed water and this wastewater is discharged downstream. At best the wastewater discharged represents a quality that can be recycled for lower grade of industrial use or for agricultural use (water quality in India- status and trends).

According to Central Pollution Control Board, the annual water consumption in Indian industry is 40 billion cubic meters and the annual wastewater discharge is about 30.7 billion cubic meters. So for every cubic meter of water consumed by Indian industry, 0.77 cubic meters of wastewater is discharged. Presently, only about 10% of the wastewater generated is treated; the rest is discharged as it is into the water bodies (water quality in India- status and trends, 1999-2001). Energy requirements of chemical intensive Effluent Treatment Plants (ETPs) increase the pollution level further in total.

The comparison of inefficient water use in industry in different countries is shown in Table-1.

Table-1. Water use in industry, water quality in India- status and trends (1999-2001).

Country	Industrial water use (billion m³)	Industrial productivity (million US$)	Industrial water productivity (US$ / m³)
India	15.0	113041.0	7.5
Korea Rep.	2.6	249268.0	95.6
Sweden	0.8	74703.0	92.2
United Kingdom	0.7	330097.0	443.7

The ratio of water consumption and economic value creation in Indian industry is poor. For every cubic meter of water that Indian industry uses, it generates the least US$7.5 economic productivity.

Phenolic compounds pose a significant threat to the environment. Due to their stability and bioaccumulation, they remain in the environment for longer periods. As they have high toxicity and carcinogenic character, they cause considerable damage and threat to the eco-system in water bodies and human health [2].

The concentration of phenol from different industrial wastewater is shown in Table-2.

Table-2. Concentration of phenol in industrial wastewater [3].

Industry	Concentration of phenol (mg/l)
Coal mining	1000-2000
Lignite transformation	10000-15000
Gas production	4000
Petrochemicals	50-700
Pharmaceuticals	1000
Oil refining	2000-20000

Phenols are considered toxic for some aquatic life forms in concentrations superior to 50 ppb and the ingestion of one gram of phenol can have fatal consequences in humans. Its dangerousness lies in the effect that it has on the nervous system of living beings. In addition, they have a high oxygen demand, 2.4 mg O_2 per mg of phenol. Another additional effect is the capacity of phenols to combine with existing chlorine in drinking water, giving rise to chlorophenols, compounds that are even more toxic and difficult to eliminate. So an effective and economic treatment for eliminating phenols in water has been in urgent demand [1].

Traditional wastewater treatment techniques include activated carbon adsorption, chemical oxidation, biological digestion, etc. Nevertheless, these methods transfer the pollutant from water to another phase and hence produce secondary wastes. Phenol is also a concern in the biological stage of wastewater treatment, due to its bio resistance and toxicity to microbial population [5]. an ideal treatment can neutralize all contaminant and no leaving behind any hazardous residues. Currently, the existing treatment process generally cannot remove phenol completely. Photocatalytic process is one alternative that is expected to be able to solve the problem [2]. The researchers reported, phenol could be removed by photocatalytic process with the following advantages namely,

- Complete oxidation of organic pollutants in a few hours;
- High active catalyst adaptable to specially designed reactor system; and
- Oxidation of pollutant in ppb range.

SOLAR ULTRAVIOLET RADIATION POTENTIAL IN INDIA

In a tropical country like India ((8º 4' - 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 corresponding to Tiruchirappalli field conditions [7]. 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 [8], 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 transmittivity decreases, mainly due to clouds, but also to aerosols and dust [9]. In fact, the average percentage of UV with respect to total radiation on cloudy days is up to two percent higher than values on clear days. Since the UV radiation is not absorbed by water vapour, as much as 50% of this, or more in very humid locations or during cloudy or partly cloudy periods, can be diffuse. 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.
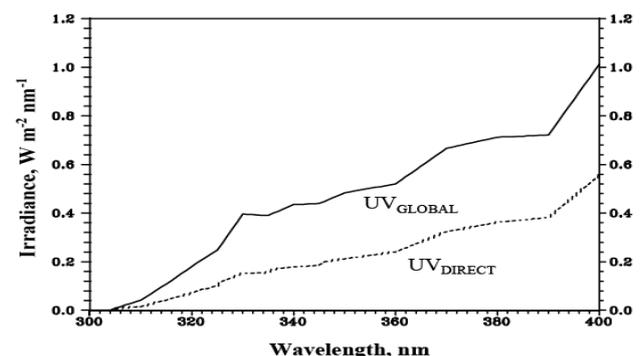
Figure-1. Ultraviolet spectrum on the earth surface.

Titanium dioxide is biologically and chemically inert; it is stable to photo and chemical corrosion, and inexpensive. TiO_2 can use natural (solar) UV radiation and has an appropriate energetic separation between its valence and conduction bands, which can be surpassed by the energy of a solar photon and therefore absorbs in the near UV light i.e. <387 nm [7].

Other semiconductor particles (e.g., CdS or GaP) absorb larger fractions of the solar spectrum than TiO_2 and can form chemically activated surface-bond intermediates,

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but unfortunately, such catalysts are degraded during the repeated catalytic cycles usually involved in heterogeneous photocatalysis. The energy needed to activate the semiconductor catalyst recommended for the solar detoxification process corresponds to UV component of the solar radiation. Selection of catalyst must be in such a way that it uses maximum fraction of solar energy [7]. Table-3 shows the Band gap energy of different photocatalysts. In order to utilize the solar energy for treatment of industrial effluents the semiconductor band gap wavelength has been matched with solar spectrum as shown in Table-3.

Table-3. Matching solar energy wavelength with band gap wavelength of semiconductor.

Semiconductor	Band gap energy (eV)	Band gap wavelength (nm)	Solar energy wavelength
TiO_2	3.0	390	UV - A
ZnO	3.2	387	UV - A
ZnS	3.7	336	UV - A
$BaTiO_3$	3.3	375	UV - A
SnO_2	3.9	318	UV - A
$SrTiO_3$	3.4	365	UV - A

SOLAR WATER DETOXIFICATION COLLECTORS

The design of solar photocatalytic collectors have much in common with those used for thermal applications with main difference being,

1) The fluid must be exposed to ultraviolet solar radiation and, therefore, the absorber must transmit UV sunlight efficiently with minimal pressure drop;
2) Temperature does not play a significant role in the photocatalytic process, so no insulation is required;
3) It must provide good mass transfer from the fluid stream to an illuminated photocatalyst or sensitizer surface in order to have a reaction rate as higher as possible; and
4) Adequate flow distribution inside the reactor must be assured, as non-uniform distribution leads to non-uniform residence times inside the reactor [11].

MATERIAL OF CONSTRUCTION

Temperatures inside solar photochemical reactors can easily reach 40-50°C, just in the case of non-concentrating or one-sun reactor, due to the absorption of the visible portion of the solar spectrum. Therefore, photochemical reactors must be able to withstand summer temperatures of around 70-80°C in order to insure that there will be no damage, which could reduce the flow.

Common materials that meet these requirements are fluoropolymers, acrylic polymers and several types of glass. Quartz has excellent UV transmission and temperature and chemical resistance, but its high cost makes it completely unfeasible for applications requiring large reactor volumes.

Fluoropolymers are a good choice for photoreactors due to their good UV transmittance, excellent ultraviolet stability and chemical inertness. Fluoropolymer materials transmit light as diffuse are poor IR-diffusers, but make an excellent visible/UV diffusers. Tubular fluoropolymers can be extruded into tubing and used as a photo reactor, are very strong and possess excellent tear resistance and are flexible and lighter than glass. ETFE (ethylene tetra fluoroethylene) and FEP (fluorinated ethylene propylene) are good candidates; ETFE has higher tensile strength than FEP, which could mean thinner-walled tubes and higher UV transmittance, resulting in cost savings since less material is used and higher photo reactor performance. Acrylics could also potentially be used as photo reactor material. Among the different fluoropolymers, Polychlorotrifluoroethylene (PCTFE) has excellent chemical inertness, UV stability etc. and is shown in Figure-2.

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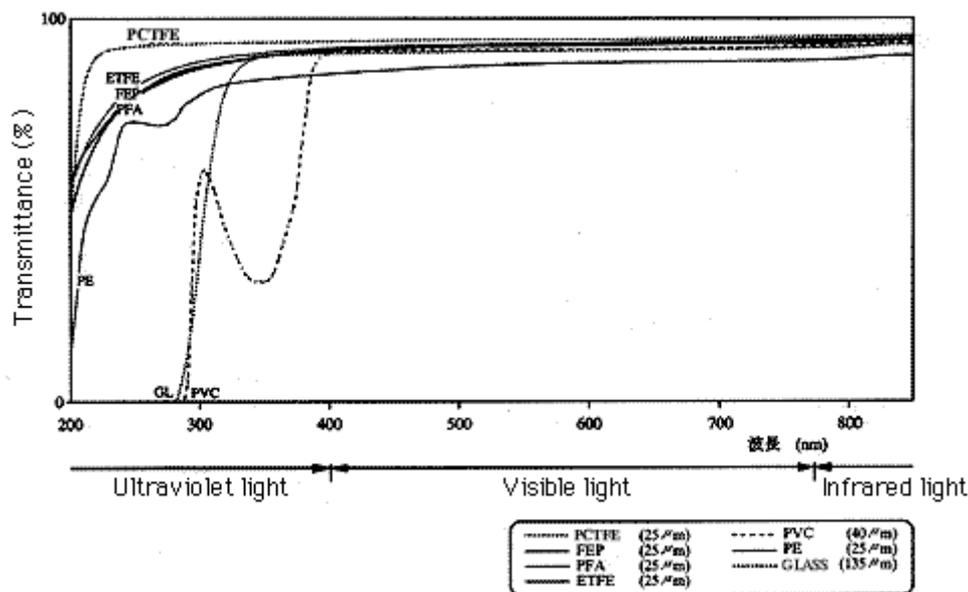
Figure-2. Transmittance of fluoropolymers corresponding to solar wavelength spectrum.

PIPING

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 photo catalytic 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 (10 years).

REFLECTOR MATERIAL

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 Aluminium is the only metal surface that is highly reflective throughout the ultraviolet spectrum. Reflectivities range from 92.3% at 280 nm to 92.5% at 385 nm.

OPPORTUNITIES

In Solar photo catalytic degradation process complete mineralization of toxic organics is possible. Removal and recovery of toxic metals is also possible. Catalyst can be activated by sunlight. It is found from literature that solar energy can degrade industrial effluent. Suitable catalyst is required. Testing of collectors for UV absorption/visible absorption is essential for utilizing actual sunlight. In many solar photocatalytic degradation techniques employed engineering aspects are not of much consideration. So there are enormous opportunities in utilizing our natural solar energy to effectively treat industrial wastewater using a UV transparent solar collector.

CHALLENGES TOWARDS COMMERCIALIZATION

Factors to consider for photocatalytic wastewater treatment include mixing regimes, mass transfer effects, reaction kinetics, catalyst (suspended or fixed) and optimal illuminated specific surface area. Elements such as modeling of momentum, mass and thermal energy balances and the determination of radiation field properties and emission models add to the complexity. In addition, other challenges relating to the practicality of reactor designs, optimal use of light sources and the development of efficient photocatalysts are evident. The high degree of interaction between transport processes, reaction kinetics and light absorption leads to a strong coupling of physico-chemical phenomena, which complicates development and modeling.

The challenge is to reduce the cost (improve performance) of solar photocatalytic processes. Progress in this area will make photocatalytic oxidation using solar or lamp driven, more competitive with other treatment options. Only reductions in the cost of solar-specific hardware (e.g., reactors and collectors) will improve the position of the solar process.

Today, several manufacturing, marketing and economic barriers still hamper commercialization of TiO_2 mediated treatment of polluted domestic and industrial waste streams. Scientific information gaps still exist to a large extent, despite vigorous research in academia.

A better understanding of the radical and redox chemistry is sought and the need exists to develop efficient, cheap and durable components in conjunction with practical reactor designs that minimize energy dissipation. Despite these seemingly insurmountable challenges, it is anticipated that photocatalysis of TiO_2 and other similar semiconductors, together with "advanced oxidation technologies", will continue to be an area of

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focus within environmental Research programs and, hopefully, produce more pilot studies.

Factors that inhibit the performance of photocatalytic oxidation include slow overall rates, low quantum yields, low-order dependence of rates on light intensity, poisoning and fouling of the catalyst, and scavenging of active oxidizing agents by spectator species. Also, solar energy experiences diurnal and annual cycles and varies with weather patterns. The water being treated can contain chemicals that block the critical wavelengths necessary for photoactivity and may require pre- or post-treatment.

EXPERIMENTATION

The experiments were carried out for different concentrations of phenol namely 20, 50, 100, 200, 300,

400, 600 ppm in an 8W UV tubular photocatalytic reactor comprising of an inner UV lamp with a diameter of about 16.0 mm and length 288 mm. A quartz tube is placed surrounding the lamp with the length of about 285 mm and diameter of 20.4 mm. The outer reactor has an inner diameter of about 31.7 mm surrounding the quartz tube. The experiments were conducted in batch mode and the photocatalytic degradation time at which phenol was completely treated was determined. The time taken for complete degradation was 5 hrs when the phenol concentration was ≤ 100 ppm. The COD was measured for every one hour time period and the results of the COD versus time are shown in Figures 3a and b.
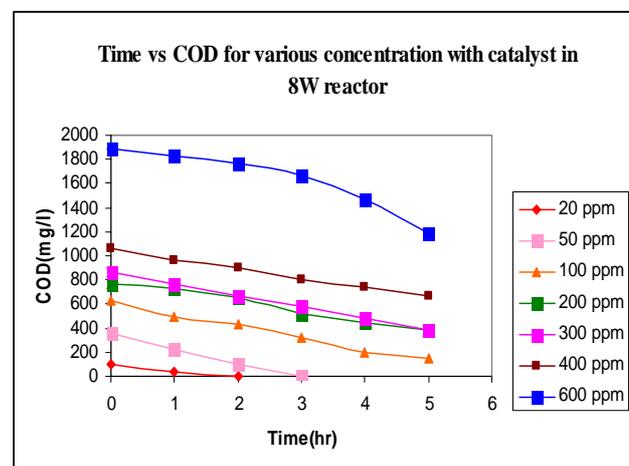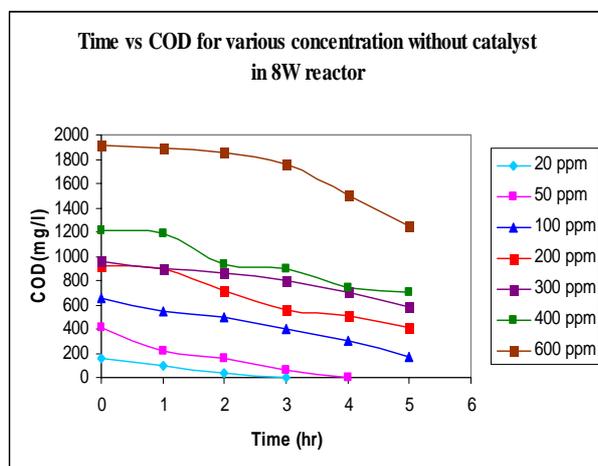
Figure-3. COD vs time for 8W batch reactor a) without catalyst and b) with TiO_2 catalyst.

CONCLUSIONS

In solar photocatalytic treatment process the engineering objectives are the focus and main innovations due to the lack of specific technological developments as the existing technology came from the solar thermal technology just with some minor modifications:

- High UV transmissivity reactor in the solar UV range.
- Solar collector upgrading design.
- Catalyst upgrading and supporting.
- Highly efficient UV reflective surface.
- Demonstration of technical and economical feasibility under real conditions.

It is technically feasible to remove a wide range of organic and inorganic compounds from contaminated water using a photocatalytic process. However, at the current state of development only a few applications are near to being commercially viable. This number could be expanded with significant progress by the improvement of the photo-efficiency of the process. In order for a solar process to compete with comparable systems using electric lamps, significant progress must be made in reducing the cost of solar collectors. Suitable catalyst could be

employed to utilize the maximum amount of solar UV radiation. To make the process more effective solar UV and solar visible could be coupled in such a way that initial treatment by solar UV radiation and then utilizing solar visible light using suitable catalyst.

From the experimentation it is revealed that for photocatalytic treatment using 100 ppm of phenol wastewater employing 0.2 g/l of TiO_2 as catalyst and employing 8 W UV lamps it is possible to reduce the COD completely in a 5 hour time period. For a solar photocatalytic treatment, using 100 ppm of phenol wastewater employing 0.2 g/l of Titanium dioxide as catalyst an experiment was conducted in the month of December from 11.30 a.m to 5.30 p.m in repeated trials under actual solar radiation in Tiruchirappalli field conditions. The COD was monitored for every one hour time period and complete degradation of phenol wastewater was possible in 4 hours. The results indicate that even in the month of December when the solar intensity was quite low it proved that the degradation of phenol was possible in 4 hours by employing agitation of the reaction mixture.

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