Phenol Waste Water Treatment Using Solar Photo catalytic Treatment in Industry

Balaji Ramachandran[1], Gullipalli Sushma[2], Patta Yashvardhani Rani[3], Matta bennita[2], Kirthi Bisoi[4]
[1]NoobTron Private Limited, Chennai, India
[2]Department of Mechanical Engineering, GITAM Deemed to be University, Visakhapatnam, India- 530046
[3]Department Of Electrical, Electronics and Communication Engineering, GITAM Deemed to be University, Visakhapatnam, India- 530046
[4]Department of Biotechnology , GITAM Deemed To Be University, Visakhapatnam, India- 530046.
Sridharabalaa@gmail.com

Abstract
Now-a-days demand for fresh water has been increasing rapidly. Water plays a major role in India and almost in every region of the world. Water is being wasted by the environment and manmade in several ways, one of such way is industrial wastage of water. In recent years quantity of water usage in Indian industries is growing tremendously. Water usage by industries is leading to create severe water crisis. This aims of this research is to treat wastewater containing recalcitrant /non-biodegradable compounds that cannot be completely treated by conventional treatment technologies/ biological methods employed in industry. In an attempt to increase the efficiency of degradation of the impurities present in the wastewater and to improve the economics of the treatment, the work was carried out on the degradation of untreated effluent of industry waste water using heterogeneous photo catalytic treatment. Pharmaceutical water discharge influence mainly on aquatic ecosystem and also shows its major impact on soil ecosystem, so it is important to treat this wastages. Out of these processes, Photo catalytic process is one of most effective and cost effective method as it relies on the activation of semiconductor that is resulting in the generation of electrons and holes to destroy the pollutants and wastage present in the water. Readings have been taken (with & without catalyst) on the experimental set up (from NITT) - Photo catalytic process**.** This paper examines all kind of industrial pharmaceutical waste water discharges in further studies.

Keywords: Industrial wastewater, Water treatment, Pharmaceutical wastage solar photo catalytic process, Industrial waste water discharge.

INTRODUCTION

In Present upcoming generation, Water is basic requirement in all industrial processes, domestic and commercial activities, so the wastewater generated from these various processes contains various contaminants depending upon process, mainly pharmaceutical, textile, acrylic Fiber, pesticides and other organic chemicals manufacturing industries and others [1]. Generate wastewater containing phenolic compounds and various dyes [2]. These effluents are intensely colored and are contaminated with high concentration of organic compounds such as suspended and dissolved salts and many other recalcitrant compounds. Even small concentration of these compounds present in effluent causes toxicity and foul odors to water [3]. If these effluents are improperly treated, they will pose to serious threat to all species on earth because hydrolysis of the pollutants in waste water can produce a great deal of toxic products. Degradation of these non-biodegradable organic compounds is not possible by conventional biological treatment processes [4]. Lately, there has been a lot of interest in application of the advanced oxidation processes (AOP's) for the removal of these organic compounds.

In Today's society, Waste management is significantly needed, Waste segregation in large contrasts are reflected in the problems related to the rational management of water, that cannot be dealt with in a unilateral way, but by many different procedures [5]. 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 eco-toxicology are used to combat these problems [6]. It must be noted that the time scale to resolve each problem as it arises, is always shorter. The problems derived from the toxicological effects of organic compounds, which are active at very low levels, must be resolved at the same time as water disinfection for rural communities. It is clear that innovative procedures are needed to deal with this wide range of problems, which vary notably in its application scale and the complexity of the problems [7].

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 [8]. The main problem stems from waste coming from industry, 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 [8-10]. In this general context, it 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 by two fundamental aspects:

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

· **EU Regulation 1005/2009/EC** on substances that deplete the ozone layer

· **EU Regulation (EC) No 850/2004** on persistent organic pollutants and amending, Directive 79/117/EC (Stockholm convention).

During this research, samples of the untreated effluent and final clarifier effluent was collected and tested in the environmental laboratories. The photocatalytic treatment does not transfer pollutants from one phase to another and leads to complete degradation of organic non-biodegradable compounds into simpler end products.

II. EXPERIMENTAL SET-UP

2.1 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 photo reactors 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 [11]. Acrylics could also potentially be used as photo reactor material. Among the different fluoropolymers, Polychlorotrifluoroethylene (PCTFE) has excellent chemical inertness, UV stability.

2.2 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.

2.3 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 [12]. 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.

2.4 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 [13]. 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 physicochemical 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 [14]. 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 in research. 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 [15].

2.5 EXPERIMENT

The experiments were carried out for different concentrations of phenol namely 20, 50, 100, 200, 300, 400 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

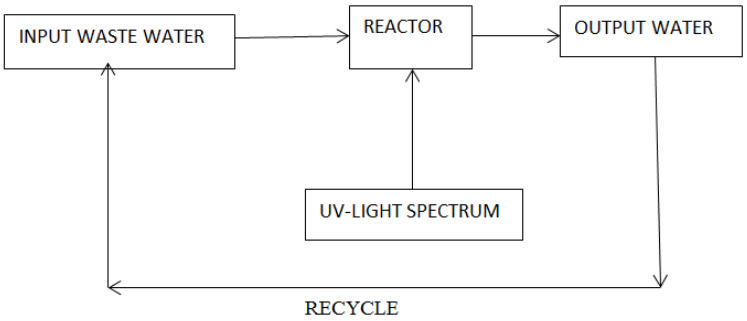

Fig.1 Photocatalytic Phenolic Wastewater Treatment

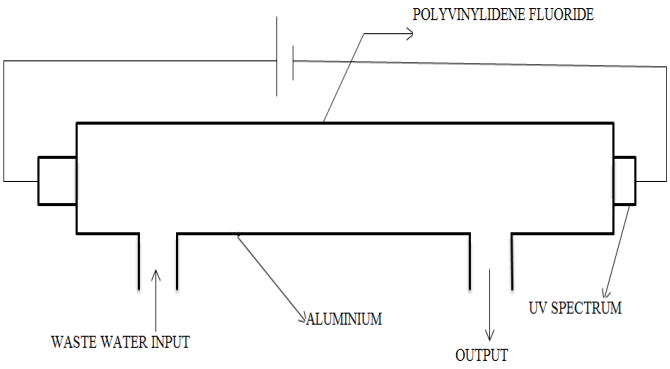

Fig.2 Schematic representation of Photocatalytic Wastewater Treatment

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 1 and 2

Fig.3 Experimental Set-up of ETD Plant

3. ENVIRONMENTAL AND PUBLIC HEALTH IMPACTS OF PHARMACEUTICALS

The risks associated with chemical contamination of the aquatic environment have become a major issue of concern for environmental scientists and engineers, as well as among the public. Drugs are the chemicals that are designed to give a certain therapeutic (biological) effect; therefore, certain environmental and public health risks can be anticipated from the exposure to the environmental pharmaceuticals. Besides, there are a few classes of pharmaceuticals that pose unambiguous impacts on the aquatic organisms, including microorganisms, phytoplankton, plants, crustaceans, fish, and insects, as well as on soil microorganisms and possibly humans. These pharmaceutical classes include:

- Cytostatic agents, immunosuppressive drugs, and some genotoxic antibiotics because of their evident cytotoxic, carcinogenic, mutagenic, and/or embryotoxic properties;
- Human and veterinary antibiotics because of their pronounced microbial toxicity and the development of antibiotics resistance in environmental bacteria including human pathogens;
- Natural and synthetic hormones because of their high efficiency, low effect thresholds and potential for endocrine disruption;
- Halogenated compounds such as iodinated X ray contrast media because of their resistance toward biodegradation and their mobility and persistence in the environment and the food web;
- Heavy-metal containing drugs and non-therapeutic medical agents because of the toxicity of the metals in certain oxidation states.

In addition, the presence of other types of pharmaceuticals, such as analgesics and anticonvulsants, in drinking water is a potential public health issue. Although the concentrations found in finished water is generally very low, it is apparent that drinking water consumption is the major route of human exposure to the environmental pharmaceuticals. Since the long-term health effects are still largely unknown for the exposure to the trace pharmaceuticals and their metabolites, especially as a mixture of biologically active compounds, the existence of these compounds in drinking water should be avoided on the basis of precautionary principle. Similarly, long-term exposure of aquatic organisms to trace pharmaceuticals in surface water may have some as-yet-known ecological impacts Pharmaceutical and personal care products (PPCPs) residues have been detected in environmental samples including groundwater, surface water, and municipal wastewater. Pharmaceutical drugs given to people as well as to domestic animals include antibiotics, hormones, pain relievers, tranquilizers, and chemotherapy chemicals given to cancer patients. Many drugs are designed to be persistent and lipophilic, so that they can retain their chemical structure long enough to do their therapeutic work. These drugs are excreted and distributed into the environment by flushing toilets as well as by spreading manure and sewage sludge onto soil. These chemicals persist in the environment; enter the food chain, bioaccumulate, biomagnify, and cause harmful effects in wildlife and humans. Because of aquatic contamination by these chemicals, bacteria and other microbes in the aquatic environment can become more resistant to these chemicals. This results in the development of more antibiotic resistant and virulent pathogens in the environment. Therefore, the persistence of pharmaceutical chemicals in the environment has become a global problem. Azithromycin, a commonly used antibiotic and urobilin, a breakdown product of bilirubin.

In the general context of the environmental problems caused by different kinds of pollutants, four different types of aqueous solutions are containing organic compounds as phenol, nitrobenzene, DCDE and water coming from the pharmaceutical industry.

Phenols have been widely used in many industrial processes, as synthesis intermediates or as raw materials in the manufacturing of pesticides, insecticides, wood preservatives, petroleum refining and petrochemicals, pharmaceuticals, paint and dye industries, organic chemicals manufacturing and so forth. Because of the great diversity of their origins, they have a great ubiquity and can be found not only in industrial wastewaters but also in soils and surface and ground waters, as a consequence of their release in industrial effluents or improper waste disposal practices and accidental leakages.

Aromatic nitro compounds are commonly used in the manufacture of pesticides, dyes and explosives, and are often detected in industrial effluents, in ambient freshwater, in ambient environments and in the atmosphere. Moreover, nitro aromatic hydrocarbons are naturally generated, as results of photochemical reactions produced in the atmosphere (in countries like Germany, Japan, Switzerland and USA nitro phenol and dinitrophenol have been detected in air and rain).

Dichlorodiethylether (DCDE) is widely used in the US in the manufacture of pesticides and pharmaceuticals, as a solvent and cleaning fluid, as a constituent of paints and varnishes, and in the purifying of oils and gasoline.

3.1.1 DEGRADATION OF PHENOL IN WASTEWATER USING ANOLYTE PRODUCED FROM ELECTROCHEMICAL GENERATION OF BRINE SOLUTION:

CONSTRUCTION:

Electrochemical activation (ECA) process concept involves the passage of high voltage current through a brine solution with a membrane interposed between the anode and cathode. As a result, this process will produce a substantial electrical potential difference, leading to the generation of two types of water namely anolyte and catholyte. The STEL system comprises an electrolytic cell made of three components: 1) the anode: an outer titanium tube coated internally with a ruthenium oxide, iridium and platinum; 2) the cathode: a central platinum rod coated with pyrocarbon; 3) an acid and alkali resistant ceramic diaphragm coated with oxides of zirconium, yttrium and aluminum fixed between the electrodes to prevent the inter mixing of solutions in the anode and the cathode chambers of the reactor, whilst not obstructing the movement of ions in the electric field. This produces both anolyte and catholyte solutions.

The schematic of the STEL ECA system are shown in Figure 1. The water was supplied at flow rate of 1 l min-1. A constant electric current (18 volts) is passed through the solution of NaCl (10%). The electron arrival in salt water at the cathode, as well as the discharge of electron from the salt water at anode are accompanied by a series of electrochemical reactions on the cathode and anode surfaces, resulting to the generation of anolyte and catholyte. After about 30 seconds, anolyte and catholyte were collected in two separate beakers. The objective of this work was to investigate the breakdown of phenol in water after they have been treated with anolyte.

3.1.2 REMOVAL OF PHENOLIC COMPOUNDS FROM INDUSTRIAL WASTE WATER BY SEMI FLUIDIZED BED BIO-REACTOR

In the treatment of phenolic waste water, it is diluted to a level such that overall concentration is reduced to about 200mg/lit. The diluted waste-water passes through the semi fluidized bed bioreactor containing immobilized culture on cellulosic triacetate polymer and the outlet treated waste water is recycled continuously. COD is measured with time. As in fluidized bed bioreactors, the semi fluidized bed bioreactor is initially seeded by introducing microorganisms and nutrients and waste water is admitted to the bed at flow rate slightly greater than the minimum fluidization velocity. The microorganisms will first grow in the suspended phase and then attach themselves to the available surface area i.e., the column wall and the fluidizing particles. The particles may consist of sand, activated carbon or coal particles. Once the particles are covered with microbes, the semi fluidized bed reactor immediately becomes operational. With the microbial growth on the bed internals, the phenolic removal efficiency of the bioreactor will not be adversely affected by changes in the temperature, flow and/or concentration flux.

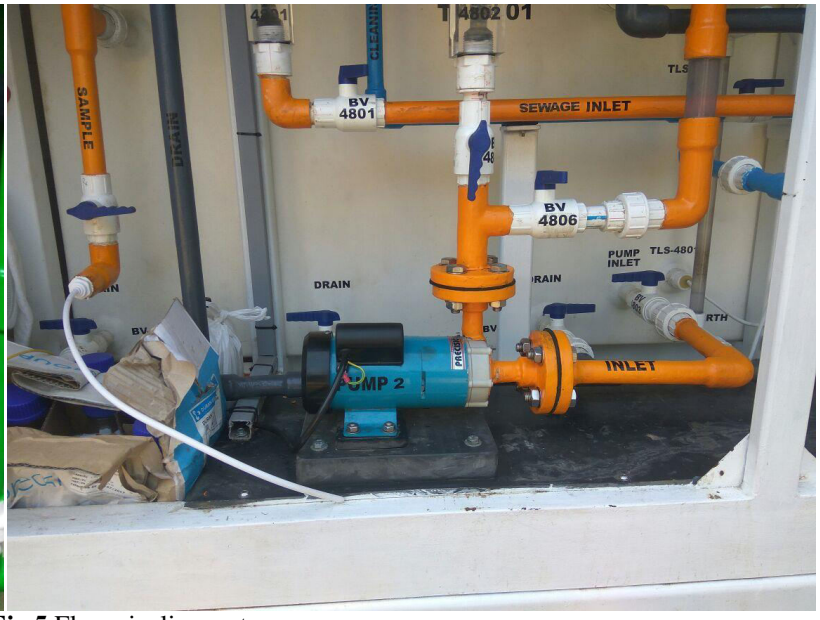

Fig.4 Level Indication system & **Fig.5** Flow pipeline system

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TABLE 1. COMPARSION BETWEEN THE DIFFERENT TYPES OF PHENOLIC WASTEWATER TREATMENT PROCESS

SI NO	PHENOL TREATMENT PROCESS	CHEMICAL USED FOR TREATMENT PROCESS	ADVANTAGES	DISADVANTAGES
1.	Phenol in wastewater discharge using the VTX process	Hydrogen peroxide	1.VTX process of treatment of phenol by oxidation of the process for removal 2.It is not harmful to the environmental	1.Time: app 5 hrs 2.Area required is more
2.	Phenol wastewater treatment with supercritical co_2	-	It is not harmful to the environmental	1.Time app:10 hrs 2.area required is more than the VTX process
3.	Degradation of phenol in wastewater using anolyte produced from the electrochemical generation	Anode: Titanium tube coated with ruthenium oxide, iridium and platinum Cathode: A central platinum rod coated with pyrocarbon Electrolyte : Nacl	Water outlet from the process produces another type of chemical but not harmful to the environmental	1.Time :2 hrs 2.area requires small than the VTX process
4.	Removal of phenolic compounds by semi-fluidized bio-reactor	Sand activated carbon (or) coal particles	It is very easy process	1.Time : 5 hrs 2. Area requires is more than the electro- chemical generation

III RESULTS & DISCUSSION

TABLE 2: EXPERIMENTAL READING (WITHOUT CATALYST)

TIME (hrs)	COD (mg/l)					
	20ppm	50ppm	100ppm	200ppm	300ppm	400ppm
0	180	400	640	900	950	1220
1	100	220	550	900	930	1200
2	50	180	500	700	900	1000
3	0	80	450	650	850	950
4	0	0	400	600	800	830
5	0	0	200	580	700	750

TABLE 3: EXPERIMENT READING (WITH CATALYST)

TIME (hrs)	COD (mg/l)					
	20ppm	50ppm	100ppm	200ppm	300ppm	400ppm
0	100	350	600	800	830	1050
1	50	200	550	700	800	1000
2	0	100	500	650	700	950
3	0	0	400	600	600	900
4	0	0	200	500	500	800
5	0	0	100	300	400	700

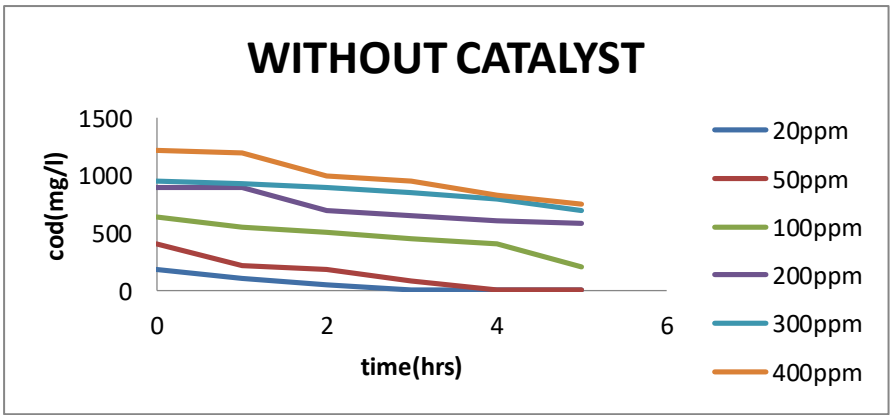

Fig.6 COD Vs Time For 8w Batch Reactor Without Catalyst

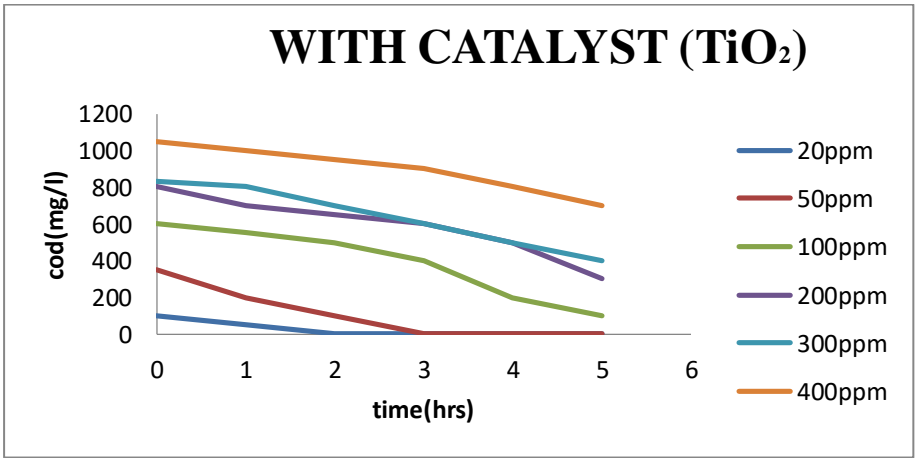

Fig. 9 COD VS TIME for 8w batch reactor with TIO_2 catalyst

From the experimentation it is revealed that for photocatalytic treatment using 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.

SOLAR WATER DETOXIFICATION COLLECTORS

India, being a tropical country, has plenty availability of sunlight so solar photocatalysis is an attractive and cost effective option for the application of this technology at industrial scale. 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;
4) Adequate flow distribution inside the reactor must be assured, as non-uniform distribution leads to non-uniform residence times inside the reactor.

DISCUSSION

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 economic 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.

COMPARISON BETWEEN THE COST ESTIMATION DIFFERENT TYPES OF PHENOL REMOVAL PROCESS

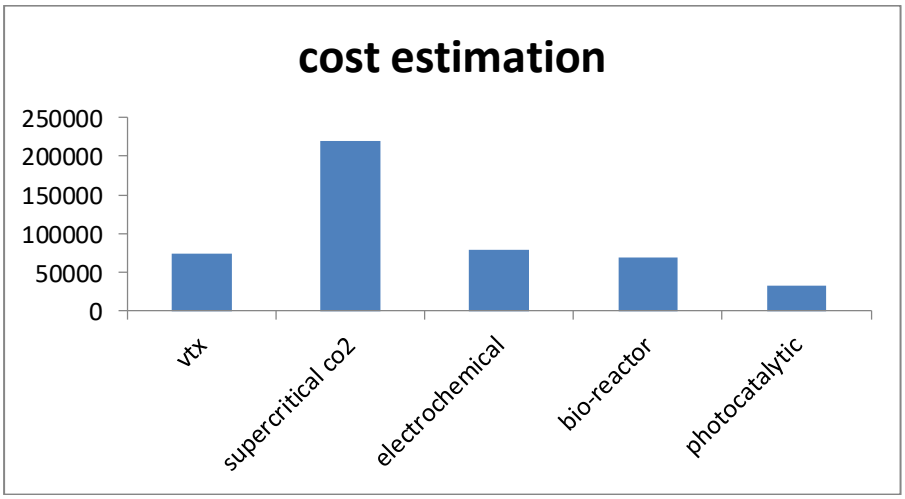

Fig.10 Comparison between the Cost Estimation Different Types of Phenol Removal Process

CONCLUSION

- Photocatalysis process is eco-friendly way to reduce the pollution load of wastewater. This process has proved its superiority to other conventional methods of wastewater treatments, in the presence of

biorecalcitrant compounds. It leads to complete destruction of hazardous contaminants and avoid transfer of pollutants from one phase to another.

- It is revealed that for photocatalytic treatment using 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. Compare to the other treatment process according to the time, area, and cost estimation it is revealed that solar photocatalytic is better.

- The reduction in COD of effluent in the UV and solar photocatalytic treatment shows the complete degradation of organic compounds into simpler end products which results in the complete mineralization of resulting solutions.

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