International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.9, No.11 pp 261-270, 2016

Solar pebble bed reactor for treatment of textile and petrochemical industrial wastewater

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Abstract : Industrial wastewater poses a hazard to our nature, mostly to the water bodies, due to the presence of various complex chemicals in it. Petrochemical wastewaters are most problematic because they contain phenols, sulphides, oil, grease and other organic components which are said to be recalcitrant i.e. they continuously cause problems to the natural sources which need to be treated in order to reuse the water. Textile industrial wastewaters are rich in colour, containing residues of reactive dyes and chemicals, high COD and TOC concentration as well as hard-degradation materials. Hence we have attempted to degrade the organic matter of the effluent using solar energy. Solar detoxification process was carried out by using a solar pebble bed reactor. Silica pebbles were coated with a TiO_2 suspension and used as a catalyst bed. Effluents were treated using solar radiation along with hourly analysis of COD and TOC for peak radiation level. Final TOC and COD values were obtained along with the values from the hourly analysis. These final readings were then compared with the initial concentrations. A significant reduction of about 60% to 70% was achieved in the TOC and COD values. Solar energy will help in less primary energy usage. There is significant reduction in the COD and TOC level.
Keywords : Silica Pebbles; Solar reactor; Textile effluent; Petrochemical effluent; Total Organic Carbon; Chemical Oxygen demand.

1. Introduction

Solar detoxification is a process where a semiconductor upon adsorption of a photon acts as a catalyst in producing reactive radicals, mainly hydroxyl radicals, which in turn can oxidize organic compounds and totally neutralize them. It completely destroys the organic and inorganic compounds in the water instead of simply removing or displacing them. Photo catalytic oxidation, using solar energy as a photon source was demonstrated by Ahmed and Ollis in 1984. The use of solar radiation for the photo catalytic oxidation of organic contaminants in waste water is fast developing application. In some cases, such as, removal of colour and reduction of Chemical Oxygen Demand (COD) in Industrial wastewater, photo catalytic oxidation may be the only environmentally benign, effective treatment available.

Petrochemical wastewater is considered to be complex and hard to treat among the industrial wastewaters. The characteristics of petrochemical industry wastewater are highly industry specific i.e. the petrochemical product manufactured at the plant. Petrochemical plants are in the business of developing substances such as hydrogen ,carbon monoxide, synthesis gas, chemicals such as ethylene and its derivatives, benzene and toluene to name a few. Therefore, each wastewater from a petrochemical plant has to be extensively characterized before deciding the viable technology for the treatment or reuse.

Dyes and dyestuffs find use in a wide range of industries but are of primary importance to textile manufacturing. Enormous volumes of effluent are generated at different stages of textile manufacturing, due to the usage of copious amounts of chemical and dyes. Wastewaters from textile industries are a complex mixture of many polluting substances like salts, acids, heavy metals, organo chlroine- based pesticides, pigments, dyes etc. Several tons of textiles required to meet up with societal demands are produced daily in this industry.

1.2 Review of Literature

Photo catalytic reactors for the treatment of liquid wastewater was studied in the presence of solar radiation and assessed that Quartz has excellent UV transmission, temperature and chemical resistance. Fluoro polymer are a good choice for photo reactors due to their good UV transmittance. Aluminium is the only metal surface that is highly reflective throughout the ultraviolet spectrum.[1]

The contribution of Nano-titania photocatalysis in prevention or reduction of environmental pollution along with the application of Nano particle photo catlytic technology in environmental safety was studied. Emphasis has been put on the application of Nano-titania photo catalytic technology in wastewater treatment.[2]

The author worked to overcome the limitations of a traditional CPC [3]**.** Major limitation was rapid increase in height for a larger aperture width and a low concentration ratio. In this study, through optical analysis, a design modification was achieved by adjusting the vertical position of the receiver. A better method for evaluating the performance of the CPC was proposed using an intercept factor to account for the total reflection phenomenon caused by the receiver. The alternatives such as new active photo catalysis for the photo catalytic zonation system are noted in this paper.[4]

The photo activity of TiO_2/pebbles was reported for the first time. Three types of pebbles were collected for this studies, black, red and white. On the basis of apparent first order rate constants the TiO_2/WL(white leached) pebbles was found 63-81 times more efficient when compared to the lowest efficiency TiO_2/BL(black leached) pebbles. The difference in photo activity of various TiO_2/pebble systems was rationalized in terms of interaction between metal oxides/ions native to pebbles and illuminated TiO_2.[5]

A novel, low cost, pebble bed photo catalytic reactor having horizontal or inclined trough collector. The collector contained TiO_2 coated, silica rich, white pebbles fixed on a flat surface in an ordered configuration to facilitate the contact between the liquid and the photo catalyst. The treatment of simulated textile wastewater showed 72% (Batch-I) and 54% (Batch-II) colour reduction and 3-35% total organic carbon (TOC) reduction. The results indicated that reactor could be successfully used for the decolourization of dyes from dyeing wastewater under sunlight.[6]

The author emphasised on the importance of knowing the Peclet number rather having a fairly good knowledge about it. Also, the importance of the dispersion model for a given model is impressed upon.[7]

A coupled solar photo catalytic-biological pilot plant system was employed to enhance the biodegradability and complete mineralization of a bio-recalcitrant industrial compound. Photo-Fenton process was employed for solar detoxification. The intermediates produced during the process were biodegradable and consequently the photo catalytic and biological processes were combined. Almost total mineralization (90% overall total organic carbon removed) was attained in the combined treatment system. Nitrification and denitrification phenomena were also observed.[8]

The concept of coupling Advanced Oxidation Process was done. Also, the study of efficiency and optimization of AOP. The importance of certain factors such choice of biological oxidant is also stressed upon.[9]

The solar degradation of effluents in board paper industries using different photo catalysts: Fenton reagent and TiO_2 was studied. p-Toluenesulfonic acid was chosen as a model compound for sulfonated pollutants already present in the incoming waters. When the real wastewater was treated with photo catalytic methods , the best performance was obtained in close circuits, when the COD values were higher. This was explained by taking into account that closure of the circuits results in accumulation of pollutants.[10]

The photo catalytic removal of colour of a synthetic textile effluent, using TiO_2 suspensions under solar radiation at pilot plant scale was tested. A synthetic dye solution was prepared by mix of six commercial textile dyes. A photo chemical rector of parallel CPC reflector with UV- transparent tubular recievers was used. The results showed that all dyes used in the experiment could be degraded successfully by photo-oxidation. The process also showed significant enhancement when it was carried out at high flows, alkaline media and high H_2O_2 concentration.[11]

The research primarily deals with the effective use of photo catalysis. Discusses in brief the feasibility of an integrated solar and bio process. The use of TiO_2 catalyst and application of solar radiation is also pointed out.[12]

In order to design an appropriate treatment system the characteristic of the wastewater generated need to be found out with reference of the following parameters; temperature, pH, total suspended solids (TSS), total dissolved solids (TDS), biochemical oxygen demand (BOD) and chemical oxygen demand (COD).[13]

The evaluation on thermal performance of CPC solar collector was studied and found that tracking solar collector exceeded the stationary one in thermal efficiency of upto 14.94% because the tracking collectors always adjusting the collector to face the sun for a normal incidence.[14]

The author reported that under optimal conditions, the extent of decolourization was 100% after different periods of time ranging from 10 to 100 minutes. The decolourization percentages differ with the difference in type of dye used in textile industry. The results indicate clearly that titanium dioxide and zinc oxide could be used efficiently in photo catalytic treatments of textile industrial wastewater.[15]

They have attempted to examine the effect of three coagulants on pharmaceutical waste water; the coagulation process for treatment of effluent of Pharmaceutical wastewater is effective. A doze of 30 mM/L $FeCl_3$, $AlCl_3$ and 60 mM/L $FeSO_4$ gives COD reduction of 85%, 81% and 86.5% respectively at optimum pH of 4, 6 and 4 respectively. [16]

We have studied the feasibility of design and performance evaluation of solar trickle down photocatalytic reactor for degradation of cypermethrin pesticide was examined. The optimum operating conditions for treatment of aqueous solution containing 100 to 600 mg L-1 of cypermethrin were observed to be H_2O_2/COD molar ratio 2, and pH 3 was maintained.[17]

The experimentations were carried out to find environmental friendly and effective solution by harnessing of solar energy through photocatalysis to degrade the contaminants present in wastewater using ZnO nano particles as photocatalyst.[18]

Numerous treatment techniques have been practiced for treating chemical effluents like chemical coagulation, precipitation, co-precipitation, air floatation, flocculation, adsorption ion exchange process, membrane process, electro-dialysis, biological process, bioremediation phyto-extraction, constructed wetland. However, these treatments are cost extensive and do not reduce the pollutants to satisfactory level.[19]

The photocatalytic decolourisation and degradation of an azo dye in aqueous solution with Fe_3O_4 as photo catalyst in slurry form have been investigated using solar light and UV .[20]

Nano titanium dioxide was prepared by sol-gel, sonochemical–hydrothermal process from a precursor of titanium iso-propoxide in the presence of polyvinyl alcohol aqueous solution.[21]

An eco-friendly synthetic method for successful preparation of FeONPs using Piper betle extract at ambient conditions was reported.[22]

The dye degradation studies catalysed by green synthesized iron oxide nanoparticles was conducted.[23]

The degradation of textile effluent using nano-composite TiO_2/SnO_2 semiconductor photo catalysts was conducted.[24]

2. Methodology

2.1 Solar Reactor

Solar treatment helps as an efficient physicochemical pre-treatment. It is necessary to modify the structure of the pollutants into less toxic and biodegradable intermediates. This then allows the subsequent biological degradation of pollutants to be achieved in a shorter time and in a less expensive method. Industrial effluent treatment using solar treatment at an initial stage helps to generate a biologically compatible effluent after elimination of the initial bio-recalcitrant compound and inhibitory intermediates. Solar photo catalytic technology is defined as that which collects solar photons and enters them in a reactor to promote specific catalytic reactions.

2.2 Parabolic trough collector

In the design of solar photo catalytic collectors the fluid is exposed to ultra-violet radiations. The absorber used transmits the UV radiations from sunlight efficiently with minimal pressure drop. Temperature does not play a significant role in the photo catalytic process. The parabolic trough collector (PTC) has the ability to capture both diffusive and direct UV radiation as compared to flat plate collectors.

2.2.1 Construction

A parabolic trough solar collector is in the shape of a parabolic cylinder which reflect and concentrate solar radiations towards a receiver tube located at the focus line of the parabolic cylinder. The receiver absorbs the incoming radiations and is transported and collected by fluid medium circulating within the receiver tube. This method of concentrated solar collection has the advantage of high efficiency, low cost and an important way to exploit solar energy directly.

The following table 1 describes the configuration of the Parabolic trough collector.

Table 1: Configuration of parabolic trough collector

Number of tubes	1
Length of the reactor tube	60 cm
Diameter of the tube	5.5 cm
Length of the PTC	91.1 cm
Volume of the tube	1425.5 cm^2
Aperture area of the collector	1.23 m^2

2.2.2 Pebble column

The column is cylindrical vessel made up of borosilicate material. The coated pebbles are filled in random arrangement. The column is then attached with inlet and outlet provisions and placed at the centre line of the parabolic trough collector.

2.3 Catalyst choice for Solar Pebble bed reactor

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

Other semiconductors (CdS, GaP) absorb larger fractions of the solar spectrum than TiO_2 and can form chemically activated surface-bond intermediates, but unfortunately, such semiconductors are degraded during the repeated catalytic cycles usually involved in heterogeneous photo catalysis. 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 is in such a way that it uses maximum fraction of solar energy.

The photo catalysts have a potential to completely oxidize a variety of organic compounds, including many highly persistent organic pollutants. Reducing conduction band electrons are more important when photo catalytic reaction is applied for hydrogen production in water splitting.TiO_2 has a wide band-gap energy of 3.0-3.2 eV. It prevents the utilization of visible-light that accounts for the most of solar energy.Table 2 shows the catalyst characteristics.

Table 2: Catalyst characteristics

Product	**TiO_2-Anatse**
Appearance	White powder
Purity	99+%
BET surface area (m^2/g)	32
Density (g/cc)	0.3
pH value of aqueous solution	7.8

2.4 Pebble collection and coating

Silica enriched white pebbles were utilised in the preparation of the coated catalyst. The pebbles were collected from Elicon Developers ,Udupi as shown in Fig 1.These pebbles were later subjected to numerous steps of pre-treatment or cleaning. Primarily, the silica enriched white pebbles were washed thoroughly in water to detach itself from dirt and mud from its surface. Further cleaning of the pebbles was achieved by preparing 0.1 M EDTA solution (300ml for every 150g of pebbles). The pebbles were later soaked in the prepared solution. The mixture was then subjected to about 4 hours of agitation which was achieved by utilising the agitator available in the Mass Transfer Lab, Department of Chemical Engineering. Pre-treated pebbles were then isolated from the agitated solution and subjected to 3 hrs of drying at 80^oC in a hot air oven.

An ethanol water (80:20 ratio) mixture was prepared to prepare a 2% suspension with the Degussa (P-25) TiO_2. This suspension was used to coat the pre-treated pebbles to obtain the coated catalyst as shown in Fig 2. The coating was achieved by spraying the suspension using a sprayer over the dried pebbles. The wet coated catalyst was then subjected to drying in the hot air oven at 70^oC for 2 hours as shown in Fig 3.Successive spraying and drying followed for five times, alternatively. The final product, heavily TiO_2 coated silica enriched pebble was obtained after the ultimate drying process.

Fig. 1: Water washed white pebbles before size reduction.

Fig. 2: Crushed Pebbles before TiO_2 coating.

Fig. 3: TiO_2 coated pebbles.

2.5 Fabrication of Reactor

The reactor was to be fitted with a pebble bed column, the column used was made of Borosilicate. The glass column was fabricated with the specification (length: 60 cm, Diameter: 5.5 cm). The fabricated column was then filled with the coated pebbles, hence completing the pebble bed column setup as shown in Fig 4.

Fig. 4: Borosilicate tube filled with TiO_2 coated pebbles (Pebble column)

2.6 Solar Pebble Bed Reactor

The Pebble Bed Reactor is used as a batch reactor, in which the effluent is filled into the tubular reactor and is kept exposed to solar radiation under the Acrylic sheet covering, in the parabolic collector as shown in Fig 5. For every one hour, 30 ml of the sample in the reactor was withdrawn and the TOC and COD levels were tested. This was done for 4 hours a day between 11 am to 3pm. This procedure was followed for 3 days for both textile and petrochemical effluents.

Fig. 5 : Pebble bed reactor setup for effluent treatment

3. Results and Discussion

3.1 Characteristics of effluents:

The initial properties of the effluents were noted before the treatment was begun as shown in Table 3 and Table 4.

Table.3: Characteristics of Petrochemical effluents

Property	Value
pH	5.94
COD	928 ppm
TOC	326.5 ppm

Table 4: Characteristic of Textile effluents

Property	Value
pH	13.43
COD	1600 ppm
TOC	703.7 ppm

3.2 Analysis of textile effluent after Solar Detoxification

The Textile effluent was treated for for 4 hours of sunlight per day. After every hour 30 ml of sample was withdrawn and the TOC and COD levels were measured. After the 4 hours of treatment the effluent was removed from the reactor, each day.

3.2.1 Characteristics of treated Textile effluent

The following table 5 shows the final properties of the treated Textile effluents after Solar detoxification method.

Table 5 : Characteristics of treated Textile effluent

Property	Value
pH	9.2
COD	532 ppm
TOC	382.8 ppm

The overall TOC reduction in Textile effluent is 46%. The overall COD reduction in Textile effluent is 67%.

3.3 Analysis of Petrochemical effluent after Solar Detoxification

The Petrochemical effluent was treated per day for 4 hours. After every hour 30 ml of sample was withdrawn and the TOC and COD levels were measured. After the 4 hours of treatment the effluent was removed from the reactor, each day.

3.3.1 Characteristics of treated petrochemical effluent

The following table 6 shows the final properties of the treated textile effluents after Solar Detoxification.

Table 6 : Characteristics of treated petrochemical effluent

Property	Value
pH	7.01
COD	344 ppm
TOC	126.1 ppm

The overall TOC reduction in petrochemical effluent is 61%. The overall COD reduction in petrochemical effluent is 63%.

3.4. Comparison of TOC reduction between Textile and Petrochemical effluents

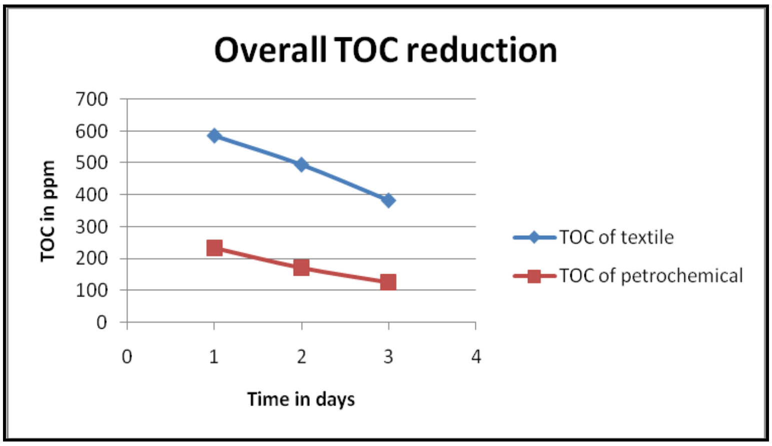

Fig. 6: Overall TOC reduction

Though the figure 6 shows steep decrease in TOC value for Textile effluent when compared to Petrochemical effluent, the overall reduction is greater for Petrochemical effluent than Textile effluent.

3.5 Comparison of COD reduction between Textile and Petrochemical effluents

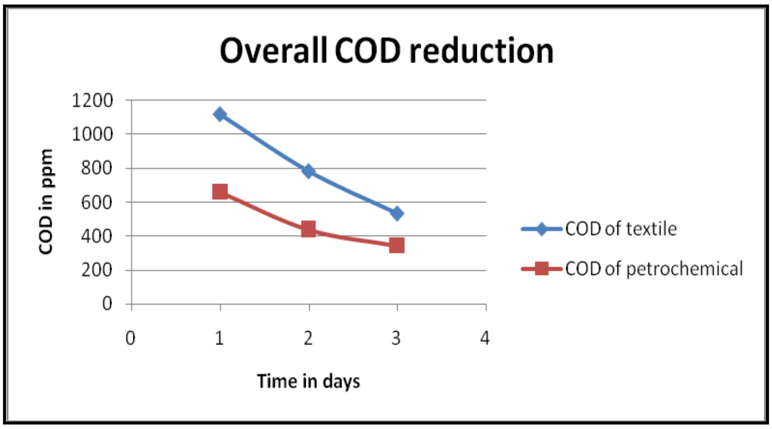

Fig. 7 : Overall COD reduction

The overall COD reduction for both textile and petrochemical effluents are almost the same after treatment as shown in Fig 7. The COD reduction in textile effluent looks drastic when compared to that of petrochemical effluent.

4. Conclusion

Textile effluents having abundance of long chain organic compounds and petrochemical effluents containing a high amount of hydrocarbons are targeted. Initial TOC, COD and pH tests were conducted to detect their respective levels in the effluents.

In order to introduce an innovative way, to bring in economic viability, a pebble bed reactor was designed, as a catalyst bed. White, silica pebbles were opted, due to its ability to activate the Degussa grade TiO_2 and also its inertness in the degradation of the TiO_2 catalyst. Pebbles were initially treated in distilled water, where in mud and other easily detachable impurities from the surface were eliminated. The pebbles were then put through the process of size reduction using a jaw crusher. The pebbles were then treated with distilled water and EDTA solution, in order to eliminated impurities. A 2 % suspension of Ethanol Water mixture in the ratio of (80-20) along with the Degussa grade TiO2 was prepared. This suspension was later coated on the pebbles by spraying it, the coating was improved by drying and spraying simultaneously for about five consecutive days.

The pebble bed reactor was then placed in a parabolic trough reactor, designed to facilitate incident rays into the reactor. An acrylic sheet, with the property of high UV transmittance was opted for and kept on the top of the collector. The reactor was treated as a batch reactor. TOC and COD analysis of each samples were conducted. A gradual decrease in the TOC and COD levels was observed through the analysis of each hourly samples. Hence, deducing that the method adopted for the treatment of the effluents under consideration is a valid and effective one.

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