Design of Photocatalytic Reactor for Degradation of Phenol in Wastewater

R. M. Abhang, Deepak Kumar and S. V. Taralkar

Abstract—The photocatalytic reactors can operate using catalyst suspended in the solution or immobilized on various supports. Photocatalytic reactors with suspended catalyst give much better contact between the photocatalyst and dissolved impurities comparing to reactors with immobilized catalyst. Titanium dioxide (TiO₂) is a promising photocatalyst, when exposed to sunlight or UV rays, it decomposes the phenol present in wastewater. The available reactors are not so efficient in terms of light contact pattern. The aim of the present study was to design the new reactor and analyze its performance for removal of phenol from water with Titanium dioxide as the photocatalyst. The various parameters were studied to observe the behavior of designed reactor like variations in the initial feed concentration of phenol, mass of catalyst, and change in the intensity of UV light & its source, and aeration of the system. The reactor performance was evaluated on the basis on change in concentration with respect to time. The performance of the reactor was studied by running the reactor in fluidized state for a known feed concentration of phenol. The designed reactor has given a better degradation of phenol up to 95.27 % within one hours of time, which when compared to existing conversion of 94 % in two hours.

Index Terms—Photo catalytic reactor, Phenol, Titanium dioxide, UV light

I. INTRODUCTION

The environmental threats due to chemical contamination in the reservoirs have become increasingly serious and directly related to industrial development. The contamination of water by phenol has been recognized as an issue of growing importance in recent years. The presence of phenols in wastewater is potentially toxic to human, aquatic and microorganism life. Phenol is well known human carcinogen and is of considerable health concern, even at low concentration. Among various contaminants, phenol and its derivatives [1] are found in many industrial wastewaters, such as coal conversion process, coke ovens, petroleum refineries, phenolic resin manufacturing, herbicide manufacturing, and petrochemicals, textile, and paper and dye industries as well as in a wide variety of industrial wastes from process involving the use of phenol derivatives resembling those of phenol [1]. There are requirements of efficient treatment systems, which could meet the regulated

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standards and economic constraints. In general, there are various processes to treat industrial wastewater containing those organic compounds. However, it is well recognized that phenolic compounds are difficult to be removed by conventional methods, which would be biological decomposition or adsorption by granular activated carbon. Hence catalytic oxidation systems [2] have been proposed by various research teams as proper alternative methods which include some advantages, such as non-toxicity, insolubility and high activity. Photo catalysts with sufficient light irradiation have been used for the decomposition of waste materials, pollutants, and harmful bacteria [3].

A successful implementation of photocatalysis requires very efficient catalysts, illumination sources and reactors. In addition, auxiliary equipment for photocatalytic reactors is of major importance to assess the effectiveness of the reactor and of the kinetic reactor modelling [2]. This requires proper characterization of the UV used, in the case of artificially powered photocatalytic reactors [2] and the characterization of the photons absorbed in the photocatalytic reactors.

The main objective of this research was to design the photocatalytic reactor & analyze the reactor performance by photocatalytic degradation of phenol in the presence of UV and catalyst 'TiO₂' is in the fluidized state and investigation of the role of main factors that affecting the process.

II. PHOTO CATALYTIC REACTOR

A. Photocatalyst

A photocatalyst is defined as a substance that is activated by the absorption of a photon and helps to accelerate a reaction, without being consumed. The Titanium dioxide TiO_2 owing to its special properties is the most frequently used photocatalyst in water and air purification processes. TiO_2 is relatively cheap, non-toxic, insoluble in water and very resistant to most chemicals. It shows the highest photocatalytic activity and resistance to so-called anodic photo corrosion. Additionally, the photocatalytic processes on titanium dioxide [4] can be also initiated by solar radiation.

B. Design Aspects of Photocatalytic Reactor

The reactor was designed on the basis of fluidized bed concept, with three phase contact pattern and also maximizing the UV irradiation area. The development of water and air treatment systems based on heterogeneous photo catalysis is an area of major technical importance [5]. The design of highly efficient photo-catalytic systems is of vital interest and one of the most desirable yet challenging goals [6],[7] in the research of environmentally friendly

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catalysts.. The main obstacle in the development of highly efficient photocatalytic reactors [6] is the establishment of effective reactor designs for intermediate and large-scale use, as demanded by industrial and commercial applications.

To achieve a successful commercial implementation, several reactor design parameters must be optimized, such as the photo reactor geometry, the type of photo-catalyst and the utilization of radiated energy [8]. A fundamental issue regarding the successful implementation of photocatalytic reactors [4] is the transmission of irradiation in a highly scattering and absorbing medium composed of water and fine TiO_2 particles. The successful scaling-up of photo-catalytic reactors involves increasing the number of photons absorbed per unit time and per unit volume.

In addition to the reactor design strategies and the catalyst selection, a number of important operating variables exist, affecting both the rate and the extent of chemical species transformation. These include semiconductor concentration, reactive surface area, particle aggregate size, concentration of electron donors and acceptors, incident light intensity, pH, and temperature.

With the need to develop new photo-catalytic reactors, there is also the issue of establishing performance indicators to enable the comparison of photo-reactor performance on the basis of photochemical and thermodynamic principles. In the case of water treatment, it can be stated that current technologies concerning photo-catalyzed oxidative degradation processes can be considered as practical alternatives to existing waste water treatments [7],[9]. Photocatalysis has already found applications in small to medium sized units in the treatment of contaminated ground waters and in the production of ultrapure water for pharmaceutical and micro electronic industries.

C. Three Phase Fluidized Reactor

When the reactor consists of three phases that is liquid, solid and gas, it's called as three phase reactor. The feed is in liquid form, catalyst is in solid form and air is in the gaseous form, enters the system by aeration done to support the photocatalysis [10].

It should also be noted that, three-phase fluidized bed reactors, which could provide intimate contact among gas, liquid, and solid phases, have gained increasing attentions in a wide range of industrial applications. These kinds of reactors have various advantages, such as simplicity in construction & operation, low operating cost and flexibility in liquid & solid phase residence times. Furthermore merits of having intimate contact between the phases, high degree of mixing among phases, high values of effective interfacial area and overall mass transfer coefficient and flexibility of introducing continuously catalyst would also be reasons for employing three-phase fluidized beds in many industrial applications [10]. The fluidized bed promises a good contact pattern for the catalyst and the feed, so it can be effectively applicable for the degradation of phenol.

D. Design and Fabrication of Photocatalytic Reactor

The reactor was designed in form of sandwiched chambers to utilize UV light efficiently. The reactor has staged contact pattern, the inlet chamber is the first stage where catalyst

makes contact with feed. The second stage is the contact made in the two compartments located at the ends.

The chambered construction was thought in order to increase the maximum residence time of the fluid. The two stages allow the feed to be treated more efficiently with through mixing. The area marked as "1" is the inlet for the feed; it uses the counter flow pattern for the contacting of the feed and catalyst. Below this section there two tubes which are perforated with 2 mm holes from which compressed air will pass provide bubbling agitation for above section (1). Due this bubbling the catalyst bed will be suspended and will act turbulent fluidized bed. The area marked as "2" is the main fluidized section were the fluidization of coated particles will take place. In this section fluidization takes place due two factors one of them is the flow of the feed from the section "1" and the other is due to the bubbling tubes present below these section. The bubbling is done because it that aeration increases the rate of was found photo-degradation by several folds. The fluid will exit the reactor from the four outlets provided at outer top face of the section "2".

The section "3" is water proof section, as it will have the UV lamps situated in it which will irradiate both "1" and "2" sections. This will allow us to lower the energy needed for irradiation. The lower section i.e. "4" is the connection section, it connects the section "1" from "2" and it allows us situate the bubbling tubes.

The section "4" is separated from section "1" and "2" by a 10 mm plate with perforations of 4 mm and 2 mm respectively. This was done in order to support the catalyst, allow distributed flow of fluid and to facilitate aeration.

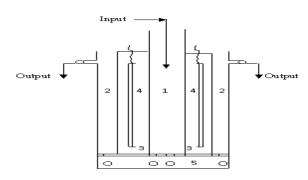
The reactor was designed with purpose of decreasing the time needed for degradation of organic pollutants such as phenol. The concept of fluidized bed allows decreasing the time by improving the area and time of contact. The reactor shown in fig.1 (a) front view & (b) fabricated reactor was constructed by using Plexi glass which has good pressure durability & also has good optical properties. The outer dimensions of the reactor are $200 \times 200 \times 1000$ mm. the reactor consists of five vertical chambers and one common lateral chamber at the bottom which connects the five chambers.

From the five vertical chambers, two adjacent compartments from the central compartment are made water proof and are sealed from all sides except from the top.

These two compartments house the UV lamps. The compartment situated at the centre is the inlet compartment. Remaining two compartments are dimensional half of the width of the central compartments, these compartments acts fluidized bed column and also as the outlet section. It has two 25 mm outlets drilled on both the faces. The UV light source and the central compartment have a dimension of $50\times200\times1000$ mm and the other two have $25\times50\times1000$ mm. The bottom compartment has the dimension of $200\times200\times50$ mm.

The reactor consists of drilled plate at the bottom of three horizontal compartments the inlet compartment consists of 4 mm drilled holes and the outlets compartments consists of 2 mm drilled holes. The reactor in the bottom compartment consists of aeration system, which is made of copper tube

with 2 mm holes on the face and at distance of 10 mm. The lengths of the tube are 190 mm and are four in number. Two are situated below the inlet section and other two are placed below at the outlet section one on each side.



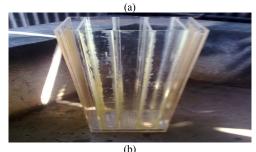


Fig.1 (a) & (b) Schematic diagram of the reactor

III. EXPERIMENTATIONS

A. Preparation of Catalysts

The catalyst used in the study was Titanium dioxide having a mol. weight of 79.90, (L R grade) supplied by Research-Lab Fine Chem. Pvt. Ltd. The catalyst was amorphous in nature and it's solubility in water is 0.5 %. The catalysts were coated [11] on the solid silica gel particles using sodium acetate (LR grade). Silica gel was used, as it is readily available & is inexpensive. The sodium acetate was used as a suitable binding agent, as it is cheap, ease of coating and also it is one of the least toxic materials used for coating of the Titanium dioxide [11], [12].

The silica gel was first separated using sieve shaker according to their sizes & the particle greater than 2.18 mesh size were taken. Mix thoroughly in 1 lit distilled water with 100 gm. Sodium Acetate and 55 gm. of TiO₂ powder (5% of solution by weight). Pour the silica gel particles into the solution prepared for 2 -3 min. & then separate the silica gel from the solution and let it dry for about 24 hrs. Repeat the procedure for multiple coats. Once done the coated silica gel weight is increased by 10 % and it can be used for the experimentation. Once the coating is done shake the coated silica for 30 sec so as to remove any lose Titina.

B. Experimental Set-up & Procedure

The set-up was designed & fabricated in the laboratory, consist of the three phase fluidized bed type of reactor (TPFBR). The designed reactor consists of the four lamps of 8 Watt, two on each side. It consists of feed tank & pump to transport the feed to reactor.

The four outlets from the reactor are put back into the feed tank. The aeration system is connected to an air header made

of copper which distributes one compressed air input to four outputs. The aeration tubes are placed into lower compartment.

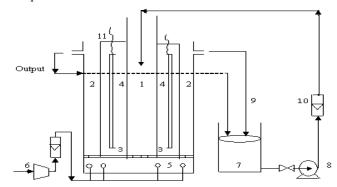


Fig.2 Experimental setup: 1- Inlet Chamber of Reactor, 2 – Outlet Chamber, 3 – UV Lamp, 4- Middle UV Chamber, 5 – Bottom Aeration Chamber, 6- Air compressor, 7- Feed tank, 8- Feed Pump, 9- Outlet Stream, 10- Rotameter, 11- UV Light connections

The parameters were selected to carry out with variations are, initial phenol concentration in feed, mass of catalyst in the reactor, intensity of UV light, UV vs. visible light, and aeration of the system. The reactor performance will be evaluated on the basis on percentage of conversion.

All experiments were carried out under ambient conditions i.e. at room temperature and 1 atm. The experiments will give the observations against the known amount of volume of feed and will operate as cyclic process.

The reactor was operated for two hours, with different feed concentrations, catalyst loading and with & without aeration and the corresponding change in concentration ware measured with regular interval of time. The intensity of UV light can be changed by decreasing or increasing the number of UV lamps. We will operate reactor first with two lamps then with four lamps.

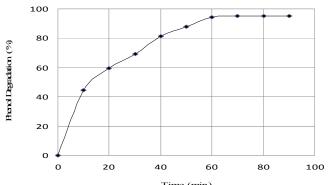
Visible light also contains some amount of low wavelength waves, so it must also support photo-degradation of phenol. So same experiment ware carried out in presence of 8 Watt fluorescent tubes and corresponding readings were taken.

IV. RESULTS & DISCUSSIONS

Phenol when contact with a photocatalyst TiO_2 in the presence of UV irradiation, it degrades and forms intermediates compounds which undergo further reaction to convert to CO_2 and H_2O . In the designed reactor, flowing velocity of fluid inside the central core part and outer part of the reactor maintained at certain level, so catalyst particles will not be escaped from the silica particle and will not be in the outlet water. The reactor was utilized continuously by varying the different parameters like known concentration, temperature, catalyst loading etc. and studied its performance and behavior.

A. Degradation of Phenol

For the initial concentration (C_o) 5 gm/lit of phenol & catalyst 0.75 gm/lit, with respect to reactor, during starting within 10 min. of time, the degradation of phenol was observed about 44 %, then as time proceeds, the degradation rate slow down & at near about 1 and half hrs the degradation ceases.



Time (min)
Fig.3 Rate of degradation of phenol with respect to time

Initially, the rate of degradation of phenol was very high as shown in fig. (3). & within two hours of run, it has decreased the concentration up to 95.27 %. The designed three phase fluidized bed reactor has helped in reduction of time for degradation of phenol photocatalytically.

B. Effect of Aeration

When the aeration system is activated, the agitation also occurs simultaneously & all the three chambers behave like a fluidized bed reactor & results were excellent. As we can see that aeration affects the degradation of phenol adversely, without aeration only 50% degradation were achieved as shown in fig. (4) and it was due to trapping of air while coming through inlet.

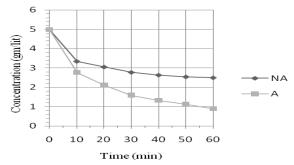


Fig.4 Effect of aeration on Phenol degradation for 5 (gm/lit) initial concentration (with and without aeration)

C. Effect of Initial Concentration of Feed

Two different Initial feed concentrations of phenol were taken for the experimentations, 4.98 gm/lit and 1.93 gm/lit. The concentration of feed was affected the rate of degradation slightly, as we can observe in fig (5), initially for high concentration, degradation was fast, but later it became sluggish as in low concentration case. But initially irrespective of concentration, the degradation was impressively fast with more than 40% conversion in 10 minutes.

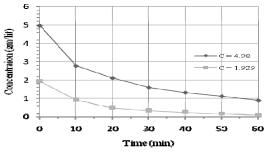


Fig. 5 Degradation of phenol at different initial concentration; i) 4.98gm/lit ii) 1.93 gm/lit

D. Effect of Mass of Catalyst in the Reactor

Three different catalyst loading 0.75 gm/lit, 1 gm/lit and 4 gm/lit were taken. Initially the degradation of phenol rate was similar in all three cases but as time proceeded, the rate slowed down. For the same initial feed concentration different catalyst loading gave different results. As expected increase in catalyst amount increased degradation, but for 4 gm/lit, the degradation was in between the 0.75 gm/lit and 1 gm/lit. That means after particular amount of catalyst loading, the degradation rate does not change with time.

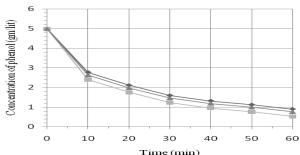


Fig. 6 Degradation of phenol at different mass of catalyst loading; i) 0.75 gm/lit ii) 1gm/lit iii) 4 gm/lit

E. E. Effect of Intensity of UV light

By using different intensity of light source i.e. 2 Watt, 4 Watt and 8 Watt UV lamps, did not increase the degradation that significantly. Initially the rate of degradation was almost equal, but later on a slight difference was observed. The increase in degradation was slight about 4%. This concludes that increasing intensity will increase the degradation of phenol.

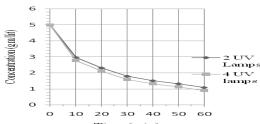


Fig. 7 Effect of UV light intensity on rate of degradation; i) 2 lamps ii) 4

F. Effect of UV vs. Visible Light

When experiment was carried out with visible light source, its phenol degradation ceased to continue at end of the run. This predicts that conversion of phenol with visible light is possible but not efficient. The effect of UV light source gives best result in the same situations. So UV lamps are the best source for phenol degradation.

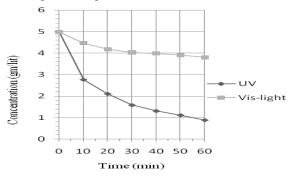


Fig. 8 Effect of UV & Visible light on rate of degradation; i) with UV ii) With Vis-light

V. CONCLUSION

When the reactor is operated, its all three chambers behaves like a fluidized bed due to aeration, thus increases the contact time with catalyst and also increases the contact area of catalyst with feed, this helps in faster degradation.

Aeration effects the degradation of phenol adversely, without aeration only 50% degradation was achieved and it was due to trapping of air while coming through inlet. The concentration of reactant affected the rate slightly as we can observe initially for low concentration degradation was fast but later it became sluggish as in high concentration case. For the same initial feed concentration, different catalyst loading gave different results.

It was observed that, the reactor thus designed has given a better degradation of phenol up to 95.27 % within one and half hours of time for 21 liters of feed, which when compared to existing conversion of 94 % in 2 hours. Thus, the reactor has worked according to acceptations, but still some modifications in scale ups are required such as change in outlet position and method of input for feed and input for putting the catalyst, traces of catalyst in the outlet stream, cost estimation etc. for large scale operation.

REFERENCES

- [1] Saber Ahmed, M.G. Rasul, Wayde N. Martens, R. Brown, M.A. Hashib, "Heterogeneous photocatalytic degradation of phenols in wastewater: A review on current status and developments", Desalination, 261, (2010) 3–18.
- [2] N.A. Laoufi, D. Tassalit, F. Bentahar, "The degradation of Phenol in water solution by TiO2 photocatalysis in a helical reactor", Global NEST Journal, Vol. 10, (3), 2008, 404-418.
- [3] S. Malato, P. Fernandez-Ibanez, M.I. Maldonado, J. Balnco, W. Gernjak, "Decontamination and Disinfection of water by solar photocatalysis: Recent overview and trends", Catalysis Today, Vol. 147 (1), 2009, 1-59.
- [4] Ramesh Thiruvenkatachari, Saravanamuthu Vigneswaran, Shik Moon, "A review on UV/TiO2 photocatalytic oxidation process", Korean J. Chem. Eng., 25 (1), 2008, 64-72.

- [5] A. Sobczynski, A. Dobosz, "Water purification by Photocatalysis on Semiconductors- A Review", Polish Journal of Environmental Studies, Vol. 10,(4), 2001, 195-205.
- [6] Ajay K. Ray, Antonie A. C. M. Beenackers, "Novel photocatalytic reactor for water purification", AIChE Journal, Vol. 44, (.2), 1998, 477-483
- [7] Ajay K. Ray, Antonie A.C.M. Beenackers, "Development of a new photocatalytic reactor for water purification", Catalysis Today, 40,1998, 73-83.
- [8] Angelo Albini, Maurizio Fagnoni, "Handbook of Synthetic Photochemistry", Wiley Publications; 1st Edⁿ, 2010, 1-9.
- [9] M. Sanchez, M.J. Rivero, I. Ortiz, "Photocatalytic oxidation of grey water over titanium dioxide suspensions", Desalination, 262, 2010, 141–146.
- [10] Sanjay P. Kamble, Sudhir B. Sawant, Vishwas G. Pangarkar, "Novel solar-based photocatalytic reactor for degradation of refractory pollutants" AIChE Journal, Vol. 50, (7), 2004, 1647-1650.
- [11] Joanna Grzechulska-Damszel, "Removal of organic impurities from water using a reactor with photoactive refill", International Journal of Photoenergy, Vol.1, 2009, 1-6.
- [12] T.K. Kim, M. N. Lee, S.H. Lee, Y.C. Park, C.K. Jung, J.H. Boo, "Development of surface coating technology of TiO₂ powder and improvement of photocatalytic activity by surface modification", Thin Solid Films, 475, 2005, 171–177.
- [13] Akira Fujishima, Xintong Zhang, "Titanium dioxide photocatalysis: present situation and future approaches" C. R. Chimie, 9, 2006 ,750–760.

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