Universal Performance Parameter for Photo-catalytic Oxidation in Slurry Phase

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Abstract:

UV radiation attenuation in a slurry phase reactor as a function of catalyst concentration and pollutant concentration is experimentally measured. It is observed that in most of the practical working ranges of the catalyst concentration as reported by the researchers, the radiation penetration in the remote regions of the reactor is not uniform and not even assured. It is also observed based upon literature review that the optimum parameters generated for slurry phase photo-catalytic reactors by the researchers are highly dependent to the reactor configuration. Here an approach is suggested to generate reactor configuration independent parameters that may be universally applicable.

Keywords: Slurry phase; UV radiation measurement; Reactor depth; Photocatalytic degradation; Universal parameter

1. Introduction

Refractory organics like lignin, cellulose, polysaccharides, phenolic material, detergents, pesticides, dyes and various organics with limited solubility and resonant ring structures are extremely resistant to biological degradation and pose difficulties in municipal and industrial wastewater treatment [1]. Conventional wastewater treatment methods are inadequate to handle the rising level of these organics in wastewater [1]. Destruction of such organics using the strong photo-produced oxidation power of TiO_2 was first reported by Frank and Bard [2]. Later researchers identified many other semiconductors having potential to be used as photo-catalyst including ZnO [3], CuO/SnO_2 [4], WO_3 [5], Au/Al_2O_3-CeO_2 [6], Fe_2O_3 [7], $CaBi_6O_{10}/Bi_2O_3$ [8], MoO_3 [9], ZnS [10,11], and CdS [11]. Conventionally TiO_2 is considered to be the most suitable photo-catalyst because of its advantages over others, which include wider direct band gap, chemical and biological inertness, photocatalytical stability, availability, ease of production and without risk to the environment and humans [12,13].

In 1980s the process of powdered TiO_2 photo-catalysis (Slurry phase reactors) got much recognition from researchers. In early 1990s Fujishima and coworkers conceived the idea of thin film based photo-catalysis for wastewater treatment [13]. Presently many modifications of photo-catalysis reactors with hybrid combinations are in use [14-17].

Today slurry phase photo-catalytic reactors are extensively used in environmental applications [18-24].The basic slurry based configuration for photo-catalysis has its own advantages including high total surface area of photo-catalyst per unit volume, ease of photo-catalysts reactivation and simplicity in process modeling [14,25]. Many researchers have investigated the process of photo-catalytic degradation of pollutants under slurry phase reactor. They have identified the main parameters involved as catalysts loading, pH, temperature, dissolved oxygen, contaminant loading, light wavelength, and light intensity [12,14]. A schematic representation of a simple slurry type reactor for photo-catalytic oxidation is as described in Fig. 1. The figure also shows the UV radiation pathway. The UV radiation may be obtained from artificial source or sun. The figure shows the simplest case of UV radiation being showered from the top surface of the reactor. Yet it is possible to have other configurations also like additional radiation sources provided on side surface [26] or even from bottom [27] in order to enhance the availability of radiation energy everywhere inside the reaction vessel. In some configurations, source of UV radiations are installed within the vessel also [22,28].

The initiation of photo-catalysis is essentially driven by the availability of specific wavelength photon. Thus transmissivity of the slurry phase is a crucial parameter in reaction kinetics so that the required radiation may be available everywhere in the slurry phase. The transmissivity of radiation in slurry phase is a complex function of catalyst concentration, turbidity and pollutant concentration. The detrimental effect of turbidity on transmission has been reported [29-31].

A real world application of photo-catalysis for wastewater treatment needs optimization of all process parameters as mentioned above. Researchers have investigated these parameters independently and have proposed their optimum values. A few notable such works are reported [32-40]. It must be realized that the process of photo-catalysis is complex and the parameters are interwoven. They cannot be optimized independently. Hence, the optimized values given by researchers are reactor configuration dependent. A holistic approach is required to optimize the process parameters. The present paper discusses the complexities and inter-dependence of operational parameters and proposes the concept of a simple universal performance parameter for a slurry phase reactor.

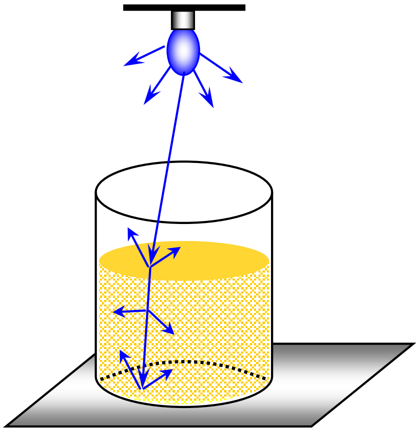

Figure 1: Schematic representation of simple slurry type photo-catalytic reactor.

1.1. The optimum catalyst dose and transmissivity of slurry phase

In heterogeneous catalytic reactions, the rate of reaction has a direct dependence on the *effective catalyst dose*. It must be recognized that the photo-catalysis phenomenon takes place essentially at the surface of catalyst. Thus catalyst dose must be rightly interpreted as catalyst surface area. Surface area is a function of particle size, shape, surface texture (morphology) and porosity. It is also important in semiconductor photo-catalysis that the electron emission effectively takes place only with the nano-size of the catalyst particle. Thus the effective catalyst loading need to be defined in terms of surface area of nano-size particles specifically. The requirement of a good catalyst is to have larger surface area with lesser mass per unit volume of the reactor content. This can be achieved by manipulating shape and surface texture of catalyst particle. Catalyst manufacturing/synthesis technologies may be researched to meet this requirement.

It must be noted that though larger surface area leads to higher reaction rate, higher dosage of catalyst may have negative impact on the reaction. It can make the water excessively turbid which will scatter the incident radiation thus reducing the radiation availability in the interiors of the reactor. The optimum catalyst loading determined thorough an experimental investigation is specific to the radiation intensity used.

The optimum catalyst loading is also dependent upon pH of the phase (water). This is because pH of solution greatly influence the agglomeration/separation of catalyst particle resulting into change in effective surface area available for reaction [29,34,35].

1.2. The optimum concentration of pollutant

Many researchers have been exploring this aspect [41,42]. Higher concentration of pollutant will enhance possibility of interaction between it and hydroxyl radical. Thus the oxidation rate will be enhanced. On the other hand, higher concentration of pollutant reduces the penetration of UV radiation thus hydroxyl radical production will be less and the overall reaction rate will reduce. The optimum pollutant concentration is a function of radiation intensity used as well as catalyst loading.

1.3. The optimum radiation intensity

Effect of light intensity on photocatalytic reaction kinetics has extensively been studied [43,44]. The ideal situation is that where sufficient photons are available on every point on the surface of the catalyst to keep all the conduction band electrons emitted at all times. This ideal situation may be referred as a saturation limit of light intensity. Anything in excess of this light intensity shall be unused.

If the irradiance is lesser than this requirement, the catalyst shall be underutilized and the reaction rate shall be less than that of maximum possible under the given set of other conditions. Yet higher light intensity shall be unutilized and will be wastage of energy. Thus optimum light intensity is also a function of catalyst loading. Catalyst particles reflect and scatter the radiation flux thus causing less flux to reach to the remote zones of the reactor. Radiation flux is also attenuated by pollutants in wastewater. Thus optimum light intensity is a function of catalyst concentration as well as organic material concentration.

2. Experimental set up

The present study has investigated the effect of catalyst dose and pollutant concentration on radiation transmission. The experimental set up is schematically shown in Fig. 2.

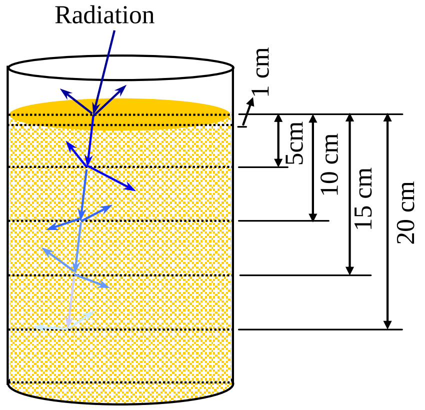

Figure 2: Measurement of UV radiation flux in slurry phase.

Here, the source of UV radiation is 125 watt lamps, manufactured by Narva (Germany). The vessel is made of borosil glass. It is filled with slurry phase prepared by dispersing TiO_2 in distilled water. TiO_2 used is of Degussa P25 (Crystal size 24.1 nm measured by XRD, and surface area 52 m^2/g measured by BET surface area analysis; reported in author's previous work [23]. Radiation is measure at the surface of slurry phase and at every 5 cm. Radiation is measured using an International Light, USA, Research radiometer, IL-1700 having range of 200-400 nm. The probe pollutant used for present study is congo red dye having λ_{max} = 498 nm.

3. Results and discussions

The effects of catalyst dosage and pollutant concentration (Congo red dye) on radiation penetration are experimentally investigated. The results are shown in Fig. 3 and Fig. 4 respectively. Fig. 3 and Fig. 4 respectively show the attenuation of UV radiation due to TiO_2 dose, and cango-red dye.

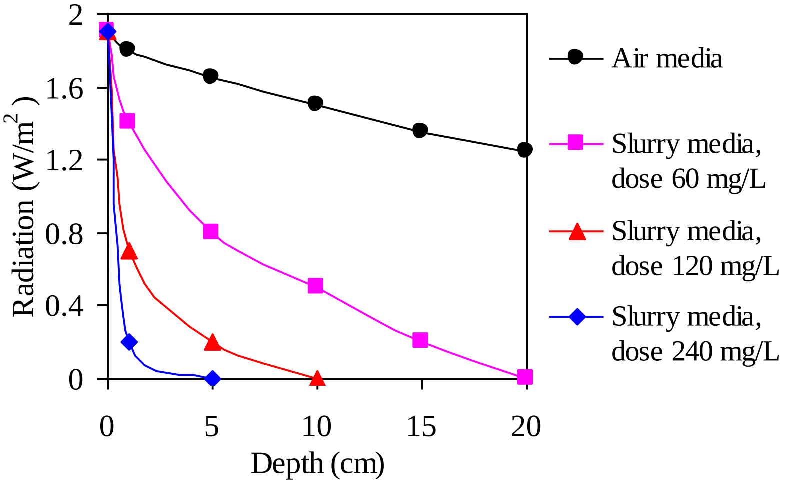

Figure 3: Transmission of UV radiation flux in TiO_2 slurry phase.

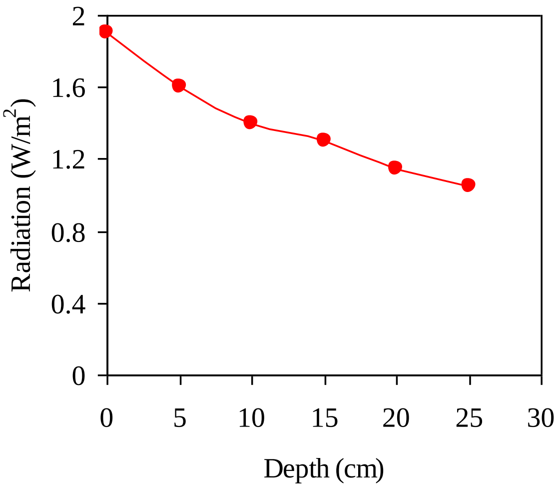

Figure 4: Transmission of UV radiation flux in dye phase.

In Fig 3 the concentration of TiO_2 used is respectively 60 mg/L, 120 mg/L and 240 mg/L. It can be seen that the TiO_2 concentration has a very profound impact on UV radiation transmission. This figure shows that the radiation intensity (or flux) decreases with the increase in the depth. When the light was irradiated through the air, even at the depth of 20 cm, the light intensity was still as high as 1.6 W/m^2, whereas the irradiation flux reduced greatly with the increase in catalyst dosage. At a catalyst dosage of 240 mg/L, the intensity of the irradiation vanished out at the depth of 5 cm, but lasted to a depth of 20 cm for a catalyst dosage of 60 mg/L.The results are dependent upon the intensity of radiation source. Fig. 4 shows the attenuation of radiation due to dye concentration 35 mg/L. Comparing Fig. 3 and Fig. 4, it can be seen that the catalyst dose has more drastic effect on radiation attenuation than dye concentration.

Some researchers have quoted the optimum value of photo-catalyst in the range of 2 to 8 g/L for various pollutants. Alhakimi *et al* [45] had highest degradation rate for potassium hydrogen phthalate at 3 g/L catalyst concentration using sun light as source of UV radiation. Sakthivel *et al* [46] quoted optimum value of 2.5 g/L catalyst dosage for acid brown 14 using sunlight. They measured UV radiation intensity at the top of the reactor as 38.2 W/m^2. Saquib *et al* [47] showed that the optimum catalyst dosage is 2 g/L for acid orange 8 using artificial UV source, yet the radiation intensity is not specified. Nevertheless, none of these investigators have undertaken the measurements of radiation intensities within reactor depths. In fact at very high concentration of catalyst, the radiation will not penetrate to the interiors of reactor. The reaction will only take place just in the region of the top. Yet since constant mixing is maintained throughout the duration of the experiment, the entire bulk of the polluted slurry undergo the reaction. However the results thus obtained shall be extremely dependent upon the reactor configuration and operation conditions. Nair *et al* [48] worked on kill of E. Coli group of microorganisms in water using slurry type photo-catalytic reactor. They measured the light intensity at the surface of reactor and accepted their results to be reactor configuration dependent; realizing the above-mentioned limitation.

In order to obtain reactor configuration independent kinetic parameters and efficiency for slurry type photo-catalytic reactor, the radiation attenuation function for the given concentration of catalyst and wastewater must be experimentally worked out. This will make it possible to estimate the radiation flux at any location in the reactor. Thus the radiation profile in the reactor can be determined. The reaction kinetics and efficiency can be determined point wise everywhere in reactor and can be integrated. Otherwise the average radiation flux value can be determined from the radiation profile and the same can be used for kinetic calculations and efficiency estimation.

It is also possible to arrange the light sources so as to obtain almost uniform radiation flux everywhere in the reactor. In either case this will enable the estimation of reactor configuration independent kinetic parameters and efficiency of the process.

In the most general form, the photo-catalytic reaction rate can be described as

$$\frac{dC}{dt} = \frac{(C_o - C_t)}{\Delta t} \tag{1}$$

Where C_0 and C_t are the concentrations of pollutant initially and at time t. The expression (1) is specific to the design and operating parameters including surface area of catalyst particles, concentration of organic material, average intensity of radiation, pH etc. If dC/dt is defined in terms of per unit surface area of catalyst, per unit concentration of organic material, per unit intensity of light for specific pH and operating conditions, the reaction rate shall be independent of constraints like reactor configuration and shall be universally acceptable.

4. Conclusions

It is advantageous for the researchers as well as the plant designers to determine a radiation attenuation function for the catalyst concentration and pollutant concentration being used by them. This will help researchers to precisely optimize their parameters and plant designers to optimize their design. The major problem associated with the slurry type photo-catalytic reactors is that the optimum values of parameters determined through the experimentations are reactor configuration and operating conditions dependent. They inhibit their universal applicability. However if the reaction rate, as given by equation (1) in its simplest form, is defined with the set of conditions mentioned along with, can be taken as reactor configuration independent and can be applied universally.

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