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Research Article

Immobilized Nano TiO_2 for Photocatalysis of Acid Yellow-17 Dye in Fluidized Bed Reactor

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Abstract

The UV photocatalytic decomposition of Acid Yellow-17 dye by TiO_2 immobilized on Chitosan and Cellulose Acetate were studied. The catalyst used was nanosized TiO_2 prepared by sol-gel technique. The batch studies with free catalyst and the immobilized catalysts were carried out and it is found supports used in immobilization do not offer diffusional limitations. Kinetics of degradation of the dye by immobilized TiO2 nanoparticles followed first order kinetics in the range of concnetrations studied. The effect of factors like catalyst loading, initial dye concentration, liquid flow rate on the degradation of Acid Yellow-17 was studied in a fluidized bed flow reactor operated in a batch recycle mode with the nanoparticles immobilized on cellulose acetate film.. Fluidized bed reactor with catalysts supported on cellulose acetate flakes may be considered as an efficient photoreactor.

Keywords: *Acid yellow-17; TiO_2, immobilized nanoparticles; photocatalysis; fluidized bed reactor*

1. Introduction

The textile industry is a significant contributor to many national economies, encompassing both small and large-scale operations worldwide. It is second largest employment generating sector in India. Textile processing generates many waste streams, including liquid, gaseous and solid wastes, some of which may be hazardous. The nature of the waste generated depends on the type of textile facility, the processes and technologies being operated, and the types of fibers and chemicals used. The textile industry uses high volumes of water throughout its operations, from the washing of fibers to bleaching, dyeing and washing of finished products. On average, approximately 200 liters of water are required to produce l kg of textiles. The large volumes of wastewater generated also contain a wide variety of chemicals, used throughout processing(Parvati et al.,2009). These can cause damage if not properly treated before being discharged into the environment. High concentrations of textile dyes in water bodies stop the reoxygenation capacity of the receiving water and cutoff sunlight, thereby upsetting biological activity in aquatic life and also the photosynthesis process of aquatic plants or algae (Zaharia et al., 2009).

The removal of toxic compounds from the textile wastewater is a very important task. Various physical, chemical and biological treatments are applied for the purpose. Biodegradation methods are effective in reducing the biological oxygen demand of the effluent, but nearly 53% of the colors are resistant to microbial attack. Hence, advanced oxidation processes like ultraviolet (UV), UV/H_2O_2, UV/ozone (Arslan et al,1999) with a photocatalyst have been researched extensively. The capability of the process to completely convert all the organic pollutants to ultimate products (CO_2 and H_2O) makes it attractive. The excellent photoactivity makes TiO_2 a perfect photocatalyst for wastewater treatment(Chong et al,2010) . The unique property of nanoparticles is the high surface to volume ratio; having more sites for achieving photocatalytic property enhancements. Hence use of nanoparticles of TiO_2 which have semiconductor properties, in the degradation of compounds present in the wastewater is researched upon(Sylvia et al,2008).

The band gap energy of 3eV makes TiO_2 very good semiconductor. UV light irradiation can excite electron from valence band to conduction band creating an equivalent hole in the valence band. The photon incident on the catalyst should have energy greater than the band gap. Hence two possible oxidation processes can occur during the photocatalytic reactions(Ahmed et al(2008).

(i) water can be oxidized to hydroxyl radicals by photogenerated positive holes and then these react with organic substrates to produce oxidized species.

(ii) The organic substrate can be directly be adsorbed on the catalyst leading to oxidation of the substrate directly on the surface.

Despite the effectiveness of the heterogeneous catalyst, the commercialization of the process is difficult due to the high operating cost. The nanosized particles of TiO_2 limit the practical application of the catalyst as it is very difficult to recover the catalyst from the slurry. The fine

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solid particles can also lead to increase in turbidity leading to reduced UV light penetration into the reactor. Hence an alternative is necessary to retain the fine catalyst particles. This led to immobilization of catalyst on solid supports.

The fluidized bed reactor provides better contact for the photo catalyst and reactant fluid. The reactor also enables better UV penetration into photo catalyst reactor and good exposure of the UV light to catalyst. This can help in improving the heterogeneous reaction.[Zulfakar et.al,2011]. Thus in the present study fluidized bed reactor with TiO_2 immobilized on solid supports like cellulose acetate and chitosan are used for photocatalysis of Acid Yellow-17(AY-17) dye in contaminated water.

2. Materials and Methods

2.1 Preparation of TiO_2 photocatalyst

TiO_2 nanoparticles were prepared by Sol-gel method, which included drop wise addition of 50 ml of 20%(v/v) solution of titanium (IV) isopropoxide in isopropanol into 20ml mixture of isopropanol and water(1:1) with vigorous stirring. After adjusting the pH to 2–3 with concentrated H_2SO_4, the resulting solution was stirred until a transparent TiO_2 sol was obtained. Later the sol was oven dried for 12hrs at 100^0C and calcined at 450^0C for 3hrs before use.

2.2 Preparation of TiO_2 immobilised on Cellulose acetate

Cellulose Acetate solution was prepared by dissolving 1 g of Cellulose Acetate in 8.3 ml of Acetone. 0.5 g of TiO_2 was added and stirred for uniform concentration. The viscous solution is spread uniformly on glass plates for drying. TiO_2 Immobilized on Cellulose Acetate films were cut into small pieces of 1cm*1cm.

2.3 Preparation of TiO_2 immobilised on Chitosan

Chitosan beads were prepared according to Wan Ngah's methods with further modifications. In order to increase the mechanical strength of chitosan, it was cross-linked with gluteraldehyde.

Chitosan solution was prepared by dissolving 1 g of chitosan flakes into 50 ml of 5% (v/v) acetic acid solution. 250ml of 1 mol/l NaOH solution was prepared. 1ml Gluteraldehyde was added to the NaOH solution.

0.5g of TiO_2 was added to the chitosan solution, mixed well to obtain uniform solution.

The viscous chitosan- TiO_2 solution was added drop wise using syringe into precipitation bath containing NaOH solution. This ensures that the acetic acid within the chitosan gel is neutralized and thereby coagulates the chitosan gel to spherical uniform chitosan beads.

2.4. Reactor for batch studies

The photoreactor for batch photocatalysis consists of a reactor with magnetic stirrer placed in between two vertically placed 18W UV-A lamps enclosed within an aluminum chamber. Air was continuously passed through the solution during the course of reaction. Batch experiments were conducted with 100ml dye solution of required concentration and the catalyst in free and immobilized form.

2.5. Fluidized bed flow reactor in batch recycle mode

A 261 ml fluidized bed flow reactor was housed in a aluminum chamber and exposed to two 18W UV lamps. Cellulose acetate flakes or Chitosan beads immobilized with the catalyst were fluidized by air, by passing air at a flow rate of 1.5lpm from the bottom. The Acid Yellow dye solution was pumped from a 1000 ml reservoir into the reactor by a peristaltic pump. The effluent from the reactor was recycled back into the reservoir, from which it is pumped back to the reactor. The pH of the Acid Yellow dye solution was adjusted to 3 before starting the reaction. Following the photodegradation, samples were collected from the reservoir at regular intervals of time for the analysis of the dye by absorbance measurement using UV–Vis spectrophotometer (U-2000, Hitachi) at 418 nm wavelength. Studies were carried out by varying the flow rates, initial concentrations and catalyst loadings to observe their effects on the degradation.

3. Results and Discussion

3.1 Effect of immobilization and kinetics of photocatalysis with immobilized catalyst

The time course variation of percentage degradation of the dye with free catalyst and catalyst immobilized on cellulose acetate flakes and chitosan beads during batch photocatalysis are presented in Fig.1. Catalyst loading was 0.5g. For experiments with free catalyst 0.5g of TiO_2 particles were used. In case of immobilized catalyst, one gram of the support containing 0.5g of catalyst was used. It is observed from Fig.1 that the rate of photocatalysis with free catalyst was slightly higher as compared to those with and immobilized catalysts, but the difference in rates is very minimal. It shows that diffusional limitations with these supports are very less and these supports can be efficiently used in photocatalytic applications. Almost complete degradation of the dye took around 3 h with free catalyst and 5h with immobilized catalysts.

The batch reactor time course data of concentration vs time were found to fit first order kinetic model for photocatalysis of AY-17 dye by TiO_2 immobilized on Cellulose acetate films and chitosan beads. The first order rate constants are 0.6576 h^{-1} and 0.8736h^{-1} respectively for photocatalysis by catalyst immobilized on Cellulose acetate and Chitosan respectively. First order rate constants imply that the rate would be faster with catalyst immobilized on Chitosan as compared to that with cellulose acetate. Fig. 1 also shows a marginally higher rate with catalyst immobilized on chitosan as compared to that with cellulose acetate. But it was observed that chitosan beads disintegrate on long time exposure to water. So for further experiments with fluidized bed reactor cellulose acetate was used as support for TiO_2.

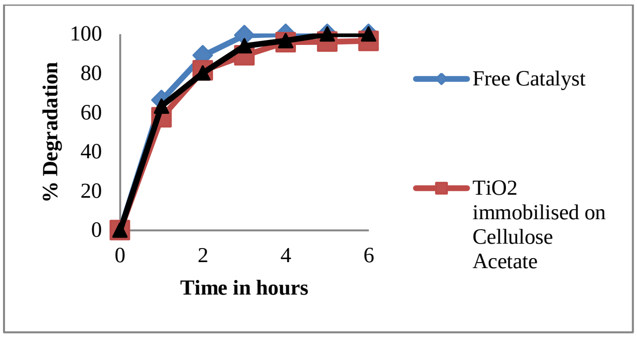

Fig. 1: Effect of Immobilisation on photocatalysis of AY-17 dye in batch reactor. Experimental Conditions: pH 3,dye concentration: 10ppm, catalyst loading:0.5g, amount of support=1g

3.2 Studies on fluidized bed flow reactor under batch recycle mode

3.2.1 Effect of Initial dye concentration

The study on the photocatalytic degradation of Acid Yellow-17 by TiO_2 immobilized on Cellulose Acetate by changing the inlet dye concentration was carried out with 3g of TiO_2 immobilised on 5g of Cellulose Acetate. Acid Yellow-17 dye (pH=3) was pumped from a reservoir containing 100ml of dye solution, through the reactor at 38 ml/min in a recycle mode. Fig.2 shows that the rate of degradation of Acid Yellow-17 dye decreased with increasing initial dye concentration. This may be due to the hindrance to UV light penetration at higher inlet dye concentration. It was found that only 5 ppm and 10 ppm dye could undergo complete degradation in 11 hours.

3.2.2 Effect of catalyst loading

Effect of catalyst loading on the rate of degradation during UV photocatalysis was studied by varying the TiO_2 catalyst loading in the range of 0.3 g to 5 g in fluidized bed reactor. Initial dye concentration used was 10 ppm, inlet flow rate to the reactor was 38 ml/min with continuous air flow of 1.5 lpm and the initial pH was 3. It can be observed from Fig 3 that the rate of photocatalysis increases with the increase in catalyst loading.1000ml of 10ppm dye was degraded to around 95% in 7h with 3 and 5g of the catalyst. Initial rate of photocatalysis is very high with 5g of catalyst as compared to 3g catalyst. When the catalyst loading was decreased by 1/10th (3g to 0.3g), the percentage degradation after 7h irradiation has reduced to less than 1/3rd(95% to 30%). With the increase in catalyst loading, the active sites for the pollutant to get adsorbed also increases, thereby increasing the rate of degradation. But when the catalyst loading is very high, it blocks the penetration of UV light, thereby hindering the photocatalysis. Hence there is an optimum catalyst loading for maximum rate of degradation.(.Zulfakar et al.,2011). The effect of blocking of UV penetration by increase in catalyst loading is reduced by fluidization and thus the rate of degradation has continuously increased with increase in catalyst loading.

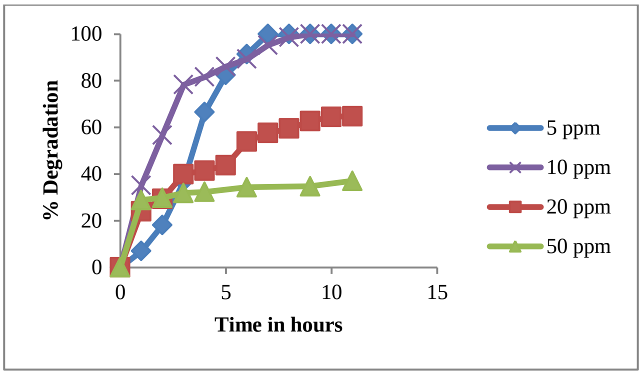

Fig. 2: Effect of Initial dye Concentration on photocatalysis in fluidized bed reactor

3.2.3 Effect of liquid flow rate

The experiments were conducted at 38 ml/min and 96 ml/min of liquid flow rate to study the effect of flow rate on degradation of AY-17 dye by TiO_2 immobilized on Cellulose Acetate. Initial dye concentration was 10ppm, catalyst loading=3g and initial pH=3. The rate of degradation increases with decrease in the flowrate. Increase in flow rate can have two opposing effects on rate of photocatalysis. With the increase in flow rate, rate of degradation may increase due to reduction in external mass transfer limitations. But increase in flow rate can also reduce the contact time between the catalyst and the dye by reduction of residence time in the reactor. It can be observed from Fig 4 that, higher degradation is achieved with decreased flow rate. As the flow rate increases, the residence time for the dye in the reactor increases, leading to enhanced contact between the dye and the catalyst. Though the initial rates of degradation seems unaffected by increased flow rate, lower rate is observed at later times. In the present situation, contribution of liquid flow rate for reduction of mass transfer limitations seems negligible. The air flow rate of 1.5 lpm keeps the catalyst fluidized, thereby eliminating the mass transfer limitations.

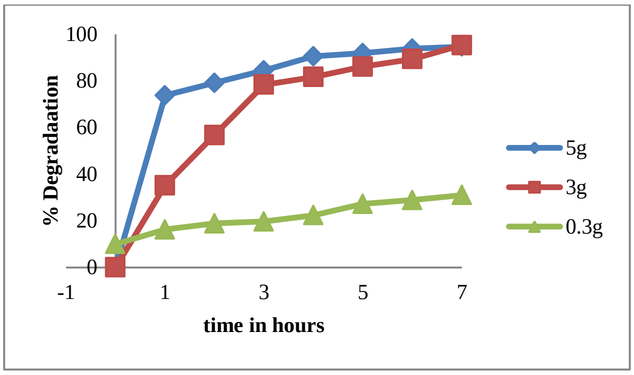

Fig.3. Effect of catalyst loading on photocatalysis in fluidized bed reactor

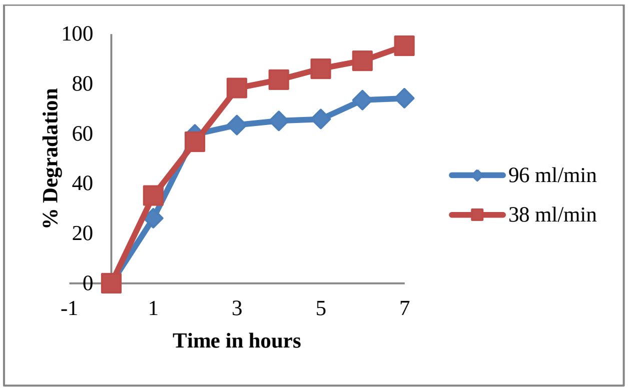

Fig.4. Effect of liquid flow rate on photocatalysis in fluidized bed reactor

Conclusions

Supports like chitosan and cellulose acetate flakes do not offer any diffusional limitations for photocatalytic process and the TiO_2 catalyst immobilized on these supports show almost equal efficacy as the free TiO_2 catalyst for photocatalytic degradation of AY-17 dye in contaminated water. Photocatalysis of AY-17 dye by TiO_2 immobilized on Cellulose acetate films and Chitosan beads follow first order kinetic model. Rate of degradation of AY-17 dye decreased with increase in initial dye concentration, decrease in catalyst loading and decrease in flow rate. More than 95% removal of 10ppm dye from 1000ml solution can be achieved within 7h in a fluidized bed reactor with TiO_2 immobilized on cellulose acetate flakes under UV light irradiation. Fluidized bed reactor with catalysts supported on Cellulose acetate flakes may be considered as an efficient photoreactor.

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