Process Safety and Environmental Protection xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Process Safety and Environmental Protection

journal homepage: www.elsevier.com/locate/psep

Modeling and optimization of a sono-assisted photocatalytic water treatment process via central composite design methodology

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ABSTRACT

This work focuses on modeling and optimization of a sono-assisted photocatalytic decolorization process of a model pollutant, azo dye C.I. direct red 16 (DR16). In the process, a high temperature thermal decomposition nano synthesized titanium dioxide (TD-TiO_2) was applied as photocatalyst. Central composite design (CCD) methodology was used for designing the experiments, modeling and optimization of the process. A quadratic model was established to describe dependency of the decolorization efficiency (*DE*), as the model response, to some effective operational parameters, i.e. the catalyst dosage, pH and the dye initial concentration. The ANOVA analysis confirmed that all of the variables have significant influence on the model response. Under the established optimum conditions, 92.4% *DE* was achieved after 45 min; however, to access desirable mineralization efficiency, the process should be continued up to 120 min. All withdrawn samples from the reaction media during the process showed no antibacterial activity, which indicates safety of the treated effluent for disposal into the environment. Also studies showed that the process proceeds via two parallel branches of photolysis and photocatalysis, where propagation of the ultrasonic waves into the reaction media plays a vital promoting role on the latter branch.

Keywords: Nano TiO_2; Photocatalysis; Experimental design; Modeling; Optimization; Mineralization

1. Introduction

Conventionally, process engineers wish to determine the important levels of design parameters so that; related responses can reach to optimum values. The optimum can be either a maximum or minimum of a function of the design parameters (Aslan, 2007). To optimize a photocatalytic system, the conventional one-factor-at-a-time (OFAT) approach is mostly used to reveal the effects of one parameter after another. Although this conventional method is widely acceptable, reported results may be insignificant and have less predictive ability if condition of one of the operating parameters is changed. When a combination of several independent variables and their interactions affect the process-desired responses, as the case of photocatalytic systems, application of design of experiments (DOE) accompanied with statistical and response surface analysis can be an effective strategy (Chong et al., 2009a; Fu et al., 2009; Khataee et al., 2011; Lizama et al., 2002). Compared to the OFAT approach, the DOE has pre-determined experimental points that are distributed uniformly throughout the study domain. This allows indication of process optimum conditions and identification of the parameter interactions, where they can be interpreted using statistical software, such as Design Expert® software (Chong et al., 2010).

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http://dx.doi.org/10.1016/j.psep.2014.07.004
0957-5820/

The fundamentals of the heterogeneous photocatalytic process, using TiO_2 particles, have been extensively reported (Chong et al., 2010; Fujishima et al., 2000; Gaya and Abdullah, 2008). The process is initiated by the exposure of TiO_2 particles to the UV light to excite an electron from the valence band (VB) to the conduction band (CB), resulting in formation of the high-energy electron–hole pairs (exiton). The highly oxidative valence band holes (redox potential of 2.8 V) may react directly with the surface-sorbed organic molecules or indirectly via the formation of hydroxyl radicals (Konstantinou and Albanis, 2004). The reaction of the photo-generated holes with the hydroxyl ions and water molecules adsorbed on the TiO_2 surface can yield hydroxyl radicals (da Silva et al., 2003; San et al., 2002). In addition, the conduction band electrons are negative enough to reduce the present dissolved oxygen molecules in solution. The generated hydroxyl radicals are powerful oxidizing agents that attack organic pollutants present on or near the TiO_2 surface (Fujishima et al., 2000). In this regard, dissolved oxygen plays an important role in the TiO_2 photocatalysis process as an electron scavenger to prevent the electron–hole recombination (Chong et al., 2009b).

Efficiency of the photocatalytic oxidation can be hindered severely by two main factors: mass transfer limitations and fouling of the solid catalyst (Gogate and Pandit, 2004). If the photocatalytic oxidation is run in presence of ultrasonic irradiation (sonication), the rate of hydroxyl radical generation will be increased (chemically via the cavitation process and physically via increase in the catalyst surface exposed to light irradiation). Also through this, mass transfer resistance is diminished due to the acoustic streaming and turbulence created by the ultrasonic wave propagation. Moreover, generated turbulence helps in cleaning the catalyst which cause the increase in the efficiency of the photocatalytic oxidation process (Gogate and Pandit, 2004; Cheng et al., 2012; He et al., 2011).

The aim of the present study is modeling and optimization of a sono-assisted photocatalytic decolorization of a model pollutant, direct red 16 (DR16), in aqueous media based upon central composite design (CCD) methodology. The used photocatalyst is nano titanium dioxide particles, synthesized using thermal decomposition method (TD-TiO_2) (Chin et al., 2010). For modeling, some applied operational parameters i.e. the catalyst dosage, pH and dye initial concentration were considered as the variables, and the decolorization efficiency percentage (*DE*) as the relevant response. Analysis of variance, statistical regression and response surface analysis were done and also optimum conditions were determined and confirmed. Under the optimum conditions, extents of the aromatic degradation and mineralization obtained by the modeled sono-assisted photocatalytic system were assessed and in this regard some details of the process were clarified.

2. Experimental

2.1. Chemicals

The azo dye, direct red 16 (DR16), $C_{26}H_{17}N_5Na_2O_8S_2$ (C.I. 27,680, MW 637.26) was purchased from Alvan Sabet company (Iran), 99% pure (mass fraction). DR16 is a two azo dye in which chromophore part of the molecular structure contains azo linkage and shows a strong absorbance in the visible region at 520 nm, while the absorbance peaks of the benzene and naphthalene rings appear in the UV region (290 and 224 nm). The dye structure and spectrum has been presented elsewhere (Saien et al., 2009). Sulfuric acid and sodium hydroxide used to adjust the pH of solutions were Merck products. Titanium tetraisopropoxide $((CH_3)_2CHO)_4Ti$ was supplied by Aldrich with purity more than 97%. Deionized water (Millipore) was used in all the experiments.

2.2. Catalyst preparation

The nano photocatalyst was synthesized via a high temperature thermal decomposition (TD) method (Chin et al., 2010). Titanium tetraisopropoxide (TTIP) under temperature of 95 °C was carried into a tubular electric furnace working under temperature of 900 °C using argon (4.3 L/min) and air (43 L/min) flows. An alumina tube (0.45 m in length and 0.02 m in diameter) was placed inside the electric furnace. A water-cooled particle collection device was installed downstream of the alumina tube, to collect the synthesized nano photocatalyst powders.

2.3. Catalyst characterization

X-ray diffraction (XRD) was recorded on a DMAX-2500 (Rigaku Inc.; focal spot size: 5 mm^2) diffractometer using a Cu rotating anode with a scan rate of 2°/min. The anatase content fraction (f_A) was determined from the integrated intensity of the anatase and rutile phase diffraction lines (I_A and I_R), using the following equation (Spurr and Myers, 1957).

$$f_A = \frac{0.79I_A}{I_R + 0.79I_A} \quad (1)$$

For scanning transmission electron microscopy (TEM), the materials were deposited onto a carbon foil supported by a copper grid. The TEM analysis was carried out using a CM-30 microscope (Philips; operated at 300 kV, image resolution <0.23 nm). The powder specific surface area (SSA, m^2/g) was determined by nitrogen adsorption (>99.999%) at 77 K on a Micromeritics Tristar 3000 apparatus using the BET method. Also, pore volume distribution was determined from the desorption isotherms (Micromeritics ASAP 2010 Multigas system) using the Barrett–Joyner–Halenda (BJH) method. Assuming monodispersed, spherical primary particles, the BET-equivalent particle diameter (d_{BET}) was calculated using Eq. (2) (Spurr and Myers, 1957), where ρ is the particle density, which is 3.84 g/cm^3 for the TiO_2 anatase crystalline. Fig. 1 shows the XRD spectrum and TEM image of the used catalyst. The determined specific physical characterizations of the nano particles are as: SSA = 134.4 (m^2/g), d_{BET} = 11.63 (nm), pore volume = 41.69 × 10^{-4} (cm^3/g), pore size = 7.14 (nm) and f_A = 0.966.

$$d_{BET} = \frac{6000}{\rho \times SSA} \quad (2)$$

2.4. Sono-photo-reactor and experimental procedure

A schematic of the reactor and its belongings is presented in Fig. 2. A cylindrical handmade sono-photo-reactor of glossy stainless steel was used with capacity of 1.25 L and dimensions of 90 mm diameter and 200 mm height. The light source (165 mm body length and 80 mm arc length) was a 250 W mercury lamp with a wavelength range of 280–400 nm and the maximum emission of 365 nm (measured by a TOPCON UV-R-1 spectroradiometer). The lamp was placed in a quartz tube

Please cite this article in press as: Soleymani, A.R., et al., Modeling and optimization of a sono-assisted photocatalytic water treatment process via central composite design methodology. Process Safety and Environmental Protection (2014), http://dx.doi.org/10.1016/j.psep.2014.07.004