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Photocatalytic degradation of chlorhexidine—A chemical assessment and prediction of optimal condition by response surface methodology

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ABSTRACT

Present study demonstrates an intensive experimental study on the photo-mineralization of an antiseptic drug component, chlorhexidine digluconate in batch slurry photo reactor in presence of ultra-violet light and using titanium dioxide as catalyst. Chlorhexidine digluconate belongs to the typical class of antiseptic drug components that generally used in disinfectants, cosmetics and pharmaceutical products. This study aims to analyze the influence of operating parameters, and their interactive effect on the overall removal efficiency of the targeted drug component from waste stream, and prediction of the optimum condition for up-scaling the technique and design of the photocatalytic reactor. Response surface methodology has been used to develop a multi-variant regression model and to assess the influence of individual parameters as well as the interactive effects. Substrate to catalyst ratio, UV intensity and medium pH were chosen as independent variables to optimize the percent removal of chlorhexidine digluconate as response. Optimal conditions obtained from statistical analysis at substrate to catalyst ratio 1.25, UV intensity 87.5 $\mu W\ cm^{-2}$ at pH 10.5 have shown percent removal of 67.47 with desirability factor of 0.989. Model predicted values were found in good agreement with the experimental values, and the behavior of the model equation has supported the experimental observation with minor deviation. Separate validation experiment at predicted optimal condition ascertained the high predictive ability of the model equation.

1. Introduction

In present context of waste management and recovery of resources, severe environmental concern is emerging because of natural water contamination by drugs residues and their metabolites. These chemical compounds are so designed that, they are physiologically active and resistant to biodegradation, which substantially increase their foot print in the aquatic environment and are categorized as 'pollutant' [1,2]. The principal track of these pharmaceutical into the environment is through its ending-up in soil, surface waters and ground water after their excretion from humans or animals via urine or feces through the sewage system [3,4] In addition to metabolic excretion, disposal of expired drugs from hospitals, pharmaceutical industries and common households, also introduce them into fresh water resources. Several studies have reported in details the direct inflowing of pharmaceuticals in the sewage treatment process [5] and their adverse effect on the aquatic life [6–8].

Chlorhexidine (CHD) compositions are in use all over the world for more than 50 years and is used primarily as its salts like the dihydrochloride, diacetate and digluconate in disinfectants (disinfection of skin and hands), cosmetics (adhesive to creams, tooth pest, deodorants and antiperspirant), and pharmaceutical products (preservatives in eye drops, active substance in wound dressing and antiseptic mouth washes) [9]. Systemic oral administration of CHD formulations on rats have shown that, receiving 50–200 mg/kg body mass in drinking water for 90 days produce evidence of histiocytosis of the mesenteric lymph nodes [10]. It is also reported as environmentally hazardous, toxic to aquatic organisms, sewage microorganisms and responsible for long term adverse effects in aquatic environment [9].

To avoid the hostile buildup of drug components in aquatic environment, researches are underway to develop effective detoxification techniques to ensure complete destruction of the drug residues. To maintain the environmental standard of discharged effluents, technical and industrial developments for removal of pharmaceuticals have become obligatory to the pharmaceutical industries. Photo-mineralization of the pharmaceuticals sensitized by semiconductor photocatalysis is a rapidly expanding area of research [11–14], which has been proven

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beneficial in removal of a wide range of challenging contaminants. The photocatalytic detoxification approach is attractive as the effluent produced is harmless to the environment. Moreover, the photo mineralization process, by principle being destructive in nature, requires less downstream processing and can be easily controlled [15]. Compared to other destructive technologies like, chlorination, ozonation, H_2O_2-Fe oxidation, those normally depend on the use of strong hazardous chemicals; this approach is recognized as quite safe and promising [15]. Intensive studies on photocatalysis using nano-TiO_2 as catalyst have already been published for treatment of the pharmaceutical components in waste water [16–19], but study on photocatalytic degradation of CHD using nano-TiO_2 is scanty [20]. Present study aims at the photocatalytic degradation of the CHD rich formulation and optimization of the process using response surface methodology (RSM) for 'up scaling' the adopted technique and setting up of a novel type photoreactor.

Response surface methodology (RSM) is a useful statistical method commonly used for experimental design and widely applied to model and optimize several wastewater treatments, like photocatalytic [21,22], and electro-Fenton [23–25]. In RSM approach, the effects of multiple process variables can be evaluated simultaneously, as well as the interactions can also be predicted on the desired response [26]. RSM is a collection of statistical and mathematical techniques used in developing, improving and optimizing a process in which response is of interest that is influenced by several variables and the objective is to optimize this response. It defines the effect of independent variables and the combination effect. This methodology performs a minimum set of experiments in an experimental matrix, with improved statistical interpretation possibilities and indicating the significance of process parameters interaction. Face Centered Central Composite Design (FCCD) is one of the most frequently used designs for optimization of photocatalytic treatment process [27] which leads to a strong estimation of the optimum response. It contains an imbedded factorial or fractional factorial design with points that is augmented with a group of axial point that allow estimation of curvature. RSM has also been used in photocatalytic removal of miscellany pharmaceutical agents [27–31]. In this work the objective is to investigate the effect of different process parameters and interactive effects for optimization of the percent removal of CHD from aqueous matrix using the RSM approach. Chlorhexidine digluconate is well known and widely used antiseptic component for human and veterinary applications but few reports are available pointing to the adverse effect of this drug component. This compound is primarily used as an antiseptic component up to certain concentration level [20]. Above that level its adverse effect becomes intense and can exhibit adverse toxic effects on aquatic life [9,10,20]. This study aims to point out about the adverse effect of CHD as well as the efficiency of photocatalytic degradation process in reducing the level of this drug component from process stream. Novelty of this study is in the choice of the substrate as chlorhexidine digluconate since; no publication is still available attempting to study the efficiency of photocatalytic degradation for this particular class of antiseptic component. To our knowledge, no such information available in the published literatures regarding optimization of the operating process parameters on photocatalysis of antiseptic CHD using TiO_2 as photocatalyst by RSM. Present work is focused on the effect of parameters (substrate to catalyst ratio, pH, UV intensity) on extent of CHD degradation in batch slurry photo reactor. At the outset, suitable conditions for optimizing the CHD degradation was obtained experimentally and then fitted in the quadratic model for optimization. This study not only provides information for predicting and optimizing the degradation process of CHD, but also can provide scheme of a new method to deal with antiseptic drug pollution.

2. Experimental

2.1. Materials

Chlorhexidine digluconate ($C_{22}H_{30}Cl_2N_{10}{\cdot}2\ C_6H_{12}O_7$, FW 897.8) 20% aqueous solution was provided by Sigma-Aldrich and was used without further purification to prepare the simulated solutions to standardize the analytical process. Its structure is shown in Fig. 1. Titanium dioxide photocatalyst nano-powder (Aeroxide®P25, particle size 21 nm with surface area (BET) 35–65 $m^2\ g^{-1}$, from Sigma–Aldrich) was used as received. All experimental runs were carried out with ultrapure water from Arium® Pro VF (Sartorius Stedim Biotech) of 18.2 MΩ cm resistivity. All other chemicals, unless mentioned were procured from E. Merck, India.

2.2. Batch study of the photocatalytic degradation of chlorhexidine digluconate

Chlorhexidine digluconate of varying concentration (0.5–1.5 mg L^{-1}) was dissolved in the DI water to simulate the synthetic pharmaceutical waste water. To study the process of photocatalytic degradation of chlorhexidine digluconate, batch study in a slurry photo reactor (100 mL) was conducted with varying concentration of the substrate (CHD) (0.5–1.5 mg/L) and the catalyst (TiO_2) (0.1–0.4 mg/L). Experimental runs were performed in the following ranges, substrate to catalyst ratio: 1–5; UV intensity: 50–125 μW cm^{-2} and pH of the reaction matrix: 4–10.5. The reactor details are given in our previous study [20]. Dissolved oxygen concentration was maintained 8.24 mg/L at the 25 °C. In present study, experimental runs were monitored, and analyzed by residual chlorhexidine digluconate concentration in the reaction mixture as a function of time. All experimental runs were repeated thrice to check the reproducibility of the experimental results.

For overall understanding of the process, different controlling parameters like, UV intensity substrate to catalyst ratio and the pH of the reaction mixture were varied. Each batch studies were conducted for 1 h (at 400 rpm) with sample collection at each 5 min interval. To ascertain the complete catalyst removal, aliquot was centrifuged (4 °C, 11,000 × *g*, 5 min) and supernatant was collected for subsequent analyses.

2.3. Analytical procedures

Chlorhexidine digluconate concentration of the reaction mixtures was determined by spectrophotometer at 275 nm [32]. To maintain the accuracy of measurements and to illustrate the product pattern, repeat measurements were done in RP-HPLC system (Cyber Lab, Millbury, USA) with 'Zorbax SB Phenyl column', (4.8 mm × 250 mm, 5 μm, Agilent, USA) at 25 °C with eluent flow rate of 0.5 mL min^{-1} at UV absorbance of 275 nm [33]. The mobile phase used was methanol (60%) and water (40%) and injection volume was 20 μL. Residual CHD concentrations were measured from the peak areas as obtained in HPLC chromatogram. The process efficiency was evaluated in terms of the percent removal of the CHD (R%) from reaction matrix and estimated following Eq. (1), where, C_i is the initial concentration of the CHD and C_f is the final

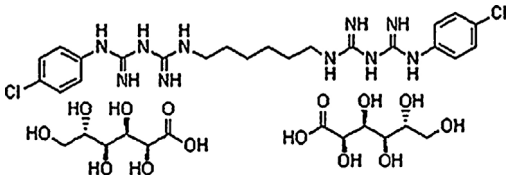

Fig. 1. Structure of chlorhexidine digluconate (CAS: 18472-51-0).