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Photocatalytic degradation of pharmaceutical wastes by alginate supported TiO_2 nanoparticles in packed bed photo reactor (PBPR)

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ABSTRACT

In recent years deposal of pharmaceutical wastes has become a major problem globally. Therefore, it is necessary to removes pharmaceutical waste from the municipal as well as industrial effluents before its discharge. The convectional wastewater and biological treatments are generally failed to separate different drugs from wastewater streams. Thus, heterogeneous photocatalysis process becomes lucrative method for reduction of detrimental effects of pharmaceutical compounds. The main disadvantage of the process is the reuse or recycle of photocatalysis is a tedious job. In this work, the degradation of aqueous solution of chlorhexidine digluconate (CHD), an antibiotic drug, by heterogeneous photocatalysis was study using supported TiO_2 nanoparticle. The major concern of this study is to bring down the limitations of suspension mode heterogeneous photocatalysis by implementation of immobilized TiO_2 with help of calcium alginate beads. The alginate supported catalyst beads was characterized by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDAX) as well as the characteristic crystalline forms of TiO_2 nanoparticle was confirmed by XRD. The degradation efficiency of TiO_2 impregnated alginate beads (TIAB) was compared with the performance of free TiO_2 suspension. Although, the degradation efficiency was reduced considerably using TIAB but the recycle and reuse of catalyst was increased quite appreciably. The kinetic parameters related to this work have also been measure. Moreover, to study the susceptibility of the present system photocatalysis of other three drugs ibuprofen (IBP), atenolol (ATL) and carbamazepine (CBZ) has been carried out using immobilized TiO_2. The continuous mode operation in PBPR has ensured the applicability of alginate beads along with TiO_2 in wastewater treatment. The variation of residence time has significant impact on the performance of PBPR.

1. Introduction

Wastewaters from pharmaceutical industries and from households contain lots of drugs especially antibiotics are vigorously entering to water environment. Therefore, threats due to pharmaceutical drugs to the aquatic life as well as all living element become major concern of research work (Carballa et al., 2004; Hirsch et al., 1998; Ternes, 1998; Kidd et al., 2007; Lange et al., 2001; Oaks et al., 2004). For remediation of a disease pharmaceutical drugs are frequently used and thereafter without alternation major part of those medicines enters to the environment through municipal sewage system. Moreover, sometime medicines are thrown into environment directly and pharmaceutical wastes from the respective industries directly disposed off to the water bodies (Hirsch et al., 1998; Ternes, 1998; Kidd et al., 2007; Halling-Sørensen et al., 1998). As a result a gradual growth pharmaceutical component is observed in water environment. However, it is impossible to separate pharmaceutical compounds i.e. antibiotics, hormones, steroids, etc. through wastewater treatment and cannot be degraded by means of biological treatment (Daughton and Ternes, 1999; Zwiener and Frimmel, 2000). Several groups of researcher have adopted photocatalysis in presence of nanoparticle, one of the main categories of advanced oxidation process (AOP) to eliminate detrimental effects of pharmaceutical compounds (Klavarioti et al., 2009).

Heterogeneous photocatalysis in presence of nanoparticle mainly TiO_2 has become a promising pathway for separation of several micropollutants form wastewater streams (Devipriya and Yesodharan, 2005; Woo et al., 2009; Zayani et al., 2009; Hsu et al., 2008; Calza et al., 2006; Sakkas et al., 2007; Zhang et al., 2010; An et al., 2011; Sarkar et al., 2014a,b). Small size nanoparticle provides

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higher surface to volume ratio thus it offers better surface reaction. Titanium oxide nanoparticle is used frequently due to its strong oxidizing power, higher photo stability and non-toxic nature (Gupta and Tripathi, 2011). Many researchers have highlighted many advantageous sides of photocatalysis in presence of TiO_2 nanoparticle although the scale up of heterogeneous photocatalysis process is the main challenging task. The recovery and reuse of TiO_2 nanoparticle at the end of photocatalysis process is the main obligation of photocatalysis process and eventually it is very tedious job in practice.

The problem related to the larger scale implementation of heterogeneous photocatalysis is cumbersome separation and recycling of photo catalyst during the wastewater treatment. This problem can be obliterated by implementation of immobilization of TiO_2 on solid support. The immobilization is very simple and easy to execute for immobilization of cells and enzyme (Santos et al., 2008). However, mentioned method by Santos et al. (2008) can be adopted to entrap TiO_2 nanoparticle. Moreover, it is necessary to develop a cost effective and environment friendly entrapment method so that it can be easily adopted by research fraternity. Harikumar et al. (2011) described that calcium alginate was nontoxic, biodegradable, non-immunogenic, water insoluble and thermally irreversible type of polymer matrix which could provide better support for immobilization of nanoparticle. Therefore, calcium alginate beads can be used for environment friendly immobilization of TiO_2 nanoparticle and those photo active beads should be used in wastewater treatment in large scale.

The main goal of this current research work is to develop an immobilized photocatalytic system to remove pharmaceutical components from the wastewater. The current research group has already established that photocatalysis in presence of TiO_2 nanoparticle is very much effective in removal of anti-biotic like chlorhexidine digluconate (CHD) (Das et al., 2014, Sarkar et al., 2014a,b). Although, the last successful attempt of photocatalytic degradation of CHD has been done using suspension of photo catalyst (Das et al., 2014, Sarkar et al., 2014a,b) but it prevails some limitations which have been described earlier. As per literature survey, this research work has made the first attempt to implement immobilized TiO_2 using alginate in the field of pharmaceutical wastewater treatment and at the same time elimination of disadvantages of suspension mode has been tried so far. Furthermore, a new concept of packed bed photo reactor (PBPR) has been introduced here in which nanoparticle impregnated alginate beads have been used as packing material. Introduction of PBPR has been made to eliminate the major limitation of batch mode during treatment of large volume of wastewater as PBPR has been operated in continuous mode. Moreover, to ascertain the applicability of immobilized system as well as PBPR, the present research work has tried to carry out photocatalytic degradation of different drugs in continuous mode. Other three pharmaceutical drugs i.e. ibuprofen (IBP), atenolol (ATL) and carbamazepine (CBZ) which have also some other detrimental effects on environment (Hapeshi et al., 2010, Georgaki et al., 2014), were also treated with immobilized TiO_2 system to check the viability of present treatment method using PBPR.

2. Experimental

2.1. Chemical and reagents

Titanium dioxide photocatalyst nanopowder Aeroxide®P25 (mixture of rutile and anatase, 718467) of particle size 21 nm with surface area (BET) 35–65 $m^2\ g^{-1}$ from Sigma-Aldrich, were used as photo catalysis. Chlorhexidine digluconate solution (20% w/v), Ibuprofen ($CH_3H_{18}O_2$, purity ≥ 99%), atenolol and carbamazepine ($C_{15}H_{12}N_2O$) were purchased from Sigma-Aldrich to prepare the simulated solutions for experimental purpose. All experiments were carried out with ultrapure water from Arium® Pro VF (Sartorius Stedim Biotech) of 18.2 MΩ cm resistivity. All other chemicals i.e. sodium alginate, calcium chloride (di-hydrate) were purchased from Sigma Aldrich Chemical Co., USA.

2.2. Immobilization of TiO_2 in calcium alginate beads

The titanium dioxide impregnated beads were prepared by entrapping TiO_2 nanoparticles in the calcium alginate beads. About 100 mL of casting solution was prepared by mixing 4.0 g (4%) of sodium alginate powder and 1.0–4.0 g of TiO_2 nanoparticle in ultrapure water and stirring until a homogenous solution was achieved. First, TiO_2 nanoparticle was added to 100 ml water and stirred for 30 min to form homogeneous suspension and then sodium alginate was introduced in that solution. The mixture (100 mL) was injected drop wise into 400 mL $CaCl_2$ solution (0.5 M) using a syringe (10 mL) with a needle (0.8 mm in diameter, 38 mm in length) to form TiO_2 impregnated alginate beads (TIAB). The TIAB were cured in the $CaCl_2$ solution for overnight at room temperature and then rinsed with ultrapure water for several times. Prepared TIAB stored in ultrapure water and kept in 4° C for future use. Blank beads were also prepared by above mentioned method but without TiO_2 addition.

2.3. Adsorption and photocatalysis

The photocatalytic degradation using suspension mode of TiO_2 was carried out under artificial UV source in a quartz reactor in the batch mode. The experimental details have been already described by Das et al. (2014) and Sarkar et al. (2014a) in suspension mode. The batch study using TIAB was carried out maintaining the favorable conditions similar to the batch study in suspension mode. The pH and the temperature were maintained at 10.5 and 30° C and substrate to catalyst ratio (S/C) was fixed at 2.5. The irradiation time for both systems maintained for 1 h. With certain interval aliquot solution was piped out from the reaction broth to measure the concentration of antibiotic, CHD. For the adsorption process, same type of experimental study was carried out as mentioned above but without UV irradiation. To increase the efficacy of TIAB and to eliminate the limitations of batch mode operation, the photocatalysis has been carried out in continuous mode using Packed Bed Photo Reactor (PBPR). The present mode of operation has been illustrated schematically in Fig. 1. The residence time (τ) and all other physical parameters were selected according to the best removal condition achieved in batch mode. To maintain constant temperature during the photocatalysis reaction the reactor is jacketed for the circulation of coolant and to protect UV

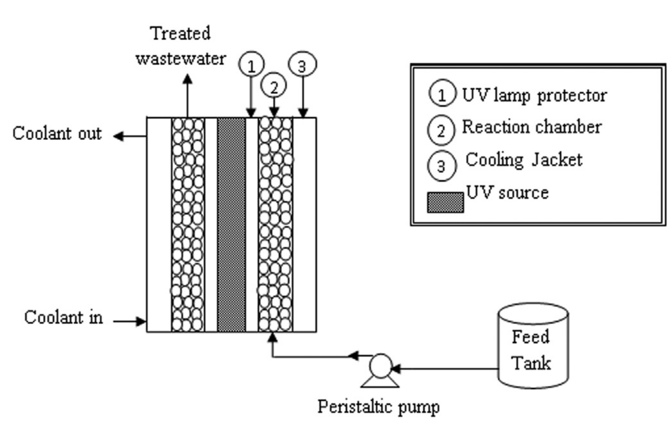

Fig. 1. Schematic representation of PBPR.