



Research article

Photocatalytic degradation of carbofuran by TiO₂-coated activated carbon: Model for kinetic, electrical energy per order and economic analysis



M.A. Vishnuganth^a, Neelancherry Remya^b, Mathava Kumar^{c,*}, N. Selvaraju^a

^a Department of Chemical Engineering, National Institute of Technology, Calicut, 673 601 Kerala, India

^b School of Infrastructure, Indian Institute of Technology, Bhubaneswar, 751 013 Odisha, India

^c Department of Civil Engineering, Indian Institute of Technology, Madras, 600 036 Tamil Nadu, India

ARTICLE INFO

Article history:

Received 16 March 2016

Received in revised form

8 June 2016

Accepted 11 June 2016

Keywords:

Carbofuran

GAC supported TiO₂ catalyst

Photocatalysis

Kinetic model

Electrical energy per order

Cost analysis

ABSTRACT

The photocatalytic removal of carbofuran (CBF) from aqueous solution in the presence of granular activated carbon supported TiO₂ (GAC-TiO₂) catalyst was investigated under batch-mode experiments. The presence of GAC enhanced the photocatalytic efficiency of the TiO₂ catalyst. Experiments were conducted at different concentrations of CBF to clarify the dependence of apparent rate constant (k_{app}) in the pseudo first-order kinetics on CBF photodegradation. The general relationship between the adsorption equilibrium constant (K) and reaction rate constant (k_r) were explained by using the modified Langmuir-Hinshelwood (L-H) model. From the observed kinetics, it was observed that the surface reaction was the rate limiting step in the GAC-TiO₂ catalyzed photodegradation of CBF. The values of K and k_r for this pseudo first-order reaction were found to be 0.1942 L mg⁻¹ and 1.51 mg L⁻¹ min⁻¹, respectively. In addition, the dependence of k_{app} on the half-life time was determined by calculating the electrical energy per order experimentally (E_{EO} experimental) and also by modeling (E_{EO} model). The batch-mode experimental outcomes revealed the possibility of 100% CBF removal (under optimized conditions and at an initial concentration of 50 mg L⁻¹ and 100 mg L⁻¹) at a contact time of 90 min and 120 min, respectively. Both L-H kinetic model and E_{EO} model fitted well with the batch-mode experimental data and also elucidated successfully the phenomena of photocatalytic degradation in the presence of GAC-TiO₂ catalyst.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The application of pesticides to reduce the loss in yield by pests become a regular practice in modern agriculture throughout the world. The extensive use of pesticides to increase the yield has released their traces in aquatic environment. However, the major sources of pesticide release into the environment includes effluents from pesticide formulating and manufacturing plants, direct surface runoff from agricultural fields, leaching, disposal of empty containers, equipment washing etc. The presence of higher level of pesticides in any food supplement including drinking water has been well recognized as toxic, mutagenic and carcinogenic. In many rural areas of developing countries including India, the major

source of drinking water rely on open and tube wells located close to the agricultural fields. Most of these water supplies were made after simple chlorination process, which compromises the quality of water for drinking in these localities. On the other hand, several of the pesticide formulations have been known to be biorefractory and recalcitrant in nature and therefore, biological treatment of agro industrial effluents has been often perturbed and sometimes banned (Mahalakshmi et al., 2007; Lopez-Alvarez et al., 2011).

Carbofuran (2, 3-dihydro-2, 2-dimethylbenzofuran-7-yl methylcarbamate, CBF), one of the broad spectrum carbamate pesticide and nematicide, has been in use against foliar pests, observed in fruit, vegetable and forest crops. It accounts about 12.4% of the total insecticide produced every year in developing countries (Lu et al., 2011). CBF is an inhibitor of acetyl cholinesterase, an enzyme vital to the functioning of the control nervous system, and it is a potential endocrine disruptor. CBF has high solubility in water (700 mg L⁻¹) and it has high mobility in soils (Lopez-Alvarez et al.,

* Corresponding author.

E-mail address: mathav@iitm.ac.in (M. Kumar).

2011). Several researchers reported the presence of CBF in open and ground water samples far from agricultural fields. Therefore, it is very important to develop a cost-effective treatment technology for the successful removal on CBF and similar other pesticides from water and wastewater. Hydrolysis and microbial degradation of CBF appear to be the important methods of removing pesticides in the environment. However, these processes require long time for CBF degradation in aqueous solutions (Katsumata et al., 2005).

A variety of effective treatment techniques such as Fe (III) aqua complexes as photocatalyst (Katsumata et al., 2005), Ultra sound (Ma et al., 2010), Fenton process (Ma et al., 2009), Photocatalysis by semiconductor oxides (Mahalakshmi et al., 2007) etc. have been proposed for aqueous CBF removal. It has been well recognized that semiconductor mediated photocatalytic oxidation of aqueous phase organic compounds is a successful and convenient alternative to conventional methods. Among the semiconductor materials, TiO_2 has been a promising photocatalyst due to its high photocatalytic activity, resistance to photocorrosion and high biological immunity (Mahalakshmi et al., 2007; Lu et al., 2011). On the other hand, rapid and efficient decomposition of organic pollutants in a photocatalytic process can be increased by loading the photocatalyst on a suitable fine adsorbent. Among the TiO_2 adsorbent complexes, a composite of TiO_2 /Carbon is found suitable (Li et al., 2008; Zhang et al., 2011) due to the presence of extra adsorbent material. The additional surface area from the adsorbent transfers the organic pollutant(s) more efficiently to the TiO_2 surface where it could be rapidly degraded by photo-activated TiO_2 (Li et al., 2006). Although the basic principles of photocatalysis by TiO_2 /Carbon are well established, the effects of several keys parameters such as catalyst dosage, initial concentration of target organic compound, medium pH and the expression of the kinetics of the system are not clearly addressed in the case of CBF removal (Gu et al., 2010; Saïen and Khezriano, 2008). In the past, the first-order/pseudo-first-order reaction kinetics was mainly used for describing the behavior of organic pollutant degradation in aqueous system. The kinetic behavior of the first-order reaction, affected by the initial organic content, could be described by a modified Langmuir-Hinshelwood (L-H model) (Da Silva and Faria, 2003). The apparent rate constants (k_{app}) of the L-H model depend on the initial concentration of the CBF, TiO_2 concentration, pH and other parameters. The variation in the k_{app} also leads to affect the Electrical Energy per Order (E_{EO}) (which is a term used to estimate electrical energy efficiency) of the system. The appropriate Figure-of-merit is the Electrical Energy per Order (E_{EO}) that is defined as the number of kilowatt hours of electrical energy required to reduce the concentration of a pollutant by one order of magnitude (90% in 1 m^3 of initial wastewater). The various factors like efficient quality goals, maintenance, control, flexibility etc., have to be considered in the wastewater treatment technology. Although these factors are important, economics play a predominant role in the overall process.

This work was focused to establish a kinetic model that relates the initial concentration of CBF and its degradation in GAC- TiO_2 photocatalysis system. Moreover, the work has been extended to validate the kinetic model developed, evaluate the figure of merit- E_{EO} with respect to the initial CBF concentration and economic analysis of the GAC- TiO_2 photocatalytic process for CBF removal.

2. Materials and methods

2.1. Chemicals and reagents

CBF used throughout this work (HPLC grade >98% purity) was purchased from Sigma-Aldrich, India. The other chemical reagents used in this study, i.e. titanium tetra isopropoxide (99.9%),

hydrochloric acid (37%), pure absolute ethanol ($\geq 99\%$), were supplied by Chemind Chemicals, India and they were used without further purification. The GAC with particle size fraction between 0.6 mm and 2.38 mm was supplied by Southern Carbon and Chemicals, India.

2.2. GAC- TiO_2 composite preparation

The GAC- TiO_2 photocatalyst was prepared using a wet chemical process. Initially, TiO_2 sol gel solution was prepared using 5 mL of titanium tetra isopropoxide mixed with 50 mL of absolute ethanol and 1 mL of 37% HCl. Subsequently, 250 mL double distilled water was added with desired stoichiometric amount of prewashed GAC. Then the prepared material was homogenized using a magnetic stirrer for 30 min and the homogenized mixture was kept in a water bath at 80°C for 2 h. Later, it was cooled to room temperature and washed with pure water. Finally, the GAC- TiO_2 photocatalyst was dried above 100°C and calcined under nitrogenous atmosphere. The prepared dry catalyst was analyzed using a scanning electron microscopy with electron dispersive spectroscopy (SEM-EDS) to study the extent of TiO_2 coating on the surface of the GAC (Vishnuganth et al., 2015).

2.3. Experimental set-up

Batch-mode photocatalytic degradation experiments were conducted in a custom-made lab-scale double walled cylindrical reactor. The dimensions of the reactor were as follows: 9 cm outer diameter and 34 cm height. The schematic diagram of the batch photocatalytic reactor is shown in Fig. 1. The photocatalytic reactor was incorporated with UV lamps, overhead stirrer and required sample collection ports. The working volume of the system was maintained as 1.9 L. The UV light was provided using 4 low pressure mercury UV lamps (254 nm, Hitech Ultraviolet, Mumbai and circumferentially placed in the reactor) with maximum output of 14 W and an intensity of 40 mW cm^{-2} for each lamp. An electronic overhead stirrer was operated at 200–300 rpm to mix the contents

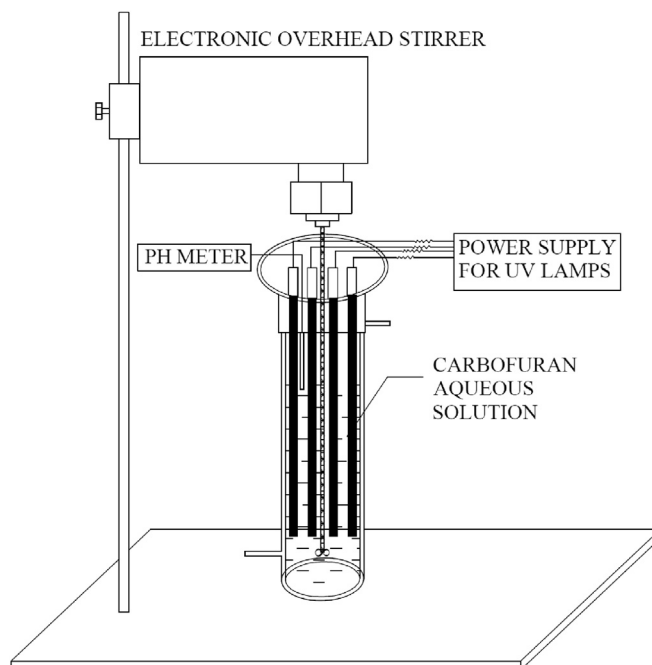


Fig. 1. Schematic diagram of the batch photocatalytic reactor.

Download English Version:

<https://daneshyari.com/en/article/7479511>

Download Persian Version:

<https://daneshyari.com/article/7479511>

[Daneshyari.com](https://daneshyari.com)