Photocatalytic degradation of terbuthylazine: Modelling of a batch recirculating device

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ABSTRACT

A thin layer photocatalyst using chitosan to immobilize TiO$_2$ on a glass fiber woven roving material was successfully used for photocatalytic degradation of terbuthylazine, s model s-triazine herbicide. The reaction was conducted in a photocatalytic recirculating reactor with the photocatalyst inserted as a removable module. The experimental reaction system employed in this study was composed of an annular photoreactor with the immobilized TiO$_2$/chitosan layer and the radiation source and the second part of the reaction system only used for the aeration or the reaction mixture, both operating in unsteady conditions. The kinetic model is based on a simplified consecutive degradation of terbuthylazine to cyanuric acid through intermediate products. The model of the annular reactor is represented by a hyperbolic partial differential equation solved by method of characteristics; the model of the aeration vessel is given by an ordinary differential equation. The proposed model represents a simple way to describe a complex recirculating reactor system operating in unsteady conditions.

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1. Introduction

Persistent organic pollutants (POPs), like pesticides, are not easily degraded by conventional degradation methods, making advanced oxidation processes like photocatalysis increasingly interesting to many researchers [1–6].

Research on photocatalysis is mostly based on TiO$_2$ suspended nanoparticles in fluid phase contaminated with organic pollutants, allowing for the largest surface area and efficient photocatalytic degradation. The lack of the photocatalysts selectivity allows a very wide range of their application [7–12]. Retrieval or separation of suspended photocatalytic nanoparticles from the fluid phase is the major drawback of this process [13–16]. Regeneration is also a challenge in the case of suspended nanoparticles making the photocatalyst poisoning another issue, as well environmental contamination [17–21].

Immobilization of TiO$_2$ is a common way to solve these issues [17,22]. The specific surface of a thin layer is very small compared to the reactor, which can, including the external mass transfer limitations, lead to a 70% reduction in photocatalyst performance compared to the suspension reactors. Immobilized layers offer the possibility of easier photocatalyst modifications, as well as regeneration [17,23–28]. Regardless, for industrial application, the photocatalyst needs to be removable, allow easy maintenance and off site regeneration. It also needs to withstand harsh operating conditions of industrial water and prepared from easily available and cost effective materials, also avoiding the risk of additional pollution. TiO$_2$ and chitosan as the photocatalyst binder are quite common and widely available materials, suited for such applications [29–42].

This study presents the development of a mathematical model of the photocatalytic recirculating reactor with an immobilized photocatalytic layer described in a previous paper [43]. The experimental reaction system comprised two parts. An annular photoreactor, with the immobilized TiO$_2$/chitosan layer and the central radiation source. Since process variables were not only time dependent, but also dependent on the position along the reactor length, the reaction system could not be considered homogenous and solved as a batch reactor as it is usually done [44,45]. The annular part of the reactor system was described using a hyperbolic differential equation. The equation was simplified by variable substitution, expressing both the reactor length and reaction time as the residence time with the Courant number being equal to 1. The second part of the system was used for aeration of

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Nomenclature

Symbols

A_r	Frequency factor, min^{-1}
c_0	Initial concentration of terbuthylazine, $mg\ dm^{-3}$
$c_{(CYA)}$, $c_{(MP)}$, $c_{(TBA)}$	Concentration of the indicated compounds, $mg\ dm^{-3}$
c_i	Concentration of compound i, $mg\ dm^{-3}$
E_a	Activation energy, $kJ\ mol^{-1}$
k_1, k_2	Reaction rate constants (Eq. (1)), min^{-1}
n	Order of the reaction, dimensionless
Q_R	Recirculation flow rate, $dm^3\ min^{-1}$
Q_A	Aeration flow rate, $dm^3\ min^{-1}$
r_{TBA},	Rate of reactant consumption
r_{MP}, r_{CYA}	Rate of the intermediate products or reaction product formation (Eqs. 2–4), $g\ dm^{-3}\ min^{-1}$
RMSD	Root mean square deviation, dimensionless
R^2	Correlation coefficient, dimensionless
t	Irradiation time, min
T	Reaction temperature, $°C$
u	Linear velocity of the solution, $dm\ min^{-1}$
v_0	Volumetric flow, $dm^3\ min^{-1}$
V_m	Volume of the aeration vessel, dm^3
V_r	Total volume of the reactor, dm^3
X_{TBA}	Terbuthylazine conversion, %
$Y_{CYA,\ TBA}$	the reaction yield of cyanuric acid, %
z	Axial position along the length of the reactor, dm

Greek letters

ρ	Volume density of the catalyst, $g_{cat}\ dm^{-3}$
τ	Residence time of the reaction mixture, min
τ_m	Residence time of the reaction mixture in the aeration vessel, min
$\tau_{r,}$	Total residence time of the reaction mixture in the annular reactor, minDAD diode array detector

Abbreviations

CYA	Cyanuric acid
DAD	Diode array detector
DPA	6- deisopropylatrazine (6-chloro-N^2-ethyl-1,3,5-triazine-2,4-diamine according to IUPAC)
DTB	Desethylterbuthylazine (6-chloro-N^2-(tert-butyl)-1,3,5-triazine-2,4-diamine according to IUPAC)
HPLC	High performance liquid chromatography
LC/MS	Liquid chromatography mass spectrometry
MP	Intermediate products
PHCD	Photocatalytic degradation
PHL	Photolytic degradation
TBA	Terbuthylazine
TDA	Acetamideterbuthylazine (N-(4-(tert-butylamino)-6-chloro-1,3,5-triazin-2-yl)acetamide according to IUPAC)
TBH	Hydroxyterbuthylazine (4-tert-butylamino-6-ethylamino-[1,3,5]triazin-2-ol according to IUPAC)

the reaction mixture without any photocatalyst. This part can be approximated as a mixed flow stirred-tank operating in unsteady state. Since process variables were not only time dependent, but

also dependent on the position along the reactor length, the reaction system could not be considered homogenous.

2. Experimental set up

2.1. The batch recirculating photocatalytic device

Photocatalytic degradation experiments were carried out using a custom made batch recirculating photocatalytic device presented in Fig. 1. The outer walls of the reactor, as well as the heat exchanging shell, were made of borosilicate glass tubes (i.d. 6 cm). The inner tube was a removable quartz cuvette (o.d. 2.5 cm, cutoff at 195 nm). An *Osram Puritec germicidal HNS G5* lamp (8W, 254 nm) was axially mounted inside the quartz cuvette and centered along the entire length of the photoreactor. The terminal ends of the bulb were blackened with Teflon tape in order to ensure uniform emission of radiation. The other part of the reactor setup was a vessel used for aeration of the reaction solution using controlled air flow from an air compressor. Recirculation of the reaction solution was driven by a peristaltic pump (*Gilson, Model Miniplus Evolution*) and a thermostatic flow bath (*Julabo, Model ED – Heating Immersion Circulator*) was used to ensure isothermal conditions inside the reactor. The photocatalyst module consisted of a thin TiO₂/chitosan layer deposited on the commercial glass fiber woven roving material (*KELTEKS, RT 360*) and mounted on an inox steel frame. The photocatalytic module was placed closed to the inner side of the outside reactor walls facing inwards. The preparation of the photocatalyst layer was described in our previous paper [43].

The thermostatized reaction mixture was recirculated through the reactor system until adsorption equilibrium of the model component on the photocatalyst. The reactor effluent was analyzed as described elsewhere [43] to determine concentration of terbuthylazine and degradation products. Place and sampling intervals were chosen to ensure adequate data for the mathematical model validation. Experiments were conducted until complete degradation of terbuthylazine was achieved, which took up to 120 min.

2.2. Identification of the reaction intermediates

In order to confirm one of the possible reaction mechanisms of terbuthylazine degradation some products of the photocatalytic degradation were identified using LC/MS on samples normally used to monitor the progress of reaction, which were otherwise analyzed on HPLC [43]. The identification was conducted on an *Agilent 1260 HPLC* system with a DAD detector coupled with an *Agilent 6420 QQQ* mass spectrometer. Representative samples from degradation experiments were used for degradation products identification by measuring the molar mass of compounds compared to already known degradation products. The relative retention times were confirmed on the DAD detector before the MS detector for correlation. The retention time of cyanuric acid was identified using the pure substance.

3. Results and discussion

3.1. Identification the intermediate products formed in the photocatalytic and photolytic degradation of terbuthylazine

Using the LC/MS analysis, the following degradation products were identified and subsequently quantified using HPLC in the experiments (Fig. 2): 6-deisopropylatrazine (DPA), desethylterbuthylazine (DTB), acetamideterbuthylazine (TDA) and hydroxyterbuthylazine (TBH).

Compounds illustrated in Fig. 2a–c (hereafter called DPA, DTB i TDA) are specific for a photocatalytic reaction leading to a