DEGRADATION OF TRICLOSAN FROM AQUEOUS SYSTEMS USING A PHOTOCATALYTIC MEMBRANE REACTOR

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ABSTRACT

Nowadays there is an increased concern regarding the triclosan (TCS) – 5 chloro – 2 – (2,4 – dichlorophenoxy) phenol persistence, toxicity and potential negative impact upon the environment. TCS is used on a large scale for personal care products fabrication and therefore is present within the wastewater treatment plants discharged effluents and sludge. Due to its persistence and toxicity, UV/TiO_2 photocatalysis coupled with membrane processes for catalyst recovery is representing a promising treatment method for aqueous systems with TCS content. The degradation of triclosan using a photocatalytic membrane reactor utilizing photocatalyst in suspension was studied. The proposed treatment sequence consists of two main steps. First one is heterogeneous UV/TiO_2 photocatalysis followed by the second - photocatalyst separation using a polymeric membrane and its reuse within the next treatment cycle together with fresh photocatalyst addition in order to assure optimum photocatalyst dose. UV/TiO_2 photocatalysis was performed in the following working conditions: pH = 6.5, catalyst optimum dose [TiO_2] = 200 mg/L, time t = 90 minutes. Photocatalyst separation was realized using an ultrafiltration polymeric membrane (12% polysulfone) at a working pressure of 2 bars until a concentration ratio of ½ was achieved. The membrane played a double role both in photocatalyst separation and as barrier for remanent pollutant and degradation by-products molecules. It was found that proposed treatment sequence is efficient for five cycles with no need of membrane cleaning / replacement and with TCS degradation efficiencies varying from 99.72% (1^{st} cycle) to 93.52% (5^{th} cycle). The photocatalyst consumption was reduced with 52% in comparison with classic UV/TiO_2 photocatalysis processes.

Keywords: PMR, triclosan, photocatalysis, TiO_2 anatase

INTRODUCTION

Triclosan (TCS) 5 chloro-2-[2,4-dichlorophenoxy] phenol is an antimicrobial agent used on a large scale for the personal care products. The effluents and sludge discharged by wastewater treatment plants are the main sources for TCS presence within the aquatic

environment but TCS removal via conventional wastewater treatment processes presents low efficiencies [1].

In the last period there is an increased concern related to TCS persistence and potential negative impact [2]. TCS can undergo direct photolysis with production of 2,8-dichlorobenzo-p-dioxine, substance known as carcinogenic [3]. Moreover the methyl triclosan formed via biological methylation can be more lipophilic and bio accumulative compared with TCS [4]. The risk assessment showed that TCS presence within surface water can affect aquatic organisms [5].

Due to TCS persistence and toxicity, advanced oxidation processes constitutes an intense studied alternative for TCS degradation. This is sustained also by the fact that wastewater treatment plants are in general not equipped for advanced removal of pharmaceuticals and personal care products compounds being designed mainly for removal of carbon, nitrogen, phosphorus based compounds.

TiO_2 based photocatalytic systems proved to be an adequate technique for degradation of refractory pollutants both due to its high oxidative potential and economic and environmentally friendly characteristics compared to other classic oxidants. Therefore, TiO_2 photocatalysis is considered a promising technology for degradation of organic pollutants from groundwater and industrial wastewater. The advantages of TiO_2 photocatalysis are represented by high reaction rate and good photo - efficiency even at relatively low irradiance. Nevertheless, due to its inactivity in visible spectra, its use is not suitable within large scale processes. Moreover photocatalytic systems using TiO_2 in suspension needs an additional process for catalyst separation / recovery [6].

A promising method for solving the issues related to photocatalyst separation is represented by the use of photocatalytic membrane reactors (PMRs). PMRs are hybrid reactors in which photocatalysis is coupled with a membrane process. The membrane is playing a double role, as barrier, for both photocatalyst and remanent substrate [7]. PMRs can be split in two main categories: PMRs with TiO_2 in suspension and PMRs with TiO_2 fixed on a support.

The main operational parameters that are influencing photocatalytic processes efficiency are: reactor design, radiation wavelength and intensity, photocatalyst dose, pollutant initial concentration, temperature, pH, oxygen content, presence of dissolved salts. The most important advantages of using PMR with TiO_2 in suspension are [8] [9] [10]: easy separation of photocatalyst particles from treated solution and possibility to recover the photocatalyst and reuse it within subsequent treatment cycles.

Taking into account presented advantages it can be concluded that PMRs are representing a promising alternative for treatment of water polluted with organic compounds.

EXPERIMENTAL PART

The used reagents were: TCS (Aldrich), TiO_2 anatase (Merck), NaOH (Merck) and H_2SO_4 (Merck) used for correction of pH, Na_2SO_4 (Chimreactiv) and n-hexane (Fluka) for preparation of samples.

A 12% polysulfone membrane was prepared via phase inversion technique using the following reagents: polysulfone resin (Acros Organics), n-methylpyrrolidone (Merck), polyvinylpyrrolidone (Fluka), polyethyleneglycol (Scharlau).

Experimental installation used was a PMR utilising TiO_2 in suspension with two main components (see figure 1):

1. Heraeus type photo-reactor equipped with:
    a. medium pressure Hg lamp TQ 150 with the photon flow determined by ferrioxalat actinometry of $I_0 = 1.05 \times 10^{-6}$ einstein s^{-1}
    b. cooling jacket made of quartz transparent to UV radiation
    c. reaction vessel, $V_u = 400$ cm^3, with magnetic recirculation pump
2. Koch LabCell CF1 (CrossFlow membrane separation) with the following main operational characteristics:
    a. membrane diameter = 76 mm
    b. maximum working pressure = 35 bar
    c. maximum working temperature = 70 ˚C
    d. made from stainless steel

Figure 1 Experimental PMR installation

Wastewater samples with an initial concentration of $[TCS]_0 = 1.86$ mg/L were first subject to heterogeneous photocatalysis in the following working conditions pH = 6.5, $[TiO_2] = 200$ mg/L, $t_{irr} = 90$ minutes. The resulted effluent was entered into the

membrane module at a working pressure of 2 bars until a concentration ratio of ½ was achieved. Separated photocatalyst was subsequently reused within the following treatment cycle together with some fresh catalyst in order to assure the required TiO_2 initial concentration of 200 mg/L. Gas chromatography coupled with ion trap mass spectrometry (GC-ITMS) was used for TCS analysis.

RESULTS AND DISCUSSIONS

Experimental results on TCS removal are presented in table 1:

Table 1 TCS concentrations vs. treatment cycles

Cycle	[TCS], µg/L		
	Influent	UV Reactor Effluent	Membrane Module Permeate
1	1860	36.5	5.26
2	930	20.5	4.64
3	925	24.1	15.51
4	927	52.1	35.12
5	928	81.4	60.15

The obtained results showed that after 5 cycles TCS degradation efficiencies in the heterogeneous photocatalysis stage are approaching the 90% value, which indicates that there is a need for total replacement of the photocatalyst and repeat of treatment sequence.

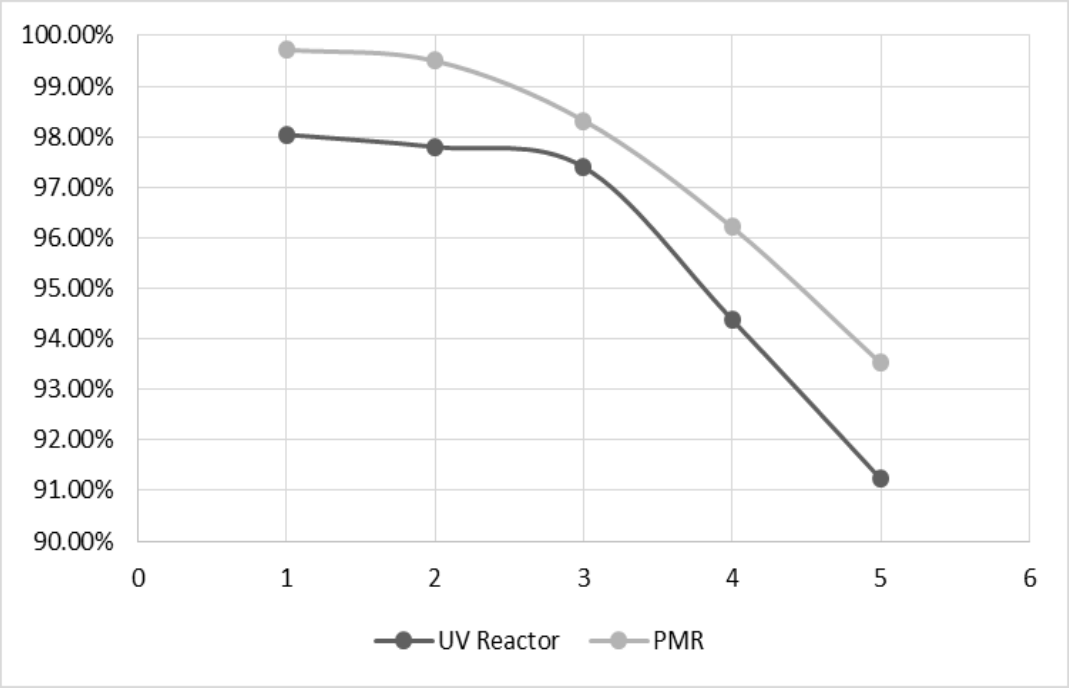

Figure 2 TCS removal efficiencies vs. treatment cycle

The differences between inflow and outflow of membrane module can be explained by TCS adsorption on TiO_2 particles and / or its retaining in the membrane. Analysing the data it can be said that membrane is playing a double role, both in photocatalyst separation / recovery and remanent pollutant removal.

In order to determine the TiO_2 quantity required to be added within 2^{nd} -5^{th} treatment cycles the photocatalyst concentration was determined based on total suspended matters indicator for feeding solution, UV post-treatment effluent and concentrate resulted from membrane module. For 1^{st} treatment cycle 80 mg TiO_2 were used (corresponding to a concentration of 200 mg/L). For each further cycle it was found that a quantity of 32 mg fresh TiO_2 has to be added in order to keep TiO_2 concentration about 200 mg/L.

Photocatalyst separation was performed within the membrane module using a polymeric 12% polysulfone membrane. Working pressure was 2 bars and separation process was conducted until a concentration ratio of ½ (50%) was reached. The average flows through membrane for each of five separation cycles are presented in figure 3.

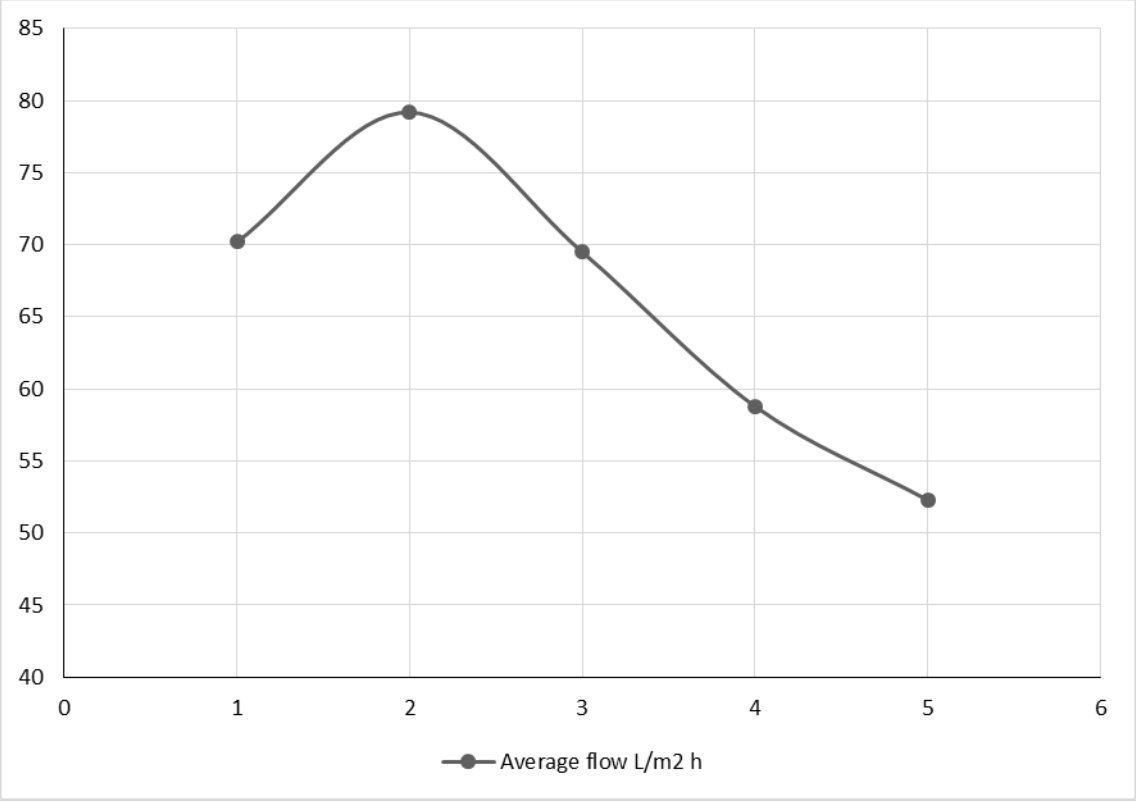

Figure 3 Average flow vs. separation cycle

Maximum flow was registered for the 2^{nd} treatment cycle due to the forming a filtering layer at membrane surface, making the membrane behave similar to a filter press. The flows are then decreasing due to the clogging until a value of 75% of maximum flow. This can lead to the need of membrane replacement if separation time becomes too long. Regarding the membrane clogging it was evaluated based on the following equation:

$$\% \text{ clogging} = (J_{2,i} - J_{2,f})/J_{2,i} \times 100 \quad (1)$$

where:

$J_{2,i}$ – distilled water flow through membrane before TiO_2 suspension passing through membrane at 2 bar pressure

$J_{2,f}$ – distilled water flow through membrane after TiO_2 suspension passing through membrane at 2 bar pressure

Based on the above mentioned equation the clogging percentage was calculated as 16.2%.

Summarising the above mentioned data it can be said that the use of proposed treatment flow resulted in TCS removal (>93%) and reduction of fresh photocatalyst consumption (52%) compared with classic photocatalytic reactors. In the table2 are presented material balance data for one treatment sequence (five cycles) using an experimental laboratory scale PMR installation utilising TiO_2 in suspension.

Table 2 Material balance for one treatment sequence

INPUT		OUTPUT		
Wastewater	1200 mL	Treated water	1095 mL	
TiO_2 1st cycle	80 mg	TiO_2	153.9 mg	
TiO_2 2nd-5th cycles	128 mg			
		LOSSES		
		UV Reactor		
		Treated water	60 mL	5.00 %
		TiO_2	49.3 mg	23.70 %
		Membrane module		
		Treated water	45 mL	3.75 %
		TiO_2	4.8 mg	2.31 %

CONCLUSIONS

The TCS degradation from aqueous systems was studied using a laboratory scale PMR. Chosen configuration was PMR with photocatalyst in suspension that presents the following advantages compared with PMR with photocatalyst immobilised on/in membrane:

- Possibility to reuse the photocatalyst in comparison with classic heterogeneous photocatalytic processes. It was obtained a reduction of photocatalyst consumption of 52%.
- Decrease of treatment cost mainly due to reduction of fresh TiO_2 consumption but also due to decrease of energy consumption - no need for additional classic processes for photocatalyst separation.

Proposed treatment sequence has two main stages. First one is a heterogeneous photocatalysis followed by photocatalyst separation using a polymeric membrane and its reusing in the next treatment cycle together with addition of fresh photocatalyst in order to assure the optimum needed dose.

Performed experiments showed that the treatment cycle can be repeated five times with TCS removal efficiencies above 93%. The removal efficiencies varied from 99.72 % (1^{st} cycle) to 93.52 % (5^{th} cycle) with no request of membrane replacement / cleaning.

Removal efficiencies after passing through membrane module are higher, for each of five cycles, than those after heterogeneous photocatalysis, proving that the membrane is playing a double role both in photocatalyst separation and pollutant removal.

In the photocatalyst separation process, the flows through membrane were specific to ultrafiltration domain. The membrane clogging was calculated based on average distilled water flows before and after photocatalyst suspension passing through membrane, resulting a clogging ratio of 16.2 %.

As a final conclusion it can be said that laboratory scale experiments confirmed the fact that PMRs are representing a promising alternative for treatment of wastewater with organic pollutants content.

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