Photocatalityc degradation of atrazine using TiO_2 encapsulated in alginate microbeads

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Introduction

Atrazine has been one of the most widely used selective triazine herbicide in controlling broadleaf and grassy weeds for many years. It is an endocrine –disrupting chemical with a life time of days to years, depending on the environment in which it is present (D.A. Goolsby, 1997). Although its usage is now being regulated by law in most European countries, and therefore banned in certain way, it can still be found in aquatic ecosystems thanks to its low degradability and persistence (Kruger, 1993; Graymore, 2001). In the past years, there have been used different oxidation processes for treating organically polluted waters. As one of those processes photocatalyc oxidation has shown to be effective in degrading atrazine, which is achieved through dechlorination, dealkylation and deamination (Pelizzetti et al., 1990, 1991, 1992a). Involving photocatalysts is speeding up this degradation process and titanium dioxide is one that is being used most often. There are many studies of using various photocatalysts such as ZnO, Fe_2O_3 (M. Lackhoff, 2002), $Na_4W_{10}O_{32}$ (I. Texier, 1999) and others, but TiO_2 has proven to be the most efficient among these. Titanium dioxide (TiO_2) as a photocatalyst in atrazine degradation process has shown to form 2, 4, 6-trihydroxy-1, 3, 5-triazine (cyanuric acid) rather than proceeding to its complete mineralization (P.L. Yue et al., 1993), during which several intermediates are being formed.

In this study the atrazine degradation was conducted using TiO_2 encapsulated in alginate microbeads and we also studied the effect of different TiO_2 concentrations, different microbeads' size and their quantity in the examined solution, on degradation rate.

Material and methods

Atrazine was obtained from the respective source - Institute for the application of nuclear energy, Belgrade, with 98% purity and was used without any further purification. A stock solution of atrazine was prepared in methanol (Arachem reagensi, Belgrade) and stored in dark prior to its use in the experiments. Photocatalyst, titanium dioxide (TiO_2), was purchased from company Degussa (P25; Aeroxide TiO_2, Germany). The atrazine stock solution was prepared as 10 mg/L and also 1 mg/L in distilled water and also kept in dark. The alginate used for making microbeads was obtained from SIGMA Chemical CO. and is of medium viscosity.

The forming of microbeads was conducted by Nisco Encapsulator (electrostatic droplet generator) and additional pump (Harvard Apparatus Pump 11) to provide the demanded alginate solution flow. In

order to obtain certain microbead size there were used two different needle sizes (0.5 and 0.35mm), the applied potential was 5 kV and alginate solution (1, 1.5 and 2% of alginate) flow rate was 0.250 mL/min. There were used two different distances between needle tip and collecting solution ($CaCl_2$) – 2.5 cm and 1.5 cm. The size of microbeads was determined by light microscope (Leica DMLS with camera DC300 and software EM1000), giving microbeads' size from 100 to 1000µm. The same set up was used for the formation of TiO_2/alginate microbeads (Figure 2).

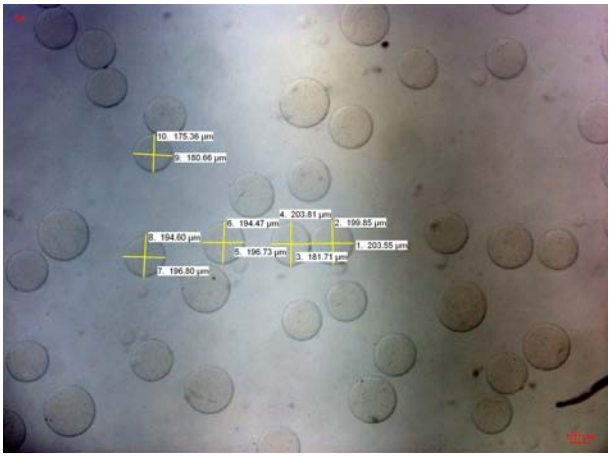

Figure 1. Alginate (1.5%) microbeads of 200µm in diameter

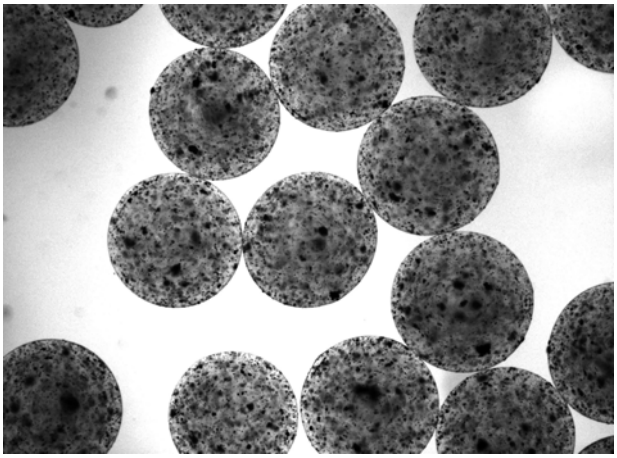

Figure 2. TiO_2(0.05%)/alginate(1.5%) microbeads of 500µm in diameter

The experiments with different concentrations of TiO_2 (0.05%, 0.1%, 0.5%), different quantity of microbeads (5g, 8g and 16g), initial pH 4.5 and constant UV intensity, were performed in 250mL Pyrex glasses, with 100mL of atrazine stock solution, surrounded with two ultraviolet (UV) lamps (Philips), each having 18W. The glasses with reaction mixture were positioned on the magnetic stirrer (tip) with optional stirring adjustment. There was no pH adjusting during the experiments, nor were any other compounds used in order to enhance the degradation efficiency.

The concentration of atrazine was determined using T70 UV/VIS spectrophotometer (PG Instruments Ltd) with setting wavelength spectrum between 190 and 400 nm and following the changes in absorbance values throughout the experiment. Detection of atrazine was conducted at 221nm.

Results and discussion

During 2h irradiation of atrazine solution (1 mg/L) with 5 g TiO_2(0.05%)/alginate(1.5%) microbeads, it was noticeable that atrazine was being degraded 98% at the end of the experiment, and that the highest degradation rate is being reached after 45 minutes (Figure 3). Afterwards the degradation has slowed down and reached its total degradation at the end of the experiment (Tab. 1).

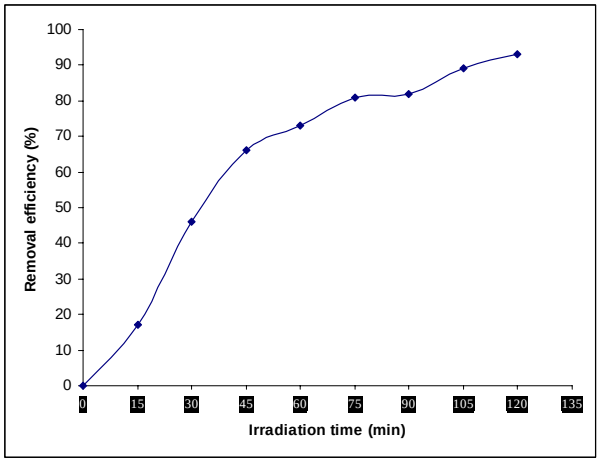

Figure 3. Atrazine (1 mg/L) removal efficiency during irradiation period

Irradiation Time (min)	Absorbance (nm)	Removal Efficiency (%)
0	0.360	0
15	0.299	17
30	0.196	46
45	0.119	66
60	0.095	74
75	0.070	81
90	0.065	82
105	0.041	89
120	0.012	97

Table 1. Atrazine (1 mg/L) removal efficiency during irradiation period

Since the parallel experiments were conducted with and without alginate microbeads in reaction mixture, this has shown that there is slight difference in degrading atrazine during time. While comparing these two, the degradation efficiency was higher in favor of solution with microbeads.

It has also been tested the difference between using the same concentration of TiO_2 (0.5%) in alginate (1.5%) microbeads and different quantity (8 and 16 g) of microbeads in the atrazine solution (10 mg/L). It has been shown that there is a slight difference in atrazine degradation in these two experiments, but not significant (Figure 4).

During the experimental period of three months, while using the same TiO_2/alginate microbeads in replicates throughout the experiments of atrazine degradation, with different TiO_2 loading and storing them properly (in $CaCl_2$ solution and in refrigerator) when they have not been used, non of the TiO_2/alginate microbead undergone any change.

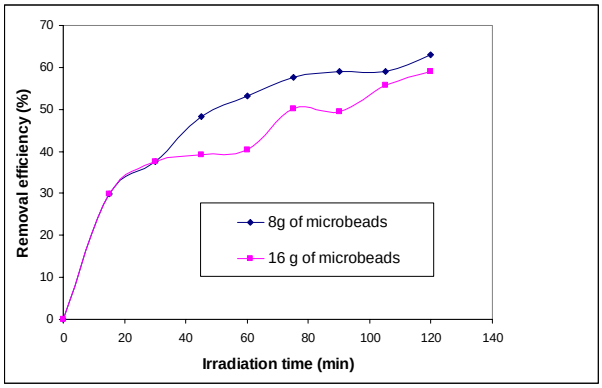

Figure 4. Degradation efficiency with different quantity of microobeads

While doing the spectrophotometric detection of atrazine, some other peaks were perceived, during elapsing of examination period which was likely due to presence of PCO degradation intermediates, i.e. CIAT, CEAT, CAAT, ammeline or any other compound that wasn't identified.

Conclusions

This research denotes that using TiO_2 encapsulated in alginate microbeads is a very feasible way of using this photocatalyst in performing photocatalytic oxidation as a pretreatment in detoxifying and degrading triazine herbicide, atrazine. The degradation is proven to depend on catalyst and initial herbicide concentrations, and quantity of alginate beads in the reaction solution. The most important indication of conducted experiments is that microbeads have shown to have great stability and durability, since there was no loss of any of their features during two months period of their reusage.

Acknowledgment

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