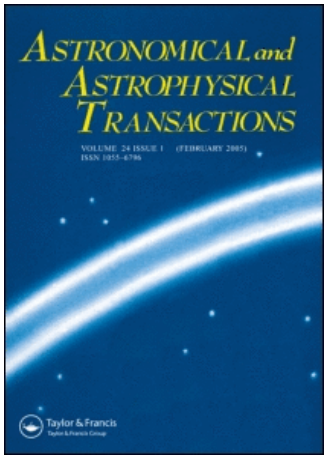

Astronomical & Astrophysical Transactions
The Journal of the Eurasian Astronomical Society
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453505

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Online Publication Date: 01 December 2003
To cite this Article: Kuburovic, Natasha D., Valent, Vladimir J. and Todorovic, Marija S. (2003) 'The use of the solar energy in photochemical and photocatalytic processes', Astronomical & Astrophysical Transactions, 22:6, 887 - 890
To link to this article: DOI: 10.1080/10556790310001612490
URL: http://dx.doi.org/10.1080/10556790310001612490

Astronomical and Astrophysical Transactions
Vol. 22, No. 6, December 2003, pp. 887–890

THE USE OF THE SOLAR ENERGY IN PHOTOCHEMICAL AND PHOTOCATALYTIC PROCESSES

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(Received 25 November 2002)

The increasing use of the Earth's natural resources has generated increasing disposal of waste products and contamination of the environment. Many of these products are organic chemicals. Characteristic examples of waste products in the atmosphere, hydrosphere and soil are insecticides, herbicides and pesticides used to protect crops, accidental leakages and spills, and the continual discharge of waste by products in effluent streams from petrochemical and essential industries. To purify these contaminated atmospheres, hydrosphere and soil a procedure and process has been developing with minimal specific consumption energy from a renewable energy source. This paper will provide a survey and analysis of the parameters, thermal efficiency and conversion energy in the use of solar energy in the photochemical and photocatalytic degradation processes of organic effluents. As a consequence of the use of solar energy in the degradation of these effluents, a conceptual solution of a technical–technological and photocatalytic process is given for effluents which are located in watercourses and soil in Yugoslavia.

Keywords: Solar energy; Photochemical processes; Photocatalytic processes

1 INTRODUCTION

A long time ago, natural resources were considered as God's gift with little awareness or need to protect them. Now it is necessary to develop procedures and processes for purification of contaminated atmospheres, hydrosphere and soil, using as little energy as possible from renewable energy sources.

The topic of this paper describes one of these methods. We consider the degradation of organic pollutants in aqueous environments as a result of sunlight, which is the radiation source, and titanium dioxide, which is the catalyst. The compounds which occur in the environment (alcohols, ketones, phenols, amines, polychlorinated biphenyls (PCBs), pesticides, etc.) degrade and we obtain non-toxic compounds: waters carbon dioxide and simple mineral acids (Crittenden *et al*., 1995). A reactor model using Langmuir–Hinshelwood type of kinetics (Crittenden *et al*., 1995) was employed to assess the reactions in the destruction of organic compounds. The best results were achieved when the destruction was performed with

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ISSN 1055-6796 print; ISSN 1476-3540 online
DOI: 10.1080/1055679031000161249O

hydrogen peroxide (H_2O_2) as it accepts electrons more easily than molecules of oxygen (Blake *et al.*, 1991; Ollis *et al.*, 1991; Peterson *et al.*, 1991). Adding H_2O_2 in a high concentration reduces the rate of chemical reaction, because photolytic destruction of H_2O_2 takes place (Blake *et al.*, 1991; Peterson *et al.*, 1991). As a catalyst we used the novel anatase titanium dioxide (TiO_2) powder called Hombikat UV100. The maximum photonic efficiency that could be attained with Hombikat UV100 is about four times that of the usual TiO_2 powder owing to the large surface area of the agglomerate (250 $m^2\ g^{-1}$) (Gerisher, 1979; Kormann *et al.*, 1988; Hilgendorff and Bahnemann, 1995; Lindner *et al.*, 1995). The superior results obtained with Hombikat UV100 are found only for sunlight of wavelengths length below 400 nm. This wavelength is a prerequisite for the process (Lindner *et al.*, 1995).

2 PILOT PLANT AND DISCUSSION

Solar radiation that reaches the Earth's surface is more than sufficient to meet our needs for energy. Degradation of organic pollutants of the water is one way of using concentrated solar radiation (Elbella *et al.*, 1992; Todorovic and Kosi, 1996; Todorovic *et al.*, 1997; 1999). The concept of a technical–technological facility for degradation of organic pollutants is given in Figure 1.

Based on this concept, parameters such as the temperature, the rate of inflow, the flow, the thermal efficiency of receiver and the active power of receiver can be determined from mass and energy balances (Ecim and Todorovic, 1999) and so can the parameters that are involved

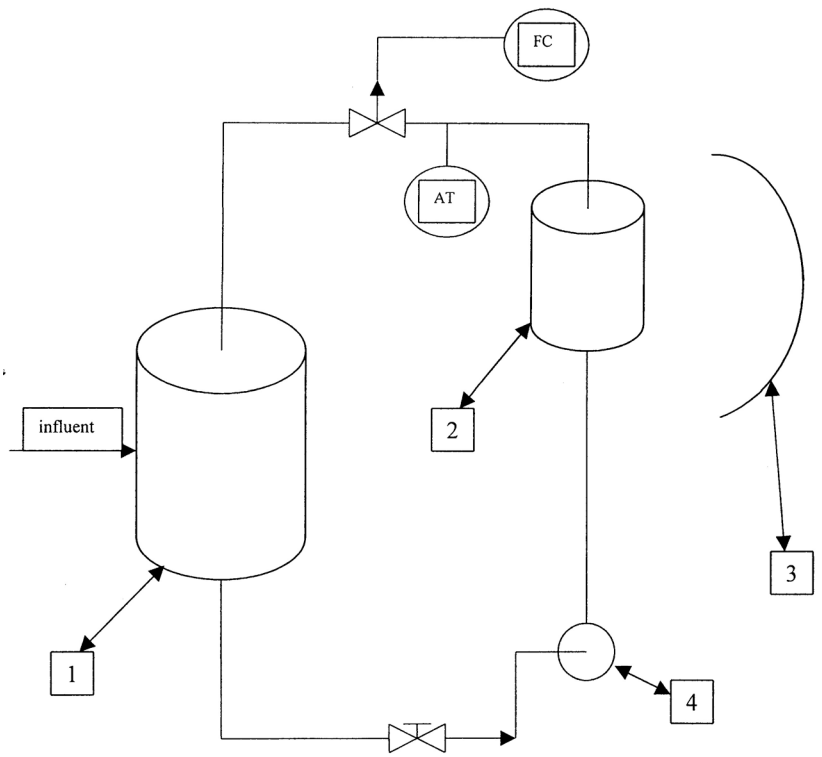

FIGURE 1 Diagram of the technical–technological facility for degradation of organic pollutants: 1, storehouse; 2, receiver (photochemical reactor); 3, concentrator; 4, pump; FC, fluid flowmeter; AT, site of collecting the specimen.

with chemical transformation in the receiver (Crittenden *et al*., 1995) such as the empty-bed contact time (EBCT), the rate of destruction, the adsorption constant and the Langmuir rate constant.

3 CHEMICAL TRANSFORMATION IN THE REACTOR

A rapid photocatalytic reaction occurs when the reactor (Ollis, 1991) is illuminated with ultraviolet radiation. The kinetics of photocatalysis is given by the Langmuir–Hinshelwood form rate expression (Crittenden *et al*., 1995).

$$r = -\frac{Kk[C]}{1 + k[C]}, \tag{1}$$

where $[C]$ is the influent organic concentration, K is the Langmuir rate constant and k is the apparent adsorption constant.

The adsorption constant can be estimated using the equation

$$k = \frac{([C]_s[C])^{-\beta RT/V_m}}{[C](1 - [C]_s/[C]^{-\beta RT/V_m})}, \tag{2}$$

where $[C]_s$ is the aqueous solubility of a compound, R is the gas constant, T is the absolute temperature, V_m is the liquid molar density of the organic compound at the normal boiling point and β is a fitting constant.

The value of β is determined using experimental data of a reference compound by linear regression on the following equation:

$$-\beta \frac{RT}{V_m} \ln\left(\frac{[C]_s}{[C^0]}\right) = \ln\left(\frac{k_{ref}[C^0]}{1 + k_{ref}[C^0]}\right), \tag{3}$$

where the adsorption constant, k_{ref}, of the reference compound can be obtained by fitting the destruction data of the reference compound to the equation

$$\frac{\text{EBCT}}{\ln([C^0]/[C])} = \frac{1}{Kk} + \frac{1}{K}\frac{[C^0] - [C]}{\ln([C^0]/[C])}. \tag{4}$$

In Eq. (4), $[C^0]$ is the influent organic concentration. The apparent adsorption constant evaluated from Eq. (2) can then be used in Eq. (4) to predict the EBCT required for a certain level of organic destruction.

A linear form of the expression for the Langmuir rate constant given by

$$K = \frac{I}{A + I}(1 + B[C^0])K^0, \tag{5}$$

where I is the intensity of ultraviolet radiation, A is a half-saturation constant (when $I = A$, then $K = \frac{1}{2}K_{max}$), B is a fitting constant, $[C^0]$ is the influent organic concentration and K^0 is a constant which accounts for the effects of the type of organic compound, catalyst (semiconductor, photocatalyst and support), catalyst dosage, reactor configuration, etc.

Equation (5) is used to determine the constants A, B and K^0 which we used to calculate K_{ref} by regression:

$$\frac{I}{K_{\text{ref}}} = \frac{1}{K^0_{\text{ref}}} I - B \frac{I[C^0]}{K_{\text{ref}}} + \frac{A}{K^0_{\text{ref}}}. \tag{6}$$

The Langmuir rate constant K_{ref} of the reference compound, can be obtained by fitting the destruction data of the reference compound to Eq. (4).

4 CONCLUSION

This pilot plant can be used for degradation of organic contaminants in water under ambient conditions. These contaminants include alcohols, aldehydes, carboxylic acids, ketones, amines, phenols, thioethers, surfactants, mercaptans, PCBs, herbicides, pesticides (dichlorodiphenyltrichloroethane, Lindane, etc.), dioxins, solvent compounds (trichloroethylene, PCE, etc.) and fuel constituents (benzene, toluene, ethylbenzene, etc.). Degradation is in most cases complete (99.999%) (Crittenden *et al*., 1995). Photocatalysis mineralizes organic compounds into non-toxic forms: simple mineral acids, carbon dioxide and water. It is expected that this experimental process could be applied in the degradation of organic effluent which can be located in watercourses and soil in Yugoslavia.

We have been employing technology which uses concentrated solar radiation combined with less expensive optical components of small area, high efficiency and considerably more expensive energy converters (Elbella *et al*., 1992; Todorovic and Kosi, 1996; Todorovic *et al*., 1997; 1999). Because of this we managed to reduce the cost of this process compared with technologies that use non-focused solar radiation.

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