

Research Article

Treatment of Pesticides in Wastewater by Heterogeneous and Homogeneous Photocatalysis

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The effect of different heterogeneous and homogeneous photocatalytic systems on the oxidative degradation of mepiquat chloride in aqueous solutions was investigated. In the case of heterogeneous reactions, the influence of five factors was studied: the type of catalyst, photocatalyst concentration, pH, pesticide concentration, and the presence of H₂O₂ and/or Fe³⁺. For homogeneous catalysis, other factors were studied: the oxidising agent and the light source. Nearly complete degradation of mepiquat chloride was obtained after about 180 minutes in the presence of an acid medium (pH3) using a UV-A lamp and TiO₂P-25 catalyst (0.5 g/L), for an initial pesticide concentration of 10 ppm. Degradation rates corresponding to homogeneous photocatalysis were lower compared to those corresponding to the use of TiO₂ as the photocatalyst.

1. Introduction

Removing refractory organic pollutants from wastewaters is an important issue given the fact that most of them are toxic, mutagenic, and/or carcinogenic, even in low concentrations, and are a real health threat to humans, animals, as well as to the environment [1]. Heterogeneous and homogeneous solar photocatalytic detoxification methods (TiO₂/H₂O₂, Fe³⁺/H₂O₂) have recently shown great promise for the treatment of industrial wastewater, groundwater, and contaminated air [2].

Mepiquat chloride or 1,1-dimethylpiperidine chloride, also known as DPC, is a new plant growth regulator that can be used on a variety of crops and exerts a variety of effects. It works by inhibiting gibberellic acid synthesis, reduces internode length, hastens maturity, and retards abscission [3]. In addition, DPC is used to prevent the lodging of winter

wheat; for apples, it can increase calcium absorption, reduced by depression disease; for citrus, it can increase the sugar content. In agrochemical products, it is formulated as an emulsifiable concentrate, a water dispersible granulate and as a technical product. This pesticide was first registered in the USA in 1980 to be used as a growth regulator of cotton, and in 1997 it was reregistered by the Environmental Protection Agency (EPA) for its use in the USA [4]. Currently, it is formulated as an emulsifiable concentrate at concentrations lower than 5% (w/v) [5].

Mepiquat chloride has the molecular formula C₇H₁₆ClN and a molecular weight of 149.66 g/mol. Figure 1 presents the structural formula of 1,1-dimethylpiperidine chloride.

Mepiquat chloride is labelled as a potential groundwater contaminant by the DPR (Department of Pesticide Regulation), because it has the potential to move into groundwater based on its water solubility, ability to bind to soils (K_{oc}),

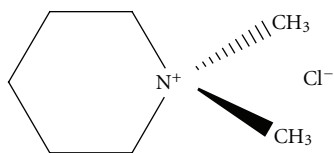


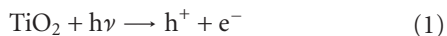
FIGURE 1: Structural formula of 1,1-dimethylpiperidine chloride.

and half-life. Its acute toxicity is classified as moderate by the IRIS (Integrated Risk Information System) of the US Environmental Protection Agency.

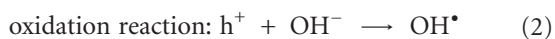
In recent years, new and more severe regulations coupled with enforcement against wastewater discharges have been established in most industrially developed countries [6]. This is why various technologies have been developed for the advanced treatment of wastewater containing pollutants that cannot be removed by conventional treatment processes. Destructive oxidation methods such as heterogeneous photocatalysis ($\text{TiO}_2/\text{UV-A}$), ozonation, $\text{H}_2\text{O}_2/\text{UVB}$, photo-Fenton, and sonolysis are considered very attractive since they transform hazardous pollutants into compounds with a reduced impact on the environment [7]. Also, among advanced oxidation processes, homogeneous and heterogeneous photochemical oxidation processes have proven their efficiency in the degradation of refractory organic pollutants [8].

Photocatalysis implies the acceleration of a photoinduced reaction by the presence of a catalyst [9]. Photoinduced reactions are activated by the absorption of a photon with sufficient energy, that is, equal to or higher than the band-gap energy (E_{bg}) of the catalyst [10]. The absorption leads to a charge separation due to the promotion of an electron (e^-) from the valence band of the semiconductor catalyst to the conduction band, thus generating a hole (h^+) in the valence band.

The activation equation can be written as:



In this reaction, h^+ and e^- are powerful oxidising and reducing agents, respectively. The oxidation and reduction reactions can be expressed as:



In order to sustain a photocatalysed reaction, e^- - h^+ recombination subsequent to the initial charge separation must be prevented as much as possible [11].

Heterogeneous photocatalysis may be considered a viable alternative for the removal of refractory organics due to several important advantages such as: complete mineralization or formation of more readily biodegradable intermediates when complex organic compounds are treated, no need of auxiliary chemicals, no residual formation, easily operation and maintenance of the equipment [12].

Heterogeneous photocatalysis leads to the mineralisation of organic carbon using a semiconductor catalyst in suspension or as a thin film. One advantage of the photocatalytic

process is its mild operating conditions and the fact that it can be powered by sunlight, thus significantly reducing the amount of electric power required and therefore the operating costs [13]. Heterogeneous photocatalysis is influenced by catalyst loading, initial pollutant concentration, pH, radiant flux, aeration, the presence of other substances or impurities, and photoreactor geometry [14].

The most widely used semiconductor catalyst in photoinduced processes is titanium dioxide (TiO_2), because it is chemically and biologically inert, photocatalytically stable, relatively easy to produce and to use, able to efficiently catalyze reactions, cheap, and without risks to the environment or humans [15].

Homogeneous photocatalysis uses UV radiation in combination with chemical oxidising agents such as hydrogen peroxide or ozone.

2. Experimental

2.1. Light Sources. For the photocatalytic degradation of mepiquat chloride, a G23 Radium Ralutec UVA lamp (9W/78, 350–400 nm, $I = 1.3517$ ein/min) and a Radium Ralutec VIS lamp (9W/71, $I = 0.5898$ ein/min) were used.

Actinometry was used to determine the exact radiation intensity of both lamps within the vessels. The radiation intensities obtained for the UVA and the VIS lamp were 1.3517 ein/min and 0.3517 ein/min, respectively. After 10–15 uses of the lamps, it was necessary to repeat the actinometric determinations to check that the lamp intensity remained constant.

2.2. Vessels and Reagents. For the photocatalytic experiments, a solution of mepiquat chloride pesticide was used. As catalysts, $\text{TiO}_2\text{P-25}$, $\text{TiO}_2\text{UV-100}$, $\text{TiO}_2\text{-A}$, TiONa , and ZnO were studied.

A photochemical reactor (Figure 2) with volume of 500 mL was used to carry out the experimental tests. The reactor was covered with a black cloth to avoid interactions with ambient light.

2.3. Procedures and Analyses. In the initial 300 mL aqueous solution of the pesticide ($C = 10$ mg/L), different quantities of catalysts were added. The reaction solutions were magnetically stirred in the dark for 30 min until adsorption/desorption equilibrium was reached. The solutions were then irradiated under UV light with continuous magnetic stirring. A fixed quantity of each mepiquat chloride solution was taken at regular time intervals during the illumination period and filtered through a syringe filter to analyse the amount of pesticide remaining in the solution. DPC concentrations during the experiments were monitored by a Total Organic Carbon Analyzer (Shimadzu), in order to measure the mineralisation of the pesticide.

3. Results and Discussion

3.1. Mepiquat Chloride Degradation by Heterogeneous Photocatalysis. The influence of five experimental factors was

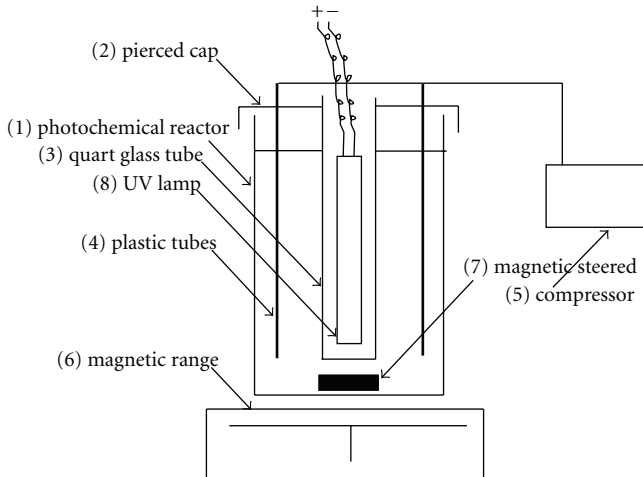


FIGURE 2: Photocatalysis experimental setup ((1) photochemical reactor, (2) pierced cap, (3) quart glass tube, (4) plastic tubes, (5) compressor, (6) magnetic range, (7) magnetic steered, (8) UV lamp).

studied: the type of catalyst, photocatalyst concentration, pH, pesticide concentration, and the presence of H_2O_2 and/or Fe^{3+} . The experiments were conducted by varying one factor and keeping the others constant.

3.1.1. *Influence of the Type of Catalyst.* Five types of catalysts were investigated in this study: TiO_2P-25 , TiO_2 UV-100, TiO_2-A , $TiONa$, and ZnO ; the results are plotted in Figure 3.

The corresponding amounts of catalyst were added to 10 ppm solutions of mepiquat chloride in order to obtain a dose of 0.5 g catalyst/L and then irradiated with UV-A light. From Figure 3, it can be seen that the TiO_2P-25 catalyst exhibited the best behaviour in the degradation of mepiquat chloride and was thus considered the reference catalyst. The increase of the TOC values in the case of the ZnO catalyst might be assigned to the desorption of the pesticide from the ZnO surface, taking into consideration that the adsorption of mepiquat chloride on this material is less intense in comparison with the other photocatalysts.

3.1.2. *Influence of Catalyst Concentration.* The influence of catalyst concentration was studied for the TiO_2P-25 catalyst, which was chosen as the reference.

The degradation experiments were conducted using the same pesticide concentration (10 ppm), the same UV-A lamp, and different concentrations of the same photocatalyst. The results are depicted in Figure 4.

As expected, Figure 4 shows that the most advanced pesticide degradation occurred when heterogeneous photocatalysis was conducted with a higher dose of the catalyst (TiO_2P-25).

3.1.3. *Influence of pH.* The influence of the pH of the solution was studied by conducting the photocatalyst experiments with 0.5 g/L TiO_2P-25 catalyst in 10 ppm mepiquat chloride solution, using the UV-A lamp but adjusting the solution pH

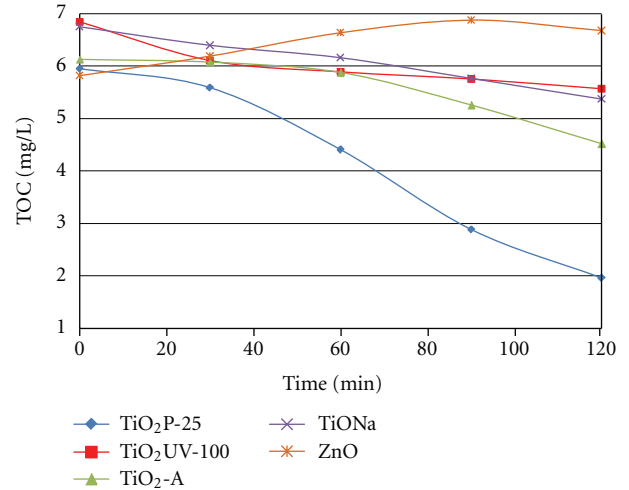


FIGURE 3: Pesticide degradation by heterogeneous photocatalysis using different catalysts (initial conditions: 10 ppm mepiquat chloride, 0.5 g/L catalyst, UV-A lamp).

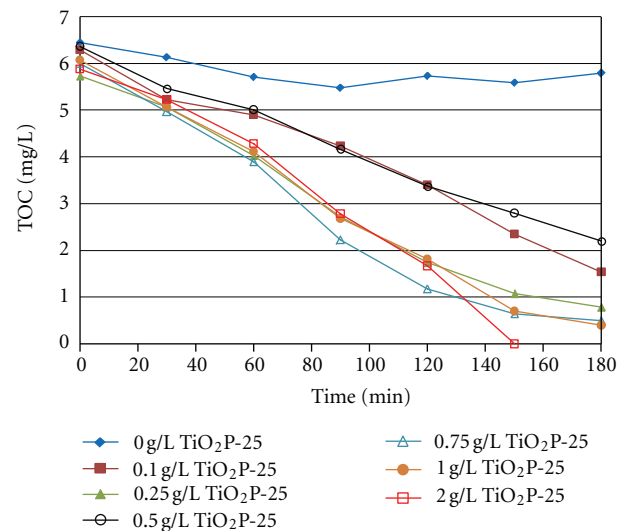


FIGURE 4: The TiO_2P-25 dose influence on the degradation of mepiquat chloride (initial conditions: 10 ppm mepiquat chloride, 0.5 g/L TiO_2P-25 , UV-A lamp).

from acidic values (pH3, 4, and 5) to basic values (pH8, 9, and 11)

Figure 5 illustrates the variation in TOC/TOC(0) values over time at different pH values. The positive effect of acidic pH on pesticide degradation noted in the figure can be assigned to the fact that the TiO_2 surface is positively charged when the solution pH is lower than 6.8, thus facilitating the photocatalytic process [9].

3.1.4. *Influence of the Mepiquat Chloride Concentration.* The influence of the mepiquat chloride concentration on the photocatalytic process was studied using the TiO_2P-25 catalyst. The degradation experiments were conducted using pesticide solutions of various initial concentrations, the same

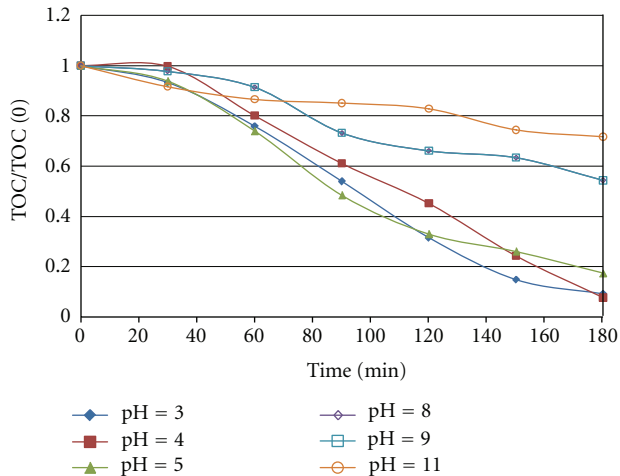


FIGURE 5: Pesticide degradation over time at different pH values of the initial solution (initial conditions: 10 ppm mepiquat chloride, 0.5 g/L $\text{TiO}_2\text{P-25}$, UV-A lamp).

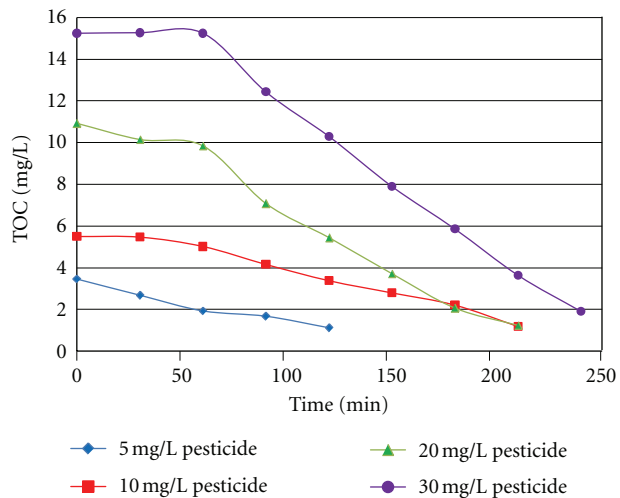


FIGURE 6: Behaviour of different concentrations pesticide solutions during heterogeneous photocatalysis using UV-A light and 0.5 g/L $\text{TiO}_2\text{P-25}$ as the catalyst.

UV-A lamp, and the same photocatalyst concentration (0.5 g/L). The results are shown in Figure 6.

3.1.5. The Influence of H_2O_2 or Fe^{+3} . The next step of this study focused on enhancing the photocatalysis reaction by adding H_2O_2 or Fe^{+3} in different concentrations to the initial solution.

Figures 7 and 8 show pesticide degradation during photocatalysis with $\text{TiO}_2\text{P-25}$, facilitated by H_2O_2 and Fe^{+3} , respectively. The best degradation rate was obtained when the $\text{TiO}_2\text{P-25}$ photocatalysis was used alone. It was noted that no enhancement was obtained by adding H_2O_2 or Fe^{+3} at any dose.

3.2. Mepiquat Chloride Degradation by Homogeneous Photocatalysis. Homogeneous photocatalytic oxidation of the

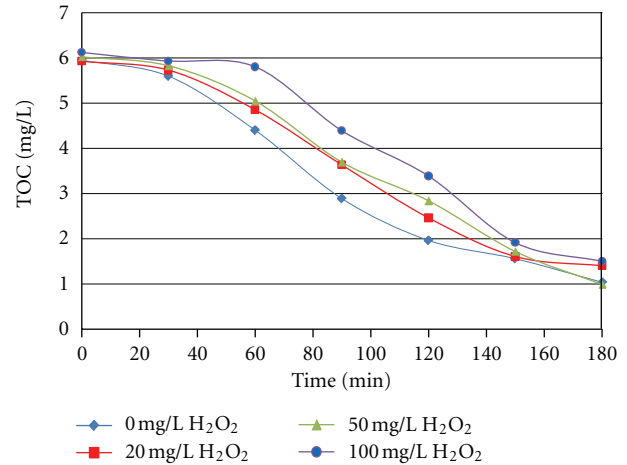


FIGURE 7: Heterogeneous photocatalysis of mepiquat chloride in the presence of $\text{TiO}_2\text{P-25}$ and H_2O_2 (initial conditions: 10 ppm mepiquat chloride, 0.5 g/L $\text{TiO}_2\text{P-25}$, UV-A lamp).

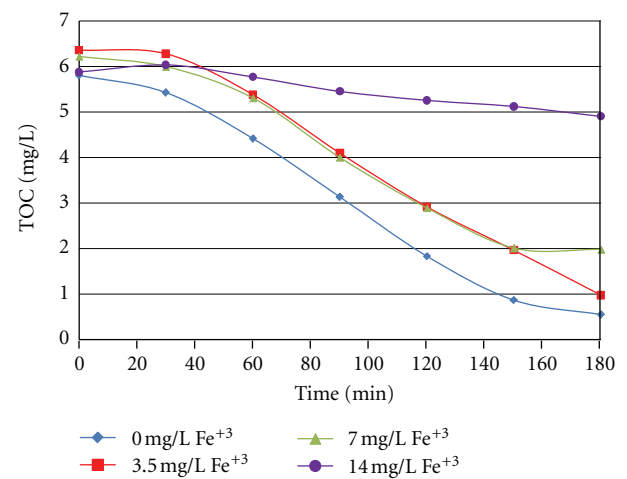


FIGURE 8: Heterogeneous photocatalysis of mepiquat chloride in the presence of $\text{TiO}_2\text{P-25}$ and Fe^{+3} (initial conditions: 10 ppm mepiquat chloride, 0.5 g/L $\text{TiO}_2\text{P-25}$, UV-A lamp).

pesticide was also tested using two oxidising agents: a photo-Fenton agent ($\text{H}_2\text{O}_2 + \text{Fe}^{+3}$) and a ferrioxalate agent (potassium oxalate + $\text{H}_2\text{O}_2 + \text{Fe}^{+3}$) in various concentrations. The influence of light was also studied using UV-A and VIS lamps, respectively. The results are depicted in Figures 9 and 10, respectively.

In the case of the photo-Fenton reagent, the best results were obtained when less oxidant was used: 50 ppm H_2O_2 and 3.5 ppm Fe^{+3} . When more photo-Fenton agent was used, lower values for pesticide decontamination were obtained.

With the ferrioxalate reagent, an excellent degradation rate was obtained when visible light was used, as can be seen in Figure 11, this being economically reliable. When using the UV-A lamp, photodegradation results were comparable with those achieved for photo-Fenton homogeneous catalysis.

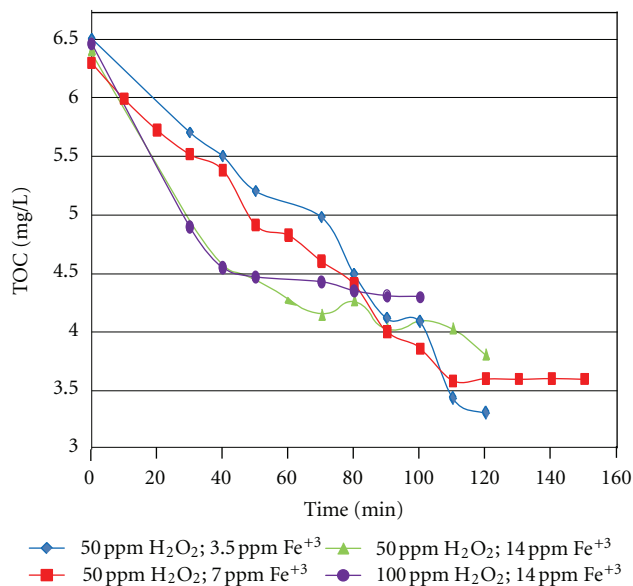


FIGURE 9: Homogeneous photocatalysis of mepiquat chloride using the photo-Fenton agent (initial conditions: 10 ppm mepiquat chloride, UV-A lamp).

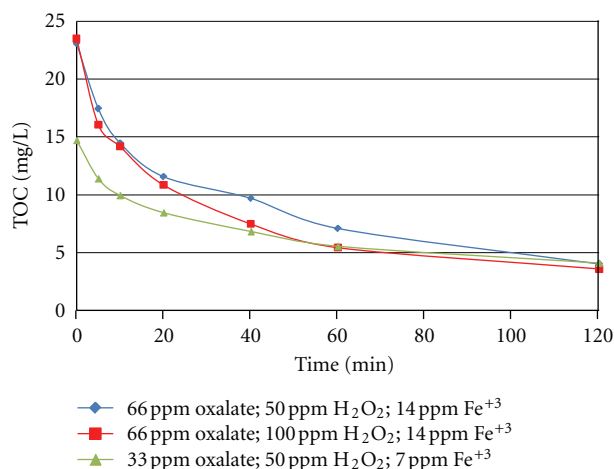


FIGURE 10: Homogeneous photocatalysis of mepiquat chloride using the ferrioxalate agent (initial conditions: 10 ppm mepiquat chloride, 0.5 g/L $\text{TiO}_2\text{P-25}$, UV-A lamp).

4. Conclusions

- (i) The present study demonstrated the possibility of oxidative degradation of persistent organic pesticides by heterogeneous photocatalysis.
- (ii) Nearly complete degradation of mepiquat chloride was obtained after about 180 minutes in the presence of an acid medium (pH3) using a UV-A lamp and the $\text{TiO}_2\text{P-25}$ catalyst (0.5 g/L), for an initial pesticide concentration of 10 ppm.
- (iii) The remnant pesticide concentrations were higher when homogeneous photocatalytic oxidation was involved, in comparison with levels obtained in a

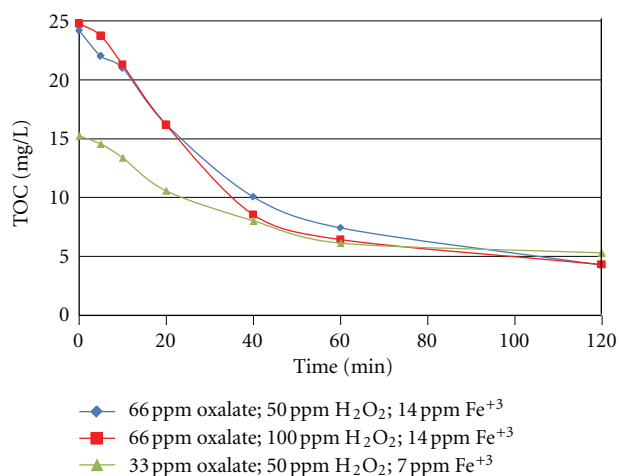


FIGURE 11: Homogeneous photocatalysis of mepiquat chloride using the ferrioxalate agent (initial conditions: 10 ppm mepiquat chloride, VIS lamp).

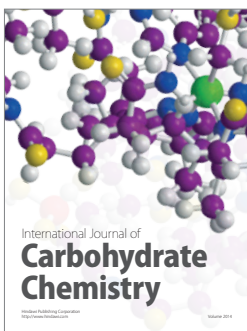
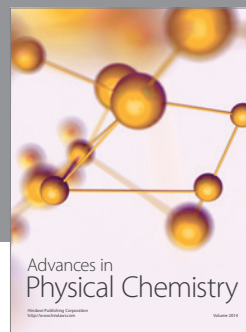
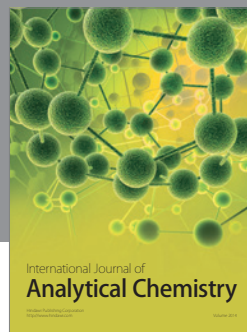
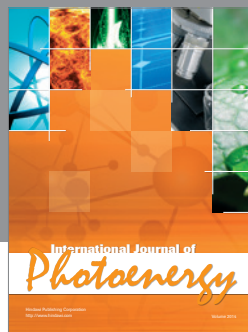
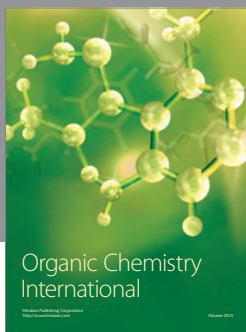
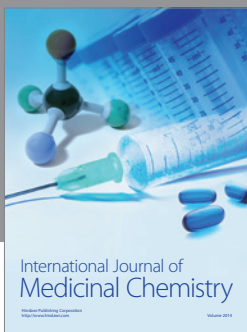
heterogeneous photocatalytic degradation process based on TiO_2 .

- (iv) Degradation rates corresponding to homogeneous photocatalysis were lower compared to those corresponding to the use of TiO_2 as the photocatalyst. In this way, the remnant concentrations of mepiquat chloride were below the drinking water level of comparison for acute and chronic risk range for infants and children (6 ppm), but as a consequence of the heterogeneous photocatalysis degradation process, this remnant concentration was about 10 times lower than the abovementioned level (0.54 ppm for 0.5 g/L $\text{TiO}_2\text{P-25}$, $C_i = 10$ ppm pesticide).
- (v) Moreover, we tested the possibility of reusing $\text{TiO}_2\text{P-25}$ three times and found comparable photocatalytic activity for the solids with each use. The TiO_2 Degussa was recovered by simple washing, providing an economic advantage to this process.
- (vi) Our study succeeded in achieving the task of finding a suitable photocatalytic system to provide a mepiquat chloride remnant concentration in accordance with EPA standards.

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