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Methomyl degradation in aqueous solutions by Fenton's reagent and the photo-Fenton system

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Abstract

The chemical degradation of pesticide methomyl in water by Fenton (H_2O_2/Fe^{2+}) and photo-Fenton (H_2O_2/Fe^{2+}/UV) processes was investigated. A laboratory set-up was designed to evaluate and select the optimal oxidation process. The degradation rate is strongly dependent on the pH, initial concentrations of the pesticide, H_2O_2, Fe^{2+}, and $[H_2O_2]_0/[Fe^{2+}]_0$ ratio. The effect of these parameters has been studied and the optimum operational conditions of these two processes were found. The optimum conditions were obtained at pH 3 for the H_2O_2/Fe^{2+} and H_2O_2/Fe^{2+}/UV. The kinetics of degradation was found to follow first-order reaction rules. The photo-Fenton system proved to be the most efficient and occurs at a much higher oxidation rate than Fenton system and allows achieving 100% degradation of methomyl in 30 min of reaction time. The results of the study showed that photo-Fenton process was an effective and economic treatment process for methomyl under acidic conditions by producing higher mineralisation efficiency in a relatively short radiation time compared to Fenton process.

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1. Introduction

The pesticide and chemical industries are considered to generate wastewaters containing toxic and sometimes non-biodegradable compounds that remain in the environment even after their wastewaters have been subjected to conventional processing [1].

Methomyl, which has been classified by the WHO (World Health Organization), EPA (Environmental Protection Agency, USA), and EC (European Commission) as a very toxic and hazardous pesticide [2], is highly soluble in water (57.9 g/l, 20 °C). It also has a low-sorption affinity to soils and can therefore easily cause groundwater contamination in agricultural areas [3]. Methomyl is widely used all over the world because of its powerful control of many different pests [4]. It is a commonly used insecticide in Morocco on a wide range of tomato crops. Methomyl, *S*-methyl *N*-(methylcarbamoyloxy) thioacetamidate, belongs to the carbamate family of pesticides, for some of which photocatalysis by TiO_2 and photo-Fenton has already been described [5].

In recent years, advanced oxidation processes (AOPs) have been intensively investigated for the treatment of waters and wastewaters. AOPs, defined as processes generating hydroxyl radicals ($OH^\bullet$), are considered to be promising alternatives to conventional processes due to their efficiency in oxidizing a great variety of organic contaminants [6]. The Fenton and photo-Fenton systems have been widely applied in the treatment of non-biodegradable wastewater in the filed of AOPs [7,8].

Oxidation with Fenton's reagent is based on ferrous ion and hydrogen peroxide, and exploits the reactivity of the hydroxyl radicals produced in acidic solution by the catalytic decomposition of H_2O_2 [9]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \qquad (1)$$

Hydroxyl radicals may be scavenged by reaction with another Fe^{2+}:

$$OH^\bullet + Fe^{2+} \rightarrow OH^- + Fe^{3+} \qquad (2)$$

Fenton reagent appears to be a very powerful oxidizing agent. Besides, the process is simple and non-expensive, taking place at low temperatures and at atmospheric pressure [10]. The chemicals are readily available at moderate cost and there is no need for special equipment.

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In photo-Fenton process in addition to the above reactions the formation of hydroxyl radical also occurs by the following reactions (Eq. (3)) [11]:

$$Fe^{3+} + H_2O + h\nu \rightarrow OH^{\bullet} + Fe^{2+} + H^{+} \quad (3)$$

The rate of organic pollutant degradation could be increased by irradiation of Fenton with UV or visible light (photo-Fenton process). The illumination leads not only to the formation of additional hydroxyl radicals but also to recycling of ferrous catalyst by reduction of Fe^{3+}. In this way, the concentration of Fe^{2+} is increased and the overall reaction is accelerated. Among the AOPs, the oxidation using Fenton's reagent and photo-Fenton's reagent has been found to be a promising and attractive treatment method for the effective degradation of pesticides.

The main objective of this study is to analyse the feasibility of degradation of methomyl by Fenton and photo-Fenton processes. The influence of different operational parameters (pH, H_2O_2, Fe^{2+}, methomyl concentration, and optimal $[H_2O_2]_0/[Fe^{2+}]_0$ ratio) which affect the efficiency of Fenton and photo-Fenton reactions, in methomyl oxidation was also investigated.

2. Experimental

2.1. Reagents

Methomyl ($C_5H_{10}N_2O_2S$) in the purest form, is available from Merck Chemical Company Darmstadt. Fig. 1 shows the chemical structure and UV spectrum of this molecule. Ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$) used as a source of Fe^{2+} was purchased from Fluka. Hydrogen peroxide solution (35%, v/v) in stable form was provided by Panreac. The pH of the pesticide solution was adjusted by using H_2SO_4 or NaOH (Merck). All reagents employed were not subjected to any further treatment. Water used throughout was ultrapure deionized water.

2.2. Photoreactor

All experiments (photochemical decomposition alone and combined with hydrogen peroxide, Fenton's reagent oxidation and photo-Fenton system) were performed in a well stirred, batch, cylindrical photoreactor with a total volume of 500 ml. The reactor is made of glass and does not contain any metal parts. The outside of the reactor was covered with an aluminium sheet. At the top, the reactor has inlets for feeding reactants, and ports for measuring temperature and withdrawing samples. The reactor was open to air with a Teflon-coated magnetic stirring bar placed at the bottom to provide proper mixing.

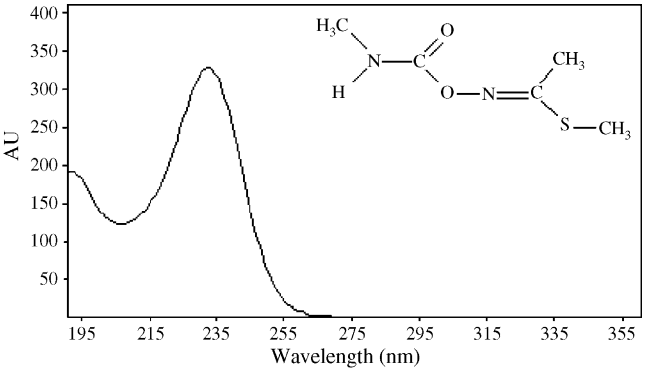

Fig. 1. Chemical structure and UV spectrum of methomyl ($\lambda_{max} = 231$ nm).

Specifically, for the photochemical experiments, a high-pressure mercury lamp (Philips HPK, 125 W) which emitted a maximum radiation at 365 nm was used as radiation source. It was located in the reactor in axial position inside a quartz sleeve. An external jacket surrounded the reactor, and a water stream was pumped from a thermostatic bath in order to maintain the temperature at the selected value of 20 °C.

2.3. Experimental procedure and analytical methods

For every experiment conducted, the reactor was filled with 250 ml of methomyl aqueous solution at the desired initial concentrations. The required amounts of ferrous sulphate and hydrogen peroxide were added to the reactor in the Fenton's reagent oxidation experiments and in the photo-Fenton experiments. For the photo-Fenton process ($UV/H_2O_2/Fe^{2+}$), the pH value of the solution was set to 3 by adding required amounts of H_2SO_4 solution before a given weight of iron salt was added. The iron was very well mixed with the prepared pesticide solution before the addition of a given volume of H_2O_2. The time at which the ultraviolet lamp was turned on was considered time zero or the beginning of the experiment which was taking place simultaneously with the addition of hydrogen peroxide.

The quantitative and qualitative analysis of the organic compounds in the samples was performed by high performance liquid chromatography HPLC (Jasco-type). The wavelength detector was set at 231 nm. A reverse-phase column (length, 25 cm; internal diameter, 4.6 mm) ODS-2 Spherisorb (Chrompack) was used. The mobile phase was composed of acetonitrile (20%) and water (80%). The flow rate was 0.4 ml/min and the injection volume was 20 μl in all samples.

Total organic carbon (TOC) was analysed by direct injection of the filtered samples into a Shimadzu-5050A TOC analyser calibrated with standard solutions of hydrogen potassium phthalate.

3. Results and discussion

In the Fenton and photo-Fenton processes, the H_2O_2 was oxidized and $OH^{\bullet}$ was produced. The formation of $OH^{\bullet}$ depends on several factors such as pH, dose of Fe^{2+} and H_2O_2, initial concentration of the pollutant and the ratio between Fe^{2+} and H_2O_2. Therefore, the effects of the previous factors were investigated.

3.1. Chemical degradability of methomyl

To evaluate the efficiency and the benefit of each condition on the pesticide degradation experiments were carried out under the following conditions: (1) pesticide + H_2O_2, (2) pesticide + UV, (3) pesticide + UV + H_2O_2, (4) pesticide + UV + Fe^{2+}, (5) pesticide + Fe^{2+} + H_2O_2 (Fenton process),

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