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Study on the photocatalytic degradation of insecticide methomyl in water

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ABSTRACT

Photo-Fenton degradation of the insecticide methomyl in water using Fe-ZSM-5 zeolite and AlFe-pillared montmorillonite catalysts under halogen lamp light was studied. The study was performed at room temperature in a glass batch reactor under constant airflow. Both catalysts exhibited activity in the wet oxidative degradation of methomyl. The rate of photodecomposition of methomyl was measured using UV spectrometry and HPLC, while its mineralization was followed using ion chromatography (IC) and total organic carbon (TOC) analyzer. IC results showed that mineralization led to formation of sulfate, nitrate and ammonium ions during the process. Under our conditions, complete disappearance of 16.22 mg/L of pure pesticide and 100% or 80% TOC removal occurred within 4 h using 5 g/L or 1 g/L of Fe-ZSM-5 zeolite, respectively. The Fe-ZSM-5 was found to be a better catalyst. Pseudo-first-order rate constants were calculated, and the performed treatments compared.

1. Introduction

Methomyl, $C_5H_{10}O_2N_2S$, S-methyl N-[(methylcarbamoyl)oxy] thioacetimidate) is a broad spectrum insecticide which belongs to the carbamate family of pesticides. According to [1], it is a very toxic and hazardous compound and a pollutant causing environmental concerns because of its high solubility in water (57.9 g/L at 25 °C). Since sorption affinity of methomyl to soils is rather low, it can easily cause contamination of both ground and surface water resources. In addition, various amounts of methomyl have been detected in surface and ground waters across Europa and America not only during actual insecticide application but also after a long period of use [2].

AOP$_s$ [3–9] include catalytic and photochemical methods and have H_2O_2, O_3 or O_2 as oxidant. The principal active species in this system is the hydroxyl radical $^{\bullet}OH$, which is an extremely reactive and non-selective oxidant for organic contaminants [3,10] and the reduction potential of $^{\bullet}OH$ is 2.80 V [11].

Fenton's processes [4,12,13] belong to AOP$_s$ and utilize H_2O_2 activation by iron salts. The main advantage of these processes is a complete degradation of contaminants to harmless compounds such as CO_2, water and inorganic salts [4,13]. The classic Fenton's reagent is a mixture of ferrous ion and hydrogen peroxide in acidic solution or suspension [12–14]:

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

Degradation of organic pollutants by Fenton's reagent can be strongly accelerated and improved by ultraviolet radiation and visible light, or by solar radiation. This process is called the photo-Fenton reaction [6–9,14–19]. The key of photo-Fenton processes is Eq. (1). The obtained ferric ion or its complexes subsequently act as light absorbing species that produce another hydroxyl radical, while the initial ferrous ion is regained [4]:

$$Fe(OH)^{2+} + h\upsilon \rightarrow Fe^{2+} + {}^{\bullet}OH \quad (2)$$

The main advantage of the photo-Fenton process is light sensitivity up to a wavelength of 600 nm [17]. According to [10], irradiation with light $\lambda < 580$ nm affects photoreduction of Fe^{3+} to Fe^{2+} together with the production of $^{\bullet}OH$ radicals.

Methomyl has been photodegradated using AOP$_s$. Different catalysts have been used, mostly TiO_2 [5,16,20], as well as photo-Fenton reaction [14,16,21,22]. In these reactions, dissolved ferrous sulphate heptahydrate was used as a source of Fe^{2+} ions.

Recently, we have only reported as letter that methomyl can be degradated using supported iron catalysts, such as Fe-ZSM-5 zeolite and AlFe-pillared montmorillonite [23]. These catalysts have also been used for destruction of other organic contaminants [24–27]. To our knowledge, there are no other reported studies focusing on the use of Fe-ZSM-5 zeolite and AlFe-pillared montmorillonite for photodegradation of methomyl.

The purpose of the present work is to study photo-Fenton degradation of the insecticide methomyl in water using various concentrations of Fe-ZSM-5 zeolite and AlFe-pillared montmorillonite.

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The effects of operational parameters such as initial concentration of methomyl and pH were also studied.

2. Experimental procedures

2.1. Reagents

All chemicals used in the investigation were of reagent grade and were used without further purification. Analytical standard of methomyl (99.8%) was received as a present from DuPont de Nemours, USA. Hydrogen peroxide solution (30% v/v) in stable form was provided by Carlo Erba. The pH of pesticide solutions was adjusted by using H_2SO_4 (Merck). NaOH, Na_2CO_3 and $NaHCO_3$ were purchased from Merck. Acetonitrile used for HPLC analysis was HPLC grade and was provided by Fluka. Methanesulphonic acid for ion chromatographic analysis was provided by Fluka. All solutions were prepared with Millipore Waters deionized water (18.2 MΩ/cm at 25 °C) and were prepared immediately prior to use.

2.2. AlFe-pillared montmorillonite (AlFe-pillared clay (PILC) catalyst)

The AlFe-pillared montmorillonite catalyst preparation and the applied physico-chemical methods for its characterization are given elsewhere [26]. One gram of pillared montmorillonite catalyst contains 5 mmol (iron + aluminium) cations, thus the iron content amounted to ca. 14 wt.% and Fe^{3+} ions are in highly dispersed state in the AlFe-PILC catalyst [28].

2.3. Fe-ZSM-5 zeolite

Fe-ZSM-5 zeolite was obtained by solid-state exchange of ammonium ions with iron ions in commercial ZSM-5 zeolite [29]. The applied catalyst was produced by Alsi-Penta Zeolithe GmbH, Schwandorf, Germany. In the starting zeolite, the Si/Al ratio was 12. The extent of iron exchange resulted in an Fe/Al = 0.75 ratio. Thus the iron content was ca. 5 wt. % and in this case a hematite/ZSM-5 composite with Fe^{3+} ions is formed [28].

2.4. Photodegradation procedure

The photodegradation procedure is reported elsewhere [23]. A halogen lamp (Brilux, Model JCDR, 50 W, 640 cd, China) was used as a radiation source. Color temperature of the light was 3000 K, which corresponds to 575.6 nm [30].

2.5. Analytical procedure

For spectrofotometric determination during degradation of methomyl, 2.0 mL of the solution were taken at regular time intervals and their spectra recorded on a Shimadzu 1700 UV–VIS spectrophotometer in a wavelength range from 200 to 300 nm. The kinetics of methomyl degradation was monitored at 233.8 nm.

For HPLC determination, all solutions were filtered through Sartorius 0.20 μm syringe filters and were analyzed at 234 nm and at ambient temperature (25 °C) on a Hewlett Packard HP 1050 liquid chromatograph with a UV–VIS detector, equipped with a reversed-phase column type Zorbax Eclipse XDB-C18 150 × 4.6 mm (i.d.) × 5 μm. The mobile phase (flow rate 2.0 mL/min) was a mixture of acetonitrile and water (25:75, v/v). Sample injection volume was 20 μL and both samples and standards were diluted with acetonitrile. Under the above chromatographic conditions, concentrations of methomyl were determined from the peak area at $t_R = 2.0$ min.

For ion chromatographic determinations, all methomyl solutions were diluted and were filtered through Milex-GV 0.22 μm membrane filters, and were analyzed on a Dionex DX-300 ion chromatograph at ambient temperature (25 °C) with a suppressed conductivity detector. Ion chromatograph was equipped with a Dionex IonPac AS 14 column 250 × 4.0 mm (i.d.) for anion determination and Dionex IonPac CS 12 column 250 × 4.0 mm (i.d.) for cation determination. The mobile phase for anion determination was a carbonate/bicarbonate mixture (3.5 mmol/L Na_2CO_3 + 1.0 mmol/L $NaHCO_3$), flow rate 1.0 mL/min, and for cation determination, it was a solution of methanesulphonic acid (20.0 mmol/L), flow rate 1.0 mL/min. For both anion and cation measurements, sample injection volumes were 50 μL. Prior to sample measurements, blank samples of deionized water were chromatographed. Retention times for nitrate and sulphate ions were 8.0 and 12.5 min, respectively. Retention time for ammonium ion was 4.8 min.

For total organic carbon (TOC) analysis, the samples were analyzed on a Zellweger LabTOC 2100 instrument using a high-temperature combustion followed by infrared CO_2 detection.

3. Results and discussion

3.1. Photocatalytic degradation of methomyl

In our experimental work 2 types of catalyst were used: Fe-ZSM-5 zeolite in concentration of 5 g/L and 1 g/L, and AlFe-pillared montmorillonite in concentrations of 5 g/L, 3 g/L and 1 g/L. In the initial part of the experimental work adsorption studies with both catalysts were performed (Fig. 1). When AlFe-pillared montmorillonite is concerned weak adsorption was observed (Fig. 1a) whereas in the presence of Fe-ZSM-5 zeolite (Fig. 1b) stronger adsorption took

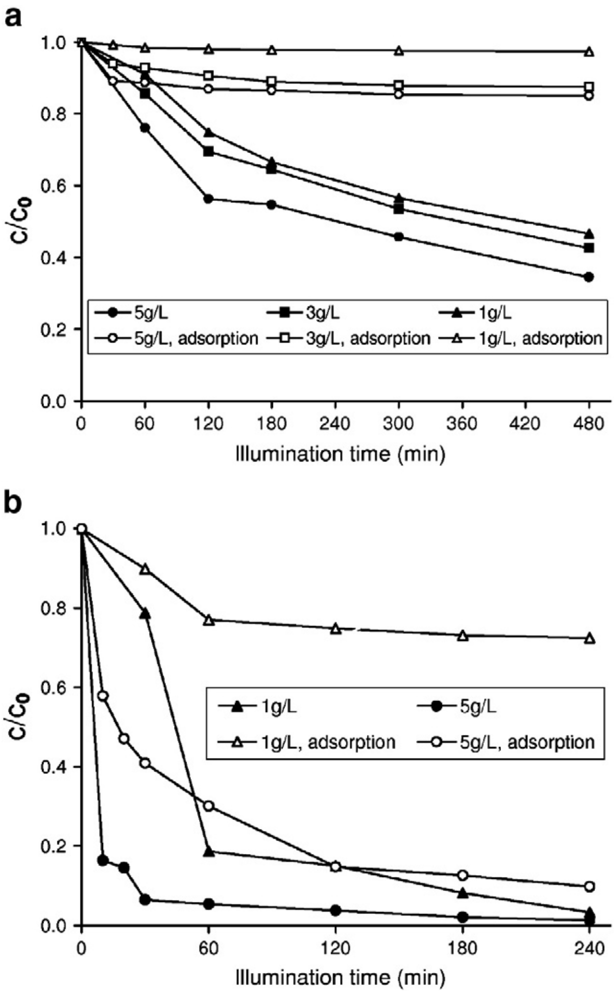

Fig. 1. Methomyl photodegradation in the presence of different catalysts: (a) AlFe-PILC, (b) Fe-ZSM-5 (methomyl concentration = 16.22 mg/L, pH = 3.7).