Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.887497

52 (2014) 3837–3842
May

Taylor & Francis
Taylor & Francis Group

Photo-Fenton method usage to organic compounds degradation

Iwona Skoczko*, Janina Piekutin

Department of Technology in Environmental Engineering and Protection, Technical University of Bialystok, 45A Wiejska Street, 15-351 Bialystok, Poland
Tel. +48 85 746 96 44; email: i.skoczko@pb.edu.pl

Received 3 June 2013; Accepted 12 September 2013

ABSTRACT

The aim of conducted research within this work was the decomposition of chosen pesticides with the use of Fenton's method supported by UV radiation and strong halogen light. The experiments were done with the use of such pesticides as chloropiryphos, metribuzyne, and metriam included in popular plant protection products. In order to support the highest possible effect of pesticides degradation, the decrease in hydrogen peroxide dose and catalyst, there was conducted the research connecting irradiation by strong halogen lamp with the power of 400 W and UV lamp with the wave length of 350 nm. In the process of pesticides removal, irradiation process was conducted during mixing of samples with Fenton's reagent. In conducted experiment, the past sell-by date chemicals were degraded in stages into simpler compounds. The conditions cause the acceleration of reaction in comparison with the one occurring without any light support. However, the processes described above are occurring slowly, which eliminates their use in practical technology of solution treatment. This thesis is proved by the research conducted by article's authors.

Keywords: Fenton method; Pesticide degradation

1. Introduction

Advanced oxidation processes (AOPs) consist of chemical oxidizing agents treatment in the presence of a particular catalyst to oxidize or degrade many pollutants. AOPs have been used for the degradation of a variety of organic pollutants, such as phenols, hydrocarbons, aliphatic and aromatic, halocarbons, ethers, ketones. [1–6].

Fenton's method is one of the chemical methods of organic pollution degradation classified to the group of AOP processes. It uses the hydrogen peroxide and iron ions, as catalyst of oxidation process. The reaction is the one of the most efficient oxidation techniques. Moreover, it leads to the catalytic degradation of hydrogen peroxide in the presence of Fe(II) or Fe(III). As a result, reactive hydroxyl radicals $^{\cdot}OH$ of very high oxidation potential reaching 2.8 V are generated [1–3]. The pH range, in which oxidation is observed, is between the

*Corresponding author.

Presented at the 11th Scientific Conference on Microcontaminants in Human Environment, 25–27 September 2013, Wisla, Poland, Organized by Department of Chemistry, Water and Wastewater Technology, Faculty of Environmental Engineering and Biotechnology, Czestochowa University of Technology

value of 3 and 4. However, the weight proportion of catalyst quantity to hydrogen peroxide amount hesitated about 1:5. Fenton's reagent is the effective oxidant of many organic substances. Hydroxyl radicals, which are formed in the Fenton's reaction, can oxidize almost all organic compounds containing hydrogen. The main advantage of Fenton's process, in comparison with other methods of chemical treatment, is the lack of H_2O_2 rests in after-reaction structure and catalytic quantity of Fe^{2+} used in this reaction. Moreover, to warm the mixture, the Fenton's reaction is conducted at an ambient temperature using the reaction heat. It is an essential advantage of this process since it does not demand the installation of heat exchanger in reactor, and the energy is used to mix and dose reagents. As a result of conducted research works [1–4,6], it was stated that UV radiation (300–500 nm) and strong light accelerates the Fenton's reaction very much. On the contrary to reaction without light support, mineralization of organic compounds is close to 100%. The reactions described in literary sources as photo-Fenton's and UV-Fenton's reactions are intensified processes on natural environment, for example, surface water exposed to sun rays or in the atmosphere.

Fenton's reaction is used to preliminarily treatment, decrease COD before past biological treatment of sewage or in order to mineralize toxic and hardly—biodegraded pollution, sewage treatment polluted by chemicals among others pesticides, in the range of degradation and mineralization of organic pollution of effluent water (mainly chlorophenols and some pesticides). In available literature, there is no information about the possibilities of using the method in preliminary oxidation of industrial sewage from pesticides production polluted by the rests of plant protection chemicals [4,5]. In many industrial plants, this sewage is pretreated in sewage treatment plant with the use of such methods as coagulation or sorption, which does not guarantee effective elimination of pesticides from process wastewater [6]. Sewage is carried to municipal wastewater treatment plant, where it affects biological treatment structure negatively causing the decrease in its general effectiveness [7,8].

The aim of conducted research presented in this paper was the decomposition of chosen pesticides with the use of Fenton's method supported by UV radiation and strong halogen light. Photo-Fenton's methods were compared to classic Fenton's reaction and dark-Fenton's method.

2. Materials and methods

In order to support the highest possible effect of pesticides degradation as well as the decrease in hydrogen peroxide dose and catalyst, research connecting irradiation by strong halogen lamp with the power of 400 W and UV lamp with the wave length of 350 nm was carried out. Irradiation process was conducted during the samples mixing with Fenton's reagent in the reactor. The experiments were done with the use of the following plant protection chemicals:

- Insect determinant—Chloromezyl 500 S.C. (in 1 L of chemical, it contains active substances: chloropiryphos 278 g and dimetoat—222 g, which are the compounds from the phospho-organic group);
- Weed-killer—Sencor 70 WG (in a form of stable granulates containing 70% of active substance of metribuzyne from the group of triazine pesticides);
- Fungicide activating emergency and prudentially Polyram 70 WG (in a form of stable granulates containing also 70% of active substance of metriam from the group of ditiocarbaminianes).

The research was done on particular substances and their mixture. Preparations samples were dissolved in treated sewage in a quantity of 50 mg/1 dm^3 of aqueous solution. The mixture of treated sewage and pesticides filled four non-pressure rectors with the 1 dm^3 capacity. Reactors were equipped with a magnetic stirrer. Afterward, Fenton's reagent was introduced into reactors. It was prepared using 5 g of Fe^{2+} and 3 g of H_2O_2. Next, the reaction environment was acidified to the pH of 3.0–3.5 with a concentrated sulfuric acid. Then, reactor's contents were mixed. The time of sewage mixing with pesticides and Fenton's reagent was measured as 1.5 h. During mixing the Fenton's method was realized in different light conditions. In the first reactor, Fenton's classical method was used. The second reactor was closed in the darkroom in order to use dark-Fenton's method. Fenton's method supported by UV irradiation occurred in the third reactor. And Fenton's reaction supported by irradiation by strong halogen lamp realized in the fourth reactor. After 90 min mixing time, every reactor contents were neutralized by the solution of $Ca(OH)_2$ to pH about 6.5–7. Next step was sedimentation of precipitated sewage sludge. Solution required also filtration by thick filters. Finally, the samples were clear. The content of the pesticides residues was determined with the use of gas chromatography method (GC/ECD/NPD and GC/MS/MS).

3. Results and discussion

The goal of conducted experiments was to consider such methods as: dark-Fenton, classic Fenton, photo-Fenton, and UV-Fenton reaction. The comparison of four analyzed methods is shown in the Fig. 1.

Tested in this paper, pesticides are popular preparations used all over the world in order to protect plants. Their presence is common in surface water and flat ground water. What is more they degrade slowly in natural environment. The half life degradation time is 20 d for metribuzyne, 48 d for metiram, and 72 d for chloropiryphos. This time gets longer for their mixture. Every preparation is dangerous for human and animal life and may cause many diseases. That is why they should be eliminated both from water and sewage so that the environment would be safe.

Conducted research clearly shows the superiority of methods supported by intensive irradiation over reactions occurred in the darkroom or those under traditional conditions. Among analyzed preparations, the compound from the phospho-organic group was degraded to the largest extent. It was the least exposed to the full degradation in conditions of 2 h mixing together with the irradiation by UV lamp 350 nm. The preparations residues showed the exposure on degradation by Fenton's reagent with the UV irradiation giving the effect of full oxidation.

Similarly, high effects of pesticides removal from solutions were observed in rectors irradiated by halogen lamp of 400 W. Metiram was easily exposed to degradation in this method. It was all removed. Degradation of metribuzyne also reached minimal statistic values at the level of 0 mg/dm^3; however, the results were rejected by *T*-Tukey's method as statistically unessential. In repeated tests that value was reached only twice. It is essential to indicate that only some researchers analyzed technological aspects of pollution degradation in water or sewage by Fenton's method with the use of sunlight (visual light), which wavelength was 290–500 nm. These are the conditions commonly occurred in natural environment. Kiwi [9] noticed that reactive indirect products are formed in natural water exposed to sunrays, which afterward take part in photooxidation reactions. These are mainly superoxide anion radicals ($O_2^{\bullet-}$), hydrogen peroxide (H_2O_2), singlet oxygen (1_{Δ} O), hydroxyl radicals ($^{\bullet}OH$), organic superoxide radicals ($RO_2^{\bullet}$) and radicals $CO_3^{\bullet-}$. Their concentration in surface water ranges from 10^{-16} mol/dm^3 for hydroxyl radicals to 10^{-8} mol/dm^3 for superoxide anion radicals and H_2O_2. Finally, they are responsible for natural degradation of many

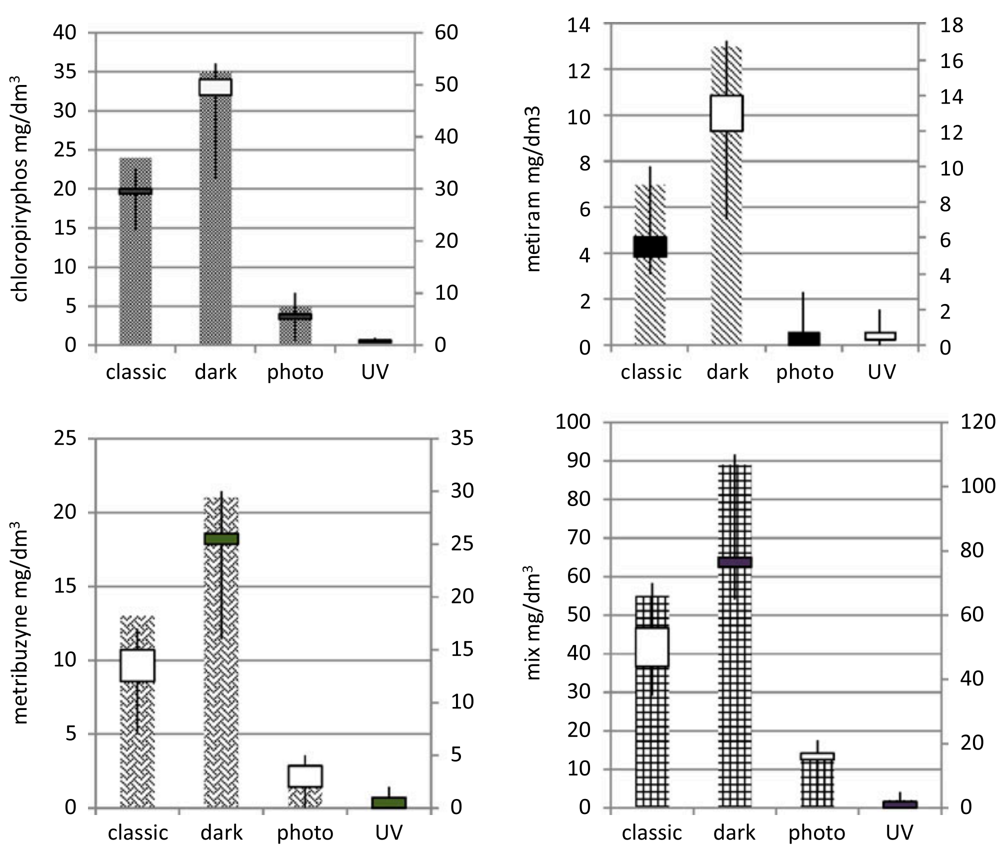

Fig. 1. Comparison of methods studied: classic Fenton, dark-Fenton, UV-Fenton, and photo-Fenton.

organic pollutants present in water. Conducted research by Skoczko and Piekutin proved that studied pesticides degradation needs high concentration of oxidants. Classic Fenton's method is not effective enough in order to dispose of toxins. That is why radicals mentioned by Kiwi were used to boost the process. In that group, the strongest oxidizing agent is a hydroxyl radical. Its concentration was intensified by irradiation. It is essential to which extent and in what way Fenton's reaction takes part in forming of these radicals. In metiram, metribuzyne, and chloropiryphos degradation took part all Kiwi's oxidants. One may notice that superoxide anion radicals may have had a huge impact in comparison with dark-Fenton. McGinnis [10] assumes that oxidants main sources in natural water are photochemical reactions connected with forming of superoxide anion radicals ($O_2^{\bullet -}$). The conditions cause the acceleration of reaction in comparison with the one occurring without any light support. That conclusion was confirmed by Skoczko and Piekutin's tests. However, the processes are occurring slowly, which eliminates their use in practical technology of aqueous solution treatment. This thesis is proved by the research conducted by article's authors, in which efficient degradation of pollution with the sunlight was observed. However, it occurred much slower than with the use of UV irradiation, which multiplies particular radicals.

Apart from the oxidants, the form and concentration of iron catalyst is also important as far as Fenton's method is considered. UV-Fenton's method used in research conducted by the author is one of the AOP methods used frequently these days in order to degrade stable pollution. In classical Fenton's reaction, formed Fe^{3+} ions are stored in the structure (only re-reduction of Fe^{3+} to Fe^{2+} is undergoing to the little extent), and after the exhaustion of Fe^{2+} ions, the reaction almost disappears. Pozdnyacov [11], Gonzalez [3], and Silva [12] observe that in UV-Fenton's reaction, under the influence of UV radiation, photoreduction of Fe^{3+} ions to Fe^{2+} is observed as well as free radicals $^{\bullet}OH$ are formed.

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

Formed Fe^{2+} ions can still react with hydrogen peroxide according to the classical Fenton's reaction generating new radicals $^{\bullet}OH$, which leads to an increase in the effectiveness of pollution degradation process. It can be precisely described by the following reaction:

$$[Fe(OH)]^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH$$

Fe^{3+} ions and hydroxyl radicals can react together according to the following reaction:

$$Fe^{3+} + {}^{\bullet}OH \rightarrow [Fe(OH)]^{2+}$$

Under the influence of UV radiation, with the wavelength of 313 nm, there is observed the photo-catalytic opposite reaction, causing the increase in radical quantity $^{\bullet}OH$:

$$[Fe(OH)]^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH$$

This dependence is used by Skoczko and Piekutin for pesticide degradation. Although only 5 mg of Fe^{2+} was added to an aqueous solution, iron transformation made it possible to reach more catalyser and more hydroxyl radicals. Presented reactions showed that the basic amount was gained in the darkroom only in the third reaction. UV irradiation intensified process, got more iron forms and hydroxyl radical. As a result, it led to better degradation of studied pesticides.

The most favorable pH for UV-Fenton's reaction amounts 2.8, with which approximately half of iron (III) occurs as Fe^{3+}, and the rest as $[Fe(OH)]^{2+}$. Below this pH value, the concentration of $[Fe(OH)]^{2+}$ decreases, while over pH 2.8—hydrated iron oxides are precipitated (III) [2]. The following reactions:

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

$$[Fe(OH)]^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH$$

are observed in UV-Fenton's process as reactions of feedback.

Bauer claims [13] that in UV-Fenton's reaction radicals $^{\bullet}OH$ are formed in result of direct photolysis H_2O_2:

$$H_2O_2 + h\nu \rightarrow 2{}^{\bullet}OH$$

However, according to Engwall [1], it plays less substantial part in this process since hydrogen oxidant shows slight absorption of photons in the range of ultraviolet.

The variety of Fenton's reaction investigated by Bauer [13] and Safarzadeh [14] supported by UV radiation is the process running in the presence of ions of carboxyl acids forming complexes with ions Fe^{3+}. These complexes are more active than ions $[Fe(OH)]^{2+}$ and while downgraded under the influence of UV rays they form organic radicals in the following reaction:

$$Fe(III)(RCO_2)^{2+} + h\nu \rightarrow Fe(II) + CO_2 + {}^{\bullet}R$$

Degraded ion Fe^{2+} can afterward form with H_2O_2 radicals $^{\bullet}OH$, while organic radical can react with oxygen undergoing further oxidization. It leads to the decrease in iron ions usage. In the conducted experiment, plant protection chemicals, which were past the sell-by date, were degraded in stages into simpler compounds. In the structure of chloropiryphos showed in the Fig. 2, at the outset of degradation process during Fenton's reaction, relative bond was broken and unfastened from the ring. As a result, it caused the forming of new carboxyl group.

Similarly, metribuzyne: 4-amino-6-tetr-butylo-3-metylotio-1,2,4-triazyn-5(4H)-on and metiram undergoing degradation, they release carboxyl groups. It can be assumed that it was one of the conditions accelerating UV-Fenton's reaction and increasing its efficiency (Figs. 3 and 4).

Despite noticeable advances in the last years, the widespread successful application of photochemical processes for the treatment and decontamination of pesticides residues in water and wastewaters has not been fully achieved. Research scientists and industrial engineers must work together to solve important practical problems in order to make it possible to apply the photo-Fenton reaction's technology on a large scale. Obtained results proved high efficiency of UV-Fenton reaction. The form of irradiation has to be employed so that total mineralization of the organic pesticides of effluents could be achieved.

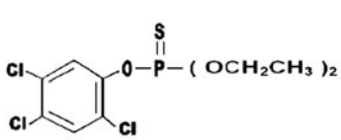

Fig. 2. Molecular structure of chloropiryphos.

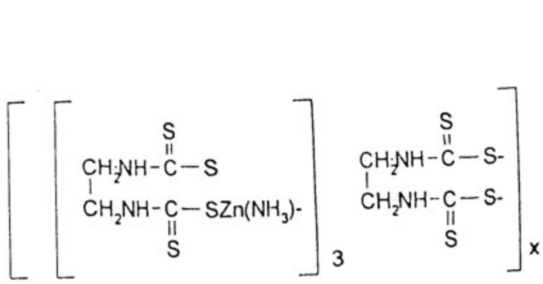

Fig. 3. Molecular structure of metribuzyne.

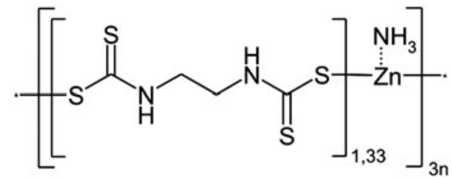

Fig. 4. Molecular structure of metiram.

4. Conclusions

(1) Among three analyzed pesticides, the chemical of lowest permanence for each of variances was Polyram 70 WG with an active substance Metriam.

(2) The highest permanence on oxidization of Fenton's reagent showed Chloromezyl 500 S.C. with active substances—chloropiryphos and dimetoat.

(3) Photo-Fenton's reactions with support of UV radiation and a strong halogen lamp, showed substantially higher efficiency in pesticides degradation comparing to the classical method and the one used in darkroom.

(4) Among the analyzed variances of Fenton's method, the highest efficiency in pesticides decomposition was reached with irradiation by UV lamp with the wave length of 250 nm.

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