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Comparative study of oxidative degradation of sodium diatrizoate in aqueous solution by H_2O_2/Fe^{2+}, H_2O_2/Fe^{3+}, Fe (VI) and UV, H_2O_2/UV, $K_2S_2O_8$/UV

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HIGHLIGHTS

- Systems based on ferrate salts are strongly dependent on the solution pH.
- Fenton-*like* system is more efficient than Fenton system in removal of diatrizoate.
- UV/$K_2S_2O_8$ system is a promising process to remove pharmaceuticals in natural water.
- Natural organic matter improves the efficiency in systems using UV radiation.

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ABSTRACT

This study centers on Advanced Oxidation Processes (AOPs) based on the use of iron salts and ultraviolet (UV) radiation for the removal of diatrizoate (DTZ) contrast medium, selected as a model compound resistant to all conventional natural and waste water treatment methods. We studied the effectiveness of Fenton's reagent, Iron (III) and Iron (VI) salts, and oxidation processes based on the use of UV radiation, UV/H_2O_2 and UV/$K_2S_2O_8$, for the degradation of DTZ in aqueous medium. With Fenton's reagent, the percentage DTZ removal was independent of the initial Fe^{2+} concentration and was most influenced by the initial hydrogen peroxide concentration. In contrast, the Fenton-*like* system was affected by both initial Fe^{3+} and H_2O_2 concentration. The effects of ferrate salt-bases methods were highly dependent on the solution pH, and a higher rate constant ($1.74 \times 10^2\ M^{-1}\ s^{-1}$) was obtained when dihydrogen ferrate species predominated in the medium. The UV/H_2O_2 system was strongly dependent on the pH and initial H_2O_2 concentration, showing a favorable synergic effect at H_2O_2 concentrations <10.0 mM. The UV/$K_2S_2O_8$ system proved to be more effective than the UV/H_2O_2 system, with higher rate constants, which were 24.0% higher for pH = 6.5 and $[DTZ]_0 = 25\ mg\ L^{-1}$. Study of the influence of the matrix on these AOPs revealed a markedly higher percentage DTZ removal and reaction rate in surface water with the UV radiation-based systems than with the iron salt-based systems. According to the total organic carbon values obtained, a high degree of mineralization was only attained with the UV/$K_2S_2O_8$ system.

1. Introduction

Conventional wastewater treatments are not adequate to treat certain chemical compounds produced by human activity, which are eventually deposited in the environment. These persistent pollutants include iodinated contrast media, notably sodium diatrizoate (DTZ), which has been detected in surface, ground, and waste waters [1–3]. In common with all contrast media, DTZ is highly polar, stable, and chemically inert and is eliminated unmetabolized after its administration. Conventional techniques used in urban wastewater treatment plants have proven ineffective for its removal [3–6], leading to the accumulation of DTZ and degradation products in the environment and their assimilation into biological systems, with poorly understood adverse effects [7–9].

It was shown the high resistant from DTZ to physicochemical process as the ozonation method and ozone joint with UV lamp and hydrogen peroxide, in which DTZ degradations were 14% and 36% respectively [10,11]. In another study based on ozone, Fenton,

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Abbreviations: ANOVA, Analysis of variance; AOPs, Advanced Oxidation Processes; CAS Number, chemical abstracts service registry number; CTB, Cytarabine; DTZ, sodium diatrizoate; HPLC, high performance liquid chromatography; LOD, limit of detection; LOQ, limit of quantification; NOM, natural organic matter; *P*, *P*-value; SW, Natural surface water; TOC, total organic carbon; UV, ultraviolet; WHO, World Health Organization.

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O_3/H_2O_2 and UV/H_2O_2, the degradation results were similar but the most effective of them were UV radiation (254 nm) and photo Fenton system with 96.6% and 64.7% of degradation in the same order [12]. All of them were realized only in ultrapure water so it is necessary to complement these studies with natural water and to broaden the investigation with other processes, which can be more efficient.

Advanced Oxidation Processes (AOPs) have aroused special interest in the search for alternative treatments for this type of component.

Various studies have reported the effectiveness of Fenton's reagent to remove organic pollutants from water [13,14].

Thereby, we have considered Fenton-like oxidizing process, in which peroxo complexes $[Fe(HO_2)]^{2+}$ and $[Fe(OH)(HO_2)]^{+}$ are formed when ferric ion comes into contact with hydrogen peroxide [15]

Nowadays, oxidation with ferrate salts is considered one of the optimal chemical treatments for waste and drinking waters due to their strong oxidizing properties, permitting their use in oxidation, disinfection, coagulation, or a combination of these processes [16–19]. Moreover, its decomposition products (ferric iron and oxygen) are non-toxic [17,19,20]. Ferrate is an energetic oxidizing agent in aqueous medium, with an oxidation potential ranging from 2.20 V in acid medium to 0.70 V in basic medium. Under acid conditions, its redox potential is higher than that of other oxidants commonly used in water treatment [20]; however, this process is usually conducted under conditions of basicity ($pH \geqslant 8$) because of the instability of ferrate at acid pH values [17,19,21]. This dependence on the pH value is mainly due to the protonated species of the ferrate ion ($H_3FeO_4^{+}$, H_2FeO_4, $HFeO_4$, and FeO_4^{2}) [19].

Ferrate can react with organic compounds, such as anilines, amines, phenols, and olefins through electrophilic oxidation mechanism [22]. Besides, Fe (VI) can be used for the degradation of inorganic pollutants such as metal-complexed cyanides, ammonia, sulfides, and metals [23–25].

Another group of Advanced Oxidation Processes of great interest are the based on the use of ultraviolet radiation (UV). UV radiation has been proposed as an effective process to degrade pharmaceutical pollutants from waters [26]. It produces a transition in molecules to a singlet excited state and possible intersystem crossing to a triplet state. In most cases, hemolysis originates radicals that initiate chain reactions and produce final products with lower molecular weight. Direct photolysis has generally demonstrated a low effectiveness to degrade organic compounds dissolved in water in comparison to processes that generate hydroxyl radicals. Thereby, the combination of UV radiation with an oxidizing agent (hydrogen peroxide, peroxydisulfate, ozone, etc.) improves the effectiveness of organic compound removal from waters [27–33].

The UV/H_2O_2 system has been applied to the degradation of a great variety of pollutants [26,29,34–40]. This system presents several advantages: (i) H_2O_2 can be readily mixed with water in all proportions; (ii) costs associated to UV/H_2O_2 system are smaller than the corresponding to other processes, for example UV/ozone; and (iii) UV/H_2O_2 processes leads in most cases to the mineralization of the organic pollutants.

Other source of radicals used with UV radiation is the peroxodisulfate anion ($S_2O_8^{2-}$) which has been used in pollutant degradation [27,41–44]. However, reactions with $S_2O_8^{2-}$ are very slow at ambient temperatures; therefore, other methods have been proposed to activate or accelerate the degradation of organic molecules [44]. These include the generation of sulfate radicals, $SO_4^{\cdot-}$ ($E_0 = 2.6$ V), by the photochemical decomposition of $S_2O_8^{2-}$. At the end of the oxidation process, sulfate anions will be generated as the end-product, which is not considered to be a pollutant. The maximum level of sulfate suggested by the World Health Organization (WHO) in the Guidelines for Drinking-water Quality is 500 mg L^{-1}. European Union standards complete and strict than the WHO standards, suggesting a maximum of 250 mg L^{-1} of sulfate anion in water intended for human consumption [45].

With this background, the present study focused on the effectiveness of AOPs based on the use of iron salts and ultraviolet (UV) radiation to remove DTZ contrast medium, which served as a model compound resistant to conventional natural and waste water treatments. The specific objectives were to study the effectiveness of Fenton's reagent, Iron (III) and Iron (VI) salts, and oxidation processes based on UV radiation, UV/H_2O_2, and UV/$K_2S_2O_8$, for DTZ degradation in aqueous phase.

2. Materials and methods

2.1. Materials

All chemical reagents used (sodium diatrizoate (CAS Number: 737-31-5), phosphoric acid (CAS Number: 7664-38-2), potassium peroxodisulfato (CAS Number: 7727-21-1), sodium sulfite (CAS Number: 7757-83-7), ferrous sulfate (CAS Number: 7782-63-0), ferric chloride (CAS Number: 10025-77-1), potassium ferrate (CAS Number: 13718-66-6), hydrochloric acid (CAS Number: 7647-01-0), sodium nitrite (CAS Number: 7632-00-0)) were of high purity analytic grade and supplied by Sigma–Aldrich. All solutions were prepared with ultrapure water obtained with Milli-Q® equipment (Millipore).

2.2. Reactor for iron salts

Experiments with hydrogen peroxide, Fe (II), Fe (III), and Fe (VI) were conducted in an opaque glass cylindrical reactor, with 1 L capacity, in constant agitation at room temperature (295 K).

2.3. DTZ degradation by Fenton process

Experiments were conducted at pH = 3.0 to guarantee the maximum concentration of $HO^{\cdot}$ radicals in the medium. The reaction inhibitor solution used was 1 mL 1000 mg L^{-1} sodium nitrite.

For DTZ, the follow-up time for the Fenton process was established by conducting preliminary experiments at different reaction times for initial concentrations of 100 mg L^{-1} DTZ and 50 mg L^{-1} hydrogen peroxide and ferrous ion. Reaction follow-up time was fixed at 5 min, withdrawing samples at 1 min intervals. In order to study the influence of the experimental variables, experiments were conducted in which the DTZ concentration (10, 25, 50, and 100 mg L^{-1}) was varied and concentrations of Fe (II) and H_2O_2 were fixed at 5 mg L^{-1}. The influence of H_2O_2 concentrations (5, 15, 25, and 50 mg L^{-1}) was studied with an initial concentration of 25 mg L^{-1} DTZ and an Fe (II) concentration of 5 mg L^{-1}, and the influence of Fe (II) concentrations (0.1, 0.5, 1.0, 5, 10, and 50 mg L^{-1}) with 25 mg L^{-1} DTZ and 5 mg L^{-1} H_2O_2.

2.4. DTZ degradation by the Fenton-like process (Fe III)

The Fenton-like process was studied in experiments conducted under the same conditions as for the Fenton method but with ferric chloride as catalyst.

2.5. DTZ degradation by Fe (VI) salts

Sodium DTZ was degraded by Fe (VI) using potassium ferrate. Previous assays showed that DTZ degradation takes place during the two first minutes; therefore, a reaction follow-up time of 5 min was established. These experiments were conducted at