



Heterogeneous photo-Fenton processes using zero valent iron microspheres for the treatment of wastewaters contaminated with 1,4-dioxane



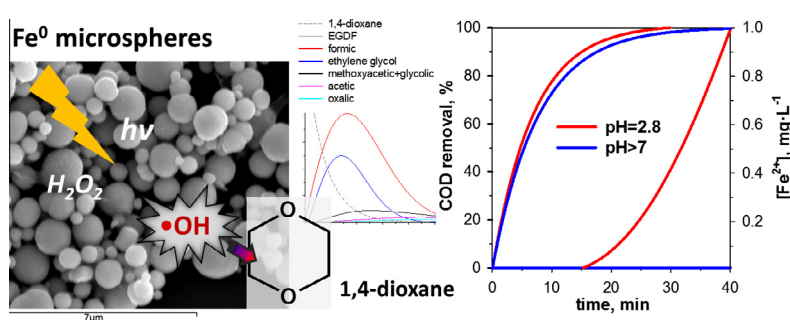
Helen Barndölk, Laura Blanco, Daphne Hermosilla*, Ángeles Blanco

Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Ciudad Universitaria s/n, 28040 Madrid, Spain

HIGHLIGHTS

- 1,4-Dioxane was successfully degraded by heterogeneous photo-Fenton on Fe⁰ microspheres.
- Influences of radiation source, pH and reagent dose were studied on synthetic waters.
- Excellent results were achieved in neutral conditions without any iron leaching.
- Efficient treatment of industrial wastewaters was performed.
- Major reaction intermediates of 1,4-dioxane were identified.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of zero valent iron (Fe⁰) microspheres for the degradation of 1,4-dioxane by photo-Fenton processes was optimized in terms of pH and reagent dosage for the successful treatment of industrial wastewaters. In addition, reaction intermediates of 1,4-dioxane degradation were studied. In UV photo-Fenton treatment of synthetic waters, complete removal of 1,4-dioxane was reached in 5 min, significant biodegradability enhancement (up to 60%) was achieved in 10 min, and an almost total COD removal was obtained after 30 min of treatment ($\geq 90\%$), whereas the presence of bicarbonate buffer (pH ≥ 7) prevented iron leaching. At different H₂O₂/COD₀ ratios the degradation of organics by UV-catalysed Fenton was in a following order: 2.625 > 2.125 > 4 > 1.625. On the other hand, solar photo-Fenton removed above 90% of 1,4-dioxane after 180 min, whereas H₂O₂/Fe⁰ ratio of 60 was found optimum. In the treatment of industrial wastewater, $\geq 99\%$ and 60% of COD were removed by UV and solar photo-Fenton respectively. Ethylene glycol and formic acid were identified as primary intermediates for the 1,4-dioxane decomposition in heterogeneous photo-Fenton. The opportunity to avoid sludge production and pH adjustments makes the Fe⁰ microspheres an efficient catalyst for the treatment of relatively alkaline wastewaters containing 1,4-dioxane. The solar driven process could be an important economical alternative to the UV catalysed process. When considering the consumption of energy and chemicals, if partial COD reduction for biodegradability enhancement was the purpose, both heterogeneous photo-Fenton processes appear to be more energy and cost-efficient than ozonation and electro-oxidation treatments.

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* Corresponding author. Tel.: +34 91 394 4645; fax: +34 91 394 4243.

E-mail address: dhermosilla@quim.ucm.es (D. Hermosilla).

1. Introduction

1,4-Dioxane is a synthetic cyclic ether traditionally used as a solvent stabilizer, detected frequently at sites where chlorinated solvents are used in degreasing applications [1,2]. It is also used as an agent or solvent in the manufacture of several products, such as paints, dyes, waxes and resins; and as a reaction media in chemical synthesis [2,3]. 1,4-Dioxane is a hazardous chemical for humans and for the environment, classified as a possible human carcinogen (B2) [4,5]. 1,4-Dioxane has even been found in consumer products; however, it occurs more commonly in wastewater and landfill leachates [2].

1,4-Dioxane is fully miscible and, thus, extremely mobile and persistent in water; therefore, its removal from industrial effluents is of great importance to avoid the contamination of natural water bodies. However, conventional wastewater treatment plants tend to fail in degrading 1,4-dioxane due to its resistance to biodegradation at ambient conditions [2,6] and it cannot be efficiently treated by conventional technologies used for solvents, such as carbon adsorption, air stripping and distillation either due to its high aqueous solubility (4.31×10^5 mg/L), low vapor pressure (37 mmHg at 25 °C) and its boiling point similar to water (101 °C) [1,2]. As a consequence, a suitable technology for its treatment is demanded.

Advanced oxidation processes (AOPs) are an efficient alternative for the degradation of refractory organics, owing to its highly reactive and non-selective primary oxidant, hydroxyl radical ($\cdot\text{OH}$) [7]. Removal of 1,4-dioxane has been already achieved using electro-oxidation [8], ozone based treatments [9,10], photocatalysis [11,12], ultrasonic decomposition in the presence of ferrous iron (Fe^{2+}) [13], and the combination of hydrogen peroxide (H_2O_2) and UV light [14,15]. High removals of chemical oxygen demand (COD) [3,16] and biodegradability enhancement [17] were also reported treating this compound by methods based on Fenton reaction.

Among AOPs, Fenton process has been reported as one of the fastest and most economical ones, using safe and environmentally benign reagents, Fe^{2+} and H_2O_2 , to produce $\cdot\text{OH}$ [18,19]. However, the production of ferric iron (Fe^{3+}) sludge and the corrosive acid pH required for the process are still important drawbacks that restrict its full scale implementation [20,21]. As an economical alternative, using solid metallic iron as a precursor of Fe^{2+} has been reported to produce less sludge, as Fe^{3+} is recycled in a so-called pseudo-catalytic zero-valent iron (Fe^0)/ Fe^{2+} system [22,23]. Moreover, using Fe^0 particles in suspension would enhance the system reactivity; however, as the treatments using iron powder are usually performed in acidic conditions, like in classical Fenton reaction, the intensive iron corrosion would still result in important dissolved iron salts concentrations that would require subsequent removal [21,24]. A promising alternative was reported by Bergendahl and Thies [24], obtaining satisfactory results using heterogeneous Fe^0 under neutral pH conditions, enabling to avoid the consequent neutralization and precipitation step.

In addition, the overall efficiency of Fenton oxidation can be significantly improved by the assistance of radiation, owing to the photo-recovered catalytic Fe^{2+} and the photo-decarboxylation of the refractory ferric carboxylate complexes [23,25]. Moreover, sunlight is an economical alternative for the expensive UV radiation, and, thus, more and more research is focusing on solar photo-reactors [26,27]. However, there are only few reports on the 1,4-dioxane treatment by photo-Fenton processes [17,28], and none of them considers the application of Fe^0 nor solar radiation.

Fe^0 is an advantageous material for photo-Fenton treatments, exhibiting high UV activation and excellent catalytic performances, while it is fit for environmental applications, as it allows working

with a greatly lesser production of residues [22–24]. In the present investigation, we propose that Fe^0 microspheres could be used in 100% heterogeneous form at neutral pH for the treatment of refractory organics in photo-Fenton process, whereby the produced Fe^{2+} remains anchored on iron surface without any production of Fe^{2+} leaching.

Therefore, the main objective of this work was to assess the degradation of 1,4-dioxane, using Fe^0 microspheres as catalyst of photo-Fenton processes assisted both by solar and UV radiation. The effect of pH and carbonaceous alkalinity were studied and the reagent dose was optimized. The biodegradability enhancement was assessed and the 1,4-dioxane decomposition products were identified. Finally, UV and solar-driven treatments of an alkaline industrial wastewater contaminated with 1,4-dioxane were carried out and the results were compared to other AOPs in terms of process performance and operation cost.

2. Materials and methods

2.1. Materials

Industrial wastewater contaminated with 1,4-dioxane came from a chemical industry (COD = 450 mg/L; pH_0 = 8.6; alkalinity = 900 mg CaCO_3 /L; conductivity = 810 $\mu\text{S}/\text{cm}$; $[\text{Cl}^-]$ = 50 mg/L). Synthetic 1,4-dioxane solutions were prepared with Milli Q grade water. 248 mg/L of 1,4-dioxane (COD = 450 mg/L) was used to simulate the industrial wastewater, while a solution of higher concentration (7300 mg/L of 1,4-dioxane) was used for the chromatographic study of decomposition products. Analytical grade chemicals were supplied by MERCK KGaA (Darmstadt, Germany) and PANREAC S.A. (Barcelona, Spain). For pH adjustments, NaHCO_3 , NaOH and H_2SO_4 were used.

Fe^0 microspheres (>98.3% Fe; <1% C; <1% N; <0.7% O) with 1 μm of particle size and 800 m^2/kg of surface area were obtained from BASF (ZVI Microspheres 800, Ludwigshafen, Germany). The structure of Fe^0 microspheres was analysed by scanning electron microscopy (SEM) – energy dispersive X-ray (EDX) spectroscopy. The analysis of the images was carried out by SEM (JEOL JSM-6400) coupled with an EDX analyser (EDS system).

2.2. Photocatalytic equipment

UV photo-Fenton experiments were performed at room temperature, using a high-pressure mercury immersion lamp of 450 W from ACE-glass (Model 7825-30, Vineland, USA) placed in a quartz glass cooling jacket and located in a vertical manner in the centre of a 2 L-vessel reactor with magnetic stirring. The light intensity on the irradiated liquid surface, recorded with UV-VIS Radiometer RM-21 (UV-Elektronik, Ettlingen, Germany), was 186 mW/cm^2 at the mid-height of the UV-lamp and 1.5 cm from the light source).

Solar photo-Fenton experiments were carried out in a 0.1 L stirring reactor placed in a Solar Simulator supplied by Newport (Irvine, USA) fitted with a Xe lamp of 1000 W/m^2 , a correction filter (ASTM E490–73a) to obtain the solar spectrum under ideal conditions, and a dark screen covering the device to prevent the escape of radiation. The light intensity on the irradiated liquid surface was 98.9 mW/cm^2 at the mid-surface of the Xe lamp (1 cm from the light source).

2.3. Experimental procedure

In UV photo-Fenton, the influence of H_2O_2 dose was studied at following ratios to the initial COD: 4, 2.625, 2.125 and 1.625 ($\text{H}_2\text{O}_2/\text{COD}_0 = 2.125$ was selected based on the stoichiometrical relation

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