More on sonolytic and sonocatalytic decomposition of Diclofenac using zero-valent iron

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ARTICLE INFO

ABSTRACT

The study is an extension of our previous work on sonolytic and sonocatalytic decomposition of Diclofenac-Na (DCF) to depict and highlight further operation parameters of significance, and to assess the effect of a novel home-made catalyst made of magnetic nanoparticles of zero-valent iron (ZVI). It was found that high-frequency was more effective than power ultrasound (20 kHz), and the efficiency was a maximum at 861 kHz, acetate-buffered pH 3.0 and air bubbling provided that samples were prepared from a pre-heated stock solution to enhance solubility of the compound. As such, 40-min sonication rendered nearly complete transformation of DCF to intermediate products that were more biodegradable than itself, but with little mineralization of organic carbon. Catalytic sono-treatment showed that the effect of the catalyst was largest in a non-buffered acidic solution and the rate of DCF elimination increased with increasing concentrations of solids up to a "critical" mass, above which it declined via the coalescence of particles and bubbles. Sonocatalysis using the "effective" solid mass also enhanced the overall degradation or mineralization of the compound as portrayed by the accumulation of chloride and nitrate ions in solution after prolonged contact. The production of excess H_2O_2 during catalysis with ZVI was attributed to the presence of additional and major routes of $^\cdot OH$ and/or H_2O_2 formation (other than water pyrolysis). The initial rate of DCF degradation in the presence of nanoparticles was found highly sensitive to the mass of solids in solution, declining sharply as the mass exceeded a "critical" effective level. A catalyst efficacy factor was defined as a function of the initial mass ratio of Fe^0 to DCF and found to be one order of magnitude larger than that obtained by using commercial microparticles with a threefold larger Fe content. The result signifies that the role of aqueous Advanced Fenton reactions (Fe^0/H_2O_2) was less significant in the presence of nanoparticles relative to that of heterogeneous reactions with reactive Fe and oxygen species on the massive surface areas with enriched reaction/adsorption and nucleation sites.

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1. Introduction

The majority of pharmaceutical wastes in water are composed of anti-inflammatory and analgesic formulations, which are used for human and animal health care as pain relievers and inflammation reducers, respectively. Diclofenac (DCF) is one of the most common anti-inflammatory pharmaceutical that is readily available without prescription and consumed world-wide for the relief of analgesic, arthritic and rheumatic pains. The compound is an emerging contaminant due to the fact that shortly after uptake it is excreted with urine in form of the original compound or one of its metabolites [1], which are only partially eliminated (0–75%) in sewage treatment facilities [2]. Hence, treated sewage effluent may contain not only the original formulation, but also

some of its metabolites (0.7–1.7 μ gL^{-1}), all of which ultimately end up in natural water systems.

The presence of DCF and its metabolic forms in aquatic systems leads to acute toxicity and liver/kidney function damage in fish [3–5]. These and the health effects associated with DCF-contaminated water have promoted the search for innovative treatment processes that target the ultimate destruction of the compound in water or transformation to harmless intermediates. The most promising such treatment alternatives are "advanced oxidation processes" (AOPs), which are recognized with their capacity to generate hydroxyl radicals (OH$^\cdot$) and sludge-free character [6]. Destruction of non-biodegradable compounds by ultrasound is a novel AOP technique, owing to the generation of OH$^\cdot$ via molecular fragmentation of water molecules during implosion of gaseous cavity bubbles. The uniqueness of ultrasound in chemistry arises also from its power to enhance mass transfer and to improve surface properties of solid particles, thus reducing chemical consumption and sludge generation rates [7].

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Current research on the degradability of DCF by ultrasound has shown that complete conversion of the compound to more readily biodegradable forms is possible, but its ultimate mineralization is not [1]. Accordingly, hybrid processes such as sono-ozonolysis and sono-catalysis are effective, as they provide complete degradation and appreciable mineralization of the compound [8–10]. The increase in efficiency by such combinations is related to factors such as enhanced mass transfer rates of gases and solutes, enlarged surface areas of solids, excess bubble nuclei and excess OH· formation.

The use of zero-valent iron (ZVI) separately or in combination with AOPs has also received much attention during the last decade, particularly for the destruction of non-biodegradable micro-pollutants. The potential of the method is based on the reactivity of iron to initiate surface chemistry and advanced Fenton reactions. In the presence of ultrasonic cavitation, ZVI is further effective via the synergy of ultrasound and surface chemistry leading to enhanced mass transport of pollutants to the metal surface with increased surface defects and active sites, the production of H_2O_2 and OH radicals via water fragmentation, and continuous cleaning of the surfaces by mechanical shear forces [10–14]. However, the addition of excess or moderate quantities of H_2O_2 is typical in most of published research related to the use of ZVI in the presence or absence of ultrasound to inducing Fenton-like or advanced Fenton reactions [15–17]. A list of aqueous and surface reactions occurring in sonicated water containing ZVI can be found in the literature [10,18].

The aim of this study was to further investigate the operation parameters of sonochemical elimination of DCF in water (e.g. frequency, pH, sample preparation, sparge gas, ultrasound dose) and to assess the effect of a home-made cost-effective catalyst in form of magnetic nanoparticles of zero valent iron (ZVI) without the addition of H_2O_2. The efficiencies of sonolytic and sonocatalytic processes were evaluated not only by the rate of DCF elimination at optimized conditions, but also by the change in chemical and biochemical oxygen demands and the extent of carbon, chlorine and nitrogen mineralization. The study also encompasses the assessment of OH· production in the presence of the catalyst and comparison of the catalyst efficacy with that of commercial microparticles of ZVI used in the previous study.

2. Materials and methods

2.1. Materials

Diclofenac sodium salt ($C_{14}H_{10}Cl_2NNaO_2$: 318.13 g mol^{-1}) was purchased from Sigma with >98% purity and used as received. The chemical structure and environmental properties of the compound were as given in our previous study [10,19-21].

HPLC grade acetonitrile, KH_2PO_4, phosphoric acid, reagent grade NaOH, $NaHCO_3$, H_2SO_4, H_2O_2, KI, ammonium molybdate tetrahydrate and KHP were all obtained from Merck, Istanbul. The zerovalent iron was made in the laboratory as nano-scale magnetic

particles coated with disordered carbon, iron carbide and graphite (ZVI-I). The chemical/physical composition and average particle size of the catalyst is as listed in Table 1. The particles were synthesized using edible supermarket oils to produce an identical product to that obtained previously by sonication of $Fe(CO)_5$ in diphenylmethane in a two-stage process [22,23]. The coating material was made of air stable $Fe_2C + C$ with a Fe to Fe_2C ratio of 4:1. As such, the product was found highly effective in eliminating TCE and PCE from contaminated water despite the air-stability of the carbon shell wrapping [24].

2.2. Analytical

DCF was analyzed using a Shimadzu LC-20AT HPLC analyzer equipped with an Inertsil ODS-3V column and a 20A UV–Vis photo diode detector set at 254 nm. The mobile phase consisted of 80:20 acetonitrile and 0.01 M KH_2PO_4 buffer flowing at 1 mL min^{-1}. Sample injection volume and retention time were set at 50 μl and 3.7 min, respectively. Alternatively, DCF was analyzed spectrophotometrically at 276 nm using a Unicam Heλios α-Double Beam Spectrophotometer with a 1 cm quartz cell.

Total organic carbon (TOC) was monitored by a Shimadzu TOC-V CSH analyzer operating in non-purgable organic carbon mode. H_2O_2 was analyzed by KI method described by Klassen et al. [25]. COD and BOD_5 were analyzed in accordance with the procedures described in Standard Methods [26]. Concentrations of Cl$^-$ and NO_3^- were analyzed using ICS-3000 Ion Chromatograph (Dionex) and that of Fe by AAnalyst 300 Atomic Absorption Spectrophotometer (Perkin Elmer). The carbon content of nanoparticles was measured using an ECS 4010 elemental combustion system (Costech Instruments).

2.3. Set-up

The reactor was either: (i) a high-frequency plate-type (500 mL), equipped with a 120 W generator (operated at 90% of capacity) and a piezo-electric transducer (22 cm^2) that emitted optionally at 577, 861 or 1145 kHz (Ultraschall/Meinhardt, Germany) or (ii) a low-frequency horn-type (150 mL) connected to a 180 W generator (operated at 30% of capacity) and a piezo-electric transducer (tip area = 1.13 cm^2) emitting at 20 kHz (Bandelin Sonoplus HD2200, Germany). Both were surrounded by water-cooling jackets to maintain constant temperature (22 ± 0.5 °C). The power inputs were adjusted such that the reactors had closely similar specific powers of 0.23 and 0.19 W mL^{-1}, respectively.

2.4. Procedure

2.4.1. Preparation of the magnetite nano-particles (ZVI-I)

Commercially refined and rapeseed corn oils and $Fe(CO)_5$ (99.5% STREM) were used as received without additional purification. A 100 mL solution of 1 M $Fe(CO)_5$ in oil was sonicated for 3 h under argon atmosphere by means of a Sonics and Materials VCX600 ultrasonic device with a direct-immersion titanium horn (surface area = 1 cm^2) and an electric generator operating at 20 kHz and 600 W, respectively. The absorbed acoustic power was measured by the thermal probe method as 0.45 W mL^{-1}. The temperature of the solution was kept at 0–10 °C by a Julabo FT-901 cooler during the reaction. The black solid product after sonication was removed by centrifugation, washed three times with dry pentane inside a N_2-filled glove box, and dried under vacuum at room temperature. Annealing of the solids was performed at 750 °C for 3.5 h under an argon flow (99.996%).

Table 1
Characteristics of the catalyst.

Characteristics	ZVI-NP
Fe (%)	29
Carbon (%)	5.6
Hydrogen (%)	0.008
Sulfur	–
Oxygen	–
Silicon	–
Diameter (nm)	20–100