



Sonochemical treatment of effluent originating from desulfurization process; validation of predictive models



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ABSTRACT

Ultrasound has been shown to have desirable effects on reactions in liquid medium. Enhancement in the reaction rates and the rates of mass transfer due to ultrasound may be attributed to its chemical and/or mechanical effects; generation of free radicals occurs with a great propensity for reaction. In this work, the degradation of specific pollutants (dibenzothiophene sulfone, carboxylic acids and acetonitrile) in the effluent originating from desulfurization process of fuel loaded with dibenzothiophene was studied by the means of ultrasonic enhanced Fenton process. Operating parameters were obtained ($[Fe^{2+}] = 1.98 \text{ mmol dm}^{-3}$, $[H_2O_2] = 20.03 \text{ mmol dm}^{-3}$, pH 3.15) using experimental design technique coupled with numerical optimization. Special emphasis was put on sonochemical process modeling. Experimental data were compared with the values obtained by the previously published model, whereas the sonochemical effectiveness factor (e_{US}) was introduced in the kinetic models to incorporate cavitation phenomena and its influence on conversions. Intrinsic rate constants for the reaction between $\cdot OH$ radicals and organic compounds (k_2) and other kinetic parameters of Fenton process were treated as independent of ultrasound, since e_{US} presents a simplification of complex cavitation steps responsible for the mineralization and degradation rate enhancement. The study resulted in the model applicable for degradation of volatile compounds as well, since pyrolysis in the cavitation bubble was included in the model as a first-order rate constant, k_p . Finally, three-frequency ultrasonic pilot reactor was utilized for the treatment of the effluent. Developed kinetic model was validated accordingly.

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1. Introduction

Nowadays many environmentally attractive alternative processes are studied in various scientific and technological fields. Novel reaction pathways are investigated in aqueous and non-aqueous media leading to applicable catalytic processes for wastewater treatment, petroleum refining, etc. One of those processes is the oxidative desulfurization process which receives a lot of attention recently as an interesting alternative to hydrodesulfurization [1–7]. In contrary to hydrodesulfurization, oxidative desulfurization is characterized by very mild process conditions, producing low and/or ultra-low sulfur diesel fuels. However, the amount of emerging wastewater (hereafter: desulfurization wastewater, DW) still presents a problem. Desulfurization wastewater originated from either the initial addition of aqueous phase in case of ultrasonic assisted oxidative desulfurization or due to the H_2O_2 degradation during the process. Certain wastewater treatment processes have been investigated

recently, including the adsorption of the sulfonic compounds from DW on the various metallic and non-metallic adsorbents and catalytic decomposition, and biological methods that includes microorganisms that use sulfur as food [8–10].

As the addition to existing treatment methods, advanced oxidation processes enhanced by ultrasonic activity appeared as an interesting alternative. Recently, the possibility of treatment of DW arising from the process of oxidative desulfurization by application of ultrasound and Fenton reagent is shown. The studied model sulfur compound was dibenzothiophene sulfone (hereafter: DBTO2) since dibenzothiophene initially present in the fuel was converted to DBTO2 during desulfurization [11].

Application of ultrasonic assisted oxidation, i.e. sonochemical processes, for wastewater treatment represents a technological challenge. Ultrasound has been shown to have desirable effects on both homogeneous and heterogeneous reactions. Enhancement in the reaction rates and the rates of mass transfer due to ultrasound may be attributed to its chemical or mechanical effects or to both simultaneously, meaning that the implosion of microbubbles, i.e. cavities, results in desirable chemical effects by generation of free radicals with a great propensity for reaction [12,13].

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Meanwhile, ultrasonic waves increase the mass transfer rate in an aqueous solution via extreme turbulence [14,15]. The sonochemical reaction scheme is quite complex. There are mainly three reaction sites: cavity interior (bubble), gas–liquid interfacial area and bulk liquid. Accordingly, two main reaction mechanisms are proposed; the substrate either reacts with the hydroxyl radical or undergoes pyrolysis [16,17]. In the interfacial region, a similar reaction occurs but in an aqueous phase. Most of the hydrophobic compounds react inside the cavitation bubble whereas hydrophilic substances react at bulk phase [18].

For all mentioned reasons, ultrasound finds its application for water and wastewater treatment. The effects of ultrasound waves on the hydrophilic chemical oxidations are due to the production of hydroxyl radicals during the cavitation-induced thermal decomposition of water. Sonochemical destruction is also effective for volatile substrates. Particularly, in the case of volatile or hydrophobic compounds, the decomposition proceeds not only via $\cdot\text{OH}$ radicals reaction, but also via direct pyrolysis in the collapsing hot bubbles. Most of the studies concerning ultrasound effects relate to the oxidation of aromatic compounds. In this case, the $\cdot\text{OH}$ radical appears as the main reagent that reacts with the organic target [19 and references therein]. Sonolysis of organic compounds in water solution is generally characterized by a rather low reaction rate constant [20], thus the enhancement of organic compound oxidation is achieved by combined techniques; ultrasound (US)/ O_3 , US/UV ('sonouv'), US/ $\text{TiO}_2/\text{H}_2\text{O}_2$, US/UV/ TiO_2 , etc., and it has been demonstrated in different studies [19,21–23]. As far as concern Fenton type processes, cavitation was found to play a supplementary role in enhancing the efficiency of Fenton processes [24,25]. In order to overcome modeling challenges due to the nature of sonicated system and sequential scale-up of ultrasonic reactors, a comprehensive algorithm was recently proposed for calculation of the sonochemical effectiveness factor and wastewater treatment modeling. The presented approach implies that ultrasound is an auxiliary source of free radicals ($\cdot\text{OH}$) in Fenton type reactions; introduction of ultrasound represents an enhancement of pollutant degradation rates. The sonochemical effectiveness factor was introduced in kinetic models as the e_{US} factor [26,27]. The e_{US} factor was modeled as a function of employed frequency, actual cavitation-related power intensity of ultrasound and a portion of the cavitationally active zone, i.e. dimensionless active volume.

In current study, reported model for e_{US} calculation and a fully developed model describing sono-Fenton oxidation were applied to describe the degradation kinetics of compounds in DW. Due to a presence of volatile compounds, pyrolysis in the cavitation bubble has been taken into account in current research. It has been shown that developed models and the underlying assumptions are valid for different ultrasonic reactor configurations and different initial composition of treated wastewater.

2. Methodology

2.1. Wastewater and auxiliary chemicals

The degradation experiments were performed with the samples of real wastewater obtained after oxidative desulfurization (hereafter: DW) and model solutions of target pollutants (DBTO₂, formic acid, acetonitrile and their mixture denoted hereafter as MDW). A typical sample of desulfurization wastewater contains: DBTO₂ ($c_0 = 16.61 \text{ mg L}^{-1}$ as matching solubility in water), carboxylic acid (formic and acetic) and acetonitrile as main pollutants. The samples were treated as received from desulfurization process (Laboratory for Petroleum Engineering, Petroleum and Petrochemical Department, Faculty of Chemical Engineering and Technology, University of Zagreb, Croatia) [11]. Model solutions

of DBTO₂, formic acid, acetonitrile and their mixture (are prepared following the usual concentration of these pollutants reported in related studies: $c_{0,\text{DBTO}_2} = 16.61 \text{ mg L}^{-1}$, $c_{0,\text{formic acid}} = 120 \text{ mg L}^{-1}$, $c_{0,\text{acetonitrile}} = 240 \text{ mg L}^{-1}$. Note that DW sample consists for both formic and acetic acid, but only formic acid was chosen as model compound for detailed kinetic study.

All reagents used in this work were analytical or HPLC grade and used without any further purification. Reagents for the Fenton type reactions were as follows; ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and hydrogen peroxide (H_2O_2 , 30%), all supplied by Kemika, Croatia. Other chemicals were as follows; sulfuric acid (H_2SO_4 , 50%) used for the pH adjustment. Standards for specific pollutants were obtained by Sigma.

2.2. Instrumental set-up and analyses

Different configurations of reactors were used for the sonication experiments: cylindrical reactor with homogenizer (HCR) and three-frequency hexagonal cell, i.e. ultrasonic pilot reactor prototype (PP) [27]. HCR was assembled using different cylindrical borosilicate glass reaction vessel with working volume from 0.1 to 0.5 L (from 4 to 9 cm in diameter, respectively), equipped with cooling water-jacket. Vessels were equipped with the magnetic stirrer to avoid dead zones near the bottom. Ultrasound was produced by using the ultrasonic homogenizer, SONOPLUS HD 3200, Bandelin, Germany, that consists of a generator, ultrasonic converter (model SH70G; including transducer, booster and horn) and a probe tip (thin plate) made of titanium alloy (TT13). Homogenizer operates at 20 kHz, with the nominal power of 200 W. The observed power efficiencies varied from 65% to 72% in different experiments. Ultrasonic probe was immersed in the reaction mixture and placed vertically in the middle of the vessel. The prototype of ultrasonic pilot reactor (PP) was assembled by Lab Air Media Ltd. (Croatia) and it consists of a hexagonal cell (reaction volume of 12.5 L) with ultrasonic transducers placed on three sides (20, 68 and 120 kHz; 320 kHz per side), corresponding generators, vessels for recirculation (30 L in total) and exhaust and pumps. The schematics of the both reactor configuration were given in our previous papers [24,26].

Experiments without sonication were performed as jar-tests in glass reaction vessels with the maximum reaction volume of 0.5 L and constant magnetic stirring (650 rpm) at room temperature ($23 \pm 4 \text{ }^\circ\text{C}$).

The pH of the reaction mixture was adjusted using the pH meter (Handylab pH/LF 12, Schott, Germany). Prior to experiments, pH was adjusted at given pH value for Fenton oxidations, which was followed by the addition of iron salt and hydrogen peroxide. The concentration of Fenton reagent was varied in certain manner to find the optimal composition (see next subsection).

Mineralization extents in DW, MDW and model solution of formic acid and acetonitrile were determined based on total organic carbon content measurements (TOC), performed by using a total organic carbon analyzer; TOC-V_{CPN} 5000A (Shimadzu). The exact concentration of DBTO₂ was monitored using GC measurements (GC-2014, Shimadzu, with wax column); temperature range for analysis was 100–270 $^\circ\text{C}$, carrier gas was N_2 (90 kPa).

In order to obtain data necessary for modeling, calorimetry was used to determine the portion of ultrasonic power utilized for cavitation [26]. Prior to calorimetric measurements, reactors were insulated by 2 cm thick polyurethane foam and a silicon foil. Temperature was measured by conductometer with integrated temperature sensor (Pt1000; Handylab pH/LF 12, Schott, Germany). The result for the cavitationally active zone (Δ_{US}) in HCR and PP was taken from the previous studies [26,27], where it was determined based on the sonochemiluminescence observation and imaging, and experimental determination based on aluminium

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