

# Wastewater Treatment with the Fenton Process

## Principles and Applications

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## 9 Toxicity of the Catalyst and Products Formed in the Process

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# 9 Toxicity of the Catalyst and Products Formed in the Process

During the heterogeneous Fenton process, a great amount of compounds is generated, which can be toxic to the environment. There is a possibility that after the treatment process, by-products with more toxic properties than parent compounds will appear [1]. Long-term use of iron oxides is friendly for the environment due to saving the natural resources in deposits. However, the lack of stability of the compound can result in its release into the environment. Katsnelson *et al.* [2] confirmed that the particle size may also affect the toxicity of the catalyst. Based on an equivalent mass dose, nanoparticles have more significant toxicity than micro-particles due to the penetration of the particles into the cell and disruption of them. Then, nanoparticles cause mechanical damage and cause local inflammation. Inside the cells, nanoparticles agglomerate and disrupt the functions of organelles and membrane transport [3]. Moreover, nano-Fe<sub>2</sub>O<sub>3</sub> can also be generated due to secondary formation [2]. Some nanoparticles are characterized by biocidal, biostatic, and even self-cleaning properties, which encourages researchers to use them in wastewater treatment despite the potential hazard [4].

Therefore, it is essential to constantly work on the stability of the catalyst used in the process and check if it poses any threat to living organisms. Studies are carried out on various types of organisms, such as bacteria, plants, and even higher animals like mammals. In the research performed on *Xanthobacter flavus* FB71, Wang *et al.* [5] noticed the inherence of toxic compounds, which can adversely affect the development after the process [5]. Büyüksönmez *et al.* [6] associated harmful effects with the production of hydroxyl and other oxygen-based radicals. The cells launched a protective mechanism against oxygen radicals, which increased catalase activity [6]. Iron oxides, commonly used as catalysts in the Fenton process, are considered to be nontoxic. Yet, it has been reported that *Ceriodaphnia dubia* accumulates nano-Fe<sub>2</sub>O<sub>3</sub> as a result of ingestion. Additionally, the compound also serves as a carrier of As<sup>5+</sup> and therefore increases toxicity [7].

The toxicity of the compounds against *Escherichia coli* and *Saccharomyces cerevisiae* was observed in the research performed by Schwegmann *et al.* [8]. They found that in the highest concentration of FeO<sub>x</sub>, the survival rate was reduced to 1 and 25%, respectively. It also needs to be noted that the decrease in viability was dose-dependent, and the antibacterial effect was strictly related to the nanosize of particles [8].

Brunner *et al.* [9], demonstrated the cytotoxicity of the Fe<sub>2</sub>O<sub>3</sub> to the rodent 3T3 fibroblast cells and human mesothelioma cell line (MSTO). They observed a cell-type specific response, as slower-growing 3T3 cells were only slightly affected by

the addition of up to 30 ppm iron oxide. However, 3.75 ppm of iron oxide reduced the cell parameters MTT-conversion and DNA content of faster proliferating MSTO cells. In addition, Pisanic *et al.* [10] noticed that the cytotoxicity of the same compound to the cell line derived from a pheochromocytoma of the rat adrenal medulla (PC12 cells). The magnetite and the other iron oxides used in nanoscale can oxidize, reducing pollutants' toxicity to mammalian cells. This research correlates the low neurotoxicity of cells with low redox activity [11].

In the heterogeneous Fenton process, contaminants are decomposed due to rapid oxidation in the presence of a catalyst [12]. In such a reaction, pollutants are transformed into simpler compounds that are usually less toxic [12,13]. However, as a consequence of incomplete mineralization also hazardous, potentially toxic compounds may occur in the effluent [12,14]. Therefore, great efforts and concerns need to be taken, as the toxicity of by-products also must be checked.

Cleveland *et al.* [15] evaluated the toxicity of effluent of degradation of bisphenol A (BPA) by carbon nanotube-supported  $\text{Fe}_3\text{O}_4$  used in heterogeneous Fenton process against *E. coli*. In addition to the nearly complete removal of BPA and significant removal of COD, they observed almost no inhibition of *E. coli* in the presence of final reaction effluents [15].

GilPavas and Correa-Sánchez [16] performed acute toxicity tests with *Artemia salina* on textile wastewater treated with a heterogeneous electro-Fenton process assisted by scrap zero-valent iron. They noted that untreated wastewater caused a 100% mortality, which also remained in the samples treated for 30 and 60 min. Because biodegradability had increased significantly, they connected the high toxicity of effluent with the formation of harmful compounds. It is worth noting that after combination with activated carbon treatment, the toxicity was reduced to 10 and 20%, respectively [16]. In another approach, GilPavas and co-workers [17] once again compared the toxicity of textile wastewater against *A. salina*. This time they utilized scrap zero-valent iron as the replacement for dissolved iron in the Fenton process. Compared with samples of untreated wastewater, they observed a 67% decrease in mortality of *A. salina*. They also compared obtained results with the mortality of *A. salina* in a pure grow medium. This ensured that the transformation of the chemical composition of treated wastewater corresponds to a decrease in toxicity [17]. Lan *et al.* [18] carried out heterogeneous photodegradation of pentachlorophenol (PCP) with goethite, hematite, and oxalate under UVA illumination. To evaluate the toxicity, they utilized a Microtox analyzer, a standardized method of measuring acute toxicity against marine bacterium *Vibrio fischeri*. In terms of light loss, which is the basis of this approach, they confirmed the detoxification of PCP. For the samples (1.2 mM) after 1 hour of treatment, they observed a decrease in the ratios of light loss from 83 and 84% to 54 and 46% for goethite and hematite, respectively. Additionally, they checked qualitatively for intermediates from PCP degradation. Interestingly, more active substances could be generated in the case of hematite than goethite. This confirms that by-products were responsible for the slightly greater toxicity of effluent obtained with hematite as the catalyst [18].

A high increase in toxicity due to the degradation of tetracycline in an ultrasound-assisted heterogeneous Fenton process with magnetite as a catalyst was reported by Hou *et al.* [19]. In a 48-hour immobilization assay with *Daphnia*

*magna*, they found a 60% mortality rate caused by a raw tetracycline solution. After 60 minutes of treatment, 100% of *D. magna* was immobilized. Observed toxicity was connected with by-products formed in tetracycline degradation, identified by liquid chromatography (LC) tandem mass spectrometry (MS). Interestingly, mentioned by-products exhibited high acute toxicity only at high concentrations, while no decayed toxicity was observed at low ones. Consequently, after 180 min of treatment, the mortality rate was only 55%, and therefore prolonging the time of reaction reduced the acute toxicity of *D. magna* [19].

The larger organisms against which scientists checked process safety are plants such as *Phaseolus mungo* and the mung bean. Saratale *et al.* [1] checked the phytotoxicity of dye effluents and products of the process and used for it the *P. mungo*. The inhibition of seed and length germination and length of the plum roots were not noticed in the products of the process. A significant deterioration of germination capacity and reduction in the length of the rootlets in the tests carried out on the sludge, and the dye was however observed [1]. Kumar *et al.* [20] performed a toxicity test, in which they noticed a change in the germination efficiency of mung bean (*Virginia radiata*) and its root length. After seven days of the test, they noticed germination of seed growth of 0.2 cm for untreated wastewater. However, in the case of treated wastewater, the seed root has grown to 28 cm, which proves a decrease in toxicity due to the Fenton process [20].

Gonzalez-Gil *et al.* [21] performed phytotoxicity tests such as acute ecotoxicity. In terms of analysis, they performed mitochondrial activity studies, chronic biological tests, and quantification of chlorophyll on *Polystichum setiferum* spores. Ecotoxicological tests noticed the high efficiency of the process by reduction of the acute toxicity of river water samples. However, chronic toxicity, which was checked in the post-treatment samples, occurred. Other unanalyzed toxic substances, probably of inorganic nature and potentially harmful to plant development, were also released [21].

Chatzimarkou and Stalikas [22] carried out the degradation of estriol with magnetite and graphene oxide composites in the heterogeneous Fenton process. Consequently, they evaluated the toxicity of products of degradation against zebrafish larvae. They did not notice a difference in the lethality of zebrafish larvae due to the Fenton treatment of estriol. Moreover, malformation of larvae also did not occur [22].

The largest organisms used in toxicity tests were mammals such as rats. The acute toxicity of the degradation intermediates was determined utilizing the TEST software. Before the process, the LD<sub>50</sub> value of about 1,650 mg/kg was considered to be toxic. Guo *et al.* [23] noticed a 50% lethal dose of the rat (LD<sub>50</sub>) and developmental toxicity. After the treatment process, intermediates LD<sub>50</sub> were described as very toxic and toxic. The LC<sub>50</sub> was significantly lower for the intermediates than in the starting dye and therefore was described as a non-toxic development factor [23].

The critical element of every process is intermediates and by-product generation, which can be hazardous to the environment. Intermediates formed as by-products of the process can sometimes be toxic, as shown in Table 9.1. The intensity of the

TABLE 9.1

## Selected Intermediates of Treatment during the Heterogeneous Fenton Process

Processes	Compounds	Intermediates of the Purification Process	Reference
Combination of ultrasonic and Fenton processes in the presence of magnetite nanostructures prepared by high-energy planetary ball mill	Acid Blue 185	2-methylpropanoic acid, Decanoic acid, Benzenebutanoic acid, tert-butyl dimethyl ester, Phthalazine, 1-phenyl, 1,2,3,4-Tetrahydroisoquinoline, 6,7,8-trimethoxy-1,2-dimethyl, 1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester, 3-ethyl-5-(2-ethylbutyl)- Octadecane	[24]
Heterogeneous oxidation by the Fenton method in an aqueous solution studied on nanometric magnetite (Fe <sub>3</sub> O <sub>4</sub> ) as a catalyst provided by a high-energy planet ball milling process	Ciprofloxacin	Acetamide, 4-(2-ethoxy-1-hydroxyallyl)phenol, 1-(tert-butyl)-3-methylbenzene, N-(4-(3-hydroxypyrrolidin-1-yl)but-2-yn-1-yl)-N-methylacetamide, 1,2,3,4,5-pentamethylbenzen, -(2,6-dihydroxyphenyl)ethenone, 1,2,3,4,5,6-hexamethylbenzene, 5,8-dimethyl-1,2,3,4-tetrahydroacridin-9-amine, 7-isopropyl-1,4-dimethylazulen, 3-diisopropyl naphthalen	[25]
Plant fluidized-bed heterogeneous Fenton process	Azo dye	Nitrobenzene, Phenol, Quinone, Propanedioic acid, 1,2-Benzenedicarboxylic Acid, propanamide, Pentanoic acid	[26]
Heterogeneous Fenton system with a nanoscale zero-valent iron	Chlorpheniramine	4-Hydroxy-4-methyl-2-pentanone, 2-Methylaminopyridine, 4-Chlorophenol, 2-Propionylpyridine, 2-Acetylpyridine, 4-Chlorophenyl-2-pyridyl ketone	[30]
Heterogeneous electro-Fenton process using Cu-doped Fe/Fe <sub>2</sub> O <sub>3</sub>	Tetracycline	C <sub>21</sub> H <sub>18</sub> O <sub>8</sub> N <sub>2</sub> Me, C <sub>21</sub> H <sub>21</sub> O <sub>6</sub> N <sub>2</sub>	[31]
Process catalyzed by magnetic porous carbon spheres derived from the chelating resin	Methylene blue	mono-chlorophenol, catechol, 2-chlorohydroquinone, iminodiacetic acid, oxalic acid, acetic acid, and formic acid	[32]
Heterogeneous Fenton with Fe-TiO <sub>2</sub> Visible	Atrazine	2-chloro-4-ethylamino-6-propanolamine-1,3,5-triazine; 2-Chloro-4-acetamido-6-isopropylamino-1,3,5-triazine; 2-hydroxy-4,6-dinitro-1,3,5-triazine; 2-chloro-4-amino-6-isopropylamino-1,3,5-triazine; 2-chloro-4-amino-6-nitro-1,3,5-triazine; 2-chloro-4-ethylamino-6-amino-1,3,5-triazine; 2-hydroxy-4-amino-6-isopropylamino-1,3,5,	[33]

<p>Degradation of diazinon from aqueous solutions by electro-Fenton process</p>	<p>Diazinon</p>	<p>-triazine; 2-chloro-4,6-dihydroxy-1,3,5-triazine; 2-chloro-4,6-diamino-1,3,5-triazine; Cyanuric acid; Ammelide; 2-hydroxy-4,6-diamino-1,3,5-triazine                  [34]                  O,O-diethyl O-(2-isopropyl-6-methylpyrimidin-4-yl) phosphorothioate; O,O-diethyl O-(2-hydroxy-6-methylpyrimidin-4-yl) phosphorothioate; diethyl (2-isopropyl-6-methylpyrimidin-4-yl) phosphate; 2-isopropyl-6-methylpyrimidin-4-ol; O,O-diethyl O-hydrogen phosphorothioate; diethyl hydrogen phosphate; 2-isopropyl-4-methylpyrimidine; 4-methylpyrimidin-2-ol; 4-methylpyrimidine; (Z)-3-imino-N-methylprop-1-en-1-amine; ethane-1,2-diamine; ethyl methyl hydrogen phosphate; methyl dihydrogen phosphate; phosphoric acid; O-ethyl O-methyl O-hydrogen phosphorothioate; O-ethyl O,O-dihydrogen phosphorothioate; phosphorothioic O,O,O-acid                  [23]</p>
<p>Pulsed discharge plasma with heterogeneous Fenton process using Fe<sub>3</sub>O<sub>4</sub> nanocomposites</p>	<p>Chloramphenicol</p>	<p>oxoammonium, 4-hydroxybenzoic acid,                  [35]</p>
<p>Wastewater treatment with heterogeneous Fenton-type catalysts based on porous materials</p>	<p>EDTA</p>	<p>IMDA, glycine, ED3A, U-EDDA, S-EDDA, EDMA, EDA,                  glyoxalic acid</p>
<p>Heterogeneous Fenton process mediated by SiO<sub>2</sub>-coated nano zero-valent iron</p>	<p>p-ASA organic arsenic contaminants</p>	<p>Analine, phenol, p-Benzoquinone, p-Aminophenol, p-Hydroquinone, Fumaric acid, Maleic acid, trans,trans-2,4-Hexadienedioic acid                  [36]</p>

process and the cost of technology selection and treatment depend on detected intermediate compounds. The type of intermediates depends on the kind of removed pollutant. Therefore, it is essential to identify and recognize by-products while determining the toxicity of the process. The most common methods of estimating the intermediates in the heterogeneous Fenton process utilize sophisticated techniques such as gas chromatography coupled with mass spectrometry (GC-MS) or high-performance liquid chromatography with a mass spectrometer (HPLC-MS). Selected results are shown in Table 1.1. Acisil *et al.* [24], noticed seven intermediates after the process, while Hassani *et al.* [25] identified ten compounds such as acetamide, 4-(2-ethoxy-1-hydroxyallyl), phenol, 1-(tert-butyl)-3-methylbenzene, and 1,2,3,4,5-pentamethylbenzene. Aghdasinia *et al.* [26] identified seven by-products, especially nitrobenzene, phenol, quinone, propanedioic acid, 1,2-benzenedicarboxylic acid, propenamide, and pentatonic, after azo dye degradation. Guo *et al.* [23] noticed the generation of the intermediates mentioned above by the reduction of the aromatic protein compounds and soluble microbial. They identified it with two methods: catalytic plasma and LC-MS. Firstly, the phenyl nitrile is reduced due to the weaker dissociation energy. In the next stage of the process, the amine group oxidation, hydroxyl addition, and carboxyl are substituted [27]. Also, it breaks down bonds in compounds such as CeN and CeC. The aromas broke the benzene ring and formation of organic (formic, acetic, and oxalic) and inorganic acids [28]. During the process, organic acids are oxidized. The final products of the process are neutral, harmless, natural compounds such as water and carbon dioxide. Hydrogen peroxide can react with aromatic organic by breaking the bond and adding or removing hydrogen to the original structure of the compound [29].

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