

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.

For more information visit www.intechopen.com



Fenton's Process for the Treatment of Mixed Waste Chemicals

Cláudia Telles Benatti¹ and Célia Regina Granhen Tavares²

¹*Faculdade Ingá – UNINGÁ,*

²*Universidade Estadual de Maringá – UEM,
Brazil*

1. Introduction

In recent years, with an increase in the stringent water quality regulations due to environmental concerns, extensive research has focused on upgrading current water treatment technologies and developing more economical processes that can effectively deal with toxic and biologically refractory organic contaminants in wastewater. In this context, in order to avoid or mitigate the possible adverse health, safety, and environmental impacts, to grantee compliance with federal, state, and local environmental laws, or only to set an example to students, many institutions of higher education have supported researches that aim to establish a treatment process for practical and economic disposal of waste chemicals. Waste chemicals in academic laboratories are by-products of research, teaching and testing activities. Waste chemicals from academic research laboratories can be considered one of the most polluting wastewaters and they pose more problems for the treatment and subsequent adequate disposal, due to their unique characteristics. These wastes are generated by laboratory operations, such as chemical analysis and research activities, including chemical and biological treatment experiments on a wide range of synthetic and natural wastewaters, and may include an abundance of unused laboratory reagents. Thus, they may present a great diversity of composition and volume, including refractory organics, toxic compounds and heavy metals, and may offer potential hazards to both health and environment.

The ultimate destination of waste is usually a treatment, storage, and disposal facility (National Research Council, 1995). The treatment of waste chemicals is typically via chemical action, such as neutralization, precipitation and reduction to yield a less toxic waste. However, in most cases, the treatment product still cannot be safely disposed of in the sanitary sewer. Most generators also adopt the practice of land filling or direct incineration of hazardous wastes. In this scenario, the development of economical methods to achieve a high degree of wastewater treatment is highly desirable.

The development and application of several Advanced Oxidation Processes (AOPs) to destroy toxic and biologically refractory organic contaminants in aqueous solutions concentrated significant research in the field of environmental engineering during the last decades. Among AOPs, the Fenton's reagent is an interesting solution since it allows high depuration levels at room temperature and pressure conditions using innocuous and easy to handle reactants. The inorganic reactions involved in Fenton process are well established

and the process has been used for the treatment of a variety of wastewaters. The high efficiency of this technique can be explained by the formation of strong hydroxyl radical ($\bullet\text{OH}$) and oxidation of Fe^{2+} to Fe^{3+} . Both Fe^{2+} and Fe^{3+} ions are coagulants, so the Fenton process can, therefore, have dual function, namely oxidation and coagulation, in the treatment processes (Badawy & Ali, 2006). It is essential, though, to investigate and set the operating conditions that best suits the wastewater that are being treated in order to achieve high degradation efficiencies.

In previous research work, chemical oxidation using Fenton's reagent was tested as a treatment method for mixed waste chemicals and optimized using a response surface methodology (Benatti et al., 2006). As predicted, the process optimization led to high COD removal (92.3%), with a high efficiency in the removal of heavy metals as a side effect. However, its major disadvantage is the production of $\text{Fe}(\text{OH})_3$ sludge that requires further separation and proper disposal, with the consequent increase in operation costs. To overcome the drawback, the knowledge of the treatment process residue characteristics is imperative to design a successful waste management plan that may guarantee the viability of the applied technology to the wastewater treatment.

Most studies focused on applying the Fenton process to wastewater treatment and do not take into account the generated residues. Using the previously optimized set of process variables, the effects of Fenton's reagent treatment of mixed waste chemicals are thoroughly discussed in the current chapter. The whole process was analysed from an environmental perspective, where the focus was not only the treatment of the wastewater, but also the characterization for correct final destination of the solids originating from the treatment process. Furthermore, the process was applied to wastewaters generated in different periods in order to study the effect of wastewater composition on the process efficiency.

This chapter also discusses about the unique nature of waste chemicals, presents different applications of Fenton's reagent on the treatment of a variety of wastewaters, and provides an insight into the Fenton's reaction mechanisms and some background on their operations conditions.

2. Theoretical approach

Advanced oxidation processes (AOPs) are based on the generation of very reactive species such as hydroxyl radical ($\bullet\text{OH}$), a nonspecific, strong oxidant which reacts with most organic and biological molecules at near diffusion-controlled rates ($>10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Büyüksönmez et al., 1999). Common AOPs involve Fenton and Fenton "like" processes, ozonation, photochemical and electrochemical oxidation, photolysis with H_2O_2 and O_3 , high voltage electrical discharge (corona) process, TiO_2 photocatalysis, radiolysis, wet oxidation, water solutions treatment by electronic beams or γ -beams and various combinations of these methods (Kušić et al., 2007). Among AOPs, Fenton's reagent has been used (either alone or in combination with other treatments) as a chemical process for the treatment of a wide range of wastewaters. Recent applications of Fenton's reagent include the pre-treatment of olive mill wastewater (Lucas & Peres, 2009), the treatment of landfill leachate (Deng & Englehardt, 2006; Zhang et al., 2005), copper mine wastewater (Mahiroglu et al., 2009), water-based printing ink wastewater (Ma & Xia, 2009) and cosmetic wastewaters (Bautista et al., 2007), the degradation of pesticide (Li et al., 2009; Chen et al., 2007), antibiotic (Ay & Kargi, 2010; Elmolla & Chaudhuri, 2009), high-strength livestock wastewater (Lee & Shoda, 2008) and organic compounds of nuclear laundry

water (Vilve et al., 2009), the oxidation of combined industrial and domestic wastewater (Badawy & Ali, 2006), the pre-oxidation of pharmaceutical wastewaters (Martínez et al., 2003), the treatment of water-based paint wastewater (Kurt et al., 2006) and cellulose bleaching effluents (Torrades et al., 2003), the degradation of the explosives 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) after iron pre-treatment (Oh et al., 2003), and the treatment of different streams of textile wastewaters, such as the treatment of hot desizing wastewaters (Lin & Lo, 1997), and the treatment of dye wastewaters (Wang et al., 2008; Gulkaya et al., 2006).

Fenton's reagent is also combined with biological process, as a pre-treatment to enhance the biodegradability of the recalcitrant compounds and lower the toxicity (Padoley et al., 2011, Mandal et al., 2010, Badawy et al., 2009) or as a post-treatment to improve the efficiency of the wastewater treatment (Ben et al., 2009, Yetilmezsoy & Sakar, 2008).

Fenton's reagent, which involves homogenous reaction and is environmentally acceptable (Bham & Chambers, 1997), is a system based on the generation of very reactive oxidizing free radicals, especially hydroxyl radicals, which have a stronger oxidation potential than ozone; 2.8 V for $\bullet\text{OH}$ and 2.07 V for ozone (Heredia et al., 2001). The Fenton's reactions at acidic pH lead to the production of ferric ion and of the hydroxyl radical (Garrido-Ramírez et al., 2010; Gallard & De Laat, 2001; Walling, 1975):



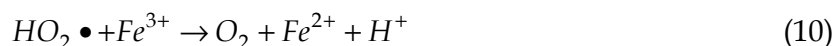
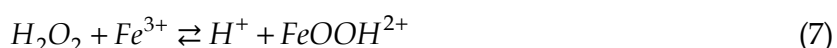
Hydroxyl radicals may be scavenged by reaction with another Fe^{2+} or with H_2O_2 (Torrades et al., 2003; Chamarro et al., 2001; Lu et al., 1999):



Hydroxyl radicals may react with organics starting a chain reaction (Bianco et al., 2011; Dercová et al., 1999):



Ferrous ions and radicals are produced during the reactions as shown below (Lu et al., 1999):



The efficiency of this process depends on several variables, namely temperature, pH, hydrogen peroxide, ferrous ion concentration and treatment time. The oxidizing potential of the hydroxyl radical is pH dependent, and varies from $E^0 = 1.8$ V at neutral pH to +2.7 V in acidic solutions (Buxton et al., 1988, as cited in El-Morsi et al., 2002). Operating pH of the system has been observed to significantly affect the degradation of pollutants (Benitez et al., 2001; Kang & Hwang, 2000; Nesheiwat & Swanson, 2000; Lin & Lo, 1997). The degree of oxidation of organics with Fenton's reagent is maximum when the pH lies in the interval pH 3–5 (Lunar et al., 2000; Lin & Lo, 1997). Hydrogen peroxide is most stable in the range of pH 3–4, but the decomposition rate is rapidly increased with increasing pH above 5. Thus, the acidic pH level around 3 is usually optimum for Fenton oxidation (Gogate & Pandit, 2004; Neyens & Baeyens, 2003). However, in order to achieve high performances, these experimental conditions must be optimized (Homem et al., 2010). Some environmental applications of Fenton's reagent involve reaction modifications, including the use of high concentrations of hydrogen peroxide, the substitution of different catalysts such as ferric iron and naturally occurring iron oxides, and the use of phosphate-buffered media and metal-chelating agents. These conditions, although not as stoichiometrically efficient as the standard Fenton's reactions, are often necessary to treat industrial waste streams and contaminants in soils and groundwater (Büyüksönmez et al., 1999).

3. Materials and methods

3.1 Materials

All chemicals employed in this study were analytical grade. All solutions were prepared in distilled-deionized water. Glassware used in metals determination was washed with detergent, rinsed with tap water, soaked with HNO_3 (~50% v/v) for 24 h, and rinsed with distilled-deionized water prior to drying.

Reagent grade H_2O_2 was standardized using iodometric titration (U.S. Peroxide, 2003) and used as purchased. A 1 M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ stock solution was prepared and standardized (Pavan et al., 1992) just before Fenton's experiments. Solutions of NaOH and H_2SO_4 were used for pH adjustments.

3.2 Sample preparation

Chemical effluents generated during the laboratory operations over a period of 17 months were monitored, collected and stored in clearly marked containers. Later on these effluents were divided into two groups and then mixed to obtain two combined samples (sample 1 and 2), produced in different periods of time that were used in the experiments of Fenton's oxidation.

3.3 Fenton's experimental procedure

The Fenton's oxidation experiments were carried out under optimal conditions established in previous work (Benatti et al., 2006): ratio $[\text{COD}]:[\text{H}_2\text{O}_2] = 1:9$; ratio $[\text{H}_2\text{O}_2]:[\text{Fe}^{2+}] = 4.5:1$ and pH 4.

Experiments were carried out in 250 mL beakers with a solution volume of 150 mL that consisted of laboratory effluent without solids separation. The effluent was continuously mixed (100 rpm) in a jar test apparatus at room temperature. Firstly the pH of the solution was adjusted to 4 with NaOH (~30% w/v), and a sample was withdrawn and centrifuged at 2500 rpm for 5 min for the separation of suspended solids and COD_0 was determined in

supernatant. The required amount of reagents was determined according to COD_0 value. The amount of $FeSO_4$ was first added to the reaction mixture. The Fenton reaction was then initiated by sequential addition of the required amount of H_2O_2 , in three steps of equal volume added at intervals of 20 min, to moderate the rise in temperature that occurs as the reaction proceeds and to minimize quenching of $\bullet OH$. The pH adjustments were performed using H_2SO_4 or $NaOH$ solutions before each reagent addition and then at each hour. The Fenton reaction time was initiated by the addition of the first required amount of H_2O_2 to the reaction mixture. After reactions were completed (4 h), precipitation of the oxidized iron as $Fe(OH)_3$ was performed by adjusting the pH to 8 and then about 15 h of clarification under quiescent conditions. Final samples of supernatant were taken for COD measurements and for determination of residual hydrogen peroxide. All experiments were performed in duplicate.

The wastewater was also characterized in terms of pH, apparent color, turbidity, total phenols, sulfate, sulfide, chloride, total phosphorous, nitrogen and metals content (Ag, Al, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb and Zn) before and after the Fenton's oxidation experiments.

3.4 Fenton's residues characterization

The Fenton's reagent residues were characterized through leaching tests, chemical fractionation and analysis of X-ray diffraction.

Sludges obtained at the end of the Fenton's process were named for ease of notation as residues 1 and 2 according to their originating effluent samples, and each one was divided into two portions. The first portion was transferred to an amber glass flask and preserved at 4 °C for leaching tests. The second one was filtered under vacuum, rinsed with distilled-deionized water to eliminate the excess of sodium hydroxide, and then dried at 105 °C. The dried solids were removed from the filter, grinded and homogenized in a porcelain mortar, and stored for chemical fractionation and analysis of X-ray diffraction.

The leaching tests were carried out according to the Brazilian methodology (ABNT, 1987a). In these tests, 100 g of sludge was filtered through 0.45 μm cellulose ester membranes, the liquid phase was stored at 4 °C and the membranes containing the solid phases were transferred to 500 mL glass beakers. Distilled-deionized water (1:16) was added along with a sufficient quantity of acetic acid (0.5 N) to adjust the pH to 5.0 ± 0.2 . The suspension was stirred for 24 h. A pre-calculated amount of distilled-deionized water was then added to the suspension, the separation of phases was performed by filtering in 0.45 μm cellulose ester membrane, and the obtained solution was mixed with the stored liquid phase initially obtained. The mixed liquor was then preserved at 4 °C for metals determination. After analysis, the residues were classified according to ABNT-10004 (ABNT, 1987b) with regard to the maximum limits obtained in the extracts.

The chemical fractionation of solid residues was carried out by use of the following sequential dissolution procedure:

- Step 1.** Exchangeable ions were removed at room temperature for 1 h with magnesium chloride solution (1M $MgCl_2$, pH 7.0) and continuous agitation in Erlenmeyer flasks, using 1 g of dried precipitate and 8 mL of extractant, according to the methodology of Tessier et al. (1979).
- Step 2.** Amorphous material was removed by acid ammonium oxalate (pH 3.0) in a 4 h extraction in Kjeldahl flasks kept in the dark and at room temperature, using 1 g of

dried precipitate and 100 mL of extractant, according to the methodology proposed by Camargo et al. (1986).

Step 3. Free Fe-oxides were removed from 0.5 g of dried samples by Na-dithionite-citrate-bicarbonate system in Kjeldahl flasks according to the methodology of Mehra & Jackson (1960).

Step 4. The residues remaining from Step 3 as well as the original samples were digested with a 2:1 mixture of nitric and perchloric acids.

Between each successive extraction, separation was performed by filtering the suspension through a 0.45 µm cellulose ester membrane. During filtration the residues were washed with distilled-deionized water. The liquid phase was transferred to volumetric flasks, diluted to mark, transferred to amber glass flasks, acidified to pH < 2 with concentrated nitric acid and preserved at 4 °C for metal determinations. The solids were transferred with a porcelain spoon and rinses of distilled-deionized water to a tare porcelain crucible and dried at 105 °C, cooled under vacuum in a desiccator, and weighed for weigh loss determinations. The solids were then crushed, manually homogenized using a porcelain spoon, dried again at 105 °C for moisture removal, and stored in a desiccator until ready for use in the next extraction step. These procedures were performed in three or more replicates.

The original dried solids as well as the solids from each extraction phase were analyzed by X-ray diffraction (XRD) using a Shimadzu D6000 diffractometer (Cu K α radiation and $\lambda = 1.54178$ Å; scanning speed 2° 2 θ min⁻¹ for the ranges 5–70° 2 θ). The mineralogical phases identification in generated X-ray diffractograms was performed by the position and intensity of diffraction planes. The amorphous phase diffractograms were determined by DXRD according to Schulze (1994), by subtraction of diffractograms intensity of original samples and of residues obtained after amorphous phase extraction.

3.5 Analytical methods

pH was measured with a Digimed-DM-20 pH meter calibrated with pH 4.01 and 6.86 Digimed standard buffers. The analyses of COD, settleable solids, total phosphorous and soluble sulfate (turbidimetric method) were performed in accordance with standard methods (APHA-AWWA-WEF, 1998). Residual hydrogen peroxide was determined by the iodometric titration method (U.S. Peroxide, 2003). Total phenols were measured according to the colorimetric method of Folin-Ciocalteu reagent (Scalbert et al., 1989). Real and apparent color, turbidity, and sulfide were measured spectrophotometrically (spectrophotometer DR/2010, HACH, Loveland, CO) using the APHA platinum-cobalt standard method, the attenuated radiation method (direct reading), and the HACH sulfide test, respectively. Chloride was determined by the silver nitrate titration method (APHA-AWWA-WEF, 1998). Nitrogen (Kjeldahl) was measured according to Adolfo Lutz Institute Analytical Norms (Normas Analíticas do Instituto Adolfo Lutz, 1985). Metallic elements (Ag, Al, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb and Zn) were determined in extracts by atomic absorption spectroscopy (Varian SpectrAA – 10 Plus).

The COD measured in the samples taken from Fenton's reactor was converted according to Eq. (11) to prevent the interference of H₂O₂ on COD analysis (Talini & Anderson, 1992).

$$\text{COD} = \text{COD}_M - R_p \times 0.25 \quad (11)$$

where COD, COD value in the sample (mg O₂/L); COD_M, measured COD (mg O₂/L); R_p, residual hydrogen peroxide in the sample (mg/L).

The percent of COD removal was then determined through the following equation:

$$\eta(\%) = \left(\frac{COD_0 - COD_E}{COD_0} \right) * 100 \quad (12)$$

where η , percentage of COD removal; COD_0 , measured COD in supernatant before oxidation (mg O₂/L); COD_E , COD value in clarified supernatant after precipitation (mg O₂/L).

4. Results and discussion

Throughout the monitoring period waste chemicals were generated as a consequence of chemical analyses and other research activities. Part of these residues is originated from chemical oxygen demand (COD), total phenols, nitrogen, protein, phosphate and sulfide determinations. Another significant part is constituted by diluted metal solutions containing Ag, Al, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb and Zn, solutions standardization, and an abundance of unused laboratory reagents. As a consequence, the samples could be described as a quite complex wastewater which comprises different chemical species in dissolved, colloidal and particulate form. The main characteristics of the raw laboratory wastewater are presented in Table 1. Results in Table 1 show that the wastewater has high organic load (COD up to 2.7 g/L) and extremely low pH (<1.0). All raw samples contained an amount of brown solids presented as settable solids.

Parameter	Unity	Sample 1	Sample 2
pH		< 1	< 1
Apparent color	Pt/Co	12700	10250
Real color	Pt/Co	7150	1020
Turbidity	NTU	4010	2960
Total COD	mg O ₂ /L	2345	2676
Total phenols	mg/L	58.6	37.9
Settable solids	mL/L	4.5	4.0

Table 1. Characteristics of raw waste chemicals

Table 2 presents the results of chemical oxidation by Fenton's reagent for both samples under optimum operation conditions. The characterization of the wastewater before and after Fenton's treatment is presented in Table 3.

Sample	Initial	End of the oxidation stage		End of the precipitation stage			
	COD mg O ₂ /L	COD mg O ₂ /L	% COD removal	residual H ₂ O ₂ mg/L	Catalytic sludge mL	COD mg O ₂ /L	% COD removal
1	898	232	74,1	13,4	40	93	89,7
2	769	176	77,1	30,0	40	166	78,5

Table 2. Results of the waste chemical treatment by Fenton's reagent.

Parameter	Unity	Sample 1			Sample 2		
		Raw supernatant	Initial effluent ^a	Final effluent at optimized conditions	Raw supernatant	Initial effluent ^a	Final effluent at optimized conditions
pH		<1	4	8	<1	4	8
Apparent color	Pt/Co	308	2205	137	503	1615	352
Turbidity	NTU	N.D.	42	10	N.D.	5	6
Soluble COD	mg O ₂ /L	1145	898	93	2576	769	166
Total phenols	mg/L	27.3	27.0	N.D.	39.8	35.9	N.D.
Sulfate	g/L	263	142	152	296	151	164
Sulfide	mg/L	0.04	0.07	0.01	0.05	0.12	0.01
Chloride ^b	mg/L	638	638	567	6523	6523	5247
Phosphorous	mg/L	203.8	90.5	0.1	394.2	233.2	0.4
Nitrogen	mg/L	1434	1038	566	38	38	N.D.
Metals:							
Ag	mg/L	1.1	1.1	0.8	1.1	1.1	1.0
Al	mg/L	18.8	5.2	1.4	6.8	6.4	4.5
Ca	mg/L	59.1	39.0	30.4	37.7	26.3	21.4
Cd	mg/L	0.3	0.3	0.3	6.9	2.3	0.5
Co	mg/L	1.2	0.8	0.8	1.3	0.8	1.0
Cr	mg/L	301.4	155.2	1.0	541.6	266.9	12.1
Cu	mg/L	1.7	0.3	0.6	4.5	2.0	0.3
Fe	mg/L	131.9	29.6	4.4	114.0	38.7	1.7
Hg	mg/L	1815.6	148.4	75.1	2769.3	70.7	99.8
K	mg/L	405.2	278.7	187.4	1084.8	646.4	645.3
Mg	mg/L	3.5	2.6	1.7	10.6	8.6	3.0
Mn	mg/L	0.7	0.6	0.5	0.8	0.4	0.1
Na	g/L	10.2	73.9	77.9	9.1	98.5	101.7
Ni	mg/L	0.9	1.2	1.1	1.1	1.3	1.1
Pb	mg/L	1.9	1.3	1.1	1.6	1.3	1.1
Zn	mg/L	0.9	0.5	N.D.	0.1	N.D.	N.D.

^a Sample after pH adjustment to 4 with NaOH (30% w/v).

^b Chloride content was determined at pH 8.

Table 3. Characteristics of the laboratory wastewater supernatant before (raw and after pH adjustment) and after oxidation at optimized conditions (N.D.: not detected).

One set of experiments was conducted as control experiments (without any addition of hydrogen peroxide or ferrous sulfate). The simple pH adjustment of the effluent to 8 did not contribute for significant COD or phenol removal. Though it was capable of minimizing the toxic metal content in solution as metal hydroxide precipitation (data not shown), it presented an undesirable effect. The raise of pH of the mixed waste chemicals to high values (pH=8) resulted, under temperatures below 20 °C, in a high instable solution, with the formation of a crystal solid phase simply by its manipulation. This is probably due to the formation of several inorganic substances, and for such substances solubility decreases with decreasing temperature.

Thus, Fenton's oxidation was conducted on wastewater without a previous precipitation of the metals. This process configuration favours the elimination of a pH adjustment step since the laboratory wastewater is highly acidic (see Tables 1 and 3) and the Fenton's reaction is also conducted under acidic conditions, with the raise of pH to 8 at the end of the process. Fenton's oxidation conducted under different conditions suggests that the presence of others metals do not interfere in the efficiency of oxidation of organic compounds by the Fenton's reagent.

Bidga (1995) describes the Fenton method as a process divided into four stages. First, pH is adjusted to low acidity, at pH value of 3–5. In this study, it was adjusted to optimum pH (pH=4). Then, main oxidation reaction takes place. The wastewater is then neutralized at pH of 7–8 and finally precipitation occurs. In this study pH=8 was adopted in order to favour the precipitation of metal species as hydroxides. Wastewater characteristics at different process stages are presented in Table 2.

During the Fenton oxidation process and, mainly, during the pH adjustment to 8, a large amount of flocks of various sizes in the wastewater were observed. According to Walling & Kato (1971), the small flocs were ferric hydroxo complexes formed by complex chain reactions of ferrous and hydroxide ions. After a period of natural sedimentation (about 15 hours), all flocs settled out in wastewater forming a catalytic sludge, whose volume is also presented in Table 2.

The supernatant separated by decantation revealed that the Fenton's reagent oxidation was efficient in degrading organic matter in both samples, reaching 89.7 and 78.5% COD removal in samples 1 and 2, respectively. Moreover, the total phenols presence was not detected after the application of Fenton's reagent. Moreover, the treated liquor under the optimized conditions showed Fe concentrations up to 4.4 mg/L. Thus, the Fe concentration could be kept below 15 mg/L, which is the maximum value for Fe concentration in disposed effluents imposed by CONAMA (Brazilian National Environmental Council) standards (CONAMA, 2008).

It is worth mentioning that great amount of NaOH were necessary to raise the pH from below 1 to 2. From this point on, the pH showed to be more sensitive to the sequential addition of NaOH solution. As a consequence, the effluent presented a high sodium concentration that increases with the raise of pH (see Table 3).

Regarding the sulfate content, the raw wastewater at pH 4 presented an initial sulfate concentration of 142 and 151 g/L for samples 1 and 2, respectively (see Table 3). Because sulfuric acid and sodium hydroxide solutions were used for pH adjustments, and ferrous sulfate was used as a catalyst in the Fenton's process, further amounts of sulfate resulted from the wastewater oxidation. Thus, the sulfate concentration still remained extremely high at the end of the process, reaching 152 and 164 g/L for samples 1 and 2, respectively. Although the Brazilian legislation does not directly limit its concentration for effluent discharge, the CONAMA Resolution No. 357 (CONAMA/2005) states that effluents must not give to the receiving waters characteristics different from those used in their classification. This resolution does not include the sulfate concentration as a parameter to be monitored, probably due to the fact that the damage caused by sulfate emissions is not direct, since sulfate is a chemically inert, non-volatile, and non-toxic compound. However, high sulfate concentrations can unbalance the natural sulfur cycle (Silva et al., 2002; Lens et al., 1998). The accumulation of sulfate rich sediments in lakes, rivers and seas may cause the release of toxic sulfides that can provoke damages to the environment (Ghigliazza et al.,

2000). In addition, the release of sulfate-rich wastewaters in sewage systems may cause the inhibition or even the collapse of the biological treatment system. Thus, a post treatment system is required to bring the sulfate levels of the treated wastewater to values that are less than the maximum allowable limit set by the local regulatory authority (1000 mg/L) in order to allow its discharged directly to the municipal biological treatment facilities.

Regarding the metal content, the Fenton's reagent process presented as a side effect the removal of certain elements, such as chromium (up to 99.4%) and aluminum (up to 73.1%).

Fu et al. (2009) studied the removal of heavy metal ions in metal-EDTA complexes by Fenton and Fenton-like reaction followed by hydroxide precipitation, and achieved high removal efficiencies while conventional technologies, such as hydroxide, sulfide and dithiocarbamate-type precipitants could hardly work for it. Although Fenton-like process presented higher efficiency than Fenton process, at optimal operation conditions ($[\text{H}_2\text{O}_2]_0 = 141 \text{ mM}$, $[\text{Fe}^{2+}]_0 = 1.0 \text{ mM}$, $[\text{Fe}^{3+}]_0 = 1.0 \text{ mM}$, initial pH 3.0 and precipitation pH 11.0), the removal efficiency of Ni(II) were above 92% for the two systems.

Mahiroglu et al. (2009) investigated the treatability of combined acid mine drainage (AMD) – Flotation circuit effluents from copper mine via Fenton's process and pointed out that heavy metals in the AMD could also be reduced to very low levels via Fenton reactions by taking part in oxidation steps.

Despite the results, the heavy metals content in the treated liquor still exceeded the maximum allowable limits for effluent discharge according to the CONAMA Resolution No. 397 (CONAMA/2008), especially for mercury, lead, chromium and silver, whose limit for disposal are 0.01, 0.5, 0.5 and 0.1 mg/L, respectively This stresses the need for an additional treatment for the removal of the remaining heavy metals prior to discharge to the environment.

Finally, the application of the Fenton's reagent in the destruction of organic compounds in mixed waste chemicals generated a dark brown slurry phase mainly constituted by heavy metals-Fe(III)-iron sludge, with a formation of 267 mL of sludge per liter of oxidized wastewater. This slurry phase presented a percentage of total suspended solids between 2.4 and 2.5% (w/w).

Thus, the overall result of the waste chemicals treatment by Fenton's Reagent is the production of an aqueous solution with a substantially lower total carbonaceous load. However, the treated liquor still presented levels of heavy metals and sulfate that were too high to meet discharge standards. Thus, the Fenton's reagent cannot be applied as a stand-alone treatment option, but it can be used in combination with other treatment techniques. Finally, it is noteworthy that a potentially hazardous solid residue is obtained as a by-product of the Fenton's treatment. Hence, it is important to characterize this material for proper waste management, satisfying environmental and health related criteria.

As a first approach to characterize the solids originating from the Fenton's process, this study focused on identifying the metals present in the residues, on their crystal structure, on the specific chemical bond in which electrons are delocalized and mobile, and on their magnetic properties. As a second approach, and in order to complement the physical characterization of the residues, leaching tests were also performed in order to obtain correct predictions of elements possible mobilization process in the environment.

The results of metals determination in these residues (Table 4) showed that the predominant metals are silver, chromium, mercury and iron. The main source of the first three ones is COD analysis. Iron is mainly a result of the Fenton's process, once it is used as a catalyst of

the reaction and undergoes precipitation after oxidation. Regarding cadmium, the results of effluent characterization (Table 3) showed that sample 1 presented an initial concentration of 0.3 mg/L, which was kept constant after the equalization and oxidation stages of effluent treatment. In consequence, this element was not detected in the originating residue from the Fenton's process (Residue 1).

Metal	Residue 1	Residue 2
Ag	30157.1	38678.3
Al	2184.5	362.0
Ca	1827.7	1839.4
Cd	ND	480.0
Co	61.2	50.2
Cr	20747.2	28395.0
Cu	210.0	538.8
Fe	400065.2	324171.4
Hg	70430.1	96926.7
Mn	221.7	282.6
Ni	49.8	36.4
Pb	57.2	11.3
Zn	96.3	50.1

Table 4. Total element determinations (mg/kg) in samples (N.D.: not detected).

Fig. 1 shows the X-ray diffractograms obtained for the studied residues. This figure shows that the amorphous phase is predominant in the material. Besides the amorphous material identified as 2-line ferrihydrite (Cornell & Schuvertmann, 1996), the presence of the crystalline phases HgCl (calomel) and AgCl (chlorargyrite) was identified in both residues. The three solid phases detected by X-ray diffraction are also the ones that present the highest concentration considering the total metal content presented in Table 3. Although the studied residues were produced by the oxidation of mixed laboratory wastewaters generated in different periods, they present similar characteristics.

The knowledge of the total concentration of metals in residues of Fenton's process is, however, not enough to evaluate their environmental impact. Addressing the chemical form of the element instead of the total trace element concentration renders the information gained through careful analysis much more valuable (Cornelis & Nordberg, 2007). The mobility of trace metals, as well as their bioavailability and related ecotoxicity to plants, depends strongly on their specific chemical forms or ways of binding (Quevauviller et al., 1997). Consequently, it is necessary to determine the solubility of these metals, which depends on the way of their association in residue.

Generally speaking, the sequential extraction of trace elements adopted in this study uses a series of chemical reagents, each time stronger, under specific conditions, to dissolve one or more specific phases from the solid sample, while preserving others. In the extract it is possible to speciate elements solubilised during the dissolution. By studying the distribution of the metals between the different phases, their contamination risks can be ascertained, because it is possible to divide a specific metal into fractions of increasing stability.

Thus, in order to study the distribution of the metals in residues and the phases to which they are bound, a sequential extraction procedure was designed based on the characteristics

of the Fenton's process as well as on the analysis of the X-ray diffractograms presented in Fig. 1. In this procedure, the total metal content is divided into four fractions of increasing stability: exchangeable (Fraction 1), amorphous iron oxide (Fraction 2), crystalline iron oxide (Fraction 3), and inert or residual (Fraction 4). The solubility of the metals in the residues can be associated with their extraction, decreasing in the order of extraction sequence. In this sense, samples with a higher metal content in Fraction 1 will be potentially more dangerous than those that present a lower content in this fraction.

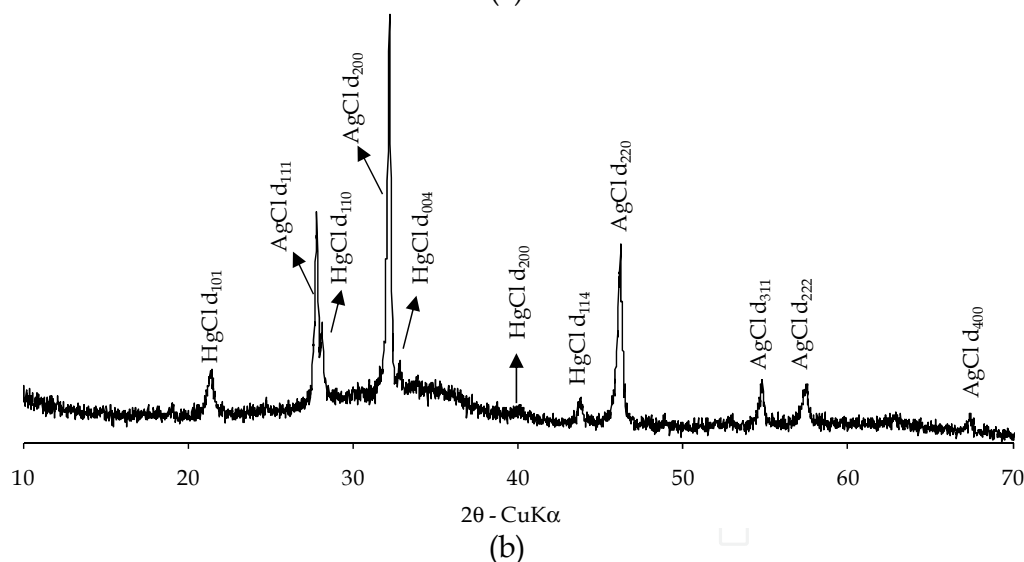
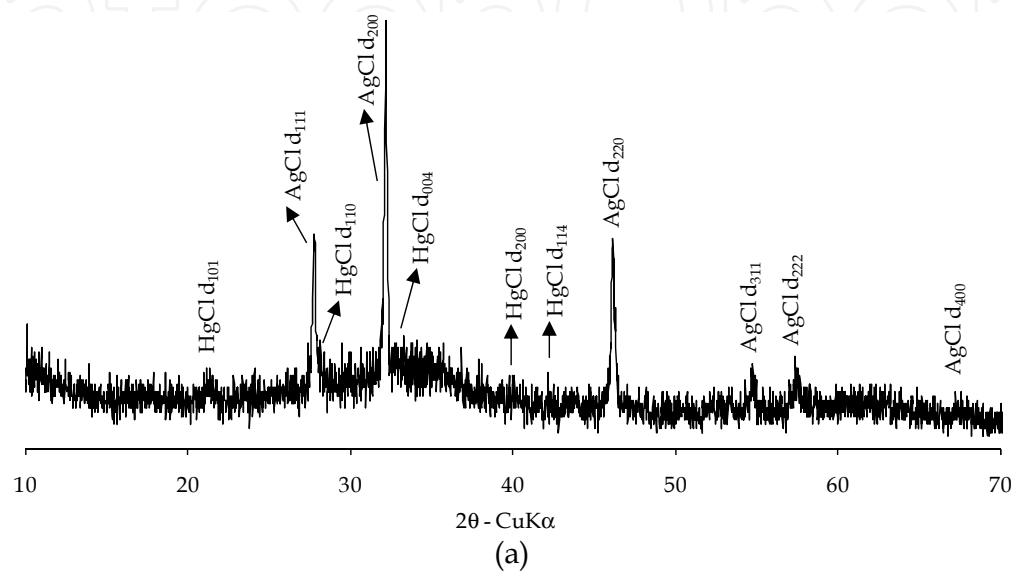


Fig. 1. X-ray diffractograms of the residue of Fenton's process: (a) Residue 1 and (b) Residue 2.

Metals extracted in Fraction 1 (exchangeable) correspond to those weakly absorbed, in particular to those retained in the residue surface with a weak electrostatic force. Changes in water ionic composition greatly affect the sorption-desorption processes of this fraction. Fraction 2 contains metals bound to amorphous iron oxide and corresponds to the reactive part of the iron compounds of the residues. Fraction 3 contains metals bound to crystalline iron oxide. This extraction favours the preferential orientation of remaining metals when

submitted to X-ray diffractometry. Fraction 4 (inert or residual) contains primary and secondary minerals, mostly silicates, titanium and aluminum oxides, which can retain metals in their crystalline structure, removed from the laboratory wastewaters. These minerals are not expected to be released in a reasonable space of time in nature's normal conditions. Metals of this fraction are chemically stable and biologically inactive.

Fig. 2 shows the weight loss of the sample after each stage of the sequential extraction method adopted. As can be seen, the last two phases of the sequential extraction (crystalline iron oxide and residual), the less reactive fraction of the residues, represent only a small percentage in mass, about 11.2 and 16.6% for Residues 1 and 2, respectively. In fact, the residues originating from the Fenton's process is mainly constituted of amorphous material (over 80%) and most metals are co-precipitated to this fraction.

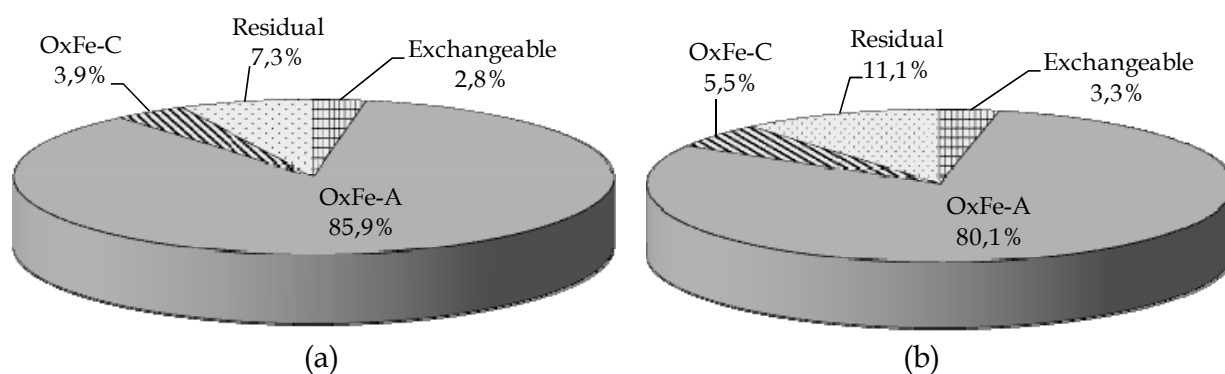


Fig. 2. Mass fractionation (% in mass) of Residues 1 (a) and 2 (b). Exchangeable, amorphous iron oxide (OxFe-A), crystalline iron oxide (OxFe-C), and final residual.

Table 5 presents the results of metals concentration in the different fractions of the studied residues. Fig. 3 shows the metal partitioning, in percentage of the total amount, found in the residues fractions. As can be seen, the sum of the four fractions (Table 5) is reasonably similar to the total contents obtained after digestion of the original samples (Table 4), indicating that no significant loss occurred during the sequential dissolution procedures, with recoveries of 96–100% in all cases. Thus, it is reasonable to assume that the dissolution procedure adopted was reliable for metals partitioning, increasing the confidence of the obtained data.

Several elements were detected in Fraction 1 (exchangeable), such as silver (0.2%), chromium (0.1%), copper (3.8%), iron (0.004%) and mercury (20.5%) of Residue 1; silver (0.1%), cadmium (5.2%), chromium (1.1%), copper (1.1%), iron (0.01%), mercury (31.6%) and zinc (0.2%) of Residue 2. These metals were associated to soluble salts as chlorites or sulfates, or simply absorbed to the residues surface.

Generally, both studied residues presented a similar distribution of metals at the different fractions obtained by the sequential dissolution procedure employed. Fig. 3 shows the chemical fractionation of each residue. With regard to silver, this element was mainly associated to the residual fraction of both residues (over 97% extraction). Elements like aluminum, calcium, cobalt, chromium, iron, manganese, nickel and zinc were predominantly found in the amorphous phase of both residues. In the case of cadmium, which was detected only in Residue 2, 86.9% of the total was found in the amorphous phase and only 6.8% was found in the most stable phases, which means in the crystalline iron

oxide and residual phases. With regard to mercury, besides the exchangeable phase previously mentioned, 21.7 and 14.8% were found in the amorphous phase, 0.2 and 0.02% in the crystalline fraction and 53.5 and 49.8% in final residual, in Residues 1 and 2, respectively. In Residue 1, lead was found predominantly in the amorphous phase, representing 73.1% of the total content, and the remaining content was distributed between the crystalline (7.4%) and residual (19.3%) fractions. In Residue 2, though, lead was mainly associated with the residual fraction (99.7%); its availability was therefore low since most of it was in the insoluble form.

Sample	Metal	Exchangeable	OxFe-A	OxFe-C	Residual	Sum	% Recovery
Residue 1	Ag	75.0	35.1	107.0	29344.0	29561.1	98.0
	Al	N.D.	2051.4	68.6	56.4	2176.4	99.6
	Ca	N.D.	1739.3	16.6	64.6	1820.5	99.6
	Cd	N.D.	N.D.	N.D.	N.D.	0.0	-
	Co	N.D.	57	2.6	1.5	61.1	99.9
	Cr	28.5	19195.5	1122.5	318.0	20664.5	99.6
	Cu	7.9	190.9	0.3	6.2	205.3	97.7
	Fe	15.7	370959.6	19230.1	8634.0	398839.4	99.7
	Hg	14450.1	15263.0	140.0	37688.3	67541.4	95.9
	Mn	N.D.	210.2	6.5	4.0	220.7	99.5
	Ni	N.D.	45.6	1.3	1.2	48.1	96.7
	Pb	N.D.	41.9	4.3	11.1	57.3	99.9
	Zn	N.D.	75.4	N.D.	20.2	95.6	99.3
Residue 2	Ag	9.7	4.9	12.4	38571.0	38598.0	99.8
	Al	N.D.	323.8	5.8	29.1	358.7	99.1
	Ca	N.D.	1467.2	287.9	82.9	1838.0	99.9
	Cd	25.1	417.0	12.0	20.3	474.4	98.8
	Co	N.D.	42.5	5.3	0.7	48.5	96.7
	Cr	310.1	26745.1	725.6	145.6	27926.4	98.3
	Cu	5.6	529.6	0.1	3.2	538.5	100.0
	Fe	19.9	315243.4	4616.7	2934.5	322814.5	99.6
	Hg	30648.7	14296.5	23.6	48263.1	93231.9	96.2
	Mn	N.D.	273.1	2.4	0.4	275.9	97.7
	Ni	N.D.	33.7	1.3	0.8	35.8	98.5
	Pb	N.D.	N.D.	N.D.	11.2	11.2	99.7
	Zn	0.1	40.8	N.D.	7.9	48.8	97.3

Table 5. Metals concentration (mg/kg) in the different fractions (exchangeable, amorphous iron oxide (OxFe-A), crystalline iron oxide (OxFe-C), and final residual) of the studied residues (N.D.: not detected).

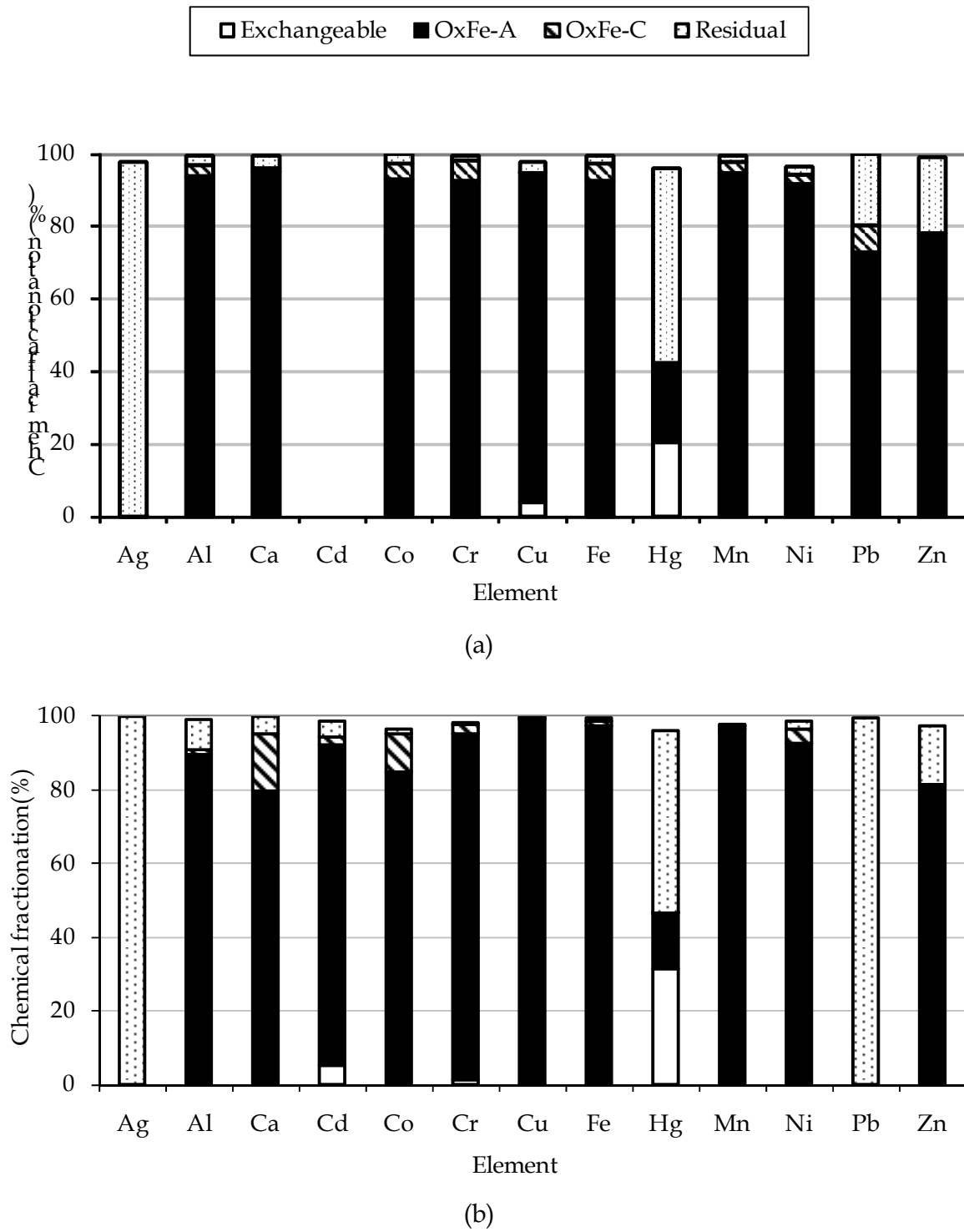


Fig. 3. Chemical fractionation of solids originating from the Fenton's process: (a) Residue 1 and (b) Residue 2. Exchangeable, amorphous iron oxide (OxFe-A), crystalline iron oxide (OxFe-C), and final residual.

Figs. 4 and 5 show the X-ray diffractograms of the studied residues. Fig. 6 shows the differential X-ray diffractograms for the amorphous phase of Residues 1 and 2.

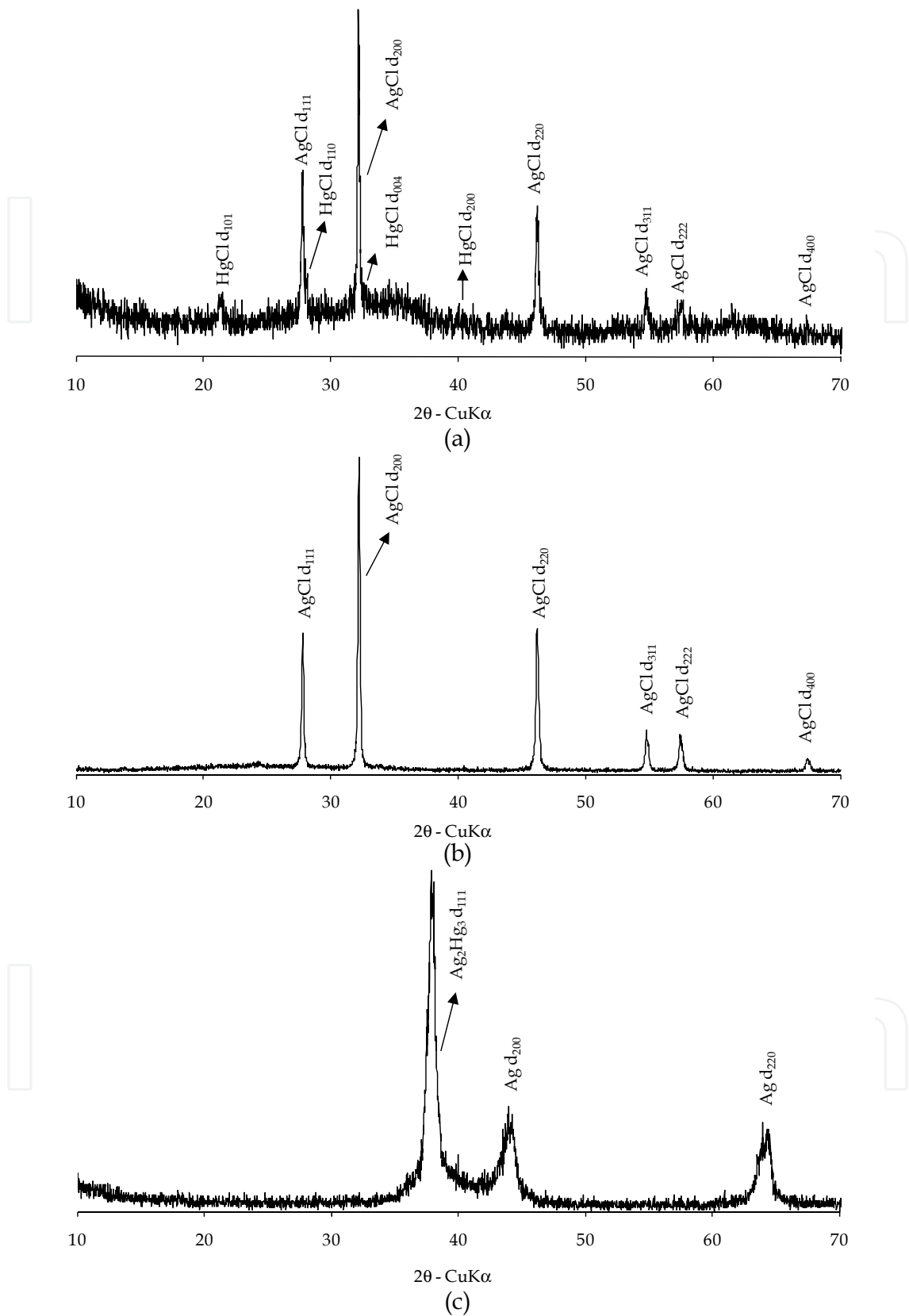


Fig. 4. X-ray diffractograms for the different fractions of Residue 1. (a) After exchangeable extraction; (b) after amorphous iron oxide extraction and (c) after crystalline iron oxide extraction.

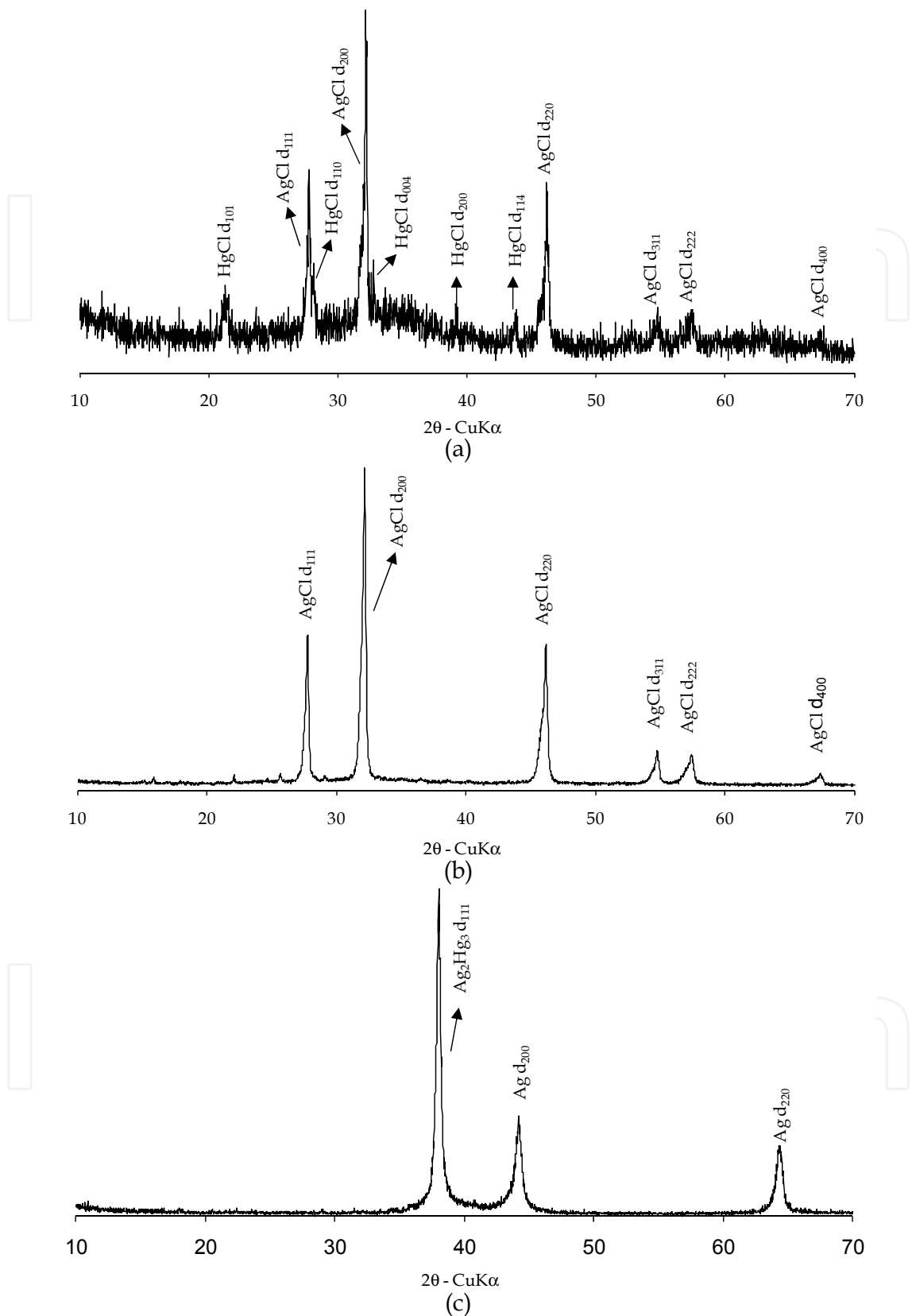


Fig. 5. X-ray diffractograms for the different fractions of Residue 2. (a) After exchangeable extraction; (b) after amorphous iron oxide extraction and (c) after crystalline iron oxide extraction.

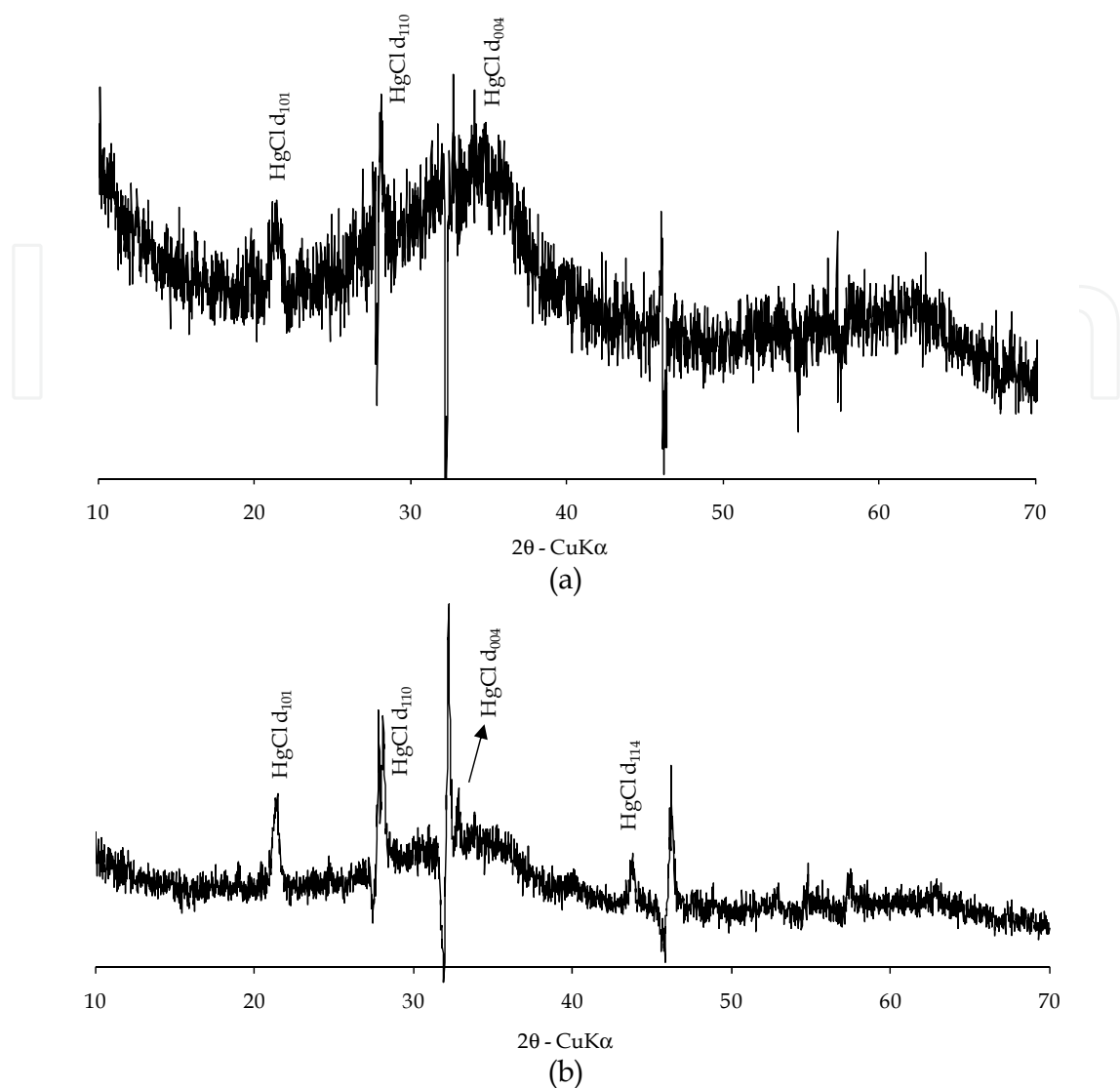


Fig. 6. Differential X-ray diffractograms for the amorphous phase and in the presence of HgCl: (a) Residue 1 and (b) Residue 2.

The position and intensity of diffraction planes indicate that there are no differences between the two solid samples. Therefore, although the wastewater samples were generated in distinct periods of time, their differences in chemical composition did not affect the mineralogical phases present in the solids resulting from their treatment by Fenton's reactions. From the interpretation of the main diffraction planes observed in the diffractograms, it was possible to identify the most likely compounds related to them. The solid residues originated from the Fenton's process presented a typical profile of material constituted predominantly by amorphous phase (2-line ferrihydrite (Schwertmann et al., 1982)), and silver and mercury compounds with well-defined crystalline structure were identified as chlorargyrite and calomel, respectively. The residual or inert fraction of the residues presented characteristics of a metallic league, formed mostly by elementary silver and mercury with minor amounts of other metals (Table 5). The Fenton's residues were originally brown, and did not exhibit detectable magnetic properties by the presence of a magnetic field, and a black coloured residual was obtained at the end of the sequential

extraction procedure. The diffractograms in Fig. 6 present the amorphous phase of the studied residues with the presence of calomel, obtained by the subtraction of diffractograms intensities of original samples (Fig. 1a and b) and of residues obtained after amorphous phase extraction (Figs. 4b and 5b). Therefore, differently to that observed for soils, acid ammonium oxalate extracted a portion of poorly crystalline crystals of calomel, besides most iron associated to 2-line ferrihydrite. The use of dithionite at the crystalline iron extraction was capable of reducing remaining mercury and silver of the selective dissolution procedure and formed a metallic league that presents diffraction planes of Ag and Ag_2Hg_3 .

From the results of the selective dissolution, the solids originated from the Fenton's process are not stable, being composed fundamentally by high toxicity metals like chromium and mercury. Hence, the results suggest that leaching of metals into the environment can occur even under mild environmental conditions.

Finally, Table 6 presents the results of metal leachability for both studied residues determined by ABNT-NBR 10005 method (ABNT, 1987a). For comparative purposes, the same table shows the maximum levels of heavy metals allowed in Brazilian non-hazardous wastes (ABNT, 1987b). Based on the obtained chemical analytical results and on the classificatory procedure proposed by ABNT-NBR 10004 (ABNT, 1987b), the solid residues from the Fenton's process can be classified as Class I—hazardous. Both residues are characterized as toxic TL (leaking test). Residue 1 received the identification codes D009 and D011, due to its mean metal concentration above the maxima permitted for total chromium and mercury, and Residue 2, D007, D009 and D011 due to its cadmium, total chromium and mercury concentration, respectively.

Metals	Element code	Residue 1	Residue 2	Limits*
Cd	D007	N.D.	0.8	0.5
Pb	D008	N.D.	N.D.	5.0
Cr	D009	13.6	18.4	5.0
Hg	D011	49.8	243.1	0.1
Ag	D012	0.2	0.2	5.0

* Identification codes and maximum established limits according to ABNT-NBR 10004 (ABNT, 1987b).

Table 6. Results of metals leachability (mg/L) for both studied residues (N.D.: not detected).

Thus, the obtained results indicate a great potential for soil, surface and underground waters contamination by heavy metals (chromium, cadmium and mercury), if the residues originated from the Fenton's process are disposed of improperly. A stabilization process of the residues is necessary prior to their disposal in the environment. Furthermore, the results indicated a high potential of silver and mercury recovery, which represent a large part of the studied residues.

5. Conclusion

Chemical oxidation using Fenton's reagent under optimum conditions has proven to be a viable alternative to the oxidative destruction of organic pollutants in mixed waste chemicals, with a COD removal of 89.7 e 78.5% in samples 1 and 2, respectively. Moreover, total phenols were not detected in the treated liquor. However, the reported results also

indicated that no single technology could be applied to mixed waste chemicals as a stand-alone treatment option once the concentration of certain inorganic constituents, such as heavy metals and sulfate, still remained high for effluent discharge.

Regarding to the Fenton's residues, they were classified as hazardous according to Brazilian waste regulations. The application of the sequential dissolution procedure indicated that the metals in the Fenton's residues are mainly constituted of amorphous material (over 80%). Furthermore, the reactive fractions of the residues (exchangeable and amorphous iron oxide fractions) retain most of remaining metals. Therefore, the Fenton's residues present great potential for environmental contamination, and require an administration system and control of their final disposal. However, Fenton's residues present great potential for silver and mercury recovery, since these elements represent a great portion of the studied residues.

6. Acknowledgment

The support provided by CAPES and by the State University of Maringá is gratefully acknowledged.

7. References

- ABNT - Associação Brasileira de Normas Técnicas. (1987a). *Lixiviação de Resíduos - Procedimento*, NBR 10005, Rio de Janeiro, R.J.
- ABNT - Associação Brasileira de Normas Técnicas (1987b). *Resíduos Sólidos-Classificação*, NBR 10004, Rio de Janeiro, R.J.
- APHA-AWWA-WEF – American Public Health Association, American Water Works Association, Water Environment Federation. (1998). *Standard Methods for the Examination of Water and Wastewater* (20th ed), ISBN 0875530478, Washington, DC.
- Ay, F., Kargi, F. (2010). Advanced oxidation of amoxicillin by Fenton's reagent treatment. *Journal of Hazardous Materials*, Vol. 179, pp. 622–627, ISSN 0304-3894.
- Badawy, M., Wahaab, R.A., El-Kalliny, A.S. (2009). Fenton-biological treatment processes for the removal of some pharmaceuticals from industrial wastewater. *Journal of Hazardous Materials*, Vol. 167, pp. 567–574, ISSN 0304-3894.
- Badawy, M.I.; Ali, M.E.M. (2006). Fenton's peroxidation and coagulation processes for the treatment of combined industrial and domestic wastewater. *Journal of Hazardous Materials*, Vol. B136, pp. 961–966, ISSN 0304-3894.
- Bautista, P., Mohedano, A.F., Gilarranz, M.A., Casas, J.A., Rodriguez, J.J. (2007). Application of Fenton oxidation to cosmetic wastewaters treatment. *Journal of Hazardous Materials*, Vol. 143, pp. 128–134, ISSN 0304-3894.
- Ben, W., Qiang, Z., Pan, X., Chen, M. (2009). Removal of veterinary antibiotics from sequencing batch reactor (SBR) pretreated swine wastewater by Fenton's reagent. *Water Research*, Vol. 43, pp. 4392–4402, ISSN 0043-1354.
- Benatti, C.T.; Tavares, C.R.G.; Guedes, T.A. (2006). Optimization of Fenton's oxidation of chemical laboratory wastewaters using the response surface methodology. *Journal of Environmental Management*, Vol. 80, pp. 66–74, ISSN 0301-4797.
- Benitez, F.J., Acero, J.L., Real, F.J., Rubio, F.J., Leal A.I. (2001). The Role of Hydroxyl Radicals for the Decomposition of p-hydroxy Phenylacetic Acid in Aqueous Solutions. *Water Research*, Vol. 35, No. 5, pp. 1338-1343, ISSN 0043-1354.

- Bham, A.A., Chambers, R.P. (1997). Degradation of high molecular weight chlorinated aromatics and aliphatics in bleach plant effluent by Fenton's Reagent. *Advances in Environmental Research*, Vol. 1, pp. 135-143, ISSN 1093-7927.
- Bianco, B., Michelis, I., Vegliò, F. (2011). Fenton treatment of complex industrial wastewater: Optimization of process conditions by surface response method. *Journal of Hazardous Materials*, Vol. 186, pp. 1733-1738, ISSN 0304-3894.
- Bigda, R.J. (1995). Consider Fenton's Chemistry for Wastewater Treatment. *Chemical Engineering Progress*, December, pp. 62-66, ISSN 0360-7275.
- Büyüksönmez, F., Hess, T.F., Crawford, R.L., Paszczynski, A., Watts, R.J. (1999). Optimization of Simultaneous Chemical and Biological Mineralization of Perchloroethylene. *Applied and Environmental Microbiology*, Vol. 65, No. 6 (Jun), pp. 2784-2788, ISSN 0099-2240.
- Camargo, O.A.; Moniz, A.C.; Jorge, J.A.; Valadares, J.M.A.S. (1986). *Métodos de análise química, Mineralógica e física de solos do Instituto Agronômico de Campinas*, Boletim Técnico no. 106, Instituto Agronômico, ISBN 8585564, Campinas, S.P.
- Chamarro, E., Marco, A., Esplugas, S., 2001. Use of Fenton reagent to improve organic chemical biodegradability. *Water Research*, Vol. 35, No. 4, pp. 1047-1051, ISSN 0043-1354.
- Chen, S., Sun, D., Chung, J.S. (2007). Treatment of pesticide wastewater by moving-bed biofilm reactor combined with Fenton-coagulation pre-treatment. *Journal of Hazardous Materials*, Vol. 144, pp. 577-584, ISSN 0304-3894.
- CONAMA - Conselho Nacional do Meio Ambiente. (2005). Resolution No. 357, March 17, 2005, São Paulo, Brazil.
- CONAMA - Conselho Nacional do Meio Ambiente. (2008). Resolution No. 397, April 03, 2008, São Paulo, Brazil.
- Cornelis, R., Nordberg, M. (2007). General Chemistry, Sampling, Analytical Methods and Speciation, In: *Handbook on the toxicology of metals*, Nordberg, G.F. (Eds.), pp. 11-38, Academic Press, ISBN 9780123694133, USA.
- Cornell, R.M., Schuwertmann, U. (1996). *The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses*. VCH Publishers, ISBN 9783527302741, Weinheim, Germany.
- Deng, Y., Englehardt, J.D. (2006). Treatment of landfill leachate by the Fenton process. *Water Research*, Vol. 40, pp. 3683-3694, ISSN 0043-1354.
- Dercová, K., Vrana, B., Tandlich, R., Šubová, L. (1999). Fenton's type reaction and chemical pretreatment of PCBs. *Chemosphere*, Vol. 39, No. 15, pp. 2621-2628, ISSN 0045-6535.
- Elmolla, E., Chaudhuri, M. (2009). Optimization of Fenton process for treatment of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution. *Journal of Hazardous Materials*, Vol. 170, pp. 666-672, ISSN 0304-3894.
- El-Morsi, T.M., Emara, M.M., Abd El Bary, H.M.H., Abd-El-Aziz, A.S., Friesen, K.J. (2002). Homogeneous degradation of 1,2,9,10-tetrachlorodecane in aqueous solutions using hydrogen peroxide, iron and UV light. *Chemosphere*, Vol. 47, pp. 343-348, ISSN 0045-6535.
- Fu, F., Wang, Q., Tang, B. (2009). Fenton and Fenton-like reaction followed by hydroxide precipitation in the removal of Ni(II) from NiEDTA wastewater: A comparative study. *Chemical Engineering Journal*, Vol. 155, pp. 769-774, ISSN 1385-8947.

- Gallard, H., De Laat, J. (2001). Kinetics of oxidation of chlorobenzenes and phenyl-ureas by Fe(II)/H₂O₂ and Fe(III)/H₂O₂. Evidence of reduction and oxidation reactions of intermediates by Fe(II) or Fe(III). *Chemosphere*, Vol. 42, pp. 405–413, ISSN 0045-6535.
- Garrido-Ramírez, E.G., Theng, B.K.G, Mora, M.L. (2010). Clays and oxide minerals as catalysts and nanocatalysts in Fenton-like reactions – A review. *Applied Clay Science*, Vol. 47, pp. 182–192, ISSN 0169-1317.
- Ghigliazza, R., Lodi, A., Rovatti, M. (2000). Kinetic and process considerations on biological reduction of soluble and scarcely soluble sulfates. *Resources, Conservation and Recycling*, Vol. 29, pp. 181-194, ISSN 0921-3449.
- Gogate, P.R., Pandit, A.B. (2004). A Review of Imperative Technologies for Wastewater Treatment I: Oxidation Technologies at Ambient Conditions. *Advances in Environmental Research*, v.8, pp. 501-551, ISSN 1093-7927.
- Gulkaya, I., Surucu, G.A., Dilek, F.B. (2006). Importance of H₂O₂/Fe²⁺ ratio in Fenton's treatment of a carpet dyeing wastewater. *Journal of Hazardous Materials*, Vol. B136, pp. 763–769, ISSN 0304-3894.
- Heredia, J.B., Terregrosa, J., Dominguez, J.R., Peres, J.A. (2001). Kinetic model for phenolic compound oxidation by Fenton's reagent. *Chemosphere*, Vol. 45, pp. 85–90, ISSN 0045-6535.
- Homem, V., Alves, A., Santos, L. (2010). Amoxicillin degradation at ppb levels by Fenton's oxidation using design of experiments. *Science of the Total Environment*, Vol. 408, pp. 6272–6280, ISSN 0048-9697.
- Kang, Y.W., Hwang, K.Y. (2000). Effects of Reaction Conditions on the Efficiency in the Fenton Process. *Water Research*, Vol. 34, No. 10, pp. 2786-2790, ISSN 0043-1354.
- Kurt, U., Avsar, Y., Gonullu, M.T. (2006). Treatability of water-based paint wastewater with Fenton process in different reactor types. *Chemosphere*, Vol. 64, pp. 1536–1540, ISSN 0045-6535.
- Kušić, H., Božić, A.L., Koprivanac, N. (2007). Fenton type processes for minimization of organic content in coloured wastewaters: Part I: Processes optimization. *Dyes and Pigments*, Vol. 74, pp. 380-387, ISSN 0143-7208.
- Lee, H., Shoda, M. (2008). Removal of COD and colour from livestock wastewater by the Fenton method. *Journal of Hazardous Materials*, Vol. 153, pp. 1314–1319, ISSN 0304-3894.
- Lens, P.N.L., Visser, A., Janssen, A.J.H., Hulshoff Pol, L.W., Lettinga, G. (1998). Biotechnological treatment of sulfate-rich wastewaters. *Critical Reviews in Environmental Science and Technology*, Vol. 28, No. 1, pp. 41-88, ISSN 1064-3389.
- Li, R., Yang, C., Chen, H., Zeng, G., Yu, G., Guo, J. (2009). Removal of triazophos pesticide from wastewater with Fenton reagent. *Journal of Hazardous Materials*, Vol. 167, pp. 1028–1032, ISSN 0304-3894.
- Lin, S.H., Lo, C.C. (1997). Fenton Process for Treatment of Desizing Wastewater. *Water Research*, Vol. 31, No. 8, pp. 2050-2056, ISSN 0043-1354.
- Lu, M.C., Chen, J.N., Chang, C.P. (1999). Oxidation of dichlorvos with hydrogen peroxide using ferrous ion as catalyst. *Journal of Hazardous Materials*, Vol. B65, pp. 277–288, ISSN 0304-3894.
- Lucas, M.S., Peres, J.A. (2009). Removal of COD from olive mill wastewater by Fenton's reagent: Kinetic study. *Journal of Hazardous Materials*, Vol. 168, pp. 1253–1259, ISSN 0304-3894.

- Lunar, L., Sicilia, D., Rubio, S., Rez-Bendito, D., Nickel, U. (2000). Degradation of Photographic Developers by Fenton's Reagent: Condition Optimization and Kinetics for Metol Oxidation. *Water Research*, Vol. 34, No. 6, pp. 1791-1802, ISSN 0043-1354.
- Ma X.J., Xia, H.L. (2009). Treatment of water-based printing ink wastewater by Fenton process combined with coagulation. *Journal of Hazardous Materials*, Vol. 162, pp. 386-390, ISSN 0304-3894.
- Mahiroglu, A., Tarlan-Yel, E., Sevimli, M.F. (2009). Treatment of combined acid mine drainage (AMD)–Flotation circuit effluents from copper mine via Fenton's process. *Journal of Hazardous Materials*, Vol. 166, pp. 782-787, ISSN 0304-3894.
- Mandal, T., Dasgupta, D., Mandal, S., Datta, S. (2010) Treatment of leather industry wastewater by aerobic biological and Fenton oxidation process. *Journal of Hazardous Materials*, Vol. 180, pp. 204-211, ISSN 0304-3894.
- Martínez, N.S.S., Fernández, J.F., Segura, X.F., Ferrer, A.S. (2003). Preoxidation of an extremely polluted industrial wastewater by the Fenton's reagent. *Journal of Hazardous Materials*, Vol. B101, pp. 315-322, ISSN 0304-3894.
- Mehra, O.P.; Jackson, M. (1960). Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate, *Proceedings of the 7th National Clay Conference*, Pergamon Press, New York, pp. 317-327.
- National Research Council, 1995. Prudent Practices in the Laboratory Handling and Disposal of Chemicals. National Academy Press, Washington, DC. ISBN 0309052297.
- Nesheiwat, F.K., Swanson, A.G. (2000). Clean Contaminated Sites using Fenton's Reagent. *Chemical Engineering Progress*, Vol. 96, No. 4, pp. 61-66, ISSN 0360-7275.
- Neyens, E., Baeyens, J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials*, Vol. 98(B), pp. 33-50, ISSN 0304-3894.
- Normas Analíticas do Instituto Adolfo Lutz. (1985). Métodos químicos e físicos para análises de alimentos (3rd ed). Editoração Débora D. Estrella Rebocho, São Paulo, BR.
- Oh, S.Y., Chiu, P.C., Kim, B.J., Cha, D.K. (2003). Enhancing Fenton oxidation of TNT and RDX through pretreatment with zero-valent iron. *Water Research*, Vol. 37, pp. 4275-4283, ISSN 0043-1354.
- Padoley, K.V., Mudliar, S.N., Banerjee, S.K., Deshmukh, S.C., Pandey, R.A. (2011). Fenton oxidation: A pretreatment option for improved biological treatment of pyridine and 3-cyanopyridine plant wastewater. *Chemical Engineering Journal*, Vol. 166, pp. 1-9, ISSN 1385-8947.
- Pavan, M.A., Bloch, M.F., Zempulski, H.C., Miyakawa, M., Zocoler, D.C. (1992). *Manual de análise química de solo e controle de qualidade*. Instituto Agrônômico do Paraná e IAPAR, Londrina, BR.
- Quevauviller, Ph. Rauret, G. López-Sánchez, J.-F. Rubio, R. Ure, A. Muntau, H. (1997). Certification of trace metal extractable contents in a sediment reference material (CRM 601) following a three-step sequential extraction procedure. *Science of the Total Environment*, Vol. 205, pp. 223-234, ISSN 0048-9697.
- Scalbert, A.; Monties, B.; Janin, G. (1989). Tannins in wood: comparison of different estimation methods. *Journal of Agricultural and Food Chemistry*, Vol. 37, pp. 1324-1329, ISSN 0021-8561.

- Schulze, D.G. (1994). Differential X-ray diffraction analysis of soil minerals, In: *Quantitative Methods in Soil Mineralogy*, J.E. Amonette, L.W. Zelazny (Eds.), pp. 412–429, Soil Sci. Soc. Amer. Misc. Publ, ISBN 0891188061, Madison.
- Schwertmann, U. Schulze, D.G. Murad, E. (1982). Identification of ferrihydrite in soils by dissolution kinetics, differential X-ray diffraction and Mössbauer spectroscopy. *Soil Science Society of America Journal*, Vol. 46, pp. 869–875, ISSN 0361-5995.
- Silva, A.J., Varesche, M.B., Foresti, E., Zaiat, M. (2002). Sulphate removal from industrial wastewater using a packed-bed anaerobic reactor. *Process Biochemistry*, Vol. 37, pp. 927-935, ISSN 0032-9592.
- Talini, I., Anderson, G.K. (1992). Interference of Hydrogen Peroxide on the Standard COD Test. *Water Research*, Vol. 26, No. 1, pp. 107-110, ISSN 0043-1354.
- Tessier, A.; Campbell, P.G.C.; Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, Vol. 51, pp. 844–851, ISSN 0003-2700.
- Torrades, F., Pérez, M., Mansilla, H.D., Peral, J. (2003). Experimental design of Fenton and photo-Fenton reactions for the treatment of cellulose bleaching effluents. *Chemosphere*, Vol. 53, pp. 1211–1220, ISSN 0045-6535.
- U.S. Peroxide (2003). Methods for residual peroxide determination: iodometric titration. Available from: <<http://www.h2o2.com/intro/analytical.html>>.
- Vilve, M., Hirvonen, A., Sillanpää, M. (2009). Effects of reaction conditions on nuclear laundry water treatment in Fenton process. *Journal of Hazardous Materials*, Vol. 164, pp. 1468–1473, ISSN 0304-3894.
- Walling, C., 1975. Fenton's reagent revisited. *Accounts of Chemical Research*, Vol. 8, pp. 125–131, ISSN 0001-4842.
- Walling, C., Kato, S. (1971). The oxidation of alcohols by Fenton's reagent: the effect of copper ion. *Journal of American Chemical Society*, Vol. 93, pp. 4275–4281, ISSN 0002-7863.
- Wang, X., Zenga, G., Zhua, J. (2008). Treatment of jean-wash wastewater by combined coagulation, hydrolysis/acidification and Fenton oxidation. *Journal of Hazardous Materials*, Vol. 153, pp. 810–816, ISSN 0304-3894.
- Yetilmezsoy, K., Sakar, S. (2008). Improvement of COD and color removal from UASB treated poultry manure wastewater using Fenton's oxidation. *Journal of Hazardous Materials*, Vol. 151, pp. 547–558, ISSN 0304-3894.
- Zhang, H., Choi, H.J., Huang, C.P. (2005). Optimization of Fenton process for the treatment of landfill leachate. *Journal of Hazardous Materials*, Vol. B125, pp. 166–174, ISSN 0304-3894.



**Organic Pollutants Ten Years After the Stockholm Convention -
Environmental and Analytical Update**

Edited by Dr. Tomasz Puzyn

ISBN 978-953-307-917-2

Hard cover, 472 pages

Publisher InTech

Published online 24, February, 2012

Published in print edition February, 2012

Ten years after coming into force of the Stockholm Convention on Persistent Organic Pollutants (POPs), a wide range of organic chemicals (industrial formulations, plant protection products, pharmaceuticals and personal care products, etc.) still poses the highest priority environmental hazard. The broadening of knowledge of organic pollutants (OPs) environmental fate and effects, as well as the decontamination techniques, is accompanied by an increase in significance of certain pollution sources (e.g. sewage sludge and dredged sediments application, textile industry), associated with a potential generation of new dangers for humans and natural ecosystems. The present book addresses these aspects, especially in the light of Organic Pollutants risk assessment as well as the practical application of novel analytical methods and techniques for removing OPs from the environment. Providing analytical and environmental update, this contribution can be particularly valuable for engineers and environmental scientists.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Cláudia Telles Benatti and Célia Regina Granhen Tavares (2012). Fenton's Process for the Treatment of Mixed Waste Chemicals, Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update, Dr. Tomasz Puzyn (Ed.), ISBN: 978-953-307-917-2, InTech, Available from: <http://www.intechopen.com/books/organic-pollutants-ten-years-after-the-stockholm-convention-environmental-and-analytical-update/fenton-s-process-for-the-treatment-of-mixed-waste-chemicals>

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2012 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](#), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen