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Microwave-assisted photo-Fenton decomposition of chlorfenvinphos and cypermethrin in residual water

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Abstract

The coupling of microwave radiation with photo-Fenton reaction for wastewater treatment was evaluated. This strategy was performed in a focused microwave digestion oven with open vessels. Ultraviolet radiation was obtained from microwave lamps (MWL) activated by microwave radiation. The operational conditions were established considering the extent of degradation of chlorfenviphos and cypermethrin used for bovine ticks (*Boophilus michoplus*) control. The results were based on residual carbon content, always comparing the procedures in the presence or absence of UV radiation. The combination of MWL and Fenton reaction degraded pesticide residues efficiently (>98%) in about 4 min.

Keywords: Fenton; Photo-Fenton; Microwave; Ultraviolet; Pesticide

1. Introduction

The agricultural activity uses chemical products for production increase, and, as consequence, it generates gaseous, liquids and solids residues that can be noxious to the environment [1]. Processes that employ great volumes of water significantly contribute with the contamination of the aqueous reservoir, mainly for the absence of treatment systems for the elevate volumes of produced liquid residues and the lack of understanding of the rural producer. Considering this context, it can be mentioned the contamination of soils and waters by pesticides employed in the bovine ticks control, which commonly produce hundreds of liters of residual solution, which could be indiscriminately discarded by the rural producer.

The use of low cost photo-oxidative processes for pesticides and insecticides degradation in natural and residual waters has been presenting good efficiency [2]. On the other hand, the main disadvantage of this kind of treatment is the need of a long time to obtain an efficient treatment [3]. The use of Fenton reaction combined with ultraviolet radiation (UV), which generates hydroxyl radical ($^{\bullet}$OH), is one of the main reason for the organic matter degradation [4].

Concentrated mineral acids followed by microwave heating [5] are an alternative for pesticide degradation in a short period of time. In 1975, Abu-Samra et al. described the use of microwave radiation as a means to complete acid-assisted wet digestions rapidly [6]. Since that time, microwave radiation for sample decomposition has become a well established technique for sample preparation. Otherwise, the acid concentration in the digests could be a drawback, owing to the detection procedure. A promising and economically feasible alternative would be the organic decomposition applying the combination of microwave-assisted heating and photo-oxidative reactions. Photochemistry in the microwave (MW) field provides an opportunity to combine chemical activation by two distinctive kinds of electromagnetic radiation. While low-energy MW radiation ($E = 0.4$–$40\ \mathrm{J\,mol^{-1}}$ at $\upsilon = 1$–100 GHz) is usually responsible for dielectric heating causing the thermal chemical activation, UV–vis radiation ($E = 600$–$170\ \mathrm{kJ\,mol^{-1}}$ at $\lambda = 200$–700 nm) initiates the excited-state reactions [7]. This combination is possible with the use of special UV lamps activated by microwave radiation (MWL), which allow accomplishing photo-degradations

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simultaneously with microwave-assisted heating. Florian and Knapp [8] proposed the use of MWL for milk sample decomposition for metals analysis. This coupling was also applied to partition and speciation studies of copper present in natural water [9].

The concern with the future of green chemistry is current and growing; several alternatives are used for the treatment of generated chemical residues, such as precipitation procedures, neutralization and distillation. Even so, presence of dissolved organic compounds in wastewater generally require procedures that degrade or eliminate the noxious characteristics of the residue, and different oxidation technologies were used, e.g. cavitation, photocatalytic oxidation, ozonation, use of hydrogen peroxide and Fenton chemistry. The mechanism of destruction in the case of different advanced oxidation techniques is similar, and some of the common optimum operating conditions point towards the synergism between these methods. In fact, the combined use of these processes should give better results as compared to individual techniques [10]. Recent reports indicate that a combination of H_2O_2 and UV irradiation with Fe(II), so-called the photo-Fenton process, can significantly enhance decomposition of many refractory organic compounds [11].

The key of photo-Fenton process is the oxidation of Fe(II) ions by H_2O_2, while one equivalent $^{\bullet}OH$ is produced ("Dark Fenton reaction" (1)). The obtained Fe(III) or its complexes subsequently act as the light absorbing species, that produce another radical while the initial Fe(II) is regained (2) and (3)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (1)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + H^+ + {}^{\bullet}OH \quad (2)$$

$$[Fe^{3+}L_n] + h\nu \rightarrow [Fe^{2+}L_{n-1}] + L^{\bullet} \quad (3)$$

The reaction (3), involving L organic linked (e.g. $RCOO^-$, RO^-, RNH^+, etc.), is more efficient than the oxidation of organic substrates via $^{\bullet}OH$ [12].

The application of Fenton reaction assisted by UV and microwave radiation comprises inherent characteristics for residues treatment, performing a fast and potentially attractive procedure. The evaluation of UV radiation to catalyze the Fenton reaction, combined with the microwave-assisted heating for the insecticide residues decomposition was the main goal of the work here described.

2. Experimental

2.1. Reagents and samples

All solutions were prepared with the use of analytical grade reagents (Merck, USA) and high-purity water (Milli-Q Water System, Millipore, Bedford, MA, USA) was used throughout. The following analytical grade reagents were used: concentrate HNO_3 (14 mol L^{-1}) and H_2O_2 (30%, m/v) (Mallinckrodt, Germany).

A 20 g L^{-1} potassium hydrogen phthalate ($C_8H_5KO_4$) stock solution was used to prepare the reference carbon solution.

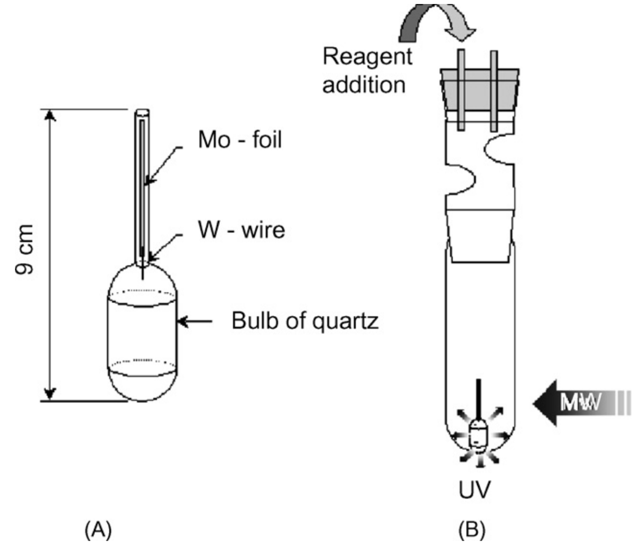

Fig. 1. (A) Schematic draw of a MWL. (B) Schematic draw of a quartz reaction vessel with MWL.

Solutions containing from 1.0 to 4.0 g L^{-1} Fe(II) were prepared from iron sulphate ($FeSO_4{\cdot}7H_2O$) (Synth, São Paulo, Brazil).

Tetramethylsilane (TMS) and dimethylformamide (DMF) were used as reference in the ^{1}H NMR spectrum, and the extracts used deuterated chloroform as solvent.

2.2. Apparatus

A focused-microwave oven with six cavities (Star System 6, CEM, Matthews, NC, USA) with a nominal power of 950 W was used for decomposition of the chemical residue.

The UV radiation is generated by immersed electrodeless Cd discharge lamps activated by the microwave radiation. A Cd low-pressure discharge MWL, developed by Florian and Knapp in cooperation with Gesellschaft für lichttechnische Erzeugnisse mbH (GLE, Berlin, Germany), was made of quartz glass, with dimensions of 90 mm high, 10 mm width, and a Mo antenna length of 35 mm (Fig. 1). The emission domain in the UV region is located at 228 nm. The radiation intensity of the MWL depends on the microwave absorbed energy [8].

A Varian (Mulgrave, Australia) Vista simultaneous inductively coupled plasma optical emission spectrometer (ICP OES) instrument with radial viewing, equipped with a concentric nebulizer, was used to accomplish the initial and the residual carbon content at the solutions before and after wastewater evaluated treatments [13]. The ICP OES operational conditions are summarized in Table 1.

The ^{1}H NMR analyses of decomposition were carried out using Bruker Instruments, model AVANCE, 400 MHz in the frequency of the hydrogen, operating at a temperature of 298 K.

2.3. Wastewater

Fenton and photo-Fenton reactions coupled to microwave radiation were evaluated to degraded a wastewater solution

Table 1
Instrumental parameters for RCC determination by ICP OES detection

Instrumental parameters	Radial ICP-OES
RF generator power (kW)	1.3
Nebulizer gas flow rate (L min^{-1})	0.6
Plasma gas flow rate (L min^{-1})	15
Auxiliary gas flow rate (L min^{-1})	1.5
Nebulizer	Concentric
Spray chamber	Cyclonic
Observation height (mm)	15
Analytical wavelength (nm)	CI 193.027

composed by 400:1 (v/v) of water containing pesticide used for bovine ticks (*Boophilus michoplus*) control. The used pesticide is a commercial concentrate, which was composed by 13.8% (m/v) chlorfenvinphos (2-chloro-1-(2,4-dichlorophenyl)-ethenyl diethyl phosphate) and 2.6% (m/v) cypermethrin (cyano(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate).

2.4. Wastewater treatment

Fenton and photo-Fenton reactions coupled to microwave radiation were carried out using from 9 to 30 mL of wastewater, that were added to the quartz vessel of microwave oven, with a mixture containing 0.5 mL of HNO_3 1.0 mol L^{-1}, plus 0.5–6.0 mL of H_2O_2 30% (m/v), and 1.0–4.0 g L^{-1} of Fe(II). The solutions were added before starting the heating cycle, and then were submitted to MW radiation from 4 to 10 min at 140 °C. This temperature was set to guarantee continuous incidence of microwave radiation during decomposition, to obtain maximum UV income. At the end of the heating program, all digests were quantitatively transferred to 50 mL volumetric flasks, which received 0.5 mL of concentrate HNO_3 before made the volume up with water.

The procedures had been carried out with and without the MWL for UV radiation outcome evaluation, and study the range of H_2O_2 and Fe(II) concentrations to improve Fenton reaction performance.

2.5. Determination of the residual carbon content

Determination of the residual carbon content (RCC) was carried out by ICP OES monitored at CI 193.027 nm [13]. A linear calibration with up to five carbon analytical solutions was prepared. Calibration standards ranging from 0.0 to 2.0 g L^{-1} were daily prepared by diluting the stock solution of potassium hydrogen phthalate.

2.6. NMR analysis

A pre-concentration of wastewater, before and after treatments, was done after the establishment of pesticide decomposition parameters, owing to ^{1}H NMR poor sensitivity. Liquid–liquid extractions were performed using ethyl ether. The mixtures were then evaporated at 25 °C for solvent removal and freeze-dried for water removal.

3. Results and discussion

Using the focused microwave oven, studies concerned with concentrations of Fe(II) and H_2O_2 were carried out with systematic experiments. Volumes among 1.5 and 6.0 mL of Fe(II) solutions containing from 1.0 to 4.0 g L^{-1}, plus volumes among 1.5 and 6.0 mL of H_2O_2 30% (m/v) were evaluated, as presented in Fig. 2. In all experiments it was added 0.5 mL of HNO_3 (1 mol L^{-1}). Fenton and photo-Fenton reactions are improved in acid medium, and acid addition was essential for pH adjustment.

All results for the wastewater solution after treatment are expressed in extent of degradation, evaluated by the RCC of the solutions. The RCC values were obtained comparing with the initial carbon content (1.8 g L^{-1} of C). In these studies, lower amounts of Fe(II) and H_2O_2 were not effective to degrade the evaluated wastewater solutions.

The results without Fe(II) addition are depicting in the two first columns of Fig. 2. It is possible to observe that about 40% of the initial carbon content of wastewater was degraded under MW radiation and H_2O_2 oxidation. When UV radiation was coupled to MW system and H_2O_2 oxidation, the UV radiation

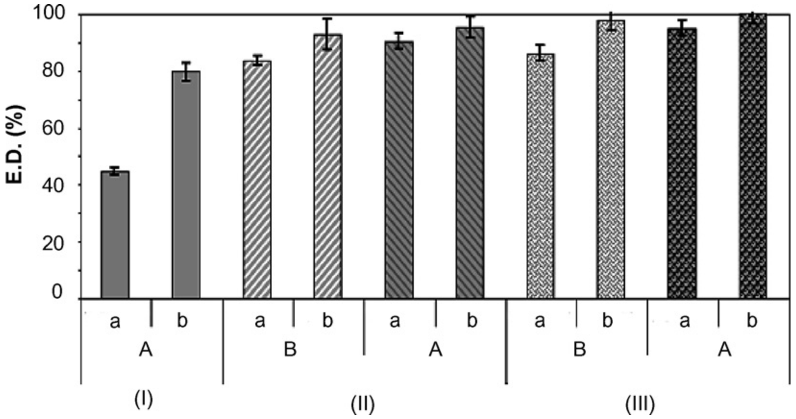

Fig. 2. Extent of degradation (ED, %) of 10 mL of wastewater (1.8 g L^{-1} of original carbon content) under 4 min of microwave radiation. Evaluation of iron and hydrogen peroxide concentrations in the microwave radiation coupled to Fenton and photo-Fenton reactions: (a) without UV; (b) with UV; (A) with 6.0 mL of H_2O_2; (B) with 1.5 mL of H_2O_2. (I) without Fe(II); (II) with 1.5 mL of Fe(II) 1000 mg L^{-1}; (III) with 6.0 mL of Fe(II) 4000 mg L^{-1}.

increases in about 100% the decomposition process compared with the previous treatment. The hydroxyl radicals generated by addition of Fe(II), Fenton reaction, improved the efficiency, reaching the maximum degradation of the wastewater, as it could be observed in the further columns of Fig. 2.

The results demonstrated that total wastewater degradation was obtained increasing the Fe(II) amount up to 4.0 g L^{-1} plus MWL. In the experimental conditions, this treatment improved in about 10% the extent of degradation compared with the treatment with 1.0 g L^{-1} Fe(II). As expected, increasing the concentration of H_2O_2 added improved the wastewater degradation. This can be explained by the effect of the $^{\bullet}$OH radicals additionally produced. An increase of hydrogen peroxide enriched the solution with photo-produced hydroxyl radicals and resulted in a decrease in RCC from the photo-oxidation. In the present work, high concentration of H_2O_2 was utilized when compared with others authors. Parra [14] and Philippopoulos and Poulopoulos [15] described that excess of H_2O_2 will react with $^{\bullet}$OH, competing with organic pollutants and consequently reducing the efficiency of the treatment. However, in the present study, this effect was not observed, mainly because H_2O_2 is consumed as oxidant during microwave radiation program.

Iron and H_2O_2 concentrations ratio that could be used to oxidize organic compounds are at present not a consensus in the literature [10]. An experimental planning was applied for better evaluation of the parameters involved in the wastewater degradation. It can be observed in the Pareto's chart (Fig. 3 (I)) that the main factor that caused significant effect on extent of wastewater degradation was UV radiation. The results of the study showed that photo-Fenton coupled to microwave radiation process was more effective to decrease the original carbon content of wastewater compared with Fenton coupled to microwave radiation process. Fig. 3 (II) shows the effects of the main factors on extent of degradation. An efficiency increase was observed when concentrations of Fe(II) and H_2O_2 were increased. This is in agreement with was previously discussed.

Furthermore, the use of MWL improves the extent of degradation in all experiments with those without them. The plot of estimated response surface (Fig. 3 (III)) shows enhanced results with higher Fe(II) concentrations. Previous reports have also concluded that increasing the Fe(II) concentration caused an increase of the degradation rate, and there is no evidence of an optimum value beyond which the rates either stabilize or become lower [16–18]. However, the utilization of higher initial concentration of Fe(II) ions may not always lead to positive effects. It is also important to consider the residual amount of the added ferrous salts along with the total concentration of the total dissolved solids (TDS). An increase in TDS effluent amount is not allowed as it leads to low gas solubility, salts ionization, and also promotes lower bio-degradation rates.

After these investigations, further research was focused on the effect of the volume of residue. Fig. 4 shows the photo-chemical behavior with decomposition time when the volume of wastewater was increased up to 30 mL. Elevated extent of degradation was attained in all procedures. Furthermore, the MWL procedure led to about a 10% increase in yield, indicating a contribution of

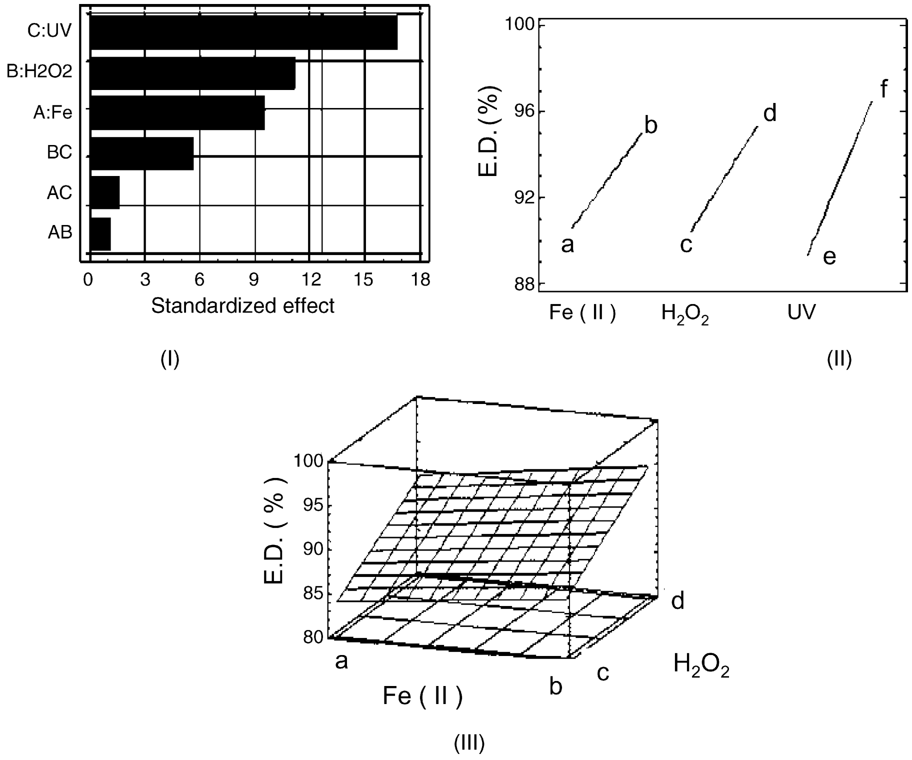

Fig. 3. Statistical analyses for evaluating the effect of Fe(II), H_2O_2, UV and its interactions on the extent of degradation (ED) of wastewater. All experiments were performed using 10 mL of wastewater solution under 4 min of microwave radiation. (I) Pareto's chart; (A) Fe(II); (B) H_2O_2; (C) UV radiation. (II) Main effect chart: (a) 1.5 mL of Fe(II) 1000 mg L^{-1}; (b) 6.0 mL Fe(II) 4000 mg L^{-1}; (c) 1.5 mL H_2O_2; (d) 6.0 mL H_2O_2; (e) without UV; (f) with UV. (III) Estimated response surface: (a) 1.5 mL of Fe(II) 1000 mg L^{-1}; (b) 6.0 mL Fe(II) 4000 mg L^{-1}; (c) 1.5 mL H_2O_2; (d) 6.0 mL H_2O_2.

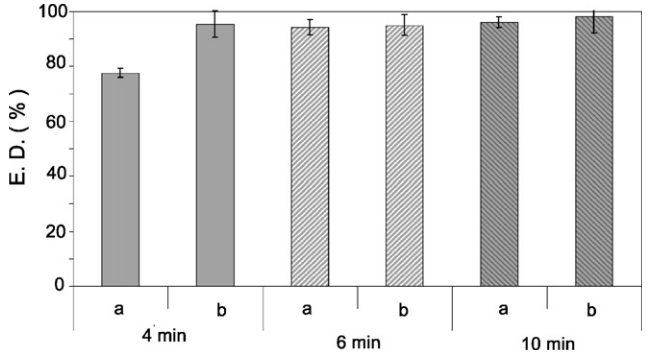

Fig. 4. Study of decomposition time in the extent of degradation (ED) of wastewater by using photo-Fenton oxidation coupled to microwave radiation: (a) without UV; (b) with UV. All experiments were performed using 30 mL of wastewater solution plus 9.0 mL of Fe(II) 1000 mg L^{-1} plus 4.5 mL of H_2O_2 30% (m/m).

the UV radiation in the reduction of the original carbon content. The UV radiation enhances radical generation, accelerating the oxidation of the organic compounds. However, Fenton processes plus microwave radiation by themselves were also efficient for wastewater organic degradation.

The photo-Fenton or Fenton process plus microwave radiation rapidly decomposed the wastewater. The coupling of microwave radiation to Fenton/photo-Fenton process shows an increment in reaction rate by at least a factor of 50 and also an improvement in the extent of degradation. In fact, with the use of microwave radiation, 95% (5% of RCC) of extent of degradation could be reached in about 4 min (Fig. 4). Adopting similar experimental conditions, but without microwave radiation, it was necessary around 5 h to attain 86% of degradation (around 14% of RCC, results not presented).

Therefore, for degradation of 10 mL of wastewater, a volume of 1.5 mL of 1.0 g L^{-1} Fe(II) solution (corresponding to 2.1×10^{-3} mol L^{-1}) + 1.5 mL of H_2O_2 (corresponding to 1.1 mol L^{-1}) was established. These conditions allowed approximately 95% of extent of degradation in a period of 4 min under treatment of photo-Fenton oxidation coupled to microwave radiation. Analysis of NMR was then accomplished to evaluate the decomposition products. Otherwise, with the use of this technique, new reaction products were not observed, suggesting the presence of the original forms even after photo-Fenton plus microwave wastewater treatment (Fig. 5). However, the considered procedure reduces in approximately 95% the original wastewater carbon contents, allowing lower impact on environment caused by its discard.

The spectra show that after photo-oxidation, the most significant reduction occurred in the aromatic and carbinolic regions. The rupture of aromatic rings has probably occurred, transforming the original product in other ones with smaller molar masses, subsequently changed to $CO_2 + H_2O$. Comparison between the spectra was possible because both were integrated compared with the same volume (2 μL) of the same DMF (8.1 ppm) sign, used as internal standard for both samples.

Sample preparation based on the proposed procedure is other possible application for metals determination by spectroanaly-

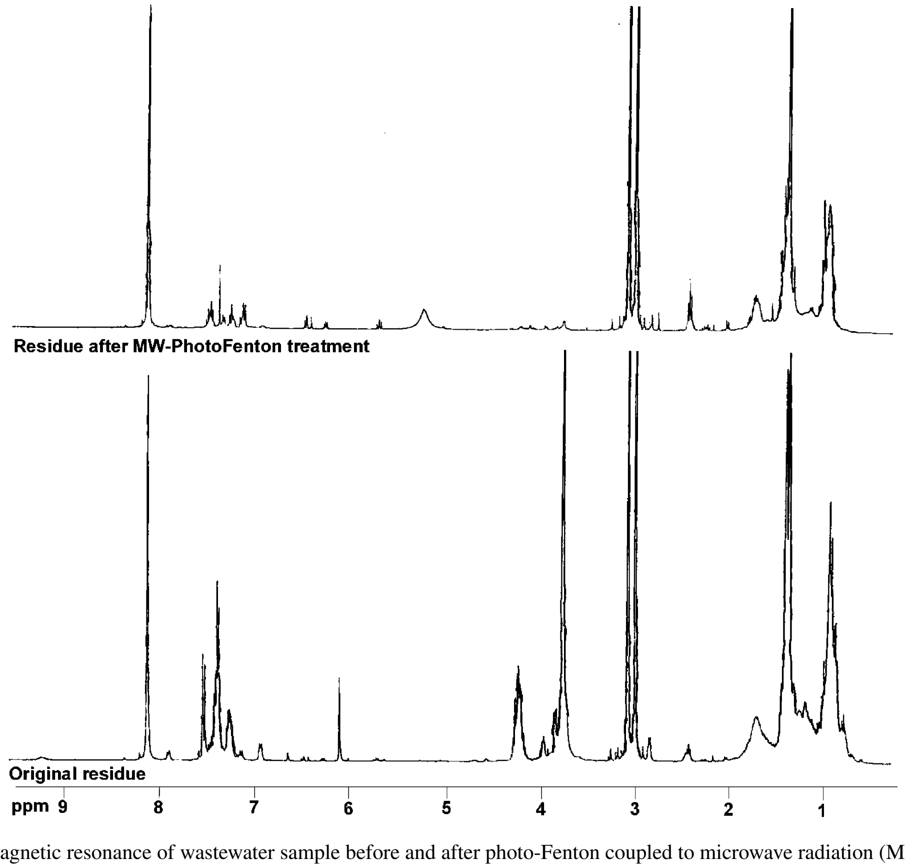

Fig. 5. Spectra of nuclear magnetic resonance of wastewater sample before and after photo-Fenton coupled to microwave radiation (MW-photo-Fenton) treatment.

sis. Adopting this alternative, small amounts of diluted mineral acids could be used. Otherwise, care should be taken owing to the high amount of iron remaining in solution, considering possible spectral interferences in techniques such as ICP OES, mainly in the lines related to Al, As and B. The spectral interferences caused by iron also affected the choice of the carbon emission line for RCC measurements by ICP OES.

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