Characterization and photo-Fenton treatment of used tires leachate

Judith Sarasa [*], Tomás Llabrés, Peña Ormad, Rosa Mosteo, José Luis Ovelleiro

Department of Chemical Engineering and Environmental Technologies, University of Zaragoza, c/María de Luna n° 3, 50018 Zaragoza, Spain

Abstract

In this study the leachates derived from used tires were firstly characterized by means of the evaluation of their organic matter content. The leachate from tire powder presented a COD value of 508 mg O_2 l^{-1} and a TOC of 214 mg Cl^{-1}. The main identified organic substances were constituents of the rubber structure: benzothiazole derivatives, phthalates, phenolic derivatives, hydrocarbons and fatty acids. The application of photo-Fenton treatment was investigated in order to obtain the maximum organic matter removal. When a solar chamber as light source was used (light intensity = 500 W m^{-2}), the best operational conditions were the following: [H_2O_2] = 3703 mg l^{-1}, [Fe^{2+}] = 92.1 mg l^{-1}, initial pH 2.7–3.0, reaction time = 100 min. After the photo-Fenton treatment at optimum conditions, the reached COD and TOC reduction was 64% and 48%, respectively. The main initial organic substances were eliminated after the reaction and no significant by-products were identified. A complementary treatment consisted of coagulation-flocculation carried out with $FeCl_3$·$6H_2O$ at pH 12 produced a maximum organic matter removal of 43% as COD and 39% as TOC. A combination of photo-Fenton followed by coagulation-flocculation enhanced the organic matter removal: a reduction of 77% of COD and 64% of TOC was attained.
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Keywords: Benzothiazole; Coagulation-flocculation; Hydrogen peroxide; Hydroxyl radical; Used tires landfill

1. Introduction

Generally, benzothiazole (BT) and its derivatives are associated to the production of tires. These compounds are mainly used as accelerators of the vulcanization in rubber production. BT derivatives are not tightly bound in the rubber matrix, therefore they may leach into soil via street runoff and reach surface waters by means of drainage systems [1]. On the other hand, BT derivatives as 3-methyl-1,2-benzisothiazole, 2(3H)-benzothiazolone, 2-mercaptobenzothiazole, 2,2′-dithiobisbenzothiazole, etc. are commonly found in wastewaters derived from rubber additives manufacturing [2].

The main environmental impact of these compounds is that they are poorly biodegradable and persistent. Benzothiazole, 2-(methylthio)-benzothiazole and 2-hydroxybenzothiazole are stable products in aquatic environments [3]. This persistent character has been also reported by Puig et al. [2], who detected benzothiazole derivatives in the water supply of Zaragoza (Spain). The origin of these pollutants was mainly attributed to a rubber

accelerators manufacturing plant, which discharges its wastewaters in a point of the Ebro River located 180 km upstream the supplying point. On the other hand, some of these compounds have toxic character. Benzothiazole is a potential toxicant to fish [4] and 2-mercaptobenzothiazole (MBT) has toxic effects to bacteria and other microorganisms [1,5].

Since a great amount of used tires have been deposited in landfills for years, the leachates from these kind of landfills have to be taken into account as a source of BT environmental contamination. It has been estimated that 250,000,000 used tires are accumulated each year in the 15 Member States of the European Union. In 1992, approximately 65% of used tires in the 12 States of EU were destined to landfills. Ten years later in 2002, this situation had completely reversed in the 15 States: approximately 65% of used tires were reused, retreaded, recycled or recovered (energy production), while less than 35% were destined for landfills [6].

Future prospects of used tires management have the target of zero landfilling in the EU, according to Council Directive 1999/31/EC [7]. Under this Directive, landfilling is no longer an option in the EU for whole tires (since 2003) or shredded tires in 2006. However, historic stockpiles are estimated to be over 1,000,000,000 within the EU, and new accumulations had been

dumped in designated landfills for many years. According to all these data, the leachates proceeding from used tires landfills can constitute an important source of pollution.

On the other hand, the toxicity of rubber tire leachates to aquatic organisms has been already demonstrated [8,9] which hinders their purification by a conventional biological treatment. Several researchers have investigated the treatment of landfill leachates by physico-chemical treatments as Fenton and photo-Fenton [10–14], coagulation-flocculation [15,16], and even the combination of both treatments to improve the organic matter removal [17–19].

Fenton's reagent is an advanced oxidation process (AOP) which generate hydroxyl radicals ($OH^\bullet$) from the catalytic decomposition of hydrogen peroxide (H_2O_2) carried out by ferrous ion (Fe^{2+}) under acidic condition [20]. Iron can also be used in the ferric state (Fe^{3+}), although $OH^\bullet$ production is slower. In this case the process is called "Fenton-like" reaction [21]. Both Fenton and Fenton-like reactions are accelerated when UV/visible irradiation is applied (photo-Fenton reaction), improving thus the degradation rates. The hydroxyl radical is one of the most reactive and strongest oxidant, which exhibits an oxidation potential of 2.80 V at pH 3. It is capable of oxidizing a great variety of organic substances such as aromatic and alkyl compounds. Its non-selective nature leads to the oxidation of the majority of compounds present in the system, including the generated intermediates [22]. The application of Fenton and photo-Fenton to landfill leachates leads to a COD degradation of 60–70% [11,14].

Coagulation-flocculation is a quick and inexpensive treatment which reaches COD removals of 50–55% when it is applied to landfill leachates. However, its application is limited by the generation of a large volume of sludge, which can be up to 45% [15]. The generated sludge needs an appropriate management as, for example, the recovery of coagulants, its reuse for other applications or a final disposal into landfills [23].

In order to obtain more information about the environmental impact of used tires leachates, one of the main objectives of this work was to characterize the leachate by means of global parameters and the identification of individual organic substances. A suitable treatment for the purification of used tires leachate was also investigated. In particular, the photo-Fenton reaction was selected due to Andreozzi et al. [24,25] demonstrated its efficiency in the removal of BT derivatives. The effect of addition of hydrogen peroxide and ferrous salt, the influence of initial pH and kind of salt (ferrous or ferric) were evaluated in order to obtain the optimum conditions. After the photo-Fenton treatment, the resultant leachate was characterized. A conventional coagulation-flocculation treatment was also investigated in order to compare the organic matter removal and to combine it with the photo-Fenton process.

2. Materials and methods

2.1. Leachate preparation

Characterization and physico-chemical experiments were carried out with synthetically prepared leachate from used car tires. The sample of leachate was obtained according to Spanish standard leaching test for hazardous waste characterization, which is based on EPA Method 1310A [26]. The leachate was obtained from Kelly Steelmark 3 Radial Tubeless used tires. The used tire was crushed to powder and passed through a sieve of 9.5 mm nominal screen size. The leaching test consisted of adding Milli-Q water as leachant to a portion of tire powder, establishing a liquid to solid ratio of 16 (w/w). The liquid–solid mixture was stirred for 24 h, maintaining a pH value of 5.0 ± 0.2 by addition of acetic acid when it was necessary. A volume of approximately 650 ml of leachate was collected by filtration of the resultant liquid over a 0.45 μm membrane filter. A representative sample of leachate was obtained by combining 25 individual leachates into one sample (composite sample) of 16 l. In order to study the influence of crushing in the leachate characteristics, an analogous sample of 6.5 l of leachate was obtained from approximately 30 g of strip shaped scrap tire following the procedure previously described.

2.2. Photo-Fenton treatment

A 100 ml of leachate from tire powder were placed in transparent glass vials, where different dosages of 1 M iron salt solution (as $FeSO_4 \cdot 7H_2O$ or $FeCl_3 \cdot 6H_2O$) and H_2O_2 (30% w/w) were added. The initial H_2O_2 dosage was based on the stoichiometric ratio with respect to the COD value assuming complete oxidation [11]. $FeSO_4 \cdot 7H_2O$ was firstly selected as source of iron due to this catalyst provided the highest efficiency to effluents derived from the manufacturing of rubber additives [27]. After the addition of reactives, the pH was adjusted to the desired value with H_2SO_4 5N. The vials were put in a solar chamber ATLAS Suntest CPS + (light intensity = 500 W m^{-2}) and magnetically stirred during all the reaction time. COD was measured each 20 min of the reaction in order to obtain the optimum conditions of treatment: initial pH, hydrogen peroxide and iron dosages, ferrous or ferric salt and time of reaction. The pH and residual H_2O_2 were also checked in time.

The effect of light was also evaluated by carrying out experiments during 27 h (1620 min) at two different conditions: under natural solar light irradiation and in absence of light (darkness). Solar light experiments were performed during sunny days at the University of Zaragoza (Zaragoza, Spain, 247 m above sea level, 41°39′ N, 1°00′29 E) and complete darkness was simulated by covering the vials with a cardboard box. The Fenton reaction was carried out as described above by addition of the optimum dosages of reactives found with the solar chamber.

2.3. Coagulation-flocculation treatment

The coagulation-flocculation experiments were performed with synthetic leachate obtained from tire powder in a Jar testing apparatus FC-6L supplied by SBS Instruments. The selected coagulant ($FeCl_3 \cdot 6H_2O$), initial dosages and operational conditions were in accordance to those recommended by Amokrane et al. [15] for the treatment of landfill leachates. Three different ferric chloride dosages were added at different recommended pH

values [28]. The desired pH was adjusted with a calcium hydroxide (Ca(OH)$_2$) solution before agitation when the experiments were performed in the alkaline region. Anionic polyelectrolyte AP-911 was added as flocculant to obtain a concentration of 2 mg l^{-1} in the leachate. The efficiency of each experiment was evaluated by measuring the COD and TOC of the resultant supernatant after sludge settling. The sludge volume (in ml l^{-1}) was also calculated after sedimentation.

2.4. Photo-Fenton combined with coagulation-flocculation

In order to improve the organic matter removal, a combination of the photo-Fenton treatment followed by coagulation-flocculation was investigated. The optimum conditions obtained in the previous experiments were applied to the tire powder leachate. The efficiency of the overall treatment was determined in terms of COD and TOC reduction.

2.5. Analytical instrumentation

pH and conductivity were measured with a Crison 507 pHmeter and a Crison Basic 30 conductivimeter, respectively. Total organic carbon (TOC) was measured using a TOC Analyzer Shimadzu TOC-V CSH. Chemical oxygen demand (COD) was determined according to "Standard Methods" [29]. In photo-Fenton treated samples, the presence of hydrogen peroxide was controlled by means of Merck Merckoquant Peroxide Test strips (range from 1 to 100 mg l^{-1}). Due to residual hydrogen peroxide constitute a positive interference in the COD analysis, it was previously removed by raising the pH up to 12 with NaOH (hydrogen peroxide dissociation constant = 1.78×10^{-12} at 20 °C [30]).

The identification of individual organic substances (semivolatile compounds) of raw and photo-Fenton treated leachate was done by means of liquid–liquid extraction and subsequent GC/MS analysis, according to "Standard Methods" [29]. The GC/MS system consisted of a Trace GC connected with a Finnigan Polaris Q Mass Spectrometer, both supplied by Thermo Electron Corporation. Semi-quantitative estimation based on peak area of anthracene-d$_{10}$ (which was added as internal standard to the extracts) was used to quantify the identified compounds.

3. Results and discussion

3.1. Characterization of the leachates

The characterization of the leachates obtained from tire powder and scrap tire was carried out by means of global parameters and the identification of individual substances. The resultant pH of both leachates was 4.9. Table 1 shows the values of COD, TOC and conductivity for both leachates. The main identified organic compounds extracted during the standard leaching test for both tire powder and scrap tire are also listed. The estimated concentration of each compound in mg l^{-1} is presented.

The leachate obtained from tire powder presents a higher content of organic matter (measured as COD and TOC) and con-

Table 1

Characterization of tire powder and scrap tire leachates: COD, TOC, conductivity and main identified organic compounds

	Leachate from tire powder	Leachate from scrap tire
Global parameters		
COD (mg O$_2$ l^{-1})	508	204
TOC (mg C l^{-1})	214	83
Conductivity (μS cm^{-1})	375	197
Identified compounds	Conc. (mg l^{-1})	Conc. (mg l^{-1})
Benzothiazole derivatives		
1,2-Benzisothiazole-3-carboxylic acid	0.482	0.414
2(3H)-Benzothiazolone	0.175	n.d.
Phthalates and related compounds		
1,2-Benzenedicarboxylic acid, diethyl ester	n.d.	0.044
1,2-Benzenedicarboxylic acid, dibutyl ester	0.158	0.291
1,2-Benzenedicarboxylic acid, butyl 2-ethylhexyl ester	0.112	n.d.
1,2-Benzenedicarboxylic acid, diheptyl ester	n.d.	0.562
1,2-Benzenedicarboxylic acid, diisooctyl ester	3.960	0.167
1,3-Benzenedicarboxylic acid, methyl ester	0.114	n.d.
1,4-Benzenedicarboxylic acid, dimethyl ester	n.d.	0.127
Aromatic derivatives		
1,2-Dimethylbenzene	0.170	n.d.
1,2,4-Trimethoxy-benzene	0.084	n.d.
Biphenyl	0.027	n.d.
Phenol, 3,5-bis(1,1-dimethylethyl)-	0.055	0.045
3,5-Bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoic acid, methyl ester	0.074	n.d.
Hydrocarbons		
1-Chlorotetradecane	1.682	0.454
3-Ethyl-5-(2-ethylbutyl)-octadecane	0.019	n.d.
Nonadecane	0.398	0.531
1,1-Bis(dodecyloxy)-hexadecane	0.287	0.391
Acids and esters		
Benzenacetic acid, methyl ester	0.197	n.d.
Propanoic acid, phenylmethyl ester	0.042	n.d.
Dodecanoic acid, Methyl ester	n.d.	0.073
Tetradecanoic acid, methyl ester	n.d.	0.107
2-Bromotetradecanoic acid	n.d.	0.023
Methyl palmitelaidate	0.191	n.d.
Palmitic acid, methyl ester	0.426	0.092
Heptadecanoic acid	0.039	n.d.
9-Octadecenoic acid, methyl ester	0.179	0.123
n-Octadecanoic acid, methyl ester	0.143	0.095
10,13-Octadecadiynoic acid	0.106	0.112
Tricosa-10,12-diynoic acid	n.d.	0.036

n.d.: not detected.

ductivity. This fact is confirmed by comparison of the identified organic substances. In general, it can be said that the number and estimated concentration of organic substances are greater in the leachate obtained from tire powder than the leachate from scrap tire. A better extraction of the organic compounds from tire

powder is a consequence of a greater contact surface between the leachant and the waste.

It is observed that many of the identified organic compounds are derived of rubber composition. Benzothiazole derivatives are used as accelerators of rubber vulcanization and phthalates are commonly used as plasticizers. Hindered phenolic derivatives such as 3,5-bis(1,1-dimethylethyl)-phenol and 3,5-bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoic acid, methyl ester are used as antioxidants. They act as radical-trapping agents and are added to the rubber to prevent degradation [30]. Chlorinated paraffins as 1-chlorotetradecane are used to decrease flammability of rubber. Hydrocarbons and fatty acids are processing aids, and they are used, for example, as dispersion agents, lubricants and homogenizers [30]. On the other hand, 1,2-dimethylbenzene (or *o*-xylene) is a motor fuel component and some of the detected hydrocarbons can be derived of road asphalt.

According to this characterization, the leachate from tire powder was thought to be more representative of a real leachate proceeding from used tires landfills, and it was selected for carrying out the experimental treatments that are described below.

3.2. Photo-Fenton treatment

Firstly, different dosages of H_2O_2 were added ranging from 1010 to 5032 mg l^{-1} in the sample. Iron dosage as Fe^{2+} was maintained at 50.3 mg l^{-1} for all the experiments ranging ratios Fe:H_2O_2 from 1:20 to 1:100 (w/w). Initial pH was adjusted to 3 with H_2SO_4 due to at this pH hydroxyl radicals exhibit the highest oxidative power [22]. A complementary experiment was carried out without hydrogen peroxide. Fig. 1 shows the percentage of COD removal as a function of time for different H_2O_2 concentrations.

For the experimented dosages, the percentages of COD removal range from 50.4 to 58.7 after 160 min of treatment. For the lower dosages (1010 and 1919 mg l^{-1} of H_2O_2) the maximum COD reduction (50.4–52.6%) was reached at 120 min of treatment. At this time, no residual hydrogen peroxide remained in the sample, which leads to stop the photo-Fenton reaction. When higher dosages of hydrogen peroxide are added, a remaining concentration is always observed after 160 min: for initial dosages 2844 and 3703 mg l^{-1}, the residual concentration is
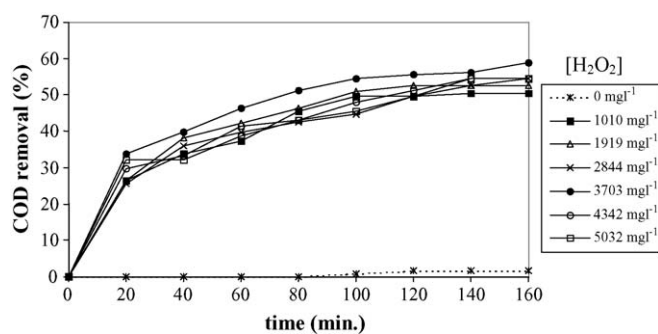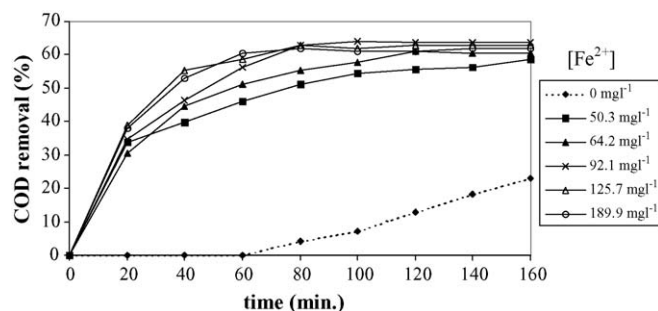
Fig. 1. Percentages of COD reduction at different concentrations of H_2O_2 during the photo-Fenton reaction with solar chamber (initial pH: 3.0; light intensity: 500 W m^{-2}; [Fe^{2+}] = 50.3 mg l^{-1}).

Fig. 2. Percentages of COD reduction at different concentrations of Fe^{2+} during the photo-Fenton reaction with solar chamber (initial pH: 3.0; light intensity: 500 W m^{-2}; [H_2O_2]: 3703 mg l^{-1}).

10–30 mg l^{-1}; 4342 and 5032 mg l^{-1} lead to a residual concentration of 30–100 mg l^{-1}.

Generally, it can be said that the degradation rate of organic compounds increases as H_2O_2 dosage increases until a critical hydrogen peroxide concentration. When a higher concentration than the critical is used, the H_2O_2 itself contributes to the OH$^\bullet$ scavenging capacity [31]. In this case, the reaction of hydrogen peroxide with hydroxyl radicals hinders any further degradation of organic matter [11]. Fig. 1 shows that the maximum COD reduction (58.7%) is obtained with a H_2O_2 concentration of 3703 mg l^{-1} and the addition of higher dosages do not enhance the efficiency of the photo-Fenton treatment. According to these results, a dosage of 3703 mg l^{-1} of hydrogen peroxide was considered the optimum.

The optimization of ferrous iron dosage was carried out at initial pH 3 and 3703 mg l^{-1} of H_2O_2. The concentration of iron was increased from 50.3 (iron concentration settled on the previous experiments) to 189.9 mg l^{-1} in the sample. A complementary experiment was carried out without adding ferrous salt. Fig. 2 shows the effect of iron dosage on the percentage of COD removal as a function of time.

As it was mentioned above, a dosage of 50.3 mg l^{-1} leads to a remaining hydrogen peroxide concentration of 10–30 mg l^{-1} after 160 min. For the dosages 64.2 and 92.1 mg l^{-1}, no residual hydrogen peroxide was present in the sample at 140 min of treatment, whereas for the higher dosages this fact was observed at 120 min. As it can be seen in the figure, dosages higher than 92.1 mg l^{-1} do not improve the COD reduction, probably due to Fe^{2+} reacts with OH$^\bullet$ as a scavenger [11]. For this dosage, the maximum COD elimination (64%) was achieved at 100 min of treatment. The experiment carried out without ferrous salt provided a COD removal of 23.1% after 160 min. This can be explained by the formation of OH$^\bullet$ from the direct photolysis of H_2O_2, although this reaction is much slower [11].

For all the experiments in which different dosages of H_2O_2 and Fe^{2+} were combined, a gradual decrease of the initial pH of almost one unit was observed during the 160 min of treatment. This fact indicates the formation of acid compounds as intermediates during the oxidation reaction.

Once the optimum concentrations of hydrogen peroxide and ferrous salt were defined, several experiments were carried out at different initial pH values in order to obtain the optimum one.
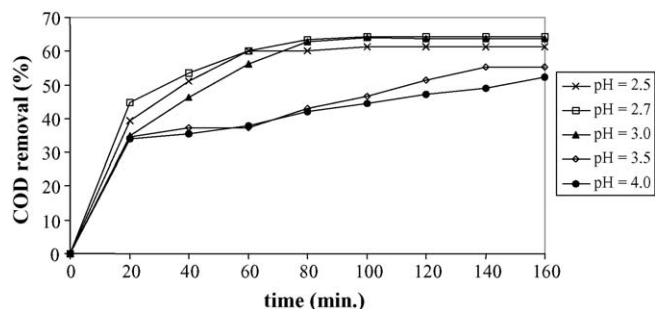
Fig. 3. Percentages of COD reduction at different initial pHs during the photo-Fenton reaction with solar chamber (light intensity: 500 W m^{-2}; [H$_2$O$_2$]: 3703 mg l^{-1}; [Fe^{2+}]: 92.1 mg l^{-1}).

Fig. 5. Percentages of COD reduction at different light exposure conditions: solar chamber (light intensity: 500 W m^{-2}), sunlight and darkness (initial pH: 3.0; [H$_2$O$_2$]: 3703 mg l^{-1}; [Fe^{2+}]: 92.1 mg l^{-1}).

In the literature it has been reported that the degradation is most efficient in the pH range of 2.5–4.0 [32]. Fig. 3 shows the effect of the initial pH on the COD removal efficiency as a function of time.

For initial pH 2.5 and 2.7, it was observed that no residual hydrogen peroxide remained in the sample at 100 min of treatment. For initial pH 3, the remaining hydrogen peroxide concentration was 30–100 mg l^{-1} at this time. However, when initial pH was 3.5 and 4.0, a residual concentration greater than 100 mg l^{-1} was detected during 160 min of treatment. Similar COD removal was reached at initial pH values 2.5, 2.7 and 3.0 after the treatment (61.4–64.2%), while the efficiency decreased when the initial pH was 3.5 and 4.0. This can be explained by deactivation of ferrous catalyst as a consequence of the formation of ferric hydroxo complexes at pH > 3 [11,22,32]. In fact, the formation of a brown precipitate was observed at initial pH 4.0, which can also difficult the absorption of UV light [11]. On the other hand, the oxidation potential of OH$^\bullet$ decreases as pH increases [22]. The maximum COD reduction (64.0–64.2%) was observed at 100 min of treatment when initial pH was 2.7–3.0. The optimum conditions which lead to the maximum COD removal along with the minimum residual hydrogen peroxide (0 mg l^{-1}) are initial pH 2.7 and 100 min of treatment.

A complementary analysis was done adding ferric chloride (FeCl$_3$·6H$_2$O) at optimum conditions, in order to determine the best source of iron (ferrous or ferric salt). As it can be seen in Fig. 4, the COD reduction obtained after 40 min is not affected by the kind of iron salt. The use of Fe^{3+} do not enhance the

efficiency of the overall reaction in terms of COD reduction, which is in accordance with the results obtained by Rivas et al. [12].

The influence of light was also investigated. Fig. 5 shows the evolution of COD removal at different light exposure situations for the optimum conditions. The photo-Fenton reaction is clearly faster using the solar chamber due to leachates are subjected to constant climatic and irradiation conditions. Nevertheless, it was observed under complete darkness and sunlight (including day and night time) that a COD elimination of 56.2–58.7% is reached after approximately 8.5 h of treatment (510 min). For both cases, a remaining hydrogen peroxide concentration was detected at this time (sunlight conditions: 30–100 mg l^{-1}, darkness: >100 mg l^{-1}). When the reaction is extended to 24 h (1440 min), the COD removal is only enhanced 1.5–2% (final COD removal of 58.1–60.1%). At this time, no residual hydrogen peroxide was present in the sample.

Fig. 6 shows the evolution of COD, TOC, pH and conductivity of the leachate as a function of time during the photo-Fenton reaction with solar chamber at optimum conditions. A high percentage of COD (45%) was eliminated after 20 min of reaction, reaching a final value of 176 mg O$_2$ l^{-1} after 100 min. TOC elimination, which indicates the formation of CO$_2$, was slower and a final value of 110 mg C l^{-1} was obtained. The pH decreased approximately one unit at 40 min, after which it was maintained constant. This indicates that acid substances were produced as intermediates at early stages of the reaction. The conductivity increased from 1248 to 1720 μS cm^{-1}, probably due to the
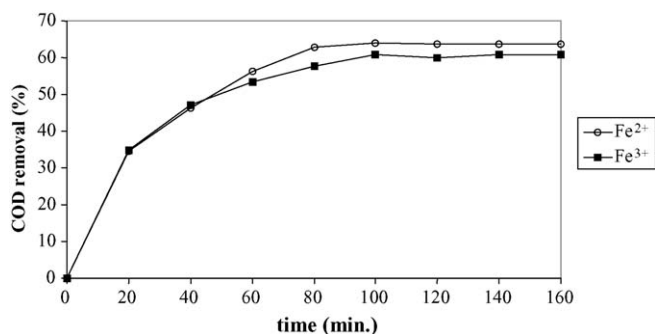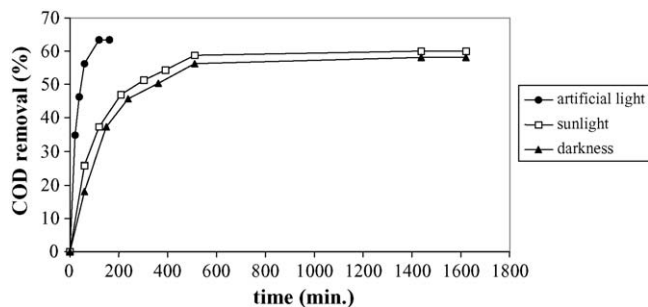

Fig. 4. Percentages of COD reduction adding ferrous and ferric salt during the photo-Fenton reaction with solar chamber (initial pH: 3.0; light intensity: 500 W m^{-2}; [H$_2$O$_2$]: 3703 mg l^{-1}; [Fe]: 92.1 mg l^{-1}).
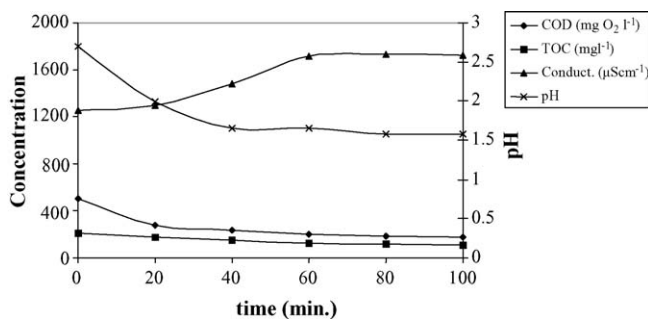

Fig. 6. Evolution of COD, TOC, pH and conductivity of the leachate during the photo-Fenton reaction with solar chamber at optimum conditions (initial pH: 2.7; light intensity: 500 W m^{-2}; [H$_2$O$_2$]: 3703 mg l^{-1}; [Fe^{2+}]: 92.1 mg l^{-1}).

Table 2
Concentration and percentage of removal of the identified compounds in the leachate from tire powder after the photo-Fenton treatment with solar chamber at optimum conditions (initial pH: 2.7; light intensity: $500\,W\,m^{-2}$; $[H_2O_2]$: $3703\,mg\,l^{-1}$; $[Fe^{2+}]$: $92.1\,mg\,l^{-1}$; time of reaction: 100 min)

Identified compounds	Conc. ($mg\,l^{-1}$)	%Removal
Benzothiazole derivatives		
1,2-Benzisothiazole-3-carboxylic acid	n.d.	100
2(3H)-Benzothiazolone	n.d.	100
Phthalates and related compounds		
1,2-Benzenedicarboxylic acid, dibutyl ester	n.d.	100
1,2-Benzenedicarboxylic acid, butyl 2-ethylhexyl ester	n.d.	100
1,2-Benzenedicarboxylic acid, diisooctyl ester	1.570	60.3
1,3-Benzenedicarboxylic acid, methyl ester	n.d.	100
Aromatic derivatives		
1,2-Dimethylbenzene	n.d.	100
1,2,4-Trimethoxy-benzene	n.d.	100
Biphenyl	n.d.	100
Phenol, 3,5-bis(1,1-dimethylethyl)-	0.034	38.2
3,5-Bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoic acid, methyl ester	0.082	0
Hydrocarbons		
1-Chlorotetradecane	n.d.	100
3-Ethyl-5-(2-ethylbutyl)-octadecane	n.d.	100
Nonadecane	n.d.	100
1,1-Bis(dodecyloxy)-hexadecane	n.d.	100
Acids and esters		
Benzenacetic acid, methyl ester	n.d.	100
Propanoic acid, phenylmethyl ester	n.d.	100
Methyl palmitelaidate	n.d.	100
Palmitic acid, methyl ester	n.d.	100
Heptadecanoic acid	n.d.	100
9-Octadecenoic acid, methyl ester	n.d.	100
n-Octadecanoic acid, methyl ester	0.045	68.5
10,13-Octadecadiynoic acid	n.d.	100

n.d.: not detected.

presence of chlorides, sulphates, etc. derived of the cleavage of organic molecules.

After the photo-Fenton treatment at optimum conditions, the resultant leachate was subjected to liquid–liquid extraction and GC/MS analysis in order to determine the degradation of the initial organic substances and the formation of by-products. The percentage of elimination of the identified substances in the raw leachate is presented in Table 2.

It was found that the photo-Fenton reaction is very efficient in eliminating the main initial organic compounds, as the most of them are not detected after the treatment. The complete elimination of benzothiazole derivatives and hydrocarbons was observed. 1,2-dimethylbenzene; 1,2,4-trimethoxybenzene; biphenyl and the majority of phthalates, acids and esters were also removed. Phenolic derivatives such as 3,5-bis(1,1-dimethylethyl)-phenol and 3,5-bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoic acid, methyl ester, remained in the leachate after the treatment due to their antioxidant character. No significant by-products were identified.
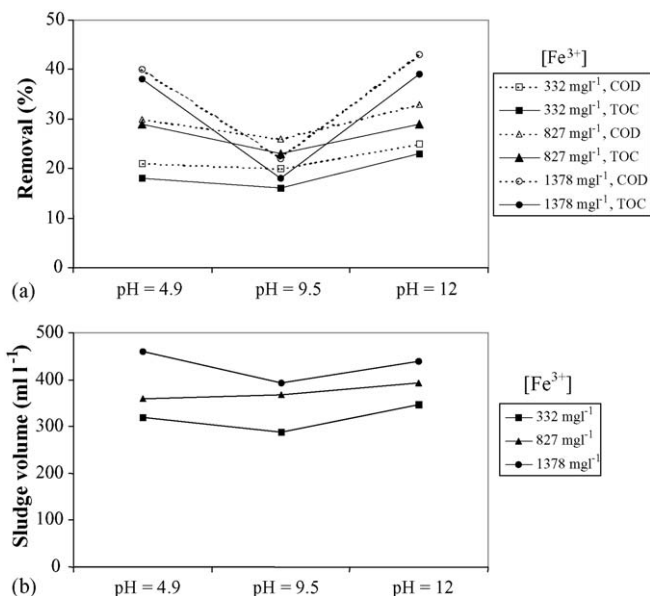

Fig. 7. Evaluation of the coagulation-flocculation treatment with $FeCl_3 \cdot 6H_2O$ at different ferric ion dosages and pHs. (a) Percentages of COD and TOC removal. (b) Estimated sludge volume (in $ml\,l^{-1}$).

3.3. Coagulation-flocculation treatment

The addition of ferric chloride ($FeCl_3 \cdot 6H_2O$) as coagulant to the tire powder leachate was experimented at three different pH values: 4.9, 9.5 and 12. The selected dosages were: 332, 827 and $1378\,mg\,l^{-1}$ of Fe^{3+}. Fig. 7 shows the percentage of COD and TOC reduction at different dosages and pH values. The sludge volume obtained after each treatment is also compared.

The more efficient treatments were those carried out at pH 12 for each experimented dosage. In general, the elimination of organic matter is lower at pH 9.5. The maximum COD and TOC elimination (43% and 39%, respectively) was produced by addition of $1378\,mg\,l^{-1}$ of Fe^{3+} at pH 12. It can be noticed that these percentages of organic matter reduction are similar to those obtained at pH 4.9 (40% and 38%, respectively). When the sludge volumes are compared, it is observed that the more amount of ferric chloride added the more sludge volume produced. In the experiments carried out with $1378\,mg\,l^{-1}$ Fe^{3+}, the sludge volume obtained at pH 4.9 ($460\,ml\,l^{-1}$) was slightly greater than the volume at pH 12 ($440\,ml\,l^{-1}$). Taking into account the sludge volume, it can be considered that the optimum coagulation-flocculation conditions are $1378\,mg\,l^{-1}$ of Fe^{3+} and pH 12.

3.4. Photo-Fenton combined with coagulation-flocculation

A complementary experiment consisted of a combination of photo-Fenton followed by coagulation-flocculation was carried out in order to obtain the maximum organic matter removal. The conditions of each treatment were the optimum ones found previously. The percentage of COD and TOC elimination after each individual treatment and their combination is compared in Fig. 8. The organic matter elimination obtained with the oxidative treatment is improved 11–15% after subsequent coagulation-
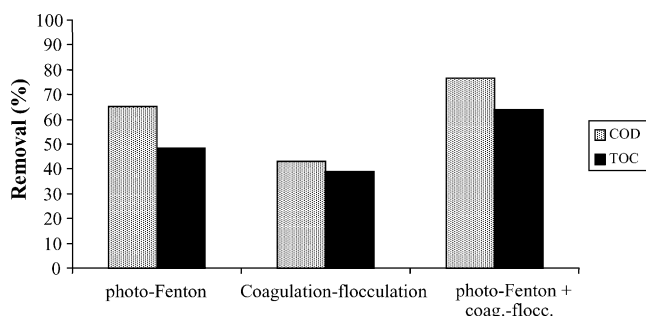
Fig. 8. Comparison of COD and TOC removal after photo-Fenton, coagulation-flocculation and photo-Fenton combined with coagulation-flocculation at optimum conditions.

flocculation. In this case, the maximum organic matter removal was 77% as COD and 64% as TOC, and a sludge volume of $133 \, ml \, l^{-1}$ was obtained.

4. Conclusions

The leachate obtained from used tire powder presents a higher content of organic matter than the one prepared from scrap tire. Its COD and TOC values were $508 \, mg \, O_2 \, l^{-1}$ and $214 \, mg \, C \, l^{-1}$, respectively. The main identified compounds were benzothiazole derivatives, phthalates, phenolic derivatives, hydrocarbons and fatty acids.

The highest COD and TOC reduction after the photo-Fenton treatment was 64% and 48%, respectively, using a solar chamber as light source. This reduction was obtained at initial pH 2.7–3.0 after 100 min of reaction with the addition of $3703 \, mg \, l^{-1}$ of H_2O_2 and $92.1 \, mg \, l^{-1}$ of Fe^{2+}. No residual hydrogen peroxide was present in the treated leachate when initial pH 2.7. A COD elimination of 56.2–58.7% can be reached after 8.5 h of treatment under darkness and natural sunlight, respectively. After the photo-Fenton reaction, the elimination of benzothiazole derivatives, hydrocarbons, acids, esters and phthalates was observed. As it was expected, phenolic derivatives used as antioxidants remained practically invariable after the treatment. No significant by-products were detected.

The coagulation-flocculation treatment of the leachate from tire powder leads to a maximum organic matter removal of 43% as COD and 39% as TOC. These results were obtained using $FeCl_3 \cdot 6H_2O$ as coagulant, with an iron dosage of $1378 \, mg \, l^{-1}$ at initial pH 12. A combination of photo-Fenton followed by coagulation-flocculation at optimum conditions produces the maximum organic matter removal of the leachate: 77% of COD and 64% of TOC.

Acknowledgment

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