Degradation of Reactive Red 120 dye by a heterogeneous sono-Fenton process with goethite deposited onto silica and calcite sand

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Abstract: The degradation of Reactive Red 120 dye (RR-120) in synthetic waters was studied. Two processes were considered: homogeneous sono-Fenton with iron(II) sulfate and heterogeneous sono-Fenton with synthetic goethite and goethite deposited onto silica and calcite sand (modified catalysts GS and GC, respectively). In 60 min of reaction, the homogeneous sono-Fenton process allowed a degradation of 98.10 %, in contrast with 96.07 % for the heterogeneous sono-Fenton process with goethite at pH 3.0. The removal of RR-120 increased when the modified catalysts were used instead of bare goethite. Chemical oxygen demand (*COD*) and total organic carbon (*TOC*) measurements showed that the highest *TOC* and *COD* removals were achieved with the homogeneous sono-Fenton process. Biochemical oxygen demand (*BOD*$_5$) measurements allowed confirmed that the highest value of *BOD*$_5$/*COD* was achieved with a heterogeneous sono-Fenton process (0.88±0.04 with the modified catalyst GC), demonstrating that the biodegradability of the residual organic compounds was remarkably improved.

Keywords: AOPs; goethite immobilization; ultrasound irradiation; azo dye.

INTRODUCTION

During the last decades, water pollution has been one of the most important environmental issues worldwide. Due to the growing demand for both goods and services, the production of solid and liquid wastes is expected to rise in the years and decades ahead and more cost-effective water treatments are needed to protect the environmental quality of the receiving water bodies.

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Industrial wastewaters can contain a variety of recalcitrant and xenobiotic substances that cannot be removed by conventional (biological) treatments. Therefore, enormous efforts have been made in recent years to improve so-called "advanced oxidation processes" (AOPs). Oturan and Aaron[1] published a review on AOPs and focused on their principles, variations and applications. As mentioned by these authors, AOPs are based on the *in situ* generation of radicals, such as hydroxyl radicals ($^\bullet$OH), that react with pollutants promoting their oxidation. The Fenton process, which is considered one of the most important AOPs, generates $^\bullet$OH by the reaction of Fe^{2+} with hydrogen peroxide (H_2O_2) at low pH values of around 3.[2] In this case, iron can be added to the system in the form of a soluble salt (*e.g.*, $FeSO_4$); this aspect is often a disadvantage since the removal of iron in the last stage of the treatment may be needed for compliance of regulations. Alternatively, iron minerals and other insoluble materials containing iron (*e.g.*, zeolites, ash) were used as catalysts in earlier studies[3–6] in so-called heterogeneous Fenton-like processes. In the past, goethite (α-FeOOH) was applied as a heterogeneous catalyst in Fenton processes for the degradation of several compounds.[7–10] These treatments were not only efficient but also had the remarkable advantage that only small quantities of iron leached from the solid phase to the aqueous phase. This means that, for such treatments, no special processes for iron removal are needed.

Heterogeneous Fenton-like processes could be combined with ultrasound irradiation to facilitate the mass transfer. Previous studies[11–13] showed that such combination improved the degradation of pollutants, thus shortening the time of the treatment. However, there are other aspects to consider; although small particles of minerals have a positive effect on the reaction rate, they can be difficult to settle and therefore not be easily separated. Perhaps an interesting option in this case, could be the deposition of the iron mineral onto a granular material which settles easily (*e.g.*, sand). Such a strategy could not only ensure good separation of the catalyst after completion of the treatment but also could help in the efficient application of this material since the use of less catalyst may lead in the same or even improved degrees of pollutant removal.

In this work, the degradation of Reactive Red 120 dye (a model azo dye) applying a heterogeneous sono-Fenton process with synthetic goethite alone and synthetic goethite deposited onto silica and calcite sands was studied. The results of these experiments were compared to those obtained by applying the homogeneous sono-Fenton process. Not only was the decrease in the concentration of the dye the subject of study, but also variations in values of *TOC*, *COD* and *BOD*$_5$ were considered. These parameters provided information on the achieved mineralization of the pollutant and the biodegradability of residual organic compounds in the solution. The possibility of the reuse of the catalyst resulting from the immobilization of goethite onto sands was also explored. This is the first rep-

ort on the use of an iron mineral deposited onto sand as the catalyst for heterogeneous (sono-)Fenton processes.

EXPERIMENTAL

Chemicals and sands

Reactive Red 120 dye, RR-120 ($C_{44}H_{24}Cl_2N_{14}Na_6O_{20}S_6$, commercial purity) was purchased from Quifatex S.A. (Ecuador) and used as received. All other chemicals were of analytical grade. Hydrogen peroxide, H_2O_2 (30 %) was purchased from Fisher Scientific. Iron(III) nitrate nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$ (>99 %) was purchased from Merck. Iron(II) sulfate heptahydrate, $FeSO_4 \cdot 7H_2O$ (>99 %), nitric acid, HNO_3 (70 %), potassium hydroxide, KOH (≥84.0 %) and sodium nitrate, $NaNO_3$ (≥99.0 %) were purchased from Sigma–Aldrich. Both silica and calcite sands were obtained from a local hardware store and their composition was confirmed by X-ray diffraction (XRD) analysis.

Preparation of goethite and the modified catalysts

Goethite was synthesized by the alkaline method.[14] Accordingly, 180 mL of a 5 M KOH solution was mixed with 100 mL of a 1 M $Fe(NO_3)_3$ solution with constant stirring at 200 rpm. Then it was diluted to 2 L with distilled water and maintained at 70 °C for 60 h. The obtained mixture was centrifuged at 4000 rpm and the separated solid phase (goethite) was washed with Milli-Q water. The resulting "synthetic goethite" was dried at 50 °C for 3 h. The synthetic goethite was deposited onto silica and calcite sands based on the method proposed by Scheidegger et al.[15] Silica sand was washed with HNO_3 and with distilled water to remove acid residues. Calcite sand was washed with distilled water. Both types of sand were dried for 24 h in an oven (110 °C). A goethite suspension was prepared by adding 1 g of synthetic goethite to 100 mL of a 0.01 M $NaNO_3$ solution, the pH was adjusted to 3.0 with HNO_3 and then stirred for 24 h at 25 °C. Subsequently, 25 g of silica sand or calcite sand was added to the goethite suspension and stirred for 24 h. The two modified catalysts (goethite immobilized onto calcite, GC and goethite immobilized onto silica sand, GS) were washed with a portion of 0.01 M $NaNO_3$ solution and with Milli-Q water. Both modified catalysts were dried at 110 °C for 24 h.

Characterization of the synthetic goethite, sands and modified catalysts

The particle size of synthetic goethite, sands (silica and calcite) and the modified catalysts was determined by laser granulometry analysis with LA-950V2 (Horiba) equipment. The specific surface area of goethite was measured by the Brunauer–Emmet–Teller (BET) method in a NOVAtouch LX[1] (Quantachrome) nitrogen adsorption apparatus. The identity of both types of sand and goethite was confirmed by X-ray diffraction (XRD) measurements with a D8 Advance (Bruker) diffractometer. The surface morphology of the sands and the modified catalysts was examined by scanning electron microscopy using PSEM Express (Aspex) equipment. Raman spectra of synthetic goethite, sands and modified catalysts were recorded in the range from 100 to 2000 cm^{-1} with a micro-Raman setup (LabRAM HR Evolution Horiba). Raman scattering was excited by a He–Ne laser at a wavelength of 633 nm. The laser beam was focused on individual particles using microscope objectives; the power on the samples was reduced by neutral density (ND) filters to prevent any photo- or thermal-modification of the materials. All Raman measurements were performed using the 600 g mm^{-1} grating (spectral resolution ≈3 cm^{-1}). The Raman scattered light was detected by a CCD camera operating at 220 K. The acquisition time per spectrum was 5 or 10 s, depending on the material.

Degradation of RR-120 in synthetic waters

Experiments of the homogeneous and heterogeneous sono-Fenton processes for the degradation of RR-120 were performed. For the homogeneous process, a 2^3 factorial experimental design was applied; two H_2O_2/$FeSO_4·7H_2O$ ratios (17.7 mM per 0.2 g L^{-1} and 20 mM per 0.3 g L^{-1}), two sonic wave amplitudes (100 and 125 μm) and two ultrasonic intensities (65 and 130 W cm^{-2}) were tested. A UP-100H ultrasonic processor (Hielscher Ultrasonics, Germany) equipped with a flow tip MS7D sonotrode was used in this step. The reactions occurred in a 250 mL flat-bottom flask of the aqueous reacting solution with an initial concentration of RR-120 ($c_{0(RR-120)}$) of 80 mg L^{-1}. The pH value was adjusted to 2.8 (optimum pH value for a Fenton reaction[16]) by the addition of a 1 M H_2SO_4 solution. The mixture was stirred with a magnetic stir bar (100 rpm) and the reacting system was cooled with a water bath to maintain the temperature in the range 20–25 °C. $FeSO_4·7H_2O$ was added to the mixture and the reaction was initiated by the addition of H_2O_2 and activation of the sonotrode. The experimental setup is shown in Fig. S-1 of the Supplementary material to this paper. The total time of sonication (reaction) was 60 min. Aliquots of 10 mL were collected at different times; to each aliquot, a 1 M NaOH solution (≈1 mL) and 0.2 g of MnO_2 were added to precipitate the iron and catalyze the decomposition of H_2O_2, respectively. The mixture was centrifuged with a WIFUG Lab centrifuge (WIFUG, Bradford, UK) at 4000 rpm for 20 min. Then the supernatant liquid was collected and filtered through quantitative filter paper and then microfilters (pore size 0.22 μm, Millipore Millex-GV). The absorbance of each solution was measured at a wavelength of 507 nm with a UV–Vis spectrophotometer (Hitachi U-1900) to calculate the concentration of RR-120 ($c_{(RR-120)}$) at each time.

The H_2O_2/$FeSO_4·7H_2O$ ratio, sonic wave amplitude and ultrasonic intensity that allowed the highest degradation of RR-120 for the homogeneous sono-Fenton process, were applied for the heterogeneous sono-Fenton process and goethite was used instead of $FeSO_4·7H_2O$. A 2^2 factorial experimental design was applied considering the H_2O_2/goethite ratio (17.7 mM//0.2 g L^{-1} and 20 mM/0.3 g L^{-1}) and the pH value (3 and 5) as variables. The pH value that allowed the highest degradation of RR-120 was selected and applied in tests with the modified catalyst (GS and GC), as sources of goethite to the reacting system. An appropriate amount of the modified catalyst (1.95 g in 250 mL of RR-120 solution), which did not slow down the magnetic stir bar in the reacting system, was used and the pH value as well as the other parameters that allowed the highest degradation of RR-120 in previous tests, were applied. Experiments of heterogeneous Fenton processes (*i.e.*, without sonication) with the modified catalysts GS and GC, were also performed.

All experiments were run in triplicate. The degradation data were plotted and the pseudo-first order rate constants were calculated.

Reuse of the modified catalysts

Three batches of synthetic water containing RR-120 (initial concentration of 80 mg L^{-1}) were treated using the previously used experimental setup. The reaction time for the treatment of each batch was 60 min. For the treatment of the first batch (1st cycle), 1.95 g of "new" modified catalyst (GS or GC) was placed into the flask and the reaction took place with the sonic wave amplitude, ultrasonic intensity, H_2O_2 concentration and pH value selected in previous tests. After the 1st cycle, the absorbance of the solution was measured and the modified catalyst recovered. The recovered modified catalyst was washed with distilled water and dried at 100 °C for 30 min. This catalyst was used for the treatment of another batch of synthetic water (2nd cycle). Again, the modified catalyst was recovered and used for another treatment (3rd cycle). A summary of the reuse tests is presented in Fig. S-2 (Supplementary material).

All experiments were run in triplicate. For the three cycles, the kinetic data were plotted and the rate constants of pseudo-first order calculated.

*Chemical oxygen demand (*COD*), biochemical oxygen demand (*BOD_5*), total organic carbon (*TOC*) and biodegradability index (*BOD_5*/*COD*)*

COD, *BOD_5* and *TOC* were measured according to the standard methods 5220-D, 5210-B and 5310-B, respectively.[17] These analyses were performed for the untreated RR-120 solution and the treated solution with the best conditions of each process (homogeneous sono-Fenton and heterogeneous sono-Fenton with synthetic goethite and modified catalysts).

RESULTS AND DISCUSSION

Characterization of synthetic goethite and modified catalysts

The granulometric analysis showed that the values of D_{80} (*i.e.*, the opening of the sieve through which 80 % of the sample could pass) were 7.4, 445.0, 1206.0, 30.4 and 372.3 μm for synthetic goethite, calcite sand, silica sand, modified catalysts GC and GS, respectively. Both modified catalysts showed smaller particle sizes than the sands used for their preparation. This reduction could be attributed to the immobilization process which involved stirring for 24 h. Such treatment could cause mechanical wear of the material due to the collisions among particles and with the flask walls. Therefore, a reduction of the particle size of approximately 69 % was observed for the silica sand, while for calcite sand it was around 93 %. As expected, the size reduction of calcite sand is more significant than that of silica sand since calcite has a lower hardness than quartz.[18] In addition, it is important to mention that is a well-known fact that calcite ($CaCO_3$) reacts in an acidic medium according to Eq. (1):

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2 \qquad (1)$$
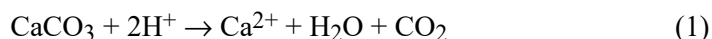
It seems that this reaction plays an important role in the reduction of the particle size, but the slow reaction rate at the pH value of immobilization does not allow the total dissolution of calcite. The specific surface area of the synthetic goethite (measured by the BET method) was 17.46 m^2 g^{-1}, which is in good agreement with a previous report.[19] Since only a small amount of goethite was immobilized onto the surface of sand particles, the specific surface area of the modified catalysts could fundamentally be attributed to silica or calcite sand. In fact, the specific surface area for the modified catalyst GC was 0.43 m^2 g^{-1}. This value is consistent with results previously reported for $CaCO_3$.[20]

Powder XRD measurements allowed the mineral composition to be estimated. The composition of the synthetic goethite was 98 % goethite and 2 % hematite. The calcite sand contained 96 % calcite ($CaCO_3$), 2 % dolomite ($CaMg(CO_3)_2$), and 2 % other minerals of the plagioclase group (albite, andesine, anorthite), while the silica sand contained 97 % quartz (SiO_2) and 3 % of minerals of the plagioclase group. The diffractograms of the materials (Fig. S-3,

Supplementary material) show typical signals attributable to goethite, calcite and quartz, as reported previously.[21–24]

The SEM micrographs of the sands and modified catalysts are shown in Fig. 1. The surface of calcite sand particles shows some roughness (Fig. 1a), while the surface of the silica sand particles seems to be smoother than the calcite particles (Fig. 1b). Such surface irregularities observed in calcite sand particles could facilitate the immobilization of goethite as suggested in an earlier work[25] for the deposition of bisphosphonates onto titanium surfaces. In fact, the micrographs of the modified catalysts GC and GS (Fig. 1c and d, respectively) show that goethite particles are abundant on the surface of calcite, while scarce goethite particles can be observed on the surface of silica. The abundance difference noticed in the SEM images is probably given by the difference in the particle size of the calcite and silica sand. Smaller particles will have a higher specific surface area and therefore offer more spots for the attachment of goethite particles.
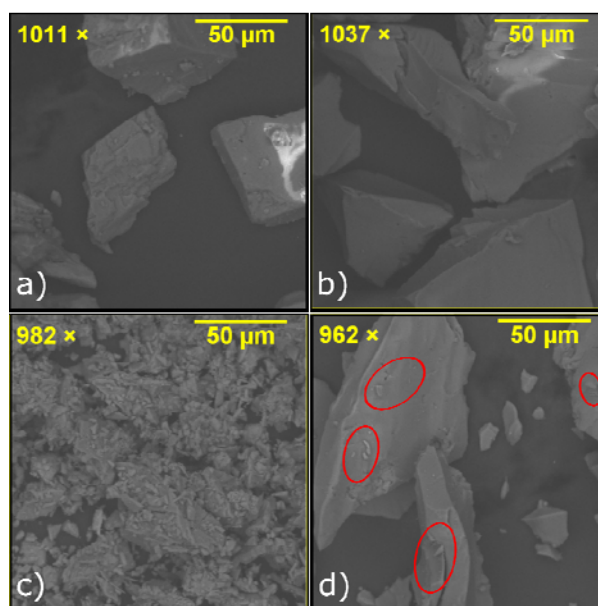

Fig. 1. SEM micrographs of: a) calcite sand, b) silica sand, c) modified catalyst GC (goethite deposited onto calcite sand) and d) modified catalyst GS (goethite deposited onto silica sand).

The identity of the sands was also confirmed by Raman spectroscopy, which is a technique that was successfully used in the past for the characterization of a variety of minerals.[26,27] The strongest band in the Raman spectrum of the silica sand appeared at 465 cm^{-1} and can be attributed to the Si–O stretching mode.[28] The most intense band in the Raman spectrum of the calcite sand, attributed to the symmetrical stretching of CO_3^{2-}, appeared at 1087 cm^{-1}, while the band at

278 cm^{-1} can be attributed to a translation mode. These Raman signals were also observed previously.[29]

The Raman spectra of both modified catalysts GS and GC were also recorded. The Raman spectrum of a mixture will be a combination of the Raman signals of the individual compounds. It should be noted that the compounds could have different "scattering cross-section". This means that, for the same concentration of two compounds, the intensity of the bands of one compound can be larger than the bands of the other one. As mentioned before, more goethite was deposited on the calcite sand than on the silica sand, a fact confirmed also by Raman spectroscopy. The Raman spectrum of the modified catalyst GC showed weak goethite signals whereas for the modified catalyst GS, no signals attributable to goethite were observed.

Despite both modified catalysts showing a yellow–orange coloration (Fig. S-4, Supplementary material), the XRD diffractograms did not show signals attributable to goethite. Therefore, it could be inferred that the content of goethite in the modified catalysts was less than 1 % since this type of XRD measurements cannot detect/estimate mineral contents below 1 %. For such low content of goethite, the Raman spectra of the modified catalysts would not necessarily show signals attributable to goethite and, in fact, the Raman spectrum of the modified catalyst GS does not show bands that could be attributed to goethite. However, for the modified catalyst GC, its Raman spectrum shows weak bands with slight shifts attributable to goethite (Fig. S-5, Supplementary material). Such shifts could be expected for substances retained by adsorption on other solid surfaces.[30] The strongest Raman signals of goethite occur at 380 and 299 cm^{-1} (symmetrical stretching of Fe–O–Fe/–OH group and Fe–OH deformation, respectively[22,23]).

Degradation of RR-120 by sono-Fenton processes

For the homogeneous sono-Fenton process, the best degradation percentage of RR-120 was 98.10 % after 60 min of reaction. This degradation was obtained with a H_2O_2/$FeSO_4 \cdot 7H_2O$ ratio of 17.7 mM/0.2 g L^{-1}, a sonic wave amplitude of 100 μm and an ultrasonic intensity of 65 W cm^{-2}. Moreover, pseudo-first order kinetics was confirmed, with a rate constant of 0.8609 min^{-1}. The RR-120 degradation curve of the homogeneous sono-Fenton process is shown in Fig. S-6 (Supplementary material).

For the heterogeneous sono-Fenton process with goethite, the best degradation percentage was 96.07 % after 60 min of reaction. This degradation was obtained with an H_2O_2/goethite ratio of 20 mM/0.3 g L^{-1} and a pH 3.0. The sonic wave amplitude and ultrasonic intensity were set at the values used to obtain the highest degradation with the homogeneous sono-Fenton process. Pseudo-first order kinetics was also confirmed for the heterogeneous sono-Fenton process. The highest degradation of RR-120 was observed when the highest

amount of goethite (0.3 g L^{-1}) was used. This could be explained in terms of the available contact area among the dye solution and goethite since a higher amount of goethite provides a higher contact surface of the catalyst with the solution, thus increasing $^{\bullet}$OH production. In addition, higher adsorption of RR-120 dye on the surface of goethite at a pH value of 3.0 can be expected; under this condition, the goethite surface is protonated and the functional group FeOH^{2+} can interact with the negatively charged sulfonate groups (–SO$_3^-$) of the dye.[19] In another work with goethite as the catalyst, the highest degradation of methylene blue was achieved under alkaline conditions; the cationic nature of methylene blue was responsible for this behavior since it facilitates the adsorption on goethite at high pH values.[31] At this point, it is important to remark that adsorption can improve the degradation of pollutants, as suggested by Konstantinou and Albanis[32] for heterogeneous processes. Since heterogeneous sono-Fenton processes are based on the generation of $^{\bullet}$OH on the surface of the solid catalyst, it is reasonable to consider that adsorption of RR-120 onto goethite could be beneficial for the degradation process. However, an excessive amount of goethite could retard the degradation reaction due to an increase in the pH value of the reaction medium, as shown in Eq. (2):[11]

$$2FeOOH \rightarrow 2Fe^{2+} + O_2 + 2OH^- \qquad (2)$$

In this work, the highest goethite concentration was 0.3 g L^{-1}, which is lower than the concentration used in the study of Neppolian and coworkers[11] for the degradation of *p*-chlorobenzoic acid in a heterogeneous sono-Fenton process using goethite. They observed a slight decrease in the removal of *p*-chlorobenzoic acid when goethite concentrations higher than 0.3 g/150 mL were applied. By using lower amounts of goethite compared to the study of Neppolian and coworkers,[11] measurement distortions due to pH variations were minimized.

Degradation curves of RR-120 in heterogeneous sono-Fenton processes with goethite and the modified catalysts (GS and GC) are shown in Fig. 2.
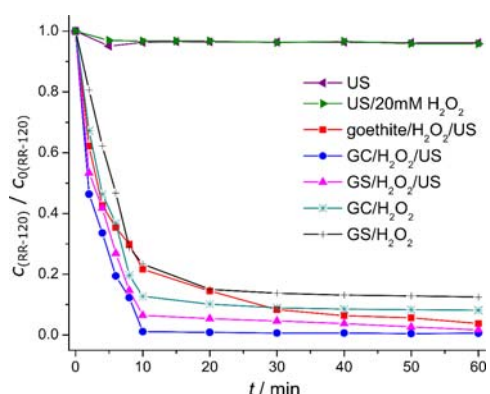

Fig. 2. RR-120 degradation curves of heterogeneous Fenton and sono-Fenton processes. The processes involved the use of goethite, H$_2$O$_2$ and the modified catalysts (goethite immobilized onto calcite, GC and goethite immobilized onto silica sand, GS). Ultrasound (US: intensity, 65 W cm^{-2} and A = 100 μm) was applied to the reacting system for the heterogeneous sono-Fenton processes. Heterogeneous Fenton processes were carried without US irradiation. Initial conditions: pH 3, $c_{0(RR-120)}$ = 80 mg L^{-1}, $c_{goethite}$ = 0.3 g L^{-1}, c_{GS} = 1.95 g/250 mL, c_{GC} = 1.95 g/250 mL, $c_{H_2O_2}$ = 3 g L^{-1}.

RR-120 degradation curves of the heterogeneous Fenton processes (*i.e.*, processes without ultrasound irradiation) are also shown. The highest degradation percentages after 60 min of reaction were achieved with the heterogeneous sono--Fenton processes with the modified catalysts GS and GC (98.32 and 99.42 % in 60 min, respectively). Without ultrasound irradiation, the degradation percentages after 60 min of reaction were 87.51 and 91.82 %, for the modified catalysts GS and GC, respectively. However, differences among the processes should not only be evaluated based on the final degradation percentages achieved after 60 min of reaction, but also considering the RR-120 degradation in time. For the heterogeneous sono-Fenton processes with the modified catalysts GS and GC, after only 10 min of reaction, the degradation percentages were 93.50 and 98.86 %, respecttively, which are degradation percentages remarkable higher than those obtained for the heterogeneous sono-Fenton process with goethite (78.39 %) or the heterogeneous Fenton processes with modified catalysts GS and GC (76.68 and 87.26 %, respectively) without ultrasound irradiation at the same time of reaction. It should be noted that in experiments involving only ultrasound as well as ultrasound and H_2O_2 (20 mM), the degradation of RR-120 was very low (less than 5 %).

A remarkable advantage of the heterogeneous (sono-)Fenton processes is that iron is introduced into the reacting system as an insoluble solid substance (goethite). This means that $^\bullet$OH are produced on the surface of goethite and subsequently released to the solution for the degradation of the pollutants. Only small quantities of goethite are dissolved and low concentrations of iron in water after the treatment could be expected.[19] After the treatment, goethite could be separated and reused, which is an important advantage over homogeneous (sono-)-Fenton processes. Although goethite is an insoluble mineral, ultrasound irradiation can lead in the disaggregation of large goethite particles and colloidal particles could be produced, thus making the separation of this mineral very difficult. Consequently, the content of iron in the treated water (fundamentally in an insoluble form), as well as its turbidity, may increase. Therefore, the aim of producing the modified catalysts was to add goethite "pasted" to sand particles and remove it together with sand particles after the treatment, thus achieving a very efficient separation of goethite. The results of tests using both modified catalysts showed a clear improvement in the degradation of RR-120.

Based on the results depicted in Fig. 2, there is no question about the fact that ultrasound irradiation enhances the heterogeneous Fenton process, an aspect that was also observed before by Zhang and coworkers.[12] This is attributed to the induction of cavitational effects which generates intense turbulence and facilitates mass transfer.[19,33] Moreover, it is accepted that cavitation bubbles form during ultrasound irradiation, and their collapse creates drastic conditions.[34] It

seems that such turbulence and extreme conditions favor the chemical reactions involved in the degradation of RR-120.

As mentioned before, the content of goethite in the modified catalysts was less than 1 %. This means that less than ≈20 mg of goethite, ≈10–15 times smaller than the amount of goethite used in the process with bare goethite, was added when the modified catalysts were used. However, the heterogeneous sono-Fenton processes with both modified catalysts were the most efficient in the degradation of RR-120. How can this be explained? It seems that two interpretations could explain the high efficiency of the modified catalysts: 1) the rise in the number of solid particles can enhance the dye degradation since solid particles promote an increase in cavitation events in the reaction system[35,36] and 2) the small size of the goethite particles deposited on the grains of sand provided a greater contact area for the reaction. Concerning the latter point, in an earlier report, Li and coworkers[37] attributed the high photocatalytic activity of alumina supported hematite to the reduced particle size of hematite on the support material.

The possibility of reusing the solid catalysts makes attractive the heterogeneous (sono-)Fenton processes. Therefore, both modified catalysts were tested for the treatment of three batches (*i.e.*, three cycles) and their catalytic performance was evaluated in terms of the achieved degradation of RR-120 after 60 min of reaction and the values of the pseudo-first order rate constants, k_{app}. The reuse of the modified catalysts in a 2nd cycle allowed degradation percentages of 93.94 and 95.05 % for the modified catalysts GS and GC, respectively. With the reuse in the 3rd cycle, degradation percentages were 74.83 and 78.39 % with the modified catalysts GS and GC, respectively.

The values of k_{app} for the sono-Fenton processes are presented in Table I. For the 1st cycle, the values of k_{app} for both modified catalysts were higher for the heterogeneous sono-Fenton process than for the heterogeneous Fenton pro-

TABLE I. Pseudo-first order rate constants (k_{app} / min^{-1}) for the heterogeneous (sono-)Fenton processes with the modified catalysts; the values of k_{app} were calculated based on kinetic data for the first 3 min of reaction; modified catalysts: GS (goethite deposited onto silica sand) and GC (goethite deposited onto calcite sand). 1st cycle means that the material was new and had not been used for a previous treatment. 2nd and 3rd cycles mean that the material was previously used for the treatment of one and two batches of the RR-120 solution, respectively

Material	Process	
	Sono-Fenton	Fenton
Goethite	0.251±0.000	–
GS (1st cycle)	0.273±0.003	0.115±0.000
GS (2nd cycle)	0.216±0.000	–
GS (3rd cycle)	0.145±0.000	–
GC (1st cycle)	0.312±0.002	0.213±0.005
GC (2nd cycle)	0.267±0.002	–
GC (3rd cycle)	0.195±0.000	–

cess. As mentioned before, a higher degradation percentage was achieved with the modified catalyst GC than with GS, and this is clearly confirmed by the values of k_{app} (0.273 ± 0.003 min^{-1} for GS and 0.312 ± 0.002 min^{-1} for GC).

As shown in Table I, the values of k_{app} for the 1st cycle are higher than those for the 2nd and 3rd cycle for both modified catalysts. It seems that goethite is gradually washed out of the sand particles due to the combined effect of ultrasound and the pH value of the medium. Certainly, iron cations transferred to the aqueous phase could trigger the formation of •OH by other chemical reactions, and such contribution may be a factor favoring the degradation of RR-120 at a pH 3.[19] The decrease in the amount of goethite on the modified catalysts could be observed by the naked eye due to the intense color of goethite and the dye adsorbed onto its surface (see Fig. S-7, Supplementary material). The intensity of the coloration decreased for the modified catalysts after the 2nd and 3rd cycles, indicating a progressive decrement in the content of goethite due to the use and reuse of the modified catalyst. Goethite, among the components of the modified catalysts, is the material with the higher adsorption capacity (see the section "Adsorption Isotherms", Supplementary material). Therefore, it is reasonable to also link the coloration due to adsorbed RR-120 to the content of goethite in the modified catalyst. The adsorption depends on the pH value of the solution[38,39] and values of the point of zero charge, pH$_{pzc}$ of adsorbents (available in the literature[40]) provide insights into the extent of such a process. Taking into account the values of pH$_{pzc}$ for goethite, calcite and silica,[40] only silica has a pH$_{pzc}$ below 3, thus the adsorptions to calcite and goethite are favored under the conditions of the heterogeneous sono-Fenton process. At a pH value of 3, RR-120 is electrostatically attracted to goethite and calcite sand while it is repelled from silica sand. This could explain the adsorption parameters presented in Table S-I (Supplementary material) and confirms that the modified catalyst GC is the best catalyst for the heterogeneous sono-Fenton process.

COD, BOD$_5$, TOC and BOD$_5$/COD of RR-120 solutions (treated and untreated)

The variation with time of the *COD* and *TOC* for the heterogeneous sono--Fenton processes is depicted in the graphs of Fig. 3. Clearly, the removals of the *COD* and *TOC* were higher for the processes with the modified catalysts than with goethite alone. The modified catalyst GC allows not only the highest degradation of RR-120 to be obtained, but also has a remarkable effect on the mineralization of the dye. The removals of the *COD* and *TOC* are indicators of the degree of mineralization of the dye (the higher the *COD* and *TOC* removals are, the higher is the degree of mineralization) and, among the heterogeneous processes, the modified catalyst GC provided also the best results in this respect.

The values of *TOC*, *COD* and *BOD*$_5$, achieved after 60 min of reaction in the sono-Fenton processes are presented in Table II. The values of *TOC* and *COD*

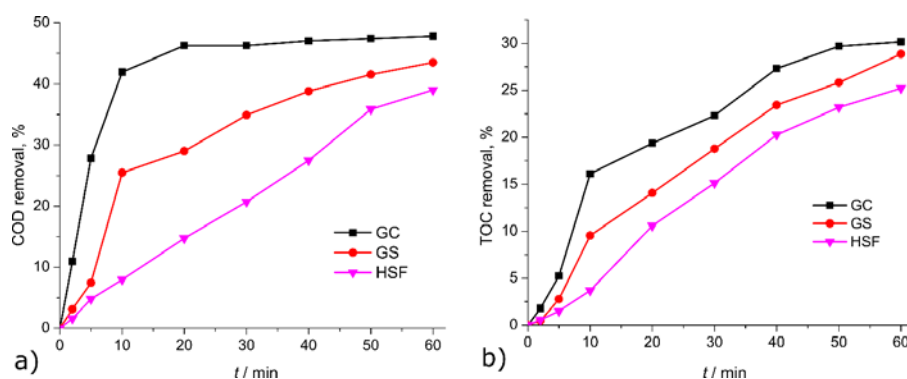decreased due to the treatments, more for the homogeneous process than for the heterogeneous processes.

Fig. 3. Variation with time of: a) chemical oxygen demand (*COD*) and b) total organic carbon (*TOC*) for the heterogeneous sono-Fenton process with goethite (HSF) and the modified catalysts (GS and GC).

TABLE II. Values of *TOC*, *COD*, *BOD*$_5$ and the biodegradability index (*BOD*$_5$/*COD*) of the untreated RR-120 solution and the solutions treated by homogeneous and heterogeneous sono-Fenton processes

Process/Solution	*TOC* mg L^{-1}	*COD* mg L^{-1}	*BOD*$_5$[a] mg L^{-1}	*BOD*$_5$/COD
Untreated RR-120 solution (80 mg L^{-1})	28.8±0.0	126.0±0.7	6.2±5.7	0.05±0.04
Homogeneous sono-Fenton[b]	17.7±0.0	59.0±0.0	9.8±5.7	0.17±0.10
Heterogeneous sono-Fenton with goethite[b]	21.5±0.0	77.0±0.7	35.9±1.8	0.47±0.02
Heterogeneous sono-Fenton with GS[b]	20.6±0.0	72.0±1.4	43.4±5.5	0.60±0.08
Heterogeneous sono-Fenton with GC[b]	20.2±0.0	66.5±0.7	58.7±3.0	0.88±0.04

[a]The values of *BOD*$_5$ are influenced by the biodegradable organic matter contained in the seed; [b]after 60 min of reaction

On the other hand, the values of *BOD*$_5$ increased due to the treatments, leading to an increase in values of the biodegradability index (*BOD*$_5$/*COD*) of the treated solutions; *BOD*$_5$/*COD* increased from 0.05±0.04 for the untreated RR--120 solution to 0.17±0.10 for the homogeneous sono-Fenton process, and to 0.47±0.02, 0.60±0.08 and 0.88±0.04 for the heterogeneous sono-Fenton processes with goethite and the modified catalysts GS and GC, respectively. These results show that the heterogeneous sono-Fenton processes allow the condition *BOD*$_5$/*COD* > 0.40 to be reached, thus indicating that residual organic compounds in the solution are readily biodegradable.[41] These compounds could be more difficult to oxidize,[12] but they could biodegrade in a subsequent biological process (*e.g.*, in a biological wastewater treatment plant) or simply be discharged to a receiving water body, depending on their concentration. Interestingly, although the homogeneous process allowed the highest *TOC* and *COD* removals,

the achieved BOD_5/COD was under than 0.40, thus implying limitations in a subsequent biological process.

At this stage, certain details on the BOD_5 results reported in this work must be discussed. For the BOD_5 analysis, a population of microorganisms capable of oxidizing biodegradable organic matter is necessary and must be provided as "seed" to the sample.[17] The seed for the BOD_5 analysis in this study was a small (and constant) volume of domestic wastewater. Obviously, this small volume of domestic wastewater, beside microorganisms, contained biodegradable organic matter that contributes with a certain value of BOD_5 to the samples (untreated and treated solutions). Therefore, the BOD_5 of the untreated RR-120 solution should be taken carefully.

As final remarks, it is important to highlight that the TOC, COD and BOD_5 provide information concerning the degree of mineralization and the residual organic charge in an aqueous solution. The identification of the organic compounds resulting from the oxidative processes was not performed in this work and future works should focus on this issue. Quantum chemical calculations could be an excellent tool to determine the most stable species produced in this kind of oxidative processes. Data obtained in this way may be useful for a better understanding of the interactions between the catalyst surface and pollutants, as well as interactions occurring in the liquid solution.

CONCLUSIONS

The degradation of RR-120 by homogeneous and heterogeneous (sono-)Fenton processes was tested. Synthetic goethite and two modified catalysts (synthetic goethite deposited onto silica and calcite sands, GS and GC, respectively) were used for the heterogeneous processes. In all cases, the degradation of RR-120 was enhanced by ultrasound irradiation.

The highest degradation of RR-120 after 60 min (reaction time) was achieved with the heterogeneous sono-Fenton process with the modified catalyst GC (99.42 %). The homogeneous sono-Fenton process allowed the highest TOC and COD removals, but the residual organic compounds showed poor biodegradability (BOD_5/COD < 0.40). On the other hand, BOD_5/COD values higher than 0.40 were obtained with all heterogeneous sono-Fenton processes; the highest BOD_5/COD value (0.88±0.04) was obtained with the modified catalyst GC.

There are some advantages of the use of the modified catalysts in sono-Fenton processes. First, low amounts of goethite are used, and this mineral can efficiently be separated from the water after the treatment. In addition, it seems that modified catalysts promote the formation of biodegradable products, which could be a clear advantage over other AOPs. Potentially, heterogeneous sono-Fenton processes with modified catalysts of goethite (or other iron minerals) could be applied for the removal of a variety of substances including antibiotics, pesti-

cides, and other recalcitrant and xenobiotic pollutants. Future studies should focus on the design of reactors to apply heterogeneous sono-Fenton processes with these modified catalysts.

SUPPLEMENTARY MATERIAL

Additional data are available electronically from http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

И З В О Д

РАЗГРАДЊА БОЈЕ РЕАКТИВНО ЦРВЕНО 120 ХЕТЕРОГЕНИМ СОНО-ФЕНТОН ПРОЦЕСОМ ПОМОЋУ ГЕТИТА НАНЕТОГ НА СИЛИЦИЈУМ-ДИОКСИДНИ И КАЛЦИТНИ ПЕСАК

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Изучена је разградња боје реактивно црвено 120 (RR-120) у синтетичкој води. Разматрана су два процеса: хомогени соно-Фентон са гвожђе(II)-сулфатом и хетерогени соно-Фентон са синтетичким гетитом и гетитом нанетим на силицијум-диоксидни и калцитни песак (модификовани катализатори GS и GK, редом). У току 60 min реакције, хомогени соно-Фентон процес је омогућио разградњу од 98,10 %, за разлику од 96,07 % у случају хомогеног процеса са гетитом при pH 3,0. Уклањање RR-120 се повећало када су употребљени модификовани катализатори уместо самог гетита. Мерења хемијске потрошње кисеоника (*COD*) и укупног органског угљеника (*TOC*) показала су да су најбоља смањења *TOC* и *COD* постигнута хомогеним соно-Фентон процесом. Мерења биохемијске потрошње кисеоника (*BOD$_5$*) показала су да је највиша вредност *BOD$_5$/COD* постигнута соно-Фентон процесом (0,88±0,04 модификованим катализатором GK), што показује да је биоразградивост резидуалних органских материја била видно побољшана.

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