Low-cost magnetic materials containing waste derivatives as catalyst for removal of organic pollutants: insights into the reaction mechanism and odd aspects

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Abstract

Purpose
Hybrid magnetite/maghemite nanoparticles (MNP) coated by waste-sourced Bio-Based Substances (BBS) have been synthesized and studied for the degradation of phenol, chosen as model pollutant, in water.
Methods
A systematic study has been undertaken in order to rationalize MNP-BBS behavior and optimize its performance. The effect of experimental parameters, such as light irradiation, added hydrogen peroxide and the ratio hydrogen peroxide/MNP-BBS concentrations, was studied. The generation of hydroxyl radicals was assessed, and the recovery and re-cycle of the material was investigated.
Results
The obtained results indicate that the phenol degradation can be attained by both Fenton and photo Fenton processes, with higher efficiency in dark condition, in the presence of a suitable amount of hydrogen peroxide. Evidence has been obtained on the role of iron ions leached from the materials as well as of organic matter released in solution upon partial photodegradation of the organic coating. The reusability tests indicate a lower but still acceptable performance of the material.
Conclusions
The optimization of the experimental conditions to achieve the highest efficiency in substrate degradation was performed and fundamental insights into the MNP-BBS Fenton-like reaction mechanism were obtained. Furthermore, an odd aspect in the material synthesis *via* coprecipitation has been evidenced, which should be taken into account for future studies.

Keywords: magnetic nanoparticles, urban waste, Fenton, pollutants, magnetite coprecipitation synthesis

1. Introduction

The United Nations General Assembly has acknowledged access to water as a fundamental human right [1]. The need to preserve global freshwater resources and water-related ecosystems, to attain universal and equitable access to drinking water and sanitation and to prepare for water-related disasters is unwaveringly included in the targets of several of the United Nations Sustainable Development Goals [2]. Goal 6 reads "Ensure access to water and sanitation for all" [3], therefore implying the need of making big effort to secure and, when compromised, restore water quality. At this purpose an aspect raising concern is the awareness of the presence, even in effluents from water treatment facilities, of the so-called contaminants of emerging concern (CECs). They consist of a wide range of xenobiotic chemicals (from pharmaceuticals and personal care products to persistent organic pollutants used in many industrial processes).

Many of these substances have been demonstrated to be harmful to the environment, public health and aquatic systems [4] and therefore their complete removal through an effective tertiary water treatment is required. Among the available technologies that may be used to remove these pollutants advanced oxidation processes (AOPs), through the generation of highly reactive species which are able to mineralize most organic molecules, yielding CO_2 and inorganic ions as final products, have been considered a viable option [5]. Among AOPs iron based technologies, pioneered by Fenton and photo-Fenton processes [6,7] have been demonstrated to be efficient and promising for removal of organic recalcitrant contaminants [8,9]; they are based on the reaction between hydrogen peroxide as an oxidant and iron ions as a catalyst to produce highly reactive $\cdot OH$ radicals with oxidation potential of 2.8 V. Being one of the main drawbacks of Fenton (and related) processes, the need of operating at acidic pH, and the iron precipitation, relevant research effort has been directed to optimize operational parameters. A significant advance has been represented by the use, in recent years, of many Fe(III)/Fe(II) complexes, in the presence of H_2O_2, as homogeneous Fenton reagent. They have been indeed demonstrated to be able to efficiently remove several organic pollutants, especially highly toxic chemicals and recalcitrant compounds [10-14]. More recently the attention has been focused on the possibility to use magnetic iron oxides (magnetite/maghemite nanoparticles, MNP in the following), due to their unique physicochemical properties; the presence of Fe(II) can indeed improve the $\cdot OH$ radicals production through the Fenton reaction [12]. Moreover, MNP can be easily separated from the heterogeneous system at the end of the treatment due to their magnetic properties and reused for successive treatments. Recent work demonstrated the effectiveness of the magnetic iron oxides in promoting the degradation of organic pollutants under UVA irradiation [13,15]. Unfortunately, in a natural oxygen containing atmosphere, these oxides are sensitive to oxidation, yielding non-magnetic hematite and the stabilization with an organic coating is usually carried out. In general, the addition of chelating anions or polymeric complexing during the magnetite formation enhances the iron oxide stability (in particular, avoiding oxidation) [16-18].

Recently waste-sourced Bio-Based Substances (BBS) have been proposed as coating [18] for the synthesis of MNP to be tested in pollutant abatement; the choice stems from the previously observed beneficial effect of BBS on photo-Fenton pollutant degradation [19-20]. Moreover the use of residual biowaste-derived substances as source of organic coating allows the valorization of urban and/or agricultural biowastes thus re-entering them into the economic cycle, in line with the model of a Circular Economy, struggling for a zero waste approach [21].

Preliminary encouraging results have been obtained when using hybrid BBS-magnetite/maghemite nanoparticles (MNP-BBS) for the photodegradation of caffeine, chosen as CECs representative molecule [22,23]. Franzoso et al. [23] investigated different MNP-BBS with different BBS contents, demonstrating that the hybrid system MNP-BBS with the best (photo)Fenton-like activity in caffeine degradation was that containing 2% wt. of organic matter. For this reason, this work focuses on the same material in order to rationalize its behaviors and optimize its performance through a systematic study. Phenol was chosen as target substrate; the effect of experimental parameters was studied; the recovery and re-cycle of the material was investigated.

For the preparation of MNP-BBS, coprecipitation synthesis was applied, adding BBS molecules to stabilize the MNP from the natural oxidation. The coprecipitation reaction is a very widely used methodology to prepare magnetic materials containing magnetite/maghemite. Although some of the main problems relative to the optimal experimental conditions (i.e. Fe(II)/Fe(III) ratio, pH, temperature, presence or absence of molecular oxygen) were considered and discussed in the literature [24-26] some question are still open. In fact, $FeCl_3$ used as source of Fe(III) in the synthesis of magnetite, even in hydrated or dehydrated form, is highly hygroscopic and tends to absorb large amount of water from the atmosphere. This implies that the molecular weight of the salt, which is the base of the calculation for the right Fe(II)/Fe(III) ratio for the preparation of the magnetic material, changes in almost short times (few months if the reagent is stored in a shelf for chemical reactants).

The use of $FeCl_3$ containing unknown amounts of Fe(III) affects the synthesis of the magnetic phase, as part of the Fe cations can be excluded from the crystalline framework of the magnetite/maghemite phase and can remain as an amorphous, undefined hydroxo-phase containing the oxidised Fe(III) giving a red shadow to the typically brilliant black colour of magnetite/maghemite. The presence of this phase is not so trivial, since its presence can affect the reactivity of the prepared material to a great extent.

Among other effects, a plain hybrid material containing the magnetic phase surrounded by BBS shows in water the natural pH of 6, whereas the material bringing some hydroxo-Fe(III)-containing phase shows a pH in water around 3, due to Fe(III) hydrolysis. Only a deep and accurate washing treatment at very low pH allows to solubilize the undesired Fe(III)-containing phase in order to obtain the plain hybrid material whose behaviours and features are described in several papers published so far [18, 22, 23].

Moreover, the presence of Fe out-of-the-structure determines a release of Fe in solution which can act as a homogeneous (photo)catalyst in (photo)Fenton processes, and this makes complicated to assess the (photo)Fenton capacity to the hybrid nanoparticles releasing small amount of iron (heterogeneous (photo)Fenton-like process) or to the solubilized iron species derived from a non-controlled synthesis ((photo)Fenton process). The consequences of this issue are described in the following, where phenol degradation has been performed.

2. Materials and methods

2.1. Synthesis and characterization

The synthesis of the magnetic material was performed following the procedure of coprecipitation reaction. 3.7 g of $FeCl_3$ and 4.2 g of $FeSO_4 \times 7H_2O$ were solubilized in 50 mL of deionized water and stirred heating until the temperature of 90°C was reached. 10 mL of NH_3 25% followed by 1 g of BBS solubilized in 50 mL of deionized water were added to the solution which passes immediately from orange to black colour forming a thin precipitate. The solution was kept at 90°C for 30 minutes, then the suspension was separated using a magnet, the supernatant removed and fresh deionized water added to wash the powder formed. The washing procedure was performed three times in order to remove the unreacted reagents and neutralize the basic environment. At the end, the powder is put in a Petri dish and left in an oven at 70°C overnight to be dried. The powder was named MNP-BBS.

The characterization of the powder was made following a well-established procedure reported in [23]. N_2 adsorption at 77K was determined by ASAP2020 (Micromeritics) and used to evaluate the specific surface area and porosity of the aggregated powder; X-Ray Diffraction analysis was performed by X'Pert PRO MPD diffractometer (PANalytical) and used to determine the crystalline phase of the sample and confirm the presence of magnetite/maghemite (proved also by its magnetization properties); FTIR spectroscopic measurements were carried out by Vector 22 (Bruker), equipped with Globar source and DTGS detector on sample dispersion in KBr to evidence the vibrational feature of the hybrid material and confirm the presence of BBS; Thermogravimetric analysis was performed by TGA (TA Instrument) in air and in N_2 atmosphere (flux 100 mL/min, ramp 10°C from RT to 800°C) to evaluate the amount of the BBS on the nanoparticles.

The results of the characterization carried out on the synthesized material are in agreement with previously obtained characterization data [23]. Briefly, spherical nanoparticle of no more than 20 nm of diameter made of magnetite/maghemite crystals are produced. The organic matter surrounding the MNP is strongly bonded to them, as visible in the FTIR spectrum, and quantified in 23% of the particle mass, as determined by TGA. The coating causes high aggregation in the dry material presenting a specific surface area of 28 m^2/g and a interparticle mesoporous porosity of 0.08 cm^3/g.

Although all the characterization results are perfectly in agreement with those expected for the magnetite/maghemite phases, some red shadows visible, in particular, at the interface air-particles, suggest the presence of a small amount of an amorphous (not detectable by XRD) hydroxo-Fe(III) phase in the sample.

2.2. Material (photo)activity

The (photo)catalytic ability of the synthesized material was tested at natural pH (3.5) by evaluating the disappearance of the phenol (10 mg/L) varying the amount of material dispersed in water and the concentration of hydrogen peroxide in order to achieve the best experimental conditions for abatement.

Irradiation were performed in Pyrex glass cells kept under continuous magnetic stirring and was realized using a Philips lamp with maximum emission at 365 nm. Samples were subjected to Fenton and photo-Fenton processes were added with 5 ml of methanol to stop the reaction and then filtered through 0.45 μm PTFE filters to remove the catalyst.

The production of hydroxyl radicals during the irradiation of MNP-BBS was studied by Electron Paramagnetic Resonance (EPR) in the presence of 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as spin-trap. EPR spectra were recorded at room temperature with a Bruker ESR 300E X-band spectrometer and acquired by using a previously developed method [27]: 10 μL of DMPO were added to 5 mL of a 1000 mg/L MNP-BBS suspension and the resulting mixture was irradiated for 5 min. Immediately after the irradiation, the mixture was transferred in a quartz capillary tube and the EPR spectrum was recorded by using the following experimental parameters: frequency = 9.78 GHz, microwave power = 5 mW, center field = 3475 G, sweep width = 80 G, receiver gain = 1×10^5, modulation amplitude = 0.41 G, conversion time = 40.96 ms , number of scans = 30.

2.3. Analytical procedures

2.3.1 HPLC-UV

Samples were analysed with a HPLC-UV equipped with a Rheodyne injector, two Merck Hitachi L-6200, a RPC18 Lichrochart (Merck) 12,5 x 0,8 cm column and a UV/Vis Hitachi L-4200 detector at λ=220 nm. Isocratic elution with 80% phosphate buffer 10^{-2} M at pH 2,8 and 20% acetonitrile. In these conditions, retention times were 6.75 min, 1,87 min, 2,45 min, 3,03 min and 3,13 min for phenol, hydroquinone, resorcinol, 1,4-benzoquinone and catechol, respectively.

2.3.2. Fe(II) and Fe(III) analyses

Total iron and Fe(II) were detected using a colorimetric method [28] and analyses were performed using a UV-Vis Cary 100 SCAN spectrophotometer. Fe(II) was analysed using 4 mL of sample added with 1 mL of acetate buffer and 1 mL of phenantroline 0,1%. Total iron was obtained by adding an excess of ascorbic acid to the sample and using the same procedure followed for Fe(II) analysis.

2.3.3. Fluorimeter

The fluorescence spectra (as Excitation Emission Matrixes, EEMs) of the filtered solutions were obtained with a Varian Cary Eclipse fluorescence spectrofluorimeter, adopting a 10 nm slit-width. The parameters set for conducting the analysis were: λ emission 220-600 nm; λ excitation 210-500 nm.

2.3.4. Total Organic Carbon

Total organic carbon measurements carried out by a TOC-VCSH Shimadzu meter. Calibration of the instrument was performed by preparing standards of potassium phthalate.

3. Results and discussion

3.1. Use of MNP-BBS to degrade a probe molecule: the case of phenol

The photoactivity of the material was investigated in MilliQ water using phenol as a model substrate. Firstly, we evaluated phenol adsorption on the surface of MNP-BBS as a function of catalyst and model substrate concentrations and, in both cases, it was negligible.

Once excluded the phenomenon of surface adsorption, the photoreactivity was estimated by irradiating under UV-A light the phenol solution added with different concentrations of MNP-BBS; the curves plotted in Figure 1 show the obtained results.

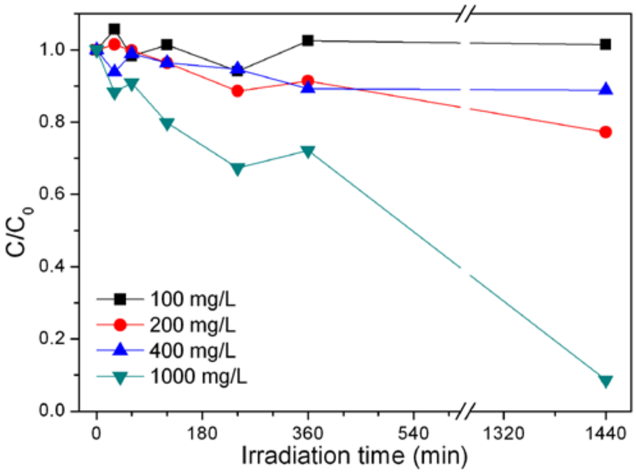

Fig.1: Degradation profiles for phenol (10 mg/L) in the presence of different MNP-BBS concentrations.

The degradation profiles evidence that the material is able to promote a significant abatement of the organic molecule only after long irradiation times (24 h) and employing catalyst at concentration of 1000 mg/L. Thus, in these experimental conditions, the material subjected to irradiation generates a very limited quantity of oxidizing species, as confirmed by EPR analysis described in the following, which provided only very weak signals related to the formation of hydroxyl radicals.

3.2. Improvement of phenol abatement through a Fenton-like process

H_2O_2 was added to the system in order to exploit MNP as source of iron and BBS as complexing agent to promote Fenton and Photo-Fenton-like processes and improve the material performance.

Firstly, the contribution of the sole oxidizing action of hydrogen peroxide to the abatement of phenol was tested. For this purpose, experiments were carried out in the absence of catalyst, using a phenol solution at 10 mg/L added with a concentration of H_2O_2 $5x10^{-4}$ M or $1x10^{-3}$ M. In both cases, H_2O_2 was not able to promote the degradation of phenol (data not shown).

Subsequently, hydrogen peroxide was added to MNP-BBS suspension following phenol degradation. In order to establish the best working conditions, experiments were carried out by varying the ratio hydrogen peroxide/MNP-BBS concentrations, keeping constant the phenol concentration.

When increasing the concentration of hydrogen peroxide up to $1x10^{-3}$ M, it was possible to obtain the complete phenol degradation within 5 minutes (see Figure 2), but in all cases the best efficiency was reached in the first 10 minutes of the reaction, i.e. immediately after H_2O_2 addition: phenol concentration rapidly decreased, as expected for a Fenton-like process, then it remained constant, probably due to the consumption of the ·OH radicals produced by iron in the presence of H_2O_2 [23, 29].

The tests obtained by adding H_2O_2 $5x10^{-4}$ M and varying MNP-BBS concentration produced excellent results and promoted the complete degradation of phenol within 5-10 minutes (Figure 2). In particular, the abatement rate increased by enhancing MNP-BBS concentration and, in the presence of MNP-BBS at 1000 mg/L, the degradation was complete in only 5 minutes.

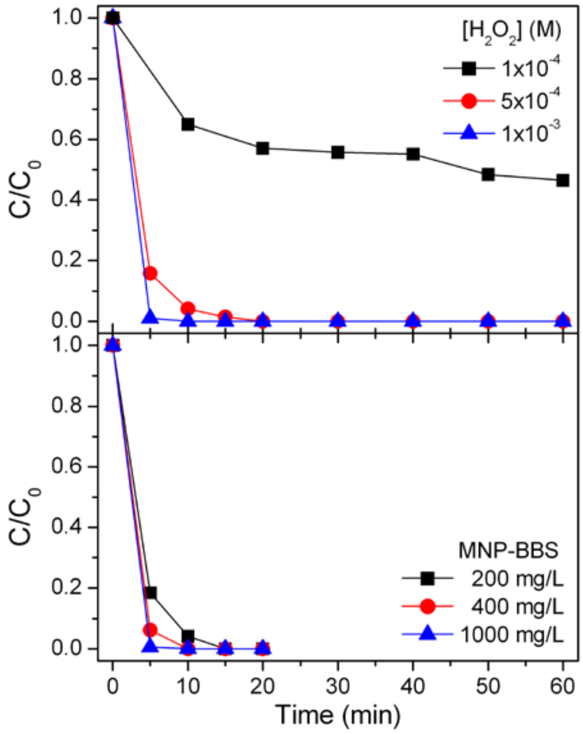

Figure 2: Degradation profiles for phenol (10 mg/L) with (a) different H_2O_2 concentrations and MNP-BBS 200 mg/L and (b) H_2O_2 $5x10^{-4}$ M in the presence of different MNP-BBS concentrations.

The last investigation was performed by keeping MNP-BBS at 1000 mg/L and working with decreasing amount of H_2O_2 in order to establish the real H_2O_2 involvement in the reaction (see Figure 3).

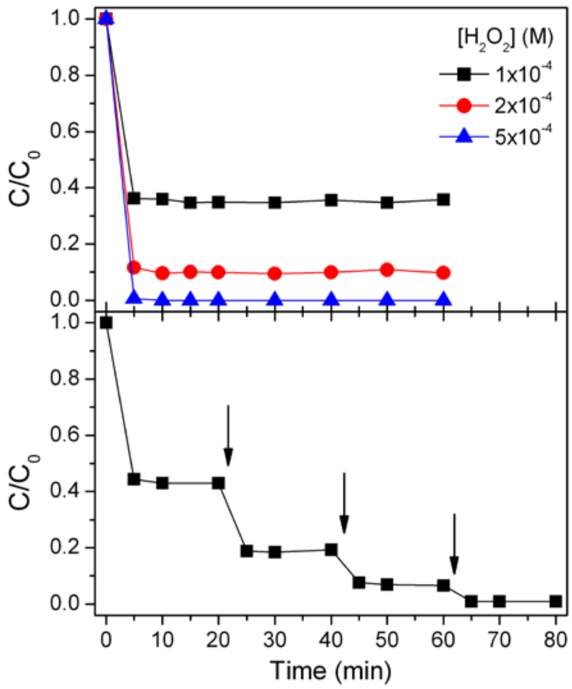

Figure 3. Degradation of phenol in the presence of 1000 mg/L MNP-BBS: top) using different H_2O_2 concentrations and bottom) following sequential addition of H_2O_2 1x10^{-4} M (indicated by arrows).

Phenol degradation profiles show that the percentage of abatement is related to the concentration of H_2O_2. Phenol completely disappears only when adding hydrogen peroxide 5x10^{-4} M, while the addition of lower concentrations of H_2O_2 allows to obtain only a partial degradation. These results suggest that the amount of OH· radicals produced by iron in the presence of H_2O_2 is not enough to promote the complete disappearance of the substrate, so underlining that the limiting factor in the reaction is the amount of hydrogen peroxide and not the amount of soluble iron. To confirm this hypothesis, a further test was carried out in the same conditions, proceeding with periodic additions of hydrogen peroxide (1x10^{-4} M) once the plateau conditions were reached (see Figure 3, bottom). The obtained results confirm that the reaction stops all the times that hydroxyl radicals are consumed and that, the addition of fresh hydrogen peroxide, allows generating further hydroxyl radicals which can continue to attack the organic substrate.

The formation of OH· radical was assessed *via* EPR measurements in the presence of DMPO as spin-trap. In agreement with the previous data, an intense typical EPR spectrum of the DMPO-OH adduct (four lines separated by 15 Gauss and with relative intensity 1:2:2:1) is clearly visible when H_2O_2 was added to the MNP-BBS solution since, in these conditions, iron released by MNP-BBS catalyses the photo-Fenton reaction and gives a high production of hydroxyl radicals. On the contrary, in absence of the catalyst, the production of OH· radical is very lower and, moreover, in the absence of H_2O_2 the generation of hydroxyl radical is negligible.

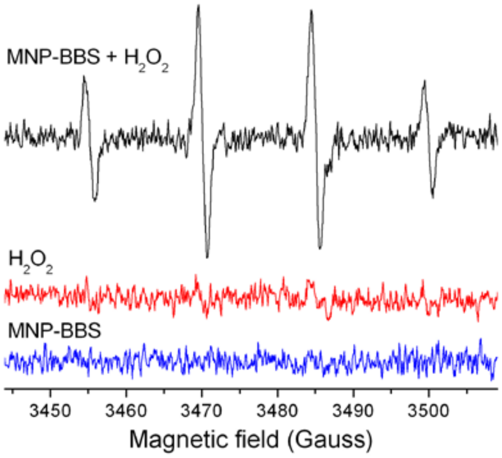

Figure 4: EPR spectra of DMPO-OH adducts generated after 5 min irradiation of MNP-BBS solutions, with and without addition of hydrogen peroxide, and H_2O_2 alone.

3.2.1. Photo-Fenton process: influence of irradiation

Further tests were carried out to define the role of light radiation in the process. For this purpose, firstly a solution of phenol at 10 mg/L was added with hydrogen peroxide 5x10^{-4} M and irradiated under UV-A light. The obtained results show that the phenol did not undergo significant degradation, in agreement with literature [30]. Subsequently, phenol degradation was performed by using the same experimental conditions employed for the Fenton-like experiments, but irradiating the samples with UV-A light, in order to assess whether the radiation influences the process efficiency. A comparison of the results obtained in the two cases is shown in Figure 5.

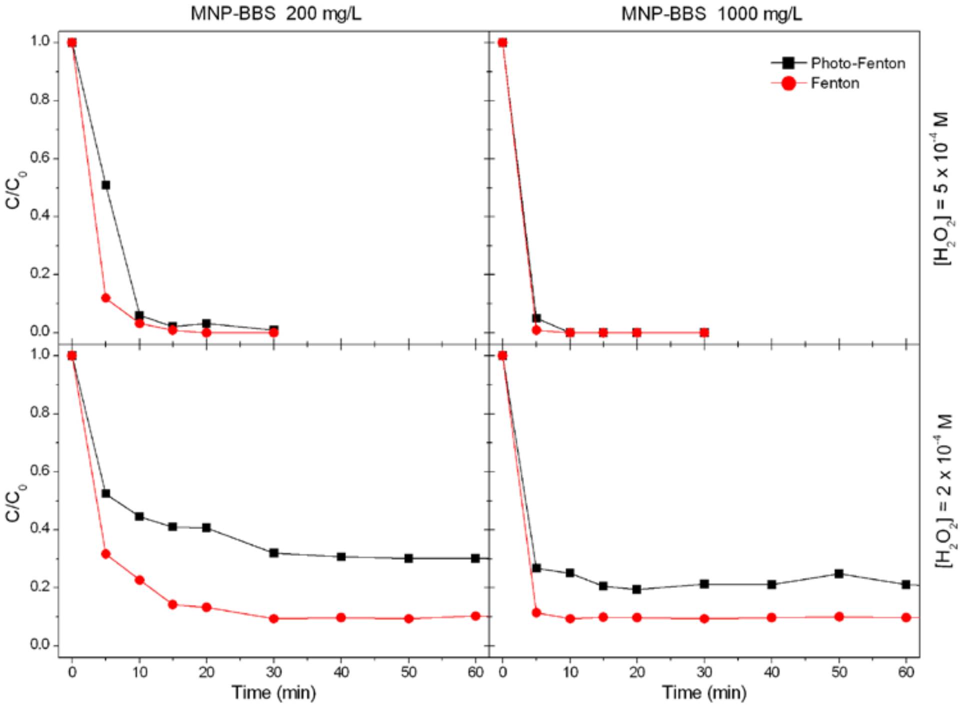

Figure 5: Phenol disappearance *via* Fenton and photo-Fenton processes with H_2O_2 5x10^{-4} M (top) and 2x10^{-4} M (bottom) as a function of MNP-BBS concentration.

The degradation curves for phenol were obtained as a result of Fenton and photo-Fenton processes performed by varying the concentrations of catalyst and maintaining constant hydrogen peroxide concentration at 5x10^{-4} M (top) or at 2x10^{-4} M (bottom). Differently from what reported in the literature [23], the use of light radiation seems to inhibit the process or, at least, does not improve the performance of the material. This effect could be explained by considering two aspects: the first one could be attributed to the absorption of the radiation by the material itself, since it shows a very dark colour even at lower concentrations; the latter could be due to the fact that the material itself undergoes photodegradation, causing the release of organic matter in solution, which could therefore compete with the organic substrate under study, thus hindering the abatement process.

3.3. Stability and re-usability: evaluation of released ions/organic matter

Once the efficiency of the method was established, a test was carried out to determine if MNP-BBS recovered at the end of the Fenton-like process could be reused to carry out a new degradation cycle. For such, once reached the complete elimination of phenol, the magnetic properties of the catalyst were used to recover it. MNP-BBS was then washed several times with MilliQ water, dried and re-used again. The degradation curves obtained from the two subsequent cycles are compared in Figure 6.

The second cycle exhibits a lower degradation efficiency: MNP-BBS is able to promote the partial elimination of phenol with 70% of abatement after one hour.

In order to assess whether the process induces changes on the organic phase that coats and stabilizes the magnetite nanoparticles, TGA analysis on the material after one working cycle and recovery was performed. The percentage of organic content, obtained from the weight loss in the range 250-700°C, is different in the two cases and can be quantified in 23% for the original sample, as stated above, and 13% for the recovered one. This change suggests that the reactive species generated during the Fenton process can also act on the organic coating of the nanoparticles inducing its partial decomposition. However, the measured loss is not directly correlated with the loss of efficiency found in the second cycle and therefore it is necessary to deepen the study of this material to understand the mechanisms in which the organic matter participates. This efficiency loss could be caused by the organic matter and the iron oxide, as both participate to the overall process. Therefore, the two aspects will be inspected separately in the following.

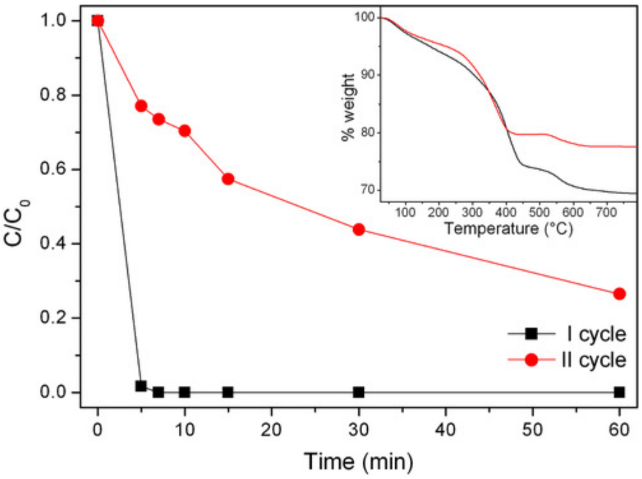

Figure 6: Phenol degradation *via* Fenton process with MNP-BBS at 1000 mg/L: **I** cycle (black) and **II** cycle (red) abatement curves. Inset: TGA curves of material as prepared (black curve) and recovered (red curve).

3.3.1. Release of organic matter

The loss of organic matter was investigated performing both TOC measurements (to investigate the amount of organics release) and fluorescence spectra (to define the nature of the organics release). TOC measured at time zero allowed to assess that the material released about 4.5 mg/L of organic carbon. TOC evolution profile over time was then followed after addition of H_2O_2 $5x10^{-4}$ M both in the dark and under UV-A irradiation (see Figure 7).

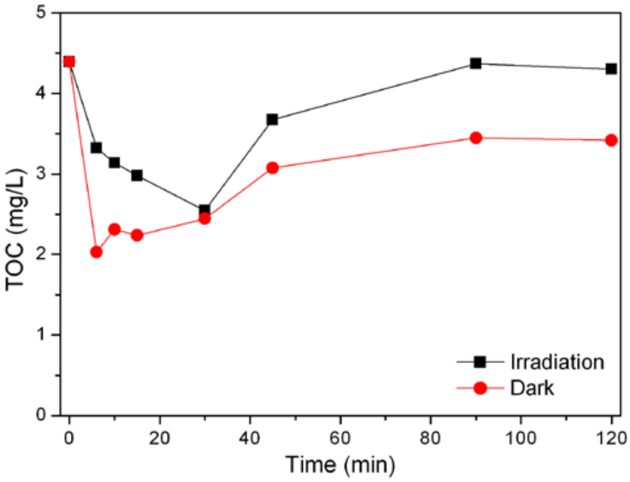

Figure 7: TOC released by the catalyst in the presence of $5x10^{-4}$ M H_2O_2

The addition of hydrogen peroxide caused the partial degradation of the organic fraction without involving its complete mineralization. At longer irradiation time, the material continues to release organic carbon in solution, suggesting that this phenomenon could also cause the release of iron species in solution deriving from the magnetic iron-containing core of the nanoparticles. Under irradiation the released TOC is higher than in the tests conducted in the dark, so implying that light could act on the material degradation as well.

We proceed by acquiring Excitation Emission fluorescence matrixes (EEMs) on the same samples aimed to understand the nature of organic matter that is affected by the action of peroxide and light. According to the literature [31], the organic substances used to coat the magnetite nanoparticles show structural similarities with the humic substances and, therefore, fluorescence matrices spectroscopy can be exploited to study properties and characteristics of these samples containing humic-like substances [32-34].

EEMs of filtered sample were recorded and are shown in Figure 8. A very intense and broad emission peak centered at excitation/emission coordinates 210/420 nm is manifest (panel A). Referring to literature [34], this signal is attributable to the presence of humic-like components. A second but less intense fluorescence peak is observed, at Ex/Em 330/ 410 nm, which could be attributed to the humic-like and fulvic-like components, too. The same signal was still maintained following 2h of UV-A irradiation (panel B), so permitting to assess that the organic matter was not photolysed.

Samples were then added with hydrogen peroxide and subjected to irradiation with a UV-A lamp (Figure 9). Following irradiation and addition of hydrogen peroxide, within few minutes we can perceive a quenching of the fluorescence with the disappearance of all signals attributable to humic-like substances. These results suggest that the action of hydrogen peroxide/light can affect the properties of some of the components of the material, destroying those responsible for the observed signals. These results agreed with those obtained by TOC measures, which showed a TOC decrease within 15 minutes after the addition of the hydrogen peroxide. Panel E and F, showed that new signals appear in samples subjected to longer irradiation times, even if with lower intensities than those observed at time zero; it implies that a prolonged irradiation could lead to the release of new fluorescent species, responsible of the increased TOC content described above (see figure 7).

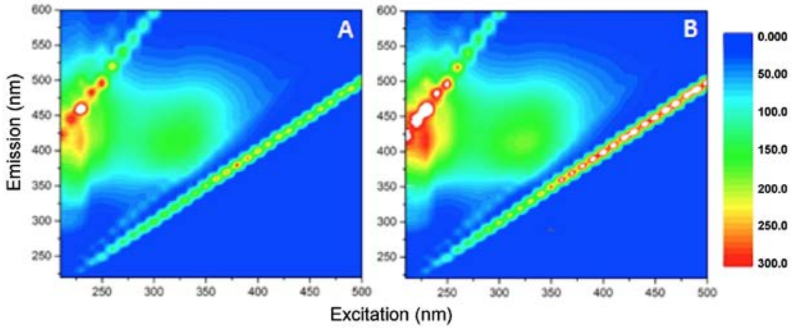

Figure 8: Excitation Emission fluorescence matrixes (EEMs) acquired on filtered sample at time zero (A) and after 2h of UV-A irradiation.

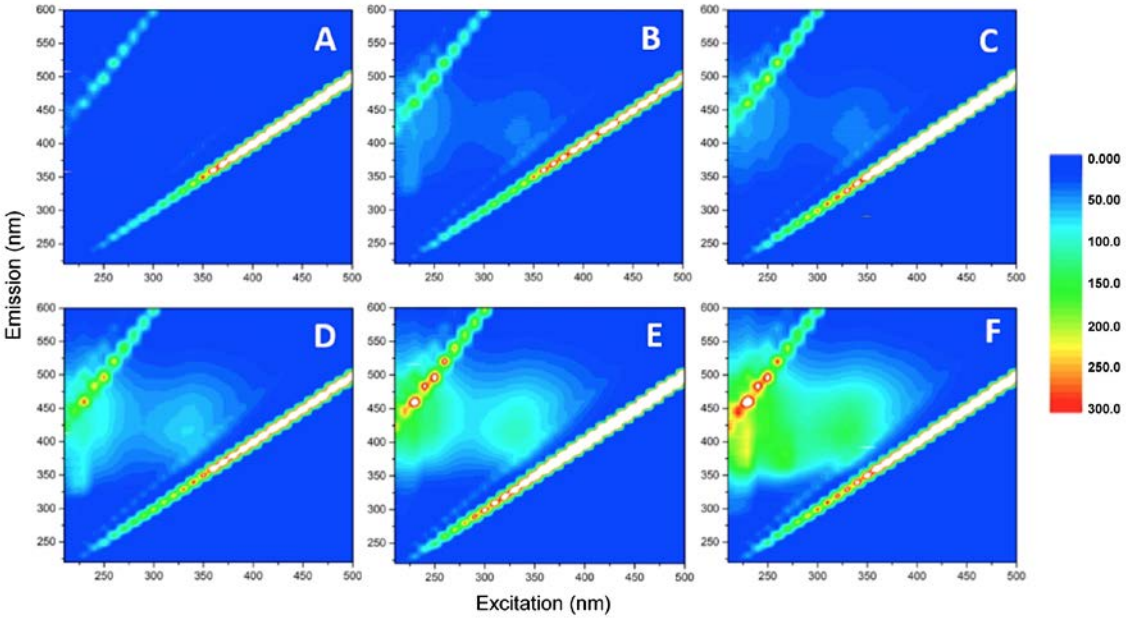

Figure 9: Excitation Emission fluorescence matrixes (EEMs) acquired after addition of H_20_2 $5x10^{-4}$ M under UV-A irradiation. Samples are measured after 5 min (A), 10 min (B), 15 min (C), 30 min (D), 60 min (E) and 120 min (F).

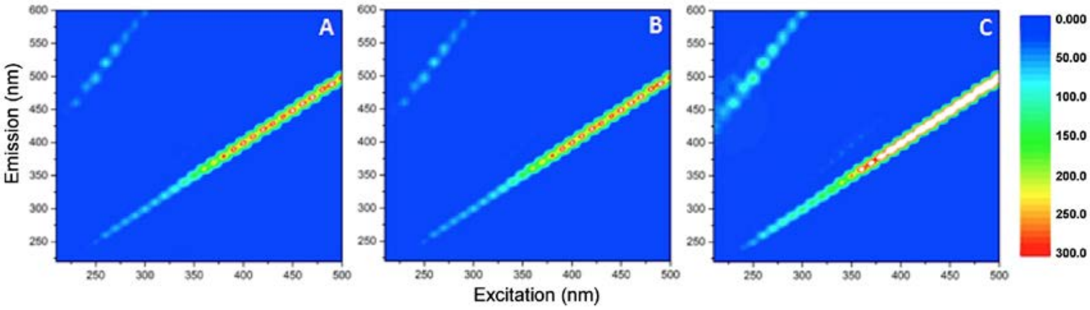

Figure 10: Excitation Emission fluorescence matrixes acquired on filtered samples following addition of H_20_2 $5x10^{-4}$ M. Samples are measured after 5 min (A), 10 min (B), 15 min (C) of H_20_2 $5x10^{-4}$ M addition.

EEMs were also acquired during the Fenton-like process and plotted in Figure 10. These images showed the disappearance of the characteristic signals after few minutes from H_2O_2 addition. Again, hydrogen peroxide, also in the dark, acts on the organic component that covers the magnetic nanoparticles, modifying their structure and/or properties.

3.3.2. Release of soluble iron

Iron oxide affects the process acting as a source of soluble iron and, therefore, the release of Fe(II) and Fe(III) in solution occurring during the process was followed. Figure 11 shows the formation and disappearance profiles of Fe(II) and total iron deriving from Fenton and photo-Fenton processes carried out in the optimized experimental conditions, i.e. in the presence of 1000 mg/L of MNP-BBS and H_2O_2 5x10^{-4} M. In both cases the total amount of released iron was 20 mg/L, while the amount of measured Fe(II) is around15-17 mg/L; Fe(II) concentration is higher than that reported in the literature [23], probably because the working pH value of 3.5 favours the dissolution of iron cations in solution [29].

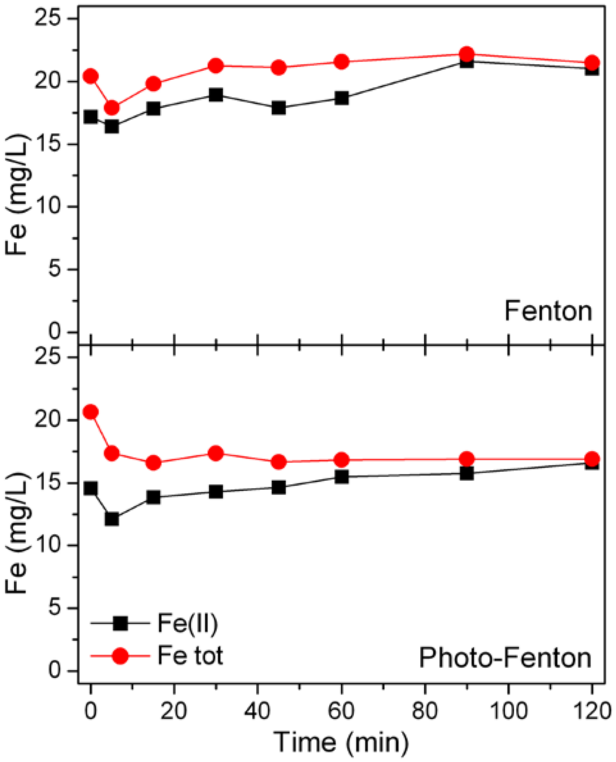

Figure 11: Fe(II) and total iron released during Fenton process (top) and Photo-Fenton process (bottom). In all cases the experimental conditions were: 1000 mg/L catalyst, 5x10^{-4} M di H_2O_2.

Some interesting suggestions to the reaction mechanism can be achieved considering the concentration of Fe(II) curves. The highest consumption of Fe(II) is recorded within 5 min, i.e. the period of time corresponding to the highest reaction rate observed in Fenton-like and photo-Fenton-like conditions.

It is worth noting a partial consumption of Fe(II) occurring in the first few minutes of the Fenton-like process, in accordance with reaction (1).

$$\mathrm{Fe^{II} + H_2O_2 \rightarrow Fe^{\,III} + OH^- + HO^{\cdot}} \quad \mathrm{k = 40 - 80\ L \cdot mol^{-1} s^{\ -1}} \qquad (1)$$

At the beginning of the process, in fact, Fe(II) is the predominant species, and the relative concentration increases during the reaction both in Fenton-like and photo-Fenton-like conditions. At the same time Fe(II) ions can be supplied by release from iron oxide (losing its protective organic coating during (photo)Fenton-like process) as its concentration in solution remains almost constant, whereas photoreduction of Fe(III) or complexation of Fe(III) by BBS explain the relative concentration decrease in solution assessed in Figure 11, where after 2h of treatment the total iron amount is measured as Fe(II).

Finally, another aspect needs to be considered to explain the activity loss shown by the sample: it is related to the reddish colour visible on the surface of the as synthesised material already described in the introduction section. The working pH of 3.5 measured in the presence of MNP-BBS suggests that iron cations hydrolysis (especially from Fe(III)) could take place during the preparation of material suspension in water as the normal working pH experimented by these suspensions should be around 5-6. If Fe hydrolysis is observed, that means that part of Fe cations has not been included in the magnetite/maghemite crystalline structure and is present at the surface of the magnetic material. This component should be responsible of the reddish colour of the powder, of the low pH observed for the suspension, and probably also of the very high reactivity of the material since iron oxo/hydroxo species could be solubilised at low pH and cause a synergistic Fenton process adding to the expected Fenton-like one. Once Fe cations out-of-the-structure are consumed (during the first reaction cycle) the reactivity is only due to the solubilisation of Fe(II) from the magnetic phase caused by BBS consumption and the reactivity slows down.

Conclusions

Phenol degradation was studied using MNP-BBS, a low cost material easy recoverable from aqueous media thanks to it magnetic feature. BBS, used as protective organic layer against magnetite/maghemite oxidation, present the advantage of complexing iron species released from the magnetic core of the material preventing their precipitation and increasing their availability during the catalyst activity. All the trials carried out indicate that the material is a suitable system to achieve the degradation of organic substrates in Fenton-like condition simply adding small amount of H_2O_2 to produce OH radicals. The reusability tests indicate a good performance of the material evidencing an odd aspect in its synthesis via coprecipitation which should be taken into account for future studies.

MNP-BBS is stable under UV-A radiation, but H_2O_2 addition induced a partial degradation of the material with the release of organic and inorganic species.

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