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Combined effect between Co and carbon nanostructures grown on cordierite monoliths for the removal of organic contaminants from liquid phase

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Carbon nanostructures were grown on the surface of cordierite monoliths using Fe or Co nanoparticles by catalytic chemical vapor deposition (CCVD) with ethanol in order to intensify the interaction of this support with organic contaminants. The materials produced were extensively characterized by X-ray diffraction, thermal analysis, elemental analysis, atomic absorption spectrometry, Raman spectroscopy and scanning and transmission electron microscopies. The materials were tested in the removal of quinoline and methylene blue from liquid solutions. Promising results were attributed to the combined effect of the hydrophobic carbon nanostructures in adsorbing the organic contaminants with cobalt metal cores that are able to promote the oxidation of the adsorbed molecules via a heterogeneous Fenton process.

Introduction

Cordierite monoliths present a honeycomb structure that consists on several parallel tubular channels separated by thin walls. They are considered excellent ceramic materials to be applied as particulate supports due to their high melting point, high temperature resistance, great chemical stability [1], high geometric external surface, high fraction of vacancies [2] and easy separation from the catalytic system [3]. However, cordierite monoliths are very hydrophilic materials [4] that do not interact appropriately with organic molecules. For this reason, carbon nanostructures were grown on their surface via CCVD (catalytic chemical vapor deposition) process in order to improve their capacity to remove organic environmental contaminants. A great advantage in the use of cordierite monoliths as support is that after reaction the material can be easily removed from the system. Recent studies describe the synthesis of carbon nanotubes (CNTs) or carbon nanofibers (CNFs) on cordierite monoliths surface. Different systems have been reported, such as CNT/ferrocene/monolith [5], CNT/CoMo/monolith [6], CNF/TiO_2/monolith [7], N-CNF/Ni/monolith [8] and CNF/Ni/monolith [4].

Carbon nanostructures are promising materials for environmental remediation due to their surface highly porous and hollow structure, large specific surface area and hydrophobic surface [9, 10]. CNTs show strong interactions with heavy metal ions [11-17], radionuclides [14, 15, 18] and organic compounds, especially hydrophobic compounds [19-21]. However, the direct use of powder CNTs is limited mainly by their difficult recovery, which may cause environmental and health problems. The most common methods to recover CNTs from liquid phase are centrifugation and filtration, both presenting important restrictions. The uncontrolled release of CNTs into the environment is of concern because of their nanometric size. CNTs can enter cells, causing damage to plants, animals, and humans [22], and their toxicology was highlighted recently [23]. Thereby, to facilitate the use and recovery of CNTs from solution, their immobilization on macroscopic supports should be an important alternative.

In this work, iron or cobalt nanoparticles were firstly supported on monoliths to catalyze carbon deposition as carbon nanostructures via CCVD. The materials were tested in the removal of organic environmental contaminants, quinoline and methylene blue, via oxidation reactions with hydrogen peroxide (H_2O_2). It is observed that the metal cores are also able to catalyze the oxidation reaction by a Fenton-like mechanism [24-30], where H_2O_2 is activated by metallic species to form HO• radicals. It is believed that the carbon nanostructures act as facilitators of the reaction by adsorbing the organic molecules prior to the oxidation by •OH radicals formed by Fe, and specially Co phases.

Experimental

Preparation and characterization of the materials

Cordierite monoliths with tubular channels were cut with dimensions of 1.0 x 1.5 x 2.5 cm and submitted to wet impregnation of metallic catalysts (cobalt or iron). Pieces of monoliths were immersed in 30 mL of $Co(NO_3)_2.6H_2O$ (Synth) or $Fe(NO_3)_3.9H_2O$ (Vetec) solution in ethanol (1.0 mol L^{-1}), for

24 h. These monoliths were then dried for 5 h in an oven at 80 ^oC. After impregnation, the materials were calcined at 650 ^oC for 3 h, producing MonoCo and MonoFe, respectively. The growth of carbon nanostructures on the surface of MonoCo and MonoFe was carried out by CCVD reaction (catalytic chemical vapor deposition) using ethanol as carbon source (N_2 as carrier gas - 100 mL min^{-1}), heating rate of 10 °C min^{-1} and final temperature of 800 °C, which was kept for 60 min. The materials produced after CCVD were named MonoCoC and MonoFeC, respectively.

The materials were characterized by XRD (Rigaku Geigerflex equipment using Cu Kα radiation), Raman spectroscopy (Bruker SENTERRA, helium-neon laser at wavelength 633 nm), thermoanalysis - TG (Shimadzu DTG 60 under air flow of 50 mL min^{-1} and a heating rate of 10°C min^{-1} up to 800 ^oC), Scanning electron microscopy - SEM (microscope LEO 1450VP), Transmission electron microscope - TEM (microscope Tecnai G2 200KV - SEI). The metal content was determined by atomic absorption spectrometry (spectrometer Hitachi-Z8200). The carbon content was measured by elemental analysis on a Perkin-Elmer equipment.

Removal of organic contaminants

The monoliths impregnated with metals, MonoCo and MonoFe and those containing carbon nanostructures, MonoCoC and MonoFeC were tested as catalysts in Fenton-like reactions in liquid phase. Organic contaminants were used as substrates in the oxidation reactions, i.e. quinoline (Sigma Aldrich), an N contaminant present in fuels and methylene blue - MB (Sigma Aldrich), a dye widely used by the textile industry.

Oxidations were carried out with 10 mg of catalyst, 100 μL of H_2O_2(aq) 30% and 10 mL of substrate solution, i.e. quinoline 30 ppm N or methylene blue 50 ppm. Quinoline and methylene blue were used as model molecules of organic environmental contaminants.

The contaminants removal was monitored by a UV-Vis spectrometer Shimadzu UV-2550. Mass spectrometry with electrospray ionization (ESI-MS) was used to identify intermediates formed throughout the degradation of Methylene Blue. ESI analyses were performed by direct infusion using a mass spectrometer model Shimadzu IT-TOF Tokyo-Japan, with two analysers together: ion trap (IT) and time-of-flight (TOF).

Results and discussion

Preparation and characterization of the materials

The cordierite monolith was initially cut and impregnated with Co or Fe, calcined (MonoCo and MonoFe, respectively) and subsequently submitted to a catalytic chemical vapor deposition (CCVD) process with ethanol as carbon source (MonoCoC and MonoFeC, respectively). **Figure 1** shows images of the monolith in different stages: in its pure form, after impregnation with cobalt nitrate or iron nitrate (MonoCo or MonoFe) and after CCVD (MonoCoC or MonoFeC). It is observed that the materials impregnated and calcined have uniform color aspect, suggesting that the impregnation with Co and Fe salts was homogeneous, including the interior walls of the monolith channels.

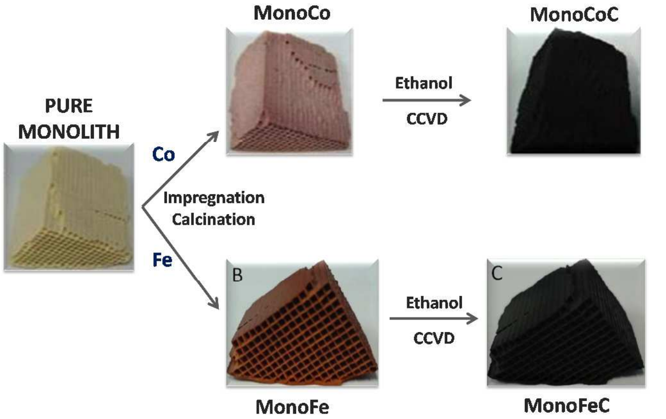

Figure 1 - Images of monoliths containing Co or Fe before and after CCVD.

The materials were characterized by XRD (**Figure 2**). The diffraction pattern characteristic of cordierite phase was identified for pure monolith and for MonoFe and MonoCo, suggesting that the structure of cordierite does not change after metals support and calcination at 650 ^oC. It is noted that both materials show predominantly characteristic peaks of the cordierite support. For the material with cobalt, MonoCo, it was not possible to identify any signs related to the metal, probably due to its high dispersion and low concentration in the sample (equivalent to 1.6 wt% as determined by atomic absorption spectrometry, AA). For the material containing iron, MonoFe, three small reflection peaks are observed (in 24, 34 and 36º) characteristic of hematite phase, Fe_2O_3, likely formed after calcination of iron nitrate at 650 ^oC. Similarly, the peaks attributed to the iron phase have also low intensity, that are related to its low concentration in the sample, 1.5 wt% by AA.

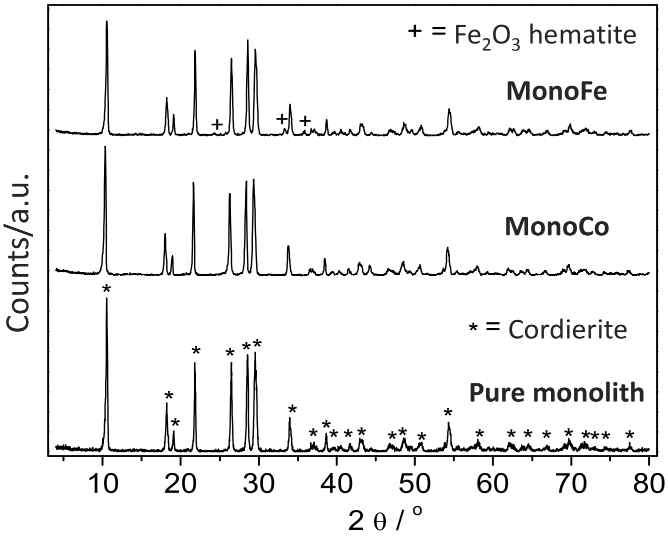

Figure 2 - X-ray diffraction patterns of pure monolith and catalysts MonoCo and MonoFe.

Figure 3 shows the results obtained by thermogravimetric analysis (TG) and elemental analysis (CHN) of the materials prepared after CCVD, MonoCoC and MonoFeC.

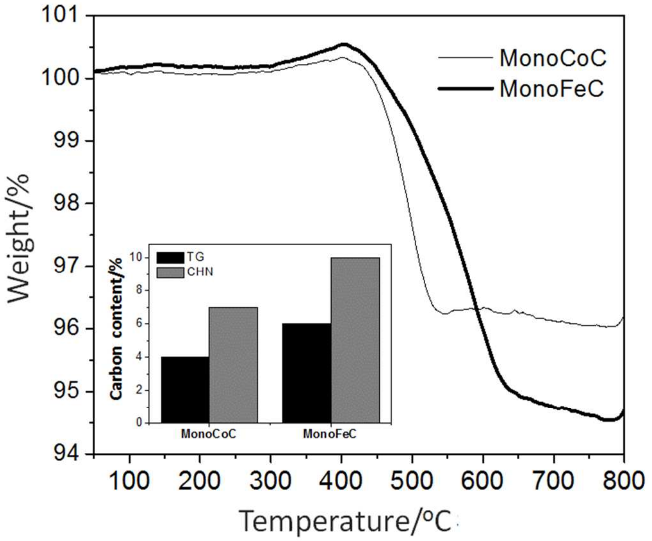

Figure 3 - TG curves obtained for MonoCoC and MonoFeC under air flow and C% determined by CHN and TG in detail.

In TG curves of **Figure 3** it can be observed a small weight gain of less than 1% between 200 – 400 °C, due to the oxidation of metals. Metal oxides formed during the calcination were probably reduced during CCVD reaction with ethanol, forming metallic Co^0 and Fe^0. During TG experiments, these reduced phases react with air oxygen as follows: $3Co^0(s) + 2O_2(g) \rightarrow Co_3O_4(s)$ / $2Fe^0(s) + 3/2O_2(g) \rightarrow Fe_2O_3(s)$. After 400 °C, it is seen a weight loss attributed to the oxidation of carbon deposits on the surface of the monoliths according to the equation $C(s) + O_2(g) \rightarrow CO_2(g)$. The weight losses can be directly related to the amount of carbon present in each material.

In **Figure 3 (detail)** it is also shown the carbon content determined by thermoanalysis (TG) and elemental analysis (CHN). The slight difference between the results obtained from TG and CHN analyses can be attributed to an overlap of events in TG experiment. The oxidation of metals (weight gain) can occur at the same temperature that the oxidation of carbon (weight loss). It is important to emphasize that TG and elemental analysis are complementary characterizations and both agree that a higher carbon amount is deposited on the surface of MonoFeC compared to MonoCoC.

The monoliths submitted to CCVD, MonoCoC and MonoFeC, were also studied by Raman spectroscopy, especially to characterize carbon deposits. The spectra obtained are shown in **Figure 4**. Both monoliths present a D band near 1350 cm^{-1} and a G band close to 1600 cm^{-1}. The D band is associated with defective carbon structures, such as agglomerates of twisted filaments and the G band is related to organized carbon structures, such as carbon nanotubes or nanofibers. The organization degree of the carbon structures formed can be measured by the ratio between the intensity of G and D bands, I_G/I_D. The I_G/I_D ratios are also shown in **Figure 4**. For MonoCoC I_G/I_D is equal to 0.48, whereas for MonoFeC, I_G/I_D = 0.28. The higher the I_G/I_D ratio the greater the organization of carbon structures. Therefore, Co has shown to be more effective than Fe to catalyze the formation of organized carbon nanostructures by CCVD.

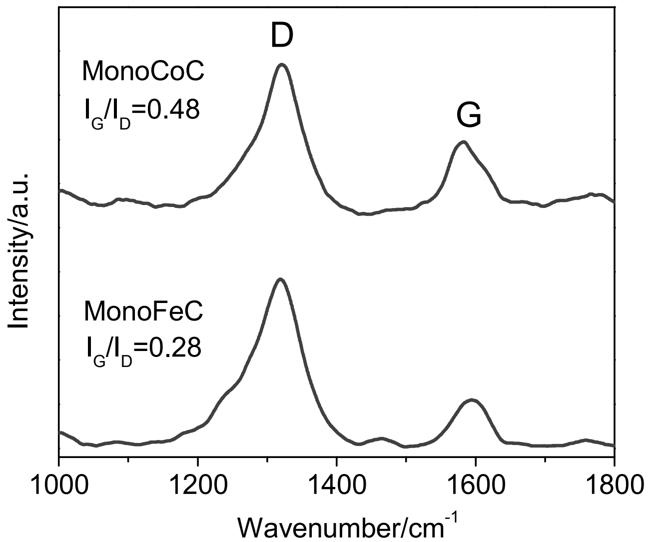

Figure 4 - Raman spectra obtained for MonoCoC and MonoFeC.

Scanning electron microscopy (SEM) was used to characterize the morphology of the materials prepared from carbon nanostructures grown on the surface of cordierite monoliths. SEM images obtained for MonoCoC and MonoFeC are shown in **Figure 5**.

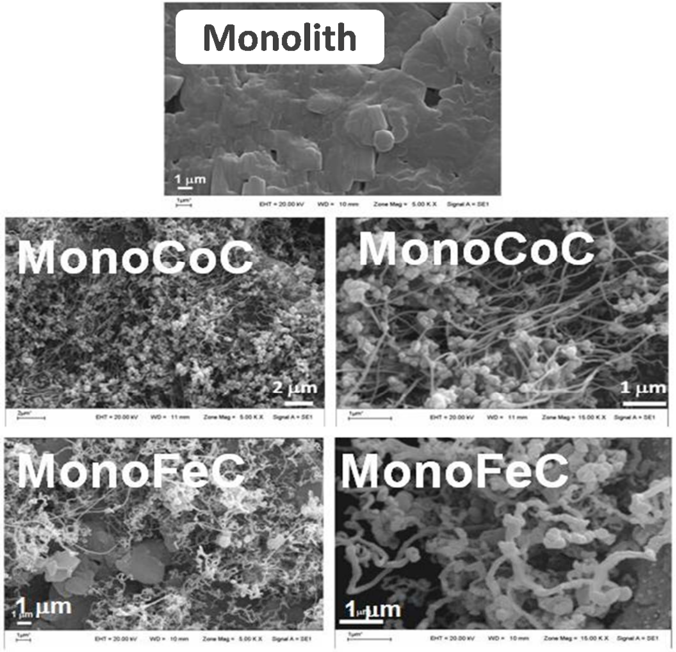

Figure 5 - SEM images obtained for the pure monolith, MonoCoC and MonoFeC confirming the formation of CNTs.

From **Figure 5** it is possible to observe that the surface of pure monolith presents a flat appearance, being composed of cordierite plates. In images obtained after CCVD for both MonoCoC and MonoFeC, it is clearly observed that the surface of the monolith is completely coated by carbon nanostructures. MonoCoC presents several filaments arranged in a linear form with at least 5 μm long and diameters between 35 and 70 nm. Filaments produced on sample MonoFeC are clearly more agglomerated and twisted, which characterizes regions of defects. Moreover, the diameters of the carbon filaments produced in MonoFeC are higher, ranging from 100 to 150 nm, what suggests that the size of cobalt nanoparticles are probably smaller than iron nanoparticles [1].

The analysis of these images are consistent with the results obtained by Raman spectroscopy (**Figure 4**), confirming that MonoCoC, which showed higher I_G/I_D ratio, presents carbon filaments more organized and with less defects than MonoFeC.

Images obtained by transmission electron microscopy (TEM) of MonoCoC and MonoFeC are presented in **Figure 6**.

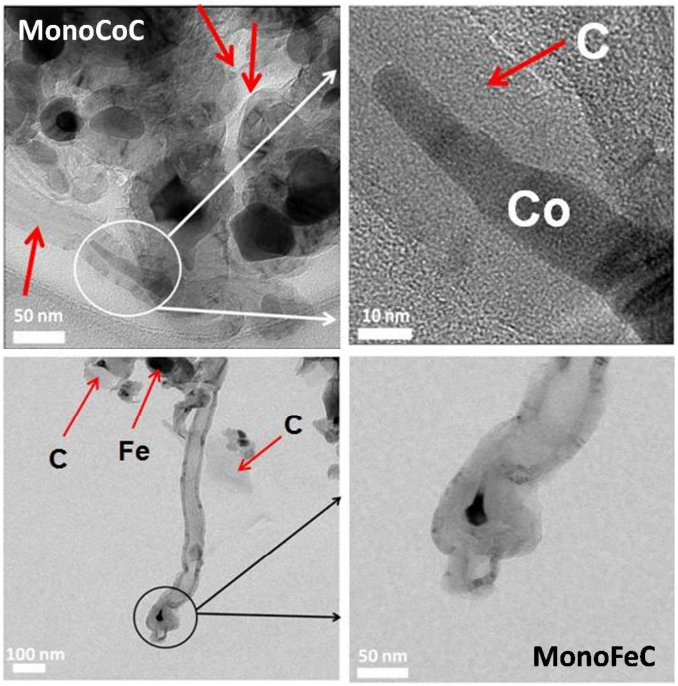

Figure 6 - TEM images obtained for MonoCoC and MonoFeC showing CNTs and metal nanoparticles in detail.

TEM images of **Figure 6** obtained for MonoCoC and MonoFeC show metal nanoparticles with diameters between 20 and 50 nm encapsulated by multiwall carbon nanotubes (MWCNT) with diameters around 30 nm. In detail, it is possible to observe metallic cores inside of carbon filaments, probably responsible for their growth on the monolith surface.

SEM and TEM images show that the carbon deposited is a mix of carbon structures, mainly as carbon nanotubes.

Removal of organic contaminants

Hereon we present studies on the use of the materials prepared in the removal of quinoline (QN) and methylene blue (MB) from liquid phase via oxidation reaction. All the materials were left in contact with the substrate solution in order to reach adsorption equilibrium before the oxidation experiments.

The efficiency of the catalyst materials containing CNTs, MonoCoC and MonoFeC, was compared to the materials without carbon, MonoCo and MonoFe.

Figure 7 shows the performance of MonoCoC, MonoFeC and materials without carbon in the removal of quinoline in liquid system.

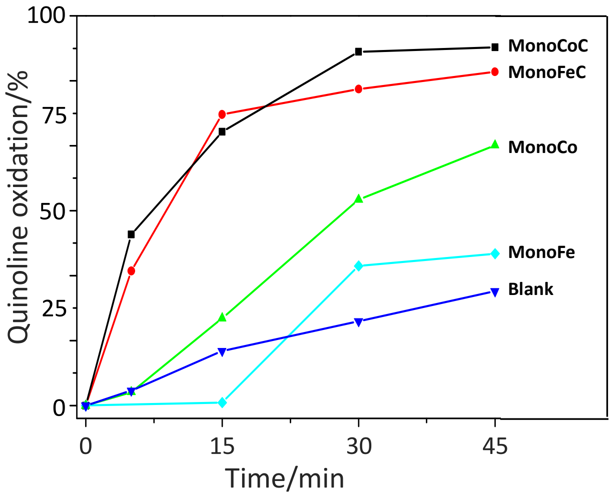

Figure 7 - Quinoline removal catalyzed by the different materials produced.

The materials containing carbon nanostructures, MonoCoC and MonoFeC, present similar activity for quinoline oxidation (~90% in 45 min) and both are more efficient than the materials without carbon. More than 70% of quinoline is already removed in the first 15 min by these two materials, while in the blank experiment (without catalyst) the reduction of quinoline concentration is less than 10% in the same period. This effect could be explained by two reasons: (i) the carbon nanostructures, very hydrophobic, allows good interaction with the organic molecules, (ii) the exposed metal catalyst, Fe and Co, used for the growth of CNTs also act as catalyst in the activation of H_2O_2, forming hydroxyl radicals ($^{\bullet}OH$), very strong oxidant, that can promote the oxidation of the organic contaminants.

Besides being less efficient than materials with CNTs, MonoCo is able to oxidize twice more content of quinoline than MonoFe. This result suggests that Co cores are more active to catalyze the Fenton-like mechanism than Fe cores in this system.

Figure 8 shows the activity of MonoCoC and MonoFeC, and the materials without carbon (MonoCo, MonoFe) in oxidation reactions of MB.

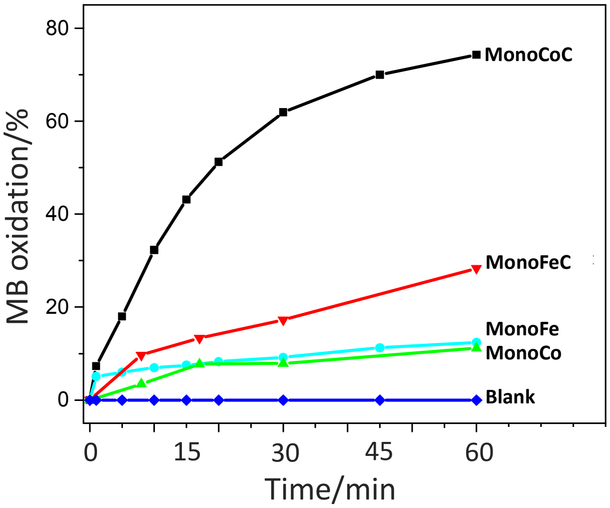

Figure 8 - Removal of methylene blue dye in the presence of the materials produced.

All the materials were first tested as adsorbents before the introduction of hydrogen peroxide and showed approximately 1 and 5% of removal in 60 min, for the materials without and with carbon, respectively. After adding H_2O_2 the conversion rates of the materials MonoFe and MonoCo reaches ~12% that are also much lower than the conversion rate of MonoFeC of 30%, and especially for MonoCoC with 74% of removal.

In this case, MonoCoC presents greater activity than MonoFeC, unlike the experiment with quinoline. However, once again, cobalt rises up as a better catalyst than iron and the presence of CNTs seems to favors the reaction. Approximately 80% of methylene blue is discolored in 60 min of reaction in the presence of MonoCoC, compared to 30% with MonoFeC and 10% with materials without carbon. This may be associated with a pre-concentration of MB on the CNTs, which favors its oxidation on the surface of the material by the exposed metallic cores, especially cobalt cores. The higher activity observed by the material with cobalt should be associated to the smaller Co particles size, very well dispersed on the monolith, thus more active for hydrogen peroxide decomposition.

The liquid phase of the MB oxidation reaction with MonoCoC was analyzed by ESI-MS (**Figure 9**). As suggested before, the available Fe and specially Co cores dispersed on the surface of the materials can promote the generation of $^{\bullet}$OH radials favoring the oxidation of methylene blue molecule.

From the mass spectra shown in **Figure 9**, it is possible to observe that not only the solution discoloration occurs, but also MB (m/z 284) is oxidized in the presence of the material MonoCoC.

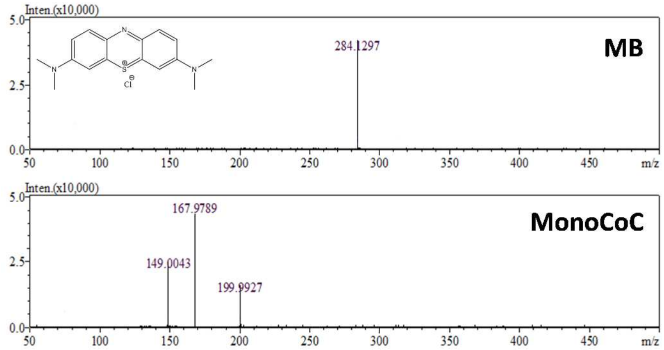

Figure 9 - Monitoring of Methylene blue (MB) oxidation by ESI-MS in the presence of MonoCoC.

Products of MB oxidation with m/z 149, 168 and 200 could be identified after 60 min of reaction. At zero reaction time, the ESI-MS operating in positive mode showed the presence of only a single cation (m/z = 284) in aqueous solution related to MB molecule. After 60 min the peak at m/z = 284 disappear, and new peaks at m/z 149, 168 and 200 can be observed. These oxidized species can be proposed from the successive hydroxylation of MB promoted by $^{\bullet}$OH radicals resulting in the rupture of the MB aromatic ring during the oxidation process [2]. The possible structures for the oxidized MB products are shown in **Figure 10**.

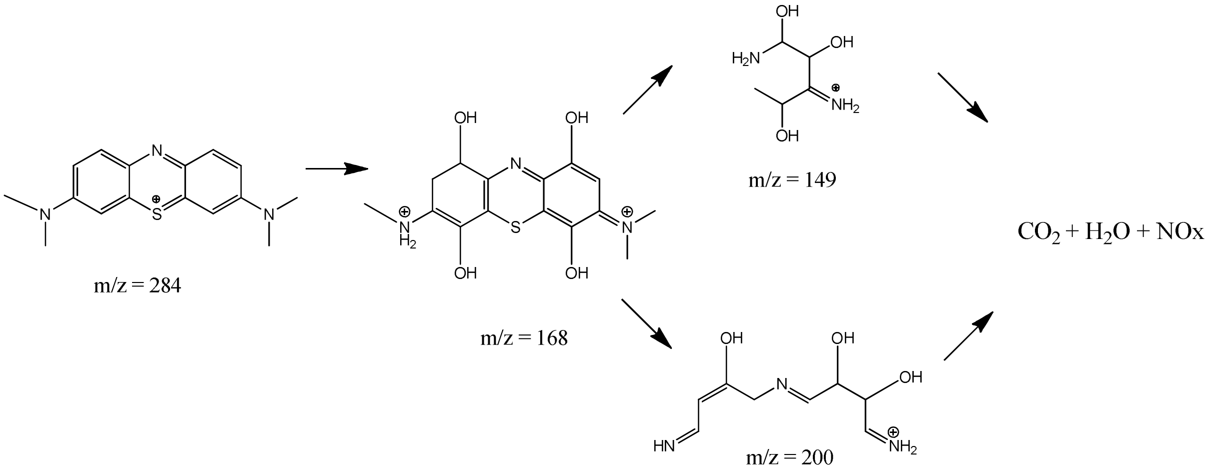

Figure 10 - Scheme of MB oxidation in the presence of the materials.

The results obtained in the catalytic tests showed very promising results. The materials produced with CNTs, especially the material containing Co, are able to intensify oxidation reactions of quinoline and methylene blue, important organic contaminants.

Figure 11 shows a schematic mechanism of the combined effect between CNTs and Co/Fe cores in the oxidation of methylene blue by the Fenton-like mechanism.

In the first frame of **Figure 11,** the material is represented by the cordierite monolith as support and carbon nanostructures and dispersed Fe or Co cores on the surface. The carbon nanofilaments are responsible for the hydrophobic portion of the material, which enables its interaction with organic molecules. The metallic cores are responsible for the Fenton-like reaction (formation of hydroxyl radicals). In the second frame of the schematic mechanism, the combined effect is shown in detail. CNTs adsorb the organic molecules (i.e. MB) and right close, $^{\bullet}$OH radicals are formed and quickly oxidize the molecules adsorbed.

Preliminary reuse experiments have shown great results with no significant decrease on the catalyst effect after two reuse cycles.

Conclusions

Results showed that carbon nanostructures could be grown on the monoliths using catalytic chemical vapor deposition process with ethanol by impregnating the surface of the monolith with iron or cobalt salts. The materials produced with carbon nanostructures supported on the surface of cordierite monoliths were applied in the removal of organic contaminants (quinoline and methylene blue) in liquid systems via oxidation reactions. Reaction studies proved that the combined effect of the hydrophobic carbon nanostructures in adsorbing the organic contaminant with the metal core that is able to promote the oxidation of the adsorbed molecules via heterogeneous Fenton system is very interesting to remove important organic contaminants, such as methylene blue, a dye widely used by the textile industry, and quinoline, a N contaminant present in fuels. Moreover, the dimensions of cordierite monoliths used as support of carbon nanostructures allows the materials to be removed from the liquid phase very easily.

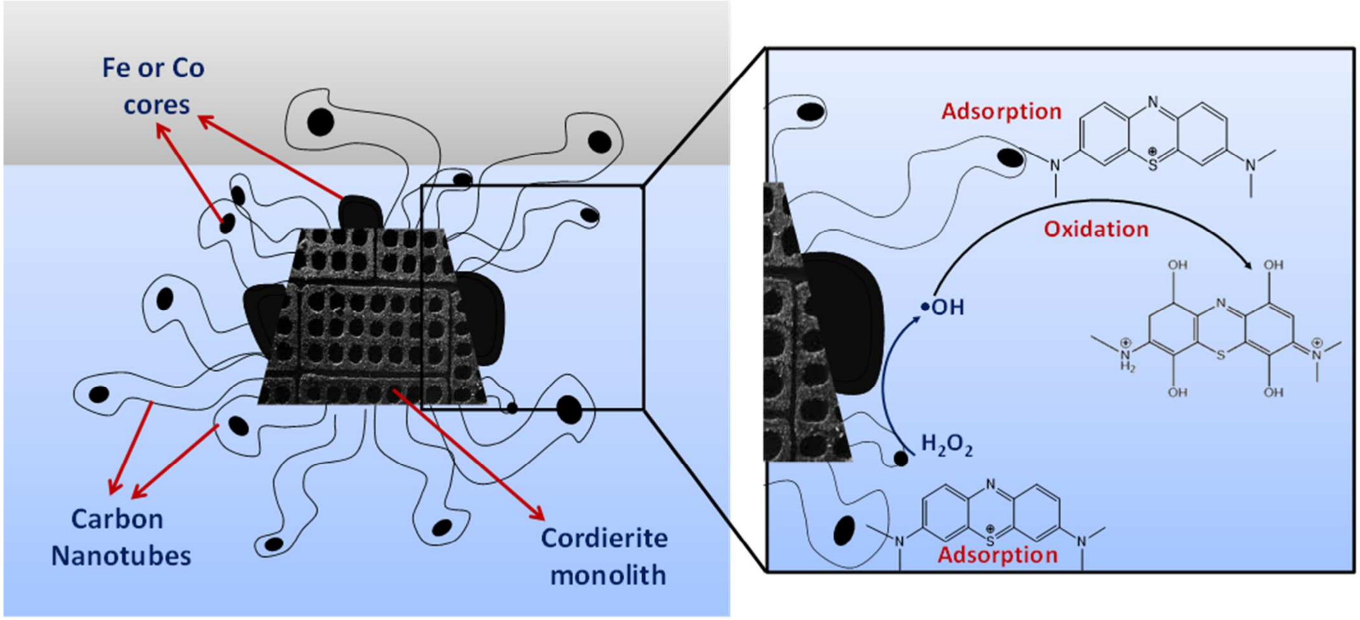

Figure 11 – Mechanism of the combined effect between CNTs and Co/Fe in Fenton-like reactions.

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Notes and references

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TABLE OF CONTENTS - GRAPHICAL ABSTRACT

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Carbon nanostructures are able to pre-concentrate organic contaminants by adsorption while metal cores catalyze the oxidation via heterogeneous Fenton-like mechanism.