## A more environmentally sustainable process to remove a wide range of endocrine disrupting chemicals from water
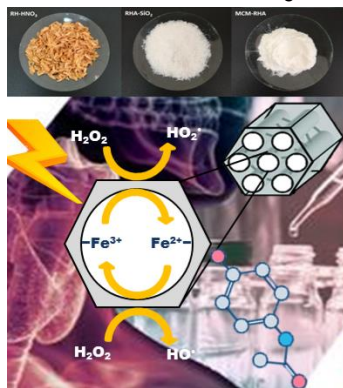
**T. Benzaquén**[1], P. Carraro[1], P. Ochoa Rodriguez[1], O. Alfano[2], G. Eimer[1]. (1) CITEQ, Maestro López y Cruz Roja Argentina, Córdoba, Argentina. tbenzaquen@frc.utn.edu.ar (2) INTEC, Ruta Nacional 168, Km. 0 - Paraje "El Pozo", 3000, Santa Fe, Argentina

Mesoporous materials of the type MCM-41 were synthesized using rice husk as precursor of silica. The MCM-41 support was then modified with Fe by the wet impregnation method. The synthetized catalysts were used as heterogeneous catalysts, in the degradation of different endocrine disruptors in aqueous medium, as herbicides (atrazine), compounds derived from the plastic industry (bisphenol A) and the pharmaceutical industry (acetaminophen), applying the photo-Fenton heterogeneous reaction $(Fe^{2+}/H_2O_2/UV-Vis)$.Thus, a stable, effective and sustainable solid was obtained which, at pH close to neutral consumed low amounts of oxidant and provided an efficient catalytic process to degrade recalcitrant organic molecules. Consequently, the heterogeneous Fenton reaction presented in this work appears as a promising pre-treatment capable to improve the biodegradability of waste water from different industry.

### Introduction

Endocrine disrupting compounds (EDCs) are contaminants with estrogenic or androgenic activity that negatively impact human and animal communities. The potential effects of these emergent contaminants in water are still uncertain and further investigation is needed to improve their efficient removal. Ordered mesoporous materials, such as MCM-41 support, are of great interest because of their well-ordered structure, large specific surface area, and their ability to interact with atoms, ions, and molecules not only on the surface but also inside the material [1]. In particular, their specific characteristics make them extremely suitable for use in the degradation of pollutants since they can allow good dispersion of the active phase, as well as easy access of bulky molecules to the active sites inside the pores [2]. The main silica precursors used in the synthesis of these materials are alkoxysilanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS). In the search for a safer, less costly and more environmentally friendly precursor, natural silica appears, especially those found in agricultural residues, which can provide an alternative source to replace commercial silica precursors. Among them, rice husks are one of the most common agricultural wastes with a global production of 600 million tons per year of rice, generating more than 100 million tons of husks [3].

On other hand, with the innovation of advanced oxidation processes (AOPs), there has been a consistent growing interest in this research field. Among the various AOPs, heterogeneous Fenton like process in combination with UV-vis light is highly ecient in wastewater treatment.

This study is to focus one such method within the AOPs, namely, heterogeneous Fenton and how it is used on the abatement of EDCs, such as, bisphenol A (BPA), atrazine (ATZ) and acetaminophen (ACE) in particular, using novel mesoporous materials synthesized with rice husk as silica precursor.

### Material and Methods

Mesoporous materials of the MCM-41 type were synthesized using rice husk as a silica precursor.

In a first stage, two previous washes of the rice husk were evaluated with water and nitric acid, obtaining silica with a high surface area for washing with acid. In order to extract the silica as sodium silicate, the resulting powder was stirred with sodium hydroxide (NaOH) aqueous solution. The resulting mixture was then centrifuged to separate supernatant and sediment. Finally, the supernatant was filtered. The silica obtained was labeled as $RHA-SiO_2$. The siliceous mesoporous material was synthesized by the hydrothermal treatment method using the silicate supernatant extracted from RHA as silica precursor and cetyltrimethylammonium bromide (CTAB) as template. MCM-41 support was then modified with Fe by the wet impregnation method. The materials were characterized structurally by X-ray diffraction (XRD) at low and high angle, texturally by adsorption-desorption of $N_2$ at 77 K, morphologically by scanning electron microscopy (SEM); and then by visible ultraviolet spectroscopy with diffuse reflectance (UV-Vis RD) and programmed thermal reduction (RTP) was inferred in the different Fe species and their interaction with the support (some of these results are not shown).

DEs degradations were performed in a multiple isothermal cylindrical batch reactors. The system

includes 4 pallets mechanical stirring to provide good mixing conditions and to ensure the adequate suspension of the catalyst in the reaction medium. The reactors were irradiated from the bottom with four tubular UV-Vis lamps (Philips Actinic BL TL-K 40W/10-R). Also, the experimental setup has a thermostatic bath connected to a temperature controller to keep the temperature constant during the reactions; and each reactor has an air diffuser device, a liquid sampling device, a thermometer and a pH control. Finally, the entire system was covered to obtain the darkness required in the Fenton reaction. Aliquots of the aqueous suspensions were collected to perform the following determinations: (i) BPA, ATZ or ACE concentration by HPLC; (ii) $H_2O_2$ by means of a modified iodimetric technique; (iii) ferrous ions and total iron with a standard spectrophotometric technique ($Fe^{2+}$-phenanthroline complex).

### Results and Discussion
*Characterization of the iron catalysts*

Table 1 summarizes the textural properties of the samples from the $N_2$ adsorption-desorption isotherms at 77 K. From the results obtained, it is possible observed that the wash with $HNO_3$ significantly improved the specific surface area compared to the water wash (216 $m^2/g$ and 27 $m^2/g$ respectively). The isotherm of the RHA-$SiO_2$-$HNO_3$ sample is shown in Figure 1.a). According to the IUPAC classification [4], the silica sample showed a type IV with a type H1 hysteresis. The pore size distribution of this sample was in range of about 15-65 Å.

$N_2$ adsorption–desorption isotherms with their corresponding pore size distribution of the MCM-RHA and Fe modified samples are shown in Figure 1.b. All the samples exhibited type IV isotherms,

typical of mesoporous structures, according to IUPAC [4], with a distinct inflection in the P/P0 range from 0.2 to 0.35, characteristic of a narrow step of capillary condensation inside the mesopores. This feature is agreement with the unimodal narrow pore size distribution, observed in Figure 1.b) (PSD). However, whereas the inflection is sharp for the MCM-41-RHA, giving account for the narrow pore size distribution, it becomes less pronounced with metal loading increasing, which indicates a bigger range in the distribution of the pore sizes (Dp) [5]. In addition, all the samples showed high specific surface (SBET) and pore volume (VTP), which are typical of mesoporous materials; nevertheless, a slight decrease in these values is observed with Fe loading increasing. Thus, it is possible to observe a small change in the pore size with the Fe loading, which is due to the increased presence of clusters and/or small particles of metal oxides finely dispersed inside the channels as well as large particles on the external surface.

The UV–Vis DRS spectra of the investigated samples are shown in Figure 2. Three bands are observed about 220–250, 300–380 and 450–550 nm. The first maximum at about 254 nm indicates that iron is linked to surface O atoms [2,6]. Thus, the second maximum at about 340 nm may be attributed to small oligonuclear iron oxide clusters (FeO)n or iron oxide nanoparticles of very small size [6]. Finally, the third maximum at about 500 nm can be assigned to larger iron oxide nanoparticles. It is known that the UV–Vis DR bands shift to shorter wavelengths when the iron species size decreases, indicating a quantum size effect. Therefore, the shifting of the UV band position observed to higher wavelengths with the Fe loading increased, suggests the presence of larger iron oxide clusters or nanoparticles.

**Table 1.** Textural properties of the synthesized samples

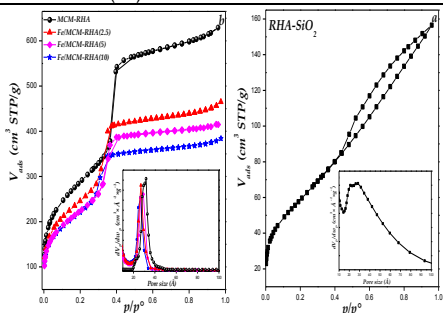| Sample | $S_{BET}$ $(m^2/g)$ | Dp (Å) | $V_{TP}$ $(cm^3/g)$ |
|---|---|---|---|
| RHA-$SiO_2$-$HNO_3$ | 216 | - | - |
| RHA-$SiO_2$-$H_2O$ | 27 | - | - |
| MCM-RHA | 1019 | 30 | 0.99 |
| Fe/MCM-RHA(2.5) | 930 | 28 | 0.74 |
| Fe/MCM-RHA(5) | 877 | 29 | 0.66 |
| Fe/MCM-RHA(10) | 843 | 28 | 0.66 |



**Figure 1.** $N_2$ adsorption–desorption isotherms of (a) RHA-$SiO_2$ and (b) synthesized samples. Inset: Pore size distribution (PSD)
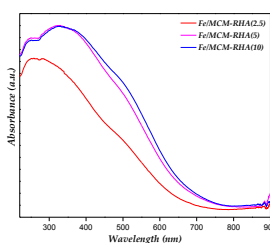


**Figure 2.** DRUV–vis spectra of synthesized samples with different Fe contents

*Catalytic evaluation of materials*

The catalytic performance for three different iron modified MCM-41 RHA solids were tested for the heterogeneous Fenton processes applied in the ATZ, BPA and ACE degradations. Before testing the catalytic activity, a series of preliminary tests were carried out (results not shown) in order to obtain the optimal reactions conditions, which maximize the degradation of contaminants and minimize the possible leaching of iron. Each

2

reaction was started by agitating the catalyst suspended in an aqueous solution of the DEs for 60 min to reach the adsorption/desorption equilibrium. In all cases, adsorption of less than 10% was observed in the solid catalysts (results not shown).

Figures 3(a), 3(b) and 3(c) show the ATZ, BPA and ACE degradation as a function of time for the different synthesized catalysts, respectively. The following reaction conditions were kept constant in the different tests (pH=5.5; $C^0_{CAT}$=1000 mg L$^{-1}$ and $C^0_{H2O2}$=95 mg L$^{-1}$, at 25 °C) in order to compare the synthesized materials and the behavior of the different pollutants. As can be seen in these figures, depending on the dispersion and size of the different iron species, the nanocomposites showed different catalytic behaviors. The catalysts with the highest metal loads showed a significant decrease in catalytic activity for all pollutants evaluated. When the Fe content was 2.5 % w/w (Fe/MCM-RHA (2.5)), the degradation of all contaminants reached its maximum value. Based on these results, as can be seen, BPA was the contaminant that reached the highest degree of degradation in 120 min. As noted above, samples with high iron loads showed a higher presence of larger iron oxide nanoparticles. These species may be blocking some sites responsible for catalyst activity. Thus, in the sample with the lowest Fe content, the active metal species would be finely dispersed in the silica structure and active for degradation.

In addition, experimental studies of iron leaching from catalyst at the end of the reaction were performed. The results obtained showed values lower than 0.8 ppm, therefore, the Fe was efficiently retained on the mesoporous surface. On the other hand, the solid can be re-used even after three cycles without loss of activity.

Thus, this mesostructure with a large specific surface and pore volume, contributes to a high accessibility and diffusion of the reactant molecules to the active sites, allowing a greater interaction between these and mesoporous structure, as well as an exploitation of the incident radiation.
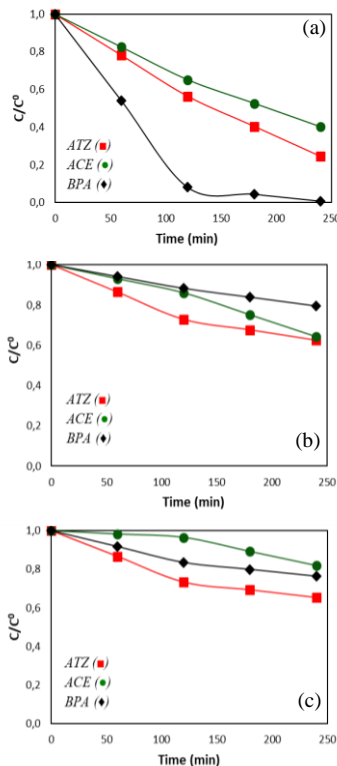


**Figure 3.** ATZ, BPA and ACE relative degradation (%) as a function of time for (a) Fe/MCM-RHA (2.5), (b) Fe/MCM-RHA (5) and (c) Fe/MCM-RHA (10).

## Conclusions

MCM-41 mesoporous silicates were synthesized using rice husks as silica precursors and modified with different Fe contents by the wet impregnation method. This appears as an effective, simple, low-cost and environmentally friendly synthesis method. All materials exhibited high specific surface, pore volume and good structural regularity, indicating that the structure was preserved after metal incorporation. These mesostructured materials have been successfully tested in the photo-Fenton heterogeneous degradation of different endocrine disruptors, such as, atrazine, bisphenol A and acetaminophen in water. The results showed that the catalyst with the lowest iron loading (2.5 %p/p of Fe) presented the highest degradation of contaminants, probably due to the presence of Fe active species, highly dispersed and interacting with the support surface. The sustainable catalysts were easily recovered and successfully reused consumed low amounts of oxidant. In all cases, the iron leaching was low and presented very good results at a neutral pH.

*References*
[1] D.Feng, Y.Feng, L. Qiu, P.Li, Y.Zang, H.Zou, Z.Yu, X. Zhang.Renewable and Sustainable Energy Reviews 109 (2019) 578.
[2] T.B.Benzaquén, N.I. Cuello, O.M. Alfano, G.A. Eimer Catalysis Today 296, (2017)51.
[3] Álvarez J., López G., Amutio M., Bilbao J., Olazar M.. Bioresource Technology 170, (2014)132.
[4] Everett D.H. (1971). Manual of symbols and terminology for physicochemical quantities and units-Appendix II. Part I. IUPAC.
[5] P.M.Carraro, V.R.Elías, A.A.García Blanco, K.Sapag, S.Moreno, M.I. Oliva, G.A. Eimer (2014). Mesopor. Mater. 191, 103.
[6] N.I.Cuello, V.R.Elías, C.E.Rodriguez Torres, M.E.Crivello, M.I.Oliva, G.A. Eimer. Micropor. Mesopor. Mater.203, (2015) 106.