

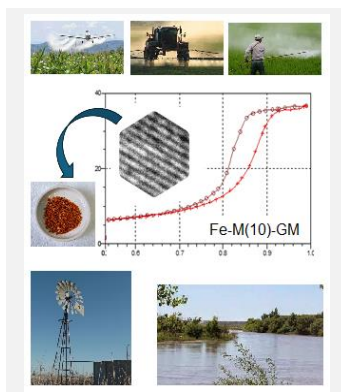
Sustainable catalysts: degradation of glyphosate in contaminated aqueous environments at room conditions

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E. Vaschetto¹, P. Ochoa Rodríguez¹, G. Eimer¹. (1) Centro de Investigación y Tecnología Química (CITEQ-UTN-CONICET), Facultad Regional Córdoba, Maestro López y Cruz Roja Argentina, 5016, Córdoba, elivaschetto@hotmail.com



Nano-structured catalysts with different Fe contents were achieved from biomass-derived renewable molding agents (glycerol and/or glyceryl monostearate) and prepared by direct hydrothermal synthesis. All the materials were characterized by XRD, N₂ adsorption, TEM, ICP-OES and UVvis-DR. The methodology of the synthesis of solids was fundamental for the development of the mesoporous structure as well as the dispersion of Fe species. By using these solids as heterogeneous catalysts in the wet oxidation reaction of the herbicide glyphosate with air at atmospheric pressure and room temperature, herbicide degradation / fragmentation levels of around 80% with 100% selectivity were reached. Thus, an advanced technology with low environmental impact for the treatment of contaminated water, which adds sustainability to the chemical industry from the use of renewable raw derived catalysts has been developed.

Introduction

In recent years there have been great advances in the field of chemistry, like the synthesis of many new substances, including fertilizers and pesticides. However, the development of this industry presents great contradictions for the environment. One of the main environmental contaminants is the herbicide: glyphosate (C₃H₈NO₅P). The most important factors in the transport of the herbicides towards natural water bodies are aerial dispersion by winds, volatilization and dragging by rainwater and irrigation. In this context, Advanced Oxidation Processes are proposed as a degradation alternative for this type of compounds in aqueous media. It has been shown that the addition of a solid catalyst to the system can promote the formation of radicals on the surface, speed up the reaction rate and improve the efficiency, drastically reducing the severity of the operating conditions [1]. In this context we propose to synthesize mesoporous silicas from renewable molding agents to be used as heterogeneous catalysts iron modified catalysts. This work deals with the use of oleochemical industry derived glycerol and glyceryl monostearate as porogens cheap and highly available from the production of biodiesel [2]. In addition, these have advantages, such as: easy removal, tendency to produce structures with thicker walls and smaller particle size solids, which would improve the porosity and stability of the material. These characteristics make them interesting for use in the synthesis of mesoporous silicas with possible industrial applications. Thus, it is proposed to develop these solids to efficiently degrade aqueous solutions of glyphosate under atmospheric pressure and room temperature conditions through wet air oxidation. By this way, the interesting results achieved in this work

allow us to propose a more sustainable advanced technology for the treatment of water contaminated with herbicides.

Material and Methods

The catalysts were synthesized by direct incorporation of the metal in the synthesis gel. Tetraethoxysilane was used as Si source, glycerol (G) or glyceryl monostearate (GM) as porogen agent, and ethanol as solvent. Hydrochloric acid (2M) was used as a pH regulator (pH=2), sodium fluoride to start the silica condensation reaction and ferric chloride as source of Fe. The synthesis procedure involves an initial stage where a solution of the porogen in ethanol with another solution of TEOS and HCl are mixed under magnetic stirring at 60°C. In a second stage, the condensation of the silica is carried out by adding the NaF salt at 60°C. Then, the necessary amount of Ferric chloride to reach a nominal molar ratio Si/Fe=10, 20 or 40 is incorporated, keeping the agitation for 3h at 60°C. The solids were identified as Fe-M(x)-G or Fe-M(x)-GM where "x" is the Si/Fe initial molar ratio. The pure matrices were synthesized for comparison.

Results and Discussion

The small-angle X-ray diffraction patterns of the catalysts synthesized showed in all cases a characteristic pattern of mesoporous materials [3]. The adsorption-desorption isotherms of representative samples, can be classified as IV type with pore diameters of the order of 8-9.7 nm being characteristic of mesoporous structures [3]. According to the results obtained by TEM, the materials presented a defined mesoporous structure, exhibiting zones whose ordering is characteristic of a hexagonal pore arrangement, with

the presence of straight mesochannels arraying along the long axis [3]. It should be remarked that both renewable porogens derived from biomass allow achieving a mesoporous structure. The UV-vis DR spectroscopy was applied to infer about the nature of iron species grown in mesoporous silicates modified with different Fe loadings. In all of the spectra, characteristic bands of the different iron species are observed [3]. It is important to note that the absorption capacity of the solids presented in this work is consistent with the metal content. Thus, the materials with higher loadings present more intense signals throughout the range of wavelengths; moreover an increase in absorbance is observed at longer wavelengths with higher Fe content. This feature is accounting for the increased formation of Fe⁺³ species in extraframework positions such as larger size iron oxide cluster and/or nanoparticles. (figures not shown).

The materials synthesized were catalytically evaluated in the glyphosate degradation reaction (Table 1). The catalysts with the highest Fe content led to the greatest degradation of the herbicide, of the order of 80% and 55% (after 15 min of reaction) for the solids synthesized using GM and G, respectively. Under conditions of atmospheric pressure and room temperature, the fragmentation

of the herbicide towards the ions: acetate, nitrate, nitrite and phosphate (characterized by ionic liquid chromatography) was achieved. The pure siliceous matrices did not show degradation of the herbicide, evidencing that the activity of the solids is referred to the presence of Fe. Glyphosate is known to form stable complexes with metallic cations [4]. As it was proposed by us elsewhere [3] (in accordance with Sheldon and Kochi [5]) Fe-glyphosate complex formed on the solid can activate molecular oxygen and, with the contribution of protons of the reaction medium, generate an active oxoiron(V) intermediate. From this, the mechanism of oxygen transfer to the substrate (glyphosate adsorbed) could be started, leading to its fragmentation and further desorption of the degradation products [3]. In this way, Fe cations in the mesoporous silica structure can act efficiently as metal centres responsible of glyphosate complex formation and beginning of oxygen transfer to substrate. Their increased presence in the synthesized catalysts with highest Fe loadings would be justifying the higher activity for Fe-M(10)-GM and Fe-M(10)-G solids (Table 1). Thus, the degradation values obtained here are very relevant, considering the importance of the use of renewable raw materials in the sustainability and economy of the processes.

Table 1. Physicochemical properties of the synthesized solids and glyphosate degradation values.

Sample	Fe content (wt%) ^a	Area (m ² /g)	Glyphosate degradation (%) ^b	Product selectivity (%)
Fe-M(40)-GM	1.69	245	63	100
Fe-M(20)-GM	2.66	265	68.92	100
Fe-M(10)-GM	4.41	323	78.85	100
Fe-M(40)-G	1.51	315	44.69	100
Fe-M(20)-G	2.71	366	51.50	100
Fe-M(10)-G	4.39	407	54.91	100

^a By ICP

^b By ionic liquid chromatography (time on stream: TOS=15 min)

Conclusions

Fe modified mesoporous materials were successfully synthesized from renewable raw material, glycerol and glyceryl monostearate. The materials were catalytically evaluated in the glyphosate degradation through wet oxidation reaction with air. The best result (around 80% of glyphosate degradation) was obtained by using a solid prepared by with molar ratio Si/Fe=10, using GM as porogen. Thus, material engineering applied to the development of advanced remediation technologies allowed the degradation of a pollutant of great global concern as glyphosate under room reaction conditions.

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