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SUPPLEMENTARY MATERIAL TO

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

SORAYA GARÓFALO-VILLALTA[1], TANYA MEDINA-ESPINOSA[1], CHRISTIAN SANDOVAL-PAUKER[1], WILLIAM VILLACIS[1], VALERIAN CIOBOTĂ[2], FLORINELLA MUÑOZ BISESTI[1] and PAUL VARGAS JENTZSCH[1]*

[1]*Departamento de Ciencias Nucleares, Facultad de Ingeniería Química y Agroindustria, Escuela Politécnica Nacional, Ladrón de Guevara E11-253, 170525 Quito, Ecuador and* [2]*Rigaku Analytical Devices, Inc. 30 Upton Drive, Suite 2, Wilmington, MA 01887, USA*

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Fig. S-1. Photograph of the experimental setup for the sono-Fenton experiments.

* Corresponding author. E-mail: paul.vargas@epn.edu.ec

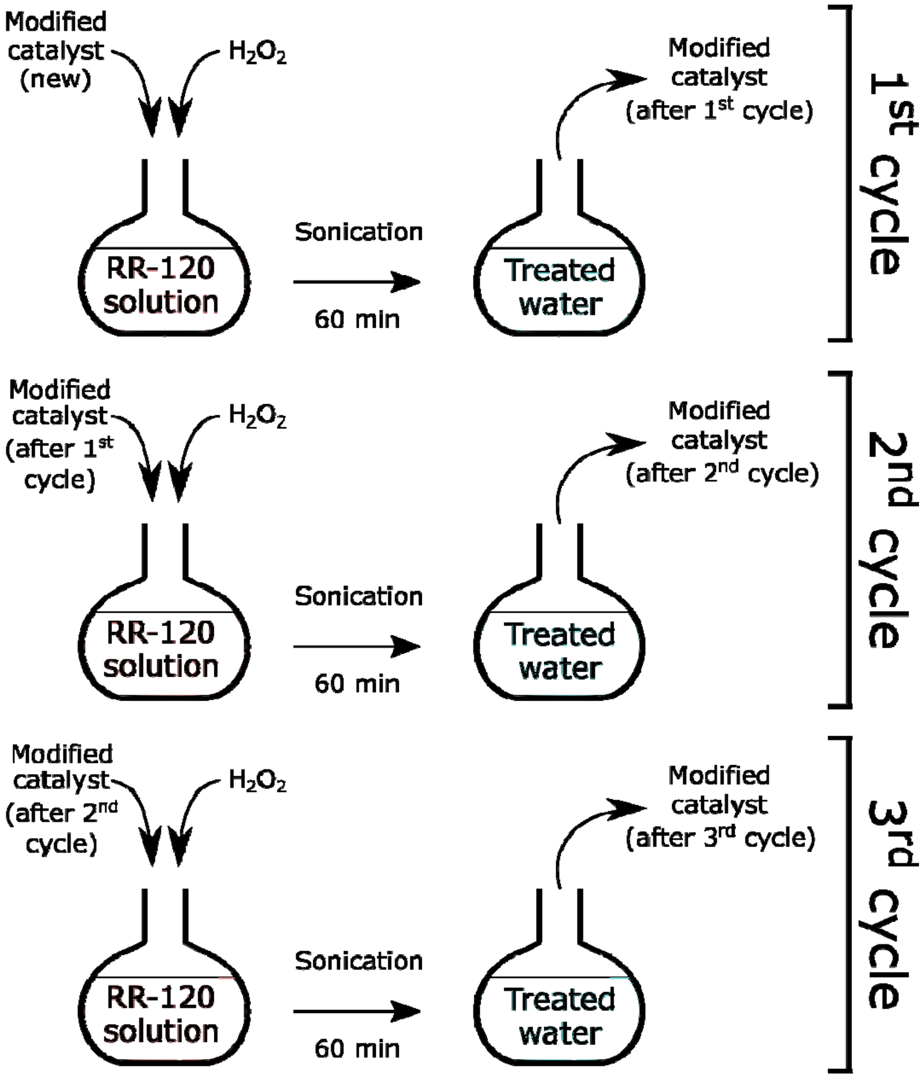

Fig. S-2. Scheme of the reuse tests of the modified catalysts.

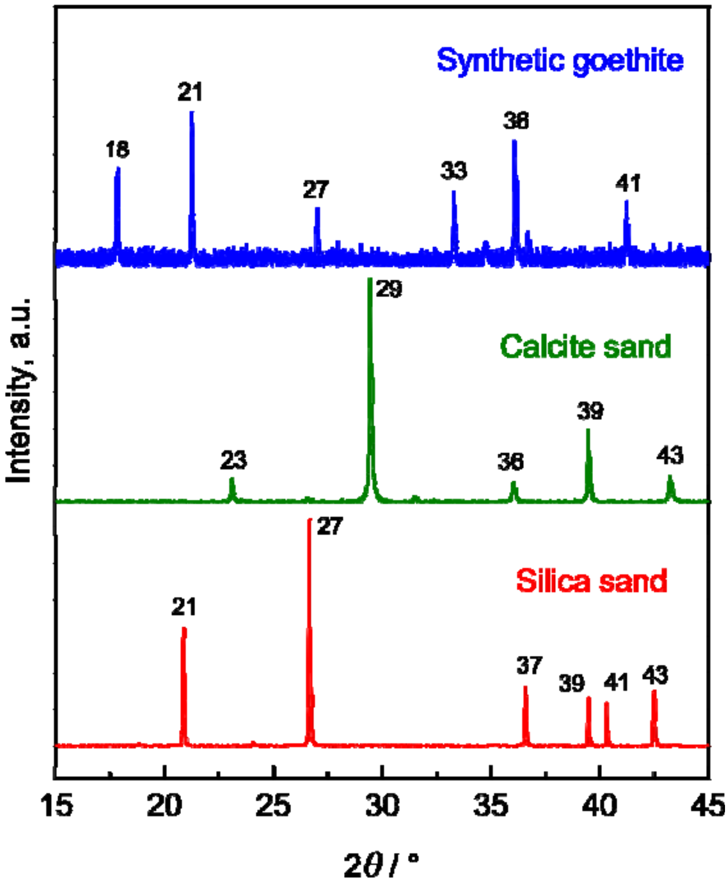

Fig. S-3. Powder XRD diffractograms of synthetic goethite, calcite sand and silica sand.

Fig. S-4. Photograph of synthetic goethite, the sands (silica and calcite) and the modified catalysts (GS and GC).

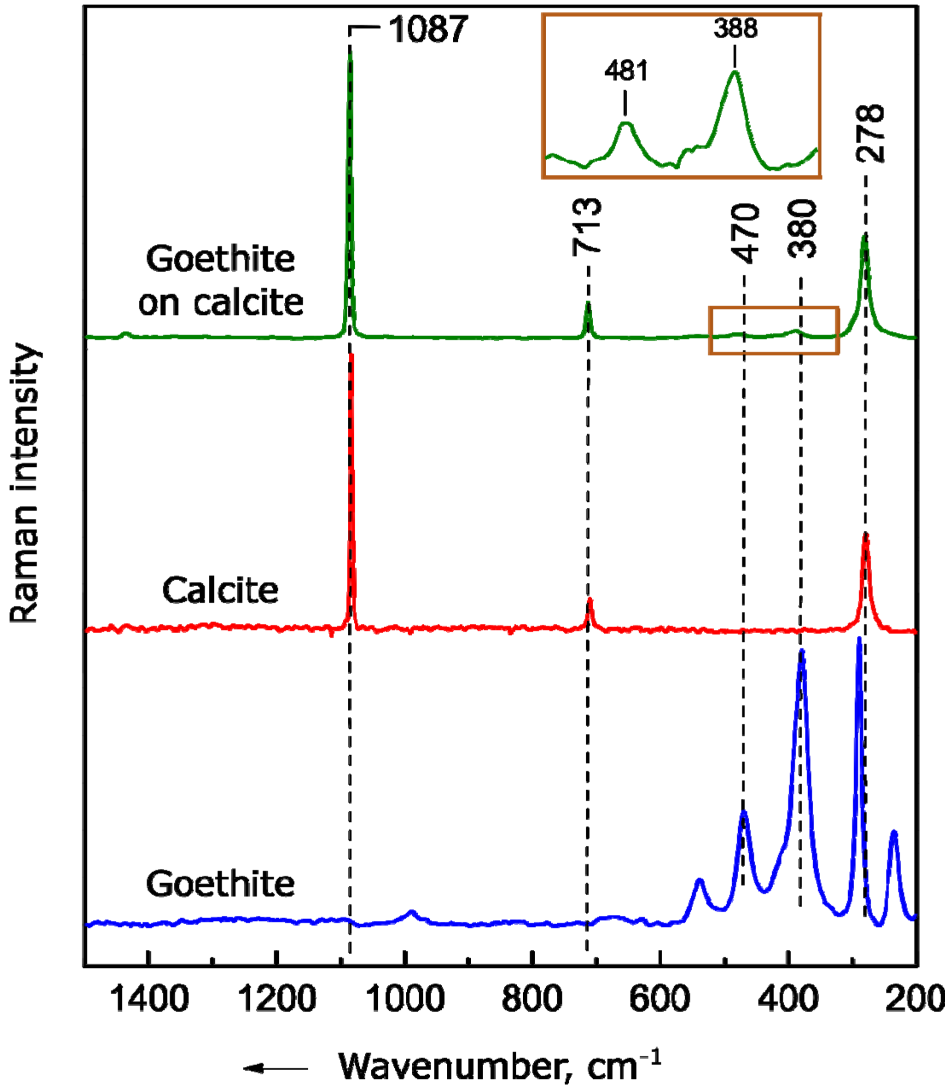

Fig. S-5. Raman spectra of the synthetic goethite, calcite sand and the modified catalyst GC (goethite deposited onto calcite sand). The box at the top shows a zoom of the Raman spectrum of the modified catalyst GC in which two weak bands attributable to goethite are visible.

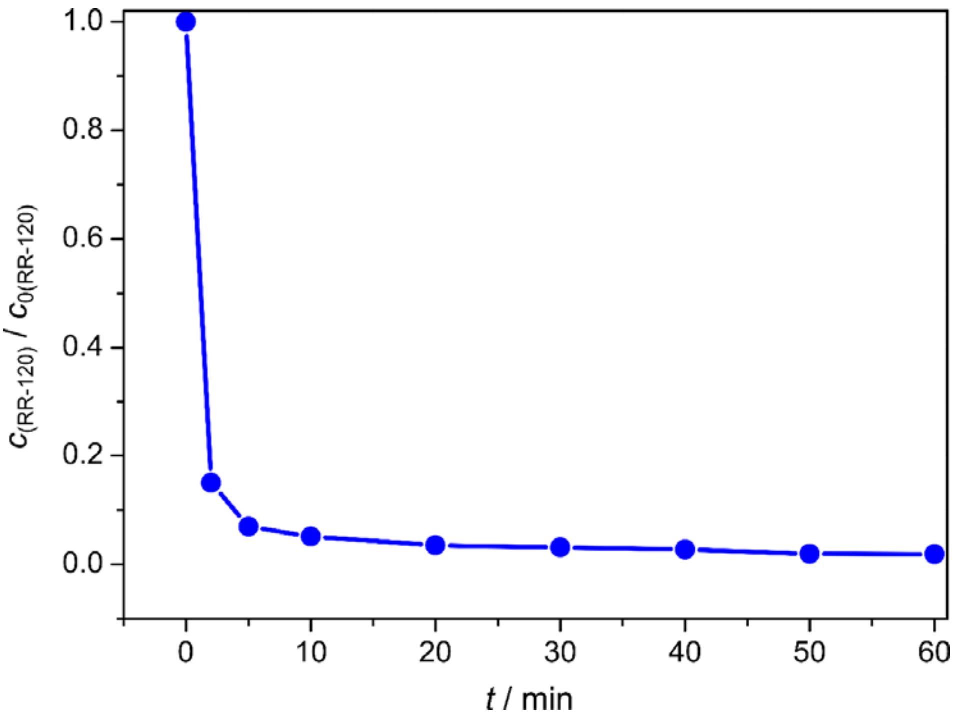

Fig. S-6. RR-120 degradation curve in the homogeneous sono-Fenton process under the best conditions ($H_2O_2/FeSO_4\cdot 7H_2O$ ratio of 17.7 mM/0.2 g L^{-1}, sonic wave amplitude of 100 µm and ultrasonic intensity of 65 W cm^{-2}).

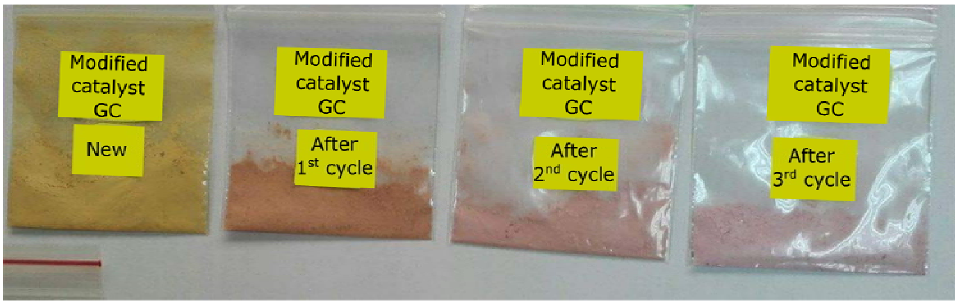

Fig. S-7. Photo of the modified catalysts GC new and after its use for the 1st, 2nd and 3rd cycle. Note the reddish coloration of the modified catalyst after the 1st cycle that decreases for the modified catalysts after the 2nd and 3rd cycles.

ADSORPTION ISOTHERMS

Adsorption tests of RR-120 onto sands and modified catalysts were performed. 250 mL of RR-120 solution was equilibrated with 1.95 g of the solid material (sands or modified catalysts) and the concentration of the resulting solution was measured by UV–Vis spectrophotometry. Six RR-120 solutions with concentrations in the range 40–140 mg L^{-1} at pH 3.0, were used in the tests. Considering the initial concentration of the solution and the equilibrium concentration of the solution for each case, the amounts of RR-120 adsorbed onto the solid were calculated. The adsorption data were adjusted to the Langmuir and Freundlich models in their linear forms that are presented in Eqs. (S-1) and (S-2):

$$\frac{c_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} c_e \quad \text{(S-1)}$$

$$\log q_e = \frac{1}{n} \log c_e + \log K_F \quad \text{(S-2)}$$

where c_e is the equilibrium concentration of the solution (mg L^{-1}), q_e is the amount of RR-120 adsorbed onto the solid (mg g^{-1}), q_{max} is maximum amount of RR-120 that could be adsorbed onto the solid (mg g^{-1}) K_L is the Langmuir constant (L mg^{-1}) and K_F (L mg^{-1}) and n are constants of the Freundlich isotherm.

The degradation of RR-120 (or any other pollutant) in heterogeneous (sono-)-Fenton processes requires the approach of the pollutant to the surface of the catalyst. Moreover, some authors suggest that the adsorption of the pollutant on the surface of the catalyst has a positive effect on the treatment.[1]

In order to evaluate the influence of adsorption of RR-120 in the degradation of this dye by heterogeneous (sono-)Fenton processes, adsorption isotherms for the sands and the modified catalysts were obtained. It was established that the equilibrium time for the adsorption of RR-120 on the modified catalysts was 60 min and this contact time was applied to equilibrate the adsorbent (sands and modified catalysts) with RR-120 solutions. The adsorption data were fitted to Langmuir and Freundlich models, and their parameters are detailed in Table S-I. These results show that the adsorption of the RR-120 dye had a better fit to the Langmuir model for all cases. In addition, based on the maximum amount that could be adsorbed (q_{max}), it is possible to say that the modified catalysts showed a greater adsorption capacity of RR-120 compared to the sands. Therefore, the contribution of goethite in the increase of the adsorption capacity of RR-120 is evidenced, which could be explained in terms of its specific surface area (the specific surface area of goethite is higher than those of silica and calcite sands).

Another important factor that must be considered in adsorption studies is the pH value of the solution; Demarchi, Campos and Rodrigues[2] in their study of adsorption of RR-120 on iron(III) doped chitosan concluded that the adsorption depends on the pH value of the solution. This is because the pH value affects the surface charge of the solid material and the ionization of the pollutants.[3] In this work, a pH value of 3.0 was used, which is lower than the point of zero charge of synthetic goethite (pH_{pzc} between 7.9 and 9.4) and calcite (pH_{pzc} between 8.0 and 10.8), and higher than the point of zero charge of SiO_2 ($pH_{pzc} \leq 2$).[4] Therefore, at a pH value of 3.0, goethite and calcite are positively charged, while silica sand acquires a negative charge. The dye in the aqueous medium was negatively charged due to the proton released from the sulfonate group. Consequently, goethite and calcite form an ionic bond by electrostatic attraction with the sulfonate group of the dye, whereas silica sand tends to repel the dye, which could also explain its low adsorption capacity.[5]

TABLE S-I. Langmuir and Freundlich parameters for the adsorption of RR-120 on sands and the modified catalysts

Material	Langmuir model			Freundlich model		
	R^2	K_L / L mg^{-1}	q_{max} / mg g^{-1}	R^2	K_F / L mg^{-1}	n
GS	0.9698	0.0249	2.0442	0.9604	0.2816	2.8176
Silica sand	0.9973	0.0569	0.8637	0.9590	0.2748	4.7059
GC	0.9902	0.0195	3.2765	0.9870	0.2724	2.2232
Calcite sand	0.9914	0.0252	1.9833	0.9542	0.2300	2.5310

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