

# Eggshell-supported Catalysts for the Advanced Oxidation Treatment of Humic Acid Polluted Wastewaters

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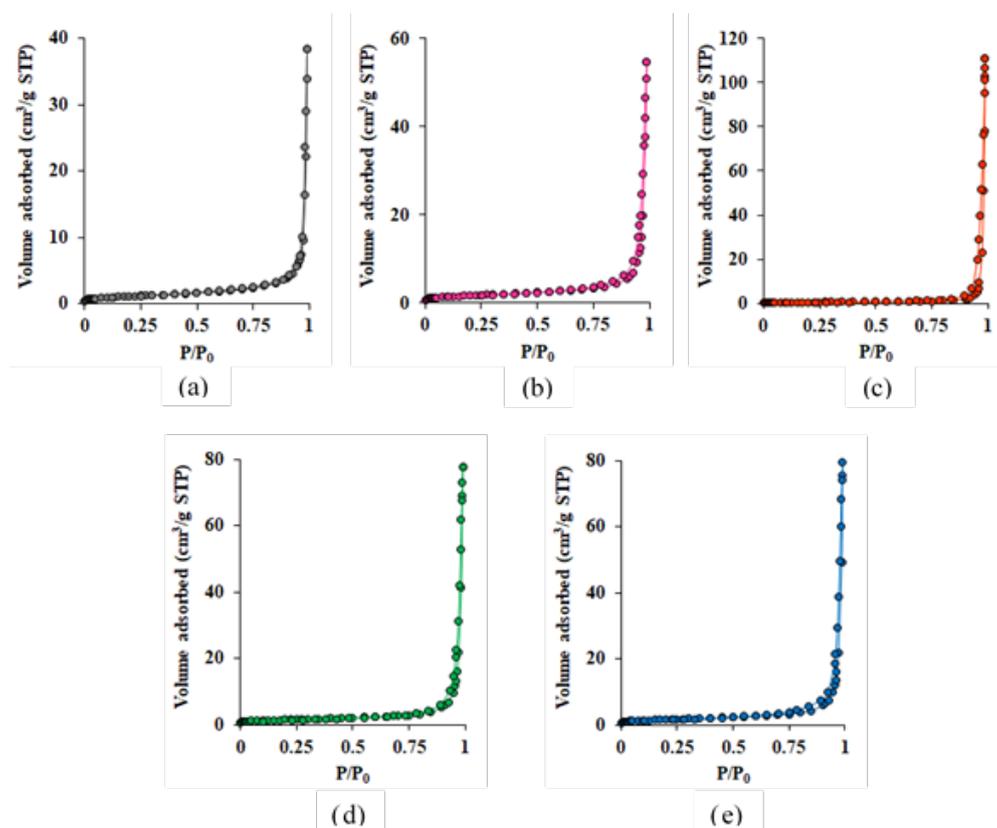
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**1. Instrumental parameters for the determination of the iron and copper content in the aqueous solution after WO treatment by ICP-MS (Table S1).**

**Table S1.** Instrumental parameters for ICP-MS.

Inductively Coupled Plasma		Mass Spectrometer	
RF power (W)	1550	Sampling cone	Nickel
Carrier gas (L/min)	1.07	Skimmer cone	Nickel
Plasma gas (L/min)	15	Peak pattern	1 point
Auxiliary gas (L/min)	0.9	Replicates	3
Sample depth (mm)	10	Sweeps/Replicate	100
Solution uptake rate (mL/min)	0.1	Integration time/Mass	0.2 s
Nebulizer	MicroMist	Analytical masses	$^{56}\text{Fe}$ , $^{63}\text{Cu}$ and $^{45}\text{Sc}$

**2. N<sub>2</sub> adsorption-desorption isotherms of the calcined eggshell and the iron and copper supported catalysts (Figure S1).**



**Figure S1.** Nitrogen adsorption-desorption isotherms at 77 K: (a) calcined eggshell, (b) Fe 5%, (c) Fe 15%, (d) Cu 5% and (e) Cu 15%.

### 3. Textural properties of the calcined eggshell and the iron and copper supported catalysts (Table S2).

**Table S2.** Textural properties of the calcined eggshell and the iron and copper supported catalysts determined by N<sub>2</sub> adsorption-desorption at 77 K.

Sample	BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Average pore diameter (nm)
Eggshell	4	0.059	50.8
Fe 5%	6	0.138	49.3
Fe 15%	2	0.071	77.5
Cu 5%	5	0.120	65.1
Cu 15%	6	0.129	65.6

### 4. Concentration of iron and copper in the samples collected at 15, 180 and 360 min of WO measured by ICP-MS (Table S3).

**Table S3.** Concentration of iron and copper in the aqueous solutions after the WO treatment of HA solution.

Sample <sup>a</sup>	WO of HA solution with Fe 5%			WO of HA solution with Fe 15%		
	Fe (µg/L)	SD <sup>b</sup>	%RSD <sup>c</sup>	Fe (µg/L)	SD <sup>a</sup>	%RSD <sup>b</sup>
15 min	1.30	0.02	1.7	9.2	0.6	6.1
180 min	2.50	0.07	2.9	10.6	0.7	6.5
360 min	9.6	0.4	3.7	145.0	1.0	0.7
Sample <sup>a</sup>	WO of HA solution with Cu 5%			WO of HA solution with Cu 15%		
	Cu (µg/L)	SD <sup>b</sup>	%RSD <sup>c</sup>	Cu (µg/L)	SD <sup>a</sup>	%RSD <sup>b</sup>
15 min	14.2	0.2	1.5	38.8	1.0	0.3
180 min	273.3	3.3	1.2	377.5	3.8	1.0
360 min	327.7	3.6	1.1	445.9	3.1	0.7

<sup>a</sup> Time at which samples were collected; <sup>b</sup> Standard deviation; <sup>c</sup> Relative standard deviation.

### 5. Chemical composition in weight percentage of the used catalysts measured by XRF (Table S4).

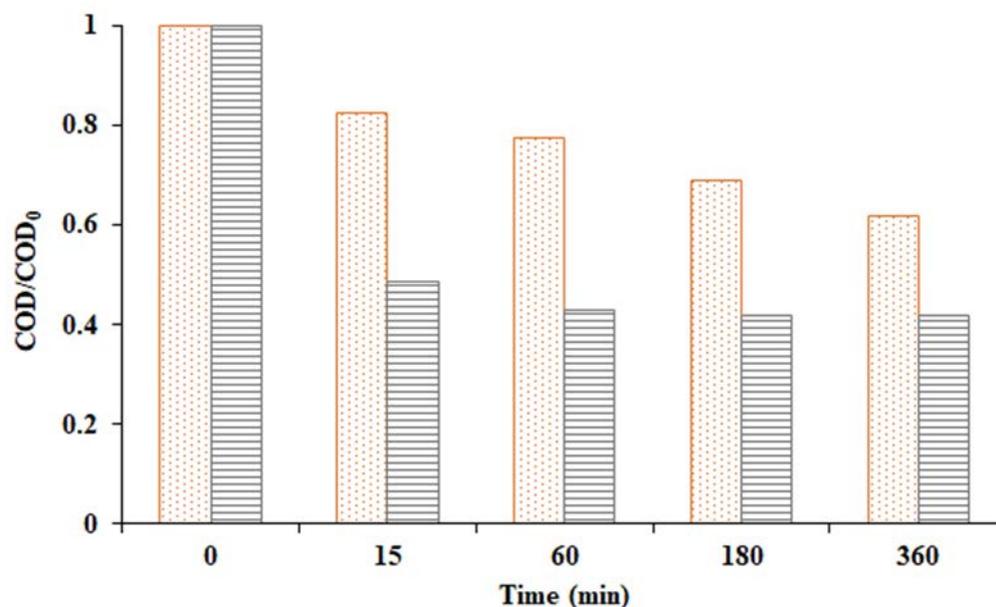
**Table S4.** Chemical composition in weight percentage of the used catalysts measured by XRF.

Element	Fe 5%	Fe 15%	Cu 5%	Cu 15%
Ca	92.90 ± 0.05	83.77 ± 0.04	93.35 ± 0.06	83.80 ± 0.02
Mg	0.86 ± 0.02	0.67 ± 0.04	0.89 ± 0.02	0.69 ± 0.01
Na	0.34 ± 0.03	0.24 ± 0.03	0.31 ± 0.03	0.29 ± 0.04
P	0.26 ± 0.02	0.25 ± 0.02	0.24 ± 0.02	0.26 ± 0.04
K	0.06 ± 0.02	0.06 ± 0.01	0.05 ± 0.01	0.05 ± 0.02

Fe	$5.41 \pm 0.02$	$14.94 \pm 0.04$	n.d.*	n.d.*
Cu	n.d.*	n.d.*	$5.10 \pm 0.04$	$14.84 \pm 0.06$

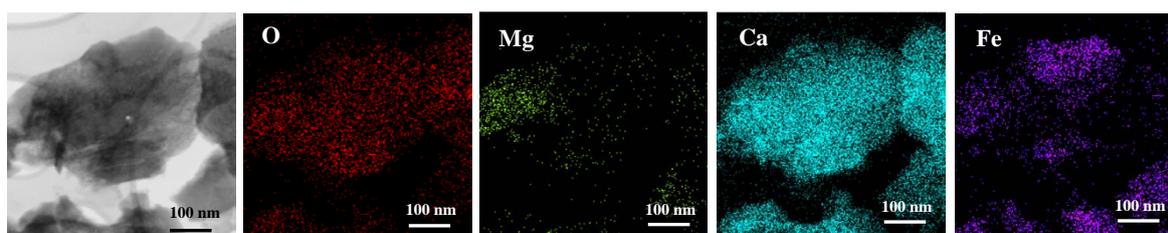
\*n.d.: not detected

### 6. Influence of a high pH value on the removal of HA using pure CaO (Figure S2).

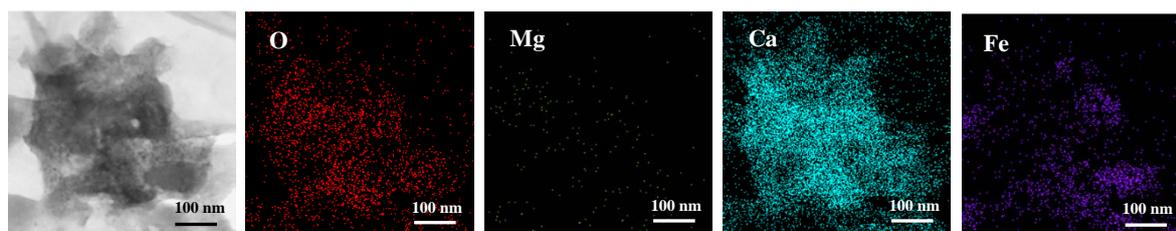


**Figure S2.** Evolution of COD concentration with time in presence of pure CaO at pH 12 (spotted area) and at pH 7.5 (horizontal lines). In all cases,  $T = 150\text{ }^{\circ}\text{C}$ ,  $P = 40\text{ bar}$ , initial COD concentration = 367 ppm and catalyst concentration = 1 g/L.

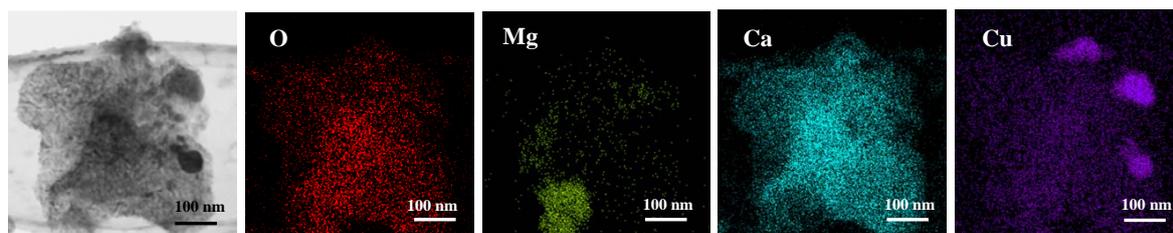
### 7. HAADF-STEM analysis of the iron and copper supported catalysts (Figure S3, S4, S5 and S6).



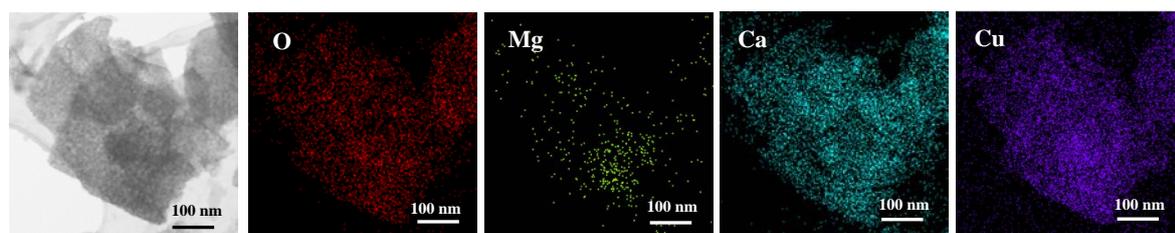
**Figure S3.** HAADF-STEM micrograph of Fe 5% and the elemental mapping of O, Mg, Ca and Fe.



**Figure S4.** HAADF-STEM micrograph of Fe 15% and the elemental mapping of O, Mg, Ca and Fe.



**Figure S5.** HAADF-STEM micrographs of Cu 5% and the elemental mapping of O, Mg, Ca and Cu.



**Figure S6.** HAADF-STEM micrographs of Cu 15% and the elemental mapping of O, Mg, Ca and Cu.