

Supplementary Materials: Chloroperoxidase-Mediated Halogenation of Selected Pharmaceutical Micropollutants

Table S1. Partial physicochemical characterization of treated water from municipal treatment plant from Puebla State.

Parameter	Value (mg/L)
Fe+2	0.178
SO4-2	90
P	14.4
P2O5	31
PO43	40.2
NO3-N	24
NO3	104
Free chloride	0.1 mg/l
Mg+2	10
Ca+2	145
BOD5	2.05
COD	651.38
Conductivity	1448 μ s/cm
pH	7.0

Table S2. Oxidation products of the CPO enzymatic oxidation

Compound	[M+H] ⁺ ó [M+Na] ⁺	Error (ppm)	mSigma	Formula	Abundance (%)
Ketoconazole	531.1536	-4.6	12.6	C ₂₆ H ₂₉ Cl ₂ N ₄ O ₄	1.75
+1Cl	565.1140	-5.4	27.5	C ₂₆ H ₂₈ Cl ₃ N ₄ O ₄	1.13
+2Cl	599.0754	-4.5	26.6	C ₂₆ H ₂₇ Cl ₄ N ₄ O ₄	1.28
Fragment	329.0460	-1.7	22.2	C ₁₄ H ₁₅ Cl ₂ N ₂ O ₃	14.13
Fragment	371.0563	-0.8	26.0	C ₁₆ H ₁₇ Cl ₂ N ₂ O ₄	7.17
Ketorolac	256.0949	7.7	8.4	C ₁₅ H ₁₄ NO ₃	0.70
Fragment	185.1107	11.6	6.3	C ₁₁ H ₇ NO ₂	1.28
Fragment	130.1519	7.2	7.9	C ₉ H ₆ O	85.23
Diclofenac *	296.0232	2.6	1.3		
+ OH	311.1697	-----	-----	C ₁₄ H ₁₂ Cl ₂ NO ₂	
+2OH	327.9714			-----	-----
+2O	325.1855				
Tetracycline	445.1620	-2.7	23.6	C ₂₂ H ₂₅ N ₂ O ₈	1.62
Ox	461.1566	-2.5	11.51	C ₂₂ H ₂₅ N ₂ O ₉	0.67
+2Cl	495.9795	84.1	285.0	C ₂₂ H ₂₁ Cl ₂ N ₂ O ₇	0.37
Sulfamethoxazole	254.06001	2.1	1.9	C ₁₀ H ₁₂ N ₃ O ₃ S	0.08
+2Cl, ring opening	323.1425	12.5	10.6	C ₁₀ H ₁₂ Cl ₂ N ₃ O ₃ S	8.65
+2Cl, fragment	309.1212	21.4	9.3	C ₉ H ₁₀ Cl ₂ N ₃ O ₃ S	8.55
+2Cl Fragment	293.1339	18.2	12.4	C ₉ H ₁₀ Cl ₂ N ₃ O ₂ S	8.93
Sodium Naproxen	231.1129	-44.8	n.a.	C ₁₄ H ₁₅ O ₃	0.07
+Na	253.0841	2.1	22.1	C ₁₄ H ₁₄ O ₃ +Na	0.54
+2 O	217.1047	-86.1	32.2	C ₁₃ H ₁₃ O ₃	5.39
+2 O and decarboxilation	261.1310	-89.6	35.8	C ₁₄ H ₁₃ O ₅	5.93

17 -Estradiol **	416	-----	-----	C ₂₄ H ₄₀ O ₂ Si ₂	-----
+1Cl	450	-----	-----	C ₂₄ H ₃₉ ClO ₂ Si ₂	-----
+2Cl	484	-----	-----	C ₂₄ H ₃₈ Cl ₂ O ₂ Si ₂	-----
Trazodone	372.1468	31.5	75.6	C ₁₉ H ₂₃ ClN ₅ O	0.12
+ Cl	406.1070	-30.9	25.3	C ₁₉ H ₂₂ Cl ₂ N ₅ O	27.34
+ 2Cl	440.0806	-30.3	30.8	C ₁₉ H ₂₁ Cl ₃ N ₅ O	16.94

* From reference [26], **From reference [27]. Error [ppm]: Absolute value of the deviation between measured mass and theoretical mass of the selected peak in [ppm]. mSigma: Combined value for the standard deviation of the masses and intensities for all peaks, given in [milliSigma].

Table S3. Toxicity test, containing of both the PhC (before and after enzymatic transformation)*.

PhC	Inhibition (%)*	
	No treatment	Enzymatic treatment
17 β -Estradiol	39.69	67.53
Diclofenac	62.11	22.68
Ketoconazole	51.29	26.55
Ketorolac	102.32	76.03
Naproxen	47.42	23.45
Sulfamethoxazole	56.70	63.66
Tetracyclin	53.61	18.81
Trazodone	52.83	20.36

* Inhibition was calculated as $[100 - \text{BOD}_{\text{dextrosa/glutamic acid}} / \text{BOD}_{\text{dextrosa/glutamic acid/PhC}}]$

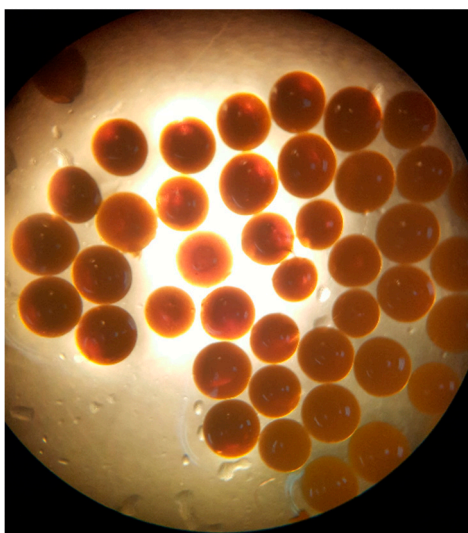


Figure S1. CPO-chitosan macrospheres prepared by precipitation and cross-linking method (scale bar 1 mm).