SUPPLEMENTARY MATERIAL TO

Comparison of the advanced oxidation processes in the degradation of pharmaceuticals and pesticides in simulated urban wastewater: Principal component analysis and energy requirements

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Text S1

All mobile phases were prepared volumetrically from individually measured aliquots and were degassed for 15 min in an ultrasonic bath before use. A mixture of phosphate buffer and acetonitrile (53:47, v/v) was used as a mobile phase for the determination of atenolol. Detection was carried out using a detector at 230 nm (Kumar et al., 2010). Atrazine was monitored at the wavelength of 220 nm and the isocratic mobile phase was pure acetonitrile and purified water (60:40, v/v) (Atarodia and Faghihiana, 2019). The chromatographic conditions used for cyprodinil were as follows: eluent A, water; eluent B, acetonitrile; gradient, 35–60% B over the first 3.5 min and then was stable for 20 min. The chromatograms were performed at 280nm (Vaquero-Fernandez et al., 2008). The mobile phase 0.1% formic acid and methanol (53:50, v/v) was used to determine the dicamba and the detector wavelength was set to 220 nm (Desipioa et al., 2019). The following chromatographic conditions were used for the enalapril assay method. The mobile phase contains a mixture of 0.02M NaH_2PO_4 buffer (pH 3.0 adjusted with H_3PO_4)

and acetonitrile in the ratio 95:5 (v/v) (Koppala et al., 2017). The analyses of the ibuprofen decay were carried out isocratically with a methanol/water (with 1% phosphoric acid) 68:32 (v/v) mixture as the mobile phase and detector wavelength was 228 nm (Loaiza-Ambuludi et al., 2013). The mobile phase for clomazone detection was methanol and water (65:35, v/v), adjusted to pH 4.0 with phosphoric acid and quantification was carried out with UV detection at 220 nm (Zanella et al., 2000). For the determination of loperamide the detector was set to 226 nm. Compound was eluted using an isocratic mobile phase consisting of 0.1% sodium-octansulphonate, 0.05% triethylamine, 0.1% ammonium hydroxide (buffer) in water:acetonitrile (45:55, v/v). The mobile phase was adjusted to pH 3.2 with phosphoric acid (Velinov et al., 2019).

Table S1. Effect of HCO_3^-, CO_3^{2-} and Cl^- ions concentrations on the removal efficiency of atenolol

Process	Concentration ion (mmol dm^{-3})	Decolorization (%)		
		HCO_3^-	CO_3^{2-}	Cl^-
UV/H_2O_2	0	**40.114**	**40.114**	**40.114**
	10.0	40.733	33.548	38.563
	100.0	45.514	46.584	37.541
	1 000.0	46.126	48.387	31.254
UV/persulfate	0	**15.473**	**15.473**	**15.473**
	10.0	16.579	10.014	13.192
	100.0	21.714	21.345	13.554
	1 000.0	22.031	21.945	10.672
Fenton	0	**50.115**	**50.115**	**50.115**
	10.0	/	/	48.374
	100.0	/	/	43.541
	1 000.0	/	/	40.051
photo-Fenton	0	**56.735**	**56.735**	**56.735**
	10.0	/	/	54.784
	100.0	/	/	50.053
	1 000.0	/	/	47.341
UV/TiO_2	0	**82.235**	**82.235**	**82.235**
	10.0	82.907	75.033	80.571
	100.0	87.254	89.378	77.497
	1 000.0	88.001	91.545	70.369

Table S2. Effect of HCO_3^-, CO_3^{2-} and Cl^- ions concentrations on the removal efficiency of atrazine

Process	Concentration ion (mmol dm^{-3})	Decolorization (%)		
		HCO_3^-	CO_3^{2-}	Cl^-
UV/H_2O_2	0	**39.619**	**39.619**	**39.619**
	10.0	41.213	31.046	37.718
	100.0	44.578	46.832	35.491
	1 000.0	45.694	47.597	30.563
UV/persulfate	0	**66.895**	**66.895**	**66.895**
	10.0	67.548	60.064	64.677
	100.0	71.639	73.347	63.046
	1 000.0	72.056	75.218	56.421
Fenton	0	**59.870**	**59.870**	**59.870**
	10.0	/	/	56.012
	100.0	/	/	54.243
	1 000.0	/	/	50.377
photo-Fenton	0	**100**	**100**	**100**
	10.0	/	/	91.407
	100.0	/	/	87.153
	1 000.0	/	/	79.055
UV/TiO_2	0	**37.655**	**37.655**	**37.655**
	10.0	38.975	30.043	36.045
	100.0	43.747	44.721	35.123
	1 000.0	44.098	46.798	29.348

Table S3. Effect of HCO_3^-, CO_3^{2-} and Cl^- ions concentrations on the removal efficiency of cyprodinil

Process	Concentration ion (mmol dm^{-3})	Decolorization (%)		
		HCO_3^-	CO_3^{2-}	Cl^-
UV/H_2O_2	0	**94.362**	**94.362**	**94.362**
	10.0	100	87.049	89.391
	100.0	100	100	84.014
	1 000.0	100	100	77.553
UV/persulfate	0	**10.846**	**10.846**	**10.846**
	10.0	11.536	7.489	10.015
	100.0	17.792	17.345	8.632
	1 000.0	18.041	18.098	6.749
Fenton	0	**67.763**	**67.763**	**67.763**
	10.0	/	/	65.637
	100.0	/	/	64.326
	1 000.0	/	/	57.721
photo-Fenton	0	**79.996**	**79.996**	**79.996**
	10.0	/	/	77.341
	100.0	/	/	74.458
	1 000.0	/	/	67.364
UV/TiO_2	0	**92.606**	**92.606**	**92.606**
	10.0	93.088	85.641	87.40
	100.0	97.397	98.377	82.17
	1 000.0	98.674	98.954	75.14

Table S4. Effect of HCO_3^-, CO_3^{2-} and Cl^- ions concentrations on the removal efficiency of dicamba

Process	Concentration ion (mmol dm^{-3})	Decolorization (%)		
		HCO_3^-	CO_3^{2-}	Cl^-
UV/H_2O_2	0	**77.818**	**77.818**	**77.818**
	10.0	79.541	70.749	76.431
	100.0	82.745	85.354	70.439
	1 000.0	83.639	87.092	65.728
UV/persulfate	0	**5.349**	**5.349**	**5.349**
	10.0	6.458	4.015	5.301
	100.0	6.941	12.466	5.587
	1 000.0	7.526	13.952	4.012
Fenton	0	**54.977**	**54.977**	**54.977**
	10.0	/	/	51.052
	100.0	/	/	50.437
	1 000.0	/	/	45.731
photo-Fenton	0	**68.024**	**68.024**	**68.024**
	10.0	/	/	66.347
	100.0	/	/	65.291
	1 000.0	/	/	87.458
UV/TiO_2	0	**83.811**	**83.811**	**83.811**
	10.0	83.359	76.047	82.578
	100.0	88.264	90.569	78.421
	1 000.0	90.021	92.515	72.693

Table S5. Effect of HCO_3^-, CO_3^{2-} and Cl^- ions concentrations on the removal efficiency of enalapril

Process	Concentration ion (mmol dm^{-3})	Decolorization (%)		
		HCO_3^-	CO_3^{2-}	Cl^-
UV/H_2O_2	0	**39.115**	**39.115**	**39.115**
	10.0	40.075	32.043	38.346
	100.0	43.547	46.721	37.921
	1 000.0	45.034	48.798	32.395
UV/persulfate	0	**15.473**	**15.473**	**15.473**
	10.0	16.639	11.397	13.459
	100.0	22.594	22.658	13.365
	1 000.0	23.012	23.092	10.021
Fenton	0	**57.115**	**57.115**	**57.115**
	10.0	/	/	55.734
	100.0	/	/	50.526
	1 000.0	/	/	47.539
photo-Fenton	0	**66.735**	**66.735**	**66.735**
	10.0	/	/	64.327
	100.0	/	/	63.568
	1 000.0	/	/	56.441
UV/TiO_2	0	**69.646**	**69.646**	**69.646**
	10.0	70.358	63.576	67.592
	100.0	74.647	76.482	64.371
	1 000.0	75.951	78.391	57.834

Table S6. Effect of HCO_3^-, CO_3^{2-} and Cl^- ions concentrations on the removal efficiency of ibuprofen

Process	Concentration ion (mmol dm^{-3})	Decolorization (%)		
		HCO_3^-	**CO_3^{2-}**	**Cl^-**
UV/H_2O_2	0	**58.747**	**58.747**	**58.747**
	10.0	59.384	51.675	56.347
	100.0	63.476	65.842	51.256
	1 000.0	64.291	67.361	49.418
UV/persulfate	0	**48.769**	**48.769**	**48.769**
	10.0	49.538	41.365	46.452
	100.0	54.247	55.879	41.376
	1 000.0	55.396	56.348	40.018
Fenton	0	**77.452**	**77.452**	**77.452**
	10.0	/	/	75.723
	100.0	/	/	74.458
	1 000.0	/	/	67.614
photo-Fenton	0	**100**	**100**	**100**
	10.0	/	/	**100**
	100.0	/	/	**100**
	1 000.0	/	/	**100**
UV/TiO_2	0	**48.747**	**48.747**	**48.747**
	10.0	49.098	41.364	47.041
	100.0	55.027	55.217	46.695
	1 000.0	55.963	57.098	41.483

Table S7. Effect of HCO_3^-, CO_3^{2-} and Cl^- ions concentrations on the removal efficiency of clomazone

Process	Concentration ion (mmol dm^{-3})	Decolorization (%)		
		HCO_3^-	CO_3^{2-}	Cl^-
UV/H_2O_2	0	**59.601**	**59.601**	**59.601**
	10.0	60.381	52.731	57.347
	100.0	65.753	66.645	54.621
	1 000.0	66.642	68.286	51.519
UV/persulfate	0	**38.587**	**38.587**	**38.587**
	10.0	39.346	31.876	36.421
	100.0	45.721	45.019	34.798
	1 000.0	46.392	46.332	29.236
Fenton	0	**58.611**	**58.611**	**58.611**
	10.0	/	/	56.491
	100.0	/	/	53.015
	1 000.0	/	/	49.382
photo-Fenton	0	**69.601**	**69.601**	**69.601**
	10.0	/	/	65.313
	100.0	/	/	64.685
	1 000.0	/	/	57.291
UV/TiO_2	0	**79.167**	**79.167**	**79.167**
	10.0	80.311	73.189	73.460
	100.0	84.465	86.356	72.319
	1 000.0	86.732	88.274	65.085

Table S8. Effect of HCO_3^-, CO_3^{2-} and Cl^- ions concentrations on the removal efficiency of loperamide

Process	Concentration ion (mmol dm^{-3})	Decolorization (%)		
		HCO_3^-	CO_3^{2-}	Cl^-
UV/H_2O_2	0	**71.391**	**71.391**	**71.391**
	10.0	72.391	65.189	67.491
	100.0	76.457	76.356	66.337
	1 000.0	77.926	88.274	59.981
UV/persulfate	0	**58.278**	**58.278**	**58.278**
	10.0	59.931	51.364	57.371
	100.0	64.275	65.279	53.956
	1 000.0	65.364	67.581	49.083
Fenton	0	**81.391**	**81.391**	**81.391**
	10.0	/	/	75.397
	100.0	/	/	74.451
	1 000.0	/	/	67.286
photo-Fenton	0	**100**	**100**	**100**
	10.0	/	/	100
	100.0	/	/	100
	1 000.0	/	/	100
UV/TiO_2	0	**82.166**	**82.166**	**82.166**
	10.0	83.176	76.347	76.639
	100.0	87.394	89.981	74.351
	1 000.0	89.852	92.654	66.082

References

Atarodia, H., Faghihiana, H., 2019. Selective photodegradation of atrazine by a novel molecularly imprinted nanophotocatalyst prepared on the basis of chitosan. J. Photochem. Photobiol. A. 382, 111892.

Desipioa, M.M., Van Bramerb, S.E., Thorpec, R., Sahaa, D., 2019. Photocatalytic and photo-fenton activity of iron oxide-doped carbon nitride in 3D printed and LED driven photon concentrator. J. Hazard. Mater. 376, 178–187.

Koppala, S., Reddy, V.R., Anireddy, J.S., 2017. User-Friendly HPLC Method Development and Validation for Determination of Enalapril Maleate and Its Impurities in Enalapril Tablets. J. Chromatogr. Sci. 1–10.

Kumar, N., Verma, N., Songh, O., Joshi, N., Singh, K.G., 2010. Estimation of Atenolol by Reverse Phase High Performance Liquid Chromatography. E-J. Chem. 7(3), 962–966.

Loaiza-Ambuludi, S., Panizza, M., Oturan, N., Özcan, A., Oturan, M.A., 2013. Electro-Fenton degradation of anti-inflammatory drug ibuprofen in hydroorganic medium. J. Electroanal. Chem. 702, 31–36.

Vaquero-Fernandez, L., Saenz-Hernaez, A., Sanz-Asensio, J., Fernandez-Zurbano, P., Sainz-Ramırez, M., Pons-Jubera, B., Lopez-Alonso, M., Epifanio-Fernandez, S.-I., Martınez-Soria, M.-

T., 2008. Determination of cyprodinil and fludioxonil in the fermentative process of must by high-performance liquid chromatography–diode array detection. J. Sci. Food Agric. 88, 1943–1948.

Velinov N., Najdanović S., Radović M., Mitrović J., Kostić M., Bojić D., Bojić A., 2019. Biosorption of loperamide by lignocellulosic-Al_2O_3 hybrid: optimization, kinetics, isothermal and thermodynamic studies. Cellulose Chem. Technol. 53(1–2), 175–189.

Zanella, R., Primel, E.G., Goncalves, F.F., Martins A.F., 2000. Development and validation of a high-performance liquid chromatographic method for the determination of clomazone residues in surface water. J. Chromatogr. A. 904, 257–262.