

SUPPLEMENTARY MATERIALS

Improvement of the Carbocatalytic Degradation of Pharmaceuticals in Water by the Use of Ultrasound Waves

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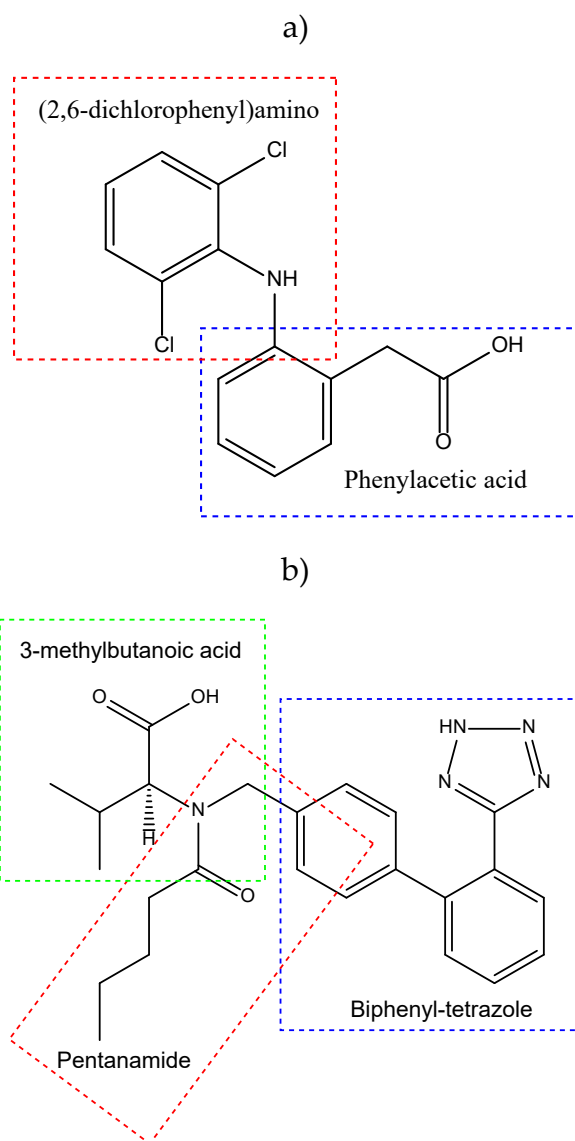
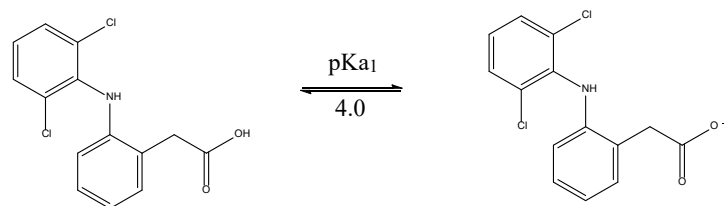


Figure S1. Chemical structure (a) Diclofenac, and (b) Valsartan.

a) Diclofenac



b) Valsartan

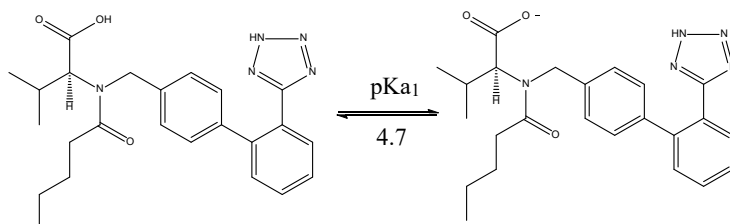
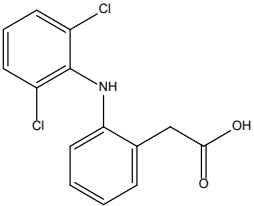
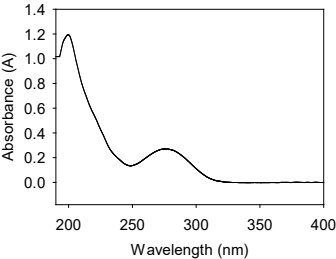
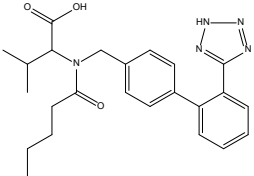
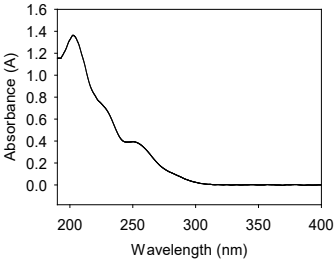


Figure S2. Structures of (a) Diclofenac and (b) Valsartan, according to their pKa values.

Table S1. Characteristics of the pharmaceuticals.

Molecular structure	Molecular weight (g mol ⁻¹)	UV/Vis absorbance spectrum	pKa	log Kow
<chem>C14H11Cl2NO2</chem> 	296.148		pKa ₁ = 4.0 (carboxylic acid) [S1].	4.51
<chem>C24H29N5O3</chem> 	435.52		pKa ₁ = 3.9 (tetrazole ring) pKa ₂ = 4.7 (carboxylic acid) [S2].	4.00

According to the World Health Organization, the prescription and consumption of antihypertensives will increase, because the number of adults with hypertension worldwide by 2025 could reach a total of 1.56 billion [S3]. Valsartan (VAL) is a pharmaceutical commonly used as an antihypertensive [S4] and it can be detected in wastewater. On the other hand, diclofenac (DCF) is a commonly used non-steroidal anti-inflammatory drug. Consequently, DFC has been detected in the surface, ground, and even drinking water [S5, S6]. Furthermore, DCF can affect rates of physiological growth and reproduction of phytoplankton [S7].

Supplementary references

- S1. Lara-Pérez, C.; Leyva, E.; Zermeño, B.; Osorio, I.; Montalvo, C.; Moctezuma, E. Photocatalytic degradation of diclofenac sodium salt: adsorption and reaction kinetic studies. *Environ. Earth Sci.* **2020**, *79*, 1–13, doi:10.1007/s12665-020-09017-z.
- S2. Siddiqui, N.; Husain, A.; Chaudhry, L.; Alam, S.S.; Mitra, M.; Bhasin, P.S. Pharmacological and pharmaceutical profile of valsartan: A review. *J. Appl. Pharm. Sci.* **2011**, *1*, 12–19.
- S3. Kearney, P.M.; Whelton, M.; Reynolds, K.; Muntner, P.; Whelton, P.K.; He, J. Global burden of hypertension: analysis of worldwide data. *Lancet* **2005**, *365*, 217–223, doi:10.1016/s0140-6736(05)17741-1.
- S4. Arvaniti, O.S.; Bairamis, F.; Konstantinou, I.; Mantzavinos, D.; Frontistis, Z. Degradation of antihypertensive drug valsartan in water matrices by heat and heat/ultrasound activated persulfate: Kinetics, synergy effect and transformation products. *Chem. Eng. J. Adv.* **2020**, *4*, 100062, doi:10.1016/j.cej.2020.100062.
- S5. Nackiewicz, J.; Gąsowska-Bajger, B.; Kołodziej, Ł.; Poliwoda, A.; Pogoda-Mieszczak, K.; Skonieczna, M. Comparison of the degradation mechanisms of diclofenac in the presence of iron octacarboxyphthalocyanine and myeloperoxidase. *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* **2023**, *287*, doi:10.1016/j.saa.2022.122113.
- S6. Shamsudin, M.S.; Azha, S.F.; Ismail, S. A review of diclofenac occurrences, toxicology, and potential adsorption of clay-based materials with surfactant modifier. *J. Environ. Chem. Eng.* **2022**, *10*, 107541, doi:10.1016/j.jece.2022.107541.
- S7. Vasantha Raman, N.; Gsell, A.S.; Voulgarellis, T.; van den Brink, N.W.; de Senerpont Domis, L.N. Moving beyond standard toxicological metrics: The effect of diclofenac on planktonic host-parasite interactions. *Aquat. Toxicol.* **2023**, *254*, 106370, doi:10.1016/j.aquatox.2022.106370.