3D-printed hybrid adsorbent monoliths for the removal of emerging organic contaminants from wastewaters

Ilias Siadimas[1], Sofia Kavafaki[1], Ramonna I. Kosheleva[1], Pavlos Efthymiopoulos[1], Georgios Maliaris[1], George Z. Kyzas [1]

[1]Hephaestus Laboratory, Department of Chemistry, School of Science, Democritus University of Thrace, Kavala, GR-654 04, Greece
Keywords: wastewater, additive manufacturing, composites
Presenting author email: kyzas@chem.duth.gr

The ever-increasing water contamination with chemically diverse pollutants by industrial, agricultural and domestic activities is one of the major challenges of modern society. Enormous amounts of treated, partially treated or untreated wastewaters are daily released to natural water bodies around the world. Numerous emerging organic contaminants of different origin, for example industrial additives, pesticides, cosmetics, personal-care products, hormones, pharmaceuticals, as well as their transformation products are ubiquitously detected in water bodies also in remote regions far from their emission sources. (Wilkinson *et al*, 2022). Due to their diverse negative effects on public health and the environment, their efficient removal from wastewater before releasing into the environment is deemed of great importance, even when present in low concentrations (Schwarzenbach *et al*, 2006). However, since conventional wastewater treatment processes were not designed to handle this class of pollutants, they are of limited effectiveness, and advanced complementary treatment techniques must be employed (Morin-Crini *et al*, 2022). Among them, adsorption is regarded as the most promising due to its versatility, high efficiency, operational simplicity, large-scale applicability, inexpensiveness, and environmental friendliness due to the lack of potentially toxic by-product formation (Rashid *et al*, 2021).

In addition to conventional adsorbents, such as zeolites, clays, silica and porous carbon, a large variety of organic, inorganic and hybrid organic-inorganic adsorbents have been developed in the past decades. Among them, polymer adsorbents and their composites exhibit distinct advantages, including high surface area, long-term physicochemical stability in water, low weight, mechanical stability, cost-efficiency, good selectivity, fast adsorption kinetics, large capacity, ease of preparation and regeneration (Pan *et al*, 2009; Jaspal *et al*, 2020). Additive manufacturing, most widely known as 3D printing, makes the creation of chemically diverse monolith adsorbents having complex porous structures possible, which can both facilitate mass transport through the pores and ensure that there is a large contact area between the material and the water contaminants (Pereira *et al*, 2021; Barman *et al*, 2023).

In this work, we report the utilization of monoliths of complex porous structure, prepared by a vat photopolymerization method, as novel adsorbents for the removal of a model drug from aqueous solutions. An acrylate-based photopolymer loaded with a carbon-based material filler was selectively solidified layer-by-layer by using light of a wavelength of 405 nm, while the adsorbent was characterized by Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray diffraction (XRD) and contact angle goniometry. Monolith's adsorption performance was evaluated by batch experiments, and the effect of pH, contact time, temperature and initial pollutant concentration was studied. The final pollutant concentration was determined spectrophotometrically. The kinetic data were fitted to the pseudo-first-order and pseudo-second-order models. The equilibrium adsorption data at different temperatures were fitted to the Langmuir and Freundlich adsorption isotherm models. The results indicate that hydrophobic 3D printed composite monoliths can be effectively employed for the removal of emerging organic contaminants from aqueous solutions.

Acknowledgement
We acknowledge support of this work by the project "Advanced Nanostructured Materials for Sustainable Growth: Green Energy Production/Storage, Energy Saving and Environmental Remediation" (TAEDR-0535821) which is implemented under the action "Flagship actions in interdisciplinary scientific fields with a special focus on the productive fabric" (ID 16618), Greece 2.0 – National Recovery and Resilience Fund and funded by European Union NextGenerationEU.

References

Barman, S.R. (2023). 3D-printed materials for wastewater treatment. *JACS Au*, 3 (11), 2930-2947. https://doi.org/10.1021/jacsau.3c00409

Jaspal, D. *et al* (2020). Composites for wastewater purification: A review. *Chemosphere*, 246, 125788. https://doi.org/10.1016/j.chemosphere.2019.125788

Morin-Crini, N. *et al* (2022). Removal of emerging contaminants from wastewater using advanced treatments. A review. *Environmental Chemistry Letters*, 20, 1333–1375. https://doi.org/10.1007/s10311-021-01379-5

Pan, B. *et al* (2009). Development of polymeric and polymer-based hybrid adsorbents for pollutants removal from waters. *Chemical Engineering Journal*, 151, 19-29. https://doi.org/10.1016/j.cej.2009.02.036

Pereira, A. *et al* (2022). Additive manufacturing for adsorption-related applications—A review. *Journal of Advanced Manufacturing and Processing*, 4(1), e10108. https://doi.org/10.1002/amp2.10108

Rashid, R. *et al* (2021). A state-of-the-art review on wastewater treatment techniques: the effectiveness of adsorption method. *Environmental Science and Pollution Research*, 28, 9050–9066. https://doi.org/10.1007/s11356-021-12395-x

Schwarzenbach, R.P. *et al* (2006). The challenge of micropollutants in aquatic systems. *Science*, 313(5790), 1072-1077. https://doi.org/10.1126/science.1127291

Wilkinson, J.L. *et al* (2022). Pharmaceutical pollution of the world's rivers. *Proceedings of the National Academy of Sciences*, 119(8), e2113947119. https://doi.org/10.1073/pnas.2113947119