

Putrescine/graphene oxide and chitosan/graphene oxide derivatives for the removal of paracetamol and ketoprofen from wastewaters

Konstantinos N. Maroulas¹, Ioannis Christodoulopoulos¹, Anastasia D. Meretoudi¹, Sofia L. Kouvalakidou¹, Ramonna I. Kosheleva¹, Ioannis Georgiou¹, Despina A. Gkika¹, Athanasios Varoutoglou¹, Irene Moschou¹, Athanasia K. Tolkou¹, Pavlos Efthymiopoulos¹, George Z. Kyzas¹

¹Hephaestus Laboratory, Department of Chemistry, School of Science, International Hellenic University, Kavala, GR-654 04, Greece

Keywords: graphene oxide, pharmaceuticals, biopolymers

Presenting author email: kyzas@chem.ihu.gr

Water treatment is a big concern for many scientists. Population growth and developments in healthcare technology are to blame for increased levels of pharmaceutical medication production and use (Date and Jaspal, 2023). However, unprocessed hospital and pharmaceutical company effluents, as well as insufficient medication waste treatment, have resulted in the discharge of medications into the environment (Gworek et al., 2020). Amongst the technologies available for pharmaceutical removal, adsorption is preferred because of ease of use, uncomplicated technology, and no toxic by-products (Al-Jubouri et al., 2022).

The current study recommends the usage of adsorbents based on graphene oxide. For their synthesis chitosan and putrescin were used in different ratios. Graphene oxide (GO) is a novel carbon nanomaterial derived from graphene and possesses several oxygen-containing functional groups, including epoxides, hydroxy groups, and carboxyl groups on its surface and at its edges (Ahmad et al., 2022). Graphene is not a viable adsorbent for many pollutants until it is modified. It is typically coated with functional groups or other compounds to boost its adsorption ability. For this reason, chitosan and putrescine were used. Chitosan, being a naturally occurring biopolymer, is cheap and has fascinating adsorption properties, because of the existence of amino and hydroxyl groups across its ring structure (Maroulas et al., 2023). Putrescine (1,4 butane diamine) is used to graft more amino groups on the composite, in order to enhance the adsorption effectiveness. Their combination is novel since it hasn't been reported in the literature and putrescin hasn't been investigated for its efficiency in adsorption processes.

Their adsorptive efficiency towards paracetamol, ketoprofen and their mixture, was evaluated by batch adsorption experiments. The effect of solution pH, contact time, temperature and initial pharmaceuticals concentration on the adsorption of the composites was determined. Two kinetic models were examined to fit the kinetics of fluoride sorption pseudo first order and pseudo second order models and the optimal pH was found by using 1.0 g/L of the adsorbent. According to thermodynamics the spontaneous nature of their adsorption was confirmed. The equilibrium adsorption data at temperatures of 30°C, 45°C and 60°C were fitted to the Langmuir and Freundlich adsorption isotherm models. The results indicate that Cs/GO@Putrescin can be effectively employed for removal of pharmaceutical residues 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

- Ahmad, A.L., Ebenezer, O.I., Shoparwe, N.F., Ismail, S., 2022. Graphene Oxide-Doped Polymer Inclusion Membrane for Remediation of Pharmaceutical Contaminant of Emerging Concerns: Ibuprofen. *Membranes* 12, 24. <https://doi.org/10.3390/membranes12010024>
- Al-Jubouri, S.M., Al-Jendeel, H.A., Rashid, S.A., Al-Batty, S., 2022. Antibiotics adsorption from contaminated water by composites of ZSM-5 zeolite nanocrystals coated carbon. *J. Water Process Eng.* 47, 102745. <https://doi.org/10.1016/j.jwpe.2022.102745>

Date, M., Jaspal, D., 2023. Pharmaceutical Wastewater Remediation: A Review of Treatment Techniques. *Ind. Eng. Chem. Res.* 62, 20492–20505. <https://doi.org/10.1021/acs.iecr.3c02451>

Gworek, B., Kijeńska, M., Zaborowska, M., Wrzosek, J., Tokarz, L., Chmielewski, J., 2020. Occurrence of pharmaceuticals in aquatic environment – a review. *DESALINATION WATER Treat.* 184, 375–387. <https://doi.org/10.5004/dwt.2020.25325>

Maroulas, K.N., Trikkaliotis, D.G., Metaxa, Z.S., AbdelAll, N., Alodhayb, A., Khouqeer, G.A., Kyzas, G.Z., 2023. Super-hydrophobic chitosan/graphene-based aerogels for oil absorption. *J. Mol. Liq.* 390, 123071. <https://doi.org/10.1016/j.molliq.2023.123071>