

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

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

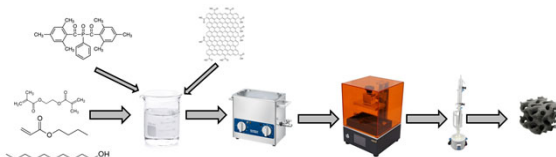
Hephaestus Laboratory, Department of Chemistry, School of Science, Democritus University of Thrace, Kavala, Greece



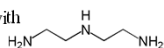
(E-mail: kyzas@chem.duth.gr)



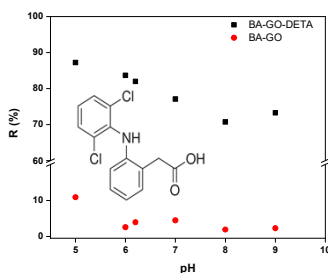
Adsorbent preparation



- 30 wt.% Butyl Acrylate, 20 wt.% EGDMA, 50 wt.% 1-Decanol.
- Ultrasonication of 0.5 wt% Graphene Oxide (GO) and 3% Irgacure 819 photoinitiator in resin mixture.
- 3D-printing of porous Gyroid-structured adsorbents via vat photopolymerization by light of a wavelength of 405nm.
- Soxhlet for 24 hours in water/isopropanol.
- DETA-modified adsorbents were hydrolyzed with HCl and then functionalized with DETA

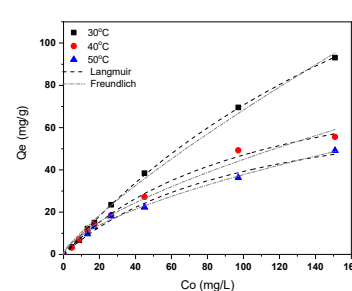


Diclofenac removal



- DETA modification enhances the adsorption efficacy (R=88% at pH=5) of Diclofenac (DCF).
- Secondary treated wastewaters are discharged at pH=7 where adsorption is also effective.

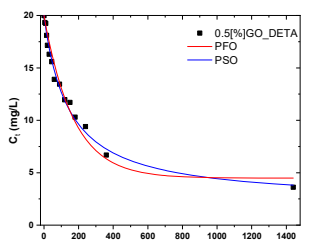
Adsorption Isotherms



Temperature	Langmuir		Freundlich	
	Qm (mg/g)	K _L (L/mg)	K (mg ¹⁻ⁿ L ⁿ G ⁻¹)	N
30°	2550.09	0.00383	0.99946	1.64262
40°	98.3315	0.00917	0.99526	2.11937
50	80.0859	0.00962	0.98878	2.15669

- Adsorption data fit better with the Langmuir isotherm model.
- GO-DETA's maximum adsorption capacity decreases with temperature

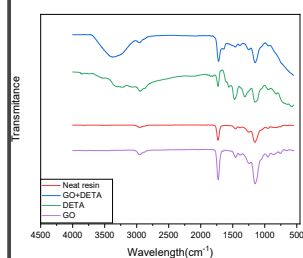
Adsorption Kinetics



	Pseudo-1 st order	Pseudo-2 nd order
k	5.91	6.99
R ²	0.97092	0.98944

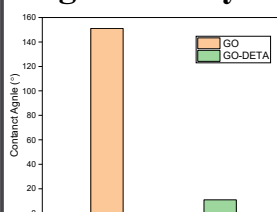
Adsorption kinetics fit better to the pseudo-2nd order model.

FTIR



The successful synthesis was confirmed.

Contact goniometry



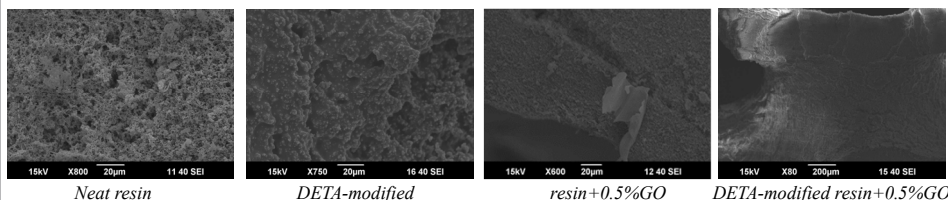
DETA-modified surface is hydrophilic, while the substrate remains super-hydrophobic leading to a very stable sorbent in aquatic media.

N₂ Porosimetry

SAMPLE	SA (m ² /g)	Pore Volume (cm ³ /g)@ST	
		avg Pore Size (Å)	P
GO	287	22.5	215
GO-DETA	232	11.9	193
Neat resin	156	11.3	130
DETA	12	6.3	62

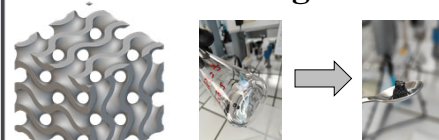
DETA presence alters porous surface and creates complex pore structures

SEM



- Sonication successfully disperses GO in the polymer matrix.
- DETA modification affects materials' surface roughness.

Advantage



The 3D printed sorbent remains intact after adsorption making its removal exceptionally effortless.

References

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

Conclusions

- Novel TPMS-shaped (Gyroid) acrylic resin/GO composite monoliths were successfully prepared by a vat photopolymerization 3D-printing technique.
- Adsorbents' efficiency was tested by batch adsorption experiments towards DCF at pH=7 (pH value of secondary treated wastewaters).
- Post-3D printing DETA-modification of the adsorbent increases by 17-fold its removal efficiency.
- DETA-functionalization of adsorbent alters its surface from super-hydrophobic to highly hydrophilic.