

3D-printed@activated carbon adsorbent materials for the removal of Diclofenac from aqueous solutions

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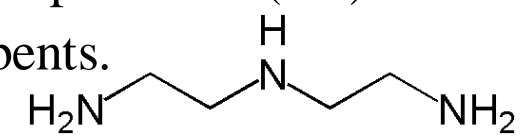
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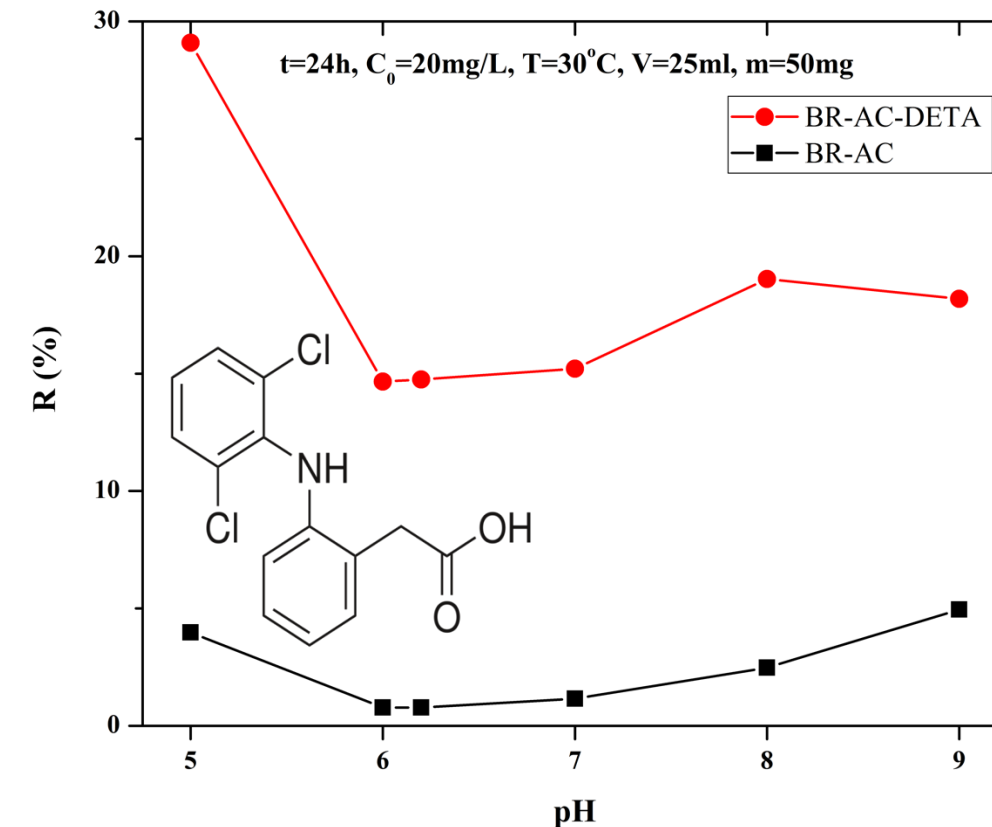
Synthesis



- Mechanical mixing of Butyl Acrylate (BA) 30wt% , EGDMA 20wt%, 1-Decanol 50 wt.% (Base Resin,).
- Addition of Activated Carbon (AC) 0.5 wt%, photoinitiator BAPO 3wt% and sonication for 15min.
- 3D-printing of porous TPMS-structured adsorbents *via* vat photopolymerization by light of a wavelength of 405nm.
- Soxhlet extraction for 24 hours in water:isopropanol 1:1 (v/v) mixture.
- DETA-functionalization of composite adsorbents.
- Drying at 50°C for 30min.

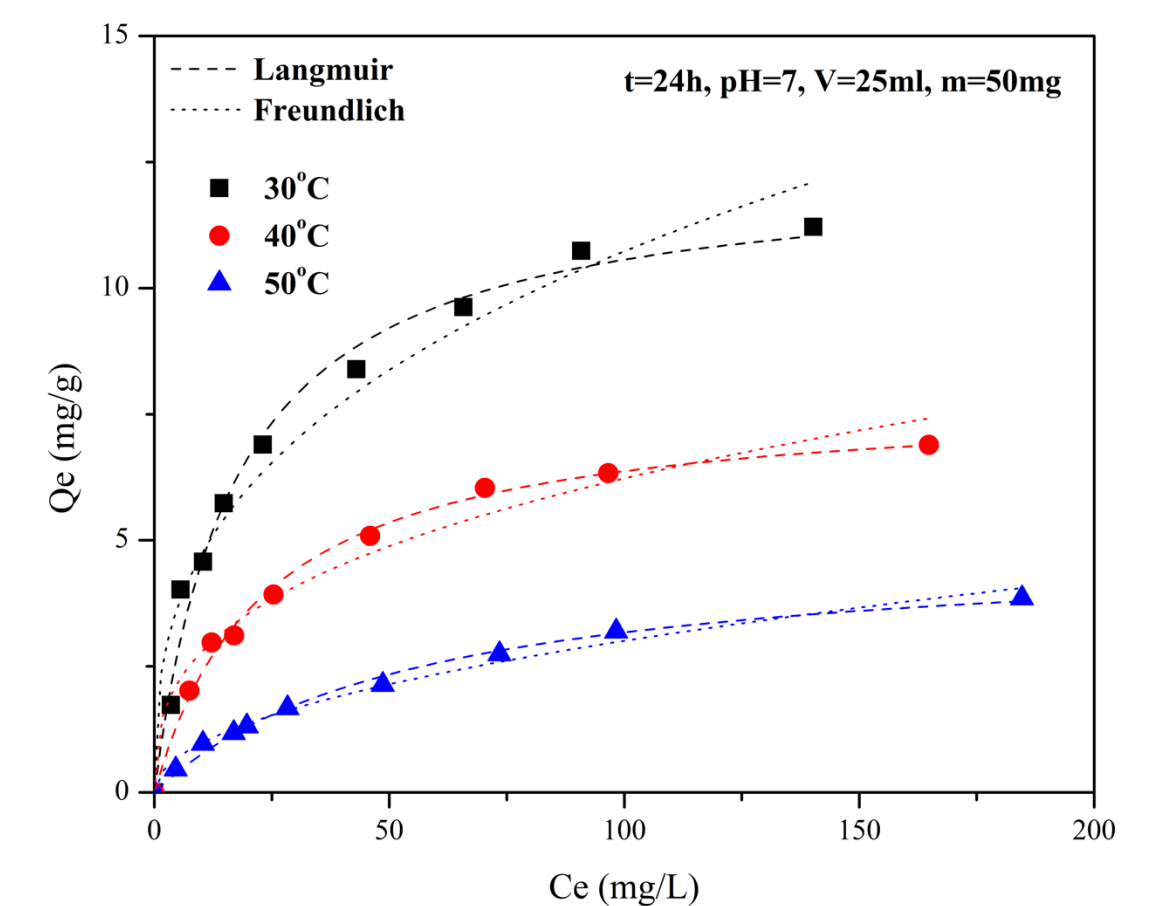


Effect of pH



- DETA modification enhances the adsorption efficiency of diclofenac (DCF) up to 19 times.
- Secondary treated wastewaters are discharged at pH=7 where adsorption is also effective.

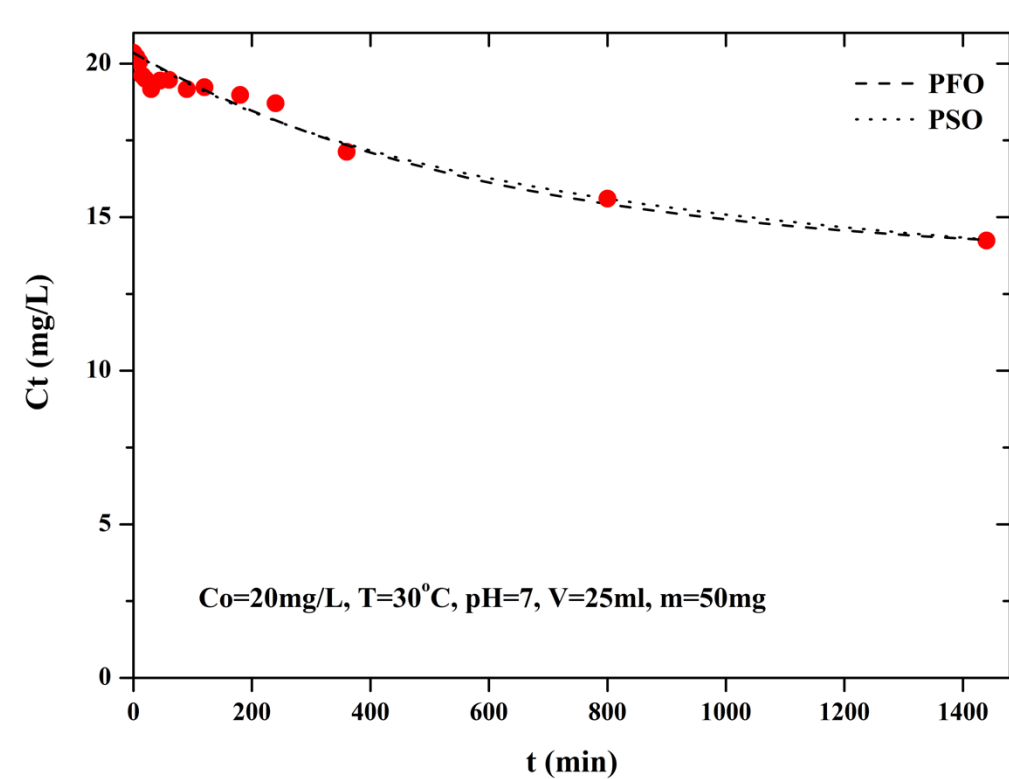
Isotherms



Temp. (°C)	Langmuir equation			Freundlich equation		
	$Q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e}$	$Q_e = K_F C_e^{1/n}$				
	Q_{max} (mg/g)	K_L (L/mg)	R^2	K_F (mg ^{1-1/n} L ^{1/n} g ⁻¹)	n	R^2
30	12.387	0.0580	0.987	2.070	2.799	0.964
40	7.865	0.0426	0.995	1.241	2.855	0.972
50	4.924	0.0181	0.993	0.318	2.049	0.986

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

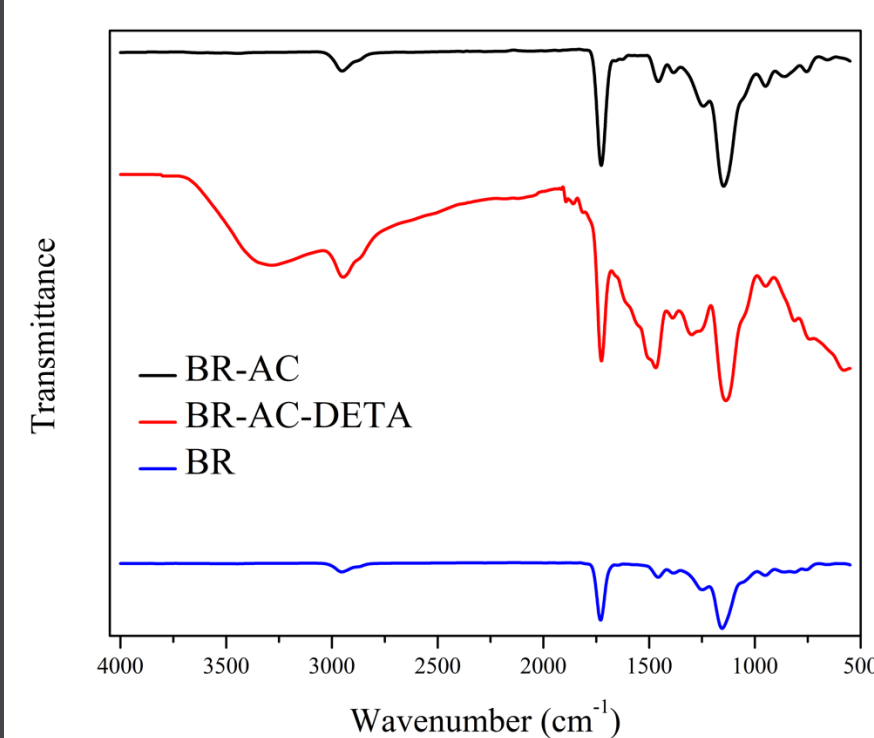
Kinetics



	PFO	PSO
$C_t = C_0 - (C_0 - C_t)(1 - e^{-kt})$	$C_t = C_0 - (C_0 - C_t) \left(1 - \frac{1}{1 + k_2 t}\right)$	
k	1.650 min ⁻¹	1.290 g ⁻¹ mg min ⁻¹
R^2	0.922	0.924

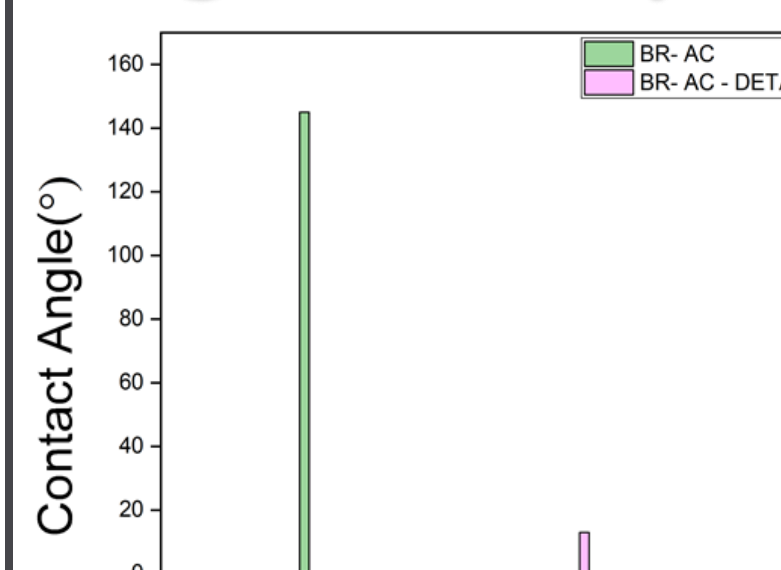
Adsorption kinetic data fit slightly better to the pseudo-2nd order model.

FTIR



The successful synthesis of AC carbon composites by vat photopolymerization, as well as their successful DETA-modification were confirmed.

Contact goniometry



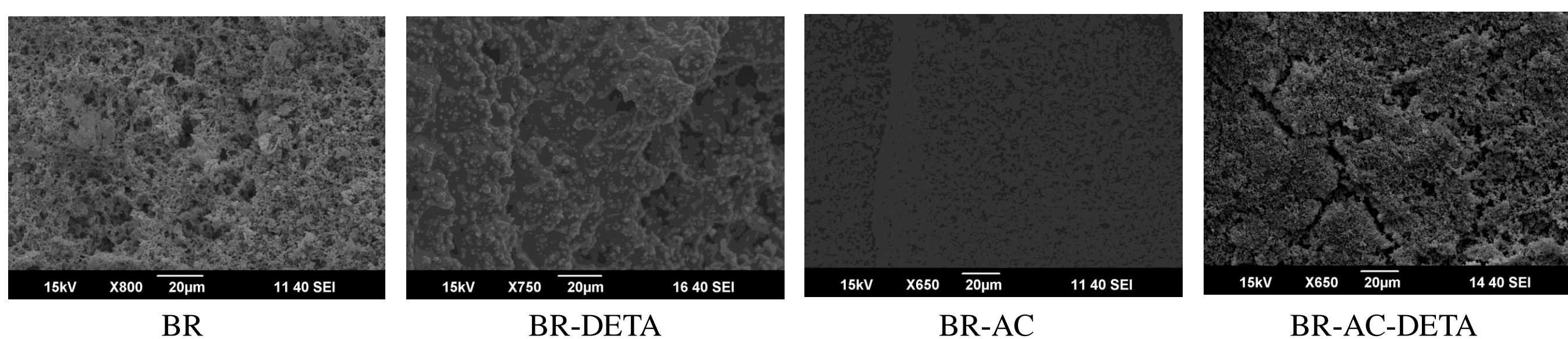
DETA-modified surface is hydrophilic, while the superhydrophobic substrate ensures adsorbent stability in aquatic media.

N₂ Porosimetry

Material	Surface Area (m ² /g)	avg Pore Size (Å)	Pore Volume (cm ³ /g)@STP
BR	156	11.3	130
BR-DETA	12	6.3	62
BR-AC	29.1	81.1	0.064
BR-AC-DETA	17.7	48.4	0.037

- DETA post-modification decreases SA, pore size and volume.
- Composite materials exhibit smaller SA and pore volume, but larger pore size.

SEM



- Sonication for 15min successfully disperses powdered AC in the polymer matrix.
- DETA modification affects materials' surface roughness.

Advantage



3D printed composite adsorbents can be easily removed from treated wastewaters after usage.

References

- 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>
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Conclusions

- Novel TPMS-shaped acrylic resin/powdered AC composite monoliths were successfully prepared by 3D-printing.
- Adsorbents' efficiency towards DCF at pH=7 (pH value of secondary treated wastewaters) was tested by batch adsorption experiments.
- Post-3D printing DETA-modification of the adsorbent increases by 19-fold its removal efficiency.
- DETA-functionalization of adsorbent alters its surface from super-hydrophobic to highly hydrophilic, and changes its pore structure.

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