RSC
Applied Interfaces

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: M. Melucci, L. Bocchi, A. Kovtun, A. Trifoglio, A. Pintus, S. Khaliha, S. Mantovani and D. Paci, *RSC Appl. Interfaces*, 2025, DOI: 10.1039/D5LF00105F.

ROYAL SOCIETY
OF **CHEMISTRY**

rsc.li/RSCApplInter

RSC Applied Interfaces

View Article Online
DOI: 10.1039/D5LF00105F

Functionalizing Graphene Oxide in Polysulfone Composite Adsorption Cartridges Through In-Flow, In Situ Treatment

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Angela Pintus,[a,b,†] Andrea Trifoglio,[b,c,†] Sara Khaliha,[b] Sebastiano Mantovani,[b] Davide Paci,[d] Alessandro Kovtun,[b,*] Letizia Bocchi,[d] Manuela Melucci.[b,*]

We present a scalable chemical method to upcycle polysulfone-graphene oxide (PSU-GO) industrial waste into customized adsorbent materials through in-situ, in flow L-Lysine functionalization of GO embeded in the polymer composite. Enanched carbamazepine removal from water is demonstrated for PSU-GOLys filled cartridges.

Graphene-based composites have shown significant potential across various applications, [1] ranging from sensors and flexible electronics, [2] advanced energy storage systems [3] and environmental remediation applications.[4] Due to its processability, water dispersibility, and superior chemical versatility, graphene oxide (GO) has been widely exploited as component in composites tailoring.[5-7] The presence of a variety of oxygenated functional groups (i.e. hydroxyl, epoxide, and carboxyl groups) on GO nanosheets surface enables the chemical functionalization through covalent chemistry, allowing for the formulation and synthesis of a wide class of modified GO-based materials with different chemical features.[8, 9] The surface chemistry tunability of GO nanosheets has recently been widely exploited to tune the adsorption properties toward water organic and metallic contaminants.[10-12] In this scenario, several examples of modification strategies have been developed, including the use of polyethyleneimine and triethyl-phosphate for toxic metal adsorption,[13, 14] polysaccharides and amino acids (AA) for targeting organic pollutants;[15-17] and cyclodextrin (CD) for the removal of per- and polyfluoroalkyl substances.[18] The adsorption mechanism has been widely explored, demonstrating that the reactivity is related to the balance of different energies contributions, including van der Waals forces (VDW), electrostatic interactions and π-π stacking interactions.[19, 20] On this line, we recently reported a study on amino acid-modified GO which demonstrates that the shape complementarity between the AA pendant and contaminant molecules enhance the hydrophobic interactions between the core of the contaminant and the amino acid side chains, eventually increasing the adsorption capacity. Among GO modified with AA, L-Lysine-modified GO (GO-Lys) showed an effective adsorption of Carbamazepine (CBZ), an antiepileptic drug of increasing concern as emerging water contaminant, with maximum adsorption capacity two order of magnitude higher than that of pristine GO.[21] As for pristine GO-Lys nanosheets, alginate-GOLys composites, showed excellent adsorption properties for a selection of organic contaminants, including Benzophenone-4 (BP4), Bisphenol-A (BPA), Diclofenac (DCF) and CBZ.[22] While a number of GO composites such as foams, aerogels, membranes have been reported in the last years,[23-25] the post-functionalization of GO nanosheets, already embedded in such composites, has been relatively unexplored, with only a few studies reporting successful modification strategies. In this context, S. de Léon et al. demonstrated that GO incorporated into photosensitive acrylic resins could be functionalized with biomolecules, thereby improving both mechanical and functional properties of the final material.[26]

Here, we demonstrate L-Lysine in-situ functionalization of GO embedded in a plastic waste material (Scheme 1), i.e. polysulfone graphene oxide (PSU-GO) granules (Fig. 1). This granuels are obtained by grinding the waste of the production of Graphisulfone® membranes [27] and have been already exploited as sorbent for drinking water treatment. [28] The chemical stability of PSU polymer requires the use of activating agents and organic solvents for surface functionalization, [29] [30] making post-production modifications under mild conditions unfeasible and thereby limiting the ability to fine-tune the surface properties and adsorption selectivity of PSU membranes. [31] [32] Here we aim at exploiting the GO nanosheets embedded in the polymer structure to tune the adsorption properties of PSU granules. In situ synthesis of GO-Lys in PSU-GO filled cartridge was performed by loop recirculation of an

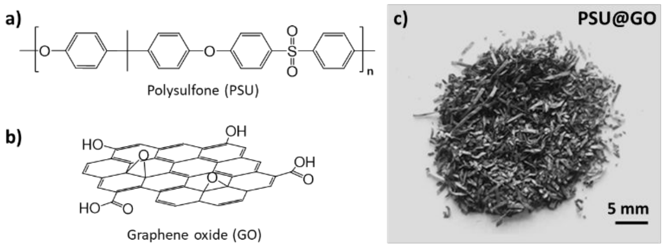


Figure 1. Chemical structures of a) polysulfone (PSU) and b) graphene oxide (GO); c) granules of composite PSU-GO.

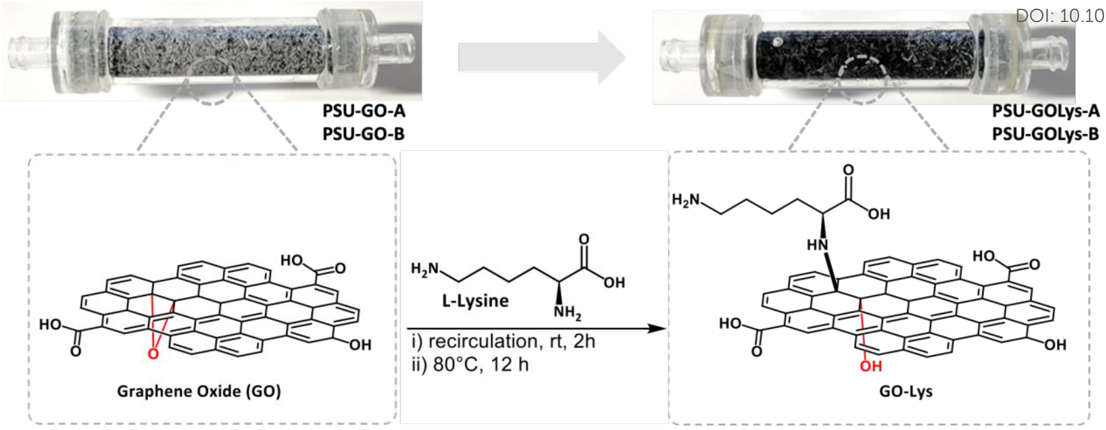
---

[a] Dipartimento di Fisica, Università di Modena e Reggio Emilia, Via Campi 213/A - 41125 Modena (MO), IT.
[b] Istituto per la Sintesi Organica e la Fotoreattività (ISOF)-CNR, via Gobetti 101, 40129 Bologna (BO), IT.
[c] Alma Mater Studiorum - University of Bologna, Department of Chemistry 'G. Ciamician', via Selmi 2, 40129 Bologna (BO), IT.
[d] Medica Spa, via degli Artigiani 7, 41036, Medolla (MO), IT.

† These authors contributed equally.

Supplementary Information available: Materials, PSU-GO functionalization with Lysine, SEM, XPS, Carbamazepine (CBZ) adsorption test in flow conditions. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/D5LF00105F



Scheme 1. In situ Lysine functionalization of GO embedded in PSU-GO granules with two different GO amount (A: 3.5% w/w and B: 10% w/w PSU/GO).

aqueous solution of L-Lysine. PSU-GO with different GO % amount (i.e. PSU-GO-A with 3.5% w/w and PSU-GO-B with 10% w/w GO/PSU ratio) were modified with Lysine by epoxide ring opening reaction (Scheme 1).[9] The reaction was carried out under basic conditions (pH 9.7) to ensure that the alpha-NH_2 of Lysine was unprotonated and available for reaction as the nucleophilic moiety.[33, 21] PSU structure does not include electrophilic groups available for direct amination, so in the exploited conditions the reaction is expected to involve only GO.[34] To optimize permeation and maximize the interaction between Lysine and GO in the porous structure of the granules, the solution of amino acid was recirculated at a constant flow of 5 mL/min for 2h (Fig. 2). Then the cartridges were kept at 80°C overnight, to facilitate the formation of stable covalent bond between Lysine and the GO surface. Finally, the modified granules were washed by passing 2.5 L of ultrapure water through the cartridge to remove unreacted residues and then air-dried before use (Section 2, ESI). Scanning electron microscopy (SEM) images provide insight into the morphology of the PSU-GO composites before and after functionalization (Fig. S2, ESI). The granules have a hollow tubular structure (Fig. 3a-b) with surface pores in the range 5-10 µm. The characteristic porous structure of the hollow fiber granules is preserved after Lysine functionalization,[27, 28] indicating that the synthetic process does not significantly alter the overall morphology of the granules.

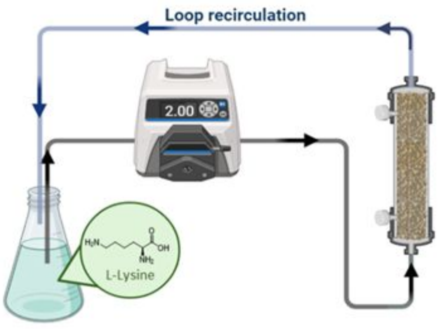


Fig. 2. Set up for in situ GO modification. The L-Lysine solution is recirculated by a peristaltic pump through PSU-GO cartridge.

ATR-FTIR spectra of PSU-GOLys composites (Fig. S3, ESI) were performed on granules before and after functionalization without highlighting any differences attributable to the Lysine grafting as most of the observed signal is ascribed to the PSU polymer. The surface chemical composition and L-Lysine loading of the PSU-GO composites were analysed by X-ray photoelectron spectroscopy (XPS). The XPS survey spectra are shown in Fig. 4 while the atomic compositions of the pristine and L-Lysine-modified PSU-GO samples are summarized in Table 1. As shown in Scheme 1, the colour of PSU-GO granules within the cartridge darkened after reacting with L-Lysine. This change can be attributed to the partial reduction of GO under the reaction conditions (basic nucleophile and thermal treatment),[35, 9] and it is confirmed by XPS analysis which show an increase in the C/O ratio from 4.2 to 4.5 for PSU-GO-A and from 3.6 to 4.3 for PSU-GO-B (Table 1). The surface of the materials predominantly consists of carbon, oxygen, sulphur and nitrogen, corresponding to i) the aliphatic C-C, C-S, and aromatic C=C regions of PSU and GO, ii) the C-O/C-O-C/C=O/S=O functionalities from both PSU and GO, iii) the sulfonated groups of PSU and GO, and iv) the nitrogen functional groups (C-N) of L-Lysine (Section 4, ESI). The successful covalent functionalization of GO is confirmed by the N 1s signal, which arises from the bound amino acid. As expected, higher L-Lysine loading was achieved for PSU-GOLys-B with higher GO extent, i.e. 10% w/w GO/PSU, with the nitrogen content increasing from 0.7% to 1.9% after functionalization, corresponding to an L-Lysine loading of about 6%. On the other hand, the nitrogen content increased from 0.8% for pristine PSU-GO-A to 1.5% for PSU-GOLys-A, corresponding to a Lys-loading of 3.5%. To confirm the successful lysine modification of PSU-GO

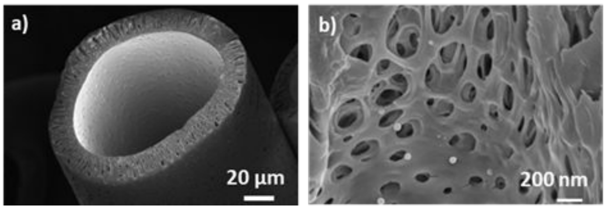


Fig. 3. SEM images of a) PSU-GO granule cross section and b) the pores.

View Article Online
DOI: 10.1039/D5LF00105F

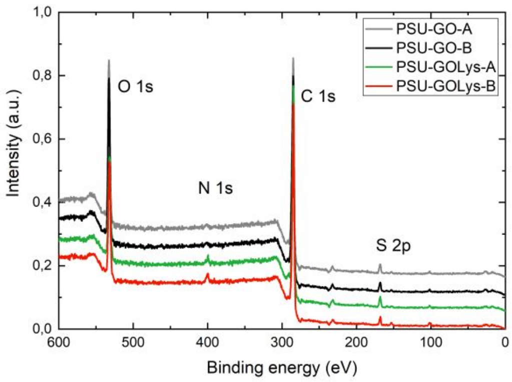


Fig. 4. XPS survey spectra of PSU-GO and PSU-GOLys composites.

Table 1. Atomic composition of PSU-GO and PSU-GOLys obtained by XPS

Composites	C (%)	O (%)	N (%)	S (%)	C/O	Loading
PSU-GO-A	78.4	18.5	0.8	2.3	4.1	-
PSU-GO-B	76.5	21.2	0.7	1.6	3.6	-
PSU-GOLys-A	78.7	17.6	1.5	2.2	4.5	3.5 %
PSU-GOLys-B	78.6	18.1	1.9	1.4	4.3	6 %

composites, we performed adsorption experiments on carbamazepine (CBZ) comparing pristine PSU-GO-A/B with PSU-GOLys-A/B. This choice was supported by both literature reports on its preferential interaction with amino acid-modified GO materials [21] [22] and by preliminary selectivity tests conducted under batch and flow conditions on a mixture of six emerging organic contaminants (Fig. S5, ESI). As expected, batch experiments revealed a significantly higher CBZ removal for GO-Lys (65%) compared to unmodified GO (13%) after 15 minutes of contact time (Fig. S6a, ESI). The same trend is observed in flow-through experiments (Fig S6b-c, ESI), carried out with the same configuration used for Lysine functionalization (Fig. 5a). PSU-GOLys-A removed 58% of CBZ compared to 35% for PSU-GO-A, while PSU-GOLys-B achieved 84% removal, compared to 60% for PSU-GO-B. The enhanced selectivity toward CBZ adsorption was then used as a functional probe to assess the effectiveness of Lysine modification in the PSU-GO composite granules. A control experiment was performed using a PSU cartridge (without GO) treated with Lysine under the same conditions used for PSU-GO composites functionalization, to exclude non-covalent interaction with the polymer and possible side-adsorption effect on CBZ. The resulting material, PSU@Lys, showed poor CBZ removal performance similar to pristine PSU, confirming that lysine functionalization requires the presence of GO for effective modification, rather than occurring through nonspecific adsorption on the polymer (Fig. S7, ESI). Fig. 5b-c presents the CBZ removal performance of pristine PSU-GO and modified PSU-GOLys cartridges under continuous flow conditions. The introduction of GO and L-Lysine into PSU led to a significant enhancement in CBZ removal efficiency compared to pristine PSU. Specifically, PSU-GOLys-A demonstrated an initial CBZ removal rate of 64%, outperforming PSU-GO-A (41%), and PSU (16%). After filtering 200 mL of CBZ-spiked water, PSU-GOLys-A maintained a removal efficiency of around 40%, while PSU-GO-A and PSU dropped to 12% and 5%, respectively. After treating 600 mL of CBZ solution, complete breakthrough occurred for all tested modules, with the total CBZ uptakes of 107.2 µg/g for PSU-GOLys-A, 27.5 µg/g for PSU-GO-A, and 6.6 µg/g for PSU (Fig. S8a, ESI). Similarly, PSU-GOLys-B exhibited the highest initial removal rate among all tested materials, reaching 87% removal efficiency. Within the first 500 mL of treated water, PSU-GOLys-B maintained a 60% CBZ removal rate, achieving complete breakthrough after treating 1 L of solution, with a total adsorption capacity of 259.5 µg/g, substantially higher than that of PSU-GO-B (66.5 µg/g) and PSU (Fig. S8b, ESI).

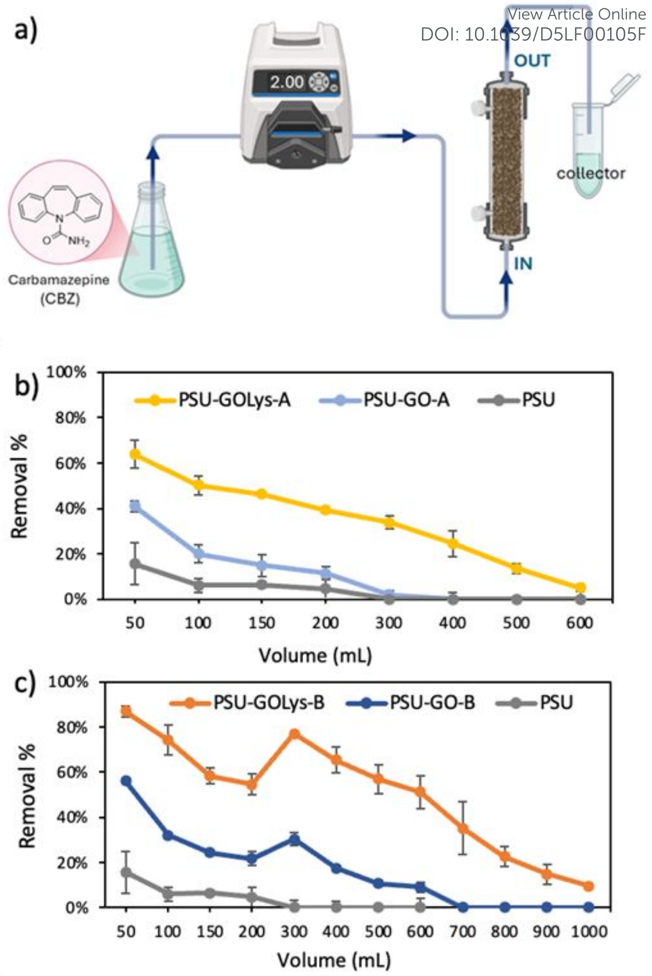


Fig. 5. a) Experimental set up used for the adsorption test of CBZ and removal performance of b) PSU, PSU-GO-A and PSU-GOLys-A and c) PSU, PSU-GO-B and PSU-GOLys-B.

In summary, we have presented a novel approach for the functionalization of GO nanosheets embedded in a polymeric matrix. The proposed protocol, which utilizes water for both synthesis and workup, was specifically developed for the preparation of PSU-GO granular composites derived from industrial plastic waste. Successful in-situ functionalization of GO with L-Lysine was confirmed by X-ray photoelectron spectroscopy (XPS) and further supported by adsorption tests on CBZ in water. The adsorption test not only validated the successful functionalization but also highlighted the potential of

View Article Online
DOI: 10.1039/D5LF00105F

PSU-GOLys cartridges for drinking water treatment, with CBZ adsorption increasing fourfold following chemical modification. The post-production modification of GO-based composites, such as PSU-GO, offers a scalable, cost-effective method to tailor the interface properties of these materials, thereby broadening their range of applications without altering the fabrication processes.

The authors gratefully acknowledge the support of this work by the projects Life-Remembrance, ENV/IT/001001 Life Resource and Environment LIFE20 'Give plastic wastes from the production of hollow-fiber membranes a second life', project PNRR MUR project ECS_00000033_ECOSISTER, 'Le materie prime del futuro da fonti non-critiche, residuali e rinnovabili' (FUTURAW, FOE 2022).

Conflicts of interest

There are no conflicts to declare.

Data availability

Notes and references

1. X. Huang, X. Qi, F. Boey and H. Zhang, *Chemical Society Reviews*, 2012, **41**, 666-686.
2. A. Razaq, F. Bibi, X. Zheng, R. Papadakis, S. H. M. Jafri and H. Li, 2022, **15**, 1012.
3. B. Wang, T. Ruan, Y. Chen, F. Jin, L. Peng, Y. Zhou, D. Wang and S. Dou, *Energy Storage Materials*, 2020, **24**, 22-51.
4. N. Devi, R. Kumar, S. Singh and R. K. Singh, *Critical Reviews in Solid State and Materials Sciences*, 2024, **49**, 72-140.
5. M. Antunes and J. I. Velasco, *Progress in Polymer Science*, 2014, **39**, 486-509.
6. W.-H. Liao, S.-Y. Yang, J.-Y. Wang, H.-W. Tien, S.-T. Hsiao, Y.-S. Wang, S.-M. Li, C.-C. M. Ma and Y.-F. Wu, *ACS Applied Materials & Interfaces*, 2013, **5**, 869-877.
7. J. Phiri, P. Gane and T. C. Maloney, *Materials Science and Engineering: B*, 2017, **215**, 9-28.
8. M.-C. Hsiao, S.-H. Liao, M.-Y. Yen, P.-I. Liu, N.-W. Pu, C.-A. Wang and C.-C. M. Ma, *ACS Applied Materials & Interfaces*, 2010, **2**, 3092-3099.
9. S. Guo, S. Garaj, A. Bianco and C. Ménard-Moyon, *Nature Reviews Physics*, 2022, **4**, 1-16.
10. X. Wang, Y. Liu, H. Pang, S. Yu, Y. Ai, X. Ma, G. Song, T. Hayat, A. Alsaedi and X. Wang, *Chemical Engineering Journal*, 2018, **344**, 380-390.
11. K. Thakur and B. Kandasubramanian, *Journal of Chemical & Engineering Data*, 2019, **64**, 833-867.
12. A. I. A. Sherlala, A. A. A. Raman, M. M. Bello and A. Asghar, *Chemosphere*, 2018, **193**, 1004-1017.
13. S. Mantovani, S. Khaliha, L. Favaretto, C. Bettini, A. Bianchi, A. Kovtun, M. Zambianchi, M. Gazzano, B. Casentini, V. Palermo and M. Melucci, *Chemical Communications*, 2021, **57**, 3765-3768.
14. X. Liu, J. Li, X. Wang, C. Chen and X. Wang, *Journal of Nuclear Materials*, 2015, **466**, 56-64.
15. Y. Qi, M. Yang, W. Xu, S. He and Y. Men, *Journal of Colloid and Interface Science*, 2017, **486**, 84-96.
16. G. Moro, S. Khaliha, A. Pintus, S. Mantovani, M. Feltracco, A. Gambaro, T. D. Marforio, M. Calvaresi, V. Palermo, M. Melucci and C. Zanardi, *Materials Today Chemistry*, 2024, **36**, 101936.
17. S. Mantovani, T. D. Marforio, S. Khaliha, A. Pintus, A. Kovtun, F. Tunioli, L. Favaretto, A. Bianchi, M. L. Navacchia, V. Palermo, M. Calvaresi and M. Melucci, *Environmental Science: Water Research & Technology*, 2023, **9**, 1030-1040.
18. F. Tunioli, T. D. Marforio, L. Favaretto, S. Mantovani, A. Pintus, A. Bianchi, A. Kovtun, M. Agnes, V. Palermo, M. Calvaresi, M. L. Navacchia and M. Melucci, 2023, **29**, e202301854.
19. H. Yan, H. Wu, K. Li, Y. Wang, X. Tao, H. Yang, A. Li and R. Cheng, *ACS Applied Materials & Interfaces*, 2015, **7**, 6690-6697.
20. V. Georgakilas, J. N. Tiwari, K. C. Kemp, J. A. Perman, A. B. Bourlinos, K. S. Kim and R. Zboril, *Chemical Reviews*, 2016, **116**, 5464-5519.
21. S. Mantovani, S. Khaliha, T. D. Marforio, A. Kovtun, L. Favaretto, F. Tunioli, A. Bianchi, G. Petrone, A. Liscio, V. Palermo, M. Calvaresi, M. L. Navacchia and M. Melucci, *Chemical Communications*, 2022, **58**, 9766-9769.
22. F. Tunioli, S. Khaliha, S. Mantovani, A. Bianchi, A. Kovtun, Z. Xia, M. S. S. Bafqi, B. S. Okan, T. D. Marforio, M. Calvaresi, V. Palermo, M. L. Navacchia and M. Melucci, *Journal of Environmental Chemical Engineering*, 2023, **11**, 109566.
23. Y. Ma and Y. Chen, *National Science Review*, 2014, **2**, 40-53.
24. G. Nassar, E. Daou, R. Najjar, M. Bassil and R. Habchi, *Carbon Trends*, 2021, **4**, 100065.
25. J. Ma, D. Ping and X. Dong, 2017, **7**, 52.
26. A. S. de León, M. de la Mata, F. J. Delgado and S. I. Molina, 2022, **307**, 2100784.
27. M. Zambianchi, S. Khaliha, A. Bianchi, F. Tunioli, A. Kovtun, M. L. Navacchia, A. Salatino, Z. Xia, E. Briñas, E. Vázquez, D. Paci, V. Palermo, L. Bocchi, B. Casentini and M. Melucci, *Journal of Membrane Science*, 2022, **658**, 120707.
28. S. Khaliha, F. Tunioli, L. Foti, A. Bianchi, A. Kovtun, T. D. Marforio, M. Zambianchi, C. Bettini, E. Briñas, E. Vázquez, L. Bocchi, V. Palermo, M. Calvaresi, M. L. Navacchia and M. Melucci, *Environmental Science: Water Research & Technology*, 2024, **10**, 1097-1107.
29. E. Avram, B. Elena, L. Cornelia and I. and Druta, *Journal of Macromolecular Science, Part A*, 1997, **34**, 1701-1714.
30. N. E. Temnikova and O. V. Stoyanov, *Polymer Science, Series D*, 2024, **17**, 140-148.
31. O. S. Serbanescu, S. I. Voicu and V. K. Thakur, *Materials Today Chemistry*, 2020, **17**, 100302.
32. O. Dumbrava, A. Filimon and L. Marin, *European Polymer Journal*, 2023, **196**, 112316.
33. C. B. Rosen and M. B. Francis, *Nature Chemical Biology*, 2017, **13**, 697-705.
34. M. D. Guiver, G. P. Robertson and S. Foley, *Macromolecules*, 1995, **28**, 7612-7621.
35. N. G. de Barros, A. C. Gonzaga Neto, K. B. Vaccioli, H. R. V. Angulo, L. G. de Andrade e Silva, S. M. Toffoli and T. S. Valera, 2023, **9**, 73.

View Article Online
DOI: 10.1039/D5LF00105F

Data availability

Electronic Supplementary Information. Materials, PSU-GO functionalization with Lysine, Scanning Electron Microscopy (SEM), X-Ray Photoelectron spectroscopy (XPS), Carbamazepine (CBZ) adsorption test in flow conditions, Experimental conditions for CBZ analysis “This material is available free of charge via the Internet at http:// https:/rsc.org.”