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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 embedded in the polymer composite. Enhanced carbamazepine removal from water is demonstrated for PSU-GOLys filled cartridges.

Graphene-based composites have shown significant potential across various applications,<sup>1</sup> ranging from sensors and flexible electronics,<sup>2</sup> advanced energy storage systems<sup>3</sup> and environmental remediation applications.<sup>4</sup> Due to its processability, water dispersibility, and superior chemical versatility, graphene oxide (GO) has been widely exploited as a component in composite tailoring.<sup>5–7</sup> The presence of a variety of oxygenated functional groups (*i.e.* hydroxyl, epoxide, and carboxyl groups) on the GO nanosheet 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.<sup>8,9</sup> The surface chemistry tunability of GO nanosheets has recently been widely exploited to tune the adsorption properties toward water organic and metallic contaminants.<sup>10–12</sup> In this scenario, several examples of modification strategies have been developed, including the use of polyethyleneimine and triethyl-phosphate for toxic metal adsorption,<sup>13,14</sup> polysaccharides and amino acids (AA) for targeting organic pollutants,<sup>15–17</sup> and cyclodextrin (CD)

for the removal of per- and polyfluoroalkyl substances.<sup>18</sup> The adsorption mechanism has been widely explored, demonstrating that the reactivity is related to the balance of different energy contributions, including van der Waals forces (VDW), electrostatic interactions and  $\pi$ - $\pi$  stacking interactions.<sup>19,20</sup> On this line, we recently reported a study on amino acid-modified GO that demonstrates that the shape complementarity between the AA pendant and contaminant molecules enhances 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 an emerging water contaminant, with the maximum adsorption capacity two orders of magnitude higher than that of pristine GO.<sup>21</sup> 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.<sup>22</sup> While a number of GO composites such as foams, aerogels, and membranes have been reported in the last years,<sup>23–25</sup> 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 León *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.<sup>26</sup>

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). These granules are obtained by grinding the waste of the production of Graphisulfone® membranes<sup>27</sup> and have been already exploited as sorbents for drinking water treatment.<sup>28</sup> The chemical stability of the PSU polymer requires the use of activating agents and organic solvents for surface functionalization,<sup>29,30</sup> making post-production modifications

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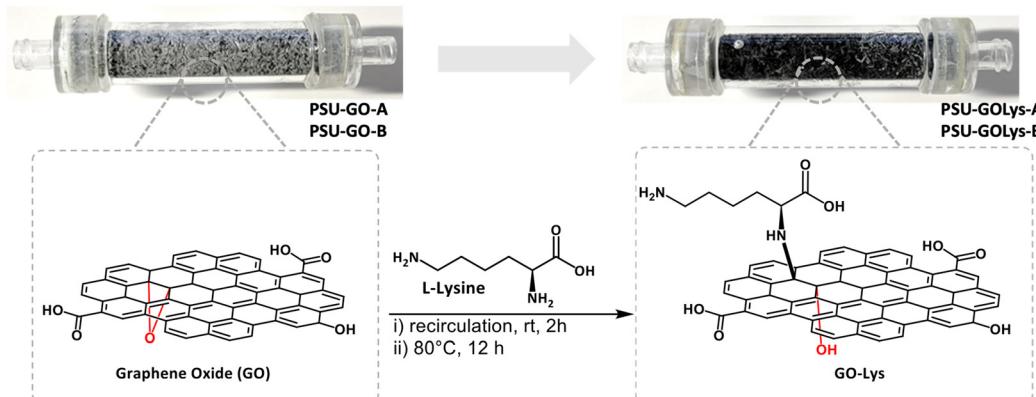
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† Electronic supplementary information (ESI) available: Materials, PSU-GO functionalization with lysine, SEM, XPS, and the carbamazepine (CBZ) adsorption test under flow conditions. See DOI: <https://doi.org/10.1039/d5lf00105f>

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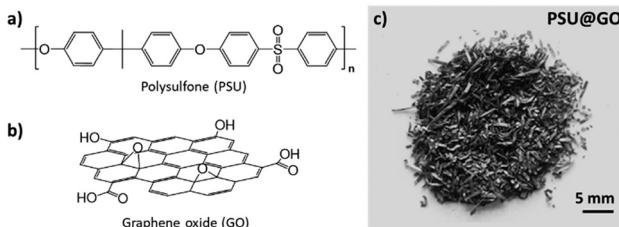


**Scheme 1** *In situ* lysine functionalization of GO embedded in PSU-GO granules with two different GO amounts (A: 3.5% w/w and B: 10% w/w PSU/GO).

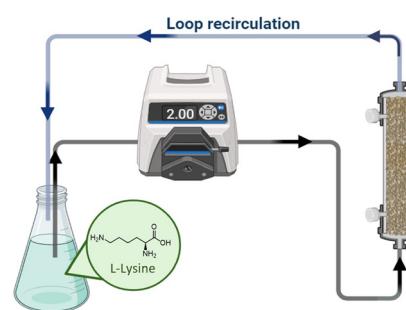
under mild conditions unfeasible and thereby limiting the ability to fine-tune the surface properties and adsorption selectivity of PSU membranes.<sup>31,32</sup> Here, we aim at exploiting the GO nanosheets embedded in the polymer structure to tune the adsorption properties of PSU granules. *In situ* synthesis of GO-Lys in PSU-GO filled cartridges was performed by loop recirculation of an aqueous solution of L-lysine. PSU-GO with different GO % amounts (*i.e.* PSU-GO-A with 3.5% w/w and PSU-GO-B with 10% w/w GO/PSU ratios) were modified with lysine by an epoxide ring-opening reaction (Scheme 1).<sup>9</sup> The reaction was carried out under basic conditions (pH 9.7) to ensure that the alpha-NH<sub>2</sub> of lysine was unprotonated and available for reaction as the nucleophilic moiety.<sup>21,33</sup> The PSU structure does not include electrophilic groups available for direct amination, so in the exploited conditions the reaction is expected to involve only GO.<sup>34</sup> 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<sup>-1</sup> for 2 h (Fig. 2). Then, the cartridges were kept at 80 °C overnight, to facilitate the formation of a 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 S2, 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 and b) with surface

pores in the range 5–10 µm. The characteristic porous structure of the hollow fiber granules is preserved after lysine functionalization,<sup>27,28</sup> indicating that the synthetic process does not significantly alter the overall morphology of the granules.

ATR-FTIR spectra of PSU-GOLys composites (Fig. S3, ESI†) were recorded 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),<sup>9,35</sup> and it is confirmed by XPS analysis that shows 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



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



**Fig. 2** Set up for *in situ* GO modification. The L-lysine solution is recirculated using a peristaltic pump through the PSU-GO cartridge.



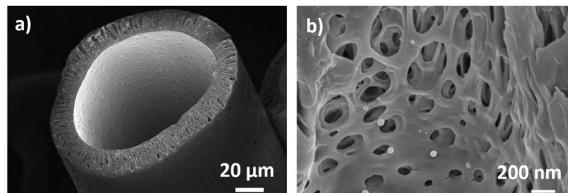


Fig. 3 SEM images of a) the cross section of a PSU-GO granule and b) the pores.

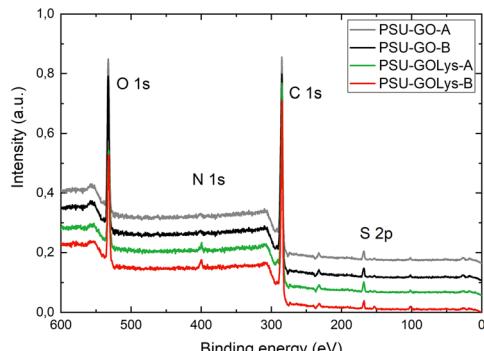


Fig. 4 XPS survey spectra of PSU-GO and PSU-GOLys composites.

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%

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 S4, 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 a 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 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<sup>21,22</sup> 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 and 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 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 composite functionalization, to exclude non-covalent interactions with the polymer and the 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 and c present 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

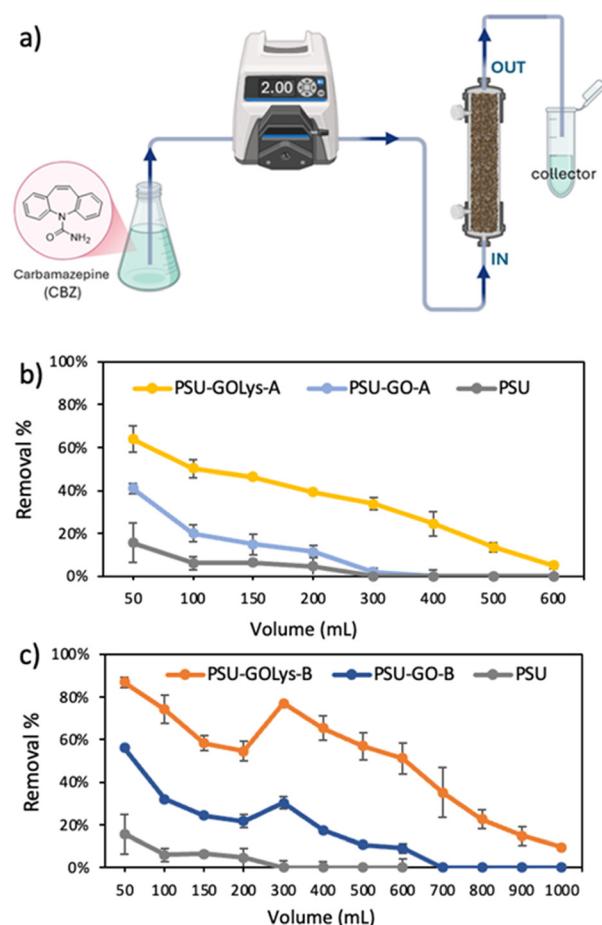


Fig. 5 a) Experimental setup used for the adsorption test of CBZ and the removal performance of b) PSU, PSU-GO-A and PSU-GOLys-A and c) PSU, PSU-GO-B and PSU-GOLys-B.



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 retained a removal efficiency of around 40%, while that of PSU-GO-A and PSU dropped to 12% and 5%, respectively. After treating 600 mL of the CBZ solution, complete breakthrough occurred for all tested modules, with a total CBZ uptake of  $107.2 \mu\text{g g}^{-1}$  for PSU-GOLys-A,  $27.5 \mu\text{g g}^{-1}$  for PSU-GO-A, and  $6.6 \mu\text{g g}^{-1}$  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 retained a 60% CBZ removal rate, achieving complete breakthrough after treating 1 L of the solution, with a total adsorption capacity of  $259.5 \mu\text{g g}^{-1}$ , substantially higher than those of PSU-GO-B ( $66.5 \mu\text{g g}^{-1}$ ) and PSU (Fig. S8b, ESI†).

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 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.

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## Data availability

ESI† Materials, PSU-GO functionalization with lysine, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), the carbamazepine (CBZ) adsorption test under flow conditions, and experimental conditions for CBZ analysis.

## Conflicts of interest

There are no conflicts to declare.

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