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Effective and sustainable removal of a model fluorescent brightener using bicarbonate-loaded polyelectrolytes in a closed-loop CO₂ cycle

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Fluorescent brighteners (FBs), currently recognised as emerging contaminants, require effective removal from aquatic environments. However, no practical methods exist due to their high water solubility, the formation of toxic byproducts upon decomposition, and the lack of repeatable absorbent regeneration. This study demonstrates the efficient removal of a fluorescent brightener from water using cationic polyelectrolytes loaded with bicarbonates. Poly(allylammonium bicarbonate) (PAAm-BC), obtained from commercially available poly(allylamine) (PAA) by capturing carbonic acid, effectively removed disodium 4,4'-bis(2-sulfostyryl)biphenyl (DSBP) from water through ion exchange. The removal efficiency reached nearly 100%, independent of the molecular weight of PAAm-BC. The bicarbonate-loaded polymer incorporated DSBP as an electrostatic cross-linker; the incorporated DSBP aligned within the polymer composites, generating directional regions in their morphology. Under basic conditions (pH 12), the composites completely released DSBP, regenerating PAA, which reloaded bicarbonates upon CO₂ introduction and enabled subsequent removal. This reversible removal process, achieved through repeated basification and CO₂ introduction in a closed-loop CO₂ cycle, is potentially applicable to a wide range of anionic pollutants and offers a promising strategy for improving aquatic environments.

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Introduction

Anthropogenic contaminants have severely degraded the global environment through improper treatment and increasing emissions from households, facilities and industries. Emerging contaminants include micro- and nanoplastics from waste plastics, per- and polyfluoroalkyl substances (PFAS), liquid crystal monomers, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, radionuclides, toxic agrochemicals, synthetic pesticides and antibiotic resistance genes in modified bacteria.^{1,2} These pollutants disperse into the atmosphere, infiltrate soil and run off into rivers and oceans,^{3,4} where they undergo further degradation and solubilisation. Consequently, they cause serious diseases through contaminated food and water and *via* the food web, leading to biodiversity loss and ecosystem disruption.⁵

Fluorescent brighteners (FBs) have recently emerged as overlooked contaminants. Although their toxicity was noted decades ago, they long received little attention, as they were considered safe and unlikely to cause serious effects such as carcinogenicity, mutagenicity or teratogenicity.^{6–9} However, recent studies report that FBs can induce diseases, including

gene mutations and eczema, and are now recognised as thyroid hormone-disrupting chemicals.^{10,11} Among them, disodium 4,4'-bis(2-sulfostyryl)biphenyl (DSBP) is the most widely used FB and serves as a benchmark for assessing FB pollution in aquatic environments. DSBP exhibits higher toxicity than synthetic surfactants such as alkyl- and alkylbenzene sulfonates (ABSs), and even greater toxicity than PFAS, due to its strong binding affinity for human transthyretin, where it acts as a thyroid hormone ligand through its two sulfonate groups.¹⁰ DSBP has also been shown to interact with the estrogen receptor¹² and with human serum albumin (HSA).¹³ Given that HSA is the most abundant carrier protein in the circulatory system and delivers substances to diverse organs, the high DSBP–HSA affinity poses significant risks to multiple organ systems.^{14,15}

DSBP is a common additive in industrial and household products, including detergents, dyes, fibres, plastics, papers, cosmetics and food,^{3,16–23} as well as in medical and agricultural applications.^{24,25} Its high structural stability and poor biodegradability^{6,26–28} promote bioaccumulation, while its high solubility in water (17.6 g L⁻¹ at 20 °C) makes its removal from aquatic environments difficult. Several approaches have been attempted for DSBP removal, including chemical methods such as detoxification by photodegradation,^{17,28–30} oxidation with hypochlorite³¹ and complexation with viologen.³² However, these approaches can generate secondary pol-

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ing 3.57×10^{-3} mmol) was added to the PAAm-BC solution (10 mL containing 0.0357 mmol of AAm-BC) at 25 °C with stirring. The mixture was stirred for 3 min at 25 °C, then allowed to stand at this temperature for 10 min without stirring, and subsequently subjected to light scattering to measure scattering intensity and hydrodynamic size, as well as UV analysis to determine transmittance.

FE-SEM observations

Precipitates were obtained by adding DSBP (80.2 mg, 0.143 mmol) dissolved in water (4 mL) to a PAAm-BC solution prepared from PAA (106.2 mg of a 15 wt% solution, corresponding to 15.93 mg (0.279 mmol) of AA) in water (78 mL) through CO₂ introduction. The precipitates were isolated by suction filtration and dried under vacuum for 3 h. The resulting yellow polymer composite powder was then subjected to FE-SEM measurements at 0.7 kV without coating.

Removal of DSBP

Water (77.0 mL) was added to PAA (105.1 mg of a 15 wt% solution, corresponding to 15.77 mg (0.276 mmol) of AA and 89.3 mg of water), resulting in $[AA]_0 = 3.58 \times 10^{-3}$ mol L⁻¹. CO₂ was introduced into the solution at 25 °C with stirring by bubbling at a flow rate of 300 mL min⁻¹ for 30 min to obtain a PAAm-BC solution. DSBP (79.0 mg, 0.140 mmol) dissolved in water (4 mL) was then added dropwise to the PAAm-BC solution over 8 min at 25 °C under stirring, followed by an additional 2 min of stirring at the same temperature. Sodium hydroxide (1.1094 g, 27.735 mmol) was dissolved in water (10.05 mL). At 25 °C with stirring, aliquots (0.2 mL, containing 0.552 mmol) of the NaOH solution were added sequentially to the polymer composite solution containing the precipitates until complete release of DSBP was confirmed by UV absorbance. After each 0.2 mL addition, the mixture was subjected to pH measurement and UV analysis, in which a 0.1 mL aliquot of the mixture was diluted with water (10 mL) for DSBP absorbance determination.

Results and discussion

The capture of DSBP by PAAm-BC through ion exchange was investigated by stirring the mixture in water at 25 °C for 10 min. UV analysis demonstrated that DSBP was effectively captured, serving as an electrostatic cross-linker of PAAm-BC (Fig. 2), and that this cross-linking induced aggregation of the polymer composites. Fig. 3 shows the UV spectra of the mixtures of DSBP with PAAm-BC or PAA at a DSBP molar ratio of 0.5 to the allylammonium unit (DSBP/AAm) or the allylamine unit (DSBP/AA). The DSBP–PAA mixture exhibited characteristic absorption originating from DSBP, although the absorbance decreased by approximately 25% because the strong CO₂-absorbent PAA slightly captured CO₂ from the air during handling. In contrast, the mixture with PAAm-BC showed no absorption, owing to cross-linkable ion exchange with DSBP, which resulted in incorporation of DSBP into the precipitates of their insoluble composites (Fig. S1).

Fig. 4A shows the variations in transmittance, scattering intensity (SI) and hydrodynamic size (D_h) of PAAm-BC as a function of the DSBP/AAm ratio when DSBP was added to the PAAm-BC solutions derived from *L*-PAA, *M*-PAA and *H*-PAA

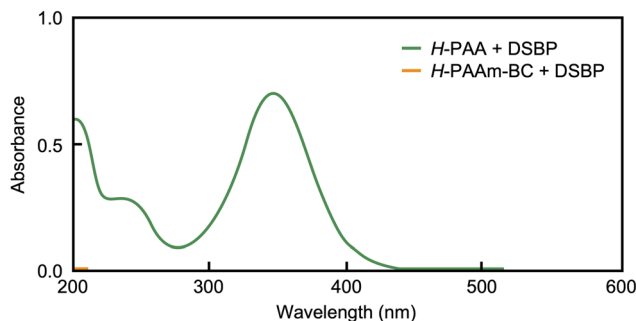


Fig. 3 UV spectra of the DSBP–PAA and DSBP–PAAm-BC mixtures. DSBP/AAm = DSBP/AA = 0.5. $[AA]_0 = [AAm-BC]_0 = 3.57 \times 10^{-3}$ mol L⁻¹.

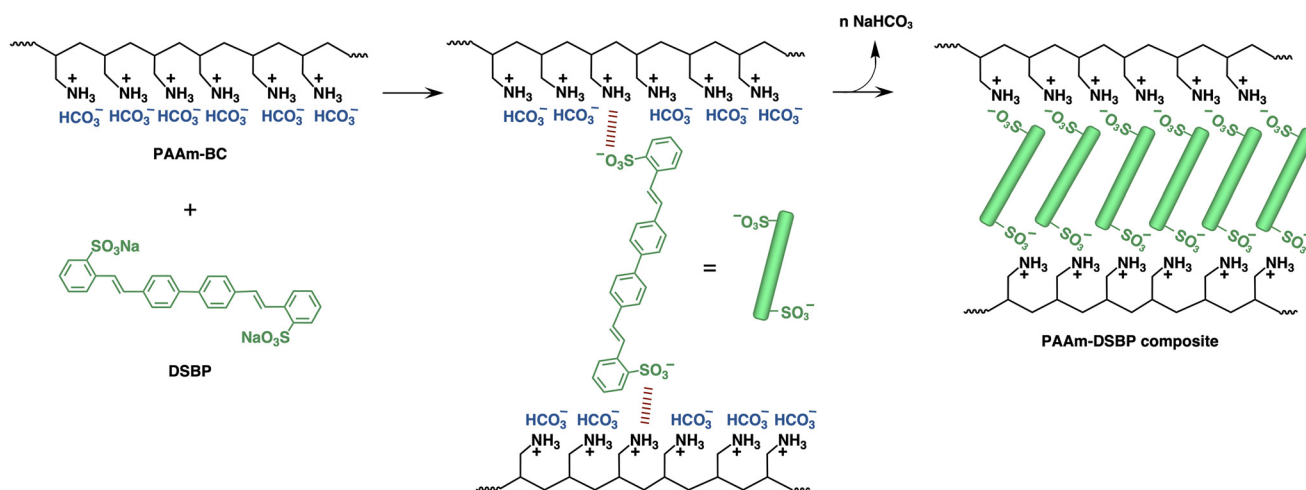


Fig. 2 Capture of DSBP by the bicarbonate-loaded polyelectrolytes through ion exchange.



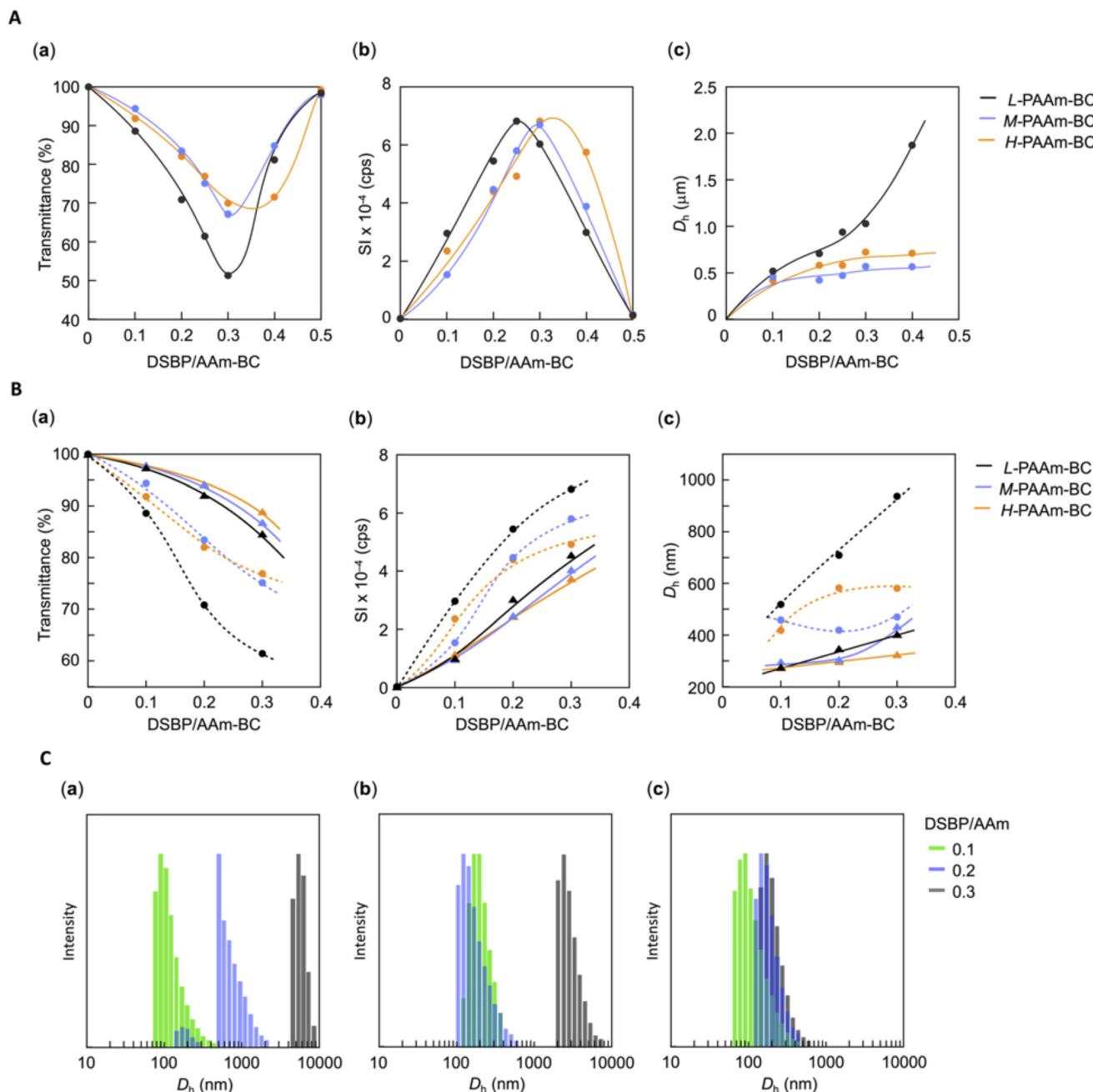


Fig. 4 (A) Variations in (a) transmittance, (b) scattering intensity and (c) hydrodynamic diameter of DSBP-captured PAAm-BC as a function of the DSBP/AAm-BC ratio. $[AAm-BC]_0 = 3.57 \times 10^{-3} \text{ mol L}^{-1}$. (B) Variations in (a) transmittance, (b) scattering intensity and (c) hydrodynamic diameter of DSBP-captured PAAm-BC as a function of the DSBP/AAm-BC ratio. $[AAm-BC]_0 = 3.57 \times 10^{-3} \text{ mol L}^{-1}$ (dashed line) and $1.78 \times 10^{-3} \text{ mol L}^{-1}$ (solid line). (C) Weight conversion distributions in light scattering for (a) *L*-PAAm-BC, (b) *M*-PAAm-BC and (c) *H*-PAAm-BC at DSBP/AAm = 0.1, 0.2 and 0.3. $[AAm-BC]_0 = 1.78 \times 10^{-3} \text{ mol L}^{-1}$.

(denoted *L*-PAAm-BC, *M*-PAAm-BC and *H*-PAAm-BC, respectively). Upon addition of DSBP, the transmittance decreased more readily and to a greater extent for the shorter PAAm-BC, suggesting that the shorter PAAm-BC chains aggregate more easily through the ion exchange with DSBP. The transmittance decreased continuously up to a DSBP/AAm ratio of 0.30–0.35 and then increased beyond this ratio due to precipitation of

the insoluble aggregates. At a ratio of 0.5, the transmittance was fully restored owing to the complete precipitation of the aggregates. Consistent with the transmittance changes, the SI exhibited maxima around a DSBP/AAm ratio of approximately 0.3. The maximum shifted to a lower ratio for the shorter PAAm-BC, indicating that the shorter chains facilitated aggregation. The D_h results revealed that *L*-PAAm-BC formed signifi-



cantly larger aggregates than *M*-PAAm-BC and *H*-PAAm-BC, suggesting that *L*-PAAm-BC tended to aggregate intermolecularly, whereas *M*-PAAm-BC and *H*-PAAm-BC primarily promoted intramolecular association.

PAAm-BC potentially facilitates intramolecular association in dilute solution. The solutions of PAAm-BC up to a DSBP/AAm ratio of 0.3, in which no precipitates were observed, were investigated in detail to clarify the aggregation behavior. Fig. 4B shows the transmittance, SI and D_h for the solutions at half the concentration of PAAm-BC. PAAm-BC showed only slight differences in transmittance and SI among the chain lengths, but a difference was discerned with increasing the DSBP/AAm ratio. In particular, *L*-PAAm-BC exhibited an increase in D_h as the DSBP ratio increased, whereas *H*-PAAm-BC showed a negligible change in D_h regardless of the DSBP ratio. In contrast, *M*-PAAm-BC initially showed D_h values comparable to those of *H*-PAAm-BC up to a DSBP ratio of 0.2; however, at a ratio of 0.3, the D_h of *M*-PAAm-BC approached that of *L*-PAAm-BC. This change implies that *M*-PAAm-BC undergoes a transition from intramolecular association to intermolecular aggregation.

The weight-conversion distribution analysis corroborated these aggregation behaviors (Fig. 4C). The distribution of *L*-PAAm-BC shifted markedly toward a higher D_h region as the DSBP ratio increased, whereas *H*-PAAm-BC exhibited only a slight shift at a ratio of 0.2 and no further shift at 0.3. In contrast, the distribution of *M*-PAAm-BC remained unchanged at a ratio of 0.2 but shifted toward a higher D_h region at 0.3. These observations indicate that the short PAAm-BC chains form insoluble complexes with DSBP, subsequently promoting intermolecular aggregation, whereas the long chains undergo intramolecular cross-linking *via* DSBP and remain as single-molecular aggregates. PAAm-BC of the intermediate chain length initially undergoes intramolecular association, followed by a transition to intermolecular aggregation.

The aggregation behavior determined the aggregate size, which in turn governed the precipitation rate. This was visually confirmed from photographs of the solutions at different DSBP ratios (Fig. 5 and Fig. S2). UV analysis further revealed that all DSBP molecules were incorporated into the precipitates of the polymer composites, demonstrating complete removal of DSBP from the aqueous solution (Fig. 6). The removal efficiencies of DSBP were nearly 100%, regardless of the molecular weight of PAAm-BC.

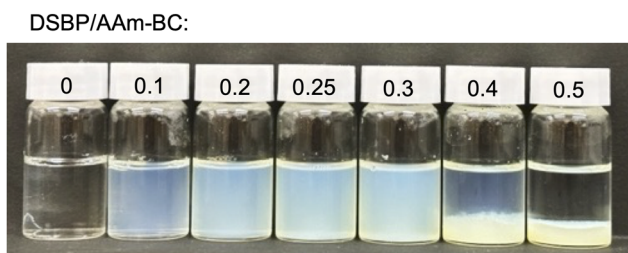


Fig. 5 A photograph of *L*-PAAm-BC solutions at different DSBP ratios.

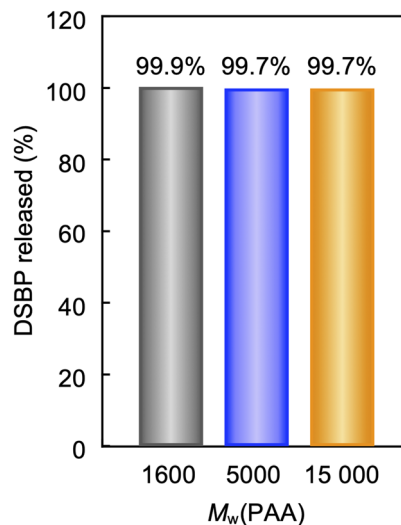


Fig. 6 Removal efficiencies of DSBP for PAA with different molecular weights. DSBP/AAm = 0.5.

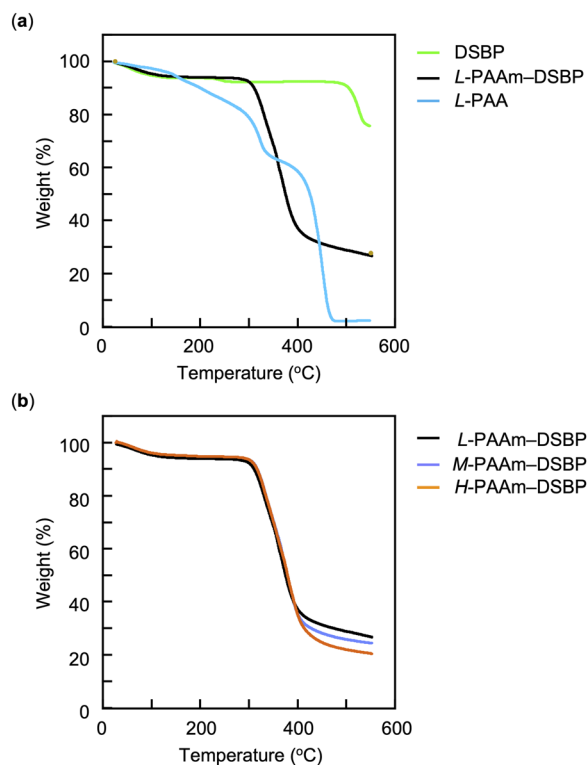


Fig. 7 TGA curves of (a) *L*-PAAm-DSBP composites (DSBP/AAm-BC = 0.5), *L*-PAA and DSBP and (b) *L*-PAAm-DSBP, *M*-PAAm-DSBP and *H*-PAAm-DSBP composites (DSBP/AAm = 0.5).

The composites with a DSBP/AAm ratio of 0.5 were isolated to evaluate thermal stability. Fig. 7 shows the TGA curves of the composites, together with those of PAA and DSBP. The composites displayed a sharp weight loss at 306.6 °C, independent of the molecular weight of PAAm-BC. This degradation corresponded to the first degradation step of PAA, observed at





Fig. 8 DSC curves of *L*-PAAm-DSBP composites (DSBP/AAm-BC = 0.5), *L*-PAA and DSBP.

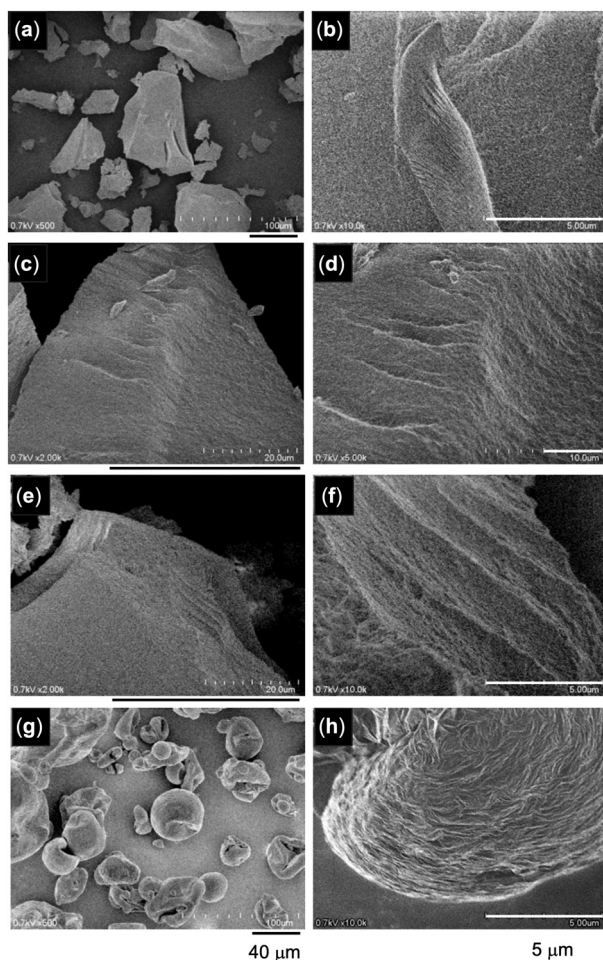


Fig. 9 FE-SEM images of (a and b) *L*-PAAm-DSBP composites, (c and d) *M*-PAAm-DSBP composites, (e and f) *H*-PAAm-DSBP composites and (g and h) DSBP. Black scale bars: 40 μm ; white scale bars: 5 μm .

307.0 $^{\circ}\text{C}$. Whereas PAA exhibited a second degradation at 422.2 $^{\circ}\text{C}$, the composites showed no further weight loss and ultimately left a residue. This incomplete degradation resulted from the high thermal stability of DSBP, which decomposed only above 500 $^{\circ}\text{C}$ (Fig. S3).

DSC analysis revealed isotropic crystalline regions with disordered orientation in the composites (Fig. 8). These regions, originating from DSBP, extended from 40 to 150 $^{\circ}\text{C}$ with a peak maximum at 88.9 $^{\circ}\text{C}$. The slightly lower melting point compared with pure DSBP suggested that the polymer chains in the composites hindered DSBP crystallisation. Melting of these regions was followed by that of the ammonium sulfonate moieties at 299.7 $^{\circ}\text{C}$. This thermal behaviour was also unaffected by the molecular weight of PAAm-BC (Fig. S4).

The DSBP incorporated into the composites strongly influenced their morphology. While pure DSBP formed spherical particles with fine surface lines, the DSBP in the composites produced a cleavage-like morphology (Fig. 9). The linear and rigid DSBP molecules aligned within the composites through cross-linking of the polymer chains, creating directional regions in the composite structure. This morphological



Fig. 10 UV absorbance of DSBP released from *L*-PAAm-DSBP composites at different pH values.

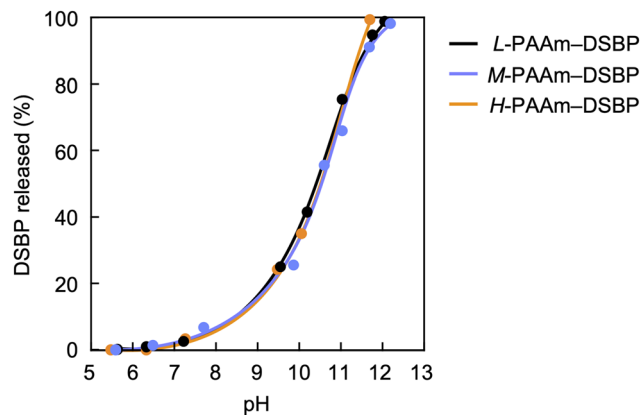


Fig. 11 Release efficiency of DSBP as a function of pH, determined from UV absorbance at $\lambda = 348 \text{ nm}$.



change suggests that DSBP not only serves as a cross-linker but also directs the internal organisation of the polymer matrix.

The composites efficiently released the DSBP under basic conditions. As shown in Fig. 10, UV absorbance originating from DSBP increased with increasing pH, indicating release of DSBP molecules from the composites (Fig. S5). Plotting the absorbance at 348 nm *versus* pH confirmed complete release at approximately pH 12 (Fig. 11). Under such strongly basic conditions, the composites dissociated completely, releasing DSBP and regenerating deprotonated PAA (Fig. 12). This pH-dependent release of DSBP was independent of the molecular weight of PAAm-BC. Introduction of CO₂ into the basic solution reloaded bicarbonate



Fig. 13 Reversible capture and release of DSBP by *L*-PAAm-BC over repeated pH-change cycles, determined from UV absorbance at $\lambda = 348$ nm.



Fig. 12 Release of DSBP from the polymer composites under basic conditions.

onto PAA, enabling recapture of DSBP. This capture and release of DSBP was completely reversible through repeated cycles of CO₂ introduction and basification, corresponding to loading and unloading of carbonic acid on PAA (Fig. 13 and Fig. S6). Thus, complete removal of this toxic additive by the bicarbonate-loaded absorbent, together with its full regeneration, was achieved in a sustainable closed-loop CO₂ cycle.

Conclusions

The bicarbonate-loaded polyelectrolyte, generated by capturing carbonic acid in water with a polymeric amine, effectively captured and removed the sulfonate-based fluorescent brightener from contaminated water through ion exchange. The bicarbonate-loaded polymer incorporated the toxic additive as an electrostatic cross-linker into the precipitates of its polymer composites. The low-molecular-weight polymer more readily captured the additive through intermolecular aggregation, whereas the high-molecular-weight polymer favoured intramolecular association. The medium-molecular-weight polymer underwent intramolecular association at low additive ratios and transitioned to intermolecular aggregation at higher ratios. The polymer composites released the fluorescent brightener completely under basic conditions, dissociating and reverting to the original polymeric amine. Upon CO₂ introduction, the polymeric amine reloaded bicarbonate and recaptured the pollutant. This reversible capture–release cycle enabled full regeneration of the absorbent through repeated CO₂ introduction and basification. The process relies on loading and unloading bicarbonate ions from the absorbent, establishing a sustainable closed-loop CO₂ cycle. This method for removing fluorescent brighteners is broadly applicable to a wide range of anionic pollutants, including sulfonate-based surfactants and dyes, per- and polyfluoroalkyl sulfonates and other toxic chemicals from diverse industrial fields such as medical care, food processing and dyeing, offering a promising approach to global environmental preservation.



- 35 M. Mustafa, E. I. Epelle, A. Macfarlane, M. Cusack, A. Burnsc and M. Yaseen, *RSC Adv.*, 2025, **15**, 12125–12151.
- 36 J. Han, X. Tang, Y. Wang, J. Li, L. Ni and L. Wang, *Water Environ. Res.*, 2017, **89**, 281–287.
- 37 I. Casero, D. Sicilia, S. Rubio and D. Pérez-Bendito, *Anal. Chem.*, 1999, **71**, 4519–4526.
- 38 A. Koutsianos, L. B. Hamdy, C. Yoo, J. J. Lee, M. Taddei, J. M. Urban-Klaehn, J. Dryzek, C. W. Jones, A. R. Barron and E. Andreoli, *J. Mater. Chem. A*, 2021, **9**, 10827–10837.
- 39 E. Yoshida, *Colloid Polym. Sci.*, 2010, **288**, 1321–1325.
- 40 E. Apuzzo, M. Agazzi, S. E. Herrera, A. Picco, G. Rizzo, C. Chavero, D. Bianchi, P. Smaldini, M. L. Cortez, W. A. Marmisolle, G. Padula, A. Seoane, M. L. Alomar, M. P. Denofrio, G. Docena and O. Azzaroni, *ACS Appl. Bio Mater.*, 2023, **6**, 4714–4727.
- 41 E. Yoshida, *RSC Sustainability*, 2024, **2**, 1837–1848.
- 42 J. Kothandaraman, A. Goeppert, M. Czaun, G. A. Olah and G. K. S. Prakash, *Green Chem.*, 2016, **18**, 5831–5838.
- 43 A. A. Olajire, *Energy*, 2010, **35**, 2610–2628.
- 44 J. Zhang, Y. Qiao, W. Wang, R. Misch, K. Hussain and D. W. Agar, *Energy Procedia*, 2013, **37**, 1254–1261.
- 45 T. N. Borhani and M. Wang, *Renewable Sustainable Energy Rev.*, 2019, **114**, 109299.
- 46 Y. Shen, C. Jiang, S. Zhang, J. Chen, L. Wang and J. Chen, *Appl. Energy*, 2018, **230**, 726–733.
- 47 D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, 1963, **11**, 431–441.

