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Self-Sustaining Supramolecular Ionic Liquid Gels for Dye Adsorption

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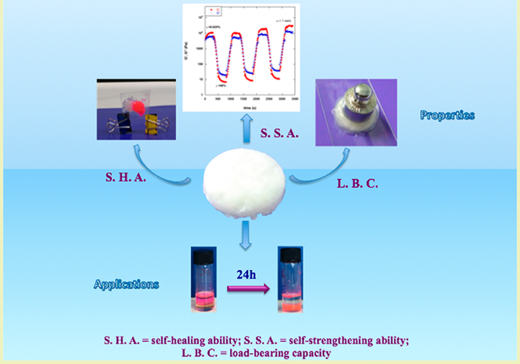
Supporting Information

ABSTRACT: Water contamination is one of the main problems of modern society, and scientific research is continuously involved in identifying solutions able to preserve this valuable source. In this context, we characterized novel ionogels formed by organic salts with different anions. In particular, they show self-strengthening behavior, a quite unusual property for supramolecular gels, and they also exhibit a good load-bearing capacity. These ionogels are able to remove cationic dyes from wastewater. Thanks to their properties, they can be used in different apparatuses like dialysis membranes and as loading in adsorption columns. In the latter case over 95% removal is achieved in less than 10 min. Interestingly, soft materials can be reused for at least 20 cycles, partially regenerated, and reused for further 15 cycles. Comparison with data previously reported in the literature shows that this is a prerogative of this system and this represents not only an improvement but also a warranty of low raw material production after wastewater treatment.



KEYWORDS: *Supramolecular gels, Ionic liquids, Dye removal, Self-sustaining gels, Recyclable materials*

INTRODUCTION

Water pollution is one of the main problems of modern society. Industrial activities cause the release of large amounts of pollutants, like heavy metals,[1] oils,[2] aromatic compounds, and among these also dyes.[3] The main consequence is the reduction of potable water that is already a limited source.

Dyes are used in different industrial sectors, from textile to printing, plastics, food, cosmetics, paper, and so on. This explains why the annual production of dyes overcomes 700 000 tons.[4] Unfortunately, notwithstanding strict environmental regulations about their discharge and improvements in dyeing processes, more than 15% of total production is yearly released in the environment. Most dyes are thermally stable and not biodegradable.[5,6] Furthermore, some of them and their metabolites are carcinogenic.[7] From an environmental point of view, they can also affect photosynthetic activity.[5]

All above drawbacks justify the growing interest of the scientific community in identifying efficient methods for dyes removal from wastewaters. Accordingly, physical, biological, and chemical methods have been proposed.[8−10] However, removal processes are in some cases conditioned by some issues like low remediation efficiency, high-running cost, and labor-intensity operation.

Among physical methods, adsorption is one of the most widely used. Different kinds of adsorbents have been proposed like polymers,[11] metal−organic frameworks,[12] carbon-based materials,[13] natural fibers,[14] and inorganic materials like halloysite nanotubes.[15] However, in the past few years, also gel phases and in particular supramolecular gels have been proposed as a viable alternatives.[16−19] They are formed by feeble and cooperative interactions established among low molecular weigth gelators (LMWGs), which result in the formation of a self-assembled fibrillary network able to trap solvent molecules.[20−22]

When they are used in dye removal, their main advantage resides in the highly porous 3D network, with high surface area and numerous adsorption sites enabling fast and effective adsorption of dyes. To this aim, different organo- and

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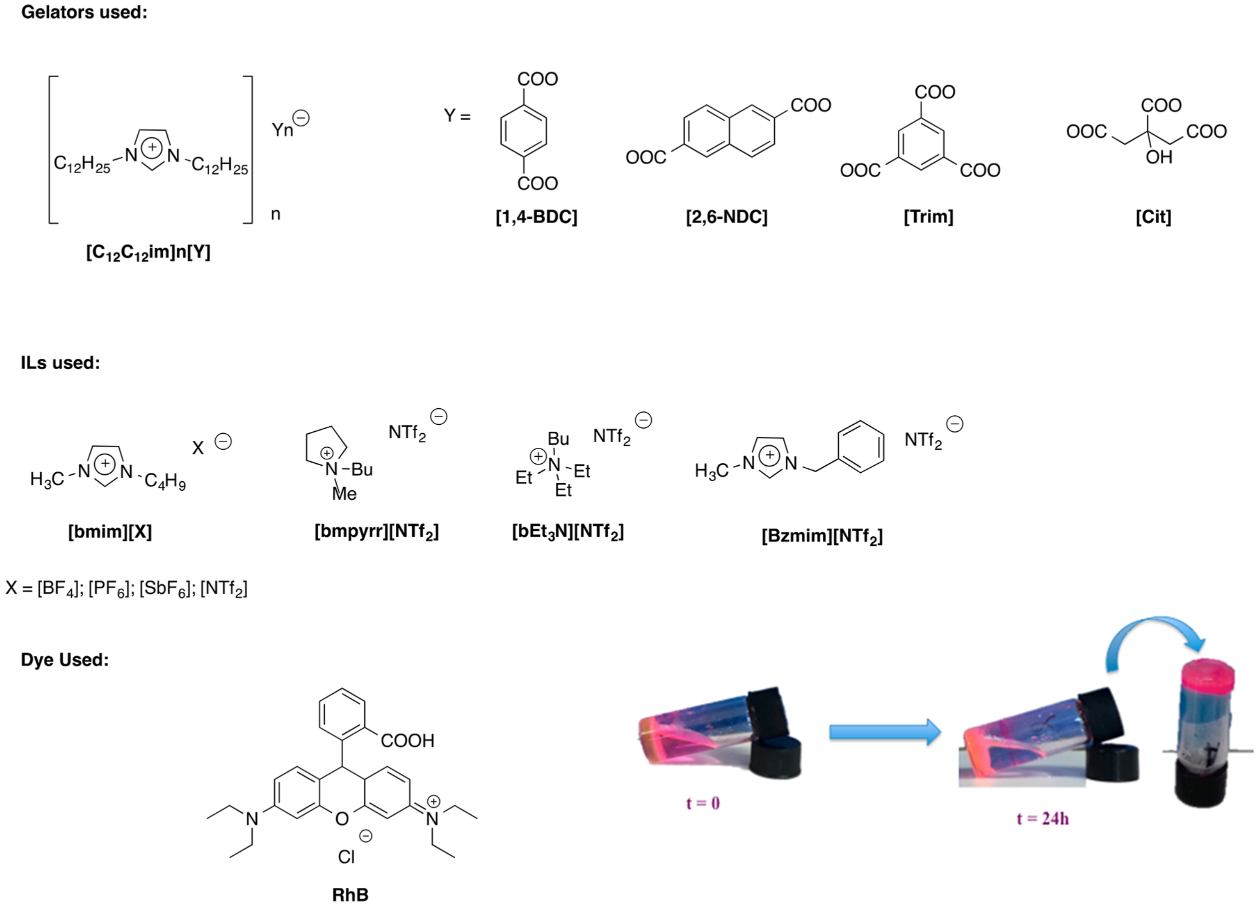
Scheme 1. Structures of Gelators, ILs and Dye Used; Schematic Representation of the Adsorption Process



hydrogelators have been synthesized and used in either their gel or xerogel phase.[16,17]

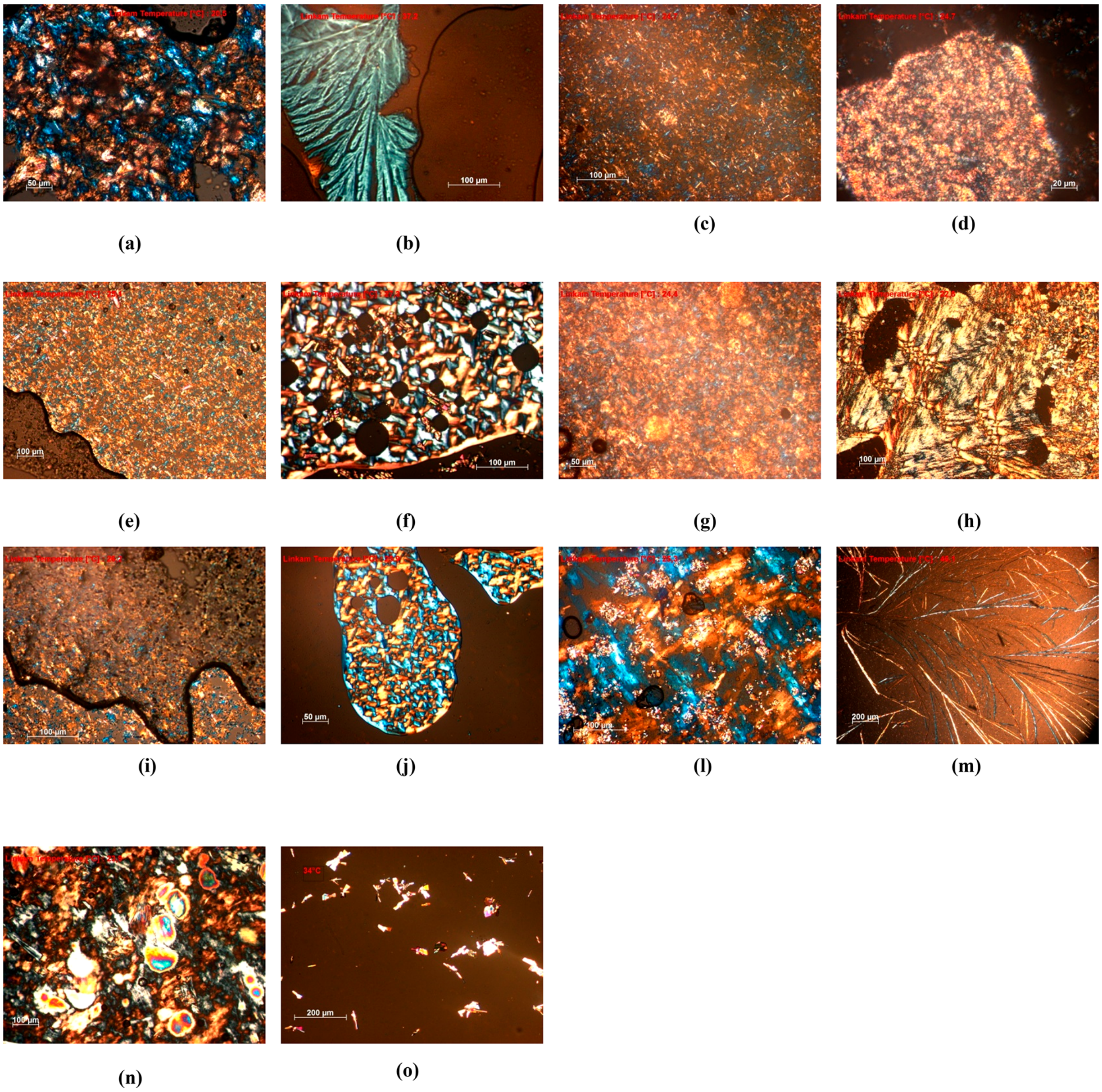
Nevertheless, if the use of gel phase rather than xerogel is taken into account, the nature and toxicity of gelation solvent must be considered. In this light, the use of ionogels, i.e., gel formed by ionic liquids (ILs), could prove a viable alternative. Indeed, ILs have attracted a growing interest in different fields of chemistry and are considered eco-friendly alternatives to organic solvents thanks to their low vapor pressure and flammability, high thermal and chemical stability.[23−25] Among others, it has been demonstrated that they are efficient extractants of dyes from wastewaters.[16,26,27] Furthermore, ILs can be conveniently used as additives to improve dyeing fibers process.[28] Ionogels formed by amino acid based gelators in [bmim][PF_6] solution have also been investigated.[29] However, even if they enabled good dye removal efficiency, no recyclability of the ionogel or its use in dynamic systems have been considered.

To address the above drawbacks, we tested new ionogels for dye removal. In particular, remembering how IL[30,31] and supramolecular gel[32−34] properties influence their applications, we investigated the gelling ability of some didodecylimidazolium-based ([$\mathbf{C_{12}C_{12}im}$]$^+$) salts differing for the anion nature. The selected cation recalls the proven gelating ability of didodecylimidazolium dicationic salts previously studied.[35] However, in this case, the lack of the aromatic spacer between the two charged heads should improve its environmental sustainability. However, carboxylate anions also awarded good gelating ability to organic salts.[35] Consequently, 1,4-benzenedicarboxylate ([**1,4-BDC**]), 2,6-naphthalenedicarboxylate ([**2,6-NDC**]), trimesate ([**Trim**]), and citrate ([**Cit**]), differing in the nature of the spacer and the number of charged heads, were associated with [$\mathbf{C_{12}C_{12}im}$]$^+$.

Gelling ability was tested both in conventional solvents and in ILs. Solvents having different polarities and hydrogen bond donor abilities were chosen. However, we used both aliphatic and aromatic ILs and, in the case of imidazolium-based ones, the effect due to a different sizes, shapes, and coordination abilities of the anion ([BF_4]$^-$, [PF_6]$^-$, [SbF_6]$^-$, [NTf_2]$^-$) was analyzed (Scheme 1).

To better modulate application of our gel phases, we first performed a complete investigation of their properties (gel−sol transition temperature, kinetic of gel phase formation, morphology, self-repairing ability, rheological behavior). The soft materials showed very interesting properties, like self-strengthening ability and good load-bearing capacity.

Then, we tested the removal efficiency of gel phases toward a cationic dye like Rhodamine B (RhB) in a static system or in a dialysis membrane or immobilized in a column as adsorbent. In the latter case, a removal efficiency of over 95% was obtained in less than 10 min. To the best of our knowledge, this is one of the few works addressing this subject, going beyond the simple static batch experiments. Finally, data collected show that our ionogels can be reused for at least 20 cycles and, after partial regeneration, for further 15 cycles allowing a low production of raw materials at the end of remediation process.



(a) (b) (c) (d)

(e) (f) (g) (h)

(i) (j) (l) (m)

(n) (o)

Figure 1. POM images of gel phases at 5 wt % of gelators at 25 °C: **(a)** **$[C_{12}C_{12}im]_2[1,4\text{-}BDC]$/DMSO** preformed gel and (b) after cooling of isotropic solution, image taken at 37 °C; (c) **$[C_{12}C_{12}im]_2[1,4\text{-}BDC]$/[bmim][$BF_4$]** preformed gel and (d) after cooling of isotropic solution; (e) **$[C_{12}C_{12}im]_2[2,6\text{-}NDC]$/[bmim][$BF_4$]** preformed gel and (f) after cooling of isotropic solution; (g) **$[C_{12}C_{12}im]_3[Trim]$/[bmim][BF_4]** preformed gel and (h) after cooling of isotropic solution; (i) **$[C_{12}C_{12}im]_3[Cit]$/[bmim][BF_4]** preformed gel and (j) after cooling of isotropic solution; (l) **$[C_{12}C_{12}im]_2[2,6\text{-}NDC]$/[Bzmim][$NTf_2$]** preformed gel aged 4 days and (m) after cooling of isotropic solution, image taken at 46 °C; (n) **$[C_{12}C_{12}im]_2[2,6\text{-}NDC]$/[Bzmim][$NTf_2$]** "fresh" preformed gel and (o) after cooling of isotropic solution, image taken at 34 °C. All images were taken at 20× magnification.

■ RESULTS AND DISCUSSION

Gelation Tests and Thermal Stability. Gelation tests were carried out both in conventional solvents and in ILs (Table S1 and S2). In general, salts used were soluble in alcohols and glycerol, but insoluble in highly polar solvents like water, phosphate buffer, ethylene, and triethylene glycols. However, in most cases, they were completely soluble in DMSO and DMF. The only exception was represented by $[C_{12}C_{12}im]_2[1,4\text{-}BDC]$ that was able to gel DMSO.

Differently, our salts were able to gel ILs. Indeed, we obtained ionogels in almost all ILs tested. In all cases, we obtained white and thermoreversible gels that remained stable to the tube inversion test[36] for at least four months at room temperature. We determined the critical gelation concentration (CGC), i.e., the minimum amount of gelator needed for gel formation. In general, this parameter ranged from 1.2 up to 5.0% wt, without particular effect due to the different anion nature or salt stoichiometry.

We also measured temperatures corresponding to gel−sol transition (T_{gel}) at the CGC, using the lead-ball method.[37] These values ranged from 16 up to 39 °C (see Supporting Information and Table S2).

To compare properties of gels obtained, we chose a common concentration (5 wt %), which was used to perform the full characterization of gel phases.

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Table 1. Values of G', G'', tan δ, and γ at the Point of Moduli Inversion Obtained as Average Values of Three Measurements on Three Different Aliquots of Gels at 5 wt % (Values at γ = 0.025% and ω = 1 rad/s)

gel	G'	G''	tan δ	γ at $G' = G''$
$[C_{12}C_{12}im]_2[1,4\text{-}BDC]$/DMSO	5900 ± 1000[a]	1500 ± 500[a]	0.25 ± 0.07[a]	49.8 ± 0.5
$[C_{12}C_{12}im]_2[2,6\text{-}NDC]/[Bzmim][NTf_2]$ (4 nights)	4800 ± 960	2500 ± 300	0.54 ± 0.05	0.54 ± 0.09
$[C_{12}C_{12}im]_2[2,6\text{-}NDC]/[Bzmim][NTf_2]$ (1 night)	1100 ± 400	500 ± 140	0.48 ± 0.03	0.63 ± 0.08
$[C_{12}C_{12}im]_2[2,6\text{-}NDC]/[bmim][BF_4]$	2600 ± 400	750 ± 340	0.32 ± 0.06	3.96 ± 0.01
$[C_{12}C_{12}im]_2[1,4\text{-}BDC]/[bmim][BF_4]$	7000 ± 500	2100 ± 200	0.30 ± 0.01	3.96 ± 0.01
$[C_{12}C_{12}im]_3[Cit]/[bmim][BF_4]$	1080 ± 60	380 ± 80	0.35 ± 0.07	3.96 ± 0.01
$[C_{12}C_{12}im]_3[Trim]/[bmim][BF_4]$	9000 ± 4000	2700 ± 700	0.32 ± 0.07	3.96 ± 0.01

[a] At γ = 0.08%.

Morphology of Gel Phases. Morphology of ionogels was analyzed by using POM investigation (Figure 1). In all cases, the analysis was performed as a function of the temperature, and after melting of soft materials, we obtained isotropic solutions.

In general, images obtained by casting preformed gels showed different features than those obtained after casting of the isotropic solutions. In this latter case, we observed more ordered structures and more pronounced differences in morphologies. Conversely, images taken from preformed gels showed quite similar textures, irrespective of solvent and gelator used (Figure 1a,b,e−h).

Comparison between POM images corresponding to **$[C_{12}C_{12}im]_2[1,4\text{-}BDC]$/DMSO** and **$[C_{12}C_{12}im]_2[1,4\text{-}BDC]/[bmim][BF_4]$** sheds light on the solvent effect. Indeed, the spherulitic network observed in DMSO (Figure 1b) changes in a thick texture in the ionogel (Figure 1d).

The anion effect is noticeable when POM images corresponding to above ionogel and **$[C_{12}C_{12}im]_2[2,6\text{-}NDC]/[bmim][BF_4]$** are compared. The $[2,6\text{-}NDC]^{2-}$ anion offers a better organization in the gel network (Figure 1f). A similar effect can be evidenced also in the case of **$[C_{12}C_{12}im]_3[Trim]/[bmim][BF_4]$** (Figure 1h). In this case, a spherulitic motif can be evidenced.

Interestingly, in the case of **$[C_{12}C_{12}im]_3[Cit]/[bmim][BF_4]$** also the cooling of the isotropic solution at room temperature awards the sample an ordered structure featured by colored phases (Figure 1j).

We also investigated the morphology of **$[C_{12}C_{12}im]_2[2,6\text{-}NDC]/[Bzmim][NTf_2]$**. For this ionogel, we performed analysis on sample rested overnight at 4 °C and on another one "aged" for 4 days. Surprisingly, morphologies detected were very different for the samples used. In the case of "fresh" ionogel, we detected a porous structure that formed small objects after cooling of the isotropic solution (Figure 1n,o). Differently, for the "aged" ionogel, we observed a thick texture with a dense lattice that under cooling of the isotropic solution gave rise to a spherulitic structure (Figure 1l,m). All above findings support the idea of a gradual reorganization of the gel network, during time, that modifies its properties and performance in the applications (see later).

Rheology Measurements. Properties of ionogels were also analyzed by performing rheological measurements. We applied classical analyses such as strain and frequency sweeps to have information about the strength of the gels.

In general, our samples featured viscoelastic behavior in dependence of the oscillation strain (γ). Indeed, a storage modulus (G') higher than the loss modulus (G'') was observed at low percentage of strain (solid-like behavior), whereas the opposite trend revealed at high percentage (liquid-like behavior). However, both moduli were independent of the angular frequency applied (ω) and higher G' values with respect to G'' ones well supported the gel nature of our samples (Figure S6).

All measurements were performed in the linear viscoelastic region (LVR). This allowed comparing properties of our soft materials, taking in consideration important parameters like tan $\delta(=G''/G')$ and the percentage of strain (γ) at which G' was equal to G'' (Table 1). γ allows evaluating the strength of colloidal forces operating in the gel network. However, tan δ represents the level of stress needed to detect the flow of a material.

Rheological measurements were performed on samples previously equilibrated for 4 days at 4 °C. However, to have information about the effect deriving from the aging of the gel phase, in the case of **$[C_{12}C_{12}im]_2[2,6\text{-}NDC]/[Bzmim][NTf_2]$**, rheology investigation was also performed after equilibrating the sample for one night.

In all cases, tan δ values were lower than 1, indicating a strong association among particles featuring gels. In general, the strength of colloidal forces decreased in the order: DMSO > $[bmim][BF_4]$ > $[Bzmim][NTf_2]$, evidencing the significant role played by the solvent nature. However, tan δ values collected in $[bmim][BF_4]$ were quite similar and show that gelator nature does not affect the stiffness of the materials.

The trend above-discussed about tan δ values is confirmed taking into account γ values. Indeed, γ values significantly decrease on going from DMSO to ILs, underlining the higher level of strain needed to break organo- than ionogels (**$[C_{12}C_{12}im]_2[1,4\text{-}BDC]$** as gelator). Notwithstanding the low number of comparisons, analysis of data collected considering **$[C_{12}C_{12}im]_2[2,6\text{-}NDC]/[Bzmim][NTf_2]$** and **$[C_{12}C_{12}im]_2[2,6\text{-}NDC]/[bmim][BF_4]$**, indicates the role played by the IL nature, as accounted for by the increase in γ value on going from the first to the second one. In general, when the IL cation is aromatic, the strength of the gel phase seems to be mainly determined by the cross-linking ability of the IL anion ($[BF_4]^-$ > $[NTf_2]^-$).[38]

Furthermore, aging of gel phases affects mechanical properties of soft materials. Indeed, data collected for **$[C_{12}C_{12}im]_2[2,6\text{-}NDC]/[Bzmim][NTf_2]$** clearly show that longer equilibration times induce a parallel increase in G' accounting for a stronger gelatinous network.

Response to External Stimuli. Ionogels were tested for their ability to self-repair after the action of external stimuli. In particular, we took into consideration their capability to re-form after being destroyed by magnetic stirring or ultrasound irradiation.

Thixotropic behavior has been widely investigated for supramolecular gels.[39] Differently, less attention has been

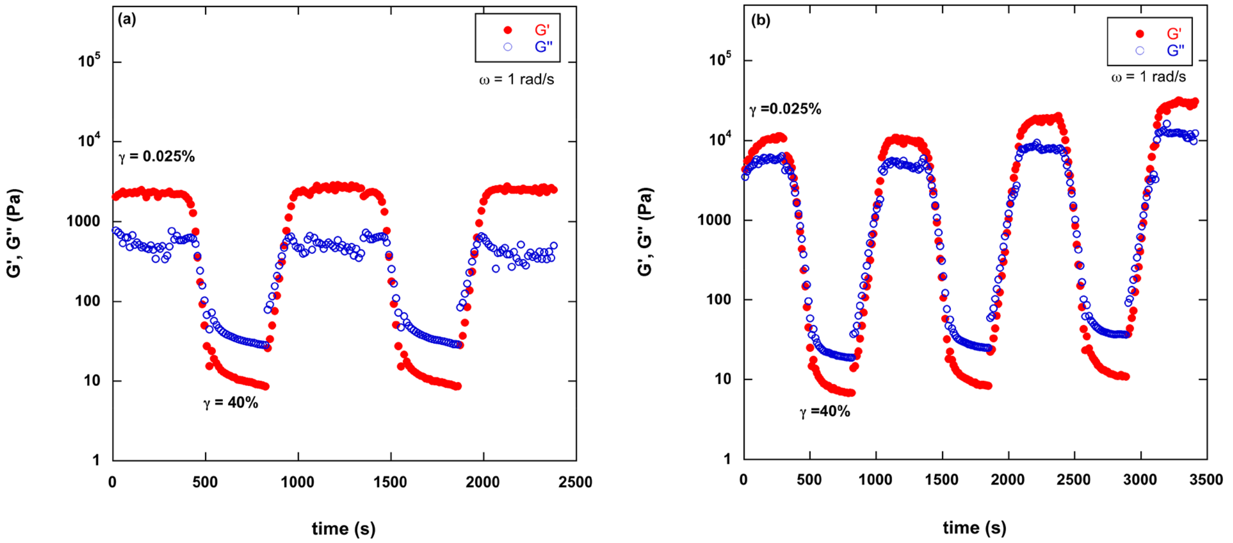

Figure 2. G' and G'' at 25 °C as a function of time and application of low ($G' > G''$ regimes, $\gamma = 0.025\%$) and destructive strain ($G'' > G'$ regimes, $\gamma = 40\%$) of (a) **$[C_{12}C_{12}im]_2[2,6\text{-}NDC]$/[bmim][$BF_4$]** at 5 wt % after 4 nights of equilibration at 4 °C and (b) **$[C_{12}C_{12}im]_2[2,6\text{-}NDC]$/[Bzmim][$NTf_2$]** at 5 wt % after 4 night of equilibration at 4 °C.

devoted to the analysis of sonotropic behavior, which recently has been evidenced in the case of supramolecular ionogels.[40] Both these properties result very interesting for applications of these soft materials. Results of both thixotropy and sonotropy tests are reported in Table S5.

In some cases, our ionogels were stable to the action of ultrasounds, while sonotropic behavior was detected only in the case of ionogels formed by **$[C_{12}C_{12}im]_2[2,6\text{-}NDC]$** in [bmim][$BF_4$], [bmpyrr][$NTf_2$], [$bEt_3N$][$NTf_2$], and [Bzmim][$NTf_2$]. Interestingly, some of these ionogels also showed thixotropic behavior. In particular, we detected the above ability in [bmim][PF_6], [bmim][BF_4], [bmim][SbF_6], [bEt_3N][NTf_2], and [Bzmim][NTf_2]. This underlines the practical potential of these ionogels that could be used under different experimental conditions without losing their performance.

Rheological investigation was further used to have a deeper understanding about the thixotropic behavior of our ionogels. The ionogel was subjected initially to conditions within LVR ($\gamma = 0.025\%$ and $\omega = 1$ rad/s) and then to destructive strain ($\gamma = 40\%$). The evolution of G' and G'' as a function of time, after cessation of destructive strain ($\gamma = 40\%$), is displayed in Figure 2 and Table 2.

Table 2. G' Recovery, at 25 °C, Measured after Cessation of Destructive Strain

ionogel		I cycle	II cycle	III cycle	IV cycle
$[C_{12}C_{12}im]_2[2,6\text{-}NDC]$/[bmim][$BF_4$]	G'	2461	2585	2483	
$[C_{12}C_{12}im]_2[2,6\text{-}NDC]$/[Bzmim][$NTf_2$]	G'	8923	9507	16734	27168

At least three destruction−recovery cycles were performed on each sample. In all cycles, we detected G' values higher than G'', confirming the gel nature of the sample. In the case of **$[C_{12}C_{12}im]_2[2,6\text{-}NDC]$/[bmim][$BF_4$]**, after three cycles, we observed 100% of G' recovery. We previously observed a similar behavior using ionogels formed by diimidazolium salts, but with a lower extent of recovery.[35]

With our surprise, a very different situation was detected using **$[C_{12}C_{12}im]_2[2,6\text{-}NDC]$/[Bzmim][$NTf_2$]**. Indeed, recovery of G' gradually increased from the first to the fourth cycle, reaching the 300% of the initial value (Table 2). This ionogel behaved as a self-strengthening gel and, to the best of our knowledge, this performance has never been reported for supramolecular gels. Rather, it has been observed for polymeric gels in response to a mechanical trigger.[41] In our case, it clearly indicates that after applying the destructive strain, the reorganization of the fibrillary network gave rise to the formation of a stronger material.

In light of this exciting result, we tested the ability to self-repair **$[C_{12}C_{12}im]_2[2,6\text{-}NDC]$/[Bzmim][$NTf_2$]** after being cut with incision. To this aim, we prepared two ionogels: a pure ionogel and a second one doped with 0.1 wt % Rhodamine B. The use of doped ionogel allowed better evidencing the renewal of the material also detectable by dye diffusion (Figure 3a).

After incision, the ionogels were put in contact and in 10 min we did not observe separation, pointing out the material restoration (Figure 3b). In addition, we clearly observed dye diffusion (Figure 3c) without any loss of self-supporting ability (Figure 3d) after 24 h.

To further study the mechanical properties of **$[C_{12}C_{12}im]_2[2,6\text{-}NDC]$/[Bzmim][$NTf_2$]**, we also investigated its self-sustaining nature. This property refers to the ability of gel phase to stand by itself without any support and retain its shape. The possibility of having self-sustaining gels has been reported for metal organogels,[42] but to the best of our knowledge, it has not been so far analyzed for ionogels.

The ionogel retained its initial cylindrical shape when it was pulled out from the container (Figure 4a). Furthermore, it showed a good load-bearing capacity. Indeed, it was able to hold metal or ceramic weights of 5, 10, 20, and 50 g (Figure 4b−e) without any compression and supported a limit pressure of about 15.9 g/cm^2.

Dye Adsorption. Once properties of ionogels were determined, we evaluated their adsorption ability. In particular, we paid attention to cationic dyes on the grounds of a recent report showing the marked selectivity of fully ionic supra-

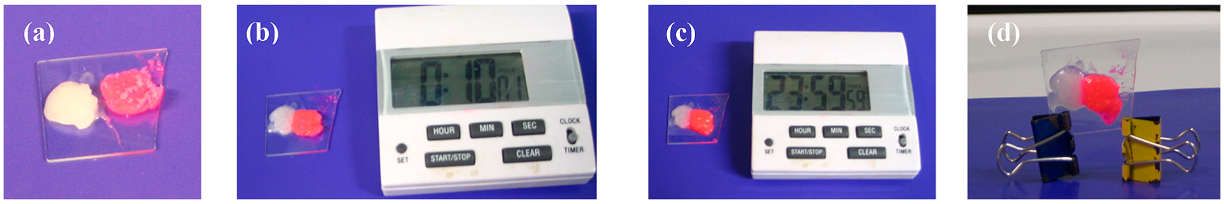

Figure 3. Self-repairing test for the **[C$_{12}$C$_{12}$im]$_2$[2,6-NDC]**/**[Bzmim][NTf$_2$]** at 5 wt % gelator at room temperature.

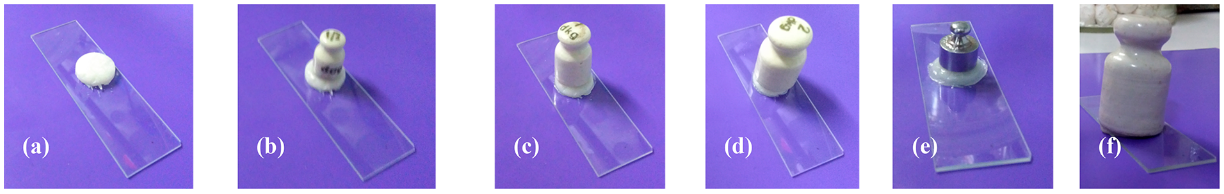

Figure 4. Test of self-sustaining ability of **[C$_{12}$C$_{12}$im]$_2$[2,6-NDC]**/**[Bzmim][NTf$_2$]** at 5 wt %: (a) without weight; (b) 5 g; (c) 10 g; (d) 20 g of ceramic; (e) 20 g of metal; (f) 50 g.

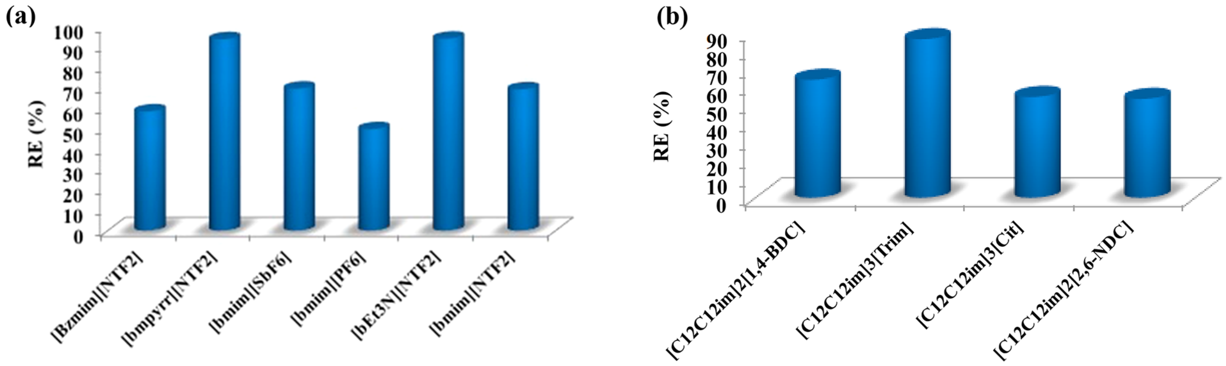

Figure 5. (a) RE of different **[C$_{12}$C$_{12}$im]$_2$[2,6-NDC]**-based ionogels, at 5 wt % as a function of IL nature and (b) RE of [Bzmim][NTf$_2$]-based ionogels, at 5 wt %, as a function of gelator nature (T = 25 °C; t = 4 h; [RhB] = 1.8×10^{-4} M). RE based on duplicate with reproducibility of 2%.

molecular gels toward such kind of dyes, and specifically we used RhB.[32]

First, we cast an aqueous solution of RhB on ionogels of **[C$_{12}$C$_{12}$im]$_2$[2,6-NDC]** in different ILs (Figure 5a and S7; Table S6).

With the only exception of **[C$_{12}$C$_{12}$im]$_2$[2,6-NDC]**/**[bmim][BF$_4$]**, which did not resist the contact with the aqueous solution, in all the other cases we observed a gradual discoloration of the aqueous phase and a concomitant coloration of the gel phases. The assessment of the residual concentration of RhB, on the grounds of a calibration curve, allowed obtaining the percentage of removal efficiency (RE) according to eq. 1:

$$\mathrm{RE} = 100 \cdot (C_0 - C_i / C_0) \tag{1}$$

where C_0 and C_i represent the initial concentration and the concentration of RhB at a given time, respectively.

RE depends on both the cation and anion nature of IL used as solvent. In particular, taking into consideration [bmim]$^+$-based ILs, RE decreases along the following trend: [bmim][NTf$_2$] ∼ [bmim][SbF$_6$] > [bmim][PF$_6$]. However, as far as the cation nature is taken into account, for [NTf$_2$]$^-$-based ILs, RE decreases along the order: [bmpyrr]$^+$ > [bEt$_3$N]$^+$ > [bmim]$^+$ > [Bzmim]$^+$, indicating a marked efficiency of aliphatic cations in the removal of the cationic dye.

As a second step, we evaluated the role played by the gelator nature. To this aim, we bore in mind that, from an applicative point of view, the material choice depends not only on its removal efficiency but also on its ease of use. In this case, the hydrophobic features of IL could play a significant role. Indeed, a hydrophobic IL, as a consequence of low water solubility, could avoid contamination of the supernatant. This is the reason why, we performed RhB removal in the experimental conditions above-discussed, using [Bzmim][NTf$_2$] as gelation solvent, notwithstanding its ionogel did not show the best performance (Figure 5a and Table S6).

Once again, data collected show that RE is affected by the gelator structure. In particular, the best removal efficiency was detected for **[C$_{12}$C$_{12}$im]$_3$[Trim]**/**[Bzmim][NTf$_2$]** while the lowest was obtained in the presence of **[C$_{12}$C$_{12}$im]$_3$[Cit]**/**[Bzmim][NTf$_2$]**. **[C$_{12}$C$_{12}$im]$_2$[2,6-NDC]**/**[Bzmim][NTf$_2$]** showed an intermediate behavior.

With the above results in mind, we decided to evaluate other operational aspects such as the time to obtain the best removal efficiency, the effect of gel's aging on the removal efficiency, the possibility of reusing the adsorption phase and loading it on a column or alternatively in a dialysis system. To analyze all above factors, we used the **[C$_{12}$C$_{12}$im]$_2$[2,6-NDC]**/**[Bzmim][NTf$_2$]** as model adsorption system on the grounds of thixotropic behavior, self-healing ability and load bearing capacity.

We first ruled out the occurrence of gel component release in the supernatant solution using ^{1}H NMR (Figure S8). Then, we performed adsorption experiments as a function of time.

We cast the aqueous solution of RhB on the gel phase and, after suitable contact time, we observed a gradual decrease of the typical adsorption band of RhB in the aqueous solution as a function of the time (Figure S9 and Table S8). Simultaneously, we detected an increased coloration of the gel phase.

Plot of RE as a function of time shows a typical hyperbolic trend, achieving over 80% of dye removal in the first 6 h. Then, RE increased slowly reaching over 98% of removal after 24 h (Figure S9b).

In consideration of the aging effect on the mechanical strength of gel phases, we verified if the same factor could affect the adsorption efficiency. To this aim, ionogels equilibrated at 4 °C, for different times (from 1 up to 7 nights), were used and their adsorption efficiency was determined after a contact time of 4 h (Table S9). Data collected demonstrate the role played by the aging of the ionogel on its ability to adsorb RhB, as accounted for by the gradual increase of RE on going from 1 up to 6 nights. This is why we performed the following tests using samples equilibrated for 4 nights, choosing a good compromise between time of equilibration and removal efficiency.

With the above information in mind, we also verified if aging preserved selectivity toward cationic dyes. To this aim, we determined the RE toward an anionic dye, like methyl orange (MO) obtaining a significantly lower RE value in 4 h, RE = 96 and 63% for RhB and MO, respectively (Figure S10).

To decrease the impact of the remediation intervention on the environment, we verified the reuse of our sorbent system. We observed that after a contact time of 24 h, the ionogel preserved its gel consistency, as assessed by the tube inversion test.[36] Furthermore, put in contact with a fresh aqueous sample, it was able to adsorb dye without any loss of efficiency (RE stayed constant at 98%) and could be reused for 20 cycles (Figure 6 and Table S10).

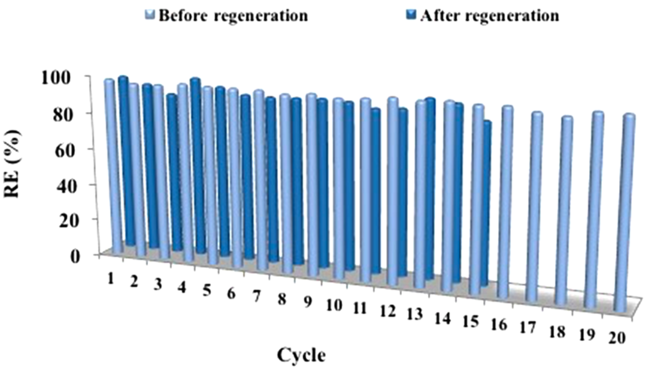

Figure 6. Cycles of reusing of $[C_{12}C_{12}im]_2[2,6\text{-NDC}]/[Bzmim][NTf_2]$ at 5 wt % in the adsorption of RhB (1.8×10^{-4} M) at 25 °C and after 24 h. RE based on duplicate with reproducibility of 2%.

Encouraged by the above results, we tried to regenerate the polluted sorbent. We observed that upon contacting the gel with one wash of two portions of MeOH (0.5 mL), it was possible to remove 65% of the adsorbed dye, without any loss of gel consistency, as assessed by the tube inversion test.[36] The partially regenerated soft material was reused for 15 consecutive cycles with a constant RE of 96% (Figure 6).

With the above results in mind, we were interested in verifying the self-sustaining nature of the polluted ionogel. This could warrant the material resistance to the weight of the polluted water passing through the solid-like phase applied, for example, as loading of a column. To this aim, we considered the ionogel obtained after 20 cycles of reusing and we repeated the procedure used to investigate the self-sustaining nature of the pure gel (Figure S11). Using both metal and ceramic weights, we confirmed that also in this case the ionogel kept its self-sustaining and load-bearing capacity, with a limit pressure of about 15.9 g/cm^2.

At this point, a comparison with similar systems previously reported in literature is mandatory. In principle, the low vapor pressure of solvent entrapped in the gelatinous network could explain why, differently from hydro- or organogels most frequently used, performances of our ionogel prove durable and better than simple ILs. Indeed, analysis of data reported about the use of ILs in liquid−liquid extraction processes, demonstrates that although they give good RE, they are rarely recycled and never regenerated.[43] For example, even if **[Bzmim][NTf$_2$]** itself (Table 3) exhibits the same RE of the corresponding gel, it cannot be completely recovered due to the more difficult phase separation of the liquid−liquid system.

We have recently demonstrated the selectivity of ionogels in cationic dye adsorption. In that case, 95% of RE was accomplished after 6 h, the gelatinous matrix was reused for 20 cycles, but no regeneration was carried out.[32]

The system more similar to ours, reported by Yu et al., used a DMSO/H_2O supramolecular gel formed by an imidazolium surfactant to remove dyes.[16] However, the above gel showed a high affinity for anionic dyes, whereas for the cationic Rh6G only about the 50% of removal was obtained after 200 h.

In our opinion, one of the key points of our system is its recyclability after regeneration. This should be a warranty of low production of raw materials at the end of the water treatment process. This is why in Table 3, some previously reported materials used in the RhB removal are reported. In particular, times of contact and removal efficiencies after material regeneration is taken into consideration.

Comparison with our results clearly shows the improvement induced by our system in this field over the ones previously reported in the literature. Indeed, RE being equal, the time of contact ranges from 0.4 up to 60 h and, in almost two cases, it was comparable to the one used by us.

However, differently from literature systems, our ionogel was the only one able to maintain its performances even after 15 cycles of reusing.

Finally, we also tested our ionogel in systems that could recall real applications. To this aim, we ensured that our gels were able to adsorb lower amounts of RhB (until 0.43 ppm) (Figure S12 and Table S11) in agreement with expected environmental levels. Furthermore, we inserted the gel phase in a dialysis system as well as loading of syringes (Figure 7). The RE values determined after contact times of 4 and 24 h using a dialysis membrane are reported in Table 4.

In the first case, the ionogel resisted to the immersion in the aqueous solution. RE values clearly demonstrate that adsorption ability increased with the diameter of the membrane (Table 4). Also in this case, we evaluated the possibility of reusing the adsorption membrane and our attempt successfully demonstrated that it could be reused up to four cycles without any loss in the removal efficiency.

Finally, the ionogel was tested as solid-like phase for a syringe. The instant elution through the column allowed obtaining a less colored solution and calculating a RE of 50% and recording the overall volume of water eluted. This result

Table 3. Regenerated Adsorbents Previously Reported in Literature for RhB and Rh6G Removal from Wastewater

adsorbent	time of contact (h)	RE (%)	cycles of reusing on regenerated material	RE after regeneration (%)
ionogel $[\mathbf{C_{12}C_{12}im}][\mathbf{2,6\text{-}NDC}]$ in $[\mathbf{Bzmim}][\mathbf{NTf_2}]$[a]	24	98	15	95
$[\mathbf{Bzmim}][\mathbf{NTf_2}]$[a]	24	98		
ionogel[32]	6	95		
dipeptide based hydrogel[44]	60	78	3	
glucose based organogels[45]	24	97	1	97
Zn-based metal−organic framework[46]	12	94	3	94
polymer-derived ceramic components[47]	24	97	3	97
amphifunctional mesoporous silica nanoparticles[b48]	6	99	10	99
graphene oxide nanocomposite hydrogel[49]	0.4	95	3	85

[a]This paper. [b]R6G.

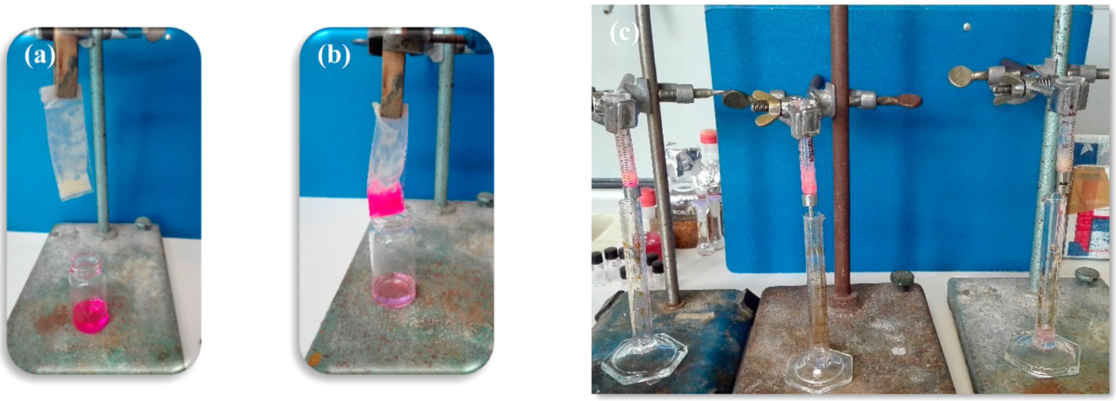

Figure 7. Picture of $[\mathbf{C_{12}C_{12}im}]_2[\mathbf{2,6\text{-}NDC}]/[\mathbf{Bzmim}][\mathbf{NTf_2}]$ at 5 wt % used in a dialysis membrane (a) before and (b) after 4 h of contact with RhB (1.8×10^{-4} M) at 25 °C and (c) sequential system of syringes.

Table 4. RE of $[\mathbf{C_{12}C_{12}im}]_2[\mathbf{2,6\text{-}NDC}]/[\mathbf{Bzmim}][\mathbf{NTf_2}]$ at 5 wt % Used in a Dialysis Membrane, after Adsorption of RhB (1.8×10^{-4} M), at 25 °C and after 24 h (RE Based on Duplicate with Reproducibility of 2%)

	RE (%) dialysis membrane (cut off = 12/14000 Da; *d* = 10 mm)		RE (%) dialysis membrane (cut off = 12/14000 Da; *d* = 14.3 mm)	
	t = 4 h	*t* = 24 h	*t* = 4 h	*t* = 24 h
I cycle	32	77	52	93
II cycle			52	98
III cycle			54	93
IV cycle			52	88

clearly restates the self-supporting nature of ionogel and its load-bearing capacity.

To further improve RE and decrease operational times, the solution of RhB was eluted through a sequential system formed by three syringes. In this case, in 10 min, we collected a clearly discolored solution and calculated a RE equal to 96% (Figure 7c).

■ CONCLUSIONS

In this paper, conjugating properties of ILs with the ones of some polycarboxylate imidazolium salts, we obtained some supramolecular ionogels able to remove cationic dyes from wastewater. Removal efficiency as well as properties of ionogels are dependent on IL and gelator nature.

Currently, the mechanism of the adsorption process for these materials is not well understood. On the grounds of previous reports,[16] we can presume a crucial role played by electrostatic interactions between RhB and carboxylate anions of gelators. However, considering the good performance of aliphatic ILs used as gelation solvent, also cation−π system interactions could positively act on the adsorption process. Differently, for aromatic ILs, π−π interactions could be pivotal in the adsorption.

Among ionogels obtained, the $[\mathbf{C_{12}C_{12}im}]_2[\mathbf{2,6\text{-}NDC}]/[\mathbf{Bzmim}][\mathbf{NTf_2}]$ showed very interesting features and performance. First, it behaved as a self-strengthening material and after application of a mechanical trigger it regained its storage modulus with an increase of the 300% in the fourth cycle. To the best of our knowledge, this is the first time that a similar behavior is observed for a supramolecular gel.

This ionogel also showed self-healing ability and a good load-bearing capacity that proved very useful in the application as adsorption phase.

In this latter context, the ionogel was tested in the removal of RhB from wastewater, using different approaches. Studies performed demonstrated that this is able to remove over 90% of dye in 4 h. Interestingly, the ionogel can be reused up to 20 cycles and, after partial restoring, it can be reused for additional 15 cycles without any loss in adsorption efficiency. This represents a significant improvement with respect to systems previously reported in literature that, after regeneration, did not show the same reusing ability.

Thanks to its self-sustaining nature and load-bearing capacity, the ionogel was also tested in systems that can replicate real applications, like a dialysis membrane and syringes. In the first case, the gel phase was reused for four cycles. In the last case, the immediate elution through the column gave a RE equal to about 50% that if performed in a serial system of three columns, allowed removing of 95% of the dye in less than 10 min.

On the whole, considering the simple preparation method of our ionogels, their features and high reusability also coupled with a high adsorption rate, we expect that they could be applied for wastewater remediation using different techniques.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b03002.

> DSC traces of gelators and gels, TGA traces of gelators, RLS traces, kinetic of gel formation, strain and frequency sweeps of gels, rheological graphs, picture of dye adsorption, ^{1}H NMR and UV−vis spectra for the IL and the gelator release in water, pictures of ionogels, self-sustainability test, gelation and T_{gel} tables, tables reporting removal efficiency for the different systems studied, materials, methods and characterization data of gelators, discussion about thermal stability of gelators and gels, analysis of kinetic data about gel phase formation (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Ribeiro, C.; Scheufele, F. B.; Espinoza-Quiñones, F. R.; Módenes, A. N.; Vieira, M. G. A.; Kroumov, A. D.; Borba, C. E. A comprehensive evaluation of heavy metals removal from battery industry wastewaters by applying bio-residue, mineral and commercial adsorbent materials. *J. Mater. Sci.* **2018**, *53*, 7976−7995.

(2) Gong, Y.; Zhao, X.; Cai, Z.; O'Reilly, S. E.; Hao, X.; Zhao, D. A review of oil, dispersed oil and sediment interactions in the aquatic environment: Influence on the fate, transport and remediation of oil spills. *Mar. Pollut. Bull.* **2014**, *79*, 16−33.

(3) Hai, F. I.; Yamamoto, K.; Fukushi, K. Hybrid Treatment Systems for Dye Wastewater. *Crit. Rev. Environ. Sci. Technol.* **2007**, *37*, 315−377.

(4) Robinson, T.; McMullan, G.; Marchant, R.; Nigam, P. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresour. Technol.* **2001**, *77*, 247−255.

(5) Aksu, Z.; Tezer, S. Biosorption of reactive dyes on the green alga Chlorella vulgaris. *Process Biochem. (Oxford, U. K.)* **2005**, *40*, 1347−1361.

(6) Kiran, I.; Akar, T.; Ozcan, A. S.; Ozcan, A.; Tunali, S. Biosorption kinetics and isotherm studies of Acid Red 57 by dried Cephalosporium aphidicola cells from aqueous solutions. *Biochem. Eng. J.* **2006**, *31*, 197−203.

(7) Charumathi, D.; Das, N. Packed bed column studies for the removal of synthetic dyes from textile wastewater using immobilised dead C. tropicalis. *Desalination* **2012**, *285*, 22−30.

(8) Chakma, S.; Das, L.; Moholkar, V. S. Dye decolorization with hybrid advanced oxidation processes comprising sonolysis/Fenton-like/photo-ferrioxalate systems: A mechanistic investigation. *Sep. Purif. Technol.* **2015**, *156*, 596−607.

(9) Lin, J.; Ye, W.; Baltaru, M.-C.; Tang, Y. P.; Bernstein, N. J.; Gao, P.; Balta, S.; Vlad, M.; Volodin, A.; Sotto, A.; Luis, P.; Zydney, A. L.; Van der Bruggen, B. Tight ultrafiltration membranes for enhanced separation of dyes and Na2SO4 during textile wastewater treatment. *J. Membr. Sci.* **2016**, *514*, 217−228.

(10) Logroño, W.; Pérez, M.; Urquizo, G.; Kadier, A.; Echeverría, M.; Recalde, C.; Rákhely, G. Single chamber microbial fuel cell (SCMFC) with a cathodic microalgal biofilm: A preliminary assessment of the generation of bioelectricity and biodegradation of real dye textile wastewater. *Chemosphere* **2017**, *176*, 378−388.

(11) Deng, S.; Xu, H.; Jiang, X.; Yin, J. Poly(vinyl alcohol) (PVA)-Enhanced Hybrid Hydrogels of Hyperbranched Poly(ether amine) (hPEA) for Selective Adsorption and Separation of Dyes. *Macromolecules* **2013**, *46*, 2399−2406.

(12) Haque, E.; Jun, J. W.; Jhung, S. H. Adsorptive removal of methyl orange and methylene blue from aqueous solution with a metal-organic framework material, iron terephthalate (MOF-235). *J. Hazard. Mater.* **2011**, *185*, 507−511.

(13) Gan, L.; Li, H.; Chen, L.; Xu, L.; Liu, J.; Geng, A.; Mei, C.; Shang, S. Graphene oxide incorporated alginate hydrogel beads for the removal of various organic dyes and bisphenol A in water. *Colloid Polym. Sci.* **2018**, *296*, 607−615.

(14) Chacon-Patino, M. L.; Blanco-Tirado, C.; Hinestroza, J. P.; Combariza, M. Y. Biocomposite of nanostructured MnO2 and fique fibers for efficient dye degradation. *Green Chem.* **2013**, *15*, 2920−2928.

(15) Zeng, G.; Ye, Z.; He, Y.; Yang, X.; Ma, J.; Shi, H.; Feng, Z. Application of dopamine-modified halloysite nanotubes/PVDF blend membranes for direct dyes removal from wastewater. *Chem. Eng. J. (Amsterdam, Neth.)* **2017**, *323*, 572−583.

(16) Cheng, N.; Hu, Q.; Guo, Y.; Wang, Y.; Yu, L. Efficient and Selective Removal of Dyes Using Imidazolium-Based Supramolecular Gels. *ACS Appl. Mater. Interfaces* **2015**, *7*, 10258−10265.

(17) Okesola, B. O.; Smith, D. K. Applying low-molecular weight supramolecular gelators in an environmental setting - self-assembled gels as smart materials for pollutant removal. *Chem. Soc. Rev.* **2016**, *45*, 4226−4251.

(18) Song, S.; Feng, L.; Song, A.; Hao, J. Room-Temperature Super Hydrogel as Dye Adsorption Agent. *J. Phys. Chem. B* **2012**, *116*, 12850−12856.

(19) Takeshita, J.; Hasegawa, Y.; Yanai, K.; Yamamoto, A.; Ishii, A.; Hasegawa, M.; Yamanaka, M. Organic Dye Adsorption by Amphiphilic Tris-Urea Supramolecular Hydrogel. *Chem. - Asian J.* **2017**, *12*, 2029−2032.

(20) Draper, E. R.; Adams, D. J. Low-Molecular-Weight Gels: The State of the Art. *Chem.* **2017**, *3*, 390−410.

(21) George, M.; Weiss, R. G. Molecular Organogels. Soft Matter Comprised of Low-Molecular-Mass Organic Gelators and Organic Liquids. *Acc. Chem. Res.* **2006**, *39*, 489−497.

(22) Weiss, R. G. The Past, Present, and Future of Molecular Gels. What Is the Status of the Field, and Where Is It Going? *J. Am. Chem. Soc.* **2014**, *136*, 7519−7530.

(23) Cevasco, G.; Chiappe, C. Are ionic liquids a proper solution to current environmental challenges? *Green Chem.* **2014**, *16*, 2375−2385.

(24) Deetlefs, M.; Fanselow, M.; Seddon, K. R. Ionic liquids: the view from Mount Improbable. *RSC Adv.* **2016**, *6*, 4280−4288.

(25) Plechkova, N. V.; Seddon, K. R. Applications of ionic liquids in the chemical industry. *Chem. Soc. Rev.* **2008**, *37*, 123−150.

(26) Ravula, S.; Larm, N. E.; Liu, Y.; Atwood, J. L.; Baker, S. N.; Baker, G. A. Ionothermal synthesis of magnetically-retrievable mesoporous carbons from alkyne-appended ionic liquids and demonstration of their use in selective dye removal. *New J. Chem.* **2018**, *42*, 1979−1986.

(27) Zambare, R.; Song, X.; Bhuvana, S.; Antony Prince, J. S.; Nemade, P. Ultrafast Dye Removal Using Ionic Liquid−Graphene Oxide Sponge. *ACS Sustainable Chem. Eng.* **2017**, *5*, 6026−6035.

(28) Bianchini, R.; Cevasco, G.; Chiappe, C.; Pomelli, C. S.; Rodríguez Douton, M. a. J. Ionic Liquids Can Significantly Improve Textile Dyeing: An Innovative Application Assuring Economic and Environmental Benefits. *ACS Sustainable Chem. Eng.* **2015**, *3*, 2303−2308.

(29) Dutta, S.; Das, D.; Dasgupta, A.; Das, P. K. Amino Acid Based Low-Molecular-Weight Ionogels as Efficient Dye-Adsorbing Agents and Templates for the Synthesis of TiO2 Nanoparticles. *Chem. - Eur. J.* **2010**, *16*, 1493−1505.

(30) D'Anna, F.; Noto, R. Di- and Tricationic Organic Salts: An Overview of Their Properties and Applications. *Eur. J. Org. Chem.* **2014**, *2014*, 4201−4223.

(31) D'Anna, F.; La Marca, S.; Noto, R. p-Nitrophenolate: A Probe for Determining Acid Strength in Ionic Liquids. *J. Org. Chem.* **2009**, *74*, 1952−1956.

(32) Marullo, S.; Rizzo, C.; Dintcheva, N. T.; Giannici, F.; D'Anna, F. Ionic liquids gels: Soft materials for environmental remediation. *J. Colloid Interface Sci.* **2018**, *517*, 182−193.

(33) Rizzo, C.; Arrigo, R.; Dintcheva, N. T.; Gallo, G.; Giannici, F.; Noto, R.; Sutera, A.; Vitale, P.; D'Anna, F. Supramolecular Hydro- and Ionogels: A Study of Their Properties and Antibacterial Activity. *Chem. - Eur. J.* **2017**, *23*, 16297−16311.

(34) Billeci, F.; D'Anna, F.; Gunaratne, H. Q. N.; Plechkova, N. V.; Seddon, K. R. Sweet" Ionic Liquid Gels: Materials for Sweetening of Fuels. *Green Chem.* **2018**, DOI: 10.1039/C8GC01615A.

(35) Rizzo, C.; D'Anna, F.; Noto, R.; Zhang, M.; Weiss, R. G. Insights into the Formation and Structures of Molecular Gels by Diimidazolium Salt Gelators in Ionic Liquids or "Normal" Solvents. *Chem. - Eur. J.* **2016**, *22*, 11269−11282.

(36) Raghavan, S.; Cipriano, B.: Gel Formation: Phase Diagrams Using Tabletop Rheology and Calorimetry. In *Molecular Gels*; Weiss, R., Terech, P., Eds.; Springer Netherlands, 2006; DOI: 10.1007/1-4020-3689-2_9, pp 241−252.

(37) Takahashi, A.; Sakai, M.; Kato, T. Melting Temperature of Thermally Reversible Gel. VI. Effect of Branching on the Sol−Gel Transition of Polyethylene Gels. *Polym. J. (Tokyo, Jpn.)* **1980**, *12*, 335−341.

(38) McLean, A. J.; Muldoon, M. J.; Gordon, C. M.; Dunkin, I. R. Bimolecular rate constants for diffusion in ionic liquids. *Chem. Commun.* **2002**, 1880−1881.

(39) Li, J.; Geng, L.; Wang, G.; Chu, H.; Wei, H. Self-Healable Gels for Use in Wearable Devices. *Chem. Mater.* **2017**, *29*, 8932−8952.

(40) Rizzo, C.; Arcudi, F.; Đorđević, L.; Dintcheva, N. T.; Noto, R.; D'Anna, F.; Prato, M. Nitrogen-Doped Carbon Nanodots-Ionogels: Preparation, Characterization, and Radical Scavenging Activity. *ACS Nano* **2018**, *12*, 1296−1305.

(41) Ramirez, A. L. B.; Kean, Z. S.; Orlicki, J. A.; Champhekar, M.; Elsakr, S. M.; Krause, W. E.; Craig, S. L. Mechanochemical strengthening of a synthetic polymer in response to typically destructive shear forces. *Nat. Chem.* **2013**, *5*, 757−761.

(42) Karan, C. K.; Bhattacharjee, M. Self-Healing and Moldable Metallogels as the Recyclable Materials for Selective Dye Adsorption and Separation. *ACS Appl. Mater. Interfaces* **2016**, *8*, 5526−5535.

(43) Bhatt, D. R.; Maheria, K. C.; Parikh, J. Enhanced separation of toxic Blue BG dye by cloud point extraction with IL as an additive: Effect of parameters, solubilization isotherm and evaluation of thermodynamics and design parameters. *J. Environ. Chem. Eng.* **2015**, *3*, 1365−1371.

(44) Nandi, N.; Baral, A.; Basu, K.; Roy, S.; Banerjee, A. A dipeptide-based superhydrogel: Removal of toxic dyes and heavy metal ions from waste water. *Biopolymers* **2017**, *108*, e22915.

(45) Zhang, X.; Song, J.; Ji, W.; Xu, N.; Gao, N.; Zhang, X.; Yu, H. Phase-selective gelators based on closed-chain glucose derivatives: their applications in the removal of dissolved aniline/nitrobenzene, and toxic dyes from contaminated water. *J. Mater. Chem. A* **2015**, *3*, 18953−18962.

(46) Wu, M.-K.; Yi, F.-Y.; Fang, Y.; Xiao, X.-W.; Wang, S.-C.; Pan, L.-Q.; Zhu, S.-R.; Tao, K.; Han, L. An Ultrastable Metal−Organic Framework with Open Coordinated Sites Realizing Selective Separation toward Cationic Dyes in Aqueous Solution. *Cryst. Growth Des.* **2017**, *17*, 5458−5464.

(47) Zeydanli, D.; et al. Polymer-derived ceramic adsorbent for pollutant removal from water. *J. Am. Ceram. Soc.* **2018**, *101*, 2258−2265.

(48) Shinde, P.; Gupta, S. S.; Singh, B.; Polshettiwar, V.; Prasad, B. V. Amphi-functional mesoporous silica nanoparticles for dye separation. *J. Mater. Chem. A* **2017**, *5*, 14914−14921.

(49) Soleimani, K.; Tehrani, Abbas D.; Adeli, M. Bioconjugated graphene oxide hydrogel as an effective adsorbent for cationic dyes removal. *Ecotoxicol. Environ. Saf.* **2018**, *147*, 34−42.