Combining Carbon Materials and Ionic Liquid Gels to Boost Simultaneous Removal of Emerging Pollutants from Wastewaters

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Water bodies contamination is a pressing issue of modern society, exacerbated by the large structural variety of contaminants. This explains the interest toward developing systems able to remove from wastewater different contaminants, with different susceptibility to removal methods. Consequently, herein hybrid ionic liquid gels, based on 1,3:2,4-dibenzylidene-D-sorbitol (DBS), doped with graphite, carbon nanotubes, graphene, and graphene oxide, are described. First, the gel–sol transition temperatures (T_{gel}), rheological and self-healing properties are determined. These gels are then used as sorbent materials and, for the first time, for removing mixtures of pollutants of different classes, namely the dyes rhodamine B and methyl orange, the drugs diclofenac and carbamazepine, or the endocrine disruptor bisphenol A, to simulate real wastewaters. Interestingly, hybrid gels prove efficient in removing single and mixed pollutants. The best performing gel is reusable for at least 12 consecutive cycles, without any intermediate washing. It can also be embedded in adsorption columns or dialysis membranes, to treat larger volumes of wastewater. Here, this gel achieves an adsorption capacity of 117 and 66 mg g^{-1} for rhodamine B and bisphenol A in mixture, with a distinct preference toward cationic contaminants, exhibiting competitive performance with most systems previously reported.

1. Introduction

The treatment of water bodies, for the removal of pollutants, is a pressing need in present-day society, considering that water is an indispensable and limited resource. The concomitant consequences of urban and industrial activities contribute to the occurrence in water of different kinds of pollutants, with diverse structures and thus susceptibilities to removal methods such as dyes, metals, and anions.[1,2]

Recent focus has been laid to the removal of the so-called emerging pollutants,[3,4] which are increasingly occurring compounds in wastewaters, whose presence in water bodies or wastewaters is in many cases still not regulated.[5] Emerging pollutants include endocrine disruptors as bisphenol A,[6] pharmaceutically active compounds[7] or products deriving from cosmetics.[8,9]

The growing awareness of this issue has led to a large body of literature, dealing with the removal of such pollutants from aqueous solutions. However, the vast majority of these works focus on the removal of single pollutants,[10] while real wastewaters are mixtures of many contaminants, with different structures and stability. This is further complicated by synergistic or antagonistic interactions involving each contaminant and the adsorbent surface.[11] Consequently, it is desirable that the methods used to remove pollutants from water are efficient and active toward these multicomponent mixtures.[12]

To address this topic, different methodologies have been used, from photocatalysis,[13] to photoelectrocatalysis,[14] advanced oxidation,[15] and adsorption.[11,12] This latter has the advantages of requiring relatively simple equipment, low energy consumption and operating cost.[16]

Regarding the simultaneous adsorption of pollutants, the most pursued strategy employs bifunctional sorbents, endowed with sites specifically active toward different species like for example, metals and neutral emergent contaminants.[2,11] For instance in a citric acid-crosslinked β-cyclodextrin polymer used to remove bisphenol A (BPA), methylene blue (MB), and Cu(II) ions, the cyclodextrin cavities remove BPA by inclusion, while MB and Cu(II) ions are adsorbed at the citric acid surface.[17] A similar approach was employed in using EDTA-crosslinked cyclodextrins for the adsorption of metal ions and dyes, in which the EDTA groups complex the metals cation while the cyclodextrin moieties include the dye.[18]

In other cases, non-functionalized materials achieved significant removal of different kinds of pollutants. Such is the case, for instance, of tea waste biomass, used to remove Cr(VI) and phenol.[19]

Among the different materials capable of adsorbing pollutants from water, supramolecular gels are playing an increasingly important role.[20] These are solid-like materials originated by

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the self-assembly of small molecules, known as gelators, in dilute solutions, forming a sample-spanning network underpinned solely by non-covalent interactions, entrapping high amounts of solvent.[21,22]

In the context of adsorption, the properties of the gels can be easily tuned by judicious choice of gelator and solvent, driving their affinity to the adsorption of different classes of pollutants. In general, the solvent plays a major role in determining the properties of a gel, and a recent development in this field is constituted by the obtainment of supramolecular gels in non-conventional solvents, like deep eutectic solvent (DES) or ionic liquids (ILs), known as eutectogels[23] and ionic liquid gels,[24,25] respectively. These combine the peculiar features and high solubilizing ability of the above solvents, with the supramolecular structure of the gel, that offers cavities in which adsorbed species can be accommodated. In this context, we have successfully employed supramolecular gels in DES and ILs, differing for the nature of both gelator and solvents, for the adsorption of dyes,[26,27] iodine,[28] Cr(VI),[29] sulphur-,[30,31] and pharmaceutically compounds[32,33] as well as emerging pollutants.[34]

Another possible way to ameliorate the properties of supramolecular gels, is the incorporation of nanomaterials, which albeit not participating in the self-assembled network, can improve the mechanical, thermal,[35] electrochemical[36] or antioxidant properties[37] of the gel. On this subject, we have found that carbon-nanomaterial-doped ionic liquid gels can successfully remove various pharmaceutically active compounds from water.[32,33]

Obviously, supramolecular gel properties and performance heavily depend on the gelator features and we recently demonstrated that ionic liquid gels formed by 1,3:2,4-dibenzylidene-D-sorbitol, (DBS), are efficient and highly recyclable sorbents for the removal of BPA.[34]

DBS bears both aromatic and hydrogen bond donor functionalities,[38] which can in principle be harnessed in the adsorption of different kinds of contaminants, capable of establishing $\pi-\pi$ stacking or hydrogen bond interactions with the surface of the gel. It has been previously used to obtain sorbent phases for wastewater decontamination,[38] but to the best of our knowledge, it has never been used in combination with carbon nanomaterials and for the simultaneous removal of mixed pollutants. In this context, it could prove efficient as its aromatic nature could drive the interaction with carbon nanomaterials, giving rise to supramolecular gels having features and performance completely different from the ones of the corresponding pristine gels. On the other hand, the bifunctional nature of the gelator, due to the presence of both aromatic rings and hydroxyl groups, could be efficiently exploited in the contemporary catching and removal of different contaminants.

Based on these considerations, we prepared hybrid supramolecular ionic liquid gels of DBS (from now on HILGs), doped with different carbon nanomaterials such as graphite, graphene, graphene oxide, and single walled carbon nanotubes. As solvents for the gels, we used ILs differing for the cation and anion, in which DBS is able to gel,[34] such as [bmim][BF$_4$], [bmim][PF$_6$], [bmim][NTf$_2$], [bmpyrr][NTf$_2$], and [bmpip][NTf$_2$], reported in **Figure** 1. The aromatic or aliphatic nature of IL cation, as well as the different IL anion coordination ability could

in turn affect not only properties of hybrid ionic liquid gels, but also their performance.

The HILGs obtained were characterized by their gel-solution transition temperature (T_{gel}) and rheological features. To have full insights about their removal ability, the gels were then used as sorbents to remove from water different types of pollutants such as cationic and anionic dyes, namely rhodamine B (RhB) and methyl orange (MO) respectively, as well as emerging pollutants[3,39] like the endocrine disruptor bisphenol A (BPA) or pharmaceutically active compounds such as diclofenac (DFC) and carbamazepine (CBZ), whose structures are depicted in Figure 1. All these compounds have widely proven to have adverse toxic effects on humans and environment. In particular, synthetic dyes as RhB and MO exert toxic effects especially on aquatic organisms,[40] while BPA interferes with the endocrine systems in humans.[41] In addition, DCF and CBZ have been identified among the most dangerous compounds able to exert chronic effects on aquatic organisms.

First, we evaluated the adsorption performance of our hybrid gels toward solutions of single pollutants. Then, we assessed their behavior toward binary mixtures of pollutants of different types, to have a more realistic picture of their removal efficiency for the treatment of actual wastewater. We considered the following mixtures: RhB/BPA, RhB/DCF, RhB/CBZ, and MO/BPA. This would give insights about the ability of these hybrid gels in acting toward cationic/neutral and anionic/neutral systems.

Surprisingly, among all tested HILGs, DBS:graphite/[bmpyrr][NTf$_2$], embedding the cheapest carbon material, proved to be the best performing one. Consequently, we first investigated its recyclability. Then, it was also used as loading of columns and embedded in a dialysis membrane, to treat a much larger volume of polluted water and to simulate real systems.

Data collected show that our systems show good performance in the removal of pollutants mixtures and in the case of cationic/neutral ones. Interestingly, the most efficient hybrid gel can be reused for at least 12 consecutive uses, without any intermediate washing and it shows competitive performance with respect to adsorption systems so far reported in literature also in terms of recyclability. These results further the pursuing of sustainable development goals 6 (clean water and sanitation) and 11 (sustainable cities and communities).

2. Results and Discussion

2.1. Gelation Tests and Determination of Gel–Sol Transition Temperatures

As already mentioned, for the preparation of hybrid gels, we doped DBS-based ionic liquid gels with different carbon nanomaterials. We tested different ILs that were chosen on the grounds of their structural features, but also for the previous observed ability of DBS to harden some of these solvents.[34]

To prepare hybrid gels, we first prepared a nanocomposite of DBS and carbon nanomaterials, by grinding them in a mortar, until obtaining uniform power. Then, we carried out gelation tests by dispersing the nanocomposite in the suitable amount of IL by sonication, and then subjecting the mixture obtained to a heat–cool cycle. Based on previous results,[32,34] for all the gels
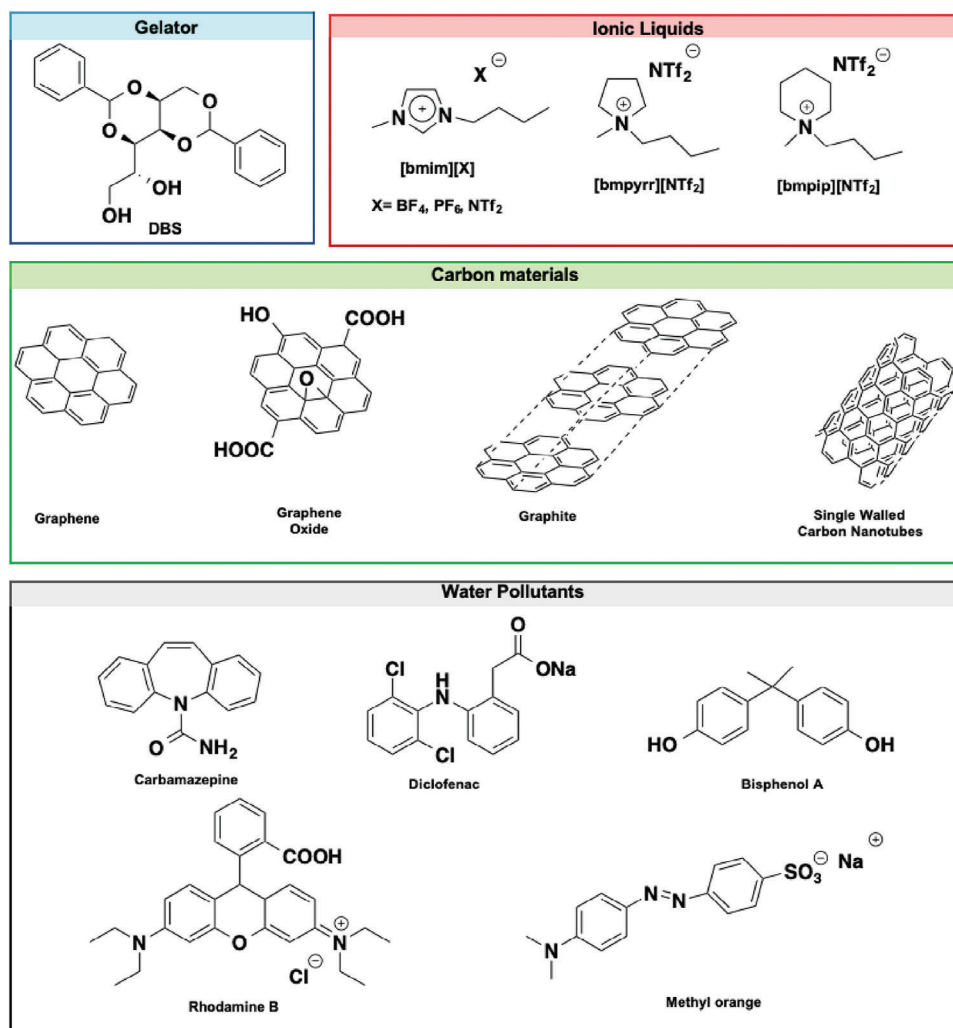
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Figure 1. Structures of gelator, ionic liquids, carbon nanomaterials, and water pollutants considered.

we employed a concentration of 3 wt.% of DBS and of 0.1 wt.% of carbon materials.

Initially, we used cheap graphite as doping materials for our gels. Subsequently, the effect of incorporating different carbon nanomaterials was investigated only for the gel based on DBS/[bmpyrr][NTf$_2$], due to its highest efficiency as sorbent (see later). The results of the gelation tests are reported in **Table 1**.

A first look at the results reported in Table 1, points out that the presence of graphite enhances gelation in the case of the DBS/[bmim][BF$_4$] system, which does not form a gel in the absence of the carbon nanomaterial. In the other cases, the gel formed either in the presence or in the absence of graphite. To further investigate the influence of this latter on the properties of the ionic liquid gels, we determined the gel-solution transition temperatures by the falling drop method.[42]

For HILGs, T_{gel} changes from 51 up to 78 °C. In general, for graphite-based gels, T_{gel} increased as the anion coordination ability decreases, as accounted for by values collected in [bmim$^+$]-based ILs. On the other hand, anion being the same ([NTf$_2^-$]), T_{gel} significantly increases going from aromatic ([bmim][NTf$_2$]) to aliphatic ILs ([bmpip][NTf$_2$] and [bmpyrr][NTf$_2$]). However, this

Table 1. T_{gel} in the presence and absence of carbon materials, outcome of thixotropy tests.

Gel	T_{gel} [°C][a]	T_{gel} without material [°C][b]	Thixotropy
DBS:Graphite/[bmim][NTf$_2$]	63	65	no
DBS:Graphite /[bmim][BF$_4$]	51	–	yes
DBS:Graphite /[bmim][PF$_6$]	71	70	yes
DBS:Graphite /[bmpip][NTf$_2$]	75	69	no
DBS:Graphite /[bmpyrr][NTf$_2$]	74	80	no
DBS:Graphene/[bmpyrr][NTf$_2$]	73	80	yes
DBS:Graphene OX/[bmpyrr][NTf$_2$]	69	80	yes
DBS:CNT/[bmpyrr][NTf$_2$]	78	80	yes

[a] T_{gel} were reproducicle within ± 1 °C; [b] Values taken from ref. [34].

parameter stays constant independently from the structure of the aliphatic cation, probably indicating that cation-π interactions, between IL cation and graphite, play a major role in stabilizing gel phases.
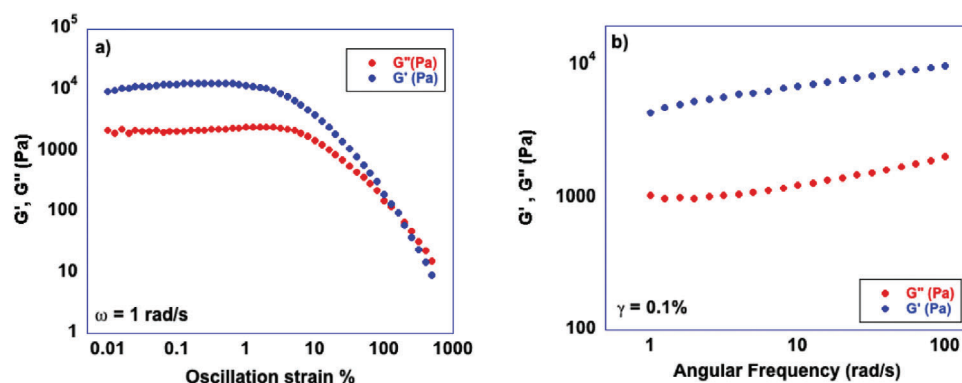
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Figure 2. Plots of a) strain and b) frequency sweep measurements at 25 °C, for the DBS:Graphite /[bmpyrr][NTf$_2$] hybrid ionogel.

As far as data as a function of carbon materials are concerned, comparable T_{gel} are obtained using graphite or graphene (≈73 °C), whereas graphene OX and CNTs induce a significant decrease and increase in the above parameter.

With the only exception of DBS/[bmpip][NTf$_2$], for which we detected a higher T_{gel} for the HILG than for the ILG (75 °C and 69 °C for HILG and ILG, respectively), comparison between values collected for pristine materials and graphite-based HILGs, as a fuction of the IL nature, show these are comparable or only slightly lower. This suggests that that inclusion of carbon materials in the gels causes only minor or negligible disturbance to the gel network, as accounted for by comparable values obtained. In addition, comparison among the T_{gel} of the hybrid materials obtained in [bmpyrr][NTf$_2$], shows that the influence due to the presence of the carbon material is minimal for DBS:CNT/[bmpyrr][NTf$_2$], but in the other cases a general decrease in T_{gel} is observed, with the largest variation detected in the case of graphene OX.

2.2. Self-Repairing Ability and Rheological Investigation

Next, we probed the response of the hybrid gels to mechanical stress, induced by contacting the gel with a magnetic stirrer (5 min at 400 rpm). After being subjected to the mechanical stimulus, the gel was kept at rest overnight to verify if it spontaneously formed again. The results reported in Table 1 shows an articulate behavior, affected both by the nature of the carbon material and the IL anion.

Graphite-doped gels obtained in [bmim][BF$_4$] and [bmim][PF$_6$] exhibited thixotropic behavior, whereas the ones obtained in NTf$_2$-based gels were not, irrespective of the IL cation, aliphatic or aromatic. Thixotropic behavior may result by a complex interplay of different factors, however in gels it is generally ascribed to hydrogen bonds between functionalities present in the gelator-solvent system, which are destroyed by mechanic stress and reform spontaneously after the stress ceases, without undermining the integrity of the fibers.[43]

In particular, the effect of the IL anion can be ascribed to the different cross-linking degree of the anions, that is, the potential number of hydrogen bond that they can accept, which decreases on going from the more symmetrical [BF$_4^-$] and [PF$_6^-$] anions to the [NTf$_2^-$] one.[44,45] Thixotropic ability decreases in parallel

as the latter anion would favor to a lesser extent the restoration of the full hydrogen bond network. However, IL being the same ([bmpyrr][NTf$_2$]), the above scenario changes with the nature of the carbon material. Indeed, the ability to restore after the action of a mechanical stimulus is fully recovered in the presence of the other carbon materials.

On the grounds of the above results, we investigated the mechanical properties of selected HILGs by strain and frequency sweep rheological measurements. In particular, we focused on the effect exerted by the incorporation of different carbon nanomaterials, and consequently, we chose to perform these measurements on the [bmpyrr][NTf$_2$]-based gels. Such investigations aim to gather insight on the mechanical resistance and flexibility of the gels, as well as confirming their nature of true gels.

To this aim, we carried out these experiments at 25 °C, using gels at the common concentration of 3 wt.% in DBS, doped with 0.1 wt.% of carbon nanomaterials. Strain sweeps were carried out at a frequency of 1 rad s^{-1}, whereas frequency sweeps were carried out at an oscillation strain of 0.1%. These values fell within the linear viscoelastic region. From these measurements, we determined the values of G′, storage modulus and G′′, loss modulus, indicative of solid-like and liquid-like rheological response, respectively. Moreover, we also determined the loss tangent (tanδ), that is, the G′′/ G′ ratio, related to the strength of intermolecular interaction underpinning the gel network, as well as the strain at crossover point, γ_c, which is the maximum strain tolerated by the sample without breaking, and hence gives information on the mechanical strength and flexibility of the gel.[46] Plots relevant to rheological measurements are reported in **Figures 2** and **S1** (Supporting Information), while the rheological parameters obtained are summarized in **Table 2**.

Looking at the results reported in Table 2, shows that the presence of carbon nanomaterials in the DBS-based ionogels is not detrimental from a rheological point of view. In particular, the values of tan δ, reminiscent of the extent of intermolecular interaction within the gels,[47] appear almost independent from the presence or absence of materials, suggesting that the materials do not interfere with the establishment of the DBS-based gel network. The parameters most affected by the presence of carbon nanomaterials are γ_c and G′. In particular, γ_c and hence the flexibility of the hybrid gels, increases along the order, graphene = GO = native gel < CNT << graphite. Interestingly, while the incorporation of nanostructured carbon materials like graphene and graphene

Table 2. G′ and G″ at $\gamma = 0.1\%$ and $\omega = 1$ rad s^{-1}, tan $\delta = $ G″/G′ and values of γ_c at G″ = G′ for DBS/[bmpyrr][NTf$_2$] gels (3 wt.%) doped with 0.1 wt.% or carbon materials, at 25 °C. Error limits are based on average of three different measurements with different aliquots.

Material	G′ [Pa]	G″ [Pa]	tan δ	γ_c [%]
None[34]	85 000 ± 20000	19 000 ± 5000	0.23 ± 0.07	32 ± 8
Graphene oxide	173 000 ± 4000	26 000 ± 8000	0.167 ± 0.007	22 ± 4
Graphene	38 000 ± 15000	8000 ± 700	0.27 ± 0.05	28 ± 4
Carbon nanotubes	160 000 ± 15000	26 000 ± 8000	0.16 ± 0.04	39.9 ± 0.1
Graphite	15 000 ± 9000	3000 ± 800	0.23 ± 0.04	158.5 ± 0.7

oxide has negligible influence on the flexibility and resistance of the hybrid gels, graphite induces the most significant enhancement, with γ_c increasing by five times in magnitude. This surprising finding is consistent with a similar effect we observed when graphite was incorporated in a supramolecular ionogel of imidazolium salts in an [NTf$_2^-$]-based IL.[32] It highlights the beneficial effect due to the addition of the cheapest carbon material employed and underlines the nature of reinforcer of graphite that is a well-established reinforcer for polymer composites,[48,49] but is still largely underexplored for hybrid supramolecular gels.

Analyzing the trend of the storage modulus, G′, which is more related to the stiffness of the gel,[50] evidences a more articulate modulation of the rheological properties. In particular, G′ increases along the order graphite < graphene < native gel < CNT < GO, showing that incorporating carbon nanotubes and graphene oxide lead to significantly stiffer gels, while this parameter sharply decreases in the presence of graphite. This is consistent with the previous observation that the graphite-doped hybrid gel is the most flexible one. To further characterize our hybrid gel, we attempted to record a SEM image of the xerogel deriving from DBS:graphite/[bmpyrr][NTf$_2$] gel, after washing with ethanol to remove the solvent, according to a published procedure.[26] However, from the Image reported in Figure S2 (Supporting Information), no morphology could be inferred as the gel matrix appears to be covered by graphite, which is uniformly dispersed in the sample.

2.3. Single Pollutant Removal Tests

We then investigated the ability of the carbon material-doped ionic liquid gels to remove pollutants from water. Preliminar-ily, we verified that all hybrid gels kept their self-supportiveness after contact with water for 24 h at 25 °C (250 mg of gels with 500 µL of water). The only exception was the gel in [bmim][BF$_4$] which partially collapsed due to solubilization of IL in the aqueous phase. Consequently, we did not use this gel for adsorption tests. We carried out static adsorption experiments, by contacting for 4 h, at 25 °C, 250 mg of native and hybrid gel with 500 µL of aqueous solutions of a single pollutant having concentrations of $4.0 \cdot 10^{-4}$ M for BPA and $1.8 \cdot 10^{-4}$ M for the RhB, MO, CBZ, and DCF. Then, the residual concentration of pollutant was determined spectrophotometrically and the removal efficiency, RE (%) was determined as reported elsewhere.[28,32] For a useful comparison, we also carried out the same tests by contacting the aqueous solutions of pollutants with the same amount of IL present in each gel. A representative picture of the adsorption tests is reported in **Figure 3**, while the results obtained are reported in Table S1 (Supporting Information) and **Figure 4**.

Looking at the results reported in Figure 4a, gives a broad picture of the effect of the IL on the performance of the graphite-doped hybrid gels. The best results are obtained using the hybrid gel in [bmpyrr][NTf$_2$], with the exception of MO, for which, in any case removal efficiencies are rather low, irrespective of the IL present in the gel. Since these initial screening indicates the hybrid gel in [bmpyrr][NTf$_2$] as the best-performing one, we investigated in the same way the effect of the nature of the carbon material, by employing the ionogels in this IL, doped with graphene, GO, and CNT, obtaining the results reported in Figure 4b. In general, the highest removal efficiencies are once again observed for the hybrid gel doped with graphite, although the trend of removal efficiency as a function of the carbon material, depends on the nature of the pollutant. In particular, the two dyes describe the extreme cases, in which RE is practically the same regardless of the materials used, that is, assuming high values (> 90%) for RhB and low values (≤ 20%) in the case of MO. A more articulate behavior emerges for BPA, CBZ, and DFC, in which case the highest efficiency is observed for the graphite-doped gels, and the lowest ones for the gel doped with graphene. In any case, the best-performing sorbent is the DBS-[bmpyrr][NTf$_2$] hybrid gel doped with graphite. Finally, comparing the RE% obtained after 4 h upon contact with neat ILs, reported in Table S1 (Supporting Information), shows that for all pollutants the RE% is always higher than for the gels. Interestingly, the trend of the extraction efficiency for the pollutants for a given ILs, is the same as in gels, that is, MO < DCF < CBZ < RhB. However, the advantage of
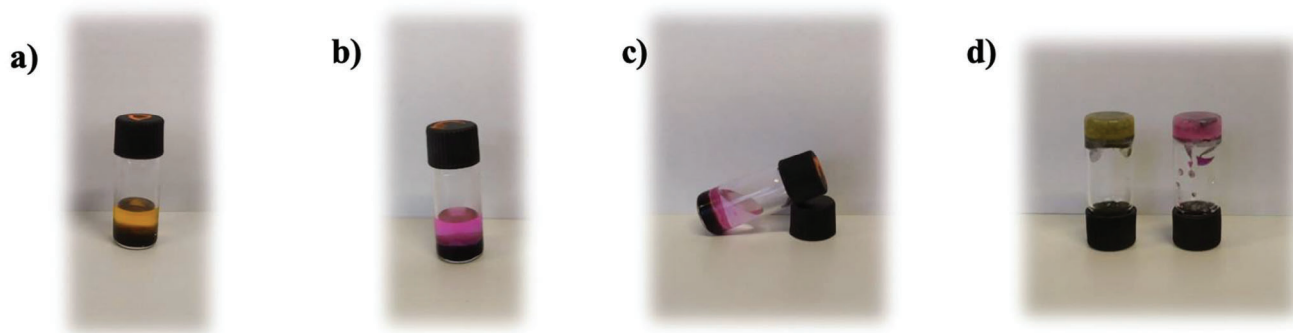

Figure 3. Photo of hybrid gels in contact with RhB and MO water solution a,b) at $t = 0$, c,d) after 4 h.

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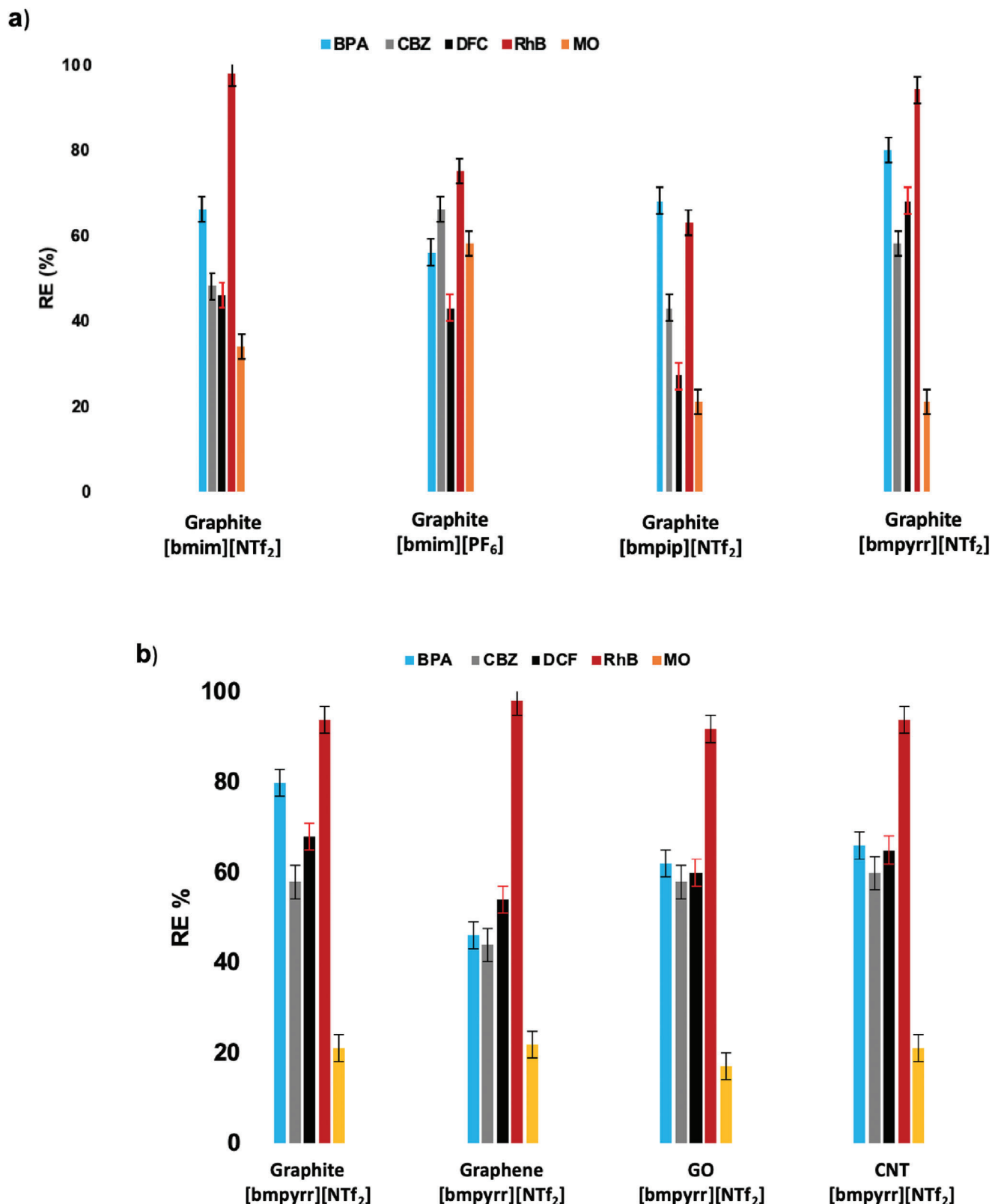SUSTAINABLE
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Figure 4. Plots of RE%, at 4 h, for aqueous solutions of pollutants after contact with a) hybrid ionogels doped with graphite and b) and hybrid ionogels in [bmpyrr][NTf$_2$] doped with different materials.

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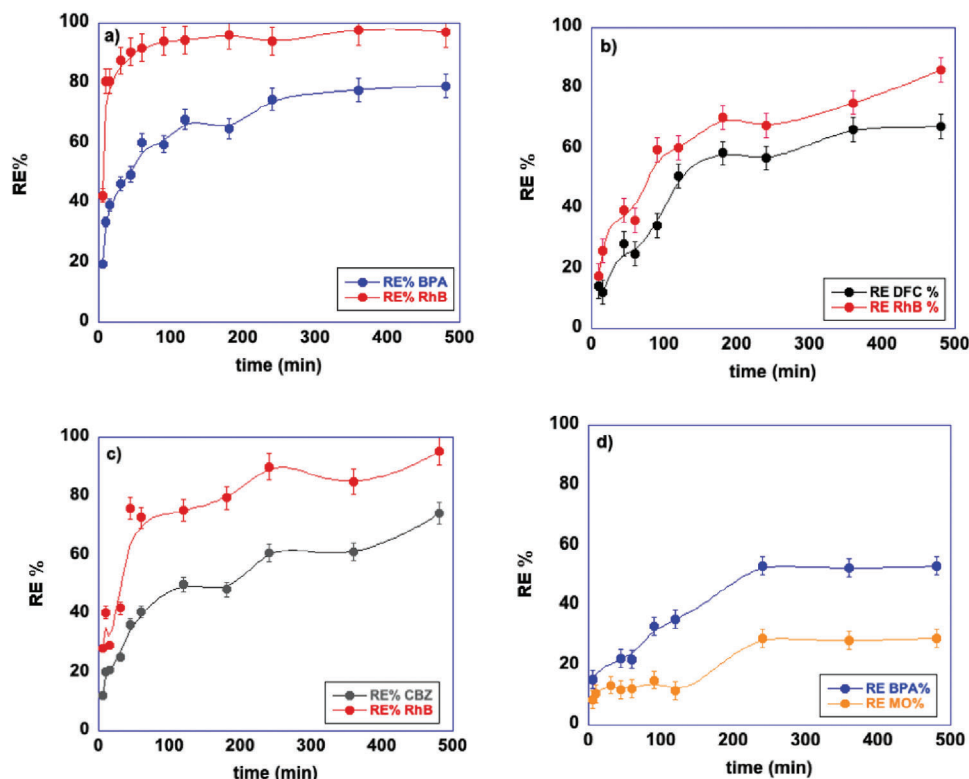**ADVANCED
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Figure 5. Plots of RE%, as a function of time, relevant to the adsorption of aqueous binary mixtures of a) RhB/BPA, b) RhB/DCF, c) RhB/CBZ and d) BPA/MO, over the DBS:Graphite /[bmpyrr][NTf$_2$] hybrid gels. RE% are average values of triplicate experiments and are reproducible within ± 4%. Lines are drawn as mere visual aid.

using gels over the liquid–liquid extraction with ILs is the much easier separation of the solid-like pollutant laden gel, compared with the liquid phase of the ILs. This hypothesis was further verified by contacting all the hybrid gels with D$_2$O for 24 h, to assess the potential leakage of IL into the aqueous phase. The ^{1}H-NMR spectra of the aqueous phases, added with maleic acid as internal standard together with enlargement of the region comprised between 0.5 and 3.6 ppm in the inset, is reported in Figure S3 (Supporting Information) while the values obtained are reported in Table S2 (Supporting Information). The amounts of IL released after 24 h is limited, for the [NTf$_2$$^-$]-based ILs to the range 0.5–1 wt.%, while it soars to 13 wt.% in the presence of the hydrophilic anion [BF$_4$$^-$] Furthermore, it is important to consider that hydrolysis of fluorinated anions different from [BF$_4$$^-$], and the consequent formation of HF, is negligible at room temperature.[51] In fact, [NTf$_2$$^-$] anions are stable in water, even under sonication.[52]

2.4. Adsorption Tests for Pollutants Mixtures

Since real wastewaters contain several pollutants of different kind, we tested the performance of the gels toward aqueous solutions consisting of mixtures of pollutants. We chose pollutants with negligible overlap in their UV–vis spectrum, namely RhB/BPA, RhB/DFC, RhB/CBZ and MO/BPA. To this aim, we carried out adsorption tests of each pollutant mixture over the DBS:Graphite /[bmpyrr][NTf$_2$], by determining the removal effi-

ciency as a function of time. The results obtained are reported in **Figure 5** and Table S3 (Supporting Information).

The plots reported in Figure 5 clearly show how the adsorption kinetic of each pollutant is affected by the presence of the other, as they compete for the adsorption sites of the gel. In particular, RhB is adsorbed faster in the presence of BPA as a second component, reaching a plateau RE% of 90% in 30 min (Figure 5a), whereas in the presence of DFC, the RE% of RhB goes down to 60%, and the adsorption process is significantly slower, now requiring 90 min to reach the maximum value. This suggests that DCF exerts an antagonistic effect[11] on the adsorption of RhB, that can be explained by the presence on DCF of strong hydrogen bond accepting moieties such as a carboxylate and an amino group, which can establish hydrogen bonding with RhB, making this latter less available to interact with the gel surface by hydrogen bonding. Accordingly, looking at the values of RE% obtained at 4 h reported in Figure 4b, reveals that the adsorption of RhB is substantially unaffected by the presence of BPA, with RE% amounting to 94% in both cases. Conversely, in the presence of DFC, the RE% of RhB goes down to 68%.

An intermediate situation is found when RhB is mixed with CBZ, in which case a slowing down of the adsorption of RhB occurs, however with no reduction in removal efficiency.

Looking at the results obtained for BPA leads to similar conclusions. In particular, the adsorption of BPA is only slightly affected by a strong competitor for adsorption sites like RhB (RE% for BPA = 80% and 75% in the absence and presence of RhB, re-
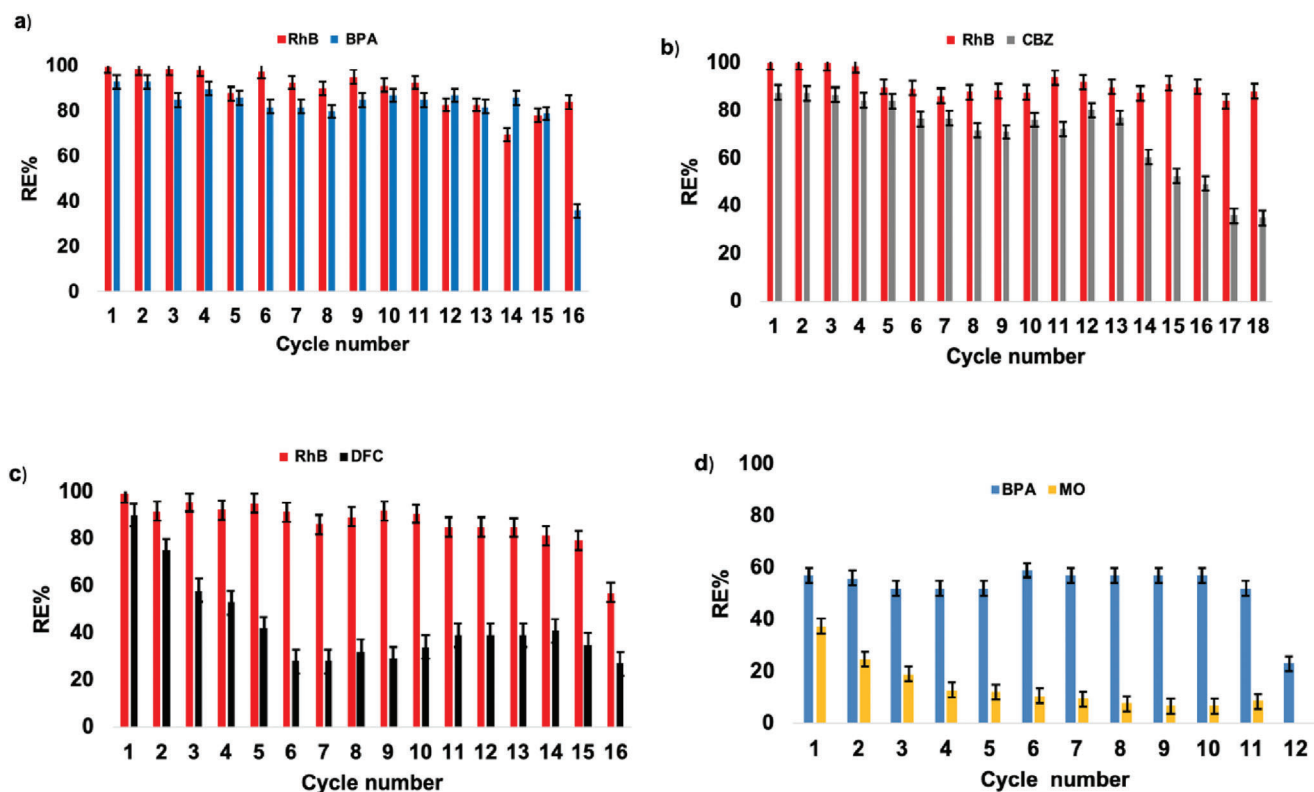
Figure 6. Plots of RE% obtained reusing the DBS-[bmpyrr][NTf$_2$]/graphite gel as sorbent for a) RhB/BPA, b) RhB/DFC, c) RhB/CBZ, and d) BPA/MO mixtures, for 24 h at 25 °C. RE% are average values of triplicate runs and are reproducible within 4%.

spectively), confirming negligible interactions between RhB and BPA. Conversely, the fraction of BPA adsorbed drops to 60% in the presence of MO. However, MO does not appear as a strong competitor for adsorption sites, as its removal efficiency never exceeds 30%. This observation can be explained once again by considering that the anionic dye MO exerts an antagonistic effect, decreasing the ability of BPA to interact with the gel surface by hydrogen bonding. The importance of hydrogen bonding in the adsorption of dyes has been previously demonstrated in literature,[53] also in the case of related native[30,34] and hybrid[32] ionic liquid gels as sorbents.

To further investigate the adsorption ability of the gel, we went on to evaluate the sensitivity of the removal efficiency to temperature. To this aim, we determined the removal efficiency of the same gel, at 40 °C, toward the RhB/BPA mixture, after 24 h of contact. The RE% amounted to 99% and 54% for RhB and BPA, respectively, evidencing that the performance of the gel is substantially maintained only with a slight reduction for BPA.

2.5. Reuse Tests

From a sustainability standpoint, it is desirable that the gel phase can be reused without any intermediate washing. Consequently, we went on to evaluate the reusability of the best performing hybrid gel, namely DBS-[bmpyrr][NTf$_2$]/graphite. To this aim, after an adsorption run, using binary mixtures of pollutants, the supernatant aqueous phase was removed and replaced with a new

batch of aqueous mixture. Contact between the hybrid gel and the aqueous phases was maintained for 24 h, at 25 °C. This procedure was repeated until a significant reduction in removal efficiency occurs for at least one component of the mixtures. The results obtained are reported in **Figure 6** and Table S4 (Supporting Information).

The results summarized in Figure 6 show in general a good degree of recyclability of the hybrid gel, although its behavior appears markedly influenced by the nature of the components of the aqueous mixture. More specifically, we found the best reusing performance when gel is contacted with the RhB/BPA and RhB/CBZ mixtures (Figure 6a,b). In both cases, RhB is removed almost entirely from the aqueous phase, at the RE% keeps practically constant over 15 or 16 adsorption runs. Moreover, 90% of BPA is removed without loss in efficiency over 15 cycles, after which a pronounced drop in RE% is observed. Similarly, for CBZ a high RE% is maintained for five cycles, followed by a slight decrease in the adsorbed amount which reaches a still good value of 80%, maintained until the 13th reuse. After that RE% decreases regularly, halving at the 18th cycle of reuse.

Examining the plot reported in Figure 6c, reveals a different trend for the RhB/DCF mixture. In particular, while RhB exhibits the same behavior previously described, with RE% > 96% over 15 cycles, the efficiency for DFC decreases regularly, passing for 90% to 40% in only six cycles. Thus, CBZ is adsorbed in higher amounts than DCF. In contrast with what happens in fully ionic hybrid gels in aromatic ILs,[32] this result cannot be ascribed to the different π-surface area of these molecules, given the high

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Table 3. RE% of RhB/BPA mixture over [bmpyrr][NTf$_2$]/graphite gel on sequential columns at 25 °C.

	RE_{RhB} [%][a]	RE_{BPA} [%][a]
cotton	23	0
1st column	22	0
1st column[b]	49	5
2nd column[b]	82	32

[a] RE% are average values of triplicate runs and are reproducible within ± 4%;
[b] Elution after the solution was contacted 3 min with the gel.

Table 4. RE% after adsorption of aqueous mixtures of pollutant by DBS-[bmpyrr][NTf$_2$]/graphite gel embedded in a dialysis membrane.

Mixture	RE_{RhB} [%]	RE_{CBZ} [%]	RE_{DCF} [%]	RE_{BPA} [%]
RhB/BPA	83			97
RhB/CBZ	90	67		
RhB/DCF	78		36	

affinity of the gel toward BPA. The marginal role played by $\pi-\pi$ interactions is also consistent with the aliphatic nature of the IL in our gel. Instead, we propose that such findings can be ascribed to the anionic nature of DFC. Indeed, this gel appears to adsorb selectively neutral and cationic species over anionic ones, as also demonstrated in the case of the MO/BPA mixture (Figure 6d). In this case, the removal efficiency toward the anionic dye is the lowest detected and regularly decreases at each cycle of reuse, reaching only 10% after six cycles.

2.6. Adsorption Tests in Different Devices

To probe the performance of our gels in a more realistic setting, we used it as loading for columns to treat flowing aqueous phases. As a model mixture, we used the one which gave us the best results, namely the RhB/BPA one. In particular, we filled three columns with 500 mg of gel each and then 3 mL of solution were eluted on the first column. The eluate obtained was then poured on the second one and the procedure was repeated another time. To avoid leaching the gel outside the column, it was necessary to interpose a layer of cotton (1 g) between the gel and the open end of the column. Thus, we determined the RE% after elution in each column, taking account also the contribution of the cotton alone. The results obtained are reported in **Table 3**.

At first, we allowed the solution to freely flow through the gel, but the RE% obtained was very low, due to the insufficient contact time. For this reason, we next allowed 3 min of contact prior to elution of the treated mixture. The results obtained show that sequential elution on columns has both pros and cons compared

with the static adsorption experiments. On the one hand, a nett RE% of 59% is achieved for RhB, in only after only 6 min of treatment. On the other hand, the RE% for BPA is much lower, reaching only 32% after the same time. In any case, however, the volume of solution treated (3 mL) was larger than the one used in the static adsorption runs (500 μL) and the time of contact was significantly lower.

Finally, to further assess the performance of our hybrid gel in the treatment of much larger volumes of pollutant mixture, we embedded 1 g of hybrid gel within a dialysis membrane (d = 21 mm; flat width = 35 mm, 12,000 Da). Then, we immersed the gel-embedded membrane in a beaker containing 20 mL of RhB/BPA aqueous solution, maintaining contact for 24 h, at 25 °C. Representative pictures of the experimental setup are reported in **Figure 7**, while the results obtained are summarized in **Table 4**.

The results reported in Table 4 reveal that both RhB and BPA are almost completely removed from the solution, which is notable, given that the volume of solution treated is 40 times larger than the one present in the previous static adsorption experiments.

Encouraged by these results, we also applied the same procedure to the adsorption of pollutants from other mixtures, namely RhB/CBZ and RhB/DFC. In the first case, we observed good to high removal efficiencies for both components. Finally, the results obtained in the presence of RhB/DFC mixture, once again point out that the anionic drug DFC is adsorbed in a much smaller fraction than its cationic counterparts, confirming the trend already shown in the kinetic runs and in the reuse experiments alike. Looking at these results as a whole, shows that the trend observed are not only maintained upon carrying out the adsorption from larger volume of solutions, but also amplified, in terms of the different affinity of the gel sorbent phase to the
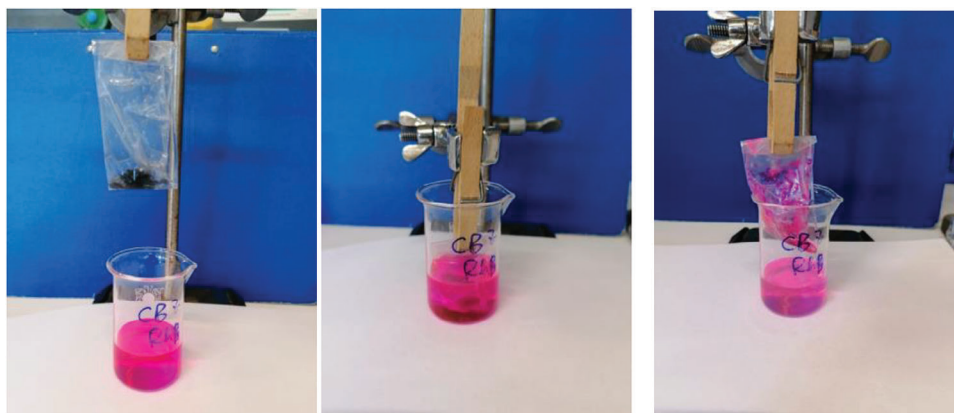

Figure 7. Representative picture of adsorption of aqueous mixture of pollutant by DBS-[bmpyrr][NTf$_2$]/graphite gel embedded in a dialysis membrane.
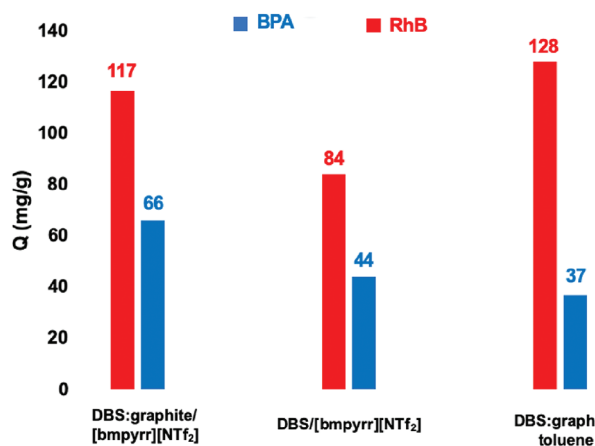
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Figure 8. Results of saturation experiments at 25 °C, in the presence of the DBS:graphite/[bmpyrr][NTf$_2$] 3 wt.%, DBS/[bmpyrr][NTf$_2$] 3 wt.%, DBS:graphite toluene 3 wt.%.

pollutants. Nevertheless, our hybrid gels show good removal performance on treating mixture with a diverse range of pollutant, making it a promising material for the efficient treatment of real wastewaters.

2.7. Comparison with Literature

To better assess the performance of our material in the wider context of sorbents for the treatment of wastewaters, we now compare our results with the ones reported in literature for related systems. To this aim, we first determined the amount of pollutant which saturates the best-performing gel, DBS:graphite/[bmpyrr][NTf$_2$], considering the BPA/RhB mixture. We contacted 250 mg of gel with 25 mL of the pollutant mixture solution, for 24 h at 25 °C, and determined the amount of pollutant adsorbed. Given the much higher amount of pollutant present, only partial adsorption took place. We determined the amount of pollutant adsorbed in terms of adsorption capacity Q, defined as the mg of pollutants adsorbed per gram of gelator, Equation (1).

$$Q = \frac{(C_0 - C_e) \, V}{m} \qquad (1)$$

where C_0 is the initial concentration of pollutant and C_e is its equilibrium concentration of BPA expressed in mg mL^{-1}. Furthermore, m is the mass in g of the gelator and V the volume of solution, expressed in mL. In this way, we found a saturating amount equal to 117 mg g^{-1} for RhB and 66 mg g^{-1} for BPA.

Given the above results, it can be interesting to evaluate the advantages deriving from the presence of graphite and the IL, by performing the same saturation experiments with the gel of DBS/[bmpyrr][NTf$_2$] (3 wt.%), devoid of carbon material, and the organogel of the DBS:graphite in toluene (3 wt.%), devoid of IL. It is indeed reported in the literature that DBS gels in such solvent.[54] The results obtained are reported in **Figure 8**.

Analysis of the results reported in Figure 8, clearly shows that the presence of both the carbon material and the IL is beneficial. In particular, in the absence of graphite, the adsorption ability

of the gel significantly decreases for both RhB (Q = 84 mg g^{-1} compared with 117 mg g^{-1}) and BPA (44 mg g^{-1} compared with 66 mg g^{-1}). On the same line, while the organogel of the DBS:graphite composite in toluene practically retains the same adsorption ability of the ionic liquid gel (Q = 128 mg g^{-1} compared with 117 mg g^{-1}), it shows a drastically reduced adsorption ability for BPA, (Q = 37 mg g^{-1} compared with 66 mg g^{-1}). With this information at hand, we can now compare our results with those reported in the literature. For a meaningful comparison, we limited our choice to works sharing with our gel, the removal of at least one contaminant as component of the mixture. We have compiled such examples, alongside our results in **Table 5**.

Examination of the results reported in Table 5, shows that in general, our gels require more time, but are more efficient in terms of adsorption capacity, compared with most of the other systems reported.

In particular, when we compare the adsorption capacity of our gels with the one of a pillar-[5]-arene- based polymer,[55] (entry 1 and 2), we find that the adsorption capacity for the same pollutant, BPA, is almost one order or magnitude higher (Q = 66 and 6.5 mg g^{-1}, respectively). Comparing the results obtained toward cationic dyes, the performance of our gel is still superior, although the dyes considered are different, namely RhB and MB (Q = 117 and 6.5 mg g^{-1} for RhB and MB, respectively). It is important to note though, that this work focused on the adsorption of a very dilute solution of remarkably four pollutants at the same time, including also 1-naphthylamine (1-NA) and the drug propanolol (Prop).

Similar conclusions can be made when we compare our results (entries 1 and 3) with the ones obtained for a cyclodextrin-grafted cellulose,[56] employed for the adsorption of a three-component mixture, featuring BPA, MB and Cu^{2+} cations. Also in this case, we find a much higher adsorption of BPA for our gel, (Q = 66 and 0.97 mg g^{-1}) whereas the performance of our gel is comparable for the cationic dyes, (Q = 117 and 122 mg g^{-1} for RhB and MB, respectively). Moreover, when we compare the performance of our hybrid gel with the one of a graphene oxide-polyvinyl alcohol composite,[57] used as sorbent for a binary mixture of dyes the cationic MB and the anionic MO (entries 1 and 4), we find that the adsorption capacity for RhB in our case is lower than the one for the polymer composite (Q = 117 and 231 mg g^{-1} for RhB and MB, respectively), while this latter shows no observable propensity for the adsorption of the anionic dye. As previously described, also in our case we found a preference for cationic over anionic species in terms of adsorption, although our hybrid gels exhibited a low but appreciable adsorption toward MO.

Finally, we compare our results with sorbents based on functionalized cyclodextrins, in which the cavity of the macrocycle includes one contaminant as guest. In particular, a citric acid-crosslinked β-cyclodextrin polymer,[17] shows a lower adsorption capacity for BPA compared with our gel (Q = 34.7 and 66 mg g^{-1}, entries 1 and 5), in a comparable contact time. Similar conclusion can be drawn by comparing the performance of our gel with a functionalized β-cyclodextrin,[58] (entries 1 and 6) in which the adsorption capacity for BPA was much lower (Q = 16.9 mg g^{-1} in mixture with MB and 21.4 mg g^{-1} with MO). It is worth noting that in this case the pH was regulated to 4 and 11 to optimize the adsorption conditions. The performance of our gel is inferior to the one of a Zr(IV)-β-cyclodextrin coordination

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Table 5. Comparison between the best results obtained in this work and in related systems in the literature.

Entry	Sorbent	Pollutant mixture	Time [h]	Pollutant-Q [mg g^{-1}]
1	DBS-[bmpyrr][NTf$_2$]/graphite gel[a]	RhB/BPA	24	Rhb-117
				BPA-66
2	Pillar-[5]-arene-polymer[55]	BPA/1-NA/Prop/MB	0.083	BPA-6.5
				1-NA-6.4
				Prop-7.5
				MB-6.5
3	Biomass-derived aerogel[56]	MB-BPA-Cu(II)	1	MB-122
				BPA-0.97
				Cu^{2+}−20
4	Graphene-oxide composite[57]	MB-MO	0.5	MB-231
				MO-Negligible
5	Citric acid-crosslinked β-cyclodextrin polymer[17]	BPA-MB- Cu(II)	20	BPA-34.7
				MB-44.8
				MO-27.30
6	Functionalized β-cyclodextrin[58]	BPA-MO	2	BPA-20.7 and 16.9
		BPA-MB		MB-22
				MO-21.4
7	Zr(IV) cross-linked carboxymethyl β-cyclodextrin[59]	BPA-EST-Cu(II)	0.16	BPA-78.8
				EST-182
				Cu(II)−220

[a] This work.

polymer,[59] which removed the same amount of BPA (Q = 66 and 68.8 mg g^{-1}, entries 1 and 7) but a much shorter time, 10 min instead of 24 h. The other components of the mixture, estradiol (EST) and Cu(II) were removed also with very high values of Q.

It is also useful to compare the performance of these different systems in terms of reusability. In our case, we could reuse the hybrid gel, for 12 cycles, without requiring any intermediate washing. Conversely, in the works reported in Table 5, where recycling was attempted, the adsorbent reuse never exceeded 5–6 cycles, and in most of them, the adsorbent was washed with a solvent or solution, in between each cycle.[17,57–59] In the only one case where such intermediate washing was not required, the material was reused six times.[55]

In the light of the above considerations, our hybrid gel shows competitive performance with most systems reported in the literature for simultaneous adsorption of similar pollutants.

3. Conclusion

The novelty of this work stands in the first use of DBS-based hybrid supramolecular gel for the simultaneous adsorption of different kinds of pollutants from wastewater, which conjugates adsorption efficiency and very good recyclability to a straightforward preparation.

As for HILGs properties, data collected show that their thermal stability is affected by the IL anion coordination ability and cation ability to give cation-π interactions with gelator. Furthermore, the presence of carbon nanomaterials heavily affects the rheological and mechanical properties. In particular, graphite significantly enhanced the mechanical resistance and flexibility of the native gel, whereas the incorporation of carbon nanotubes led to stiffer gels.

The use of hybrid gels as sorbents for binary mixtures of pollutants, namely RhB/BPA, RhB/CBZ, RhB/DCF, and

BPA/MO, demonstrates that the best performing gel was the DBS-graphite/[bmpyrr][NTf$_2$] one. Interestingly, in perfect agreement with economic aspects of sustainability, this gel was obtained by incorporating the cheapest material. Analysis of its removal efficiency as a function of time shows that both synergistic and antagonistic effects can be detected in dependence of pollutant nature. In particular, antagonistic effects are exerted by anionic pollutants.

As previously stated, the DBS-graphite/[bmpyrr][NTf$_2$] gel displayed good recyclability and could be reused for at least 12 consecutive cycles without loss in performance and need for intermediate washing.

In addition, this gel could be successfully embedded in a dialysis membrane to treat a larger volume of solution, achieving adsorption capacity of 117 and 66 mg g^{-1} for RhB and BPA, respectively. Comparison with the literature reveals that our gel has a comparable or superior performance for BPA removal compared with other systems previously reported in literature also in terms of recyclability. These considerations support our intention, in the next future, to expand the range of materials to be embedded in the gel matrix, with the aim to enhance efficiency and applicability.

4. Experimental Section

Materials: Commercially available D-sorbitol, benzaldehyde, single walled carbon nanotubes (TCI, >55%) graphite powder (Fluka, ≥ 99.0%), graphene oxide (Sigma 4–10% edge-oxidized), graphene platelets (IoliTech, 99.5%, 11–15 nm) bisphenol A (BPA), methyl orange (MO), rhodamine B (RhB), diclofenac sodium salt (DCF), and carbamazepine (CBZ) were used without further purification. Ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF$_4$], IoliTech, 99%), 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$], IoliTech, 99%) 1-butyl-3-methylimidazolium

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bis(trifluoromethanesulfonyl)imide ([bmim][NTf$_2$], IoliTech, 99%), N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ([bmpyrr][NTf$_2$], IoliTech, 99%), and N-butyl-N-methylpiperidinium bis(trifluoromethanesulfonyl)imide ([bmpip][NTf$_2$] IoliTech, > 98%) were obtained from commercial sources, dried at 60 °C at reduced pressure for 1 h and stored in a desiccator under Ar and over CaCl$_2$ before usage. DBS was prepared according to reported procedures.[60]

Preparation of Carbon Material-DBS Nanocomposites: The suitable amounts of DBS and carbon materials were weighed and intimately mixed by grinding in a mortar, until obtaining a uniform powder.

Gelation Tests: The suitable amount of nanocomposite was weighed in a screw-capped vial (diameter 1 cm) together with the appropriate IL (≈250 mg), and the mixture was dispersed under ultrasonication, (20 kHz, 200 W) for 10 min. Then, it was heated at 80 °C for 1 h, under magnetic stirring. The hot dispersion was sonicated for further 10 min. Subsequently, the mixture was kept at 4 °C overnight. Gel formation was assessed by tube inversion test.[47]

T$_{gel}$ Determination: T_{gel} was determined by the falling drop method.[42] A vial containing the preformed gel was placed upside-down in a water bath. The bath temperature was raised gradually (1 °C min^{-1}) until the gel collapsed and flow was observed. T_{gel} values were reproducible within 1 °C.

Rheological Measurements: Typical rheological measurements were carried out on a strain-controlled rheometer equipped with a Peltier temperature controller and a plate–plate tool. Strain and frequency sweep measurements were carried out at 25 °C, on three different aliquots of gels, within the linear viscoelastic region. In particular, strain sweeps were performed at a frequency of 1 rad s^{-1}, while frequency sweeps at a fixed oscillation strain of 0.1%.

SEM Images: Samples for the SEM images were obtained by casting the gel into an aluminum stab and washing it with ethanol, to remove the ionic liquid, according to a published procedure.[26] SEM images were obtained on a PRO X PHENOM electronic scanning microscope, operating at 5 kV.

Adsorption Tests: Aqueous solutions of RhB and MO were prepared by dilution of suitable stock solutions. Aqueous solutions of BPA, CBZ and DCF were prepared by dilution of stock solutions of in methanol. These latter were diluted in water to achieve the desired concentration, maintaining the amount of methanol to 3% (v:v). Typical adsorption tests were carried out in vials by placing onto 250 mg of preformed gel (3 wt.%), 500 μL of pollutant aqueous solution. After a suitable time, an aliquot of solution was withdrawn, diluted and then the relevant UV-spectrum was recorded. The residual concentrations of pollutant were determined based on calibration curves previously determined. The initial concentration of the aqueous solutions of pollutants was equal to $1.8 \cdot 10^{-4}$ M, with the exception of BPA for which a concentration of $4.0 \cdot 10^{-4}$ M was used. The same procedure was followed for the adsorption of pollutants from their binary mixtures.

Gel recycling experiments were carried out by removing the aqueous phase after an adsorption run and replacing it with a fresh batch of pollutant solution. The residual concentrations of pollutants were determined as described above.

For adsorption of mixtures of pollutants carried out in a dialysis membrane (d = 21 mm; flat width = 35 mm, cut off = 12,000 Da) this latter was filled with 1 g of gel and immersed in 20 mL of pollutant aqueous for a contact time of 24 h. Adsorption tests on column, were carried out according to a published procedure.[34]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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