

# Design of environmentally friendly eutectogels as efficient materials for wastewater treatment

*Salvatore Marullo,<sup>†</sup> Alessandro Meli,<sup>†</sup> Nadka Tz. Dintcheva,<sup>‡</sup> Giulia Infurna,<sup>‡</sup>*

*Carla Rizzo,<sup>†</sup> Francesca D'Anna<sup>†\*</sup>*

*<sup>†</sup>Università degli Studi di Palermo, Dipartimento di Scienze Biologiche, Chimiche e*

*Farmaceutiche, Viale delle Scienze, Ed. 17, 90128 Palermo, Italia*

*<sup>‡</sup>Università degli Studi di Palermo, Dipartimento di Ingegneria, Viale delle Scienze Ed. 8, 90128*

*Palermo, Italy*

## **Abstract**

Contamination of water resources is a pressing concern of modern society and identification of possible solutions represents a challenge for the current scientific research. Materials used for wastewater treatment should be themselves of low environmental impact, to minimize the process footprint. With the above premises in mind, we obtained supramolecular gels of L-amino acids in the deep eutectic solvent formed by choline chloride and phenyl acetic acid. After gel full characterization, determining gel-sol transition temperature and investigating gelation kinetics, rheological properties and morphological features, a deep and careful analysis of their application as sorbents for the removal of cationic dyes from aqueous solutions was performed. In particular, considering that the nature of wastewater can change in dependence on the source and the water contaminants, we analyzed both the effect of the *pH* and dye nature. Furthermore, performance of soft materials was investigated as a function of volume and concentration of wastewater and related to the nature of the gelator.

Data collected demonstrate that the best removal efficiency, for all dyes used, can be obtained with L-Phenylalanine-based eutectogel. This gel can be reused for at least 9 times without loss in

efficiency, also in the presence of mixtures of dyes. Interestingly, from an applicative point of view, this gel can be used as loading of a column proving able to decolorize large volumes of flowing solutions, achieving the 85% of removal efficiency in only 10 minutes and allowing its reuse for at least 4 times with only minor drop in efficiency.

## **Introduction**

The improvement of modern living standards arising from widespread industrial development, comes with the price of less desirable consequences like the impoverishment of fossil energy sources and pollution of air and water bodies. Consequently, the scientific community is placing intensive effort to devise and implement changes in the production chain to ensure a more sustainable development. More in particular, some pollutants raise concern because they are environmentally harmful even at low concentration and are also recalcitrant to conventional water treatment methods. Industrial dyes fit this description, and are mainly present in wastewaters originated by textile and paper industries.<sup>1</sup> Dyes are often carcinogenic, mutagenic and relatively hard to remove with conventional water treatment methods, due to their stable aromatic structure.<sup>2</sup> A number of alternative methodologies have been employed to this purpose so far, like flocculation, photocatalysis and adsorption.<sup>3</sup> This latter is widely regarded as the most promising in terms of cost-effectiveness and simplicity of use.<sup>1</sup> <sup>4</sup> Among the various materials that can be used as sorbents, nanostructured materials have recently gained much interest, owing to their high surface area, high uptake capacity and often selectivity. These include materials such as carbon nanotubes,<sup>5</sup> graphene oxide<sup>6</sup> and supramolecular gels.<sup>7</sup> Supramolecular gels are materials originated from the self-assembly of small molecules (LMWGs) in dilute solution. As a result, the aggregation leads to a sample spanning self-assembled network, capable of entrapping the solvents by capillary forces, generating solid-like materials.<sup>8,9</sup> A distinctive feature of supramolecular gels is that these materials are underpinned solely by non-covalent, reversible interactions. This, in principle, endows gels with reversible response to external stimuli and the ability to self-heal after being broken down. Gels are frequently classified depending on the

solvents by which they are constituted, distinguishing, for instance, between hydrogels and organogels, featuring water and organic solvents, respectively.

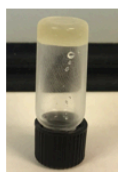
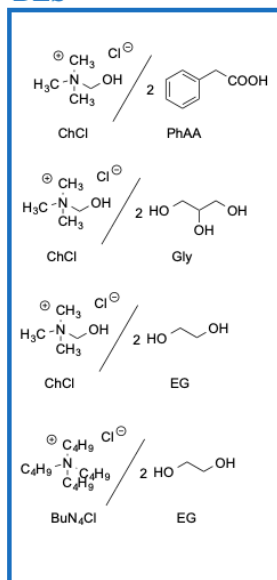
The development of non-conventional solvents, driven by sustainable chemistry, has impacted also the field of gels, giving rise to gels in ionic liquids known as ionic liquid gels<sup>10</sup> (ILGs) and, very recently, in deep eutectic solvents (DES),<sup>11-14</sup> yielding eutectogels.<sup>15-18</sup>

Specifically, DES are mixtures of compounds with a definite melting point, lower than any individual component. From the standpoint of Green Chemistry, DES possess convenient properties such as low vapor pressure and flammability. Moreover, they are often composed by cheap, readily available compounds with little or no toxicity. Finally, their preparation only requires mixing the components without need for synthetic or purification steps.

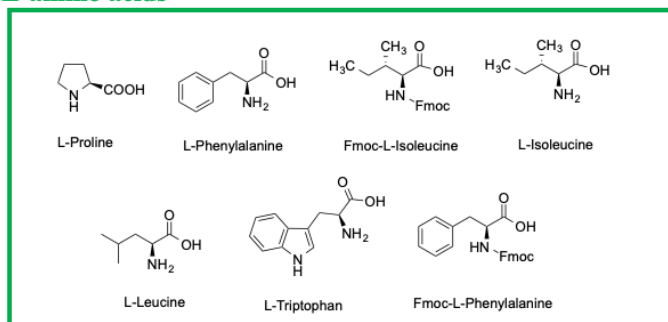
Supramolecular gels have proven successful to remove a diverse range of dissolved pollutants or oil spills from water.<sup>7</sup> In this context, we have recently shown that these materials allow fast and thorough removal of dyes from water with high recyclability,<sup>19, 20</sup> fuel desulfurization,<sup>21</sup> as well as remediation of Cr(VI) polluted waters.<sup>22</sup> Although the obtainment and use of ionic liquid gels has recently gathered a certain interest,<sup>10, 23-27</sup> the attention for eutectogels is less common,<sup>15-18, 26, 28-30</sup> These can be ideal candidates as materials for environmental applications, considering the very low toxicity of solvent components. The above advantage hires a further value if also gelator is non toxic and derives from renewable sources.

With the above premises in mind, our main goal was the obtainment of fully natural eutectogels to be applied as sorbents for the removal of dyes from wastewater. In particular, we considered as gelators amino acids bearing both aliphatic and aromatic side chains (Chart 1), and investigated their gelling ability in DES differing for both HBD and HBA nature (Chart 1). Changing the above structural features can affect properties of supramolecular gel phases, but also the removal efficiency, as a consequence of the supramolecular interactions established with water contaminants.

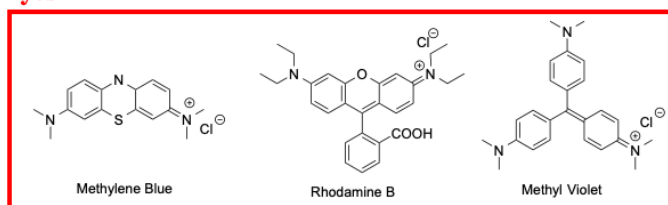
## DES



## L-amino acids



## Dyes



**Chart 1.** DES, L-amino acids, dyes used and representative picture of an eutectogel.

The gels obtained were characterized by standard gelation tests and gel-sol transition temperature ( $T_{\text{gel}}$ ). Gelation kinetics were investigated by opacity measurements, while rheological properties were studied by strain- and frequency sweep measurements. Moreover, we obtained morphological information by Polarized Electron Microscopy (POM) and Scanning Electron Microscopy (SEM). Then, we deeply analyzed the application of our eutectogels as sorbents for the removal of cationic dyes, namely Rhodamine B, Methylene Blue and Methyl Violet from water. The cationic dyes were different for size, shape and  $\pi$ -surface. All these factors might play a pivotal role in determining results of adsorption process.

Sorbents were firstly tested using aqueous solutions having different  $pH$ . Indeed, this parameter can significantly vary in dependence on the wastewater source. Then, we assessed materials performance using both single and mixed dye solutions and considering both static and flowing adsorption systems. Furthermore, using static conditions, we analyzed both the effect of dye concentration and volume of wastewater used.

Data collected evidence how the obtained eutectogels worked better in acidic solutions. Among, different materials, L-Phe-based eutectogel proved able to remove 90% of Rhodamine B and Methyl

Violet after 24 and 6h of contact, respectively. This eutectogel showed good performance also in the presence of mixed dye solutions, that better mimic real samples. In static conditions, it can be reused for at least 9 cycles, without intermediate washing and loss in performance. Furthermore, it can be used as loading of a column and, the sequential system formed by two columns, allows treating large volume of water, removing 85% of dyes in 10 minutes and can be reused for 4 cycles with only minor drop in efficiency.

## **Experimental section**

### *Materials*

Commercially available choline chloride, phenylacetic acid, L-proline, L-tryptophan, L-isoleucine, L-leucine, L-phenylalanine, Fmoc-L-phenylalanine, Fmoc-L-isoleucine, Methyl Violet, Rhodamine B and Methylene Blue were used without further purification.

### *General procedure for the preparation of DES*

The suitable amounts of phenylacetic acid and choline chloride were weighed in a round bottom flask. The resulting mixture was heated at 60 °C for 30 minutes and stirred until obtaining a limpid liquid, which was then dried under reduced pressure at 60 °C for 1 hour and kept in a dessiccator over calcium chloride.

### *General procedure for the preparation of eutectogels*

Gels were prepared by weighing into a screw-capped sample vial (diameter 1 cm) the suitable amounts of amino acid and DES. The sample vial was heated in an oil bath at 80 °C for 30 minutes, during which a clear solution was obtained. The vial was then rapidly cooled at 4 °C and then left to stand at room temperature. The tube inversion test method was used to assess gel formation.<sup>31</sup>

### *T<sub>gel</sub> determination*

$T_{gel}$  were determined by the falling drop method. A vial containing the preformed gel was placed upside-down in a water bath. The bath temperature was raised gradually (1 °C/ min) until the gel collapsed and flow was observed.<sup>32</sup>  $T_{gel}$  values were reproducible within 1 °C.

### *Opacity Measurements*

Opacity measurements were recorded with a spectrophotometer. The opacity of the gel phases was determined with UV-Vis measurements as a function of time, at a wavelength of 568 nm at 25 °C. Samples for a typical measurement were prepared by injecting into a quartz cuvette (light path 0.2 cm) the limpid hot solution of salt, recording spectra until gel formation. The gel phase obtained at the end of the measurement was stable after the tube inversion test.<sup>31</sup>

### *Rheology measurements.*

Rheological measurements were recorded on a strain-controlled rheometer using a Peltier temperature controller and a plate-plate tool. For a typical measurement, the gel was formed in a plastic blister pack, then placed between the shearing plates of the rheometer. Strain and frequency sweep measurements were carried out at 25 °C, on three different aliquots of gels.

### *POM measurements*

Eutectogels at 3 wt % of the gelator were cast between two glasses to record the POM images.

The instrument used was an Optika B-353 PL microscope equipped with crossed polarisers, and an Optika camera interfaced to a computer with Optika Vision Pro Software.

### *SEM measurements.*

SEM images were acquired on an instrument with an operating voltage of 20 kV. Samples were prepared by placing xerogels on an aluminum stub. Xerogels were obtained following a procedure

reported in literature.<sup>33,34</sup> In particular, gels were thoroughly washed with ethanol to remove the DES, and then converted to xerogels by freeze drying.

### *Dye Adsorption tests*

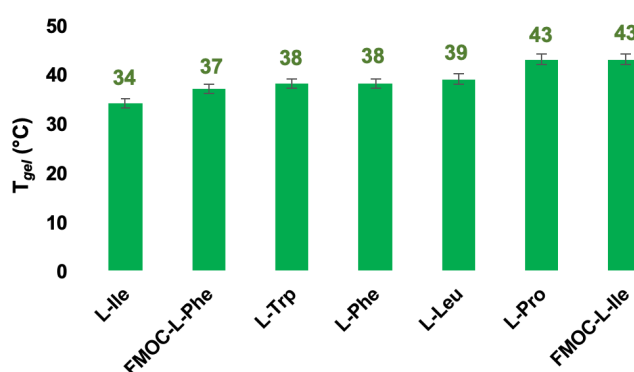
Dye adsorption tests were firstly carried out in vials by placing onto the 250 mg of preformed eutectogel (3 wt %), 500  $\mu$ L of a  $1.8 \cdot 10^{-4}$  M aqueous solution of dye. After a given time, an aliquot of solution was withdrawn, suitably diluted, then the relevant UV-vis spectrum was recorded. Concentrations were obtained based on calibration curves obtained by measuring the absorbance of aqueous solutions of the dye at increasing concentrations. The removal efficiency of gels was also investigated in a gel column using a previously reported procedure.<sup>20</sup> To this aim, 1g of eutectogel were placed on the bottom of a column, ( $\varnothing=4$  cm), whose septum was previously covered with a layer of sand. Blank experiments assured that no dye was adsorbed by the sand alone. Then, 3 mL of aqueous solution of the dye was added from the top of the column. An out flow of discolored water from the bottom of the column was observed and it was introduced again in a next column containing another aliquot of gel. This procedure was repeated a third time when clear water out flowing from the column was observed. The experiment was performed under atmospheric pressure and at 25 °C.

## **Results and discussion**

Firstly, we tested the gelling ability of the L-amino acids considered, in DES different both for HBD and HBA nature. To this aim, a mixture containing the opportune amounts of L-amino acid and DES, was heated under stirring until obtaining a clear solution, rapidly cooled down at 4 °C, then left at room temperature. The formation of a gel was assessed by the tube inversion method.<sup>31</sup> The results are reported in Table S1.

Examination of results reveals that we obtained gels only in the DES ChCl/PhAA 1:2. These gels were opaque, and stable at room temperature for at least 2 months. A representative picture of one eutectogel is reported in Chart 1.

For a useful comparison, we chose a common concentration of 3 wt % to characterize the gels. To assess the thermal stability of our gels, we determined the gel-sol transition temperature ( $T_{gel}$ ), by means of the falling drop method,<sup>32</sup> obtaining the results reported in Figure 1.



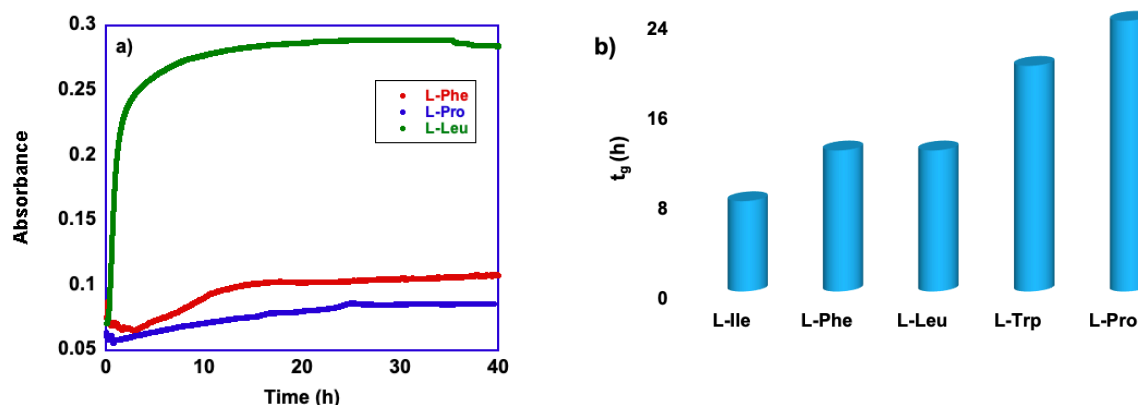
**Figure 1.**  $T_{gel}$  of the L-amino acid-based eutectogels in ChCl/PhAA 3 wt %.  $T_{gels}$  for the L-Ile and L-Trp-based gels are taken from Ref. 16.

Looking at the plot reported in Figure 1 reveals that the thermal stabilities do not span a large range of temperatures, given that the lowest and highest values differ for about 10 °C.  $T_{gels}$  increase in the order L-Ile < L-Fmoc-Phe  $\approx$  L-Trp  $\approx$  L-Phe  $\approx$  L-Leu < L-Pro  $\approx$  L-Fmoc-Ile and no obvious structural trend can be extracted, even by considering aliphatic and aromatic amino acids separately. However, comparing the  $T_{gels}$  obtained for the L-Ile and L-Pro-based gels, as well as the ones of gels based on amino acids with aromatic side chains, like L-Trp, Fmoc-L-Phe and Fmoc-L-Ile, shows that variations in the alkyl chain in aliphatic amino acids leads to higher differences in  $T_{gel}$  compared with what happens by changing the aromatic portion of the amino acid side chain. As the aliphatic amino acids differ for the organization of the side chain, the result obtained indicates that a lower conformational



freedom gives rise to more stable gels. On the other hand, notwithstanding small differences detected in  $T_{gel}$ s corresponding to gels formed by aromatic amino acids (cfr. Fmoc-L-Phe, L-Trp, L-Phe), adding a bulky aromatic group like Fmoc on the gelator structure, impacts the  $T_{gel}$ s differently, depending on which amino acid is considered. Indeed, going from the gels formed by L-Phe and Fmoc-L-Phe,  $T_{gel}$  does not substantially change, whereas the opposite occurs for L-Ile and Fmoc-L-Ile, in which cases the same structural variations leads to the lowest and highest  $T_{gel}$  determined. From these findings, we can infer that the presence of both aliphatic and aromatic moieties leads to the most thermally stable eutectogel.

To have information about the rate of gel formation, we studied the gelation process by means of opacity measurements, carried out by UV-vis spectroscopic measurements. It is worth noting that for the gels formed by the two protected aminoacids, namely Fmoc-L-Phe and Fmoc-L-Ile, gelation at 25 °C was too slow to be followed by UV-vis spectroscopy. Plots of kinetic opacity measurements are reported in Figure 2a.



**Figure 2.** a) Plots of opacity measurements as a function of time, at 25 °C for some eutectogels considered and b) times required to reach a plateau in absorbance,  $t_g$ . Values of  $t_g$  for L-Ile and L-Trp are taken from Ref. 16.

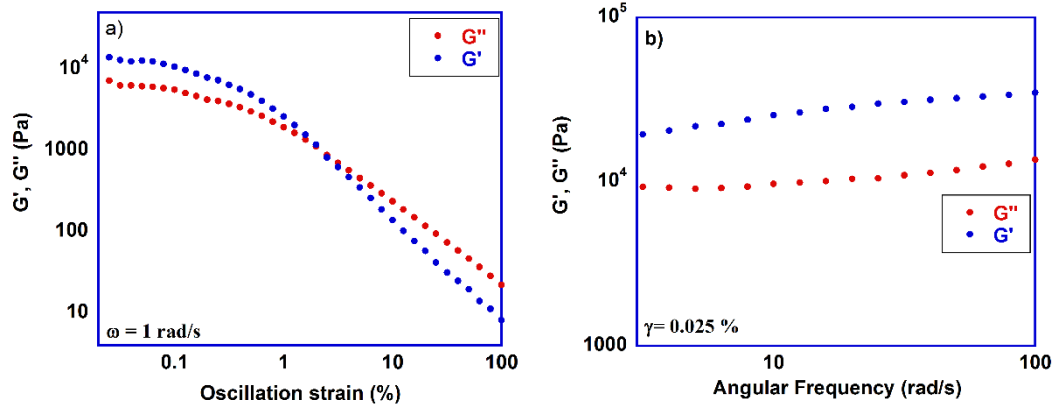
Kinetic plots reported in Figure 2a show that in all cases gelation follows a single step mechanism, with no clear evidence of induction times. This is in agreement with what we observed in our previous

work for the L-Ile and L-Trp-based eutectogels, at the same concentration.<sup>16</sup> A closer inspection of the plot reveals that the L-Leu based gels display a much higher plateau opacity than those formed by L-Pro and L-Phe, suggestive of a higher crystallinity and presence of polydisperse structures.<sup>31</sup> Further comments can be made by comparing the times at which a plateau in absorbance is reached ( $t_g$ , Figure 2b), which allows us to assess the differences in gelation rates.

In particular, gelation time decreases on going from the L-Pro to the L-Ile based eutectogels, following the order L-Pro > L-Trp > L-Leu  $\approx$  L-Phe > L-Ile ( $t_g = 24, 20, 12.5, 12.5$  and 8 h for L-Pro, L-Trp, L-Leu, L-Phe, and L-Ile, respectively). In general, we can observe that the eutectogel formed by the amino acid bearing the shortest alkyl side chain, L-Ile, forms faster.

On the other hand, the presence of a bulky aromatic group in the side chain slowed down gelation, as shown considering the L-Trp and the Fmoc-protected amino acid based gels. Interestingly, we observed a similar trend, at least from a qualitative point of view, when considering the gelation rate of ionic liquid gels formed by L-amino acid based salts.<sup>35</sup>

A fundamental aspect of gels to be considered for a given application is constituted by their rheological properties. Such measurements provide the necessary confirmation of the gel nature of the materials investigated, and information on their mechanical behavior and strength. For this reason, we carried out oscillatory rheology measurements, namely strain- and frequency sweeps on our eutectogels, at 25 °C. All the measurements were performed within the linear viscoelastic regime, and the relevant plots are reported in Figure 3 and S1.



**Figure 3.** Representative plots of a) strain- and b) frequency sweep measurements at 25 °C for the eutectogel formed by L-Phe in ChCl/PhAA 1:2, at 3 wt %.

From the rheological measurements, we can observe that in all instances the storage modulus  $G'$ , which accounts for solid-like rheological response, is higher than the loss modulus  $G''$ , over a wide range of oscillation strain. Furthermore, both moduli are practically constant over a considerable range of angular frequencies and again,  $G'$  keeps higher than  $G''$ . All these findings are well established hallmarks of gel-like rheological behavior and confirm the gel nature of our materials.<sup>31</sup> In addition, from these measurements, we can acquire information on the mechanical properties of the materials by considering two further parameters, *i.e.* the strain at the crossover point ( $\gamma_c$ ) and the loss tangent ( $\tan \delta$ ). The former is the amount of strain required to mechanically break the gel, under a given frequency, while the latter is the ratio between the moduli, ( $G''/G'$ ) and is correlated to the strength of colloidal forces underpinning the gel. In this case, a lower value of  $\tan \delta$  indicates the occurrence of stronger interactions. We report all the rheological parameters obtained in Table 1.

**Table 1.**  $G'$ ,  $G''$ ,  $\tan \delta = G''/G'$  at  $\gamma = 0.025\%$  and values of  $\gamma$  at  $G' = G''$  ( $\gamma_c$ ) for eutectogels investigated at 3 wt % of concentration at 25 °C. Error limits are based on average of three different experiments with different aliquots.

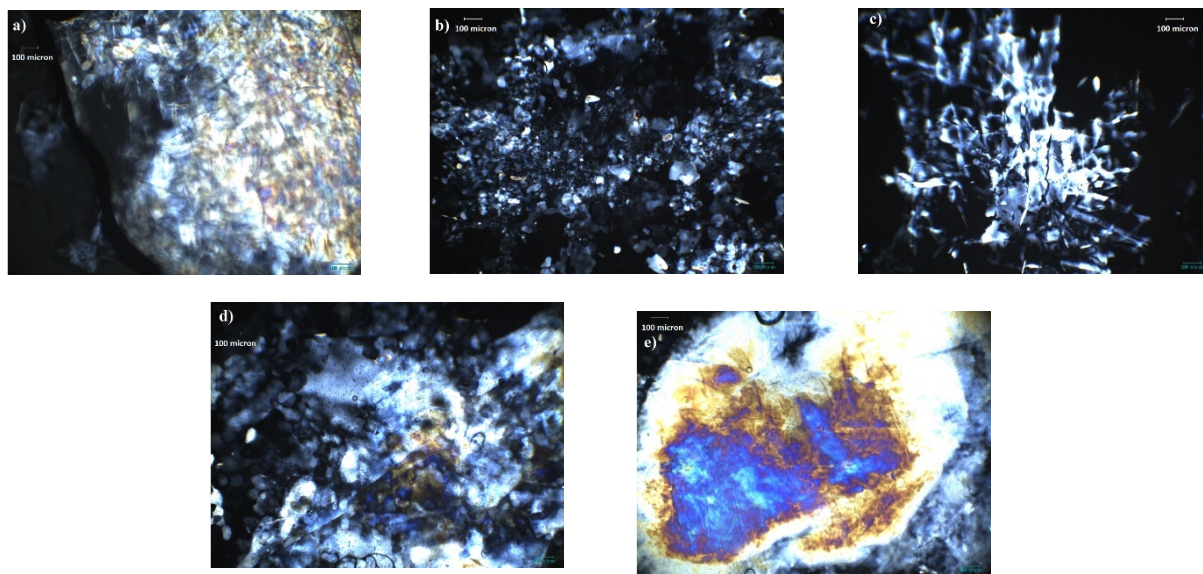
<b>Gelator</b>	<b><math>G'</math> (Pa)</b>	<b><math>G''</math> (Pa)</b>	<b><math>\tan \delta</math></b>	<b><math>\gamma</math> at <math>G' = G''</math> (<math>\gamma_c</math>, %)</b>
L-Trp <sup>a</sup>	1160±40	840±90	0.68±0.02	0.55±0.02
L-Pro	8900±1700	3710±70	0.42±0.09	0.80±0.01
L-Ile <sup>a</sup>	11000±3000	8000 ±1000	0.60±0.04	1.57±0.05
L-Phe	130000±20000	7800±700	0.62±0.15	2.00±0.10
L-Leu	15600±800	11200±700	0.72±0.08	0.81±0.06
FMOC-L-Phe	50300±200	27000±7000	0.52±0.13	1.60±0.10
FMOC-L-Ile	350000±88000	110000±40000	0.40±0.10	6.32±0.09

[a] From Ref. 16

A first glance at results reported in Table 1, points out that in all cases  $\tan \delta$  is lower than 1, suggestive of strong colloidal forces within the self-assembled network. Furthermore, the eutectogel formed by L-Trp is the weakest, while the one formed by FMOC-L-Ile stands out as the strongest, as inferred by all the three rheological parameters connected with the gels strength, namely  $\tan \delta$ ,  $\gamma_c$  and  $G'$ . Notably, in this case the  $G'$  value is one order of magnitude higher than those we obtained for ionic liquid gels.<sup>19, 20, 34, 35</sup>

In general, the presence of the bulky aromatic group Fmoc on the amino acid side chain, improves the gel strength, expressed by the  $G'$  and  $\tan \delta$ . Interestingly, the stronger gel exhibits a very low gelation rate and reminiscent of what we found for the  $T_{gel}$ , also in this case the increase in strength is much more pronounced for L-Ile, compared with L-Phe. Conversely, the gels formed by amino acid with aliphatic side chains, (L-Leu, L-Ile and L-Pro) show comparable mechanical strength, again expressed by  $G'$  and  $\tan \delta$  values.

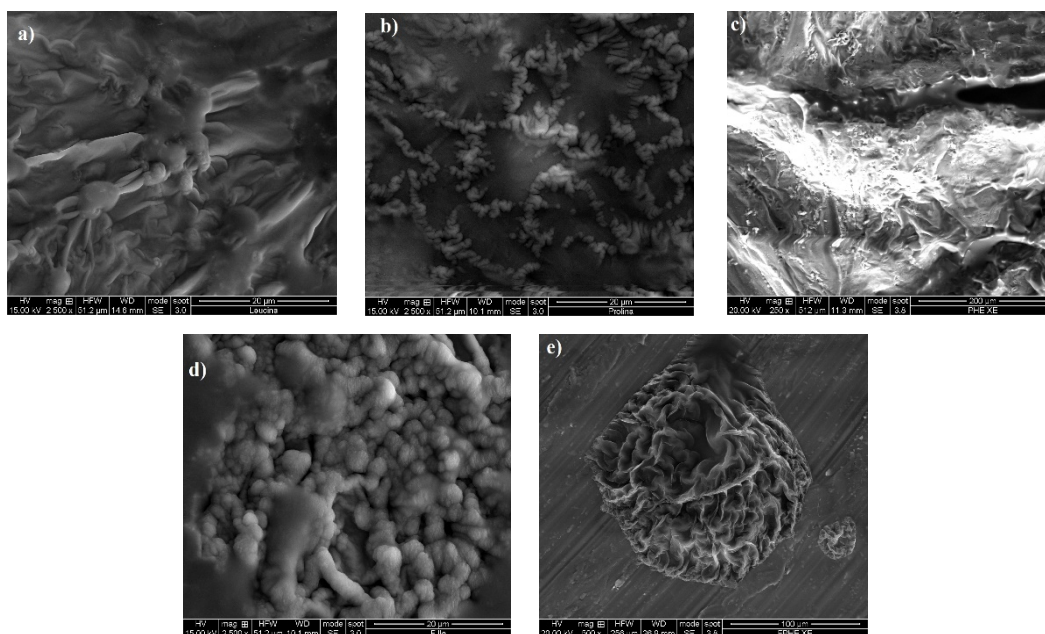
We then probed the morphology of the eutectogels by obtaining POM images, which are reported in Figure 4.



**Figure 4.** POM images obtained for the eutectogels in ChCl/PhAA, 3 wt % formed by a) Fmoc-L-Ile, b) L-Leu, c) L-Pro, d) L-Phe, e) Fmoc-L-Phe. Scale bar is 100  $\mu\text{m}$ .

Looking at the POM images reported in Figure 4, we can infer that in all cases the gels are characterized by the occurrence of regular-shaped objects. Moreover, the two gels formed by the two Fmoc protected amino acids, show clear evidence of anisotropy, similar to liquid crystals (Figure 4a,e).

To gain further information about the morphology of our eutectogels, we obtained SEM images of their xerogels, prepared by removing the DES by washing with ethanol. It is important to note that the formation of xerogels may result in a change in the pore size of the materials, due to effects of drying or sample preparation.<sup>36</sup> However, since all gels were subjected to the same treatment, the images obtained can still be used to gain a meaningful qualitative comparison of the morphology of the materials. SEM images recorded from the xerogels are reported in Figure 5.



**Figure 5.** SEM images obtained for the eutectogels in ChCl/PhAA, 3 wt % of gelator formed by a) L-Leu, b) L-Pro, c) L-Phe, d) Fmoc-L-Ile, e) Fmoc-L-Phe.

Analysis of the SEM images reported in Figure 5, highlights a pronounced influence of the amino acid used on the morphology of the relevant eutectogels. In particular, the gel formed by L-Leu exhibits the occurrence of large intertwined fibers connected by spheroidal structures (Figure 5a). Conversely, the gels composed by L-Pro and Fmoc-L-Ile (Figure 5b and 5d) are characterized by uniformly sparse spherical objects, whereas gel formed by Fmoc-L-Phe (Figure 5e) is characterized by network of fibers further coiled into honeycomb shaped structures. Finally, the L-Phe (figure 5c) based gel features a very thick appearance, and no particular morphology could be inferred. It is worth noting that the SEM images relevant to the L-Ile and L-Trp at the same concentration displayed different morphologies.<sup>16</sup> This wide diversity of morphologies from amino acid based self-assembled materials has been recently pointed out in the literature.<sup>37</sup> Furthermore, in the attempt to relate morphology to  $T_{gel}$ s and mechanical strength, we observed that, higher  $T_{gel}$  values and stronger gel phases were featured by the presence of spheroidal structures in the gelatinous network.

### Dye removal by adsorption

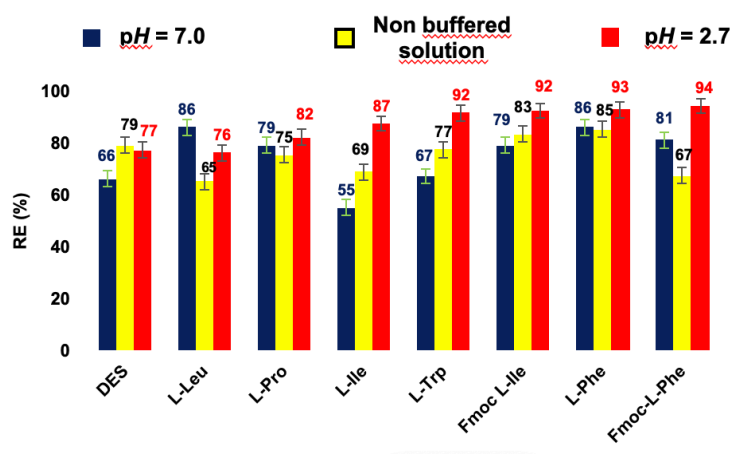
Our main goal was the use of eutectogels in wastewater treatment. Consequently, we firstly put in contact 250 mg of each eutectogel with 500  $\mu\text{L}$  of an aqueous solution of Rhodamine B (RhB,  $1.8 \cdot 10^{-4}$  M), at 25  $^{\circ}\text{C}$  for 24 hours, to verify the adsorption ability and the stability of soft materials to the contact with the aqueous solution.

Furthermore, bearing in mind differences in waste deriving from the nature of the source, we investigated also the effect of the  $\text{pH}$  of the aqueous phase, using solutions buffered at  $\text{pH}$  2.7 and 7.0 in addition to a non-buffered one. For a useful comparison, we carried out the same experiments also by using 250 mg of DES alone. In all cases, eutectogels kept their consistency also after an extend contact with the aqueous sample.

By recording the UV-vis spectra of the aqueous phase, on the basis of the Lambert-Beer law, we obtained the removal efficiency according to equation (1):

$$\text{RE (\%)} = \frac{C_0 - C(t)}{C_0} \cdot 100 \quad (1)$$

where  $C_0$  is the initial concentration of dye in the aqueous solution and  $C(t)$  is the dye concentration at a given time in the aqueous phase. The results obtained are summarized in Figure 6.



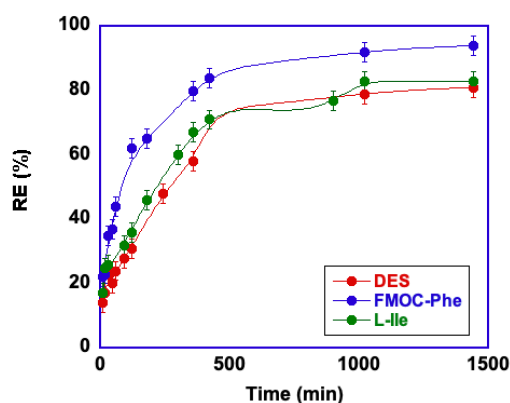
**Figure 6.** RE% of RhB ( $1.8 \cdot 10^{-4}$  M) by eutectogels and DES after 24 h, at 25  $^{\circ}\text{C}$  using aqueous solutions at different  $\text{pH}$ .

RE% are reproducible within  $\pm 3\%$ , based on triplicate tests.

Looking at the results reported in Figure 6, it is possible to evidence some recurring trends. In particular, for each gel, the  $pH$  of the aqueous phase affects the removal efficiency of RhB, and, with the exception of the gel formed by L-Leu, the highest efficiency was found by using the acidic solution. This can be explained considering that a basic aqueous phase could induce partial dissolution of the DES due to deprotonation of phenylacetic acid. It is noteworthy that, at this  $pH$ , the dye is removed by the gels more efficiently than the liquid DES.

Moving to the different efficiencies of the gel phases, values for RhB from the acidic solution increases following the order L-Leu < L-Pro < L-Ile < L-Trp  $\approx$  Fmoc-L-Ile  $\approx$  L-Phe  $\approx$  Fmoc-L-Phe. Interestingly, with the exception of L-Trp-based eutectogel, higher efficiencies were detected in the presence of mechanically stronger gels, as accounted for by  $G'$  values. The above result is different from the one we previously collected by using ionogels for dyes or Cr(VI) removal and sheds light on the effect of the solvent nature in determining materials performance.<sup>20, 22</sup> Furthermore, taking in consideration the side chain structure of the gelators, the above trend evidences a clear superior performance of the gels formed by amino acids with aromatic side chains over those with aliphatic ones, suggesting that adsorption of RhB, in this case, is mainly driven by  $\pi$ - $\pi$  stacking interactions. To obtain further insight on the adsorption process, we determined the removal efficiency for each gel, as a function of time, upon contact with a solution of RhB at the same concentration, at 25 °C. The results obtained are reported in Figure 7 and S2.



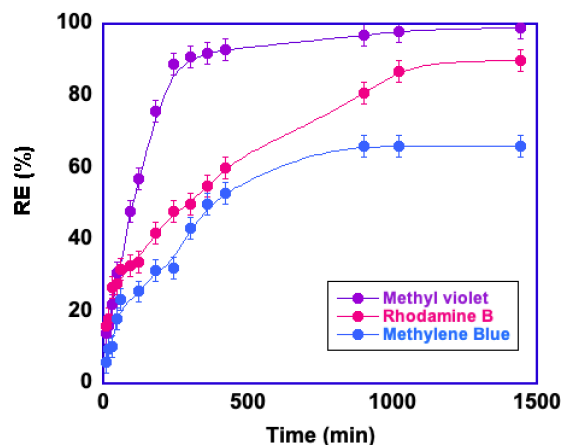


**Figure 7.** RE% of RhB ( $1.8 \cdot 10^{-4}$  M) by L-Ile- and Fmoc-L-Phe based eutectogel, at 3 wt % of gelator, as well as the DES as a function of time, at 25 °C using buffered aqueous solutions at  $pH= 2.7$ . RE% are reproducible within  $\pm 3\%$ . Lines are drawn as mere visual guide.

These plots reveal that the removal efficiency obtained by using eutectogels is never lower than that of the DES, and that, in all cases, a constant efficiency after 24 hours is detected, which indicated that the equilibrium has been reached.

In general, also the experiments as a function of time show a faster and more thorough removal by eutectogels based on amino acids with aromatic side chains, such as L-Phe, Fmoc-L-Phe and Fmoc-L-Ile, compared with the other gels. However, visual inspection revealed precipitation of the dye on the surface of the gels formed by Fmoc-L-Phe and Fmoc-L-Ile. For this reason, we carried out the next investigation using the L-Phe-based gel.

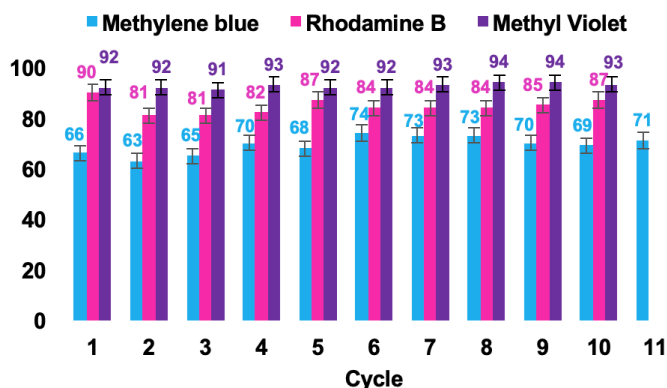
In general, one of the main issues, affecting the treatment of wastewater deriving from textile or paper industry, derives from the concomitant presence of different dyes. This is the reason why we tried to assess the adsorption efficiency towards different dyes and we put into contact the L-Phe-based eutectogel also with aqueous solution of Methylene Blue (MB) and Methyl Violet (MV), at initial concentrations of  $1.8 \cdot 10^{-4}$  M and  $5.0 \cdot 10^{-4}$  M, respectively. The RE were determined in separate experiments as a function of time, over 24 h, obtaining the results reported in Figure 8.



**Figure 8.** RE% of RhB ( $1.8 \cdot 10^{-4}$  M), MB ( $1.8 \cdot 10^{-4}$  M) and MV ( $5.0 \cdot 10^{-4}$  M) by 3 wt % L-Phe based eutectogel as a function of time, at 25 °C, using aqueous solutions buffered at pH= 2.7. RE% are reproducible within  $\pm 3\%$ . Lines are drawn as mere visual guide.

The trends of RE (%) in Figure 8 clearly show an increase in removal efficiency and in the rate of adsorption on going from MB to MV. This can be related to the concomitant increase in the  $\pi$ -surface area, further confirming the importance of  $\pi$ - $\pi$  interactions between the dyes and the aromatic groups of the amino acid, in driving the adsorption process.

Obviously, considering such kind of application, the possibility of sorbent reusing together with the above claimed environmentally friendly nature, plays a pivotal role. Indeed, in perfect agreement with sustainability requirements, this will prevent the formation of large amount of waste. With the above premise, we went on to test the recyclability of the gel phase keeping in contact, the L-Phe based eutectogel with an aqueous solution of each dye for 24 hours, at 25 °C. Then, after determining the removal efficiency, the aqueous phase was removed and replaced with a fresh batch of dye solution. The results obtained for the three dyes are reported in Figure 9.



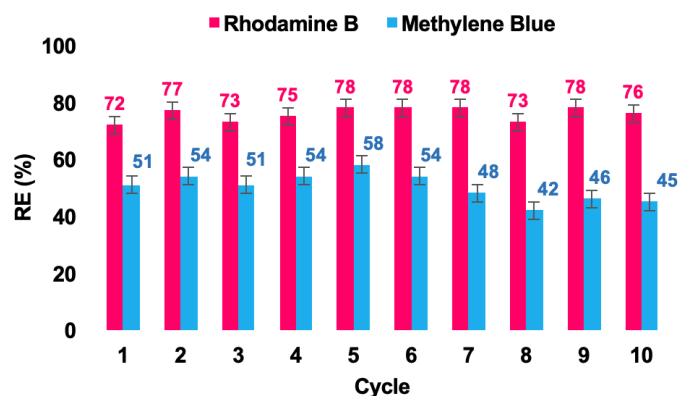
**Figure 9.** RE% obtained on recycling the 3 wt % L-Phe based eutectogel, at 25 °C, in the presence of different dyes, using aqueous solutions buffered at  $pH=2.7$ . RE% are reproducible within  $\pm 3\%$ .

Results obtained highlight that the L-Phe based eutectogel has a good degree of recyclability and can be used for at least ten cycles without obvious loss in removal efficiency. It is worth noting, however, that no further recycle was attempted after those reported in Figure 9, due to partial collapse of the gel after the last cycle. On this regard, we also checked if the gels could sustain the weight of an aqueous phase without breaking. To this aim, we put each eutectogel in contact with 500  $\mu\text{L}$  of water for 10 days. In all cases the gel maintained their characteristics, as assessed by the tube inversion test. A peculiar feature of our system resides in the possibility to be reused without any intermediate washing, avoiding in a real system both solvent and energy waste.

To demonstrate the general recyclability of our eutectogels, we also carried out the recycling of all the other gel phases using aqueous solutions of RhB. The results of this investigation, reported in Figure S3, confirms the good recyclability of all the gel phases considered in this work except for the L-Leu based gel, in which case a significant drop in efficiency occurs after the first cycle.

Recycling tests were also performed using mixtures of dyes. To this aim L-Phe eutectogel was put in contact with an aqueous mixture of dyes, for 24 hours at 25 °C. In particular, we employed an equimolar mixture of Rhodamine B and Methylene Blue ( $1.8 \cdot 10^{-4}$  M). We could not use a mixture of

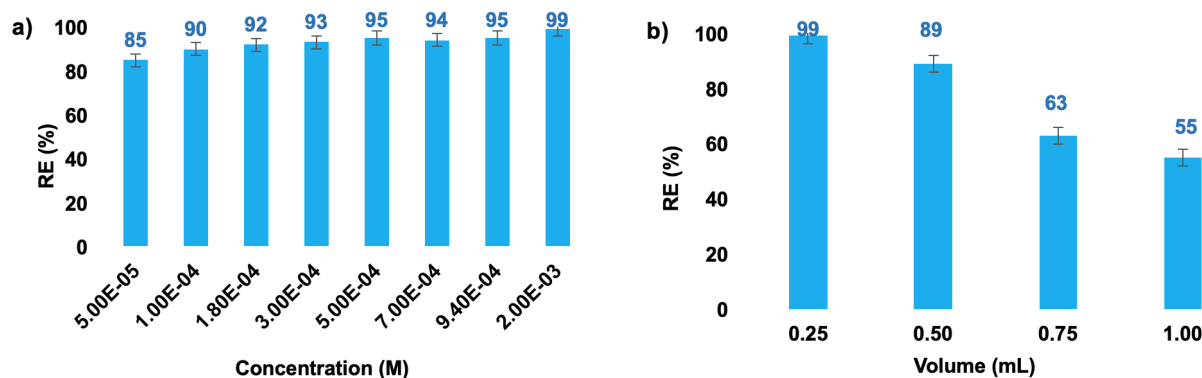
all three dyes due to partial overlap of the UV-vis absorption bands of RhB and MV. Also in this case, we reused the gel to adsorb a fresh batch of mixture, as described above, obtaining the results reported in Figure 10.



**Figure 10.** RE% obtained on recycling the 3 wt % L-Phe based eutectogel, at 25 °C, in the presence of an equimolar mixture of RhB and MB, using aqueous solutions at buffered pH= 2.7. RE% are reproducible within  $\pm 3\%$ .

Looking at the results reported in Figure 10, shows that RE (%) are lower than the ones detected for the adsorption of the single dye solutions. This can be explained by considering that the two dyes are competing for the adsorption sites in the surface of the gel. This is further supported by the different trend of removal efficiency over several cycles of reuse of the gel. In particular, for RhB the removal efficiency keeps fairly constant over ten cycles, whereas a clear drop of RE% occurs for MB after the 6<sup>th</sup> cycle, suggesting a lower ability to compete for adsorption sites, compared with RhB, according to the lower extension of  $\pi$ -surface.

To gather further information on the parameters affecting adsorption, we performed concentration- and volume dependent adsorption experiments of RhB on the same L-Phe based eutectogel. To this aim, we put the gel in contact with 0.5 mL of RhB aqueous solutions with initial concentrations ranging from  $5 \cdot 10^{-5}$  M to  $2 \cdot 10^{-3}$  M and determined the relevant RE values. The results obtained are reported in Figure 11a.



**Figure 11.** RE% obtained for RhB, at 25 °C, using aqueous solutions buffered at  $pH= 2.7$ , a) at variable initial concentrations of RhB and b) at variable volume of aqueous solution. RE% are reproducible within  $\pm 3\%$ .

The adsorption runs at variable initial concentration show that the L-Phe-based eutectogel can remove RhB over a wide concentration range with only modest variations in removal efficiency.

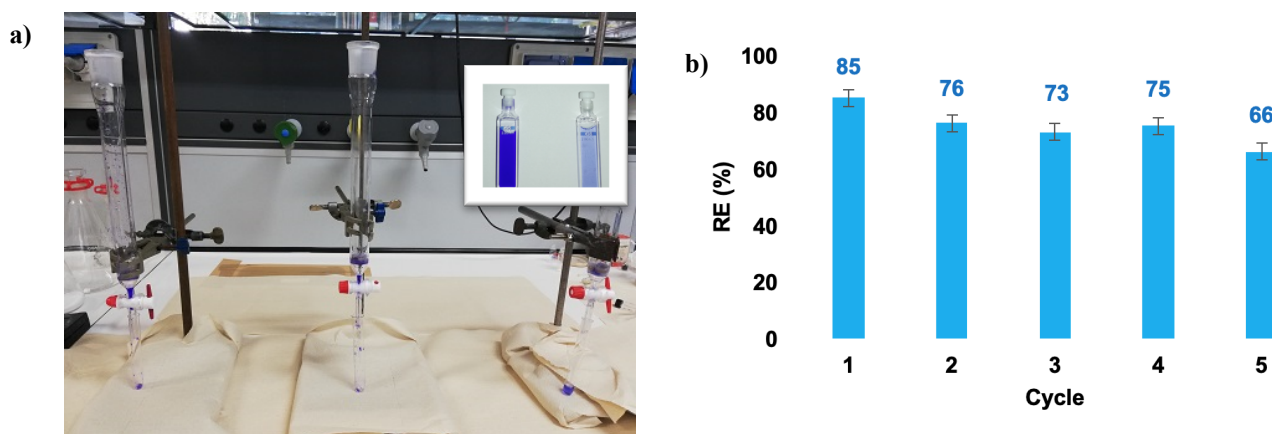
In particular, even at the lowest concentration used, the RE% amounted to 85 %, whereas we observed no saturation event over the concentration range investigated till a concentration of  $2 \cdot 10^{-3}$  M, in which case RE% of 99% is detected.

Conversely, for the adsorption experiments at variable volume, we used increasing volumes of an aqueous solution of RhB ( $1.8 \cdot 10^{-4}$  M) and then determined the RE after 24 h, at 25 °C, obtaining the results shown in Figure 11b. In this case, upon increasing the volume of aqueous phase, the efficiency markedly decreases, almost halving from 99% to 53% on going from 0.25 mL to 1 mL of solution.

Finally, we assessed the behavior of the gel in a more realistic setting, beyond the simple static batch test. To this aim, we loaded a chromatography column with 1g of gel, and then 3 mL of a MV solution were allowed to flow thorough the gel and eluted. The discolored solution was then poured back in another gel-loaded column and the whole procedure was repeated for a total of three times. Previous reports highlight that this methodology can be useful to improve removal efficiency while decreasing operational times.<sup>20, 38</sup> A representative picture of the experimental set-up is shown in Figure 12a.

Using this sequential set-up, we obtained a removal efficiency of 85%, but in only 10 minutes compared with 4 hours required by the static experiments to achieve the same level of removal (Figure 8).

Encouraged by these results, we reused the same gel loaded column with fresh batches of dye solution, using the same volume, 3 mL. The results obtained are summarized in Figure 12b.



**Figure 12. a)** Representative picture of experimental set-up used for sequential removal of dye and in the inset, quartz cuvettes containing initial Methyl Violet solutions and discolored solution after elution on three dye-loaded columns.

**b)** RE% obtained on reusing three sequential columns loaded with the 3 wt % L-Phe based eutectogel, in the presence of MV, using buffered aqueous solutions at  $pH= 2.7$ . RE% are reproducible within  $\pm 3\%$ .

The plot reported in Figure 12b evidences that the gel columns could be used four times with a small drop in RE%, whereas a more pronounced reduction in efficiency occurs on the 5<sup>th</sup> cycle, likely due to saturation of the gel phases. However, it is still worth noting that these results are obtained by processing a much larger volume of dye solution compared with the static adsorption experiments, demonstrating good potential for the scale-up of the process, in the light of developing real-life applications.

To further assess the sorption performance of our eutectogels, we now report a comparison of RE% with other systems recently reported in the literature. In particular, we compare our best results with the ones of other systems chosen for the similarity of sorbent system and experimental conditions,

focusing on system for which recycle of the sorbent has been evaluated. These are reported in Table 3.

**Table 3.** Dye removal efficiencies of our eutectogels and data from literature.

Entry	Gel or sorbent	Dye	Time of contact (h)	RE <sub>max</sub> (%)	Cycles of reuse
1	L-Phe-based eutectogel <sup>a</sup>	MV	6	92	10
2		RhB	24	90	10
3		MB	24	70	10
4	Imidazolium-based ionic liquid gel <sup>20</sup>	RhB	24	98	15
5	Diimidazolium-based ionic liquid gel <sup>19</sup>	RhB	6	97	20
6	Hemicellulose-based hydrogel <sup>39</sup>	MB	8	80	4
7	Graphene Oxide composite gel <sup>40</sup>	MV	24	90	5
8	Dipeptide-based hydrogel <sup>41</sup>	RhB	60	78	4
9	MoS <sub>2</sub> -glue sponge <sup>42</sup>	RhB	0.25	90	15

[a] This work

In general, for RhB, the performance of the L-Phe- based eutectogels is in line with the ones of ionic liquid gels of mono-<sup>20</sup> and dicationic<sup>19</sup> imidazolium salts, in terms of RE, while ionic liquid gels prove more robust and can be reused for more cycles, particularly those based on diimidazolium salt provide a faster removal (entries 2, 4 and 5). Furthermore, our eutectogel shows a better performance compared with a dipeptide-based hydrogel<sup>41</sup> in terms of efficiency, rapidity of adsorption as well as degree of recyclability (entries 2 and 8), whereas the L-Phe- based eutectogel show the same removal efficiency of a non-gel system, like MoS<sub>2</sub>-glue sponge,<sup>42</sup> although in this case the latter displays a much faster adsorption and higher number of recycles. Notably, our eutectogel yields a faster removal

of MV, compared with a graphene oxide composite gel,<sup>40</sup> and can be used more times (entries 1 and 7). Finally, our best eutectogel displays a lower efficiency for MB removal compared with a hemicellulose-based hydrogel,<sup>39</sup> although, once again, in our case the gel could be reused for a higher number of cycles (entries 3-6).

In our view, this work shows that eutectogels are suitable materials for environmental remediation, also in the light of the very low environmentally impacting nature, since they are entirely made of biocompatible components.

## Conclusions

Complying with Green and Sustainable Chemistry principles, we obtained fully natural eutectogels that were used to face the important problem of wastewater remediation. These soft materials were obtained combining the properties of DES with the ones of L-amino acids.

We observed a distinct impact of bulky aromatic groups in the amino acid side chain on the gelation kinetics and rheological properties. In particular, this impact is more pronounced considering the L-Ile-based gels compared with the L-Phe-based ones. Furthermore, we found very different morphologies for the materials obtained, as a function of the amino acid used. Then, we used the eutectogels as nanostructured sorbents for the removal of cationic dyes from water, observing a marked influence of the *pH* of the aqueous solution, with the best efficiency displayed towards acidic solutions, in which case the gels perform better than the DES itself. Interestingly, the adsorption ability is affected by the nature of gelator and can be related to mechanical properties of gels, with best performance detected for mechanically stronger gels.

The best performing eutectogel is the one based on L-Phe. This displays better removal efficiency for dyes with larger  $\pi$ -surface area, and a good degree of recyclability with single dye solution as well as binary mixtures, more similar to a real situation. This gel was also used as loading of a column, for the removal of dye from flowing water. Sequential adsorption of MV after elution on three columns



gave a RE% of 85 % in 10 minutes, and notably, the gel loaded columns can be reused four times with a minor drop in RE% and the result obtained demonstrates good potential for the scale-up of the process.

In our view, the eutectogels obtained show two main advantages perfectly fitting sustainability requirements. Firstly, these sorbent materials have a very low environmentally impacting nature, since they are entirely made of biocompatible components. Furthermore, their recycle does not require intermediate washing and this allows significantly decreasing the amount of waste deriving from the whole process.

**Declaration of interest:** There are no conflicts to declare

### **Acknowledgements**

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### **Electronic Supplementary Information**

Electronic Supplementary Information: outcomes of gelation tests, strain and frequency sweep measurements, plots of RE as a function of the time, plots of removal efficiency recycling the gel phases. This material is available free of charge at <http://www.rsc.org>.

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