A Dipeptide-based Superhydrogel: Removal of Toxic Dyes and Heavy Metal Ions from Waste-water

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Abstract

A short peptide-based molecule has been found to form a strong hydrogel at phosphate buffer solution of pH 7.46. The hydrogel has been characterized thoroughly using various techniques including field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and rheological analysis. It has been observed from FE-SEM images that entangled nanofiber network is responsible for gelation. Rheological investigation demonstrates that the self-assembly of this synthetic dipeptide results in the formation of mechanically strong hydrogel with storage modulus (G') around 10^4 Pa. This gel has been used for removing both cationic and anionic toxic organic dyes (Brilliant Blue, Congo red, Malachite Green, Rhodamine B) and metal ions (Co^{2+} and Ni^{2+}) from waste-water. Moreover, only a small amount of the gelator is required (less than 1 mg/mL) for preparation of this superhydrogel and even this hydrogel can be reused three times for dye/metal ion absorption. This signifies the importance of the hydrogel towards waste-water management.

Keywords

Peptide, Hydrogel, Supergelator, Dye absorption, Metal ions absorption.

Introduction

Supramolecular gels[1-12] belongs to a special category of soft materials due to their wide range of interesting structural and functional properties. Since past few decades, low molecular weight hydrogelators[13-15] (LMWHG) draw a significant attention to the scientists due to their ability to self-assemble among themselves by utilizing various non-covalent interactions including hydrogen bonding, π-π interactions, hydrophobic interactions, van der Waals' interactions, ionic interactions and others to form a nano/micro-fibrillar three dimensional entangled network structure. The network structure encapsulates large number of water molecules to form a hydrogel. Amino acid/peptide based gels[16-23] are endowed with variety of applications including drug delivery,[24-28] tissue engineering,[29-32] oil-spill recovery[33-35] and waste-water treatment.[36,37] They can also be used for making nanoclusters and nanoparticles,[38-40] photo-switching materials[41-43] and for other biomedical applications.[44-48]

Since the last two decades water pollution due to the textile and organic dyes is a matter of great concern to nature.[49,50] This is because many dyes are known to get reduced into toxic substances inside living organisms that can cause damage to genetic material which may affect the organism in the long run although they are often not expressed immediately.[51] On the other hand, due to discharge of large amount of metal-contaminated waste-water, effluents from several industrial operations like electroplating, mining, pigments and metal processing are also one of the major contributors to abnormal metal contamination in water sources. Inorganic effluents from the industries contain toxic metals such as Co, Ni, Cd, Cr, Cu and others, which tend to accumulate in living organisms and can act progressively over a long period of time through food chains.[52] Hence, it is essential to regulate the pollution from waste-water before disposing it to the environment to minimize human and environmental exposure to various hazardous organic and inorganic toxins. Conventional waste-water treatment processes like adsorption upon activated carbon, chemical precipitation, electrochemical techniques, ion exchange and others, have their own limitations due to their low sensitivity, incomplete removal, high-energy requirements, and production of toxic sludge.[53] Hydrogel-based soft materials offer an alternative appealing[54] for removal of various hazardous wastes from contaminated water due to their high water permeability, large surface

area for adsorption and simplicity in use. In this regard, peptide based hydrogel have gained importance in environmental applications owing to their high sensitivity towards the noxious wastes along with reusability and proper biodegradability. There are numerous examples reported by several research groups on pH responsive reusable smart hydrogels,[55,56] pH dependent selective dye absorbing novel hydrogel[57] as well as chelation induced metallo-hydrogel.[58] Many other groups have also devoted their research to explore this area.[59-64] However, there are very few gelator molecules that form gel at concentration below 0.1% (w/v).[65] These gelators are generally termed as 'supergelator'. So, it will be interesting to develop super hydrogelator, which could remove pollutants present in waste-water. This is because, very small amount of gelator molecule is needed to form the hydrogel that would act as a scavenger for toxic organic and inorganic materials from waste-water in a cost-effective way. In course of our investigation on the self-assembly of small peptide molecules, it has been found that a C-terminally protected very simple dipeptide H-Leu-Phe-OMe (Leu= L-Leucine, Phe= L-Phenylalanine) forms hydrogel at phosphate buffer of pH 7.46 with a minimum gelation concentration of 0.07% (w/v). The amino acids Leu, Phe and the free amine functionality promote gelation using different non-covalent interactions.[56] The hydrogel has been effectively used for removing both cationic and anionic toxic dyes as well as toxic heavy metal ions (Co^{2+} and Ni^{2+}) from waste-water effectively in an eco-friendly manner. Furthermore, the reusability of this hydrogelator without the loss of significant activity by changing the pH of the medium possesses an additional advantage of this gel-based absorbent.

Experimental section

Materials

All amino acids (L-Leu and L-Phe) were purchased from Sigma chemicals. 1-hydroxybenzotriazole (HOBt) and dicyclohexylcarbodiimide (DCC) were purchased from Merck and SRL, India respectively. Other chemicals used in the work were purchased from local chemical company SRL, India.

Synthetic procedure

Synthesis of Boc-Leu-OH: A solution of L-Leu (1.31 g, 10 mmol) in a mixture of dioxane (20 mL), water (10 mL) and 1(N) NaOH (10 mL) was stirred and cooled in an ice-water bath. Di-tert-butyl dicarbonate (2.39 g, 11 mmol) was added and stirring was continued at room temperature for 6 hr. Then the solution was concentrated in vacuum to about 20 mL to 30 mL, cooled in an ice water bath, covered with a layer of ethyl acetate (about 50 mL) and acidified with a dilute solution of $KHSO_4$ to pH 2-3. The aqueous phase was extracted with ethyl acetate and this operation was done repeatedly. The ethyl acetate extract was washed with water and dried over anhydrous Na_2SO_4 and evaporated in vacuum to obtain a yellowish product.

Yield: 2.1 g (8.7 mmol, 87%).

Synthesis of Boc-Leu-Phe-OMe: 2.1 g (8.7 mmol) of Boc-Leu-OH was dissolved in 10 mL of dimethylformamide (DMF) in an ice water bath. H-Phe-OMe was isolated from 4.3 g (20 mmol) of the corresponding methyl ester hydrochloride by neutralization and subsequent extraction with ethyl acetate and ethyl acetate extract was concentrated to 10 mL. It was then added to the reaction mixture, followed by 1.85 g (9 mmol) DCC and 1.37 g (9 mmol) of HOBt. The reaction mixture was allowed to come at room temperature and stirred for 3 days. The residue was taken up in ethyl acetate (40 mL) and dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 1(N) HCl (3 × 30 mL), brine (1 × 30 mL), 1(M) sodium carbonate (3 × 30 mL) and brine (2 × 30 mL) and dried over anhydrous Na_2SO_4 and evaporated in vacuum to obtain a white material.

Yield: 2.18 g (5.5 mmol, 64.4 %).

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.20-7.02 (5H, aromatic Hs, m), 6.49 (1H, NH, br), 4.79-4.75 (2H, $^{\alpha}$H and NH, m), 4.03-4.02 (1H, $^{\alpha}$H, m), 3.63 (3H, OCH_3), 3.09-2.98 (2H, $^{\beta}CH_2$, m), 1.58-1.53 (2H, $^{\beta}CH_2$, m), 1.36 (9H, Boc, s), 1.23-1.18 (1H, $^{\gamma}$H, m), 0.85-0.79 (6H, $2CH_3$, m). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 172.28, 171.80, 155.69, 135.91, 129.42, 128.65, 127.21, 80.13, 53.27, 52.37, 41.36, 38.06, 28.40, 24.80, 22.98, 22.76. **HRMS** (m/z): 415.5126 $[M+Na]^+$.

Synthesis of H-Leu-Phe-OMe: To 2.18 g (5.5 mmol) of Boc-Leu-Phe-OMe, 4 mL of trifluoroacetic acid (TFA) was added and removal of Boc group was monitored by TLC. After 8 h, TFA was removed under vacuum. The residue was taken in water (20 mL) and covered with ethyl acetate (about 50 mL) and neutralized with saturated solution of $NaHCO_3$

by using pH paper. The aqueous phase was extracted with ethyl acetate and this operation was done repeatedly. The ethyl acetate extracts were pooled, washed with water and dried over anhydrous Na_2SO_4 and evaporated in vacuum. A white material was obtained.

Yield: 1.4 g (4.8 mmol, 90.1 %).

^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): (Figure S1 in Supporting Information) δ 8.08-8.04 (1H, d, J= 13.6 Hz, NH), 7.28-7.12 (5H, aromatic Hs, m), 4.15 (1H, $^{\alpha}$H, m), 3.47-3.45 (1H, $^{\alpha}$H ,m), 3.31(3H, OCH_3), 3.14-2.80 (2H, $^{\beta}$H, m), 1.45-1.38 (1H, $^{\beta}CH_2$, m), 0.89-0.87 (1H, $^{\gamma}$H, m), 0.63-0.58 (6H, $2CH_3$, m). **^{13}C NMR** (100 MHz, DMSO-d_6): (Figure S2 in Supporting Information) δ 171.34, 169.91, 167.44, 166.11, 136.83, 136.07, 130.36, 129.02, 128.34, 128.05, 126.69, 55.44, 53.77, 52.24, 43.60, 36.35, 23.39, 22.88, 22.78, 21.68, 21.35. **HRMS** (m/z): (Figure S3 in Supporting Information) 293.0161 $[M+H]^+$.

Instrumentation Details

NMR experiments

NMR study was carried out on a Brüker DPX 400/500 MHz spectrometer at 300 K. Compound concentration was in the range 1–10mmol in $CDCl_3$ or DMSO-d_6.

Mass spectrometry

Mass spectra were recorded on a Q-Tof micro™ (Waters Corporation) mass spectrometer by positive mode electrospray ionization.

X-ray diffraction study

The hydrogel was freeze dried by using liquid nitrogen at first and it was further dried in lyophilizer to get xerogel for X-ray diffraction study. The dried powder was then placed on a glass plate and the experiment was carried out by using an X-ray diffractometer (Bruker AXS, Model No. D8 Advance). The instrument was operated at a 40 kV voltages and 40 mA current using Ni-filtered CuKα radiation and the instrument was calibrated with a standard Al_2O_3 (corundum) sample before use. For scan 5°-28°, the LynxEye super speed detector was used with scan speed 0.3s and step size 0.02°.

Field emission scanning electron microscopic study

Morphology of the reported gel material was investigated using field emission scanning electron microscopy (FE-SEM). For sample preparation, a drop of the dilute buffer solution of the gel material was placed on a microscopic glass slide and then it was allowed to dry first in the air and then under vacuum for one day to get the xerogel. After that the sample was coated with platinum. Then the micrograph was taken in an SEM apparatus (Jeol Scanning Microscope-JSM-6700F).

UV-Vis spectroscopy

UV-Vis absorption spectra were recorded on a UV-vis spectrophotometer (Varian Cary 50 Bio). For this experiment 1000 μL of aliquot was pipetted out from the dye solution throughout a time interval and the aliquot was again added to the residual dye solution for each time.

Rheology

The rheological measurement of the hydrogel of peptide P was studied under dynamic and steady shear measurement at room temperature (25 °C) on parallel-plate geometry (25 mm diameter, 1 mm gap). Rheological experiment was carried out using and Anton Paar modular compact rheometer (MCR 102). Visco-elastic measurement of the hydrogel was performed at room temperature using parallel-plate geometry (PP-25 mm, gap 0.5 mm).

Results and discussion

Gelation and Thermal Behaviour

The gelation propensities of the peptide H-Leu-Phe-OMe (**P**) has been studied by dissolving 1 mg of the compound in 1 mL of the phosphate buffer solution by the application of simple heating-cooling cycle. Below a certain temperature (T_{gel}, temperature of gelation), the complete volume of solvent is immobilized and it forms a gel. This hydrogel is thermo-reversible in nature and is stable over the pH range 5.0 to 8.0. A decrease in the pH below 5.0 triggers a gel-to-sol transition, whereas pH above 8 led to precipitation of the gelator peptide **P**. Here, all the studies have been carried out at pH 7.46. The gelation is confirmed by the inverted tube method. The gel is stable at room temperature and maintains its gel state for several months. The minimum gelation concentration (MGC) is 2.3 mM (0.07% w/v) for a

freshly prepared hydrogel without any sonication. Generally, gelators with MGC below 0.1% (w/v) fall into the category of supergelators. In this regard, this hydrogelator should be considered as a supergelator. The gel melting temperature (T_{gel}) at MGC is found to be 84 °C. For this purpose, the "tube inversion" method has been used to measure the sol-gel transition temperature (T_{gel}) of the gel phase material in buffer solution at pH 7.46. The measured temperatures are plotted against the gelator concentration to afford the plot presented in supporting information as Figure S4. The hydrogel offers potential applicability in treatment of waste-water containing organic dyes (Brilliant Blue, Congo red, Malachite Green, Rhodamine B) and inorganic metal ions (Ni^{2+} and Co^{+2}) that are widely used in textile as well as dye industries. Moreover, peptide gelators can be recovered very easily just by simple treatment with organic medium. Thus, this reported hydrogel are promising superabsorbent for removing both cationic and anionic dyes and also heavy metal ions from the water effluents.

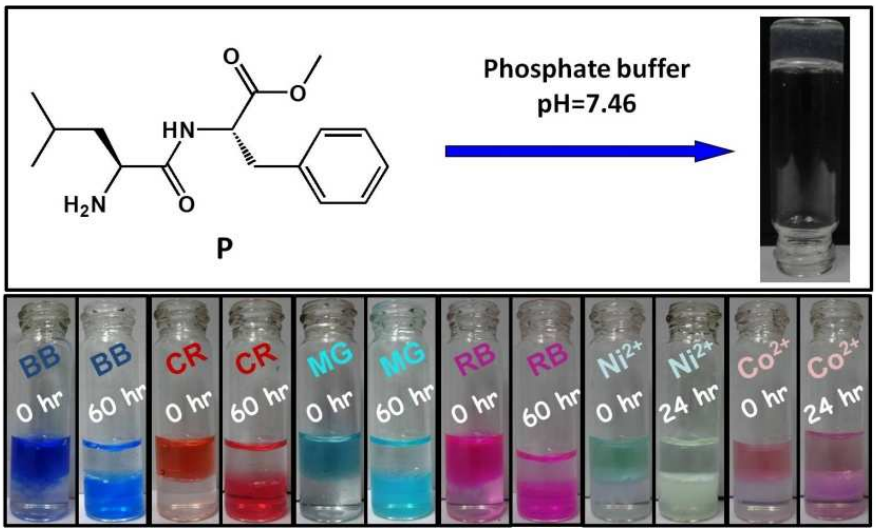

Figure 1: The upper panel shows the chemical structure of the peptide **P** and the photograph of the hydrogel from peptide **P** at 0.1% (w/v). The lower panel shows the photographs of the hydrogels before and after absorption of the dyes Brilliant Blue (BB), Congo Red (CR), Malachite Green (MG), Rhodamine B (RB) and the metal ions nickel(II) (Ni^{2+}), cobalt(II) (Co^{2+}). The concentration of hydrogels was 0.1% (w/v) for all these cases.

Morphology

To obtain insight into the morphology of the hydrogel obtained from peptide **P**, field-emission scanning electron microscopic experiment (FE-SEM) has been carried out. For the preparation of the sample, dilute buffer solution of the gel material was placed on a microscopic glass slide and then it is dried to get the xerogel. It should be taken under consideration that the sample should be in lower concentration in order to avoid the formation of fibril bundles during the drying process and also the hydrogel film generated on the slide should be thin. In Figure 2 FE-SEM images of the xerogel show nano-structured morphology in the self-assembled state. The average widths of the nanofibrils are in the range of 80±10 nm indicating a porous nanostructure with high surface area that can interact with pollutants present in its vicinity.

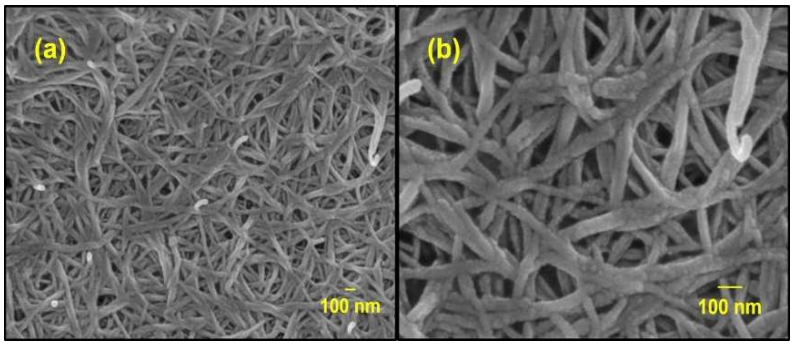

Figure 2: FE-SEM image (a) and its enlarged view (b) obtained from the hydrogel of peptide **P**.

Rheological analysis

Rheological study of the hydrogel has been performed in order to examine its mechanical strength and stability. The storage modulus (G′) and loss modulus (G″) were measured in frequency sweep experiments and are presented in Figure 3. It is evident from the plot that the storage modulus (G′) is higher than the loss modulus (G″) for this dipeptide-based hydrogel of peptide **P** and no cross-over point is found in the experimental frequency region. At 0.1% (w/v) the gel exhibits linear behaviour with respect to angular frequency in the region 8-100 rad/sec. In the experiment, almost one order higher values of storage modulus (G′) over the loss modulus (G″) suggests a soft 'solid-like' gel phase formation. The storage modulus (G′) for the gel is in the order of 8.1×10^3 Pa indicating its sufficiently high

mechanical strength. Thus, the hydrogel shows very weak dependency on the angular frequency over the experimental range. This suggests that this gel matrix has good tolerance towards external forces.

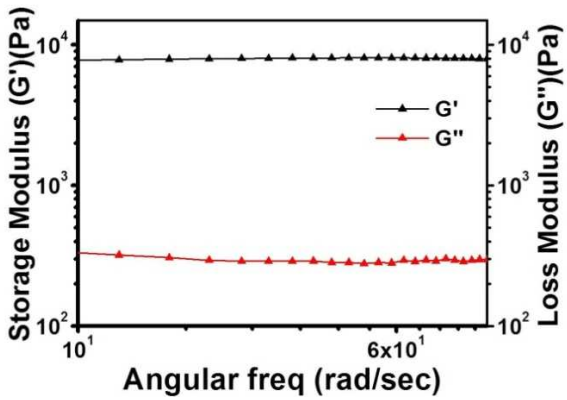

Figure 3: Frequency sweep analysis of the hydrogel from peptide **P** at 0.1% (w/v).

X-ray Diffraction (XRD) Study

The internal arrangement of the self-assembled nano-structured molecules in gel phase has been investigated by XRD analysis. Figure 4 shows the wide angle XRD patterns of the hydrogel obtained from peptide **P** in its xerogel state. In the higher angle region, peaks at 2θ= 26.47^0 and 2θ= 27.34^0 corresponds to *d* values 3.36 Å and 3.86Å respectively, characterising π-π interactions in the dried aggregates. The peaks that appeared at 2θ= 19.13^0 and 2θ= 21.07^0 corresponding to the *d*-spacing value of 4.63Å and 4.21Å respectively appeared due to the spacing between two hydrogen-bonded dipeptide strands.[22]

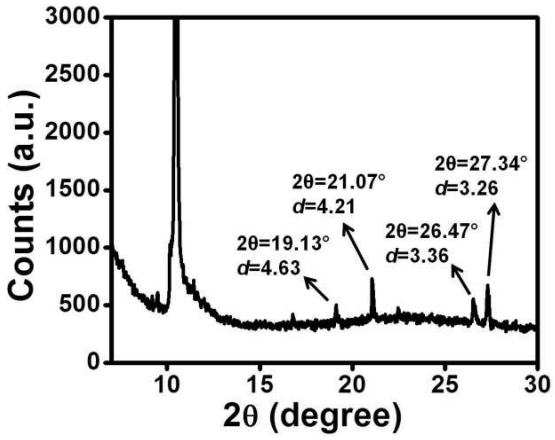

Figure 4: Wide angle X-ray diffraction pattern of the xerogel from peptide **P**.

Removal of dye and metal ion from waste-water

The effluents from various textile industries contain a large number of organic dyes and inorganic additives, which may cause acute and chronic toxicity. In addition to being toxic, dye effluents not only have negative impact on immune and reproductive systems, but these are also potential genotoxic and carcinogenic agents.[51] Heavy metal ions such as Ni^{2+} and Co^{2+} are the common constituents of runoff from mining operations and industrial effluents.[52,66] The normal limit of Ni(II) and Co(II) in drinking water are 0.07 mg/L and 0.002 mg/L respectively.[67] Severe chronic health disorders are caused due to the ingestion of these metals beyond the permitted level of concentration.[67] Hence, it is essential to safeguard the environment by eliminating such contaminants from waste-water. The hydrogel from peptide **P** has been tested for absorbing different types of toxic effluents from water with an aim to purify contaminated waste-water coming out from textile industries. For this purpose, four different dyes like Brilliant Blue, Congo Red, Malachite Green and Rhodamine B, and two metal salts nickel (II) chloride and cobalt (II) chloride have been chosen to examine their absorption into the **P** gel matrix. When the aqueous solutions of various dyes (cationic, anionic) and metal ions (Ni^{2+}, Co^{+2}) are applied over the gel, it efficiently absorbs the foreign molecules from water within a few hours leaving almost colorless water. This indicates a possible use of this gel in the waste-water treatment. Absorption of dyes and metal ions from their respective aqueous solutions has been monitored by UV-vis spectroscopy and dye/metal ion uptake capacities of the hydrogels have been determined by batch kinetic sorption experiments. For this purpose, different sets of the gel were prepared in capped vials with 1 mg of the gelator (0.1% w/v) in 1 mL of buffer solution. Solutions of dyes (8 μM) and metal ions (10 μM) are then pipetted onto the top of these gels in each set and allowed them to stand for few hours. Time dependent absorption of the dyes and metal ions from their corresponding aqueous supernatants has been monitored by UV-vis spectroscopy (Figure 5). From this plot, it is observed that the intensity of absorption maxima decreases with time for all the cases. After the application of the dye solutions over the gels, the absorption maxima of the supernatant dye solution started to decrease after 15 min and the absorption intensity continues to diminish before it reaches a saturation point after 60 hr (Figure 5a-d). Incidentally, the hydrogel can absorb all the dye used here up to 60 hr (although with different extent) before attaining a saturation limit (Figure 5a-d). On the other hand, in the case of the metal ion solutions, this gradual reduction of absorption peak occurs up to 48 hr.

Figure 5e,f indicates that after 48 hr almost complete metal ion absorption takes place. This observation is possibly due to the binding of foreign substances (dye and metal ion) with the hydrogel. This indicates the absorption of those molecules by the porous framework of the gel. The capacity of a given amount of this gel for absorbing various dyes and metal ions are quantitatively estimated and it is listed in Table 1.

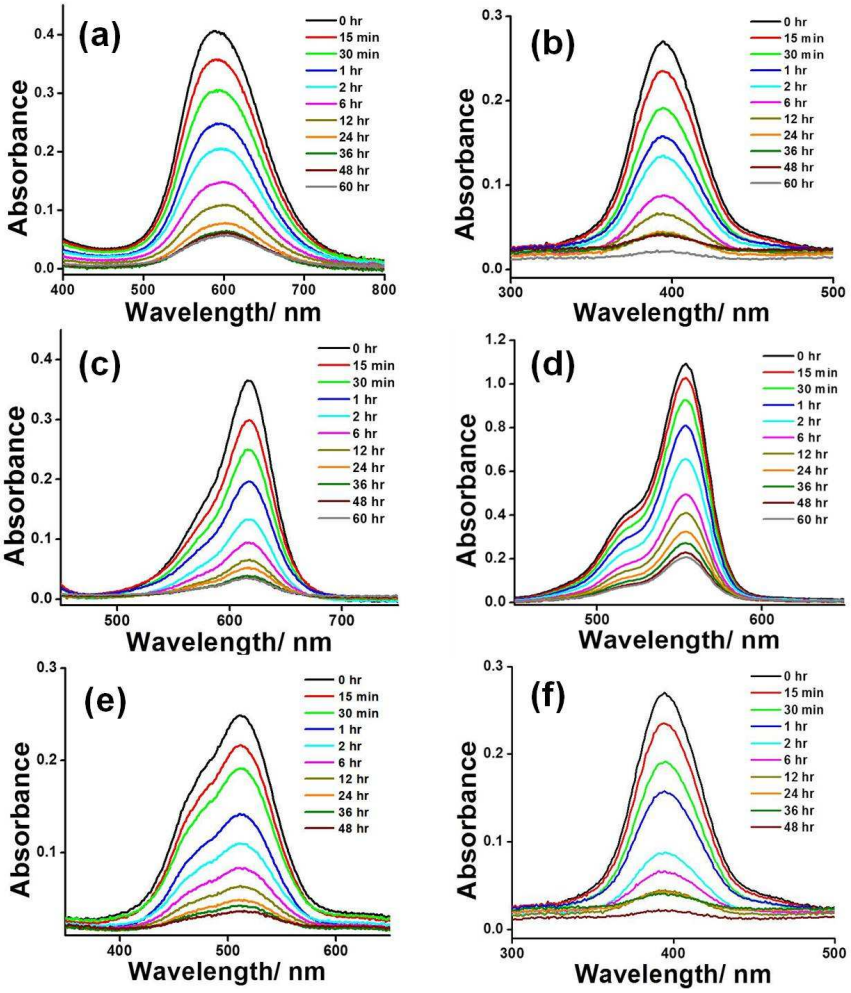

Figure 5: UV-vis absorption study of the dyes and metal ions: (a) Brilliant Blue (b) Congo Red, (c) Malachite Green, (d) Rhodamine B, (e) Co^{2+} ion, and (f) Ni^{2+} ion. For (a)-(d) the concentration was 8 μM and for (e), (f) the concentration was 10 μM.

Name of the Dye/ metal ion	Dye/metal ion absorption capacity per gram of the gelator P	Dye/ metal ion removal capacity
Brilliant Blue	490 mg	86%
Congo Red	650 mg	92%
Malachite Green	550 mg	90%
Rhodamine B	320 mg	78%
Co^{2+}	10 gm	85%
Ni^{2+}	11 gm	92%

Table 1: The maximum absorption capacity of the dyes and metal ions by the hydrogel of peptide **P**.

Reusability of hydrogel

So far, the hydrogel has been used as a purifier of waste-water containing industrial dyes and metal ions. Apart from its cost effectiveness and absorbing ability, reusability of such useful material is also important in order to its large scale utility. Industries produce gallons of polluted water every day, so there is a genuine need of huge amount of hydrogel to clean up the wastes. To check reusability, the gel was first treated with polluted water containing dyes and metal ions. After effective absorption, the gel was taken out of the vial and treated with saturated sodium bi-carbonate solution and extracted with ethyl acetate. As the metal ion and dyes are highly soluble in water and remain in aqueous part, the gelator compound being insoluble in such higher pH, goes to organic layer. The organic layer was separated, washed with brine, dried and ethyl acetate is removed in vacuum to regain the solid product. Then with the remaining compound, the hydrogel was again prepared and treated with waste-water. It has been found that using the above stated method we can use the gelator molecule for maximum three cycles. Figure 6 shows graphical representation of gelator compound remained (in percent) with respect to number of cycles in case of Brilliant Blue dye and Ni^{2+} ion. Figure S5 in the supporting information represents the same plot for the other three dyes (Congo Red, Malachite Green and Rhodamine B) and Co^{2+} ion.

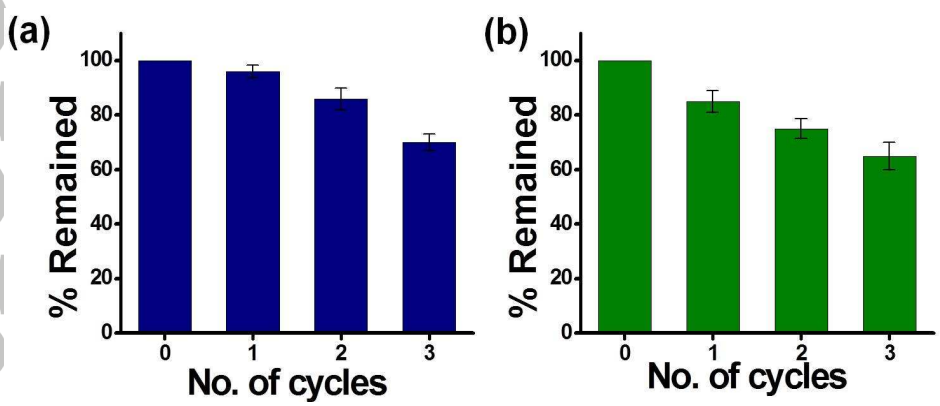

Figure 6: Bar diagram representation of reusability of gelator peptide **P** for the dye (a) Brilliant Blue and the metal ion (b) Ni^{2+}.

Conclusion

The work presented here vividly demonstrates the formation of a superhydrogel (with very low concentration of the gelator molecule) from a self-assembling N-terminally free dipeptide (H-Leu-Phe-OMe) at phosphate buffer of pH 7.46. Interestingly, this hydrogel has been used to efficiently absorb different types of toxic organic dyes (Brilliant Blue, Congo red, Malachite Green, Rhodamine B) as well as heavy metal ions from (Ni^{2+} and Co^{2+}) waste-water within a few hours. Here, only a short dipeptide is required for making a hydrogel-based absorbent material and also very small amount of the dipeptide is enough to prepare this superhydrogel. Moreover, the gelator can be efficiently reused several times without any significant loss of activity. This makes preparation and use of this hydrogel easier and profitable at the same time. Thus, it can be concluded that this short peptide-based hydrogel has wonderful applicability for removing toxic effluents from industrial waste-water in future in a cost-effective manner.

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