Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Nanoscale

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ROYAL SOCIETY OF CHEMISTRY

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Journal Name

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Sulphonated Carbon Dots-Chitosan hybrid hydrogel nanocomposite as an efficient ion-exchange film for Ca^{2+} and Mg^{2+} removal

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We have developed a hybrid hydrogel nanocomposite film via conjugation of oxidised carbon dots synthesized from 11-mercaptoundecanoic acid. The potential applicability of the film was then successfully tested for removal of Ca^{2+} and Mg^{2+} ions from solutions.

Water is the prime essential component of human life. However, the alarming rise in pollution issues originating from improper disposal of hazardous chemical wastes from paper, textile, fertilizer or petrochemical industries, electroplating plants, tanneries and slaughterhouses etc. have led to the exacerbation of the safe drinking water crisis. Another major issue pertaining to water-related problems is hardness of water caused primarily by the presence of Ca^{2+} and Mg^{2+} ions in solution. Although hard water has moderate health benefits, it is a serious problem when it comes to breakdown of costly equipments in industrial settings owing to corrosin. Therefore, the need for suitable water purification techniques to meet this global safe water crisis is in demand. Among the numerous methods available, ion exchange receives significant attention for water softening due to its high efficiency, superior regeneration power and low operational costs.[1] Ion exchange method employs ion exchange resins fabricated from organic polymer substrates.[2] Conventionally polymers such as polyaniline (PANI), polypyrrole (PPy), polythiophene (PT) and their derivatives have continued to gain much interest as chemical adsorbents owing to their ease of synthesis, porous structure, tunable morphology, good electrorheological property, unique redox chemistry, non-toxicity, insolubility in water and reversible ion (especially cation) sorption/desorption capability.[3] However, the increasing cost of their synthesis demands for alternatives to draw the same benefits at an affordable price. Moreover, typical ion

exchange resins used for water softening are derived from polystyrene crosslinked with divinylbenzene which employs the use of the harmful chemicals and harsh reaction conditions as divinylbenzene is carcinogenic and is found to cause respiratory and kidney disorders.[4] Use of nanoparticles alone for water treatment is undesirable due to difficulties in regeneration, reuse and even possible risk to ecosystem and human health.[3] Therefore the most valuable approach is to design hybrid nanocomposites using biocompatible polymers and non-toxic nanoparticles to replace the conventionally used toxic ones like titanates, Fe_3O_4 nanoparticles, etc.[5] There are already a few reports available in literature of using hybrid polymeric nanocomposites for water treatment. For instance, Musico et al. demonstrated the use of Poly(N-vinyl carbazole)-GO nanocomposite for adsorption of Pb^{2+} from waste water.[6] Zhang et al. developed a simple and novel method for the synthesis of hierarchical PANI/GO nanocomposites using 1D (uniform aligned PANI nanorods) and 2D (GO nanosheets) nanocomponents by dilute polymerization and was used as a superadsorbent material for Cr(VI).[7] It is to be noted here that these materials are all based on synthetic polymers. Among the biocompatible and biodegradable polymers, chitosan, obtained from the deacetylation of chitin, a natural biopolymer that is present in the exoskeleton of crustaceans has been able to draw significant attention due to its enhanced biocompatibility, mechanical strength, excellent adhesion and absorption ability (due to presence of hydroxyl (OH) and amine (NH_2) functional groups) due to which it can potentially bind to a variety of chemical compounds through electrostatic attraction or hydrogen bonding.[8] Carbon dots (fragments of molecules below 10 nm in size) on the other hand are a nascent class of QDs possessing far reaching potentials like chemical inertness, biocompatibility, strong and tunable fluorescence and less toxicity.[9] Our group has also developed a carbon dot rooted agarose hydrogel hybrid sensing material for optical detection and separation of heavy metal ions (Cr^{6+}, Cu^{2+}, Fe^{3+}, Pb^{2+}, Mn^{2+}).[10]

In the present work we for the first time introduce a novel carbon source (11-mercaptoundecanoic acid, MUA) for the one-step synthesis of sulphur-bearing carbon dots. These carbon dots bearing surface –SH groups were then oxidized to convert the –SH groups into $–SO_3H$ groups. Further the oxidized carbon dots were

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blended with chitosan hydrogel to form carbon dots embedded chitosan nanocomposite films. The potential applicability of these films was tested for removal of Ca^{2+} and Mg^{2+} ions from water using the principle of ion-exchange. Although a great deal of work has been done for removal of toxic ions from water based on synthetic polymers, materials for hardness (specifically Ca^{2+} and Mg^{2+} ions) removal based on biopolymers are yet to be explored. Therefore, this material we report is the first of its kind with potential to act as a biodegradable and green material for water-softening applications.

Scheme 1 illustrates the protocol being followed for synthesis of thiol functionalized carbon dots (CDs) from MUA followed by their oxidation to form sulphonated carbon dots and subsequent fabrication of polymeric nanocomposite films via conjugation of the sulphonated CDs with the biopolymer chitosan by formation of Chitosan-MUA-SO$_3$Na-CDs hydrogel.

subsequently used for gelation of the biopolymeric chitosan solution (dissolved in 3:2 mixture of acetic acid and glycerol) thereby forming a hydrogel (with a MUA-SO$_3$Na CDs concentration of 0.011 M i.e, 0.35(wt%)). This hydrogel was then washed thoroughly with Millipore water to remove any excessive carbon dots and other impurities present and was spread onto glass slides and dried at 60°C for 2 hours. Afterwards the thin films were peeled off from the slides and dessicated overnight before further characterizations. Typically the films were of thickness ~ 0.07 mm. Figure 1 illustrates the various characterizations of the Ch-SO$_3$Na-CDs films prepared. The SEM micrograph of Ch-SO$_3$Na-CDs film (Figure 1(A)) clearly shows the presence of CDs (size below 10 nm) embedded in the biopolymeric nanocomposite film.
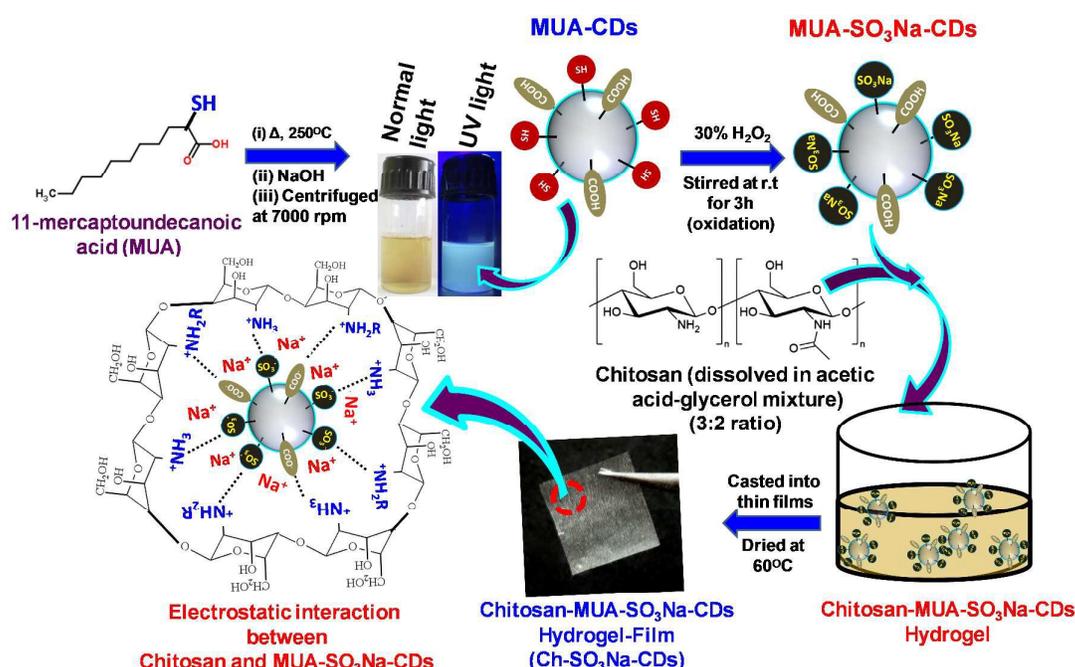
Scheme1. Schematic representation of the protocol followed for synthesis of thiol functionalized carbon dots (CDs) from MUA followed by their oxidation to form sulphonated carbon dots and subsequent fabrication of polymeric nanocomposite films via conjugation of the sulphonated CDs with the biopolymer chitosan.

The carbon dots prepared from MUA before and after oxidation were characterized using various instrumental techniques viz. UV-Visible spectroscopy, IR Spectroscopy, Fluorescence spectroscopy, Dynamic Light Scattering measurements, Powder XRD Analysis, FESEM and EDX Analysis etc. The sulphonated CDs being negatively charged with a zeta potential of -52.233 mV interacts electrostatically with cationic chitosan (positively charged due to its dispersion in acidic medium) bearing a zeta potential of +32.5 mV as shown in scheme 1 leading to its uniform distribution in the thin film.

The details of characterization are discussed in Figure S1, S2, S3 and S4 (ESI). The detailed characterization of CDs confirmed the presence of –SH and –SO$_3$Na functionalities on the CD surface before and after oxidation respectively. The oxidized CDs were then

The uniform distribution of SO$_3$Na-CDs in the chitosan film is also evident from the fluorescence microscopic image of the film (Figure 1(B)) which shows the presence of beautiful tiny blue fluorescent CD particles distributed all over the film. Evidence for successful incorporation of MUA-SO$_3$Na-CDs into the chitosan hydrogel matrix was also drawn from FTIR and TGA analysis as discussed in Figure S5 (A) and (B) (ESI). However, for control experiments blank chitosan hydrogel films were fabricated and also characterized following the same characterization techniques.

Evidence in support of successful incorporation of SO$_3$Na-CDs into the chitosan film was also drawn from the comparative powder XRD analysis and UV-Visible spectroscopy of blank and Ch-SO$_3$Na-CDs films. Comparative analysis of both the spectra shows that the blank chitosan film exhibits two distinct peaks at 2θ=10.4 (002) and

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20.1(004) degrees. On the other hand after incorporation of MUA-SO_3Na-CDs into the chitosan hydrogel matrix, a number of peaks appear along with those appearing for the blank chitosan film. The respective peaks appearing at 2θ=10.18 (002), 13.7(111), 16.6(-211), 18.5(300), 19.9(004) and 25.36(-313) matches the powder XRD spectrum of 2,4-dihydroxy-3-(phenylazo)phenyl)azo)benzenesulphonic acid sodium salt and crystallizes in monoclinic system (JCPDS Number 00-056-1960). Since the MUA-SO_3Na-CDs are in the form of the sodium salt of sulphonic acid, hence powder XRD spectrum provides the evidence for the successful oxidation of the MUA-SH-CDs to MUA-SO_3Na-CDs and also for their successful incorporation into the chitosan hydrogel matrix to form the nanocomposite films.

The UV-Visible spectrum of Ch-SO_3Na-CDs nanocomposite films exhibits a blue-shift in the absorption maxima from 275 nm to 263 nm of the characteristic peak of the blank Ch-film arising from n-σ* transitions of the −OH groups of chitosan. The hypsochromic shift observed can probably be ascribed to the increase in electron density (due to π-π* transitions of the −COO^- and −SO_3^- groups) in the chitosan hydrogel matrix owing to successful incorporation of sulphonated CDs into the hydrogel matrix.
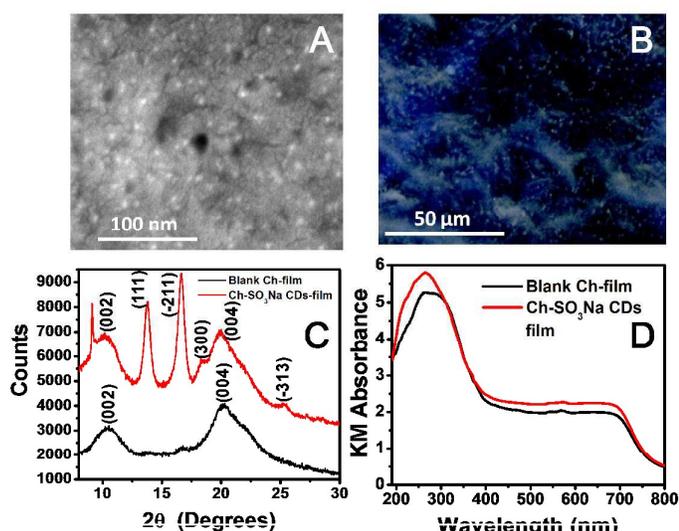

Figure 1. Systematic characterization of Ch-SO_3Na-CDs nanocomposite films involving (A) SEM micrograph, (B) Fluorescence microscopic image, (C) Powder X-Ray Diffractogram and (D) Solid state UV-Visible spectra.

The potential applicability of the Ch-SO_3Na-CDs nanocomposite films was subsequently tested in the form of a hybrid platform for removal of Ca^{2+} and Mg^{2+} ions from water based on the principle of ion-exchange. The strategy adopted for the same is a very simple one involving a dip-stand-measure technique. Ch-SO_3Na-CDs nanocomposite films of size 2 cm X 2 cm were cut and dipped in 5 x 10^{-4} M solutions of Calcium chloride ($CaCl_2$), Magnesium chloride ($MgCl_2$) and a mixture of both (in accordance with WHO standard limits for water hardness, details in ESI). The concentration of Ca^{2+} ions in solution was determined by an easy, quick and effective technique employing a Calcium Combination Ion Selective Electrode in an Accumet Excel Dual Channel pH/Ion/Conductivity Meter, XL 50

(Fischer Scientific). The measurements were recorded in millivolt mode. The detailed experimental procedure is discussed in the ESI.

Figure 2(A) shows the standard calibration curve for various concentrations of Ca^{2+} solutions. The data is being fitted logarithmically to obtain the corresponding equation and the R^2 value as displayed in the graph. The respective concentrations of Ca^{2+} ions in solution recorded at various time intervals after dipping in of the films were then calculated by plotting the potential in mV recorded, into the equation obtained from the calibration curve. The concentration of Ca^{2+} ions in solution was recorded at various time intervals starting from 0 hours to 24 hours. Figure 2(B) depicts the gradual decrease in Ca^{2+} concentration in solutions with dipped-in Ch-SO_3Na-CDs nanocomposite films and blank Ch-films recorded at various time intervals. As evident from the figure, decrease in Ca^{2+} concentration in solution was found to be faster and higher for solutions with dipped-in Ch-SO_3Na-CDs nanocomposite films as compared to those with dipped blank Ch-films thereby focusing the role played by the sulphonated CDs (SO_3Na-CDs) embedded in the nanocomposite film in Ca^{2+} removal. UV-Visible spectroscopic analysis provides experimental evidence supporting the absorption of Ca^{2+} ion from solution by the Ch-SO_3Na-CDs nanocomposite film. Figure 2(C) shows the stacked UV-Visible spectra of blank chitosan film and Ch-SO_3Na-CDs nanocomposite film before and after Ca^{2+} absorption. As evident from the spectra, in both the cases the single absorption peak of the native films viz. at 275 nm for blank Ch-film and at 263 nm for Ch-SO_3Na-CDs nanocomposite film was found to be split into three absorption peaks appearing at 306 nm, 258 nm and 203 nm for blank Ch-film and at 300 nm, 258 nm and 204 nm for Ch-SO_3Na-CDs nanocomposite film after being dipped in Ca^{2+} solution (i.e., after Ca^{2+} ion absorption). The plausible explanation of the splitting pattern might be attributed to the interaction of −OH groups of cationic chitosan with the Ca^{2+} ions for the blank chitosan film and to the interaction of negatively charged carboxylate and sulphonate groups with Ca^{2+} ions for the Ch-SO_3Na-CDs nanocomposite film. In a similar manner the removal of Mg^{2+} from solution by the Ch-SO_3Na-CDs nanocomposite film both in the pure state and in a mixture of Ca^{2+} and Mg^{2+} ions was studied by Atomic Absorption Spectroscopy (AAS) (detailed experimental procedure is discussed in the ESI). It was observed that the Ch-SO_3Na-CDs nanocomposite film could also potentially remove Mg^{2+} in addition to Ca^{2+} from solution.
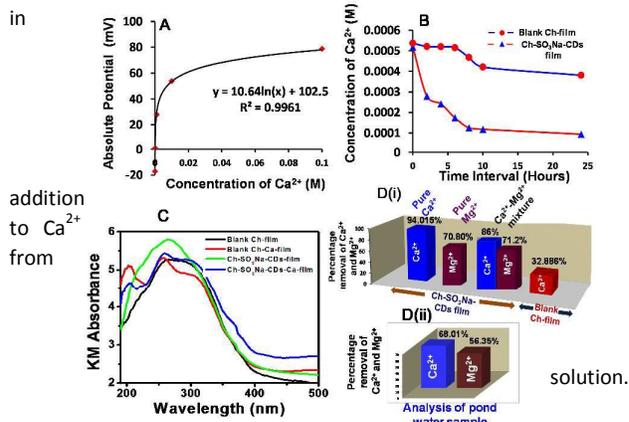

Figure 2. (A) Calibration curve for determination of Ca^{2+} in solution. (B) Plot showing the decrease in concentration of Ca^{2+} in solution with time for both Ch-SO_3Na-CDs nanocomposite films and blank Ch-films dipped solutions. (C) Comparative UV-Visible spectra of native films and those after being dipped in Ca^{2+} solution. (D)(i) Histogram plot showing the percentage removal of Ca^{2+}/Mg^{2+} from solution by Ch-SO_3Na-CDs nanocomposite films and blank Ch-films (D)(ii) Histogram plot showing the percentage removal of Ca^{2+}/Mg^{2+} from pond water sample by Ch-SO_3Na-CDs nanocomposite film.

Scheme 2. Schematic representation of the proposed mechanism for absorption of Ca^{2+} / Mg^{2+} from solu principle of ion exchange.

The extent of removal of Ca^{2+} and Mg^{2+} from solutions (Ca and Mg containing solutions as well as real environmental samples) are depicted as a histogram plots of percentage removal of Ca^{2+}/ Mg^{2+} ion versus the type of film used as shown in Figure 2(D)(i) and (ii). From the plot (i) it is clear that Ch-SO_3Na-CDs nanocomposite film has the potential to remove upto 94% of Ca^{2+} and 70.80% of Mg^{2+} from solution, whereas, on the contrary, blank Ch-film could remove only 32.9%. The adsorption capacities were determined to be 0.15gm/gm and 0.218 gm/gm of Ch-SO_3Na-CDs film for Ca^{2+} and Mg^{2+} respectively.This very well signifies the role played by the sulphonated CDs embedded in the chitosan nanocomposite film in absorption of Ca^{2+} and Mg^{2+} from solution in comparison to the blank chitosan film. Further, most importantly the material developed i.e., Ch-SO_3Na-CDs nanocomposite film has the potential to remove both Ca^{2+} and Mg^{2+} from solution and when both are present together in a mixture thereby justifying the potential of this material to be applicable for water softening purposes. In order to demonstrate the practical applicability of the material for water softening applications, we also tested its performance in real environment sample (pond water) (details of procedure described in ESI). Figure 2(D)(ii) shows the histogram plot showing the percentage removal of Ca^{2+}/Mg^{2+} from pond water sample by Ch-SO_3Na-CDs nanocomposite film. From the plot it is seen that the percentage removal of Calcium and Magnesium from pond water by the nanocomposite film was 68.01% and 56.35% respectively. Therefore it is very well justified that the material developed has potential for applicability as a water softening material.
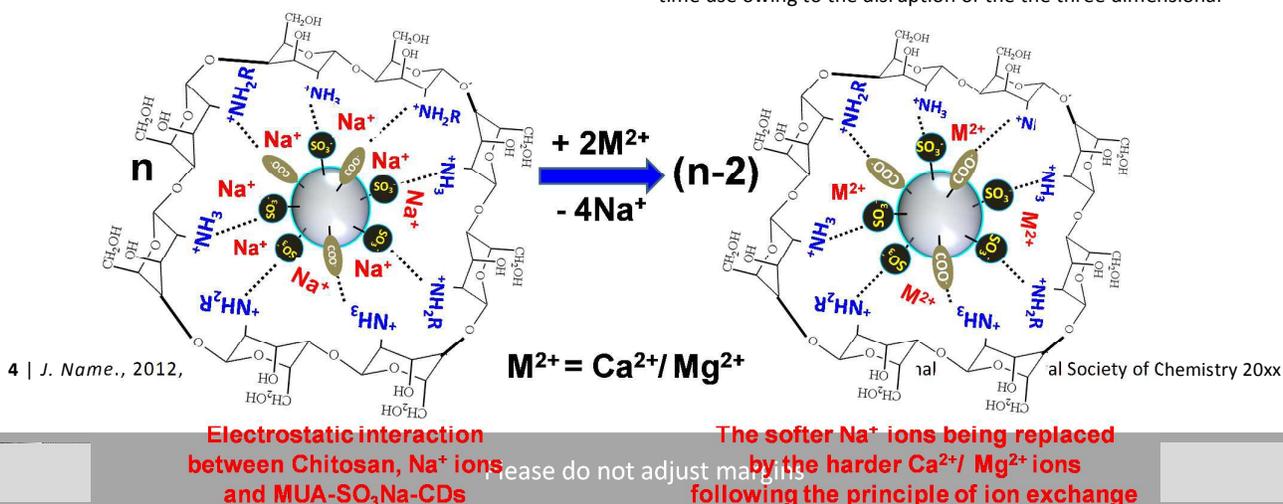
The probable mechanism underlying the entire process of absorption of Ca^{2+} and Mg^{2+} from solution by the biopolymeric nanocomposite films is believed to follow the principle of ion exchange. The schematic representation of the proposed mechanism for absorption of M^{2+} ($M^{2+}=Ca^{2+}/Mg^{2+}$) from solution by the Ch-SO_3Na-CDs nanocomposite film is shown in Scheme 2.

The amine groups of chitosan remain protonated in acidic media and therefore interact electrostatically with the negatively charged sulphonate groups on the surface of the CDs. As the sulphonated CDs are dispersed in sodium hydroxide, the CDs surface bears sodium sulphonate groups existing as an ion-pair ($Na^+SO_3^-$). Thereby Na^+ ions remain bound to the surface of the sulphonated CDs which are embedded in the chitosan film as discussed previously. The Ch-SO_3Na-CDs nanocomposite film on being dipped in aqueous M^{2+} ($M^{2+}=Ca^{2+}/Mg^{2+}$) solution enables the exchange of Na^+ ions in the hydrogel nanocomposite film matrix with the M^{2+} ions in solution. In this manner, Na^+ ions from the nanocomposite film are released into the solution and in exchange M^{2+} ions are absorbed into the hydrogel film matrix thereby assisting in the removal of M^{2+} ions from solution. The observed decrease in M^{2+} concentration in solution with blank chitosan films dipped in is proposed to be due to the fact that there is some weak interaction between the –OH groups on the chitosan film with the positively charged M^{2+} ions owing to which a percentage of ions gets absorbed into the blank chitosan film.

In conclusion, we have successfully prepared carbon dots bearing thiol (-SH) functional groups for the first time using a one-step method from a novel carbon precursor viz. 11-mercaptoundecanoic acid. The oxidation and subsequent dispersion of the CDs in sodium hydroxide gave carbon dots with sodium sulphonate groups on the surface. These oxidized CDs were used to form a hydrogel with the biopolymer chitosan and fabricated into thin films. The oxidized CDs-chitosan nanocomposite films were then successfully exploited as potential platforms for separation of Ca^{2+} and Mg^{2+} from solution based on the principles of ion exchange. The film was also successfully used to remove Ca^{2+} and Mg^{2+} from real environmental sample (pond water).

The sulphonated carbon dots-chitosan hybrid hydrogel nanocomposite film is green and can be an alternative material to toxic conventional polystyrene crosslinked with divinylbenzene generally used for ion exchange. However, the material is of one-time use owing to the disruption of the the three dimensional

$$n \xrightarrow[-4Na^+]{+2M^{2+}} (n-2)$$

$$M^{2+} = Ca^{2+}/Mg^{2+}$$

Electrostatic interaction between Chitosan, Na⁺ ions and MUA-SO₃Na-CDs

The softer Na⁺ ions being replaced by the harder Ca²⁺/ Mg²⁺ ions following the principle of ion exchange

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structure of the hydrogel upon acid treatment thereby limiting its reusability. Therefore, for the first time we report a very simple, easy, green and effective method employing a carbon nanomaterial embedded biopolymeric nanocomposite as a promising platform with anticipated potential for applicability as a water-softening ion-exchange film for removal of Ca^{2+} and Mg^{2+} from water.

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