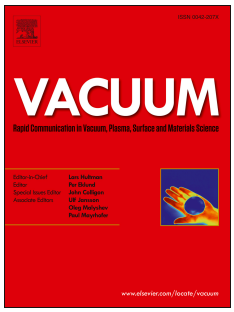
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Recent Progress in Gelatin Hydrogel Nanocomposites for Water Purification and Beyond

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Abstract

Innovative characteristics of hydrogels such as swellability, modifiability and hydrophilicity make them materials of choice for water treatment and other applications. Hydrogels have shown excellent adsorptive performance for different types of water pollutants comprising toxic dyes, nutrients and heavy metals. Among different types of hydrogel based materials, hydrogel-nanomaterials combination represent a highly viable method to further improve the properties of hydrogel for numerous applications. The combination of hydrogel and nanomaterials leads to the development of hybrid hydrogel with multifunctional network. This novel combination gives synergistic effect to the newly formed novel hydrogel materials. In this article, we briefly review the recent progress in gelatin based hydrogel nanocomposites with particular emphasis on wastewater treatment along with biomedical applications.

Keywords: Gelatin; hydrogel; nanocomposite; water treatment; biomedical applications.

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1. Introduction

Thomas Graham was first to perform the study ongels in the nineteenth century by using sol-gel chemistry [1]. He synthesized silica gel via twostep process i.e. the formation of fine particles using colloidal suspension followed by removal of solvent through evaporation. For the first time, appearance of hydrogel term in literature was noticed in 1894 and was utilized to give description about colloidal gel [2]. DuPont scientists in 1936 reported the synthesis of poly (2-hydroxyethyl methacrylate) (PHEMA) hydrogel [3]. The PHEMA hydrogel was employed for the first time in contact lens applications by Wichterle and Lim [4]. Recently most of the research is focused on smart hydrogels. Smart hydrogels show changes in swelling behavior due to variation in environmental conditions like temperature, pH, electric field and solvent composition. Hydrogels can be defined in number of different ways.In most common definition, hydrogel is a cross-linked polymeric matrix, water-swollen material with three dimensional structures [5,6]. In another definition, hydrogel may be defined as hydrophilic three-dimensional polymeric material which has the capacity of absorbing large quantity of water and retain it inside its matrices without dissolution. Hydrogels have got significant attention in the recent years, due to their use in various applications [7–12]. The flexibility of hydrogel is due to the presence of large water content and their swelling naturemakes them a smart and perfect material for different type of applications [13].

The hydrophilicity and crosslinking between network chains plays an important role in order to understand the chemistry of hydrogel and other materials. The swelling ability of hydrogel is attributed to the hydrophilic functional groups [14] (primary amidic, hydroxyl, carboxylic etc.) present in polymer matrices while crosslink between the polymer chains makes hydrogel insoluble in water. The formation of three dimensional structure of hydrogel is because of

crosslinking between the chains. The definition of hydrogel covers both the natural and synthetic material.The swelling mechanism of hydrogel can be explained on the basis of pore size of polymer network [15]. The polymer network of hydrogel can be categorized as:

(a) Nonporous

(b) Microporous

(c) Superporous

In nonporous hydrogel, mechanism of swelling in water occurs through only diffusion of water molecules in a medium.Microporous hydrogel contains pores in its structure of fewmicrons to few 100 microns that can be analyzed by microscopytechniques. The mechanism of water swelling in microporous hydrogel is considered to proceed by diffusion as well as leaching via pores.Super porous hydrogels have been recently developed [13]. They contain huge number of large-sized pores that are beneficial in getting extraordinarily high swelling kinetics. Pore size of super porous hydrogels plays big role in settling the swelling rates. Extremely porous hydrogel network have been found to exhibit faster and excessive swelling [16].

Different types of nanomaterials have been use for a number of applications [17–19]. The properties of nanomaterials such as nanoparticles are different as compared to bulk materials that make the use of nanoparticles in common user applications. It has also led to debate on safety issue of nanotechnology. The risk to the environment is reduced by the incorporation of nanomaterials into the hydrogel. This advanced combination of nanomaterials and hydrogel produces (a) structural diversity (b) property enhancements. Particularly nanocomposite hydrogels are hydrogels linked with nanomaterials via physical or covalent bond. Also, low thermal stability and poor mechanical strength are the shortcomings related to the use of hydrogels. Different type of nanomaterials such as metal nanoparticle (gold, silver), metal oxide

(iron oxide, titanium oxide), inorganic (silica, silicates), carbon nanotubes and graphene can be used with hydrogels to form hydrogel nanocomposite with improved mechanical properties and functionalities [20–27]. For example, remarkable improvements in mechanical and thermal properties were noted in hydrogel when gold nanoparticles were inserted in poly N-isopropyl amide hydrogel [28]. In another study, poly ethylene glycol/ silica based hydrogel nanocomposite was reported with improved mechanical stiffness as compared to pristine hydrogel [29]. Hence the combination of nanomaterials and hydrogels leads to innovative materials that exhibit unique characteristics not present in either component. This combined material opens new way for researchers to explore the use of these materials in many applications. The combination of hydrogel-nanomaterials can be divided into three types as [30]: (a) micro or nano hydrogel stabilized nanomaterials , (b) nanomaterials incorporated into hydrogel network by non-covalently, (c) nanomaterials incorporated into hydrogel network by covalent attachment. Recently some reviews on (a) nanocomposite hydrogels for tissue engineering [17], (b) nanocomposite hydrogel particularly on carbon nanotubes for different application [31], (c) hydrogel for removal of pollutants from aqueous solution have been published [13].

So this review will describe only the most recent progress in gelatin based hydrogel nanocomposite for pollutants removal from aqueous solution. For detailed discussion on biopolymer based hydrogels, readers are advised to read the recent reviews on hydrogels. [13,32–35]

We also review miscellaneous applications of gelatin based hydrogel nanocomposites. Our prime aim to (a) report some remarkable examples, (b) bring attention of researchers to gelatin based hydrogel nanocomposites for water purification and other applications.

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2. Structure of Gelatin

Gelatin is found in animal tissue. Long back ago as 6000 BC, it was first time utilized as glue. In 16th century, it has served as one of ingredient in a ceremonial party at the court of Henry VIII of England [36]. With time, it was synthesized at industrial scale and has found a number of applications. It has been used in various applications such as pharmaceutical industries, food and photographic. Pig skin (46%), pig and cattle bones (23.1%) and bovine hides (29.4%) are the most copious sources of production for gelatin [37]. The chemical structure of gelatin [38]can be represented as given in **Figure 1**.

Gelatin has composition similar to that of collagen. Some changes in composition are due to its manufacturing process. The formation of collagen from gelatin proceeds with the variation in composition of many amino acids. The amount and type of amino acids present in gelatin are not accurately defined. Muyonga, Cole and Duodu [39] reported 30% of proline and hydroxyproline in mammalian gelatins whereas this amount was 23% in the study of Farris, Song and Huang [40] as presented in **Table 1.** Furthermore, pig skin gelatin did not contain cysteine according to Farris et al. [40]] while its presence was reported by Bailey and Light [41].

Collagen loses its native structure during the transformation in the manufacturing process of gelatin. The change in conformation on heating of collagen fibers lead to the development of helixes type structure and partly regain their shape on cooling. Water is detained in the gelatin network leads to the formation of gel. The difference in the structure of gelatin and collagen is because of partial organization of helixes. On gelation, gelatin structure varies. The state of gel

can be determined by space arrangements and interactions. Based on these, structure can be divided into following [42]: (a) primary, single α-chain, (b) secondary, contains two single α-chains or single α-chain with a loop and (c) tertiary, three single α-chains or two single α-chains one of them in the form of a loop or single α-chain which makes two loops. The existence of primary, secondary and tertiary structure of gelatin depends upon temperature, energy and gelatin concentration.

Coppola et al. [43] characterized the structure of gelatin film by using differential scanning calorimetry. Accordingly, gelatin films may be classified into three states: (a) amorphous structure represents coil of primary chains, (b) semi-crystalized structure with coil and triple-helixes and (c) crystallized structure made of coil and triple-helixes **(Figure 2)**. This classification was according to Harrington and Rao [44] and Oakenfull and Scott [45].

The stability of secondary or triple helix structure is because of the formation of hydrogen bonds through glycine residues which are present in α-chain [46]. The triple-helical structure is preserved by different types of interactions that exist in a regular manner on chains. The hydrogen bonds are developed between hydrogen atoms of glycine and oxygen atom from carboxyl groups **(Figure 3a)** [41,42,45]

Oakenfull and Scott [45] reported the hydrogen bonding in gelatin network through -NH groups and -CO groups and hydrogen bonds due to water molecules with gelatin network. A bridge is formed by water molecules through hydrogen bonding with OH of one gelatin chain and -C=O of same gelatin chain or another gelatin chain but this opinion was contested [47]. The participation of residues in the development of hydrogen bonds was examined by Bailey and Light [42].Water molecules can form hydrogen bonding in gelatin structure by the following way: (a) with -OH of two hydroxyproline, (b) with -C=O of gelatin network and -OH of hydroxyproline **(Figure 3b)**.

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3. Gelatin Hydrogel Nanocomposites for Water Purification

Many pollutants exist in water because of the waste produced from paper and pulp, textile, tannery, plastic and food processing industries. Hydrogels have shown unique performance as adsorbent for the removal of different types of pollutants from wastewater [7–9,13]. The growth of research concerning the hydrogels in the area of environmental science increased in the recent years [13]. The different gelatin based hydrogel materials utilized for water treatment [38,48–54] are summarized in **Table 2**.

Recently, nanocomposite based on gelatin, iron oxide nanoparticles and carbon nanotube (CNT) was synthesized for the removal of cationic methylene blue (MB) and anionic direct red 80 (DR) dyes [48]. This nanocomposite has shown excellent adsorption performance for both types of dyes (**Fig. 4**). The maximum adsorption capacity 465.5 and 380.7 mg g^{-1} has been reported for methylene blue and anionic direct red 80 respectively. The percent's swelling of 83.3%, 61.2% and 55.5% were attained utilizing the gelatin gel, gelatin gel-carbon nanotube and gelatin gel-carbon nanotube-iron oxide nanoparticles nanocomposite. Hence water consumption capability of gelatin gel was decreased by the addition of either carbon nanotube or iron oxide nanoparticles.

This result may be due to the decrease in hydrophilic character of gelatin gel by the addition of iron oxide nanoparticles and carbon nanotube. The effect of dye concentration on adsorption was also studied (**Fig.5**). It was found that the adsorption capacity of the synthesized beads for both the dyes (MB and DR) increased in tandem with an increment in the concentrations of the solutions. These results were further supported by the Scanning and transmission electron

microscopy (SEM and TEM). It was observed from the images that the structure is favorable since it facilitated the higher dye adsorption in consideration of the high surface to volume ratio **(Fig. 6)**. The surface of the Gel bead was found to be relatively smooth with the absence of no particles on the top of the surface.

In this study, iron oxide nanoparticles and carbon nanotubes were found to behave as cross linker [55] in the gelatin gel network, cross linking density increased with increased in amount of carbon nanotube and iron oxide nanoparticles, resulted in the formation of three dimensional network and consequently decreased the swelling ability of nanocomposite [56].

The water retention ability of gelatin gel-carbon nanotube-iron oxide nanoparticles nanocomposite was improved by the addition of carbon nanotube and iron oxide nanoparticles to the gelatin gel. The percentages removal was 63.0%, 69.6%, and 93.1% by gelatin gel, gelatin gel-carbon nanotube and gelatin gel-carbon nanotube-ironoxide nanoparticles nanocomposite, respectively for anionic direct red 80 dye and 17.9%, 64.2% and 76.1% respectively for methylene blue dye, less as compared to anionic direct red 80 dye. The high percentage removal of anionic direct red 80 dye by gelatin gel was attributed to the presence of positive charge on the surface of gel. However, gelatin gel demonstrates electrostatic repulsion to positively charged methylene blue dye. The electrostatic attraction between polar carboxylic groups from the functionalized carbon nanotube and cationic methylene blue dye was responsible for the adsorption of methylene blue dye **(Figure 7)** onto the gelatin gel-carbon nanotube and gelatin gel-carbon nanotube-iron oxide nanoparticles nanocomposite. Likewise, iron oxide nanoparticles did not show adsorption towards the analyzed dyes, but when introduced into the gelatin gel-carbon nanotube network, it adsorbed anionic direct red 80 dye [57].

In another study, hydrogel was prepared by encapsulation of manganese peroxidase enzyme on gelatin matrix [49] using glutaraldehyde as a cross linker. This hydrogel was used for the decolorization of reactive red 195A dye from aqueous solution. The biodegradation of reactive red 195A dye was carried out in batch mode. The immobilized manganese peroxidase in gelatin gel was successfully used to achieve more than 90% decolorization of reactive red 195A dye in 5 h. The mechanism of decolorization by immobilized manganese peroxidase consists of (a) dye gelatin adsorption and (b) manganese peroxidase dye degradation [58]. The participation of enzymatic degradation in decolorization of reactive red 195A dye can be confirmed by reacting heat inactivated free and entrapped enzymes with dye molecule. The inactivated encapsulated manganese peroxidase in gel showed 1.7–2.6% decolorization in 5 h. In similar manner, no decolorization efficiency was shown by free enzyme. Hence manganese peroxidase biodegradation was the dominant mechanism for decolorization reactive red 195A dye.

A granular gelatin grafted poly (acrylic acid)/attapulgite hydrogel composite was reported as adsorbent to be used in mixed dye solution of orange G and malachite green [50]. Gelatin grafted poly(acrylic acid) hydrogel exhibited maximum adsorption capacity of 1370 mg g^{-1} and gelatin grafted poly(acrylic acid)/attapulgite (APT) hydrogel composite showed maximum adsorption capacity of 1190 mg g^{-1} for malachite green dye. Gelatin grafted poly(acrylic acid) hydrogel was synthesized by free radical polymerization using ascorbic acid (Vc)/hydrogen peroxide (H_2O_2) solution and N,N′ -methylenebisacrylamide (MBA) as redox initiator and cross linker respectively. A proposed mechanism for synthesis of gelatin grafted poly (acrylic acid) hydrogel is presented in **Figure 8.**

The hydroxyl radicals were formed via oxidation of ascorbic acid in the presence of hydrogen peroxide. The hydroxyl radicals are expected to react with hydroxyl and amino groups of gelatin, took hydrogen from hydroxyl and amino groups, led to the formation of a macroradical containing various active sites. These active sites are available for grafting of acrylic acid monomer to produce grafted chains. Finally, polymerization reaction continues, the cross linked three dimensional hydrogel networks are formed in the presence of N, N′ - methylenebisacrylamide. The optimum ratio of gelatin/acrylic acid for the formation of fine granular hydrogel was 1:4.8.

The mechanism of malachite green dye adsorption onto hydrogels was explained on the basis of zeta potential. Due to anionic nature, hydrogels showed negative zeta potential, average of -20 mV. Hence, negatively charged orange G dye was repelled by these hydrogels. The regeneration and reusability study was evaluated by taking 1000 mg L^{-1} as initial concentration of malachite green dye, 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} NaOH as desorbing and regenerating agent respectively. The adsorption efficiency remained almost the same throughout the four cycles as shown in **Figure 9**and in the fifth circle, the regeneration efficiency was reported to be 87.1 % and 93.6 % for gelatin grafted poly(acrylic acid) (GE-g-PAA/APT-0) and gelatin grafted poly(acrylic acid)/attapulgite (GE-g-PAA/APT-5, 5 is percentage of APT) respectively. This better adsorption efficiency was related to the cross linker behavior of attapulgite in polymerization process [59,60]. SEM study of the synthesized hydrogels was also carried out to study their porous surface (**Fig. 10**).

. [50]. Copyright 2015 Springer.

Recently gelatin grafted acrylamide hydrogel was prepared using graft co-polymerization method [51]. Clinoptilolite was incorporated into gelatin grafted acrylamide hydrogel network to

produce a hydrogel nanocomposite. The prepared gelatin grafted acrylamide/clinoptilolite hydrogel nanocomposite was exploited for the removal of Cd^{2+} ions from mine wastewaters and aqueous solution. The maximum adsorption capacity of 54.95 and 78.13 mg g^{-1} was determined using gelatin grafted acrylamide hydrogel and gelatin grafted acrylamide/clinoptilolite hydrogel nanocomposite respectively.

Using the ion-imprinted polymers (IIPs) technique, synthesis of 8-hydroxyquinoline-grafted gelatin/chitosan was carried out for selective adsorption and detection of lead ions [52]. Genipin was utilized as cross linker, 8-HQ-grafted gelatin and chitosan were used as monomers in the preparation of three-dimensional ion-imprinted polymers. Ion-imprinted polymers exhibited 235.7 mg g^{-1}adsorption capacity and 0.2 ng mL^{-1} detection limit for lead ion (+2).

The selection of functional monomers plays crucial role to produce identification sites for the template ions in ion-imprinted polymers technique [61,62]. The common monomers such as 4-vinylpyridine and methacrylic acid are not suitable for use in ion-imprinted polymers technique because of solubility and single functional group. These monomers are soluble in organic solvent and reduce the number of template ion in ion-imprinted polymers due to solubility. These monomers are also not perfect to work in aqueous mediums due to their hydrophobic character.

Chitosan can play a monomer role in the synthesis of ion-imprinted polymers in aqueous medium. It has issues with low adsorption capacity and selectivity due to multiple character of amino groups as cross-linker and recognition sites. Various functional groups such as primary amines, thiol, imidazole, carboxylate and peptide backbones in gelatin usually react to form composite with heavy metals [63]. 8-Hydroxyquinoline (8-HQ) can form complex through its two functional groups, bidentate chelating property, extract and remove metal ions. Hence, the

selectivity, adsorption capacity and hydrophilicity can be improved by using 8-hydroxyquinoline grafted gelatin **(Figure 11).**

This study involves the synthesis of ion-imprinted polymers through following steps: (a) hydrogel membrane formation, (b) swelling/folding and (c) chemical cross-linking, which led to the development of a three-dimensional (3D) structure of imprinted cavities with better mass transfer. Ion-imprinted polymers (IIPs) have shown better swelling capacity in comparison to non-ion imprinted polymers (NIPs) **(Figure 12)**. The yellow color of pre-polymerized membrane was due to the complex establishment of template monomer. Color turned from yellow to blue after the addition of cross linker genipin and removal of template, morphology became three dimensional (3D). BET study confirmed the average pore diameter of 2.7 nm. Hence, this simple method gave a three dimensional ion-imprinted polymers possessing fast kinetics and high adsorption capacity. Ion-imprinted polymers extraction joined with spectrophotometric method was employed for Pb (II) ions detection from real water. The intensity of absorbance was changed proportionally to amount of Pb (II) within range of 1 to 100 ng mL^{-1}.

In another study, redox hybrid hydrogel of gelatin/silica was developed by grafting of benzoquinone, to be applied for biotoxicity assay, which was performed by analyzing the water pollutants Hg^{2+}, Cu^{2+} and Cd^{2+}as role model [53]. Both microorganism E. coli and redox mediator were immobilized into matrices of hybrid hydrogel to develop a novel biosensor. The analyzed 50% inhibiting concentrations were found to be 21.2 mg mL^{-1}, 44 mg mL^{-1} and 79 mg mL^{-1} for Hg^{2+}, Cu^{2+} and Cd^{2+} respectively. UV-visible spectrophotometer, cyclic voltammetric measurements and electrochemical impedance spectroscopy was used to define the synthesized redox hydrogel. Semi-interpenetrating polymer network hydrogel was formed for sorption studies of uranyl ion, consisting of gelatin, poly (ethylene glycol), sodium acrylate and

acrylamide. Poly (ethylene glycol) diacrylate was utilized as a multifunctional crosslinker [38]. This hydrogel was synthesized in the presence of ammoniumpersulphate/N, N, N', N'-tetramethylethylenediamine as pair initiator.

Benzo-9-crown-3 doped chitosan/gelatin hydrogel has been prepared to modify the microcantilever sensor [54]. This synthesized hydrogel was applied to detect the beryllium ions (Be^{2+}) from aqueous solution. The detection was based on the deflection given by the microcantilever sensor**.**

Firstly, constant flow was maintained using 0.01 M Tris–HCl buffer solution (pH 7.04) in microcantilever coated by hydrogel film of 15 mm to obtain a balanced baseline (0 nm deflection). The detection limit for Be^{2+} by microcantilever modified by chitosan/gelatin/benzo-9-crown-3 hydrogel was found to be 10^{-11} M **(Figure 13a)**.The higher sensibility as big deflection in microcantilever is due to absorption of Be^{2+} onto hydrogel doped benzo-9-crown-3. About 1 mm response is given by microcantilever at most higher concentration of 10^{-4} M. Control tests were carried out by taking hydrogel film of 15 mm thickness without benzo-9-crown-3. No deflection was given by microcantilever on the passage of Be^{2+} solution of 10^{-4} M as indicated in **Figure 13b**. These results affirmed that deflection of microcantilever was attributed to the bond between Be^{2+} and benzo-9-crown-3.

This modified microcantilever sensor is highly selective to Be^{2+}. The high selectivity was attributed to the size of benzo-9-crown-3 (0.26 Å) [64], which are ideal to make bond with Be^{2+} in comparison to other metal ions. Be^{2+} was released from the benzo-9-crown-3 on the back circulation of buffer solution, resulted electrolyte gel came into the original position. Hence original state was taken by the microcantilever. The microcantilever modified through hydrogel exhibited reversible and selective response to Be^{2+} **(Figure 14)**.

4. Gelatin Hydrogel Nanocomposites for Miscellaneous Applications

The use of hydrogels in biomedical application is limited because of their poor stiffness and low toughness. The mechanical stiffness of gelatin based hydrogel can be improved by incorporating different nanomaterials such as graphene, carbon nanotubes, graphene oxide, and silicate nanoparticles [25,65–67]. Nanoparticles can interact through physically or chemically with polymerto increase the stiffness at their different concentrations [25,66]. Gelatin based materials have been exploited in biomedical field [68–100].

Recently, novel bio-adhesives composed of gelatin/alginate hydrogel were formulated using carbodiimide as cross linker [68]. Montmorillonite and kaolin were introduced into hydrogel matrices to enhance the sealing capability for use in hemorrhagic environment. This type of bio-adhesives was reported for the first time. Lap shear, burst strength and compression were the methods utilized to study the mechanical strength of the synthesized bio-adhesives. The optimum amount of gelatin, alginate and carbodiimide for the development of bio-adhesives was 400 mg mL^{-1}, 10 mg mL^{-1} and 20 mg mL^{-1}, demonstrated 387 mmHg of burst strength. The burst strength of 25% and 50% was found to increase with the loading of kaolin and montmorillonite respectively. The increase in burst strength by kaolin was because of micro composite structuring, while it was due to nanostructuring effects in case of montmorillonite.

Zhou et al. prepared gelatin methacrylate hydrogel and nanocrystalline hydroxyapatite to study the interaction between breast cancer cells and osteoblasts or human bone marrow mesenchymal stem cells by three dimensional biomimetic techniques [71]. Breast cancer cells growth was increased on the introduction into bio-printed matrices while osteoblasts or human bone marrow mesenchymal stem cells proliferation was suppressed in the presence of breast cancer cells. The

best percentages of gelatin methacrylate hydrogel plus nanocrystalline hydroxyapatite were 10 and 15% for the formation of matrices to analyze the interaction of osteoblasts and breast cancer cells and of human bone marrow mesenchymal stem cells and breast cancer cells respectively. Interpenetrating polymer network hydrogel of sodium alginate/gelatin incorporated cellulose nanocrystals was reported for the application in cartilage replacement [72]. The developed alginate/gelatin/cellulose nanocrystals hydrogel nanocomposite showed strain (15.2%) and strength (14.4 MPa) similar to that of natural cartilage.

Jaiswal et al. produced high mechanical stiffness and toughness for gelatin based hydrogel by incorporating very low concentration of magnetic nanoparticles [73]. This high stiffness of hydrogel nanocomposite is attributed to chemical functionality from nanoparticles. The mechanical stiffness of hydrogel nanocomposite depends on (a) size of the nanoparticles, (b) concentration of the nanoparticles and (c) concentration of the polymer.0.2 and 200 kPa are the range of mechanical stiffness obtained by controlling the above mentioned parameters. Hence this nanocomposite can be effectively used in tissue engineering and delivery of cell/protein. Garcia-Astrain et al. used maleimide capped silver nanoparticles to synthesize the hydrogel based on gelatin [85]. The storage modulus of synthesized hydrogel nanocomposite wasalmost three times higher as compared to the hydrogel having no silver nanoparticles. The application in biomedical of this bio-nanocomposite was shown by their excellent swelling, biocompatibility and drug release studies.

5. Conclusion

Hydrogels have three dimensional structure of polymer with high water absorption capacity. Poor mechanical strength is the main drawback associated with hydrogels that limit [21] their

uses in several applications. Nowadays, researchers are looking to develop hydrogels with good mechanical strength for different type of applications. From this article, we can say that the incorporation of nanomaterials into network of hydrogel is an innovative way to procure robust hydrogels with good mechanical properties for advanced applications. In this article, recent developments in gelatin based hydrogel nanocomposite for water purification has been reviewed. Water purification is a burning topic these days and gelatin based hydrogel nanocomposites have very high potential to be used in water purification. Some insights on the usage of gelatin based hydrogel nanocomposite for biomedical applications has also been provided. Expectantly, literature highlighted in this article could give innovative ideas in the field of gelatin based hydrogel nanocomposite for several other applications.

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Table 1

Amino acids composition of the pig skin gelatin as reported by Farris et al. [37]. Adopted from [37].

Amino acid	Percentage	Amino acid	Percentage
Isoleucine	1.02	Valine	1.90
Hydroxyproline	9.80	Tryptophan	-
Glycine	32.20	Serine	3.40
Cysteine	-	Phenylalanine	1.38
Asparagine	0.60	Lysine	2.65
Alanine	11.05	Tyrosine	0.35
Hydroxylysine	0.75	Threonine	1.80
Histidine	0.45	Proline	13.10
Glutamic acid	7.10	Methionine	0.32
Aspartic acid	4.42	Leucine	2.35
Arginine	4.96		

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Table 2: Various gelatin based materials used for water treatment.

Gelatin Based Material	Dye	Gelatin Based Material	Ion
Gelatin gel/carbon nanotube/ironoxide nanocomposite	Methylene blue and anionic direct red 80 [46]	Gelatin grafted acrylamide/clinoptilolite hydrogel nanocomposite	Cd^{2+} [49]
Manganese peroxidase/gelatin hydrogel	Reactive red 195A [47]	8-Hydroxyquinoline-grafted gelatin/chitosan hydrogel`	Pb^{2+} [50]
Gelatin grafted poly(acrylic acid)/attapulgite hydrogel composite	Malachite green and orange G [48]	Gelatin/silica/benzoquinone hydrogel	Hg^{2+}, Cu^{2+} and Cd^{2+} [51]
		Gelatin/poly(ethylene glycol)/sodium acrylate/acrylamide hydrogel	UO^{2+} [34]
		Benzo-9-crown-3 doped chitosan/gelatin hydrogel	Be^{2+} [52]

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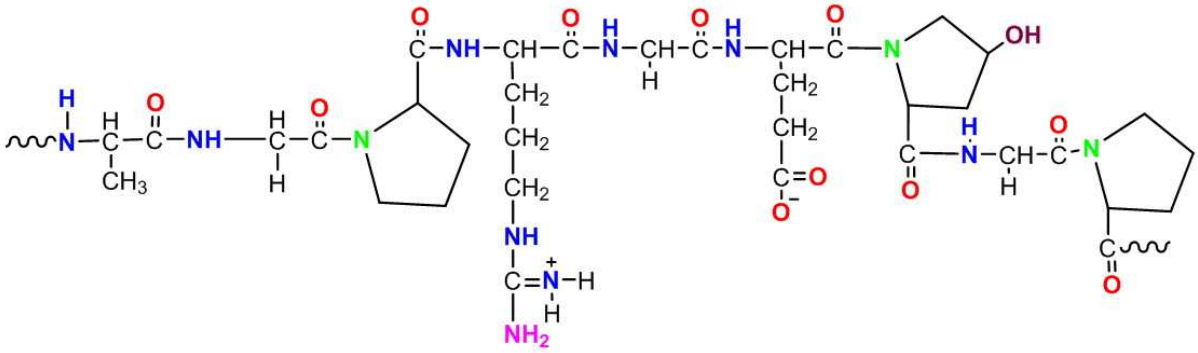


Figure 1. Representation of gelatin chemical structure [38]. Reprinted with permission. [38]. Copyright 2015 Springer.

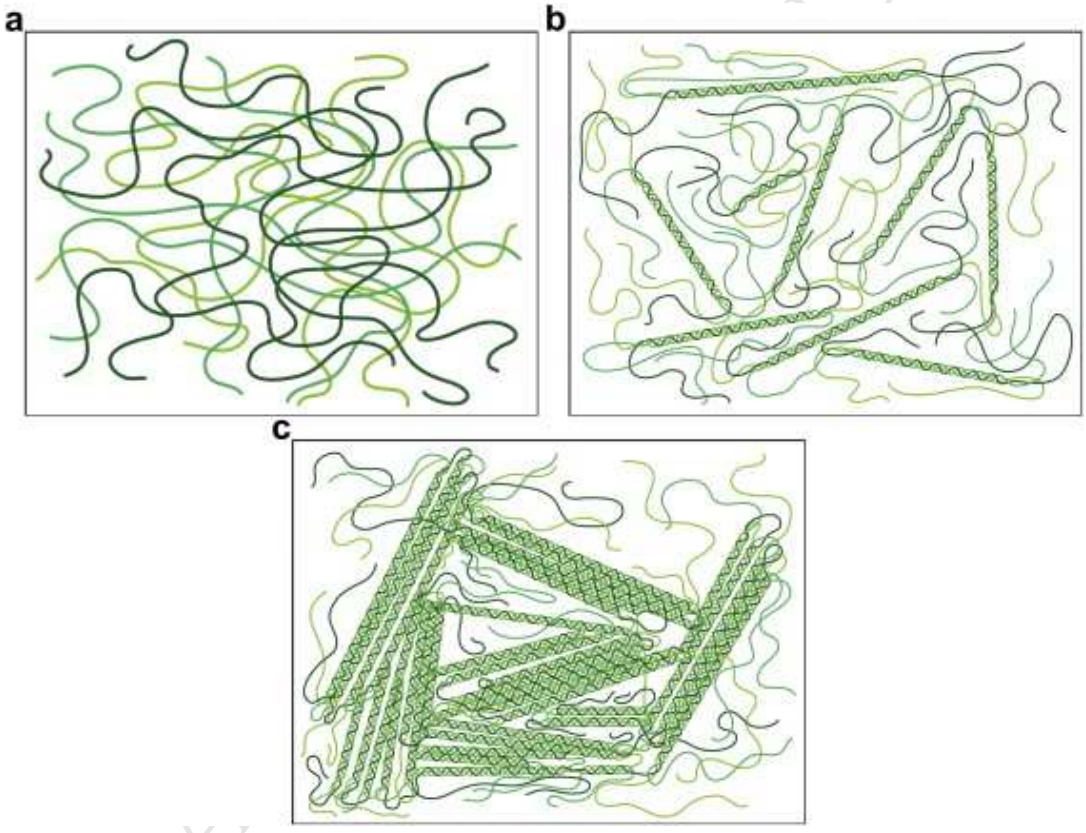


Figure 2. Gelatin film structure (a) amorphous chains, (b) semi-crystalized of triple helixes and coils, (c) packets composed of triple helixes and coils [43]. Reprinted with permission. [43]. Copyright 2012 Elsevier.

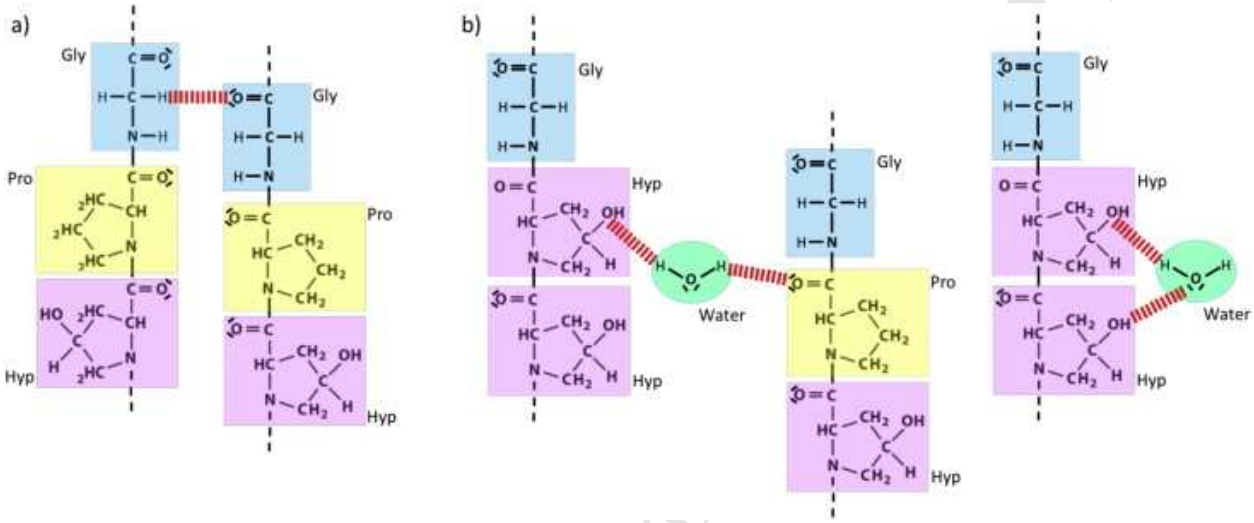


Figure 3. Hydrogen bond (represented by dotted lines) (a) between gelatin strands and (b) among gelatin strands and water molecules [36]. Reprinted with permission. [36]. Copyright 2015 Elsevier.

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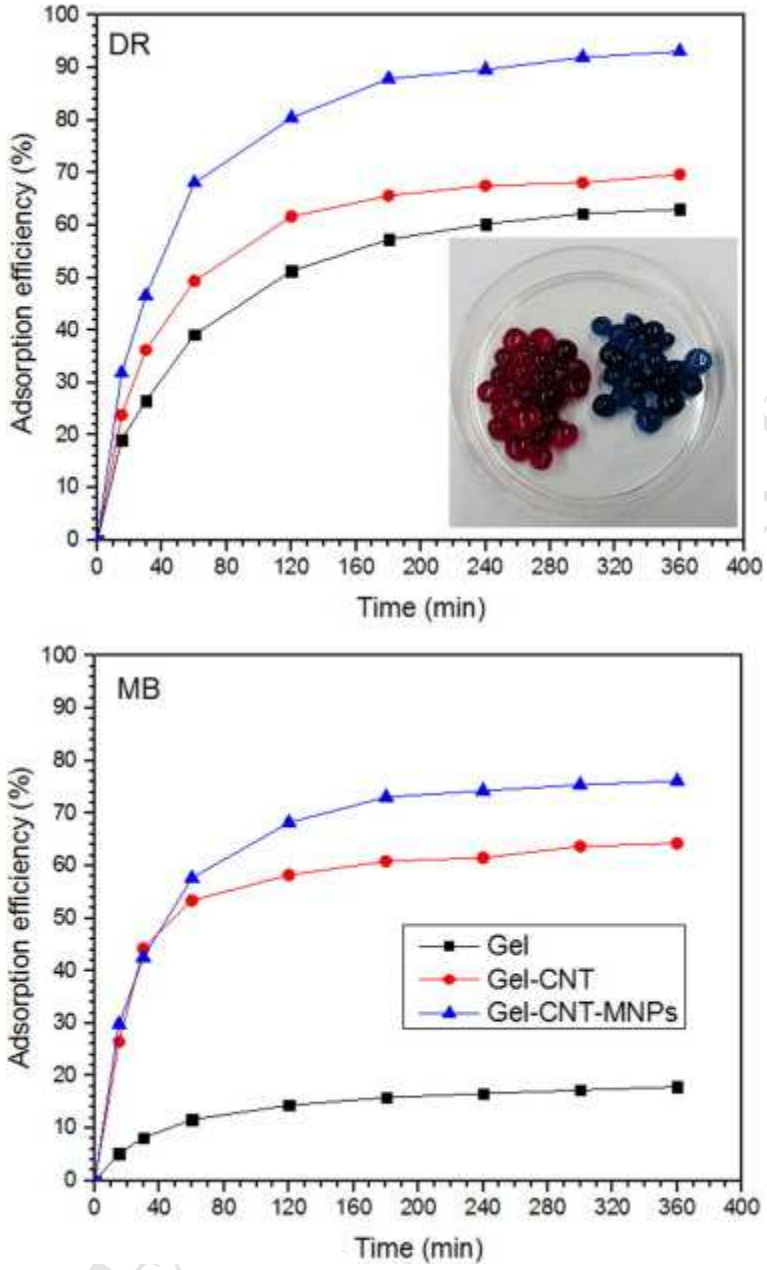


Figure 4. Effect of time on DR and MB adsorption efficiency of the prepared bead and the nanocomposite beads, insect shows the dyes adsorbed nanocomposite beads (Gel-CNT-MNPs). [In these experiments, 0.05 g of nanocomposite beads were immersed in 50 mL of dyes solutions (500 mg.L^{-1}), at 21 °C.]. Reprinted with permission. [48]. Copyright 2017 Elsevier.

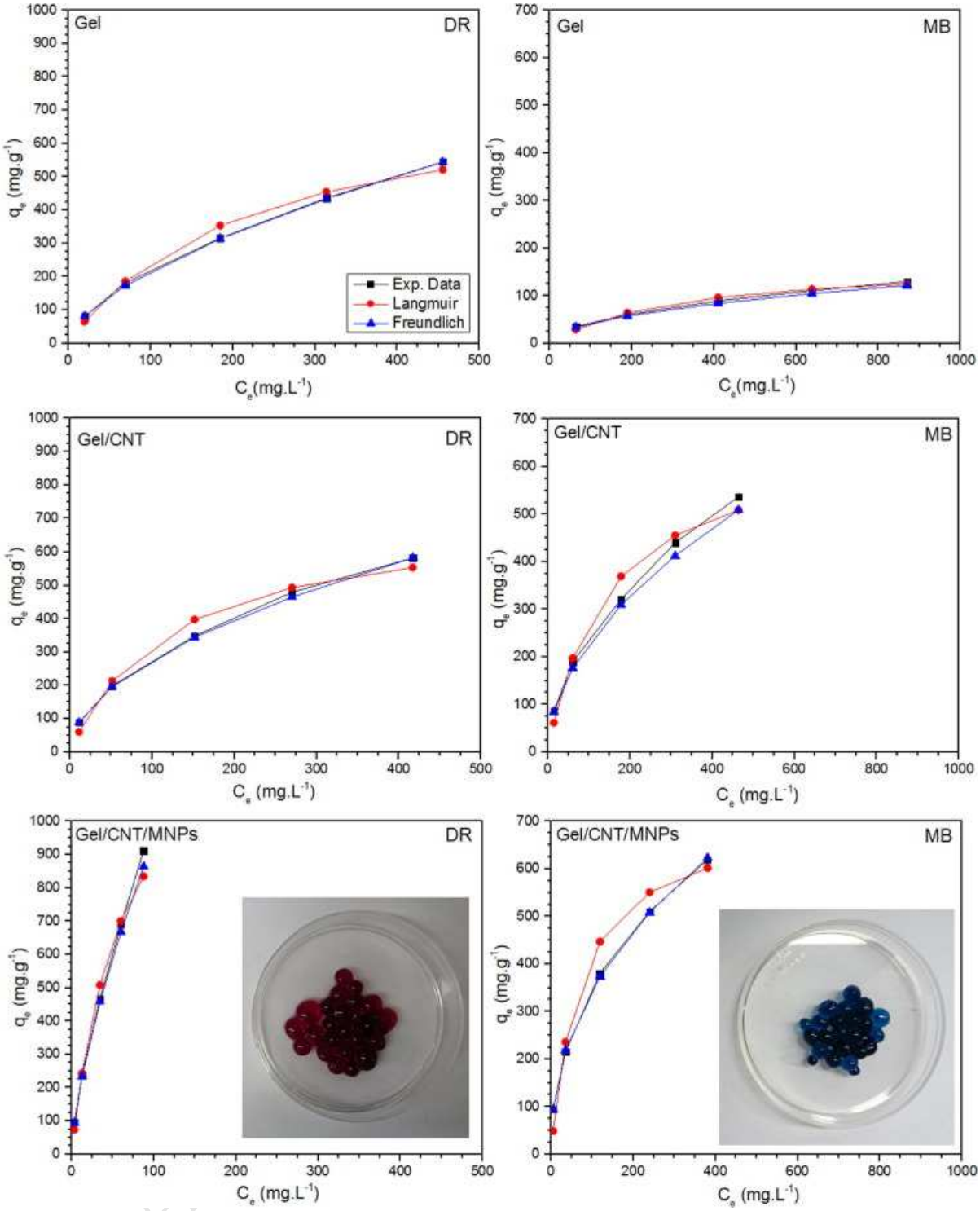


Figure 5. Effect of initial dyes concentration on adsorption efficiency of the prepared bead and the nanocomposite beads and the results of the applied isotherm models (i.e., Langmuir and Freundlich) [In these experiments, 0.05 g of nanocomposite beads were immersed in 50 mL of dyes solutions for 360 min, at 21 °C.]. Reprinted with permission. [48]. Copyright 2017 Elsevier.

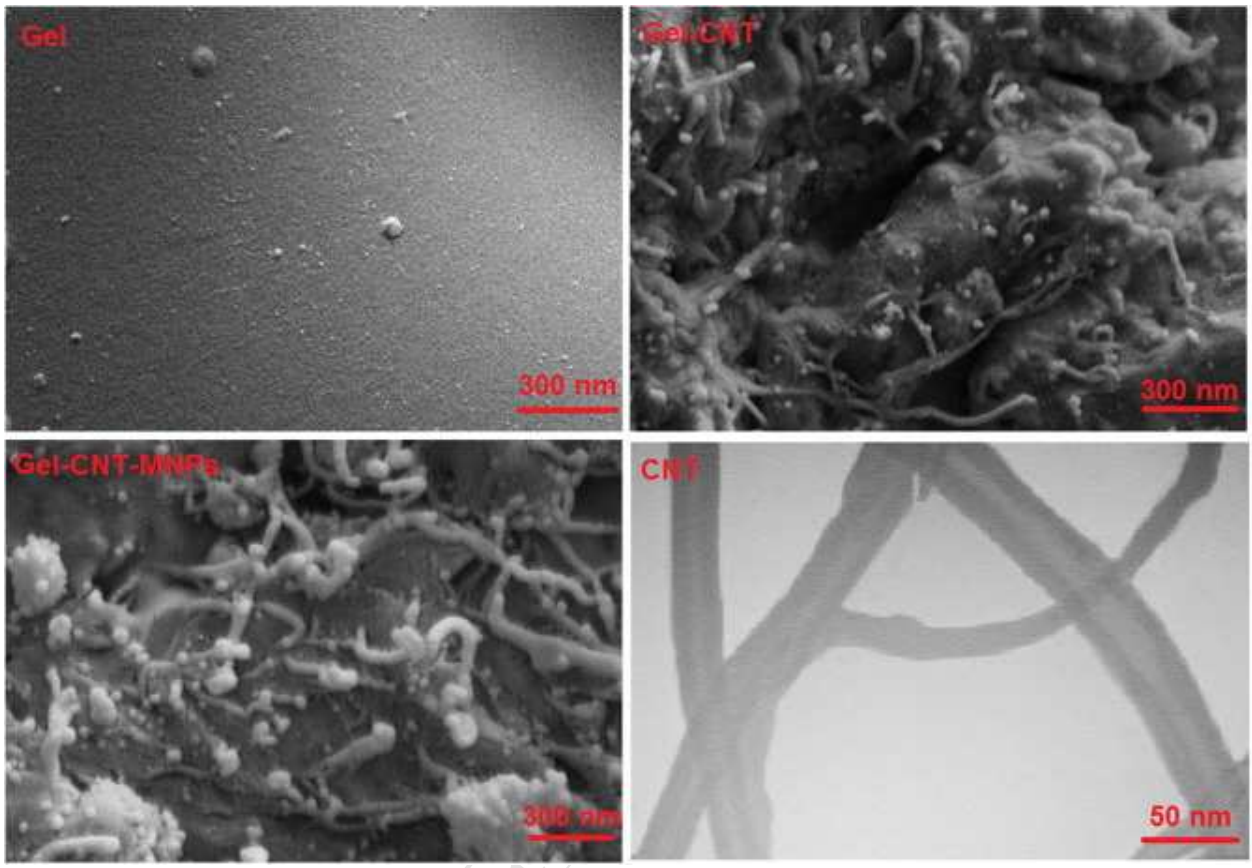


Figure 6. SEM images of the prepared the Gel bead, and Gel-CNT and Gel-CNT-MNPs nanocomposite beads with the TEM image of carboxylic acid functionalized CNT.Reprinted with permission. [48]. Copyright 2017 Elsevier.

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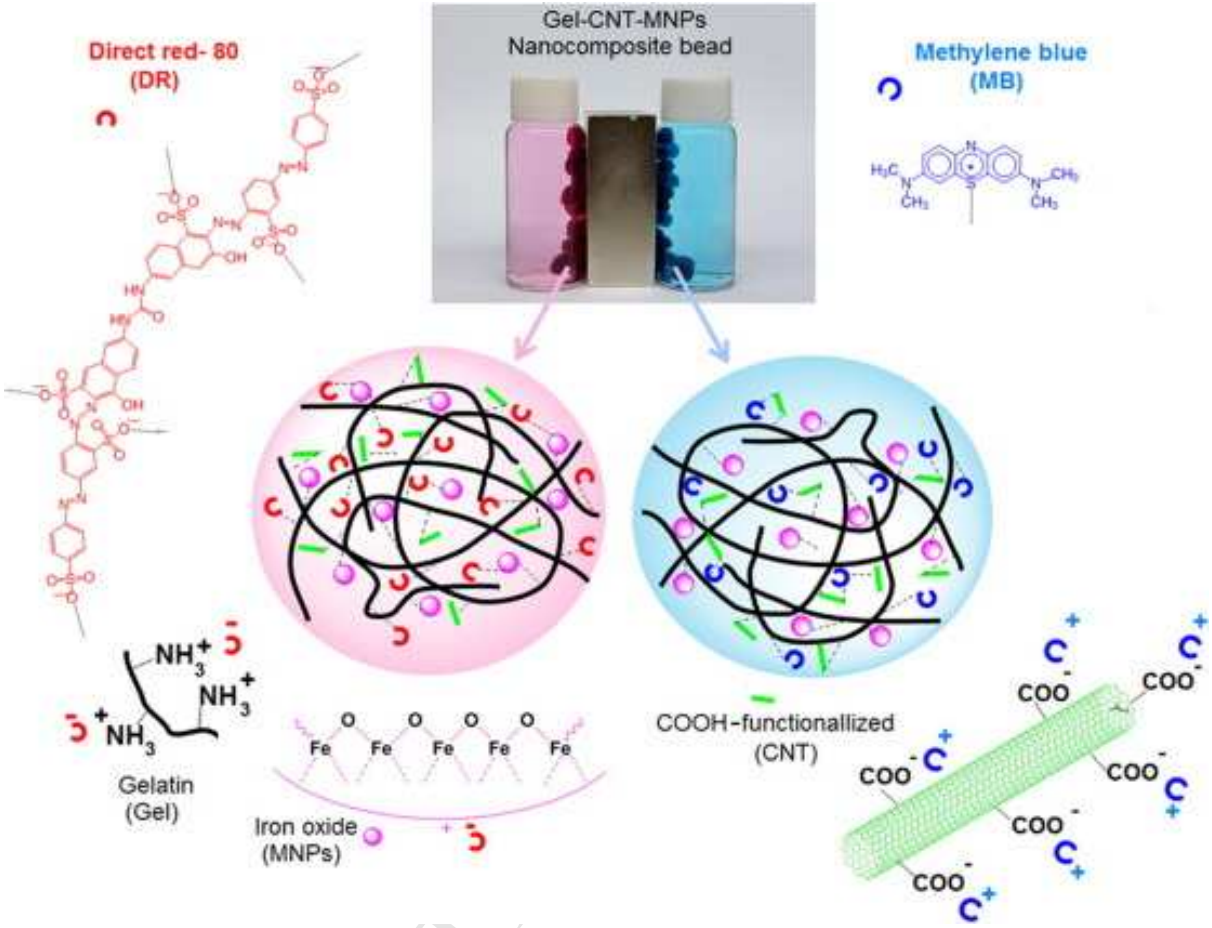


Figure 7. The proposed mechanism for direct red 80 and methylene blue adsorption by the synthesized gelatin gel-carbon nanotube-iron oxide nanoparticles nanocomposite [48]. MNPs: Magnetic nanoparticles, CNT: Carbon nanotube. Reprinted with permission. [48]. Copyright 2017 Elsevier.

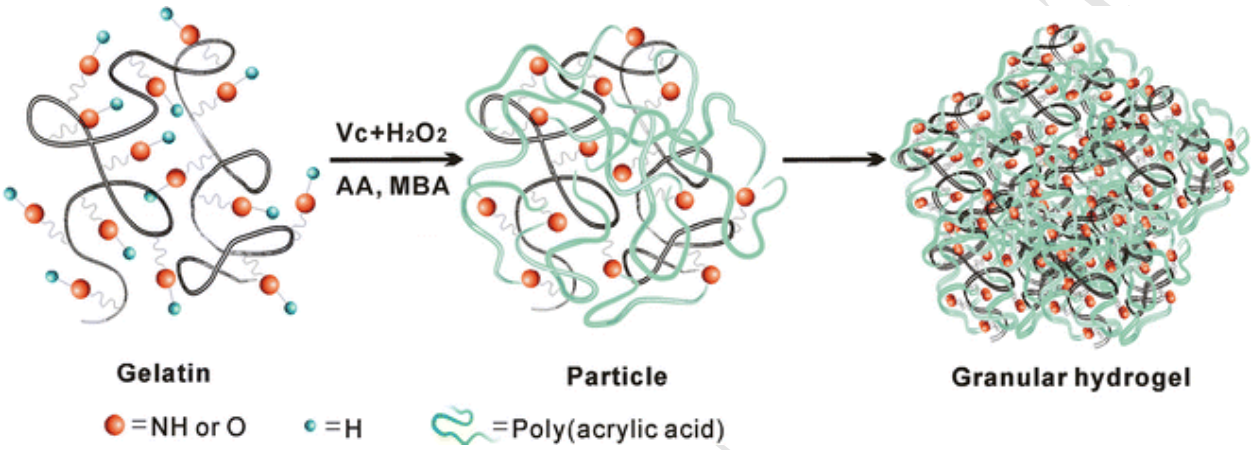


Figure 8. Schematic presentation for the synthesis of gelatin grafted poly(acrylic acid) granular hydrogel by a redox-initiated free radical grafting polymerization [50]. Vc: Ascorbic acid, H_2O_2: Hydrogen peroxide solution, MBA: N, N′ -Methylenebisacrylamide. Reprinted with permission. [50]. Copyright 2015 Springer.

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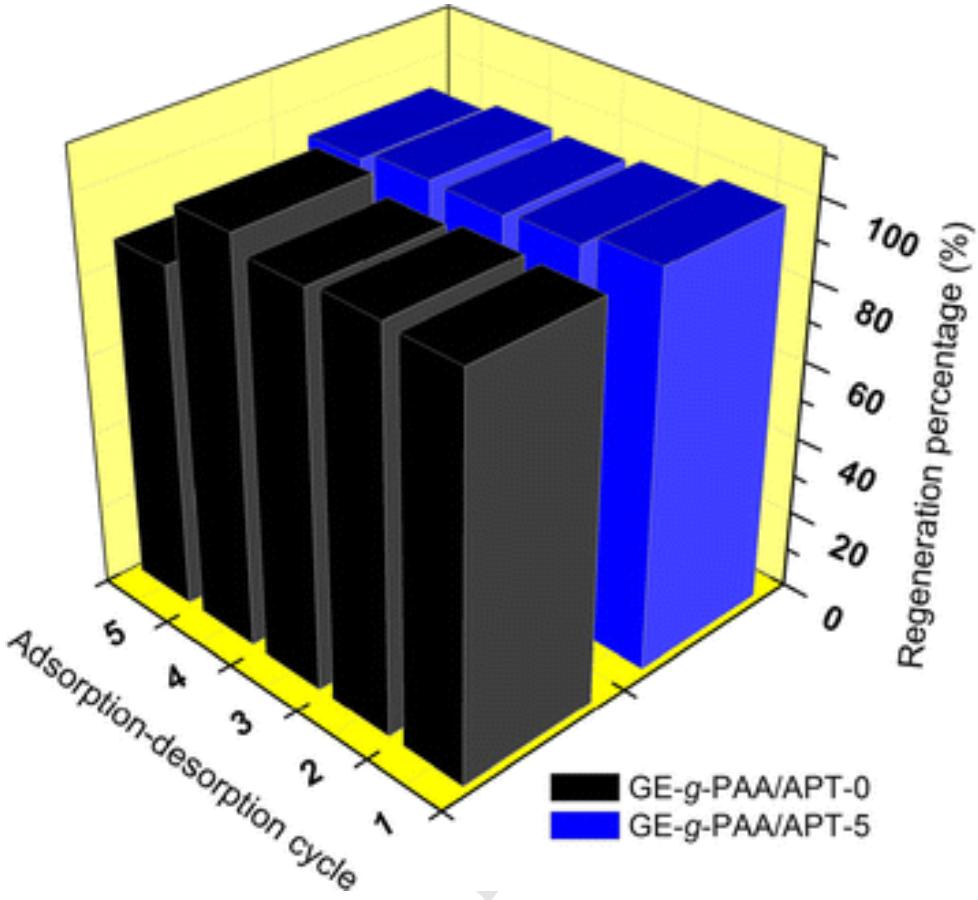


Figure 9. Adsorption–desorption cycles for gelatin grafted poly (acrylic acid) (GE-g-PAA/APT-0) and gelatin grafted poly (acrylic acid)/attapulgite (GE-g-PAA/APT-5) [50]. GE-g-PAA/APT-x, x is the percentage of APT**.** Reprinted with permission. [50]. Copyright 2015 Springer.

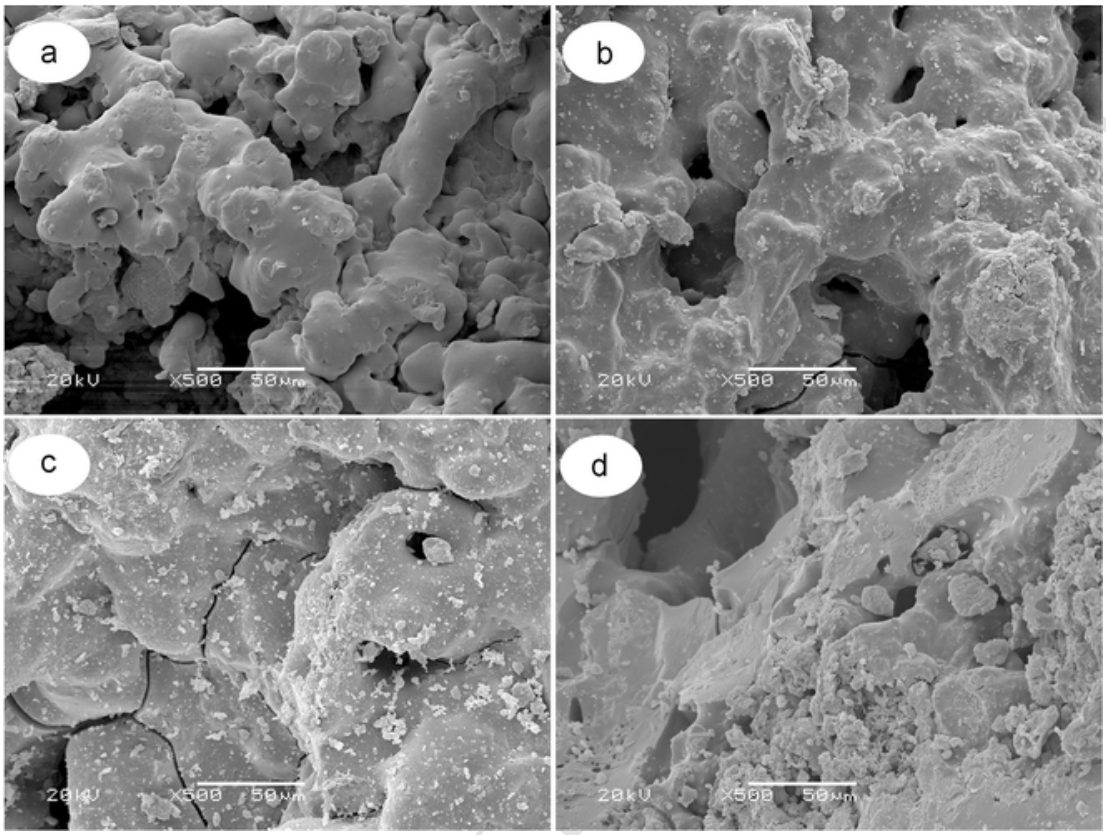


Figure 10. SEM images of (a) GE-*g*-PAA/APT-0, (b) GE-*g*-PAA/APT-5, (c) GE-*g*-PAA/APT-10, and (d) GE-*g*-PAA/APT-15. Reprinted with permission. [50]. Copyright 2015 Springer.

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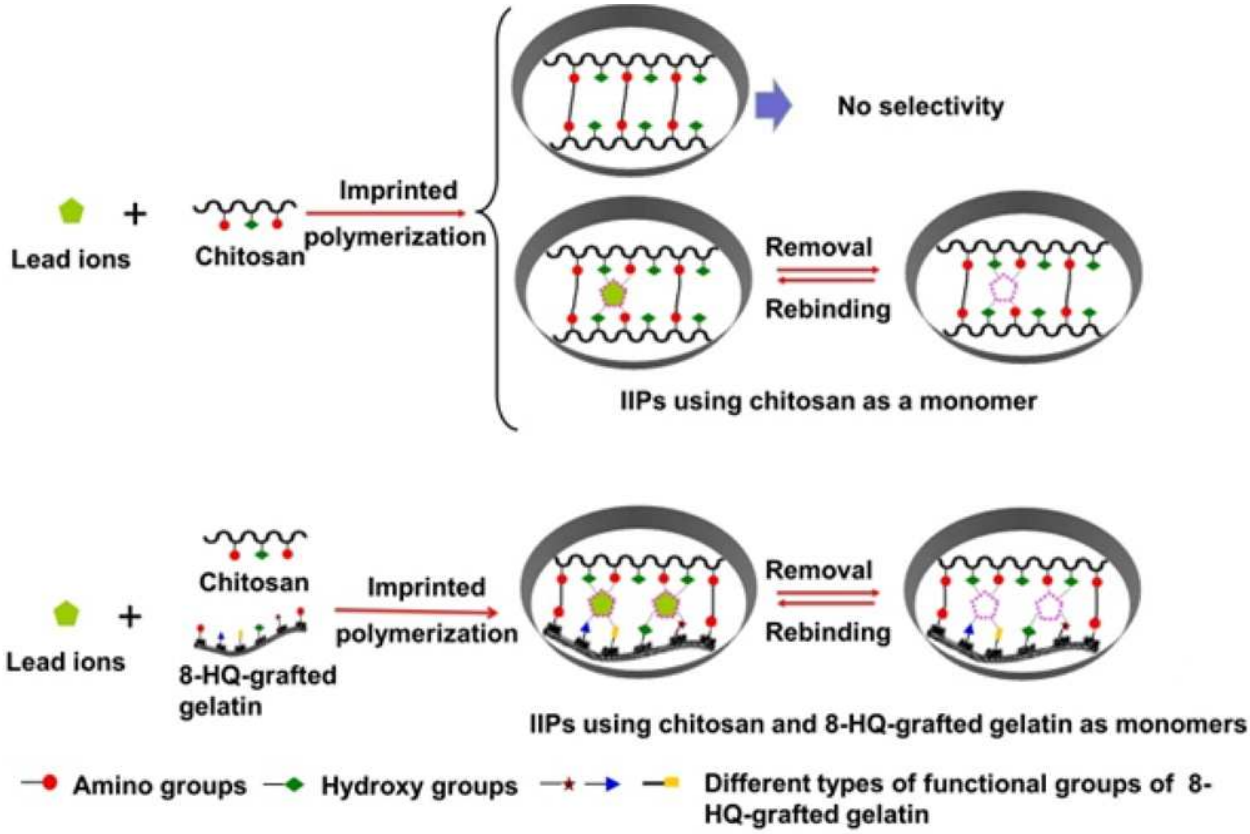


Figure 11. Improvement in selectivity of imprinted cavities by utilizing 8-Hydroxyquinoline grafted gelatin (8-HQ-grafted gelatin) [52]. Reprinted with permission. [52]. Copyright 2016 American Chemical Society.

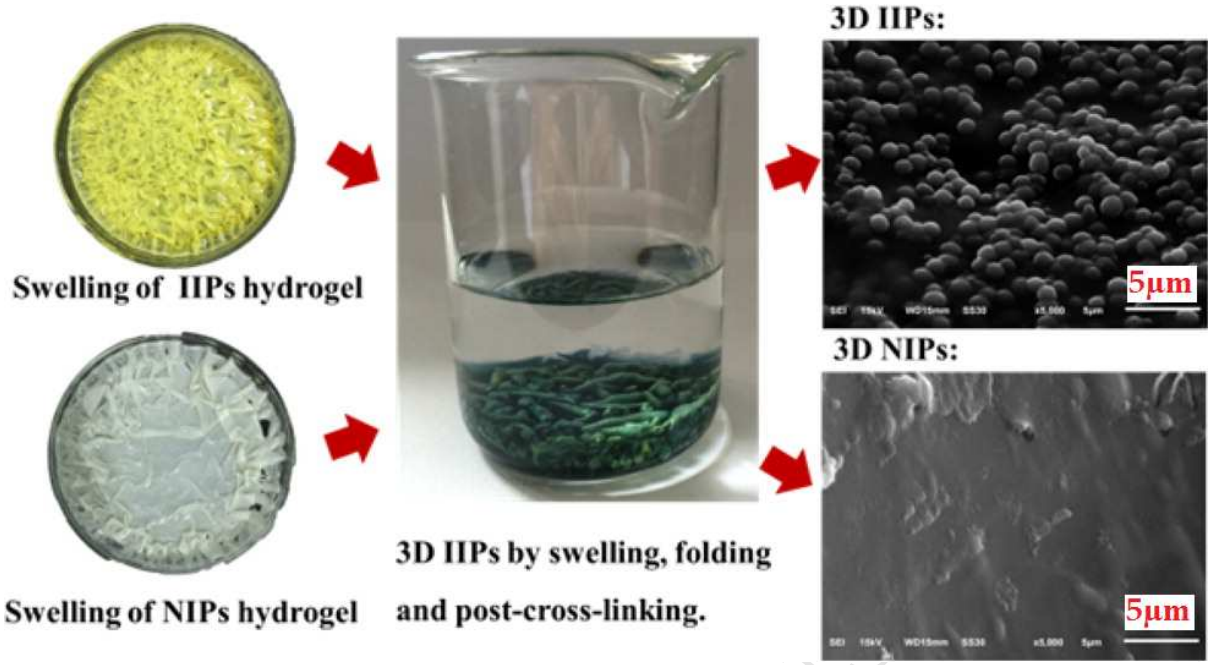


Figure 12. Photographs and SEM micrographs of three dimensional ion-imprinted polymers (3D IIPs) and three dimensional non-ion imprinted polymers (3D NIPs) [52]. Reprinted with permission. [52]. Copyright 2016 American Chemical Society.

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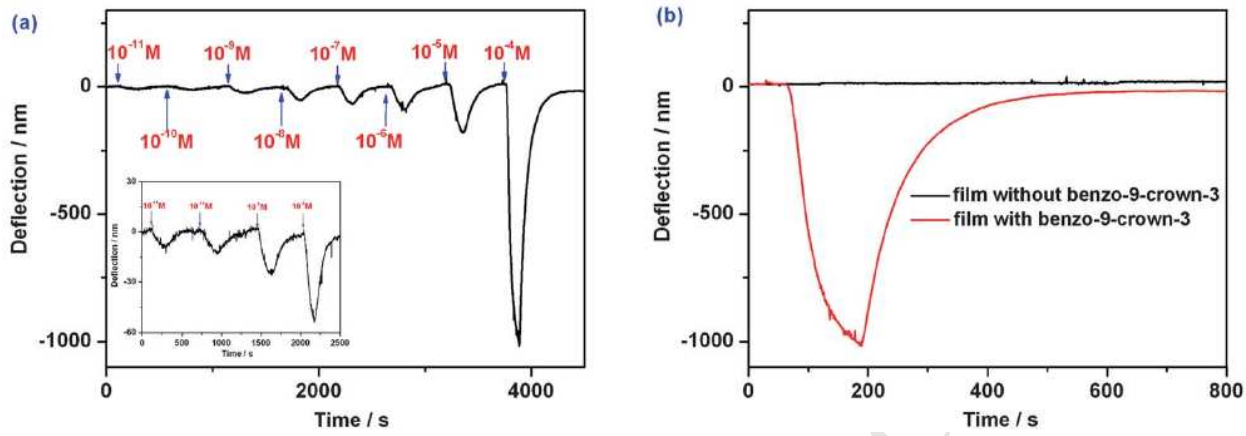


Figure 13. (a) Bending response for hydrogel layer coated in silicon microcantilever on the passage of various concentration of Be^{2+} from 10^{-11} M to 10^{-4} M with 0.01 M Tris–HCl buffer solution (pH 7.04). The inset depicts the magnified curve, (b) Bending response for hydrogel layer coated in silicon microcantilever with and without benzo-9-crown-3 [54]. Reprinted with permission. [54]. Copyright 2012 Royal Society of Chemistry.

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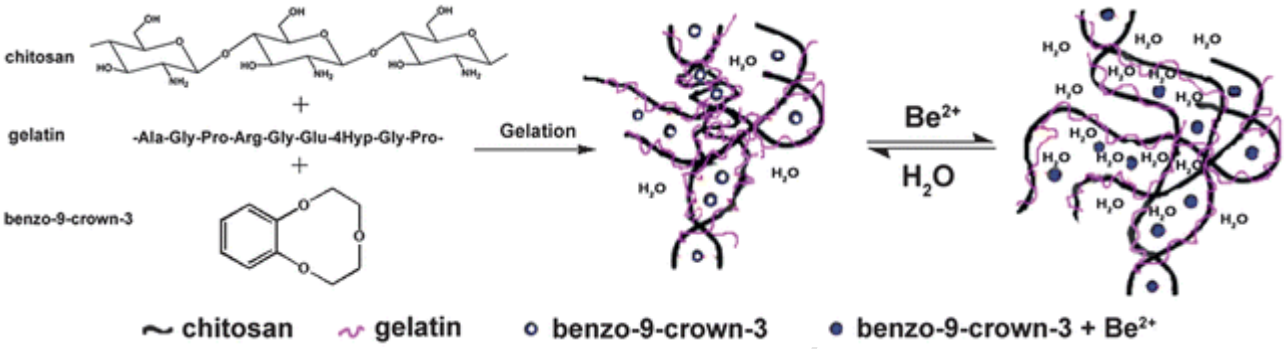


Figure 14. Schematic presentation for the synthesis of hydrogel and binding with Be^{2+} [54].

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Highlights

- Recent advances in Gelatin Hydrogels are provided.
- Different cross-linking between Gelatin and other materials are highlighted.
- Gelatin Hydrogel Nanocomposites Explained in Details
- Nanocomposites improve the mechanical and chemical stability of Gelatin
- Different applications are discussed.

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Recent progress in gelatin hydrogel nanocomposites for water purification and beyond

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