


# Applications of nanocomposite hydrogels for biomedical engineering and environmental protection

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Received: 10 August 2017 / Accepted: 11 October 2017 / Published online: 1 November 2017  
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**Abstract** Nanocomposite hydrogels are polymeric networks that possess a unique property of hydration. The presence of alcohols, carboxylic acids and amides as hydrophilic moieties in structure of nanocomposite hydrogels enhances their stiffness and water-absorbing capacity. Addition of cross-linker in the synthesis of hydrogels increases their stability under extreme conditions of temperature, pH and pressure. Natural polymer-based nanocomposite hydrogels are biodegradable, highly hydrophilic and possess good mechanical strength. Gelatin, chitin, cellulose, pectin, carrageenan, starch and alginate are natural polymers commonly

used to fabricate nanocomposite hydrogels. Nanocomposite hydrogels have special characteristics such as high swelling rate, selectivity and stimuli-sensitive nature. Here we review nanocomposite hydrogels for environmental protection and biomedical engineering. Applications in biomedical engineering include drug delivery agents, wound dressing, tissue engineering and antibacterials. Applications in environmental protection include ion exchangers, adsorption, photocatalysis and soil conditioning. Many nanocomposite hydrogels show excellent adsorption selectivity for heavy metal ions: Cu<sup>2+</sup> up to 30.35 mg/g, Pb<sup>2+</sup> up to 35.94 mg/g, and Zn<sup>2+</sup> and Fe<sup>3+</sup> up to 94.34 mg/g. Xanthan gum-based nanocomposite hydrogel has removed 96% dye from industrial effluent as reported. In addition, most of the nanocomposite hydrogels showed better adsorption capacity for pollutants in the pH range from 5 to 7. The nanocomposite hydrogels could also be regenerated and successfully utilized for several times. Nanocomposite hydrogels are therefore good bio-absorbent materials for environmental detoxification.

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**Keywords** Nanocomposite hydrogels · Environmental protection · Biomedical engineering · Adsorption · Photocatalysis

## Introduction

### Nanocomposite

The field of nanosize (1–100 nm) materials had attained great attention of scientists in recent time. These dimensions in nanosize range make possible to design and create new application-based nanocomposites materials with great improvement in their physical and chemical properties (Sharma et al. 2017c). Nanocomposite consists of inorganic

(host) and organic component and vice versa. Nanotechnology has emerged as an important tool to approach processes which involves the environmental and biological systems. In particular, molecular network of nanocomposite hydrogel has been covalently cross-linked with nanoparticles (Caló and Khutoryanskiy 2015). Table 1 shows various types of gels with their properties, uses and examples.

## Hydrogels

The hydrogels are also known as “aqua gels.” These gels are composed of hydrophilic polymer chains. Due to 99% water retention, hydrogels are flexible in nature. Hydrogels are composed of hydrophilic functional groups having ability to absorb water and solute molecules. These “smart gels” are stimuli-sensitive and thus show active response if there is a small change in external environment or stimuli. Due to the presence of many hydrophilic functional groups (OH, COO), hydrogel shows good swelling response, capillary action, osmotic pressure and water diffusion. Swelling ability of the hydrogels can be controlled by many parameters, e.g., nature of cross-linking (chemical or radiation), polymerization techniques and the presence of functional groups. Temperature, pH, electric field, ionic strength and light are some external factors which enhance the responsiveness of the hydrogels (Brannon-Peppas and Peppas 1991; Liu et al. 2008; Roy et al. 2010).

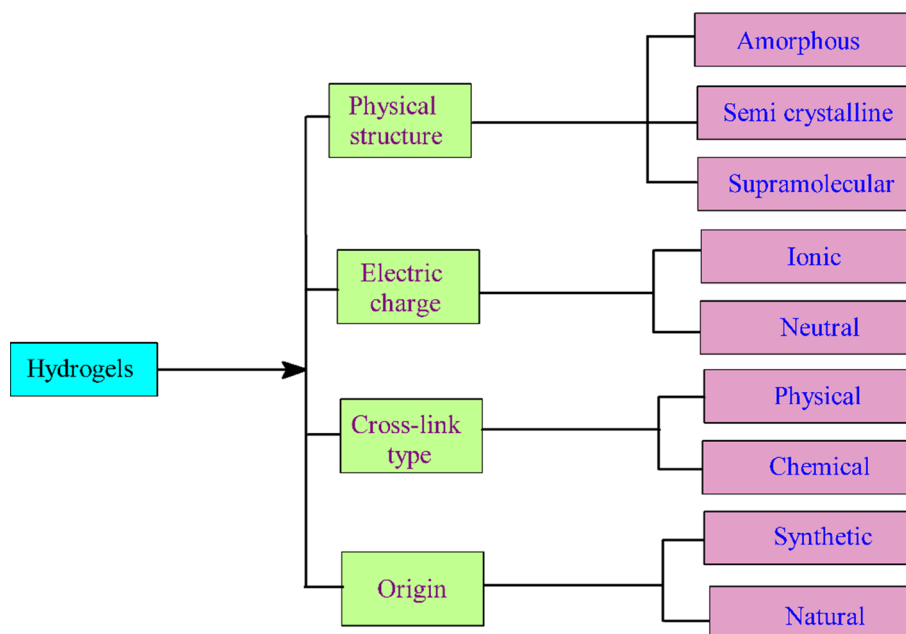
Hydrogel shows dual nature and possess different properties at macroscopic and microscopic scale. On macroscopic scale, hydrogels are solids and possess definite shape and do not flow. But on microscopic scale, hydrogels behave like solutions. Hydrogels can trap water-soluble molecules. So hydrogels have been used as molecular filters in biological sciences. Thus, hydrogels are indispensable in electrophoresis (Tanaka et al. 2005). Figure 1 shows classification of hydrogels into different categories based on their structure, charge and origin (Alzari et al. 2011).

The electrically charged hydrogels comprise of anionic ( $\text{CO}_2^-$ ,  $\text{SO}_3^-$ ) or cationic moieties ( $\text{NR}_3^+$ ) (Billiet et al. 2012). According to initial synthesis materials, hydrogels can be organized as bio- or synthetic polymer-based hydrogels. But nowadays, scientists show special interest in biopolymers-based hydrogels because of their biodegradability and biocompatibility. Such hydrogels are composed of biopolymers including chitosan, cellulose, carrageenan, alginate, collagen, xanthan gum, chitin, gum arabic and modified biopolymers (Mahdavinia et al. 2006; Chang and Zhang 2011). Hydrogels are found to be valuable in many applications, e.g., in tissue engineering used as scaffolds (Mellati et al. 2014), cell culture (Discher et al. 2005), to absorb urine in disposable diapers, contact lenses, controlled drug delivery (Nair and Laurencin 2007) and wastewater treatment (Zainal et al. 2009).

**Table 1** Properties, uses and examples of different types of gels: xerogels, organogels, hydrogels and nanocomposite hydrogels

Types of gels	Properties	Uses	Examples	References
Xerogels	Porous materials, produces dense glass, formed from a gel by drying	Used as reinforced filler, as an adsorbent, in catalysis, chromatograph packing columns, cosmetics, pharmaceuticals and paints	Examples: silica gel, dried gelatin and rubber	Permetti et al. (2007)
Organogels	Non-glassy, thermoplastic, types of interactions involved are weak non-covalent interactions and charge transfer interactions	Used in pharmacy, food and cosmetics	Examples: mineral and vegetable oils	Kumar and Katare (2005)
Hydrogels	Known as “aqua gels,” flexible, good swelling rate, good capillary action, osmotic pressure and water diffusion, solids at macroscopic scale and possess definite shape and do not flow	Used as scaffolds in tissue engineering, disposable diapers and agriculture	Examples: hair gel, plant water crystals	Ahmed (2015)
Nanocomposite hydrogels	Highly hydrated polymeric networks, biocompatible, possess more elasticity as compared to hydrogels, exhibit high strength and high heat resistance	Used in drug delivery, sensors, actuators, tissue engineering, as antibacterial agent and wastewater treatment	Chitosan-g-poly(acrylamide)/Zn, starch/poly(alginate acid-cl-acrylamide)/Fe/Zn	Gaharwar et al. (2014)

**Fig. 1** Classification of hydrogels into different categories according to their physical structure (amorphous, crystalline, supramolecular), electric charge (ionic, neutral), cross-linking types (physical, chemical) and origin (synthetic, natural)



### Organogels

Organogels are non-glassy thermoplastic solid materials composed of liquid organic phase entrapped in polymer chains, e.g., mineral oils and vegetable oils. Organogels are generally used in pharmacy and cosmetics (Visintin et al. 2005). Low molecular mass gelators with functional and chiral moieties have attracted attention in material science. Many functional modules successfully integrated into low molecular mass gelators with diverse applications, e.g., in light harvesting, energy and charge transfer, enzyme and chiral or molecular shape selection. Gelators self-assemble into nanoscale superstructures, e.g., fibers, rods, and ribbons. The types of interactions involved in gelators to assemble are weak non-covalent interactions (hydrogen bonding, pi–pi, van der Waals, coordination) and charge transfer interactions. Various organic solvents used for gelation were 1-butanol, 1-octanol, butyl acetate, tetrachloromethane, benzene and toluene. In salicylideneaniline derivative, cholesterol moieties were incorporated. Salicylideneaniline derivatives have functionalities with prominent fluorescence, photochromic, thermochromic, solvatochromism, liquid crystals and nonlinear optics (Xue et al. 2007).

### Xerogels

Xerogels are porous materials with pore size 1–10 nm. Xerogels are formed from a gel by drying. At elevated temperature, xerogels produce dense glass. Bagasse is the main waste of the sugar processing. Bagasse can be classified as fly ash or bottom ash. Bagasse fly ash can be used as low-cost adsorbent for the removal of phenolic compounds,

pyridine, dyes and heavy metal ions. In spite of these, bagasse ash is rich in silica which is used as raw material for silica gel and powder production. Silica gel exhibits many potential applications, e.g., as reinforced filler, as an adsorbent, in catalysis, in chromatograph packing columns, in cosmetics, in pharmaceuticals and in paints. Silica gel is a rigid three-dimensional network. According to preparation process, silica gel can be classified into three different types as aquagel (water-filled pores), xerogel (the aqueous phase in the pores is vanished by evaporation) and aerogel (supercritical process to vanish aqueous phase). Highly purified silica xerogels were prepared from bagasse ash by sodium silicate process with acidic treatment for gelation (Kamath and Proctor 1998; Kalapathy et al. 2000; Gupta and Ali 2004; Mall et al. 2005).

Graphene-based chitosan and graphene/chitosan/Mn<sub>3</sub>O<sub>4</sub> xerogels were prepared by incorporation of chitosan and Mn<sub>3</sub>O<sub>4</sub> into graphene sheets. Graphene/chitosan xerogels have non-covalent interactions at structural level and shows high adsorption capacity for heavy metal ions removal. At high temperature, uniform distribution of Mn<sub>3</sub>O<sub>4</sub> in graphene network can be obtained. The porosity of chitosan helps to form graphene/chitosan/Mn<sub>3</sub>O<sub>4</sub> nanocomposite with superior electrochemical performance, good cycling stability and low inner resistance (Chen 2012).

### Nanocomposite hydrogels

Hydrogels are 3-dimensional structure materials having hydrophilic polymer chains. Hydrogels are cross-linked to form matrices with high water retention. Hydrogels have promising applications in several fields because of their

tunable physical, chemical & biological properties, high biocompatibility and versatility in fabrication. In spite of these significant features, hydrogels still possess many shortcomings, e.g., poor mechanical strength, low strain, low thermal stability, which restricts area of applications of hydrogels. As a result of these limitations, trials have been made by researchers to redesigning new nanocomposite hydrogels with improved and unique properties (Wei et al. 2010; Datta et al. 2013; Annabi et al. 2014; Janas et al. 2014). Nanocomposite hydrogels are highly hydrated polymeric networks also known as hybrid hydrogels. Nanocomposite hydrogels possess superior chemical, biological, electrical and physical properties (Gaharwar et al. 2014).

Recently, nanocomposite hydrogels have attracted considerable attention due to their accelerated response and capability of action at a distance. The high strength and deformability become an interesting mystery, which focuses on the nanocomposite hydrogel structural studies aspect.

### Modified nanocomposite hydrogels

Nanocomposite hydrogels are hydrated polymeric networks which possess more elasticity as compared to hydrogels. A wide range of natural and synthetic polymers are used to compose nanocomposite hydrogels network. Combining the organic and inorganic parts to fabricate nanocomposite hydrogels results in improved chemical, biological, swelling/deswelling and physical properties (Song et al. 2015). Nanocomposite hydrogels exhibits various superior properties, e.g., high strength, good modulus and high heat resistance (Yano et al. 1993; Shin et al. 2009).

To obtain nanocomposite hydrogels, wide range of nanoparticles are combined with the polymeric networks, e.g., polymeric nanoparticles dendrimers, hyperbranched polyesters), carbon-based nanomaterials (carbon nanotubes, graphene, nanodiamonds), inorganic/ceramic nanoparticles (hydroxyapatite, silicates, calcium phosphate) and metal/metal oxide nanoparticles (gold, silver, iron oxide) (Adhikari et al. 2012; Goenka et al. 2014).

### Carbon-based nanocomposite hydrogels

Carbon-based nanomaterials: carbon nanotubes, graphene, buckminsterfullerene (C60) and nanodiamonds are being investigated for fabrication of nanocomposite hydrogels. Carbon-based nanocomposite hydrogels exhibit high mechanical toughness and electrical conductivity. Aforesaid properties make them suitable for use in tissue engineering, biomedicine, biosensing, drug delivery and environmental detoxification (Engineering et al.; Kuilla et al. 2010).

### Carbon nanotubes-based hydrogels

Carbon nanotubes were first reported in 1991. Carbon nanotubes are one of the widely used inorganic components embedded in polymeric hydrogels to enhance their inherent properties. Carbon nanotubes can be classified in two categories: multiwall and single wall. Both types of carbon nanotubes are investigated for biomedical and biotechnological applications. To enhance the dispersion of the carbon nanotubes within the nanocomposite network, carbon nanotubes surfaces are modified with amines (NH<sub>2</sub>), hydroxyls (OH) and carboxyls (COOH) polar groups. To improve the solubility of the carbon nanotubes in aqueous solutions, single-stranded DNA (ssDNA), proteins and surfactants can be used (Ma et al. 2010).

Carbon nanotubes can enhance the mechanical properties of the hydrogels because of their chemical/thermal stability, excellent mechanical properties and electric properties (Iijima 1991; Liu et al. 2010). Carbon nanotubes also introduce multiresponsiveness to the hydrogels. Covalent or non-covalent binding of carbon nanotubes to the hydrogel matrix has been utilized in the fabrication of nanocomposite hydrogels (Zhang et al. 2011).

Another method to activate the surface of carbon-based nanomaterials is to graft polymer chains onto the carbon nanotube surfaces. In this process, the carbon nanotube surface is surrounded by polymeric network and called as the surface-grafted polymer (Siengchin and Karger-Kocsis 2012).

### Graphene-based hydrogels

Graphene is a two-dimensional allotrope of carbon. Graphene is the basic structural element of other allotropes, e.g., graphite, charcoal, carbon nanotubes and fullerenes. Graphene has high mechanical strength and excellent efficiency to conduct heat and electricity (Xu et al. 2010). Because of good electrochemical properties and excellent mechanical strength, graphene and graphene oxide have been used for the preparation of nanocomposite hydrogels. Graphene-induced nanocomposite hydrogels possess improved strength and stimuli-responsive properties (Novoselov et al. 2004).

Nanocomposite hydrogel can be readily prepared via covalent or non-covalent cross-linking between graphene oxide and hydrogel matrix. These undergo pH-induced sol–gel transition and can be used for selective drug release under physiological conditions (Bai et al. 2010). By developing quantum dots and nanoribbons, graphene can be made luminescent (Elias et al. 2009; Park and Ruoff 2009; Bonaccorso et al. 2010). Graphene can be made photoluminescent by combining electron–hole pairs. Because of photoluminescence, light transmittance and high charge mobility make graphene applicable in magnetic resonance imaging (MRI)

and biomedical imaging. In spite of mechanical and electrical properties, graphene with proteins/peptides will be useful for tissue engineering applications (Sant et al. 2012; Bae et al. 2014). The graphene/chitosan/poly(vinyl alcohol) nanofibrous scaffolds were prepared for wound-healing applications (Lu et al. 2012).

#### Carbon quantum dots-based hydrogels

Carbon quantum dots are nanomaterials of carbon. The nanocomposite hydrogels fabricated with carbon quantum dots show low toxicity and environmentally friendly nature, and are of low cost and synthesized by simple synthetic routes (Sharma et al. 2017b). The chitosan/carbon dots nanocomposite hydrogel shows blue color fluorescence. When chitosan/carbon dots matrix is combined with agarose, the solid sensor platform forms. The agarose hydrogel incorporated into carbon quantum dots forms thin films for separation of heavy metal ions (Hoare and Kohane 2008). The direct determination of silver ions using luminescent carbon quantum dot hydrogels with different superficial moieties (*passivate*-CQDs with carboxylic groups, *thiol*-CQDs and *amine*-CQDs) were prepared using a low molecular weight hydrogelator. The use of the gels results in substantial fluorescence improvement and also influences selectivity. The most selective system for  $\text{Ag}^+$  ion recognition proved to be those having carboxylic groups on their surface. The fluorescent sensing was due to strong  $\text{Ag}-\text{O}$  interaction which quenches the photoluminescence of *passivate*-CQDs through charge transfer (Cayuela et al. 2016). The functionalized graphene oxide quantum dots–poly(vinyl alcohol) hybrid hydrogels were used for optical detection of  $\text{M}^{2+}$  ions ( $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$ ) in aqueous solution. It was observed that the hybrid hydrogel prepared with amine functionalized graphene oxide quantum dots was the most stable. Amine functionalized graphene oxide quantum dots–PVA hybrid hydrogel when immersed in the solutions of  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  renders brown, orange and blue coloration of the solutions detecting the presence of ions in the solution. The minimum detection limit observed was  $1 \times 10^{-7}$  M using UV–visible spectroscopy (Baruah and Chowdhury 2016).

A solid and green film of carbon dot-loaded alginate gels was used for detection of  $\text{Cu}^{2+}$  ions. The pores of the film allow the ion diffusion and contact with the carbon dots incorporated in the gel network, thus affecting photoluminescence behavior of the film. The photoluminescence of the film shows a sensitive and selective quenching effect to  $\text{Cu}^{2+}$  ions and is used as a fluorescent probe to identify  $\text{Cu}^{2+}$  with a detection limit up to 5 ppm (Hu et al. 2013). The chitosan–carbon dots nanocomposite was fabricated through a solvent casting method. The nanocomposite showed double applications as an antibacterial and pH-sensitive nanoagent for wound healing. The antibacterial activities and cell

viability were thoroughly studied against the *Staphylococcus aureus* bacterial species and L929 fibroblastic cell lines. The results revealed that the chitosan/CDs nanocomposites were biocompatible and non-toxic (Omidi et al. 2017).

Selective and on-site detection of  $\text{Hg}^{2+}$  ions has been reported on carbon dots incorporated nanocomposite hydrogels. The carbon dots entrapped within light-guiding hydrogels were quenched by the  $\text{Hg}^{2+}$  ions that penetrated into the hydrogel matrix by diffusion. Light confinement was observed with total internal reflection at the interface between hydrogel and neighboring aqueous solution (Guo et al. 2017). A hybrid carbon dot–hydrogel matrix was designed and used for recognition of bacteria. The carbon dot–hydrogel exhibited the high sensitivity and differentiates between bacterial species through modulation of the emitted fluorescence, depending upon their esterase secretions (Bhattacharya et al. 2017).

#### Crown ether-based hydrogels

Crown ethers are cyclic chemical structures which contain a ring with many ether groups. Mostly, crown ethers are cyclic oligomers composed of ethylene oxide. Nanocomposite hydrogels are good materials for reversible volume change responding to environmental stimuli (temperature, light, pH and electric). Poly(*N*-isopropylacrylamide) is a widely used polymer which is temperature responsive, in which phase transition in aqueous solution at lower critical solution temperature occurs. But for multiple response of nanocomposite hydrogels, poly(*N*-isopropylacrylamide) can be modified by addition of comonomers, e.g., Dibenzo-18-crown-6. The above-mentioned material exhibits thermo-sensitive and ion-sensitive properties due to the presence of ions of crown ether by forming complexes. Addition of crown ether nanocomposite hydrogel reduces swelling ratio as compared to unmodified poly(*N*-isopropylacrylamide). Swelling ratio of modified poly(*N*-isopropylacrylamide) can be enhanced by addition of potassium (Liu et al. 2015a). A crown ether derivative (4'-allyldibenzo-18-crown-6, CE) was covalently incorporated into the temperature-sensitive poly(*N*-isopropylacrylamide) (PNIPA) hydrogels by copolymerization method. The poly(*N*-isopropylacrylamide-*co*-4'-allyldibenzo-18-crown-6) (poly(NIPA-*co*-CE)) hydrogels exhibited dramatically faster deswelling rates than normal PNIPA hydrogels at a temperature (50 °C) above their lower critical solution temperatures. The temperature-sensitive poly(NIPA-*co*-CE) hydrogels was used for the removal of cations and in separation of chiral drugs (Zhang et al. 2002).

A stimuli-sensitive ion recognition nanocomposite hydrogel having incorporated benzo-18-crown-6-acrylamide (BCAm) into the thermoresponsive poly(*N*-isopropylacrylamide) (PNIPAM) hydrogel was synthesized. The nanocomposite hydrogel has been used as adsorbent for lead(II) metal



ions. The (PNIPAM-*co*-BCAm) hydrogels display good ion recognition and  $\text{Pb}^{2+}$  adsorption behavior. The crown ether joins with  $\text{Pb}^{2+}$  ions and forms BCAm/ $\text{Pb}^{2+}$  host–guest complexes, due to which the lower critical solution temperature (LCST) of the hydrogel shifts to a higher temperature because of the repulsion between charged BCAm/ $\text{Pb}^{2+}$  groups and the osmotic pressure within the hydrogel. The adsorption outcomes at various temperatures reveal that P(NIPAM-*co*-BCAm) hydrogels adsorb  $\text{Pb}^{2+}$  ions at lower temperature than at the LCST, but undergo desorption at higher temperature than at the LCST due to the “stretch-to-shrink” configuration change of copolymer networks which is triggered by the change in temperature (Ju et al. 2009).

The novel poly(acrylic acid-*co*-benzo-18-crown-6-acrylamide) (poly(AAc-*co*-B18C6Am)) hydrogel is particularly fabricated by free radical copolymerization. The nanocomposite hydrogel was found to be  $\text{Cs}^+$  ions recognizable in nature. It has been observed that acrylic acid units attracted the  $\text{Cs}^+$  ions via electrostatic attraction and the B18C6Am units are responsible to confine the attracted  $\text{Cs}^+$  by forming stable 2:1 “sandwich” complexes. The poly(AAc-*co*-B18C6Am) hydrogels shows excellent  $\text{Cs}^+$  adsorption (Yu et al. 2017).

#### *Cyclodextrin-based hydrogels*

Cyclodextrins are cyclic oligosaccharides and synthesized by the bacterial enzymatic degradation of starch. Cyclodextrin-based nanocomposite hydrogels possess novel properties, e.g., in drug delivery and to improve wound healing. The cyclodextrin-based synthesized material has good biocompatibility and adequate water retention tendency.

To form nanocomposite hydrogels, the common material required is covalent cross-linker, which restricts the area of applications and time consumption for sorption of drugs. Use of cyclodextrins as cross-linking agents improves the swelling ratio of nanocomposite hydrogels. Nanocomposite hydrogels consisting of polymers and cyclodextrins are specially synthesized to be used as wound-dressing materials. In some cases, if hydrophobic drug loading is carried out in nanocomposite hydrogels, the amount of drug can be minimum and therapeutic level may be low. This can happen due to the lack of affinity between hydrophobic and highly hydrated material. To avoid such issues, cyclodextrin can be incorporated to facilitate hydrophobic drug delivery. Cyclodextrin provides hydrophobic cavity to bind hydrophobic drug. The exterior of cyclodextrin possesses hydrophilic character with small dimensions which provide high swelling ratio to nanocomposite hydrogels (Makino et al. 1995).  $\beta$ -cyclodextrin has been used as cross-linker for synthesis of gelatin hydrogel with 1, 1-carbonyldiimidazole (CDI). The hydrogel was used for drug loading/release study of methotrexate. It was observed that drug loading/release properties

can be controlled by altering the cross-linker content (Liu et al. 2012b). The cyclodextrin (CD)-based nanohydrogels are of particular interest in the field of biomedicine. They have found new applications as actuators and self-healing materials. The non-covalent interaction present in cyclodextrin nanohydrogels shows reversibility and specificity (Tan et al. 2014).  $\gamma$ -cyclodextrin/polyamidoamines nanohydrogels have been fabricated for sustained delivery of dexamethasone. The inclusion of cyclodextrin (CD) moieties adds hydrophobic drug-complexing sites. The nanogel–dexamethasone formulation shows faster action with lower doses than the free drug (Argenziano et al. 2017). The  $\alpha$ -cyclodextrin ( $\alpha$ -CD) and poloxamines (Tetronics<sup>®</sup>) thermoresponsive hydrogels containing Rh-catalyst have been used for hydroformylation of alkenes. The presence of  $\alpha$ -CD is vital to incite the decantation of the multiphasic system once the reaction is complete (Argenziano et al. 2017).

#### **Polymer-based nanocomposite hydrogels**

Nanocomposite hydrogels are fabricated by incorporation of polymers. A wide range of polymers, e.g., homopolymers and copolymers, branched polymers, cross-linked polymers, block copolymers, graft copolymers and blends of two or more biopolymer are used as polymer matrix (Carvalho et al. 2010; Pathania et al. 2016c; Thakur et al. 2017). Above-mentioned polymers enclose hydrophilic and hydrophobic drugs along with genes and proteins. Incorporation of organic (polymer) and inorganic (clay) nanomaterials gives nanocomposite hydrogels with improved physical, chemical, electrical, magnetic, biological and swelling/deswelling properties as compared to its constituents (Kumar et al. 2015). Modified characteristics like optical properties and stimulus sensitivity can potentially be very helpful in medical (drug delivery and tissue engineering) and mechanical fields (Dash et al. 2014; Carrow and Gaharwar 2015). The polymers used in pharmaceuticals are polyethylene glycol, poly(*e*-caprolactone), polylactide, cellulose derivatives (hydroxypropyl methyl cellulose and ethylcellulose) and polysaccharides (alginate, chitosan, gelatin and polyamide) (Viseras et al. 2008).

#### *Synthetic polymer-based hydrogels*

*Poly(ethylene glycol)-based nanocomposite hydrogels* Photopolymerization is a fast and controlled method for synthesis of polymer matrix in various physiological conditions. The synthesized material can be used for drug and protein delivery, elastic tissue sealants to prevent post-surgery adhesion and in tissue engineering applications. Many synthetic and natural polymers, such as poly(vinyl alcohol), poly(ethylene glycol), gelatin, hyaluronic acid, alginate and chitosan are used to synthesize photocross-linked nanocom-

posite hydrogels. Polymeric nanocomposite hydrogels possess good chemical and biological characteristics but lack mechanical strength. Various types of inorganic nanoparticles, e.g., bioactive glasses, hydroxyapatite,  $\beta$ -tricalcium phosphate and silicate clay can be used to enhance physical and biological properties of polymeric hydrogels.

Photocross-linked poly(ethylene glycol)/silica nanocomposite hydrogels show spreading, minimum cell adhesion and proliferation. The incorporation of silica to form poly(ethylene glycol) nanocomposite hydrogel improves cell adhesion and cell spreading and increases metabolic activity of the cells. So, by the addition of silica, mechanical strength and cell adhesion property of poly(ethylene glycol) nanocomposite hydrogel can be improved (Zhang and Wang 2007).

*Poly(acrylamide)-based nanocomposite hydrogels* Polymeric nanocomposite hydrogels are widely used as smart materials for various applications. But their area is restricted because of low response and weak mechanical strength. To overcome these problems, polymer–clay nanocomposite hydrogels were fabricated. For this, polymerization of *N*-isopropylacrylamide and suspension of hectorite clay or laponite may be used.

The laponite clay may be used as the cross-linker in nanocomposite hydrogels and exhibited extraordinarily high tensibility, high transparency and ultimate strength. Modified nanocomposite hydrogel shows high elongation (above 1500%) as compared to normal nanocomposite hydrogels. The *N*-isopropylacrylamide clay nanocomposite hydrogels are more beneficial in cell cultivation. Highly deformed nanocomposite hydrogels with polyacrylamide–hectorite clay show elongation more than 2500%.

*Poly(hydroxyethyl methacrylate)-based nanocomposite hydrogels* Superabsorbent nanocomposite hydrogels can be a hydrophilic polymer which can absorb, swell and retain water in it up to hundreds of times as compared to their original weight. Inorganic mineral powders, e.g., mica, attapulgite and kaolinite, have been used for the preparation of nanocomposite with polymers to attain lower production cost and superior properties. To improve mechanical properties of the nanocomposite hydrogels, clays were incorporated into their matrix. The nanocomposite hydrogels were prepared by using 2-acrylamido-2-methylpropane sulfonic acid, 2-hydroxyethyl methacrylate, 2-(*N,N*-dimethylamino) ethyl methacrylate monomers and montmorillonite. The synthesized nanocomposite hydrogel can be used to remove main pollutants from textile, paper, plastic, leather and food industries.

The poly(2-hydroxyethyl methacrylate) nanocomposites were obtained by modified suspension polymerization of 2-hydroxyethyl methacrylate followed by in

situ coprecipitation of iron oxide inside the nanoparticle matrix yielding magnetic PHEMA (mPHEMA) nanocomposites. The prepared nanocomposites showed no toxicity. The fabricated superparamagnetic mPHEMA nanocomposites had potential to provide a possible option for magnetically assisted controlled delivery of anticancer drugs (Gupta et al. 2014a).

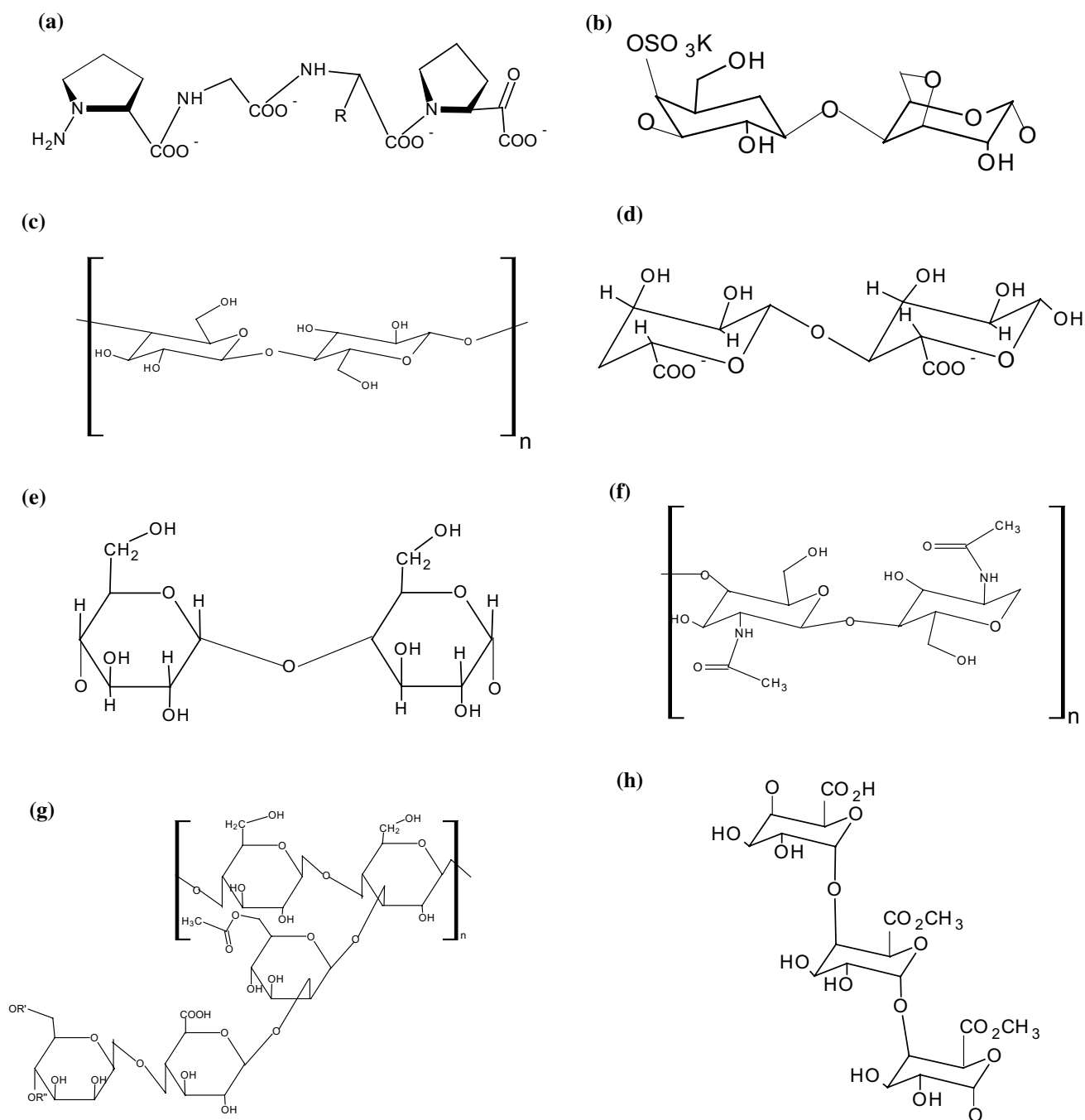
*Poly(vinyl alcohol)-based nanocomposite hydrogels* Non-ionic and water-soluble poly(vinyl alcohol) attracted the attention of researchers. Due to non-toxicity, biocompatibility and gelation ability, the poly(vinyl alcohol) has been widely used in biomedical and pharmaceutical fields (Georgieva et al. 2012). The poly(vinyl alcohol)-based nanocomposite hydrogels can be prepared by chemical and physical methods. Among physical methods, freezing–thawing is most important because of easy operation and reducing toxicity of cross-linker (Wu et al. 2011). The swelling capacity of poly(vinyl alcohol) nanocomposite hydrogels can be enhanced by the addition of ionic polymers.

To fabricate poly(vinyl alcohol) nanocomposite hydrogels, various polymers with active functional groups such as sodium alginate with carboxylate groups, carrageenan with sulfate pendants, chitosan with primary amine and poly(*N*-isopropyl acrylamide) with hydrophobic isopropyl pendants have been utilized with excellent swelling response.

#### *Natural polymer-based hydrogels*

In recent years, interest is growing in nanocomposite hydrogels which are composed of biodegradable, biocompatible and non-toxic biopolymers. In this case, chitin, chitosan, alginate and kappa-carrageenan polysaccharides are highly recommended for colon-specific drug delivery (Lee and Mooney 2012). The fact is that many substrates could be recognized by anaerobic bacteria and degraded by enzymes in the colon. Polysaccharides are worthwhile materials because these are stable in the gastric environment and effective in colon-targeted delivery (Shukla and Tiwari 2012).

There are many techniques for the removal of heavy metal ions from wastewater, including chemical precipitation, ion exchange, adsorption, membrane filtration and electrochemical treatment. But most of them have some drawbacks, e.g., high cost, less availability of instruments and complicated to handle (Fu and Wang 2011). Now polymer nanocomposite hydrogels are gaining more attention for the removal of heavy metals from the contaminated water. These nanocomposite hydrogels can swell in water and shows good adsorption capacity. The nanosized clay minerals are also introduced into the nanocomposite hydrogels so as to increase mechanical strength (Darvishi et al. 2011). Figure 2 shows chemical structures of different polymers: (a) gelatin, (b)



**Fig. 2** Chemical structures of different polymers used to synthesize nanocomposite hydrogels **a** gelatin, **b** kappa-carrageenan, **c** cellulose, **d** alginate, **e** starch, **f** chitin, **g** xanthan gum and **h** pectin

kappa-carrageenan, (c) cellulose, (d) alginate, (e) starch, (f) chitin, (g) xanthan gum and (h) pectin.

**Gelatin-based nanocomposite hydrogels** Gelatin is composed of heterogeneous mixture of single or multiple polypeptides having 50–1000 amino acids. From skin and bones, triple helix collagen is extracted. Gelatin is a protein of body which is mostly present in connective tissues, bones and ten-

dons. Gelatin can be obtained from collagen by thermal and chemical denaturation. In pharmaceutical, gelatin is used to make soft capsules, microspheres, wound dressings and adsorbent pads for surgical uses. At 40 °C, gelatin comes in sol state and forms gel when cooled down. The major drawback is that gelatin exhibits poor mechanical strength, which limits its application as biomaterial. So, to overcome this difficulty hydrothermal gelation has been used with gelatin. Hydrothermal



cite is a type of layered double hydroxide found as a natural mineral. Hydrotalcite can be synthesized by reacting aqueous solution of magnesium and aluminum chloride in the presence of sodium carbonate. The synthesized material possesses hydroxide layers of Mg and Al, which contains positive charge and requires the presence of anions to create neutral charge. The nanocomposite hydrogels of gelatin and hydrotalcite were prepared by cross-linking of glutaraldehyde (Lee and Lee 2006). Reduced graphene oxide (RGO)-gelatin nanocomposite hydrogels were fabricated using one-pot synthesis technique. The gelatin macromolecular chains were chemically cross-linked with graphene nanosheets. The gelatin acted as a reducing agent and converts GO to RGO (Piao and Chen 2016). The gelatin-silver nanocomposite hydrogels were fabricated and explored for antibacterial properties. The results revealed that biodegradable gelatin-silver nanocomposite hydrogels show promising antibacterial nature (Reddy et al. 2013). Graphene-elastin composite hydrogel actuators have been fabricated which has been found to stimuli response toward light (Wang et al. 2013a).

*Cellulose-based nanocomposite hydrogels* Cellulose is bio-renewable polymer which is abundant in nature. This possesses biodegradable and biocompatible properties. Derivative of cellulose is sodium carboxymethyl cellulose which introduces  $-\text{CH}_2\text{COOH}$  groups into main cellulose chain. Sodium carboxymethyl cellulose is water soluble due to anionic moiety and widely used in pharmacy, cosmetics and foods. Carboxymethyl cellulose can produce hydrophilic polymer which is pH responsive.

Methylcellulose is another simple derivative of cellulose which contains methyl groups substituted in place of hydrogen. Due to this substitution, the rigid crystalline structure of cellulose gets disturbed and enhances its water affinity. Methylcellulose-polyacrylamide nanocomposite hydrogel show applications in area of agriculture and act as controlled release carrier for agrochemicals (Wan et al. 2000). The cellulose nanocrystals (CNCs) polyacrylamide hydrogel was fabricated via free radical polymerization. The obtained nanocomposite hydrogels showed higher elongation ratio and enhanced tensile strength (Yang et al. 2013b). Cellulose nanocrystal-poly(vinyl alcohol) hydrogels was fabricated and showed potential for use in biomedical and tissue engineering applications (Tanpichai and Oksman 2016). A cellulose-clay hydrogel with superabsorbent properties and good mechanical performance has been used as adsorbent for methylene blue (Peng et al. 2016). Layered double hydroxides (LDH)-carboxymethyl cellulose (CMC) nanohydrogel nanocomposite has been successfully used for controlled delivery of ibuprofen (Barkhordari et al. 2014).

*Chitin-/chitosan-based nanocomposite hydrogels* Chitin is a modified polysaccharide which contains nitrogen. The repeating unit present in chitin is *N*-acetyl-*D*-glucosamine which is linked with covalent beta-(1-4) linkage. Chitosan is also one of the most abundant natural biopolymers which can be derived from deacetylation of chitin (Kumar et al. 2016). Chitosan find uses in pharmaceutical and medical applications (Kamari et al. 2016). Because of its excellent antacid and antiulcer properties and gel- and film-forming characteristics, chitosan is greatly used as good carrier in drug delivery system. Chitosan may form spherical gel beads with anionic molecules (Bitar et al. 2012).

Chitin/graphene nanocomposite hydrogels can be prepared by simple sonication. Chitin/graphene nanocomposite hydrogels found application in areas such as water remediation (Gupta et al. 2015), protein sorption, tissue engineering, food wrapping and drug delivery. For electroanalysis, chitin/graphene nanocomposite is improved by addition of dihydroxybenzene. The bonding between hydrogen of dihydroxybenzene and exfoliate edge of graphene sheets help to enhance electroanalytical property of synthesized nanocomposite hydrogels (Ifuku 2015).

*Starch-based nanocomposite hydrogels* Starch is useful as raw material for industrial purposes because of its low cost, environmentally friendly nature and biodegradability. Starch can be modified by hydrolysis, oxidation, grafting and esterification (Naushad et al. 2016a, b). But incorporation of vinyl monomers in starch by grafting is most effective. Recently, montmorillonite, an aluminum silicate, is widely used to enhance the properties of nanocomposite hydrogels of polymers. Montmorillonite contains cations and reactive groups on its surface to exchange with external matrix components. Various starch graft copolymers focused for the preparation of inorganic-organic superabsorbent nanocomposite hydrogels for environment applications. It is extremely important to remove highly toxic and polluting heavy metal ions from water system. Thus, nowadays natural polymers (cellulose and starch graft copolymers) are used for heavy metal ions removal. To remove copper (II) and lead(II) ions from water, the starch-grafted acrylamide/montmorillonite was fabricated. For its synthesis, *N*, *N*-methylenebisacrylamide cross-linker and cerium ammonium nitrate as an initiator were used (Bao et al. 2011). Starch/poly(alginic acid-cl-acrylamide) nanohydrogel has been synthesized by copolymerization method and used as an effective adsorbent for the removal of Coomassie brilliant (CB) blue R-250 dye (Sharma et al. 2017e).

**Carrageenan-based nanocomposite hydrogels** Carrageenan is high molecular weight polysaccharides having repeating galactose units in its structure. The repeating units are joined by alternating alpha-1,3 and beta-1,4 glycosidic linkages. The anionic kappa-carrageenan is used to form nanocomposite hydrogels applicable in drug delivery. Addition of galactose into carrageenan-based nanocomposite hydrogels provides masking of bitter taste of some drugs. Besides this, the ionic bonds between negatively charged sulfate on kappa-carrageenan and positive charge on mucin in saliva help in the adhesion properties of the final formulation. The magnetic hydrogels of iota-carrageenan containing maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) nanoparticles were synthesized. The hydrogels showed good thermal stability and swelling degree. The magnetic nanoparticle was well distributed on the surface of the hydrogels (Maciel et al. 2016). Iota-carrageenan-silver nanocomposite hydrogels were fabricated using greener process. The hydrogels have been effectively used for bacterial inactivation of *Bacillus* and *Escherichia coli* (Jayaramudu et al. 2013).

**Alginate-based nanocomposite hydrogels** Alginate has linear unbranched polymer which contains beta-(1-4) linkage between D-mannuronic acid and alpha-(1-4) L-guluronic acid. Alginate is a naturally derived copolymer which forms nanocomposite hydrogels. Due to the presence of ionic interactions, alginate forms divalent cations with  $\text{Ca}^{2+}$ . Calcium-alginate nanocomposite hydrogels are used for wound dressing and provide antimicrobial activity with silver ions. Silver-alginate nanocomposite can be synthesized by using gamma irradiation for photochemical reduction (Saha et al. 2010). Alginate-based nanocomposite hydrogels are mostly used in medical field. Because of regulation of moisture levels which lead to rapid granulation and re-epithelization of the damaged tissue, alginate can be used in wound dressings. Alginate-based dressings can be removed easily without causing trauma because of the highly hydrophilic gel nature of alginate. Alginate nanocomposite hydrogels are widely used in regeneration of various tissues and organs such as blood vessels, liver, pancreas and cartilage (Glicklis et al. 2000).

**Xanthan-based nanocomposite hydrogels** Xanthan gum is a type of hetero-polysaccharide having high molecular weight. Xanthan gum is made up of multiple glucose units. The side chain contains trisaccharide which consists of alpha-D-mannose. Alpha-D-mannose contains an acetyl group, beta-D-glucuronic acid and a beta-D-mannose terminal unit with pyruvate group linked.

Methylene blue and methyl violet are industrial waste toxic cationic dyes which have harmful effects on humans. To avoid the pollution of ecosystem by these toxic dyes, it

is important to treat the effluent. For this purpose, various polymers were used for remediation of dyes from industrial waste. Natural polymers are having potential to act as adsorbent due to non-toxicity, low cost and eco-friendly nature. Due to small size and high surface area, magnetic nanocomposite hydrogel shows good adsorbent property. Iron oxide filled in xanthan gum cross-linked polyacrylic acid nanocomposite hydrogels is used for methyl violet adsorption from water system (Banerjee and Chen 2007). Sol-gel method is the common process for synthesis of hybrid material by adding inorganic part on polymer matrix. Because of uniform shape, size and functional properties, silica nanoparticles are dispersed in polymer matrix. Xanthan gum/polyacrylamide/silica nanocomposite hydrogel is developed to eliminate lead ions and Congo red dye from water efficiently (Ghorai et al. 2012).

**Pectin-based nanocomposite hydrogels** Pectin is also known as pecticopolysaccharide which contains galacturonic acid. Homogalacturonans can be formed by linear chains of  $\alpha$ -(1-4) linked D-galacturonic acid. Pectin is a main component of agriculture waste and can be used as a support for metal ion separation due to cost-effective and eco-friendly nature. Pectin binds effectively with metal ions for detoxification and develops insoluble precipitates of heavy metal ions. Pectin contains  $-\text{CO}_2\text{H}$  groups which interact with heavy metal ions for ion exchange (Gupta et al. 2014b; Pathania et al. 2014). The pectin/acrylamide nanocomposite hydrogel can be synthesized by cross-link polymerization. In this, the pectin is having polyacrylamide in interstitial domain. Pectin nanocomposite hydrogels exhibit more swelling at high pH and shrink at low pH (Liu et al. 2004). By a simple free radical polymerization, pectin-poly((2-dimethylamino)ethyl methacrylate)) hydrogel was fabricated. The hydrogel networks are utilized for encapsulation of 5-fluorouracil (Eswaramma et al. 2017).

### Organic-inorganic-based nanocomposite hydrogels

Many inorganic nanoparticles are used to fabricate nanocomposite hydrogels. These inorganic materials have no toxic effects on the body. Nanoclays improve the structures and characteristics of nanocomposite hydrogels, e.g., self-healing properties, elasticity, flame-retardant structures, supergas barrier membrane and oil repellence. The nanoporous inorganic coatings, e.g., aluminum oxide ( $\text{Al}_2\text{O}_3$ ), titanium oxide ( $\text{TiO}_2$ ) and porous silicon, are used in nanocomposite hydrogels as drug carrier agents (Gultepe et al. 2010). Polymer/clay networks can exhibit complete self-healing through reconstruction of cross-links on damaged interface. Mechanical damage can be repaired without use of a healing agent. Even small parts of nanocomposite hydrogels can

be separated by cutting of same or different nanocomposite hydrogel which can be recombined together by elevated temperature. Self-healing can be achieved immediately or after long waiting time (Haraguchi et al. 2011).

In the past 10 years, research on nanocomposite hydrogels focused on the use of silicate clays as nanoparticles. The clays have been widely used because they are naturally occurring minerals and commercially available and possess a platy morphology with a high aspect ratio and considerable cation exchange capacity (Lee and Fu 2003). Clay can be used as good adsorbents because of high specific surface area, chemical and mechanical stabilities, a variety of surface and structural properties and porous network. These inorganic–organic nanocomposite hydrogels can absorb and trap ionic dyes due to the presence of ionic functional groups (Liu and Zhang 2007).

From the last few years, the inorganic nanoscale particles can be used as filler, which modifies the properties of polymers. Newly developed nanocomposites consist of a polymer and organo-clay because they usually help to improve mechanical strength and many other material properties as compared to virgin polymer or conventional composite (Li and Haraguchi 2006; Okamoto 2006). The synthetic process and molecular design of polymeric nanocomposite were first explored by Toyota group by the use of nylon 6 as the matrix polymer (Usuki et al. 1993). These modified materials are used in gas barrier film and other load-bearing applications (Vaia and Giannelis 1997). Self-assembly behaviors of polymer/clay nanocomposites have been approached to produce nanoscale polymeric materials. The linear viscoelasticity in distributed nanofiller forms is caused due to organo-clay network (Hussain 2006).

### Metal- and metal oxide-based nanocomposite hydrogels

Combining polymer hydrogels with nanoparticles (metals, non-metals and metal oxides) provides superior functionality to the nanocomposite material (Kumar et al. 2014, 2017a). An example is silica nanoparticle–hydrogel composite modified polyethylene glycol to enhance tissue adhesive property, mechanical stiffness and bioactivity (Skelton et al. 2013; Liu et al. 2014).

The synthesis of metal nanocomposite hydrogels gained attention because of their optical, electrical and catalytic properties. Because of swelling and shrinking properties, the hydrogel nanocomposites exhibit number of applications, e.g., microfluidic flow, muscle-like actuators, biosensors, drug delivery and switchable electronics (Sheeney-Haj-Ichia et al. 2002; Lee and Braun 2003).

The inculcation of metal nanoparticles into nanocomposite hydrogels results in improvement in mechanical properties as well as physiochemical properties, e.g., polymers having magnetic nanoparticles acquire magnetic

characters. Similarly, inculcation of silver/gold nanoparticles into a polymer matrix exhibits excellent antimicrobial properties. The major aspect of nanocomposite hydrogels network is to develop in situ and ex situ synthesis of nanoparticles. Well-defined free spaces between the gel networks are called as nanoscopic domains which provide tremendous growth of the nanoparticles without their aggregation. Nanocomposite hydrogels networks are much efficient to load metal/metal oxide nanoparticles (magnetite), which provides stabilization to the particles and prevents oxidation (Zhang et al. 2004).

Due to non-toxic and biocompatible nature, natural polymers are good choice for synthesis of nanocomposite hydrogels with metals. An example is chitosan can be derived from chitin by partial deacetylation, in dilute acidic solution. Chitosan exhibits poly-cationic properties with electrostatic attraction for the negatively charged gold nanoparticles. Chitosan-capped gold nanocomposite hydrogels are formed (Sugunan et al. 2005).

Gold nanoparticles when embedded in dextran were used as glucose sensors. To incorporate dextran in gold nanoparticles, firstly gold nanoparticles were modified. The dextran/gold nanoparticles were dispersed with 16-mercaptohexadecanoic acid in the presence of Tween-20. This developed –COOH groups on the nanoparticles. The 2-(2-amino-ethoxy) ethanol is allowed to react with –COOH groups to have –OH functionality through the nanoparticles. Activated –OH groups can be used by epichlorohydrin and coupled through amino groups of dextran to form dextran-coated gold nanocomposite hydrogels (Lee and Pérez-Luna 2005). Above pH 6, the chitosan is insoluble and offers an improved way to inculcate silver oxide nanoparticles. Then, silver nitrate solution is added dropwise to the chitosan solution which is prepared in acetic acid. Addition of sodium hydroxide to this solution results in the formation of black precipitate of silver oxide containing chitosan. Treatment of cotton fabric with the suspension of silver oxide–chitosan nanocomposite hydrogels imparts good antimicrobial property to the fabric (Regiel et al. 2013).

Metal nanoparticles are used as catalysts in various chemical reactions. But use of bimetallic catalyst is more significant because combination of two metals may provide better catalytic activity, selectivity and stability. Most recently, new method, microwave irradiation, provides cross-linking reaction of polyvinyl alcohol with bimetallic systems, e.g., Ag–Pt, Pt–Fe, Cu–Pd. Because of simple handling and less time consumption, microwave irradiation procedure is versatile (Miyake and Asakawa 2005; Thomas et al. 2007a).

Most widely used poly(vinyl alcohol), biocompatible polymer has been used to form nanocomposite hydrogels with metal nanoparticles. Addition of poly(vinyl alcohol) solution to silver nanoparticle suspension by citrate reduction results

in the formation of yellow transparent poly(vinyl alcohol)/silver nanocomposite film after solvent vaporation (Mbhele et al. 2003).

## Properties of nanocomposite hydrogels

### Swelling and deswelling

The highly porous structure of nanocomposite hydrogel enables them to get swell in the presence of water. Because of excellent swelling behavior, nanocomposite hydrogels get distinguished from hydrogels. By swelling, nanocomposite hydrogels imbibe surrounding solution instead of being dissolved. Swelling and deswelling property shows good result for controlled release in drug delivery.

Swelling percentage ( $P_s$ ) can be calculated as:

$$P_s = \frac{W_s - W_d}{W_d} \times 100$$

where  $W_s$  is the weight of the wet nanocomposite hydrogel and  $W_d$  is the weight of the dry nanocomposite hydrogel.

The nanocomposite hydrogels have good tissue compatibility and solute permeability. The monomer composition of nanocomposite hydrogels influences diffusion characteristic owing to many drugs loaded to the matrix. These consist of hydrophilic substances, hydrophobic substances, micromolecules (charged or neutral) and macromolecules. There are two methods for drug loading: (a) Monomer of nanocomposite hydrogel is mixed with drug and initiator without the use of cross-linker. Then, this solution is allowed to polymerize and trap drug in matrix. (b) In the second method, a nanocomposite hydrogel is placed in drug solution to get swell. Drug loading can be calculated as:

$$\text{Lower limit (swollen phase)} = \frac{V_s}{W_p} \times C_0$$

Upper limit (swollen and polymer phases)

$$= [(V_s + KV_p)/W_p] \times C_0 a$$

where  $V_s$  and  $V_p$  are absorbed solvent and dried polymer volume,  $W_p$  is dried polymer weight,  $K$  is partition coefficient, and  $C_0$  is drug concentration

Due to the absorption of water in matrix, desorption of drug takes place by diffusion (Song et al. 1981).

### Stimulus sensitivity

Nanocomposite hydrogels formed of polymers can change their shape and volume and are stimuli responsive. This change occurs due to the variation in surrounding environment, e.g., pH, light, magnetic field, electric field. But

because of facile tuning of their properties, only temperature-responsive nanocomposite hydrogels are most investigated. Poly(*N*-isopropyl acrylamide) nanocomposite hydrogels have low critical solution temperature. At low critical solution temperature, coil form of poly(*N*-isopropyl acrylamide) nanocomposite hydrogels gets converted into compact globular state. Hence, nanocomposite hydrogels formed of poly(*N*-isopropylacrylamide) undergo a reversible volume change at same transition temperature in water. Stimuli-sensitive nanocomposite hydrogels show various areas of applications, e.g., drug delivery, biomaterials, sensors and cell cultivation (Keener et al. 2011).

### Mechanical strength

Nanocomposite hydrogels are mechanically tough and shows stretching and bending. Nanocomposite hydrogels can be composed of clay and polymers with excellent mechanical properties. The mechanically tough nanocomposite hydrogels provide potential applications in biomedical engineering and electronic devices (Haraguchi 2011). The nanocomposite hydrogels synthesized by free radical polymerization of acrylamide in the presence of clay particles exhibit extraordinary stretching property and mechanical toughness (Haraguchi et al. 2005).

Recently, nanocomposite hydrogels can be prepared by blending clay and sodium polyacrylate. Tetrasodium pyrophosphate is used to prevent aggregation of clay particles. There is great effect of higher molecular weight polymers to form mechanically tough nanocomposite hydrogels. Polymers with high molecular weights get dispersed in clay particles. Polyacrylate anions show adsorption on the edge of the clay particles (Takeno and Kimura 2016).

The gel strength can be enhanced by various methods, e.g., surface cross-linking, creating composite and nanocomposites. In surface cross-linking process, the acidic group of acrylic acid combines with various multifunctional compounds, e.g., ethylene glycol, glycerin and epichlorohydrin. The cross-linking density on hydrogel surface enhances gel strength.

Synthesis of hydrogel composite is a second process for improving strength of gel. Addition of kaolin, montmorillonite and hydrotalcite to the matrix of acrylic monomer shows cross-linking. Cross-linking is formed between hydroxyl group of clay and carboxylic group of acrylic acid. Cross-linking reduces swelling rate of material but increases the gel strength. Nowadays, a third process has been introduced by which we can develop clay-incorporated nanocomposite hydrogels. New intercalated structures can be created by diffusion of clay (Haraguchi et al. 2002; Kabiri and Zohuriaan-Mehr 2003).



## Tensile property

Generally, nanocomposite hydrogels can be stretched more than 1000% from its original length. Elongation of nanocomposite hydrogels depends upon type of clay, cross-linker and polymers used in the synthesis. As similar to clay, graphene oxide is also a layered structure which contains hydroxyl and carboxyl groups and epoxides on its surface. Hence, tensile strength of nanocomposite hydrogels can be improved by incorporating graphene. The graphene oxide/polyallylamine hydrochloride nanocomposite hydrogels are synthesized with high tensile strength due to the presence of covalent bonds. The high tensile strength resulted due to the combination of high surface area of graphene oxide and the presence of interfacial interaction between graphene oxide and polymer matrix (Pan et al. 2011).

Poly(acrylic acid)/graphene oxide nanocomposite hydrogel is synthesized by in situ polymerization. The synthesized poly(acrylic acid)/graphene oxide nanocomposite hydrogel exhibited high elongation with 300% which is four times higher than that of polyacrylic acid hydrogel. Cross-linker used in nanocomposite hydrogels is *N,N*-methylenebisacrylamide (Wang et al. 2013b).

The multiwalled carbon nanotubes exhibit stiffness, strength, conductivity and chemical stability. Carbon nanotubes form ultrahigh-strength materials. Fibrous material is used as reinforcement fillers to form nanocomposite materials. Good physical properties and high aspect ratio of carbon nanotubes make them suitable for nanocomposite synthesis. Double- and triple-wall carbon nanotubes have great strength and modulus of 13–46 GPa and 0.73–1.33 TPa, respectively, and have been used for fabrication of nanocomposite hydrogels (Wei et al. 2009).

## Technologies adopted for synthesis of nanocomposite hydrogels

Generally, nanocomposite hydrogels can be synthesized from either synthetic polymers or natural polymers. Synthetic polymers show hydrophobic characteristic and possess good chemical strength as compared to natural polymers. Their excellent mechanical strength provides the durability. Natural and synthetic polymers having linear water-soluble chains can be cross-linked to form nanocomposite hydrogels in various ways such as linking of polymer chains, using ionizing radiations, electrostatics and crystalline formation. The main four parts for the preparation of nanocomposite hydrogels are polymer, monomer, cross-linker and initiator. To control polymerization heat, some diluents can be used such as water and some other aqueous solutions. Nanocomposite hydrogels are prepared by polar monomers. According to their starting materials, they can be divided into natural polymer, synthetic

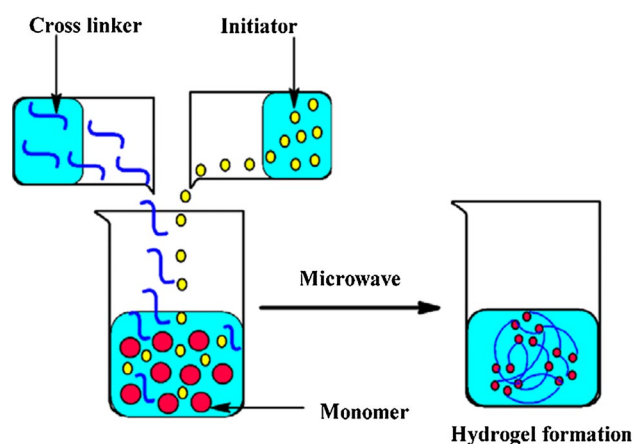
polymer and combinations of the two. Figure 3 shows microwave-assisted greener synthesis of nanocomposite hydrogel. The various techniques adopted for synthesis of nanocomposites hydrogels are discussed in following sections.

## Free radical chain polymerization

Chain or step polymerization is the method for synthesis of nanocomposite hydrogels. But free radical chain polymerization is the most commonly used method of synthesis. In free radical chain polymerization technique, hydrophilic monomers having carbon with double bond can be utilized. In such process, firstly homolytic dissociation of weak bonds of initiator occurs and produces active radical center. Active radical centers show propagation through carbon double bonds of various monomer units and form polymer chains. Combination of two active radical centers results in termination of polymerization process. Addition of cross-linker causes propagation of two radical chains so as to produce cross-link between chains (Chiefari et al. 1998). Table 2 shows list of synthetic monomers with abbreviation and chemical structure used in nanocomposite hydrogels synthesis.

## Copolymerization

To form nanocomposite hydrogels, various monomers follow free radical copolymerization with the help of cross-linking agents. The active centers propagation for polymer chains depends upon the type of monomers, solvent system used and reaction conditions employed such as light (photoinitiators), heat (thermal initiators) and gamma radiations. But in the case of radiation, polymerization initiators are not required. Peroxides and azo compounds are the examples of thermal initiators. Peroxides and azo compounds show



**Fig. 3** Microwave-assisted greener synthesis of nanocomposite hydrogel by addition of initiator and cross-linker into monomers. Monomers joined with each other by macromolecular chains to form hydrogel



cleavage with the help of reducing agents (ferrous salts, sodium metabisulfite) and some oxidizing agents (ammonium persulfate and hydrogen peroxide). In the case of radiation polymerization, the source of radiations includes cobalt 60, cesium 137 and electron beams. In copolymerization, various solvents used are ethanol, water and benzyl alcohol. Solvents can be removed further by swelling of nanocomposite hydrogels in deionized water.

### Grafting

In some cases, grafting technique is required for the formation of nanocomposite hydrogels. In grafting, free radicals generate on the surface of support which polymerized with monomer. Grafting is done by means of covalent bonds. Various techniques may be used to create free radicals on surfaces, e.g., ionizing radiation, peroxide formation, by ceric ions and radical transfer. Other examples of grafting techniques are chemical grafting, enzymatic grafting, free radical grafting, photochemical grafting, ionic grafting and radiation grafting.

Table 3 shows various grafting techniques with characteristics required for synthesis of nanocomposite hydrogels.

Hydroxypropyl methylcellulose–polyacrylamide/laponite nanocomposite hydrogels have been fabricated by grafting. Acrylamide is grafted onto hydroxypropyl methylcellulose using methylenebisacrylamide cross-linker and laponite nanoclay. The synthesized nanocomposite hydrogel has been used to remove crystal violet dye from water. Acrylic monomer, e.g., methacrylic acid and acrylamide, is grafted on high-density polymers (polyethylene, polystyrene) by gamma radiations. The source used for radiation was Co 60 followed by aqueous solution of monomer. The reaction was done in the absence of air and the presence of Mohr's salt. This limits homopolymerization of monomers (Mansoori et al. 2010).

### Bulk polymerization

In bulk polymerization, monomer-soluble initiators are required for polymerization. An example is vinyl monomers can be used for the preparation of nanocomposite hydrogels. Bulk nanocomposite hydrogels can be synthesized

with one or more types of monomers and by addition of small amount of cross-linking agent. This polymerization reaction is initiated with radiation, ultraviolet or chemical catalysts. The choice of a suitable initiator depends upon the type of monomers and solvents used. The polymerized nanocomposite hydrogel can be fabricated in a wide variety of forms, e.g., films, membranes, rods, particles and emulsions. Bulk polymerization is a simple technique, which involves monomer and monomer-soluble initiators. The viscosity of reaction mixture increases with the conversion, which is produced during the polymerization. The bulk polymerization of monomers makes a homogeneous nanocomposite hydrogel and produces glassy, transparent and hard polymer matrix. But when allowed to remain in water, the glassy hard matrix gets swollen and becomes soft and flexible (Ahmed 2015).

### Cross-linking

In the aforesaid process, the ionic or neutral monomers get mixed with the multifunctional cross-linking agent. Polymerization is enhanced thermally by UV irradiation or by the use of initiator. The synthesized nanocomposite hydrogels are washed with distilled water to remove the monomers, oligomers, cross-linking agent, initiator, soluble polymer and other impurities. Due to phase separation, the heterogeneous nanocomposite hydrogel is formed and the amount of water during polymerization become more than the water content in swelling. Typical solvents used for solution polymerization of hydrogels include water, ethanol and benzyl alcohol.

The poly(ethylene glycol) immobilized to a poly(vinyl alcohol) to form nanocomposite hydrogels where acetal or urethane linkages have been reported. Nanocomposite hydrogels cross-linked with glutaraldehyde by using MgCl<sub>2</sub>, toluene, sulfonic acid (DMSO based) as an acid catalyst. The hydroxyl group of poly(ethylene glycol) was converted into aldehyde or isocyanate. After that, poly(ethylene glycol) immobilized to poly(vinyl alcohol) nanocomposite hydrogel by aldehyde or urethane linkage. Application involved is reduction on thrombogenicity of cardiovascular biomaterials (Llanos and Sefton 2000).

**Table 2** List of synthetic monomers with abbreviation and chemical structure used in nanocomposite hydrogels synthesis

Monomer	Abbreviation	Chemical structure
Acrylic acid	AA	CH <sub>2</sub> =CHCOOH
Methacrylic acid	MA	CH <sub>2</sub> =C(CH <sub>3</sub> )COOH
Vinyl acetate	VAc	CH <sub>2</sub> =CHCOOCH <sub>3</sub>
Methyl methacrylate	MMA	CH <sub>2</sub> =C(CH <sub>3</sub> )COOCH <sub>3</sub>
Methoxyethyl methacrylate	MEMA	CH <sub>2</sub> =C(CH <sub>3</sub> )COOCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>
Hydroxyethyl methacrylate	HEMA	CH <sub>2</sub> =C(CH <sub>3</sub> )COOCH <sub>2</sub> CH <sub>2</sub> OH

**Table 3** Various grafting techniques required for synthesis of nanocomposite hydrogels and their characteristics

Grafting technique	Characteristics
Chemical grafting	Chemical grafting involves the uses of different chemical initiators or initiator systems such as ammonium persulfate (APS), potassium persulfate (PPS), ceric ammonium nitrate (CAN) + nitric acid and ferrous ammonium sulfate (FAS) for grafting (Holloway et al. 2013)
Ionic grafting	Cationic polymerization is a type of chain growth polymerization in which a cationic initiator transfers charge to a monomer which then becomes reactive. Cationic polymerization is used in the production of polyisobutylene and poly(N-vinylcarbazole). Anionic polymerization involves the polymerization of vinyl monomers with strong electronegative groups. This polymerization is carried out through a carbanion active species. Anionic polymerizations are used in the production of polydiene synthetic rubber (Haas et al. 1957)
Radiation grafting	Radiation grafting involves bonding of different organic substrates together by making use of radiations as initiator source. The substrates were immersed in an aqueous solution and irradiated with proper ionizing radiation; for example, gamma radiation from a cobalt-60 source has been used as ionizing radiation for synthesis of isotactic polypropylene-g-N-vinyl-2-pyrrolidone (Sehga and Rattan 2010)
Free radical grafting	In free radical grafting, a polymer forms by the successive addition of free radical building blocks. Free radical polymerization is a key synthesis for obtaining a wide variety of different polymers and material composites
Photochemical grafting	Photochemical grafting reactions can be initiated by photoelectron emission into the reactant liquid. The UV-induced photochemical grafting of terminal alkenes to semiconductors has been studied because it provides a facile, non-destructive method to covalently bond organic molecules to a wide variety of semiconductors including Si, diamond, SiC and metal oxides (Franking et al. 2012)
Enzymatic grafting	Enzymatic polymerizations have attracted much attention because they offer mild reaction conditions besides the occurrence of enzyme immobilization within the formed hydrogel. Suitable enzymes capable of initiating radical reactions comprise peroxidases and laccases (Nieto et al. 2010)

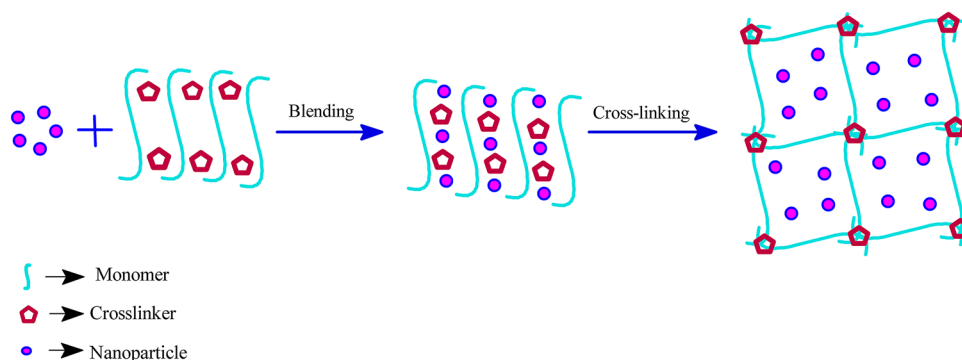
**Fig. 4** General method of cross-linking technique for synthesis of nanocomposite hydrogels by incorporation of nanoparticles, monomers and cross-linkers

Figure 4 shows general method of cross-linking technique for the synthesis of nanocomposite hydrogels by incorporation of nanoparticles, monomers and cross-linkers.

### Suspension polymerization

Suspension polymerization technique is an advantageous method especially when the products are powder or microspheres, so that grinding is not required. Most commonly water-in-oil (W/O) process is chosen as compared to oil-in-water polymerization and known as inverse suspension. Dispersion of monomers and initiators is carried out in the hydrocarbon phase to form homogeneous mixture. The dispersion is thermodynamically unstable and requires continuous agitation and hydrophilic-lipophilic balance agent.

In suspension polymerization method, monomers were dissolved in boiling alcohols and then dispersed in water.

Due to emulsion copolymerization, acrolein and hydroxyethyl methacrylate nanocomposite hydrogels were formed. Appropriate cross-linking agent and emulsifier are required in suspension polymerization (Mathur et al. 1996).

### Polymerization by irradiation

High-energy radiations like gamma rays and electron beams are used as an initiator to prepare the nanocomposite hydrogels of unsaturated compounds. The irradiation polymerization results in the formation of radicals on the polymer chains. Radiolysis of water molecules results in the formation of hydroxyl radicals, which also attacks the polymer chains and results in the formation of macro-radicals. The main advantage of the radiation initiation is the production of comparatively pure and initiator-free nanocomposite hydrogels.

## Freezing–thawing process

The freeze–thaw technique has been used to form microporous as well as macroporous matrices. To form microporous matrices, photopolymerizations of hydrophilic monomers are carried out around ice crystals. Freezing–thawing technique helps to increase pore size of nanocomposite hydrogels. Widening of pore size occurred by the formation of crystalline matrix and immediate cooling of homogeneous aqueous solution of monomers. Monomers used in this process were hydroxyethyl methacrylate, acrylic acid (AA), methacrylic acid (MAA) and acrylamide. These were cross-linked with ethylene glycol dimethylacrylate. To form macroporous matrices, a crystalline compound (sucrose) is dispersed in monomer solution before to get polymerized. An example is poly(vinyl alcohol) nanocomposite hydrogels can be prepared by freeze–thawing method. Various solvents used in freeze–thawing process are water, dimethyl sulfoxide and organic solvent–water mixtures. A novel method for the preparation of expanding poly(vinyl alcohol)/polyelectrolyte nanocomposite hydrogels has been reported. Solid polyelectrolyte particles are added to a poly(vinyl alcohol) solution and treated at low temperature for gelation. Such nanocomposite hydrogels exhibit high strength and expanding capacity. When polyfunctional monomers are copolymerized with hydroxyethyl methacrylate, novel nanocomposite hydrogels were formed. An example is poly(vinyl alcohol)-acrylamide/hydroxyethyl methacrylate nanocomposite hydrogel shows pH sensitivity, while the poly(vinyl alcohol)–methacrylic acid/hydroxyethyl methacrylate nanocomposite hydrogel can be used as dentin bonding agent, which shows interaction between the carboxyl group and calcium to enhanced bonding (Yang et al. 2008).

## Microwave-assisted method

Microwave-assisted method is a convenient and fast method for the synthesis of nanocomposite hydrogels. Microwave radiations enhance rate of reaction for some organic reactions. The radiation energy can be absorbed by whole volume of material uniformly and directly. Microwave-assisted method is convenient and fast for the synthesis of nanocomposite hydrogels. Cross-linking of poly(vinyl alcohol) at low temperature using microwave radiations can be possible. Poly(vinyl alcohol) is cross-linked with carbon nanotubes to form mechanically strong nanocomposite hydrogels. Such materials can be used as actuators and supercapacitors. SnO<sub>2</sub>/graphene nanocomposite hydrogel was synthesized by microwave-assisted method. Oxidizing and reducing agents are not required in microwave-assisted method (Nadagouda and Varma 2007).

Chitosan/poly(acrylamide)/Zn nanocomposite hydrogel was synthesized in the presence of microwave radiations. The synthesized nanocomposite hydrogel was used as a drug carrier for the drug ofloxacin and as an antibacterial material (Pathania et al. 2016b).

## Applications of nanocomposite hydrogels

### Biomedical applications

#### *Drug delivery system*

Nanocomposite hydrogels are known as cross-linked hydrophilic polymers with acidic, basic or neutral monomers, which help to imbibe large amount of water. Various types of nanocomposite hydrogels have been used for different biomedical applications due to their biocompatibility and biodegradability. Nanocomposite hydrogels are used as bio-absorbent materials in surgeries, biotechnology, agricultural and pharmaceutical applications for delivery of medicines as unique carriers (Yoshida et al. 1993).

Nanocomposite hydrogels are known as controlled drug delivery agents which allow site- specific and time-controlled delivery of drugs (Hamidi et al. 2008). Drug carrier can be of different types such as nanoparticles, nanospheres (drug dispersed throughout polymeric network) or nanocapsules (drug is surrounded by a polymer structure) (Qian et al. 2010). Nanocomposite hydrogels include inorganic parts such as silver, iron oxide, clay, gold, carbon nanotubes, hydroxyapatite and tricalcium phosphate. Addition of nanoparticles to nanocomposite hydrogels reduces burst release effect and provides stability of drug as well as slower and continuous drug release (Satarkar and Zach Hilt 2008). Because of controlled swelling ratio, mesh size and diffusion coefficient of nanocomposite hydrogel, they can be good carrier to load and transport drugs. For drug delivery, nanocomposite hydrogels can act as reservoir of drug molecules with interaction between drug molecule and nanofiller. Changes in external stimuli as magnetic field, electric field, temperature and pH help to release drug from nanocomposite matrix (Zhang et al. 2010).

*N*-isopropylacrylamide is a thermosensitive hydrogel because it possesses a lower critical solution temperature. The *N*-isopropylacrylamide nanocomposite hydrogels change their shape from a swollen state at the transition temperature by increasing the incubation temperature in water. So, nanocomposite hydrogels are applied in thermosensitive drug delivery systems and separation processes (Ramteke 2012). *N*-isopropylacrylamide nanocomposite hydrogels are squeezed out at the target site by shrinking the gel in response to temperature.

Ionic nanocomposite hydrogels have high water content, which is suitable for bio-tissues. Ionic nanocomposite hydrogels have excellent potential because of changing the charge density or the nature of the ionic as bio-responsive polymers. Magnitude of response for ionic nanocomposite hydrogels can be controlled by the moieties of the polymers. Unbound water can be retained in anionic nanocomposite hydrogels allowing lot of solute transport. Acrylic acid can be used to develop formulations that release drugs in a natural pH environment (Am Ende et al. 1995).

A broad spectrum hydrophobic drug 5-fluorouracil is active against tumors of stomach, colon, lung and breast. The cytotoxic drugs come in contact with normal cells and cause disorders of bone marrow and the epithelium of the gastrointestinal tract, which limits its therapeutic effect. Controlled administration of 5-fluorouracil is used to minimize the toxic side effects by using the chitosan-based nanocomposite hydrogels as thermoresponsive delivery system. Because of long-term safety of the drugs, biocompatible and biodegradable materials are used for drug delivery system. Metallic nanoparticles are cost-effective drug delivery system which shows simplicity, stability, high efficacy and target identification from synthesis to disposal. To minimize chemical activity and oxidizing power of metallic nanoparticles, various techniques such as grafting or coating with organic species (surfactants or polymers) or inorganic layers (silica/carbon) are developed.  $\beta$ -cyclodextrin is a cyclic oligosaccharide and widely explored for affinity-based drug delivery.  $\beta$ -cyclodextrin contains hydrophobic core and is used for encapsulating small hydrophobic molecules, thus changing the properties of the drug, e.g., aqueous solubility, stability and bioavailability. It also reduces side effects of ocular irritation and unpleasant taste and smell. The cyclodextrin–agar nanocomposite hydrogels are developed for the delivery of ciprofloxacin. Chitosan-grafted cyclodextrin is used for the controlled release of the poor water-soluble drug ketoprofen. Grafted drug delivery system was developed for the delivery of variety of drugs like miconazole, 5-fluorouracil, diclofenac sodium and riboflavin. In recent times, polymeric nanocomposite hydrogel has been used as pH-sensitive drug release system (Zhang et al. 2014a).

### *Tissue engineering*

In tissue engineering, scaffolds support cell attachment, proliferation and differentiation, as well as help for cell metabolite and nutrient transportation. Nanocomposite hydrogels can be used as scaffolds for tissue regeneration, but lack in functionality and mechanical strength. Addition of different nanoparticles such as carbon nanotubes and clay can improve functionalities and mechanical properties which fulfill requirements of tissue engineering, e.g., nanocomposite hydrogel formed from sodium alginate and carbon nanotubes

exhibited biocompatibility, inflammatory response and non-cytotoxicity. Due to enhanced characteristics, nanocomposite hydrogel forms good scaffolding materials (Kawaguchi et al. 2006), e.g., gelatin is a derivative of collagen, which is the main component of skin, bone, cartilage and connective tissues. Gelatin is used in tissue engineering because of availability, biocompatibility and biodegradability (Kania et al. 1998).

Addition of organic–inorganic fillers such as clay, cellulose, graphene and carbon nanotubes improves the mechanical performance of hydrogels. Graphene oxide has oxygen-containing groups, e.g., hydroxyl, epoxide and carboxyl groups, and results in hydrophilic character. Graphene oxide/sodium alginate/polyacrylamide nanocomposite hydrogel can be prepared by a wet-spinning method. Calcium chloride solution was used as a coagulation bath. Addition of polymer contributed to improvement in mechanical strength (He et al. 2012).

Hydroxyapatite shows good biocompatibility with soft tissues, e.g., skin, gums and muscles for ideal orthopedic and dental implants. The intrinsic properties of hydroxyapatite, i.e., fragility, hardness and lack of flexibility, make it difficult to be shaped. To overcome the drawbacks of hydroxyapatite as scaffold material in tissue engineering, various polymers are used to form nanocomposites such as cellulose, sodium alginate, poly(lactic acid), chitosan and chitin. These polymers develop porous 3D scaffolds. Due to biodegradable behavior of natural polymers, these have been explored more as compared to synthetic polymer-based nanocomposite hydrogels in tissue engineering. The hydroxyapatite is a nanosized material with large surface area-to-volume ratio and shows improved properties, e.g., osteoblast adhesion, osteo-conductivity, protein adsorption and mechanical strength. Inculcation of hydroxyapatite into polymer matrix makes the material useful in tissue engineering as scaffold (Swetha et al. 2010; Sudheesh Kumar et al. 2011).

### *Wound dressing*

Wound healing is a cellular and biochemical process which occurs in four different phases: inflammation, granulation tissue formation, matrix remodeling and re-epithelialization (Baskovich et al. 2008). The major function of wound dressings is to provide the optimum healing and to accelerate the natural healing (Reddy et al. 2009). Healing of wound is strongly affected by the presence of an adequate degree of moisture within the area of wound. This forms desirable biological medium that provides conditions for the complex processes of wound healing. Metabolic activity of each cell can be enhanced and of the whole tissue which cannot occur within dry tissue (Hebeish and Sharaf 2015).

In 2007, nanocomposite hydrogel wound dressings were introduced by using the technology of polymer nanocomposites. They can keep better moist environment on the interface of wound and dressing to accelerate the healing process (Kokabi et al. 2007).

Nanocomposite hydrogels enhance wound-dressing properties by addition of functional nanoparticles into hydrogel matrix. Nanocomposite hydrogels wound-dressing materials are usually used directly on the wound to stop bleeding, relieve pain and protect the wound from infection. Wound-dressing materials, e.g., foams, pastes and films, nanocomposite hydrogels are excellent wound-dressing materials having unique properties such as good swelling, tensile strength and biocompatibility (Varshney 2007).

Nanoclay nanocomposites are good for wound dressing because of excellent swelling, good barrier against microbes penetration, improved healing process. Chitosan shows biodegradability, good biocompatibility and hemostatic properties, so it can be used in wound dressing (El Salmawi 2007).

Poly(vinyl alcohol) nanocomposite hydrogels are biocompatible and non-toxic and can absorb large amount of water without being dissolved. Because of all these features, poly(vinyl alcohol) nanocomposite hydrogels are better options for dressing applications. Main attention has been focused on the use of cellulosic fibers for biomedical applications because of their good biocompatibility. With strong acids (sulfuric or hydrochloric acid), hydrolysis of cellulosic materials forms crystalline rod-like nanoparticles called cellulose nanowhiskers (Azizi Samir et al. 2005; Li et al. 2011b). Topological gel, nanocomposite gel and double network gel are three types of hydrogels with good mechanical strength. Sodium alginate, a natural polysaccharide extracted from brown seaweed, has been used as a novel material in the wound healing. Sodium alginate can be used in the formation of “moist healing” products such as gels and foams. Sodium alginate can form nanocomposite hydrogel in the presence of divalent( $\text{Ca}^{2+}$ ) cation due to ionic cross-linking with calcium bridges between the mannuronic acid and guluronic acid (Sun et al. 2012).

#### *Antibacterial activity*

In the past years, polymer nanotechnology has developed biodegradable nanocomposite hydrogels significantly in the biomedical field: drug delivery, tissue engineering and especially in antibacterial applications (Tiwari et al. 2009). For inactivation of bacteria, inorganic-based biodegradable nanocomposite hydrogels are promising (Varaprasad et al. 2017), e.g., silver nanoparticles having excellent antibacterial properties. Silver nanocomposite hydrogel with  $\beta$ -chitin or curcumin has enhanced antibacterial efficacy (Madhumathi et al. 2010; Eid et al. 2012). Silver nanoparticles are considered as a versatile system against microorganisms.

The silver nanocomposites are considered as non-toxic and eco-friendly in biomedical applications. The antibacterial property of silver nanocomposite hydrogel is dependent on the size of particles and the swelling ratio. The innovative pH-responsive poly(methyl methacrylate-co-methacrylic acid)/silver nanocomposite hydrogel is designed. Silver-based nanocomposite hydrogel bears antibacterial efficacy against *B. subtilis* by controlling swelling ratios of nanocomposite hydrogel and the size of silver nanoparticles (Agnihotri et al. 2012; Hebeish et al. 2013). So, the polymeric nanocomposite hydrogels function as bactericide and wound-healing matrix when applied on infected burns (Murali Mohan et al. 2007).

Nanocomposite hydrogels include polymer matrix: carboxymethyl cellulose-based nanocomposite hydrogels, chitosan–polyvinyl alcohol nanocomposite hydrogel and poly(acrylic acid). Polymer-based nanocomposite hydrogel has structural similarity and is considered biocompatible. Poly(methacrylic acid) nanocomposite hydrogels are used in the fabrication of contact lenses and is pH responsive.

## **Environmental applications**

### **Adsorption**

Because of industrialization, release of heavy metal ions and persistent organic pollutants into the water resources has raised global issues. Heavy metal ions cannot degrade into harmless end products and cause toxicity. So to remove heavy metal ions from wastewater, wide range of techniques are explored. Some of them are ion exchange, chemical precipitation, adsorption, membrane filtration, electrochemical treatment (Naushad et al. 2016a, b; Sharma et al. 2017f). But some of these techniques have drawbacks, e.g., disposal of residual metal sludge or high cost. Due to high efficiency, easy handling and cost-effectiveness, adsorption technique exhibits many advantages (Keng et al. 2014; Mittal et al. 2016a). Thus, a wide variety of adsorbents have been explored in past few decades (Naushad et al. 2015). Recently, polymer nanocomposite hydrogels have received more attention as adsorbent for the treatment of heavy metal ions from contaminated waste water. The nanocomposite hydrogels have the capacity to swell in water so that they achieve high adsorption capacity and improve mechanical strength (Rai et al. 1981; Kaya et al. 2011; Xue et al. 2017).

Clay minerals with nanosized particles are introduced into nanocomposite hydrogels to enhance their mechanical strength and improve their adsorption properties. The nanoclay minerals get mixed within polymeric matrices and get cross-linked. Sol–gel method is used for the synthesis, e.g., in attapulgite/poly(acrylic acid-co-acrylamide)



nanocomposite hydrogel, attapulgite nanorods were used as cross-linkers. Modification of acrylic acid and acrylamide is done by facile inverse suspension copolymerization. Due to the presence of carboxyl and amido groups, the copolymer matrix shows improved adsorption selectivity toward heavy metal ions (Torkkeli 2003).

Nowadays, organic–inorganic nanocomposite has become very important material (Dupont et al. 2007). Many inorganic mineral micropowders, e.g., mica, attapulgite and kaolinite, have been used in the preparation of nanocomposite matrix to achieve lower costs and good properties. But poor mechanical properties of the hydrogels inhibit their applications. To improve properties of hydrogels, many layered clays were used. Different nanocomposite hydrogels, e.g., poly(sodium acrylate)/sepiolite, poly(acrylic acid)/montmorillonite, poly(*N*-isopropylacrylamide)/montmorillonite and poly(acrylic acid)/mica, were prepared. Clays have sandwich-type structures with hydrophilic nature and are suitable for use in water absorbents as additives. Montmorillonite is a naturally occurring clay and commonly used to prepare nanocomposite hydrogels, because of their good water absorption, extensive swelling in water and cation exchange capacity. Montmorillonite is a kind of loose layer, hydrophilic, swollen natural clay (Ni and Zhu 2004; Ma et al. 2007; Paranhos et al. 2007; Santiago et al. 2007).

In the textile, paper, plastic, leather, food industries, colored organic effluent is produced. Dyeing industries discharge waste effluent with colors and low biochemical oxygen demand and high chemical oxygen demand. Effluent is toxic to aquatic life and can be carcinogenic or mutagenic. There are various methods to remove dyes from water, e.g., physical, chemical and biological. But adsorption process is mostly considered to be an effective method for quick removal of dissolved dyes from an effluent. For removal of organic compounds from wastewater, many adsorbents such as natural clays, activated carbon, modified clays are used (Kadirvelu et al. 2000; Nor Hanisah et al. 2007).

In the present era, polymeric adsorbents have been widely used to recover organic pollutants from wastewater, e.g., nanocomposite hydrogels were prepared by using 2-acrylamido-2-methylpropane sulfonic acid, 2-hydroxyethyl methacrylate, 2-(*N,N*-dimethylamino)ethyl methacrylate monomers and montmorillonite. The montmorillonite content in nanocomposite hydrogels affects the removal of indigo carmine from aqueous solutions (Luo et al. 2005; Liu et al. 2009).

The presence of ionic groups in the hydrogels opens wide area of applications particularly for the removal of pollutants from wastewater. Hydrogels comprise of anionic ( $-\text{CO}^{2-}$ ,  $-\text{SO}^{3-}$ ) or cationic pendants ( $-\text{NR}^{3+}$ ). Various hydrogels have been used in combination, e.g., sodium alginate with carboxylate groups, chitosan with pentamine, carboxymethyl cellulose with anionic carboxylate

and kappa-carrageenan with anionic sulfate groups, for the removal of cationic dyes from water (Crini 2005).

Because of non-toxicity, biodegradability and biocompatibility biopolymer kappa-carrageenan can be used in various areas of research. The gelling capacity of kappa-carrageenan can be caused physically (because of  $\text{K}^+$  cation) and chemically (non-toxic genipin). In addition to biopolymers, non-ionic and water-soluble polyvinyl alcohol is also used for adsorption of crystal violet cationic dye from wastewater (Meena et al. 2009; Mahdavinia et al. 2012).

### Photocatalysis

The contaminated water from textile, paper, leather, ceramic, cosmetics, ink and food-processing industries is harmful for human life. To remove organic dyes from this contaminated effluent of industries, various methods are available. Because of high efficiency, low energy consumption and mild reaction conditions, the photocatalytic method becomes the highly focused operation of scientific communities (Ayekoe et al. 2016). Catalysts mostly used in photocatalysis are  $\text{TiO}_2$ , CdS, ZnS, ZnO, CuS and  $\text{Fe}_3\text{O}_4$ , which have great potential in wastewater industry (Kumar et al. 2017b). But these nanoparticles have some drawbacks such as non-reusability, tough handling and aggregation due to small size. To overcome these discrepancies, composite catalysts are introduced. Composite catalysts can be made by introducing carbon nanotubes, transition metals, non-metals doping, dyed sensitizers, polymers, etc. Addition of carbon material into titanium dioxide enhances the photocatalytic activity of nanocomposite for wastewater treatment, because the carbon acts as electron sinker and hinders charge carrier. To improve catalytic activity and structural stability, many other materials are also investigated. Examples are mesoporous clays, agar and polymeric sorbents. So the highly polymeric structures, i.e., nanocomposite hydrogels, attracted more attention for wastewater treatment (Li et al. 2016). Polymeric matrix enhances photocatalytic activity due to the presence of polar groups: hydroxyl, epoxide, ether and carboxylate groups. Polymeric framework provides platform for catalytic centers to achieve solar energy conversion. Poly(vinyl alcohol)/poly(acrylic acid)/ $\text{TiO}_2$ /graphene oxide nanocomposite hydrogels are prepared by polymerization of acrylic acid and ethylene glycol dimethacrylate. The condensation was proceeded between poly(vinyl alcohol) and glutaraldehyde for efficient treatment of wastewater. The photocatalytic activity of nanocomposite hydrogels was studied by decomposition process of dyes using UV radiations (Shin et al. 2002). Starch/poly(alginate-chitosan-co-acrylamide)/Fe/Zn nanocomposite hydrogel was fabricated using simple polymerization/coprecipitation technique. The nanocomposite was used for photocatalytic degradation of

**Table 4** List of various fabricated nanocomposite hydrogels with different methods of synthesis and applications

Serial number	Name of nanocomposite hydrogels	Methods of synthesis	Applications	References
1.	Polyacrylamide/chromium/montmorillonite	Cross-linking	Oil recovery	Zolfaghari et al. (2006)
2.	Polyacrylamide/laponite nanocomposite	In situ free radical polymerization	Ultrahigh tensibility	Xiong et al. (2008)
3.	Starch/acrylic acid/montmorillonite	Grafting	Removal of heavy metal ions	Güçlü et al. (2010)
4.	Poly[acrylic acid-co-poly(ethylene glycol) methyl ether acrylate]	Photopolymerization	Drug delivery	Lee and Chen (2004)
5.	Poly( <i>N,N</i> -diethylamino ethyl methacrylate)/2-hydroxyethyl methacrylate/montmorillonite	In situ polymerization	Dye removal	Dalaran et al. (2009)
6.	Fe <sub>3</sub> O <sub>4</sub> /kappa-carrageenan/poly(vinyl alcohol)	In situ coprecipitation	Cationic dye adsorption	Mahdavinia et al. (2014b)
7.	Poly(vinyl alcohol)/cellulose nanowhiskers	Freezing–thawing technique	Wound dressings	Gonzalez et al. (2014)
8.	Iota/carrageenan/Ag	Green process	Antibacterial activity	Jayaramudu et al. (2013)
9.	Graphene oxide/sodium alginate/polyacrylamide	Free radical polymerization	Dye adsorption	Fan et al. (2013)
10.	Polyacrylamide/laponite	In situ polymerization	Dye adsorption	Li et al. (2008)
11.	Poly(acrylic acid-co-acrylamide)/hydrotalcite nanocomposite	Immobilization	To remove carbon dioxide from air	Zhang et al. (2009)
12.	Chitosan/silver	In situ cross-linking	Drug delivery and antibacterial	Yadollahi et al. (2015)
13.	Graphene/poly( <i>N</i> -vinylcaprolactam) hydrogels	Frontal polymerization	–	Sanna et al. (2012)
14.	Acrylamide/sodium acrylate/hectorite	In situ copolymerization	–	Xiong et al. (2009)
15.	Poly( <i>N</i> -isopropylacrylamide)/laponite	Cross-linking	Controlled drug delivery	Wang et al. (2012a)
16.	Acrylamide/2-(dimethylamino) ethyl methacrylate/hectorite	In situ copolymerization	–	Zhu et al. (2010)
17.	Poly-( <i>N</i> -isopropylacrylamide)/alginate /laponite	In situ polymerization	Tissue engineering	Wang et al. (2011a)
18.	Polyvinyl alcohol–montmorillonite	Freezing–thawing cyclic method	Biomedical applications	Zaharia et al. (2015)
19.	Graphene oxide/bacterial cellulose	One-step in situ biosynthesis	Tissue engineering scaffolds	Si et al. (2014)
20.	Poly(vinyl alcohol)/montmorillonite	Freezing–thawing cyclic method	Wound dressing	Sirousazar et al. (2011)
21.	Poly(ethylene glycol)/silicate	Photopolymerization	Biomedical applications	Gaharwar et al. (2011)
22.	Poly(2-hydroxyethyl acrylate)/silica	Polymerization and sol–gel process	Water sorption	Pandis et al. (2011)
23.	polyacrylamide/laponite	Free radical polymerization	Oil recovery	Tongwa et al. (2013)
24.	Kappa-carrageenan-g-poly(acrylamide)/sepiolite	Grafting	Dyes adsorption	Mahdavinia and Asgari (2013)
25.	Si/poly(acrylamide)	Photocross-linking	Biomedical applications	Yang et al. (2013a)
26.	Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> /starch/poly(acrylic acid)	Grafting	Removal of dye	Pourjavadi et al. (2013)
27.	Silver/poly(acrylamide-co-acrylic acid)	Grafting	Antibacterial activity	Thomas et al. (2007b)

**Table 4** (continued)

Serial number	Name of nanocomposite hydrogels	Methods of synthesis	Applications	References
28.	Poly(ethylene glycol) methyl ether ethacrylate/dimethacrylate/iron oxide	Free radical polymerization	Hyperthermia cancer therapy	Meenach et al. (2010)
29.	Fe <sub>3</sub> O <sub>4</sub> /poly(acrylic acid–acrylamide–butyl methacrylate)	Coprecipitation reaction	Adsorbents for removal and separation of cationic dyes	Li et al. (2011a)
30.	Graphene oxide/poly(N-isopropylacrylamide)	Photopolymerization	Actuators in microelectromechanical systems	Lo et al. (2011)
31.	Graphene oxide/poly(acrylic acid)/gelatin	Thermal initiated redox polymerization	Tissue engineering	Faghihi et al. (2014)
32.	Poly-(N-isopropylacrylamide)/clay	Photopolymerization	Tactile communication, microvalves	Ferse et al. (2008)
33.	Poly(vinyl alcohol)/poly(acrylic acid)/TiO <sub>2</sub> /graphene oxide	Radical polymerization and condensation	Photocatalytic degradation	Moon et al. (2013)
34.	N-maleyl chitosan/poly(acrylamide)/montmorillonite	Free radical polymerization	Enzymatic degradation	Yu et al. (2011b)
35.	Lithium magnesium silicate hydrate/poly(N-isopropylacrylamide)	In situ free radical polymerization	Removal of crystal violet from aqueous solution	Zhang et al. (2014b)
36.	Silver/acrylic acid, poly(ethylene glycol) methyl ether acrylate	In situ polymerization	Antibacterial activity	Lee and Tsao (2010)
37.	Vinyleddmontmorillonite/malto-dextrin-co-dimethylacrylamide	Radical cross-linking	Pharmaceutical formulations	Guilherme et al. (2010)
38.	2-acrylamido-2-methylpropane-sulfonic acid/acrylic acid/laponite	In situ copolymerization	Contact lens or ophthalmic implant	Chen et al. (2013)
39.	Ag/poly(N,N-dimethylacrylamide)/poly(vinyl alcohol)	Free radical Polymerization	Antibacterial and drug release	Luo et al. (2009)
40.	Poly(acrylamide-co-sodium methacrylate)/carboxyl carbon nanotubes	Cross-linking copolymerization	Controlled drug release and tissue engineering	Liu et al. (2012a)
41.	Polyvinyl alcohol/kappa-carrageenan/magnetite	In situ polymerization	Drug delivery and antibacterial activity	Mahdavinia and Etemadi (2014)
42.	Poly(acrylic acid)/laponite	Free radical polymerization	Wound dressing and tissue engineering	Shen et al. (2014)
43.	Carboxymethyl cellulose/poly(acrylic acid)/montmorillonite	Radical graft polymerization	In vitro release of vitamin B <sub>12</sub>	Boruah et al. (2014)
44.	Poly(N,N-dimethylacrylamide)/laponite	In situ free radical polymerization	–	Wang et al. (2011b)
45.	Silver/acrylamide/gelatin	Polymerization	Antibacterial agent	Reddy et al. (2013)
46.	Sodium alginate/poly(acrylamide-co-N-vinylcaprolactam-co-acrylamidoglycolic acid)	Free radical redox polymerization	Antibacterial activity	Reddy et al. (2014)
47.	Curcumin/silver/acrylamide/2-acrylamido-2-methyl propane sulfonic acid	Redox copolymerization	Antibacterial and drug delivery	Ravindra et al. (2012)
48.	Polyacrylamide/cellulose nanocrystal	In situ polymerization	–	Zhou et al. (2011)
49.	N-isopropylacrylamide/hectorite	In situ polymerization	Biomedical applications	Wang et al. (2013c)

**Table 4** (continued)

Serial number	Name of nanocomposite hydrogels	Methods of synthesis	Applications	References
50.	Poly(2-(2-methoxyethoxy) ethyl methacrylate/oligo (ethylene glycol) methacrylate/acrylic acid)/magnetic attapulgit	Coprecipitation	Artificial muscles, biosensors and actuators	Wang et al. (2012b)
51.	2-(2-methoxyethoxy) ethyl methacrylate, oligo(ethylene glycol)/methacrylate/inorganic clay	Polymerization	Drug delivery system, artificial muscle and biosensor	Xia et al. (2015)
52.	Halloysite-sodium hyaluronate/poly(hydroxyethyl methacrylate)	Free radical redox polymerization	Colon cancer drug delivery	Rao et al. (2014)
53.	N-vinyl 2-pyrrolidone/itaconic acid/organo-clay	Free radical polymerization	Removal of basic dye	Çöle et al. (2013)
54.	Acrylamide/kappa-carrageenan/sodium montmorillonite	Solution copolymerization	Adsorption of methylene blue cationic dye	Mahdavinia et al. (2014a)
55.	Cellulose nanocrystals/poly(acrylamide)	In situ polymerization	–	Yang et al. (2014)
56.	Poly(N-[3-(dimethylamino)propyl] methacrylamide-co-acrylamide)/montmorillonite	In situ intercalative polymerization	Gardening or soil conditioning	Nie et al. (2014)
57.	Poly(vinyl alcohol) / chitosan/polyaniline	Radiation-induced cross-linking	–	Dispenza et al. (2012)
58.	Nanohydroxyapatite/poly(ethylene glycol)-poly( $\epsilon$ -caprolactone)-poly(ethylene glycol)	Hydrothermal precipitation method	Orthopedic tissue engineering	Fu et al. (2009)
59.	Poly(vinyl alcohol)/chitosan/montmorillonite	Freezing–thawing method	Wound dressing	Noori et al. (2015)
60.	Silica/organic (poly(acrylic acid))	In situ free polymerization	–	Yang and Zhao (2014)
61.	Iron oxide/poly(ethylene glycol)	Copolymerization	Biomedical applications	Sen and Puskas (2008)
62.	Silver/poly(N-vinyl-2-pyrrolidone)	In situ radiolytic method	Antibacterial activities	Jovanović et al. (2011)
63.	Polyacrylamide/methyl cellulose/calcic montmorillonite	Free radical polymerization	Slow release of fertilizers	Bortolin et al. (2013)
64.	Chitosan/poly[(acrylic acid)-co-(2-hydroxyethyl methacrylate)]/mica	Radical copolymerization	–	Noppakundiligrat et al. (2013)
65.	Oleic acid-coated iron oxide/hexa(ethylene glycol) methyl ether methacrylate/hydrophobic 2-(acetoacetoxy)ethyl methacrylate	Random copolymerization	Magneto thermally triggered drug delivery system	Papaphilippou et al. (2011)
66.	Graphene oxide/polypyrrole	One-step co-electrode position	High-performance electrochemical supercapacitor	Zhu et al. (2012)
67.	Carboxymethyl cellulose/attapulgit	Free radical polymerization.	–	Wang and Wang (2010)
68.	2-(2-methoxyethoxy) ethyl methacrylate/attapulgit	In situ polymerization	–	Wang and Chen (2012)
69.	2-hydroxyethyl methacrylate/epoxy methacrylate	Bulk polymerization	Controlled drug delivery	Wang and Wu (2005)
70.	Iron oxide/poly(ethylene glycol) methacrylate	Polymerization	Biomedical applications	Papaphilippou (2012)
71.	Fe <sub>3</sub> O <sub>4</sub> /poly(acrylamide–gelatin)	Free radical polymerization	Tissue engineering	Reddy et al. (2011)

**Table 4** (continued)

Serial number	Name of nanocomposite hydrogels	Methods of synthesis	Applications	References
72.	Carboxymethyl cellulose/succinic acid/ZnO	In situ process	Antimicrobial activity	Hashem et al. (2013)
73.	Silver nanoparticles/poly(methyl methacrylate)/poly(vinyl alcohol)	Radical mediated dispersion polymerization	Antimicrobial activity	Dallas et al. (2011)
74.	Carboxymethyl tamarind-g-poly(acrylamide)/silica	Grafting	Adsorption of methylene blue dye	Pal et al. (2012)
75.	Chitosan/poly(alginic acid)	Copolymerization	Adsorptive removal of Cr(VI) metal ions	Sharma et al. (2017d)
76.	Chitosan-g-poly(acrylamide)/ZnS	Solar irradiation	Adsorption of dye	Pathania et al. (2016a)
77.	Chitosan-g-poly(acrylic acid)/kaolin	Graft copolymerization	Effect of pH on the water absorbency	Pourjavadi and Mahdavinia (2006)
78.	3-methacryloxypropyl trimethoxysilane/glycidyl methacrylate/maleated cyclodextrin	Polymerization	Controlled delivery of 5-fluorouracil	Anirudhan et al. (2015)
79.	Magnetic/2-acrylamido-2-methyl-1-propanesulfonic/acrylic acid/maleic acid	Free radical polymerization	Adsorption of heavy metals	Souda and Sreejith (2015)
80.	Starch/dimethylacrylamide/acrylic acid/CoFe <sub>2</sub> O <sub>4</sub>	Ultrasound-induced radical cross-linking/polymerization	Biomedical applications	Lima-Tenório et al. (2015)
81.	Hyaluronic acid/poloxamer/poly(ethylene oxide)/poly(propylene oxide)/poly(ethylene oxide)	Biom mineralization	Bone tissue repair	Huh et al. (2015)
82.	Guar gum-cl-poly(acrylic acid-IPN-aniline)	Free radical aqueous polymerization	Antibacterial and dye removal applications	Sharma et al. (2015)
83.	Graphene oxide/poly(acrylamide)	In situ polymerization	Controlled drug release, biosensors and enzyme immobilization	Shen et al. (2012)
84.	Sterculia gum/polyacrylamide	polymerization	Ant ulcer drug delivery	Singh and Sharma (2008)
85.	Poly(dimethyldiallylammonium chloride)/bentonite/starch-g-acrylic acid	In situ free radical polymerization	–	Huang et al. (2009)
86.	Poly(acrylic acid-co-poly(ethylene glycol) methyl ether acrylate	Photopolymerization	Drug release	Lee and Chen (2003)
87.	Poly(acrylic acid)/bentonite/FeCo	Ultrasound-assisted in situ emulsion polymerization	Removal of organic pollutant	Shirsath et al. (2011)
88.	Polyacrylic acid/bentonite/poly-ethylene glycol	Cross-link copolymerization	Removal of Congo red and methyl violet	Bhattacharyya and Ray (2015)
89.	Chitosan/bentonite/silver and zinc oxide	Microwave-assisted synthesis	Antibacterial activity	Motshekga et al. (2015)
90.	Poly-methacrylic acid/chitosan/bentonite	Gamma irradiation polymerization	Heavy metals recovery	Khalek et al. (2012)
91.	Acrylic acid/kappa-carrageenan/multiwalled carbon nanotube	Cross-linking	Adsorption	Pourjavadi et al. (2015)
92.	Chitosan/2-hydroxyethyl methacrylate/kaolin	Grafting	Biomedical applications	Pradhan et al. (2015)
93.	Kaolinite/poly[(acrylic acid)-co-acrylamide]	Copolymerization	Adsorption of Mn(II), Cu(II) and Zn(II)	Atia et al. (2009)
94.	Carrageenan/poly(sodium acrylate)/kaolin	Graft copolymerization	–	Sadeghi et al. (2012)



**Table 4** (continued)

Serial number	Name of nanocomposite hydrogels	Methods of synthesis	Applications	References
95.	Methyl violet/poly(acrylic acid-co-acrylamide)/kaolin	Copolymerization	Sorption behavior of methyl violet	Tang et al. (2014)
96.	Pectin/carboxymethyl cellulose	Lyophilization technique	Tissue engineering	Ninan et al. (2013)
97.	Xanthan gum/polyacrylamide/silicon	Grafting	Adsorption	Ghorai et al. (2014)
98.	Xanthan gum/polyacrylic acid/ $\text{Fe}_3\text{O}_4$	Cross-linking polymerization	Adsorption	Mittal et al. (2016b)
99.	Attapulgit/poly(acrylic acid-co-acrylamide)	Cross-linking	Adsorption	Liu et al. (2015b)
100.	Chitosan/poly(acrylic acid)/rectorite	In situ copolymerization	Adsorption	Zheng and Wang (2009)
101.	Sodium alginate-g-poly(sodium acrylate-co-styrene)/illite/smectite clay	Grafting	Adsorption	Wang et al. (2013d)
102.	Tara gum/acrylic acid	Gamma irradiation	Superabsorbent	Abd et al. (2012)
103.	Pectin Zr(IV) selenotungstophosphate	Sol-gel method	Adsorption and photocatalysis	Gupta et al. (2015)
104.	Alginate/poly( <i>N</i> -isopropylacrylamide)	Gamma ray irradiation grafting	Drug delivery	Lee et al. (2004)
105.	Chitosan-g-poly(acrylamide)/Zn	Microwave radiations	Drug delivery	Pathania et al. (2016b)
106.	Starch/poly(alginic acid-cl-acrylamide)/Fe/Zn	Polymerization/coprecipitation method.	Photocatalysis	Sharma et al. (2017a)
107.	Chitosan-poly(ethylene oxide)	Cross-linking	Drug delivery	Patel and Amiji (1996)
108.	Poly( <i>N</i> -isopropylacrylamide-co-itaconic acid)/ <i>N</i> -maleyl chitosan	Cross-linking	Environmental remediation	Yu et al. (2011a)

mixture of malachite green and fast green dye (Sharma et al. 2017a). The addition of polymeric part results in adsorption of dyes, which enhances the photodegradation process. Similarly, the photocatalytic degradation of methyl orange and Congo red dyes from aqueous solution has been studied using chitosan-g-poly(acrylamide)/ZnS nanocomposite (Pathania et al. 2016a). The use of nanocomposite hydrogels as photocatalyst is a new field which still needs to be explored in coming times.

### Ion exchange

Ion exchange is the most simplest and effective method for treatment of large volumes of waste effluents containing toxic metal ions (Anirudhan and Radhakrishnan 2011; Naushad et al. 2017). In last few centuries, the inorganic and organic ion exchangers were subject of interest, but individually they suffer from many drawbacks. The inorganic ion exchangers are difficult to handle in column process and cannot be utilized in large-scale operations, whereas organic ion exchangers show poor thermal and chemical stability. To overcome these drawbacks in present times, new class of nanocomposite ion exchangers

has been fabricated. The nanocomposite hydrogels having specific functionalities in their structure behave as selective ion exchange materials to be potentially explored for wastewater treatment on large scale. The pectin thorium tungstomolybdate, polyaniline zirconium selenotungstophosphate and polyacrylamide zirconium vanadophosphate are few of the polymeric nanocomposite ion exchange materials used for wastewater treatment (Sharma et al. 2014, 2016a, b).

### Soil conditioning

Due to the lack of water, the agriculture suffers in the world. Owing to climate change and some human activities, the land becomes arid, semiarid and dry. To overcome this problem, synthetic material with good water retention capacity is required and crop productivity can be enhanced. Superabsorbent polymers retain water about 1500 g per dry gram of nanocomposite hydrogel. When nanocomposite hydrogel is used properly, they provide more than 97% water to the plants. Some examples of superabsorbent are starch/polyacrylonitrile, vinyl alcohol/acrylic acid-co-polyvinyl alcohols and acrylamide-sodium acrylate-co-polyacrylamides.

Amorphous gelatinous material is formed on hydration when absorbents were introduced into soil. These materials release water slowly into soil and dissolved nutrients. Chitosan–acrylamide nanocomposite hydrogel can be synthesized by graft copolymerization using gamma radiation for soil conditioning. In this, bulk density of the soil decreases and water retention and porosity increase with the addition of nanocomposite hydrogel (Nnadi and Brave 2011; Shahid et al. 2012). Table 4 includes list of various fabricated nanocomposite hydrogels with different methods of synthesis and applications.

## Conclusion

From the above discussion, we can conclude that the nanocomposite hydrogels are temperature and pH responsive and show controlled swelling behavior because of association and dissociation of H-bonding within polymer matrix. Swelling increases at low temperature, and at high temperature, it is collapsed. Thus, nanocomposite hydrogels show excellent swelling at room temperature. Nanocomposite hydrogels had good application in soil conditioning. The dye removal efficiency of nanocomposite hydrogels was found about 90%. Clay plays important role as good adsorbent. Swelling is responsible for dimensional change, which causes drastic change in rheological properties and phase transition. The nanocomposite hydrogels with natural or synthetic origin exhibit many characteristics such as hydrophilicity, gelation, swellability, porosity, mechanical strength, biocompatibility and biodegradability. Nanocomposite hydrogels possess wide areas for utilization: water purification, ion exchange, removal of azo dye, chromatography, enhanced oil recovery, sensor development, and immobilization of enzyme systems, agriculture, food-processing, pharmaceutical and biomedical fields. The presence of alcohols, carboxylic acids and amides as hydrophilic moieties causes stiffness and water-absorbing capacity of nanocomposite hydrogels, and cross-linker acts as resistant to dissolution in the aqueous system. Swelling causes sorption of solvent system into pores of macromolecular structure, and these can be classified as microporous, macroporous and non-porous. For swelling, two major forces are responsible: osmotic force and counter elastic force which resist elongation of macromolecules. Addition of different cross-linkers between monomers forms covalent bonds permanently which cause changes in configuration and introduce high stability than ionic bonds, hydrophobic forces and hydrogen bonds. Commonly used cross-linkers are carbodiimides, formaldehyde and glutaraldehyde. Various synthesis techniques involved are free radical polymerization, condensation polymerization, enzymatic reactions, gamma polymerization and grafting. Thus, we can conclude that nanocomposite hydrogels are next-generation materials

finding numerous applications in fields of biomedical engineering and environmental detoxification.

**Acknowledgements** This work was supported by the Deanship of Scientific Research, King Saud University, for funding through Vice Deanship of Scientific Research Chairs.

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