Gels Horizons: From Science to Smart Materials

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Polymer Gels

Perspectives and Applications

Springer

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Contents

1 Polymer-Based Responsive Hydrogel for Drug Delivery 1
Dhanabal Kumarasamy, Miltu Kumar Ghosh and Tapan Kumar Giri

2 Stimuli-Responsive Polymeric Nanoparticles for Cancer Therapy 27
Shantanu V. Lale and Veena Koul

3 The Application of High Polymer Materials in the Aspects of Seed Technology 55
Jin Hu and Yajing Guan

4 Nanogels of Natural Polymers 71
Daniela Pamfil and Cornelia Vasile

5 Polymer Gel Composites for Bio-Applications 111
Luminita Ioana Buruiana and Silvia Ioan

6 Vegetable Oils as a Chemical Platform 125
Amanda Murawski and Rafael Lopes Quirino

7 Imprinted Polymeric Gels for Pharmaceutical and Biomedical Purposes 153
Monika Sobiech and Piotr Luliński

8 Applications of Biopolymeric Gels in Agricultural Sector 185
Sumit Mishra, Nandkishore Thombare, Mohd Ali and Saurabh Swami

9 Agro-Based Polymer Gel and Its Application in Purification of Industrial Water Wastes 229
Altaf Halim Basta and Houssni El-Saied

10 Pharmaceutical Polymer Gels in Drug Delivery 249
Geeta Aggarwal and Manju Nagpal

11 Emerging Trends of Organogels in Drug Chemistry 285
Selvaraj Mohana Roopan and Duraipandi Devipriya

12 Design and Application of Injectable Gels in Tissue Engineering and Drug Delivery 311
B. A. Aderibigbe

13 Thermo-intelligent Injectable Implants: Intricate Mechanisms and Therapeutic Applications 341
Pradeep Kumar, Yahya E. Choonara and Viness Pillay

14 Gelled Microparticles/Beads of Sterculia Gum and Tamarind Gum for Sustained Drug Release 361
Amit Kumar Nayak, M. Saquib Hasnain and Dilipkumar Pal

Chapter 8
Applications of Biopolymeric Gels in Agricultural Sector

Sumit Mishra, Nandkishore Thombare, Mohd Ali and Saurabh Swami

Abstract Hydrogels are three-dimensional cross-linked polymeric network having substantial affinity for water. Classes of hydrogels which are derived from biopolymers have been widely used in number of industries because of their biocompatibility and environmental safety. In agricultural sector, they are extensively used as soil conditioners, water retainers, and bio-remediating agents. Their recent application claims customized diffusion of different materials such as fertilizers and pesticides into surrounding soil matrix. They are proving very useful for crops in efficient distribution of water with minimum wastage, and utilization of fertilizer nutrients and pesticides in targeted zones. This chapter covers the recent advances on biopolymeric gels and different aspects of their usage with respect to agricultural sector.

Keywords Polysaccharide · Gum · Hydrogel · Soil conditioner
Pesticide · Water retainer

1 Introduction

Biopolymers are polymeric materials that are obtained from living beings. According to Dr. Pat Smith, "Biopolymers are not only materials of 'green birth' but polymers with 'green death' as well." The examples of biopolymers include carbohydrates, nucleic acids, proteins, lipids, peptides, and polysaccharides. Among these, polysaccharides have large popularity owing to their manifold uses, particularly in the field of agriculture, food, pharmacotherapy and pharmacy, cosmetic, and mining industry. Polysaccharides have high molecular weight and are

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composed of one or different types of monosaccharide units arranged in linear or branched fashion via glycosidic linkages. On hydrolysis, polysaccharides give their constituent oligosaccharides or monosaccharides. Cellulose, starch, gum arabic, guar gum, alginate, chitosan, xanthan, etc., are commercially exploited polysaccharides which find application in various industries. Polysaccharides are generally heterogeneous, containing slight modifications of the repeating units. Depending on the molecular structure and chemical composition, polysaccharides have different physicochemical properties derived from their building blocks. They may be amorphous or even insoluble in water (Varki et al. 1999, 2008). When a polysaccharide is composed of same units of monosaccharides, the polysaccharide is called a homoglycan or homo-polysaccharide, but when different units of monosaccharides are present, the polysaccharides are called heteroglycans or heteropolysaccharides.

1.1 Advantages of Natural Polysaccharide

Biodegradability: Biopolymers are naturally available and are produced by living organisms. They represent truly renewable source, and they are easily degraded by microbes; hence, they do not have any unfavorable effect on the environmental well-being.

Non-toxic and biocompatible: Natural polysaccharides being biocompatible are non-toxic and can be used in different commodities, ranging from foods to pharmaceuticals and cosmetics to drug delivery.

Environment-friendly processing: Polysaccharides from various natural sources are effortlessly gathered or harvested in various seasons in substantial amounts because the processes involved in their production are mostly natural and simple.

Low cost: As there is no specialized set up or infrastructure required to produce natural polysaccharide, the cost of production is also much lower compared to synthetic material.

Easy availability: Most of the natural polysaccharides are obtained either from cropping or plants or sea; hence, they are readily available. Also, for most of them production can be increased as per demand, e.g., guar gum.

Gums are important class of biopolymers which are heterogeneous, water soluble or water swellable, high molecular weight polysaccharides extracted from terrestrial or marine plants or from microorganisms. They have gelling capability or ability to contribute viscosity to their dispersions (Abu Baker et al. 2007). Generally, gums are insoluble in nonpolar or organic solvents such as hexane, alcohols, ether, and other hydrocarbons. On hydrolysis, depending on their chemical composition, gums yield mannose, dextrose, rhamnose, xylose, arabinose, galactose, glucuronic acid, galacturonic acid, etc. Due to their unique physicochemical properties, gums have broad applications in both food and non-food industries. All applications rely on the properties given by macromolecules in

various states of hydration, but mostly depend on the properties they impart to solutions and gels.

2 Classification of Natural Polysaccharides

Natural polysaccharides are available in large amounts as they are obtained from large varieties of animals, plants, fungi and microbes, and seaweed sources; where they perform various structural and metabolic functions. Naturally obtained polysaccharides from various sources can be classified as follows (Jani et al. 2009) (Figs. 1, 2 and 3).

Based on their origin/sources, the natural gums are differentiated into four major groups. Out of these four groups, polysaccharides with plant origin are mostly utilized commercially and found in numerous day-to-day life applications.

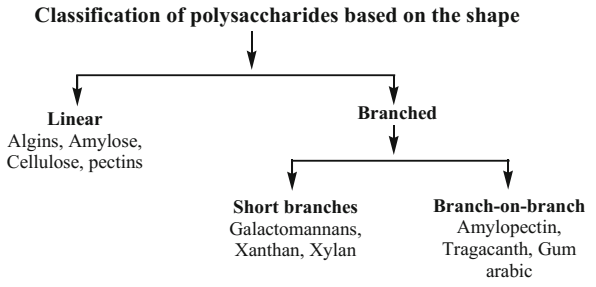

Fig. 1 Classification of polysaccharides based on the shape

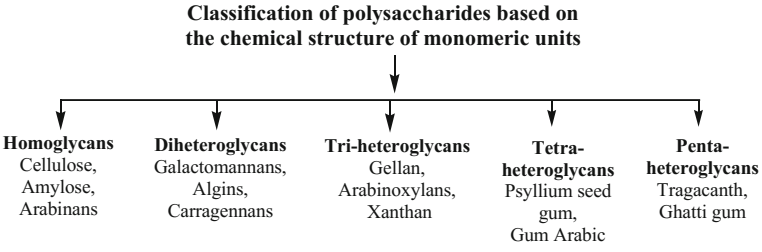

Fig. 2 Classification of polysaccharides based on the chemical structure of monomeric unit

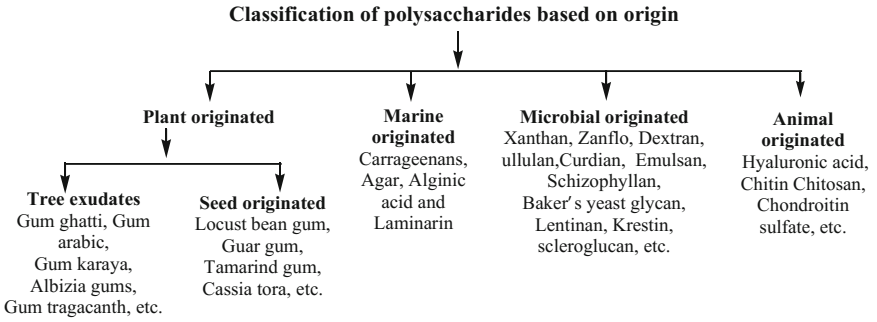

Fig. 3 Classification of polysaccharides based on origin

2.1 Polysaccharides with Plant Origin

2.1.1 Tree Exudates

Exudate gums are one of the oldest natural polysaccharides, which were already being used 5000 years ago as a thickening and stabilizing agents. Exudate gums are formed from the breakdown of internal plant tissues (mainly cellulose) in a process called gummosis. They are exudated naturally from stems, in response to mechanical wounding or after an insect, bacterial, or fungal attack. Though large numbers of gums are available, only few of them could find commercial applications and are produced or collected in substantial quantity. Some of them are discussed below:

Gum Arabic:

Gum arabic is an edible gum and approved as food additive by European Food Safety Authority with E-Number 414. This is obtained from the stems and branches of diverse subspecies of trees and shrubs of genus Acacia, in the form of dried, gummy exudates (Nishinari and Doi 2012). Gum arabic is predominantly collected from *Acacia nilotica* in India and from *Acacia senegal* and *Acacia seyal* in different parts of the world. *A. senegal* and *A. seyal* grow naturally in the semiarid sub-Saharan regions of Africa. Major gum arabic-producing countries are Sudan, Nigeria, Mali, Niger, Burkina Faso, Chad, India, Tanzania, and Kenya. Among these countries, Sudan alone produces 80% of gum arabic, followed by Nigeria which is the second largest producer (Iqbal 1993). *A. senegal* is found in some parts of India mainly in dry rocky hills of south east Punjab, in north Aravalli hills, and in other drier parts of Rajasthan and Gujarat.

Gum arabic has been extensively used as a stabilizer (Chung et al. 2016; Kong et al. 2014), thickening agent and emulsifier (Hosseini et al. 2015), micro-encapsulant (Ramakrishnan et al. 2007), in fruit coating (Addai et al. 2013), corrosion inhibitor of aluminum (Umoren et al. 2006), antioxidant (Gamal el-din et al. 2003; Al-Majed et al.2002, 2003; Abd-Allah 2002) as an adsorbent for heavy

metal (Banerjee and Chen 2007), and also used in lithography, textile, pottery, cosmetics, and pharmaceutical industries (Verbeken et al. 2003).

Karaya Gum:

The Joint Expert Committee on Food Additives (JECFA/FAO) defines gum karaya as the dried exudates obtained from *Sterculia urens* Roxburgh and other related species of Sterculia (family Sterculiaceae) or *Cochlospermum gossypium* (Mbuna and Mhinzi 2003) or other species of *Cochlospermum kunth* (family Bixaceae). The other two contributing species are *Sterculia setigera* and *Sterculia villosa*. Karaya gum is acetylated polysaccharide which on acid or base hydrolysis gives galactose, rhamnose, galacturonic acid with little quantity of glucuronic acid. *S. urens* is indigenous to India having wide distribution. It is abundantly found in the dry deciduous forests of Madhya Pradesh, Chhattisgarh, and central India. Conventionally, India is the largest producer and exporter of karaya gum, while Europe is its largest importer (Verbeken et al. 2003). Gum karaya trees are also found in Australia, Pakistan, Panama, Philippines, Indonesia, Sudan, and Vietnam. Owing to its high viscosity, acid stability, and suspension properties, it is widely used in both non-food and food applications (Verbeken et al. 2003). It is also used for the removal of heavy metals (Vinod et al. 2011), dyes, cationic dyes (Mittal et al. 2016), methylene blue (Mittal et al. 2015a, b), as an excipient for muco-adhesive drug delivery systems (Bahulkar et al. 2015), as a thickening agents (Ibrahim et al. 2010). Other major exudate gums are gum ghatti, albizia gums, salai, jhingan, moringa gum, etc.

2.1.2 Seed Derived

Seeds are also a source of polysaccharides. Most seeds contain starch as the principal food stored for use by the embryonic plant in its initial growth. Most of the plants which are used as food produce seeds with starch as a carbohydrate reserve. Few plant species produce seeds without starch food reserves, which can be harvested to produce the seed gums. More ancient seed gums were extracted from quince, psyllium, flax, and locust seeds, and some of these are still quite important.

Those gum-producing seeds that are amenable to normal agricultural production are lower in price. These are the seeds from annual plants with a normal growing season, which can be grown on agricultural land by normal methods, and which can be planted and harvested by standard agricultural machinery. In the last few decades, guar gum has emerged as very important seed gum.

Guar gum:

Guar gum is one of the outstanding representatives of green and eco-friendly biopolymers. It is a water-soluble nonionic polysaccharide isolated from the seeds of *Cyamopsis tetragonolobus* (Family leguminosae) (Whistler and BeMiller 1993). This plant is cultivated for centuries in semiarid and subtropical areas of India and

Pakistan and in some areas of North Africa and South America. Guar was introduced into the USA from India in 1903 (Whistler and BeMiller 1993). Guar is also known as "Black Gold" because its demand supply pattern has turned it into cash crop and hence a precious commodity. The main guar gum-producing states in India are Rajasthan, Uttar Pradesh, Gujarat, Tamil Nadu, Karnataka, Haryana, Punjab, Madhya Pradesh, and Andhra Pradesh. India is the largest exporter of guar gum to the world and has exported 3388.4 thousand tons of guar gum in 2013–14 (Yogi et al. 2015) to USA, Canada, China, Russia, and Germany (APEDA).

Due to its unique gelling properties and rheology, it is being widely used across various industries such as oil well drilling (Robinson et al. 1982), pharmaceuticals (Celkan et al. 2016; Vollmer 2003), textiles (Aggarwal and Sharma 2010), cement (Blackburn 2004), cosmetics (Vijn et al. 2002), food (Cretois et al. 2000), paper (Anderson et al. 1993), paint, explosives (Thombare et al. 2016), agriculture (Chandrika et al. 2014).

Tamarind gum:

Tamarind seed polysaccharide (TSP) derived from endosperm of tamarind kernels is an important natural polysaccharide. Tamarind (*Tamarindus indica*) is also known as "Indian date." Tamarind is long-lived, medium growth, bushy evergreen tree belonging to the family Fabaceae. Tamarind tree grows well in clayey, loamy, sandy, and acidic soil types, with a high drought and aerosol salt resistance (Joseph et al. 2012). This is liberally found in dry tracks of central and south Indian states, furthermore in other Southeast Asian nations.

Tamarind seed polysaccharide is a multifunctional polymer, which plays the role of stabilizer, thickener, binder (Kulkarni et al.1998), release retardant (Srinivasan et al. 2011), modifier (Kulkarni et al. 2005), emulsifying agent, and suspending agent (Deveswaran et al. 2009), as a carrier for novel drug delivery systems for oral (Alka et al. 2011; Srinivasan et al. 2011), buccal (Patel et al. 2009; Bangale et al. 2011; Jana et al. 2010), colon (Mishra and Khandare 2011), ocular systems (Rolando and Valente 2007; Mehra et al. 2010), nanofabrication, wound dressing (Patil et al. 2011; Burgalassi et al. 2000), food (Shirakawa and Yamatoya 2003; Glicksman 1996), cosmetics, confectionery, bakery, etc.

2.2 Marine Origin

Gum extraction from seaweeds which was originally practiced in oriental countries has spread to many parts of the world where shallow waters and seaweeds are abundant. The cost of production of seaweed extracts are soared up due to tedious harvesting and processing practices used in the extraction processes, which remove a large portion of the dry weight of the weeds. When harvesting is done manually, as with agar weed, or when the seaweeds are picked from beaches where they are deposited by the tides, labor costs become high. These days, advance engineering

practices are being used for harvesting and collection of seaweeds, e.g., harvesting of giant kelp (*Macrocystis pyrifera*) in California. Cut kelp is collected and lifted by a rake to the barge top where it is stacked with a claw on a drag line. By such simple mechanical means, many tons of trimmings can be harvested rapidly and brought to the processing plant on the coast. Rapid growth of the kelp beds permits retrimming within a few months. Such standard mechanical practices lower harvesting cost and tend to stabilize weed cost at the extraction point. Few important marine polysaccharides are discussed here.

Carrageenans:

Carrageenans are straight sulphated polysaccharides extracted from cell wall of red sea weed of the Rhodophyceae class. Seaweeds commonly used for the carrageenans are *Kappaphycus alvarezii* and *Eucheuma denticulatum* (McHugh 2003). These seaweeds are harvested, washed several times with seawater to remove sediments, and sun-dried until they acquire 30–40% moisture content. Major countries producing carrageenans include Indonesia, Tanzania, Malaysia, Philippines, Kenya, Kiribati, Fiji, and Madagascar. Overall business sector volume now surpasses 140,000 tons per annum with an estimation of more than $70 million (Bixler and Porse 2011). Primarily, wild-collected genera, for example, Gigartina, Chondrus, Mazzaella, Furcellaria, Sarcothalia, Iridaea, Mazzaella, Tichocarpus, and Mastocarpus, are additionally delivered as carrageenan crude materials. Carrageenan-producing nations also include Japan, North Korea, Canada, Argentina, Russia, Chile, Spain, Denmark, South Korea, France, Mexico, Portugal, Spain, USA, and Morocco. Carrageenan has numerous applications in both food and non-food industries (Hambleton et al. 2009; Necas and Bartosikova 2013) and can be utilized as stabilizer (Hsu and Chung 1999) in dairy items, for example, flavored products (Varela and Fiszman 2011), pet nourishment (McHugh 2003), newborn child sustenance, and dietary supplement refreshments. Carrageenan have been utilized to postpone microbial development in gels containing antimicrobial agent (Varela and Fiszman 2011). The capacity of suspending cocoa in chocolate milk at low concentration is special in carrageenan (Necas and Bartosikova 2013). Mostly, they are utilized as a part of pharmaceuticals, beautifying agents, printing and as a material for commercial enterprises (Cosenza et al. 2014).

Alginate:

Alginate is a water-soluble straight anionic polysaccharide, isolated from cell wall of brown algae *Ascophyllum nodosum* and *Laminaria digitata,* where it as present as magnesium, sodium, and calcium salt of alginic acid (Vu and Won 2013; McHugh 2003; Hambleton et al. 2011). Microorganisms can also produce alginate (Blanco-Pascual et al. 2014; Alboofetileh et al. 2014).

Among the world edible seaweed producers, China ranks first with a production of about five million tons and most of this is for Kombu, obtained from *Laminaria japonica* grown on hundreds of hectares on suspended ropes in the oceans. Korea mainly grows three species and produces eight million tons, and almost 50% of this

is for Wakame obtained from *Undaria pinnatifida* in a similar way to that of Laminaria in China. Japan produces about six lakh tons mainly from three species, among these species 75% of this for Nori, obtained from *Porphyra* sp.

Alginate has wide range of applications and can be used as a colloidal stabilizer, gel forming agent, and thickening agent in beverage industries (Liakos et al. 2013), as an anti-dehydrating agent on natural products such as fruits, meat, and fish (Hambleton et al. 2011; Varela and Fiszman 2011), for encapsulation of protein, DNA, drugs, cell, etc. (Ashikin et al. 2010), as a binder in fish feed, welding rods, paper, releasing agents, and immobilizing catalyst and also used in medical and pharmaceuticals, and material printing (Vu and Won, 2013).

2.3 Polysaccharides with Microbial Origin

Microbial polysaccharides are extracellular polysaccharides produced by certain microorganisms. Such gums are fashioned by selected, and perhaps carefully mutated, organisms growing on low-cost energy sources, such as grains or molasses. A variety of microbial origin gums having different physicochemical properties are already available and many more can be found. Thus, a class of fermentation gums may be developed to cater to the numerous industrial needs. Homoglycans comprising of one kind of sugar unit can be made, as exemplified in the generation of dextran. However, synthesis of enzyme-catalyzed polysaccharides from simple sugars and enzyme modification of existing polysaccharides will eventually develop and become common technique in future. Important microbial polysaccharides include:

Xanthan:

China is the world's largest producer of xanthan and exports about 66% of its produce to the world. Countries such as USA, Australia, Japan, and France are other producers and exporters of xanthan gum. Xanthan is complex extracellular bacterial exo-polysaccharide produced by the yellow-pigmented gram-negative bacteria *Xanthomonas campestris* (Ielpi et al. 1981; Ashraf et al. 2008). Xanthan is an anionic, acidic polymer produced by microbial fermentation of glucose. It is chemically composed of repeating units of pentasaccharide having two units of mannose, two units of glucose and a glucuronic acid (Becker et al. 1998). The anionic nature of xanthan is because of the presence of two acidic groups, i.e., glucuronic acid and pyruvic acid in the side chain (Sandford and Baird 1983). Xanthan is highly stable over wide range of pH and temperature and also resistant to enzymatic hydrolysis. It is highly water-soluble gum and also shown synergistic interaction with other gums. These properties are very unique to xanthan gum, and it makes it versatile hydrocolloid with applications in many industries such as pharmaceuticals as a stabilizer, film forming, thickening, gelling agent, and emulsifier. It is also used in agriculture, paint, oil, paper, cosmetics, and textile

industries. Xanthan gum finds applications in petroleum production, oil well drilling fluids, fracturing, pipeline cleaning, enhanced oil recovery (EOR), textile printing and dyeing, ceramic glazes, cleaners, slurry explosives. In food industry, it is used in dressing, dry mixing, beverages, dairy products, and baked foods. Besides, it is used in animal feed, agricultural chemicals, pharmaceuticals, and cosmetics.

2.4 Polysaccharides with Animal Origin

Chitin and chitosan:

Chitin is the second most ubiquitous natural polysaccharide after cellulose on earth. It is a hard and inelastic polysaccharide, found in invertebrate exoskeleton and internal structure. Chitin and chitosan are very promising biomaterials. The deacetylated chitin derivative, chitosan, is more useful and interesting bioactive polymer. It has many reactive amino side groups, which offer possibilities of chemical modifications, formation of a large variety of useful derivatives that are commercially available or can be made available via graft reactions and ionic interactions.

Due to its unique physicochemical properties, it is being used in number of industries such as cosmetics (Libio et al. 2016), textiles (Dutta et al. 2002), food processing (Klein et al. 2010), agriculture (Kashyap et al. 2015), photography (Dutta et al. 2002), chromatographic separations (Rhee et al. 1998), and biomedical applications such as tissue engineering (Pangon et al. 2016; Suh and Matthew 2000), burn treatment (Sohrabi et al. 2016), ophthalmology (Cheng et al. 2016), wound healing/wound dressing (Dragostin et al. 2016), and drug delivery systems (Soares et al. 2016; Pathania et al. 2016).

3 Chemical Modification of Polysaccharides

The natural raw polysaccharides have wide applications, yet there is a lot of scope to enhance their applications by improving their physicochemical properties. Properties of natural raw gum can be improved or modified by chemical methods such as grafting, derivatization, and cross-linking by least affecting its inherent properties. This is because chemical modification yields the hybrid derivatives of raw polysaccharides, which can fit into various applications (Zhang et al. 2005). For example, by synthesizing the hybrid derivatives of guar gum such as hydroxypropyl or carboxymethyl, its properties such as solubilization time, viscosity, and clarity of solution can be significantly improved (Dumitriu 2002).

3.1 Grafting

Graft copolymerization is one of the powerful tools for the modification of biopolymers as it functionalizes these natural polymers with improved and desirable properties. Therefore, these days much attention has been paid to grafting method as a tool for chemical modifications (Mishra et al. 2010; Tripathy et al. 2009). Grafting of natural gums can be done by various methods such as microwave irradiation (Pal et al. 2011; Adhikary et al. 2011), chemical initiator, or γ-radiation (Abdel-Halim and Al-Deyab 2011; Srivastava et al. 2007). The grafted polymers can be utilized in drug delivery, pharmaceuticals, and agriculture for controlled release of nutrient and agrochemicals.

3.2 Derivatization

Another method for the improvement of physicochemical properties of polysaccharides is derivatization. A large number of natural polysaccharide-based derivatives have already been synthesized and many more will be added in the future. Some of derivatized products of natural polysaccharides which are synthesized, characterized, and evaluated for their applications are dodecenyl succinic anhydride gum arabic (Wang et al. 2014) hydroxymethyl guar gum (Lapasin et al. 1991), hydroxypropyl guar gum (Lapasin et al. 1995), o-carboxymethyl-o-hydroxypropyl guar gum (CMHPG) (Shi and Zhang 2007), quaternary ammonium chitosan derivatives (De-Oliveira-Pedro et al. 2016), triazolyl-functionalized chitosan derivatives (Li et al. 2015), amphiphilic alginate-amide derivatives (Vallée et al. 2009), thiolated karaya gum (Bahulkar et al. 2015), carboxymethyl cellulose derivatives (Monier et al. 2016), metallo-terpyridine carboxymethyl cellulose derivatives, etc.

3.3 Cross-linking

Natural gums are biopolymers having numbers of free hydroxyl groups in their linear or branched long chain, which on dispersion in water form viscous solution. This is due to interaction of free hydroxyl groups of gum with water molecules by forming intra- and intermolecular hydrogen bonding, which increases viscosity of solution. Natural raw gum as such cannot be used as hydrogel due to low swelling and water-holding capacity, but it can be improved by using the synthetic cross-linkers. The cross-linker binds the chains of biopolymers by chemical or physical means and increases the stability, swelling, and water-holding capacity of hydrogels. This is because the cross-linkers undergo intra-molecular bonding with hydroxyl group of biopolymers and form a three-dimensional structure (Fig. 4).

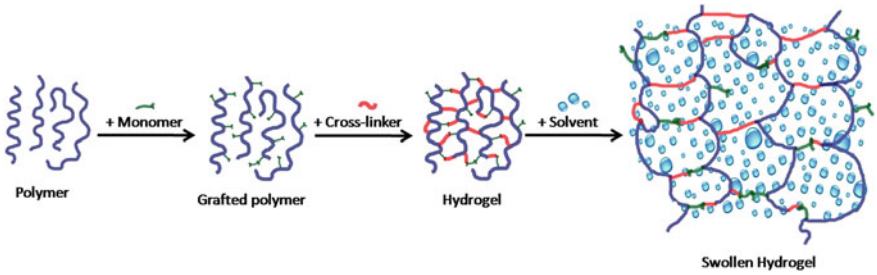

Fig. 4 Schematic diagram of synthesis of hydrogel through grafting and cross-linking

When water is added, the molecules of water are entrapped in this three-dimensional structure and cannot escape easily. Commonly used cross-linkers are methylene-bis-acrylamide, divinyl-benzene, glutaraldehyde, derivatives of ethylene-glycol-di(meth)acrylate, etc.

Hydrogels are three-dimensional matrix constituted by linear or branched hydrophilic polymers that are cross-linked chemically or physically, with the ability to absorb large quantity of water or biological fluids (Chang et al. 2010; Pourjavadi et al. 2004). Further, even in the swollen state hydrogels keep their network stable because of their cross-linked structure which imparts stability in different environments. The final properties and applications of hydrogels depend on the type of cross-linking methods used for hydrogel preparation. Important properties such as water uptake, swelling, kinetics, rheological properties, porosity, degradation rate, and toxicity are closely related to cross-linking methods (Bordi et al. 2013; Ahmed 2013). Therefore, hydrogels are synthesized to possess properties such as fast swelling, porosity, degradability. Due to these properties, they find applications in many fields such as biomedical (Pangon et al. 2016), agriculture (Pourjavadi et al. 2007), cosmetics, tissue engineering (Kim et al. 2007), drug delivery (Rodríguez et al. 2003; Zhang et al. 2002), biosensors (Adhikari and Majumdar 2004; Pourjavadi et al. 2007), and sorbents for the removal of heavy metals (Guilherme et al. 2007).

The structural strength of hydrogels depends upon the nature of bonds (Chemical or physical) between the biopolymers and the cross-linker (Kamath and Park 1993). Hydrogels can be classified on the following basis:

- Physical structure: hydrogen bonded or supramolecular, amorphous, or semicrystalline;
- Electric charge: neutral or ionic (charged);
- Cross-link: chemically or physically cross-linked;
- Responses to external stimuli: sensitive and insensitive;
- Origin: natural, semisynthetic, and synthetic.

After the first polymerization of acrylic acid and divinylbenzene in 1938, it took a decade for the first group of hydrogels to become commercially viable. These hydrogels were made of hydroxyalkyl methacrylate and other monomers having

similar structures. However, they had swelling capacity of only 40–50% and were used for production of contact lenses. HSPAN (hydrolyzed starch-polyacrylonitrile) was developed in the 1970s by USDA as first commercial superadsorbent hydrogel by alkaline hydrolysis of starch-grafted polyacrylonitrile (Buchholz and Peppas 1994). The product could not succeed because of its poor mechanical properties and high cost. The polymeric material used for hydrogel preparation affects its hydrophilicity and biodegradability. Polyacrylamides and acrylates have been extensively used over the years for synthesis of highly hydrophilic hydrogels (Laftah et al. 2011; Rodrigues et al. 2014).

However, increasing environmental concerns have led to the development of hydrogels based on natural polymers. Among natural polymers, polysaccharides have been widely used to develop hydrogels due to their high hydrophilicity, compatibility, low cost, and biodegradability (Wang and Wang 2010a, b; Wang et al. 2013). The interconnected porous structure of hydrogel materials leads to high water absorption capacity by capillary action (Kuang et al. 2011; Hemvichian et al. 2014). Various natural polymers such as starch, chitosan, chitin, pectin, gum arabic, cashew gum, and others have been used to develop hydrogels for specific use in biomedical, agriculture, biotechnological, and wastewater treatment applications (Omidian et al. 2005; Kazanskii and Dubrovskii 1992; Mekonnen et al. 2013; Rinaudo 2006; Heinze et al. 2006).

4 Applications of Hydrogels in Agriculture

In recent years, the use of biopolymer-based hydrogels in agriculture has been widely studied because they are ecologically and economically viable alternatives for soil conditioning and water and nutrient retention (Kazanskii and Dubrovskii 1992). Also, these biopolymer gels are biodegradable, non-toxic, and abundantly available and have great application potential (Sinha and Kumria 2001; Thakur et al. 2015; Thakur and Kessler 2015). Hydrogels are suitable for use in agricultural fields because of their susceptibility to degradation by physical, chemical, and microbial agents (Baldrian and Valášková 2008; Villay et al. 2012). These materials retain water and nutrients and release them over a long period of time. The rate of release of nutrients throughout the degradation of hydrogel can be made harmonious to the plant nutrient requirements.

The polysaccharides in their native form may not produce hydrogels stable enough for use as pesticide or nutrient carriers in agriculture. These hydrogels are prepared using physical or chemical methods of cross-linking or both. Various polysaccharides such as gum arabic, cashew gum, starch, and pectin have been modified by introducing vinyl groups to develop hydrogels (Fajardo et al. 2013; Sannino and Nicolais 2005; Lionetto et al. 2005; Marcì et al. 2006; Sannino et al. 2003).

Though large numbers of hydrogels have been developed at laboratory stage, only very few satisfy the requisite environment safety parameters such as

biodegradability and non-toxicity for their use in agriculture (Pillai 2010). Economic considerations also play a major role in final release of the product in the market. The use of hydrogel for water retention and as soil conditioner has been investigated long back in 1966. The commercial sale of these hydrogels started in the 1980s mainly as disposable diapers (Castel et al. 1990; Kataja et al. 1992). In later years, various reports on the structure and properties of such hydrogels were published owing to the growing interest in commercialization of these materials for use in agriculture (Buchholz and Graham 1998). The most common application method of these hydrogels in agriculture is by mixing granular hydrogel particles in soil at required concentration.

4.1 Water Retention

Globally, agriculture is predominantly dependent on rainfall. Around 65–95% of cultivated land in sub-Saharan Africa, Latin America, North Africa, East Asia, and South Asia is under rainfed agriculture (IWMI 2010). Uncertainties in frequency and pattern of rainfall in arid areas result in crop losses every year. Climate change has further aggravated the problem of water scarcity. Various methods are being employed to increase the water use efficiency in agriculture. One of the strategies is to use water retainers to grab and preserve limited irrigation or rainwater for a prolonged period. Owing to their water imbibing property, hydrogel materials are being widely investigated for water retention in agriculture. For example, in sandy areas the use of hydrogels may help in improving the water-holding capacity and thus the growth and quality of crops (Wang and Wang 2010a, b). The hydrogel particles act as miniature reservoirs through which water is drawn when required by the osmotic pressure difference. The use of hydrogels in agriculture is showing very good results. Some of the advantages of hydrogels can be listed as follows (Lee and Mooney 2001; Shalviri et al. 2010; Ulery et al. 2011):

- Reduction in requirement of water for irrigation purpose,
- Increase in availability of soil water which results in longer survival of plants under stress conditions,
- Improved fertilizer use efficiency and decreased contamination of ground water,
- Decrease in plant evapotranspiration rate,
- Improved soil physical properties such as reduced compaction and better soil aeration,
- Enhanced microbial activity,
- Prevention of excess runoff and thus reduction in soil erosion,
- Adsorption of heavy metals and reducing their effect on plants,
- Maintenance of soil moisture that helps in reducing the effects of salinity, and
- Better germination and establishment of seedlings.

Hydrogels are known for their capacity of absorbing large amounts of water. Materials commonly used as absorbents exhibit absorption capacity of around hundred times of their weight; in case of hydrogels, it increases up to thousand times. For example, Guilherme et al. (2005) synthesized a hydrogel having water absorption capacity of 1500 times. The hydrogel was prepared by copolymerization of cashew gum with acrylamide followed by partial hydrolysis of the acrylamide repeat units. Hydrogels have such high water absorption capacity due to the thermodynamic compatibility found between functional groups of hydrogel matrix and water molecules.

Most of the times, the electrically charged groups (ions) of the hydrogel material are responsible for electrostatic affinity toward water molecules during the swelling phase of absorption. Also, the hydrophobic units of the network structure interact with water molecules by weak van der Walls forces. The free water present in soil is absorbed into hydrogel by osmosis. When all the hydrophilic and hydrophobic sites are occupied, the water molecules fill the empty spaces present in hydrogel matrix. Therefore, the porosity of the hydrogel material, as well as polymer chain density and extent of cross-linking, affects the water absorption capacity of the hydrogel. On the other hand, the mechanical strength and rheological properties of the hydrogel are dependent on the degree of swelling. A high swelling capacity may significantly reduce the mechanical strength. The swelling of hydrogels by absorption of high amounts of water is the characteristic property for their use in water retention, nutrient delivery, and maintenance of various soil properties (Ramezani et al. 2013; Campos et al. 2015). Poor mechanical strength becomes significant drawback of such materials when higher and higher amount of water is absorbed (Omidian et al. 2005). Recently works have been done to overcome this problem by using materials such as nanofibrils and nanowhiskers as fillers for better mechanical strength (Rodrigues et al. 2014; Cheng et al. 2012; Spagnol et al. 2012). The use of filler material helps in obtaining hydrogels having high absorption capacity as well as mechanical strength.

Among natural biopolymers, starch has advantage for use in hydrogel preparation because it is abundant, cheaper, and suitable for chemical modification. Starch also has better plasticity and mechanical resistance. Guilherme et al. (2012) chemically modified starch with glycidyl methacrylate using 4-(*N*,*N*-dimethylamino)pyridine and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine as catalysts. The resultant product undergoes hydrogelation by free-radical reaction. The free-radical polymerization reaction was carried out in the presence of acrylic acid and acrylamide assisted by ultrasound. The material displayed 150 times absorption of its dry weight in a duration of 200 min.

Similarly, hydrogels based on gum arabic were prepared by using glycidyl methacrylate (GMA) for modification (Guilherme et al. 2007). Organic solvents and toxic reagents are no longer used for modification process and are replaced by GMA. Vinylated gum arabic has been obtained without catalyst by using water as solvent. As GMA is insoluble in water, the system was stirred at high speed at 60–65 °C. The modification reaction occurs at the interface layers of GMA and water. The hydrogel cross-linking was done by reaction with sodium acrylate and

acrylamide. The product absorbed water 500 times its dry weight and showed good mechanical strength.

Pourjavadi and coworkers used agar for development of superabsorbent hydrogels. Graft copolymerization of acrylic acid and 2-acrylamido-2-methylpropane sulfonic acid was done over agar in aqueous medium. A persulfate initiator was used along with a bifunctional hydrophilic cross-linker. The swelling capacity of the final product varied with changes in reaction parameters. Maximum of 1100 g/g water absorption capacity at optimized reaction conditions was reported by the authors (Pourjavadi et al. 2007).

4.2 Soil Conditioners

A soil conditioner is defined as any synthetic organic chemical or chemically modified natural substance that stabilizes soil aggregates, and/or favorably modifies the structural or physical properties (Aslam 1990). Synthetic polymers when used as soil conditioners improved the physical properties of soil, increased crop growth, and reduced soil erosion (Boodt 1975). The use of hydrogels in agriculture as such has not been prevalent because of high cost. Scarcity of water and desertification of soils are one of the most severe anthropogenic problems in about one-third of lands around the world. To feed the ever-growing population, it is necessary to restore these degrading lands. As these lands are also low in organic matter content, hydrogel materials when added to these soils can act as humus like substance because of their hydrophilicity and free carboxylic groups. Therefore, along with water retention, these hydrogels also increase cation exchange capacity and overall physical properties of the soils (Hüttermann et al. 2009). Hydrogels have been successfully utilized as soil conditioners in horticultural crops for increasing water and nutrient retention in sandy soils (Bouranis et al. 1995). Hydrogels affect various soil properties such as soil structure, porosity, density, texture, permeability, and water infiltration. They reduce evaporation and irrigation requirement, reduce erosion, and enhance aeration and micro-flora activity (Abd El-Rehim et al. 2004).

Hydrogel can act as reclamation agent for light sandy soils and for substrates in hydroponics as it imparts various soil properties which are present in normal arable land (Azzam 1985). The optimum concentration of application of hydrogel depends on various factors such as age and nature of the plant as well as soil properties and environmental conditions. Generally, 0.05–0.1% dry hydrogel is applied with seeds during planting (Zohuriaan-Mehr 2006). In case of forestry, hydrogel can be used during transplantation. Hydrogel can be applied over tree roots when they are transported for transplantation to prevent them from drying. Hydrogel composites have been used in dry areas of China to grow rice, soybean, sugar beet, etc. It was found that the hydrogels increased the yield of rice, soybean, and sugar beet crops (Gao 2003).

Several workers have investigated on application of hydrogels as soil conditioners. Saponified cassava-based starch-graft-poly(acrylamide) hydrogels were

evaluated for their effect on physical, chemical, and biological properties of soil and growth-related parameters of chilly (*Capsicum annum* L.) at different irrigation intervals (Parvathy and Jyothi 2012). It was reported that the moisture retained in the soil was dependent on the concentration of hydrogel which provided a controlled release of absorbed water. These hydrogels can be utilized to combat climate change mainly in moisture stress conditions as they improve the soil moisture levels and physicochemical properties. Agaba et al. (2011) reported that moisture retention by using hydrogel is effective for plantation trees in forest establishment and influences the plant growth and various soil properties such as temperature, aeration, nutrient uptake, transport, and transformation. Demitri et al. (2013) studied the feasibility of carbodiimide cross-linked cellulose hydrogels in arid areas. Three formulations of the hydrogel were used for controlled release of nutrients along with water. It was reported that the water stored in hydrogel is released as the soil dries, and thus, moisture levels are maintained for longer durations.

Hydrogels also increase the soil porosity and provide better aeration to plant roots. Chemically modified pectin-based hydrogels were studied for release of urea, phosphate, and potassium (Guilherme et al. 2010). Swelling capacity of hydrogels was measured in saline and distilled water at different pressures. It was concluded that these hydrogels can conserve moisture in a pressure range in which a large variety of horticultural crops can absorb water. Therefore, such hydrogels can be used as soil conditioners. Effect of hydrogel type and concentration on germination and growth of maize (*Zea mays*) was investigated (Abd El-Rehim et al. 2004). The plant growth parameters such as plant height, dry weight, and leaf width were increased with concentration of hydrogel. It was reported that the polyacrylate-based hydrogels improved soil physical properties and reduced the wilting period. Optimum concentration of hydrogel was investigated for its use in soils of Haouz, Morocco. Apart from the water retention capacity of the hydrogel, the study also focused on effect of pH and ions present in soil. The polymer was found to increase the water retention in soil and reduce the irrigation requirement (Bakass et al. 2001).

Hydrogels were evaluated for use as conditioners to help the establishment and growth of plant in limited irrigation conditions. Starch copolymer and polyacrylamide copolymer were studied for their effect on growth of barley and lettuce in sandy soil medium (Woodhouse and Johnson 1991). The use of hydrogel increased the period between field capacity and wilting by 300%. Total dry matter produced and the water use efficiency were also increased by hydrogel use. Effect of hydrogel on emergence and growth of seedling were studied. The starch-based hydrogels prepared by graft copolymerization with acrylic acid and acrylamide were studied. It was reported that the water-absorbing capacity of hydrogels depends on water conductivity. The use of these hydrogels increased the overall water retention capacity of soil (Chen et al. 2004). A commercial hydrogel (Stockosorb K 400) was evaluated for growth of *Pinus halepensis* seedlings in water stress conditions (Hüttermann et al. 1999). Maximum survival of plants was observed when the hydrogel concentration was highest.

Poly(AA-ethyl acrylate-vinyl acetate) hydrogel was found to increase the growth and germination of soyabean (Knypl and Knypl 1993). It has been found useful in decreasing the evaporation loss from soil and water consumption of the crop as well. When plants were inoculated with Frankia and hydrogel polymer, the root nodules showed better growth (Kohls et al. 1999). Polyacrylamide-based hydrogels were prepared by Raju and Raju (2001) and were evaluated for their soil conditioning properties. The hydrogels showed better water retention and growth in sunflower and bean crop. Hydrogels derived from guar gum have also been reported for their use as soil additive (Lokhande and Varadarajan 1992). Chu and coworkers prepared composite hydrogel made up of Polyacrylic acid and sodium humate (Chu et al. 2006). It was synthesized by acrylic acid graft copolymerization on sodium humate. The composite hydrogel was evaluated and found to have positive effect on the growth of maize crop.

Abedi-Koupai and coworkers studied the effect of hydrogel on water absorption in soil and other plant growth parameters (Abedi-Koupai and Sohrab 2004). Application of hydrogel and its effect on water retention properties of three different soils of Iran was investigated. Plant growth parameters of *Cupressus arizonica*, an ornamental plant in water-stressed conditions were also determined (Abedi-Koupai and Asadkazaemi 2006). The residual water and saturated water contents were reported to increase by use of hydrogel. Application of 6 g/kg hydrophilic polymer in sandy loam soil resulted in 2.3 times increase in available water.

Apart from crop plants, hydrogels have also been evaluated for use in cultivation of mushrooms. Sook and coworkers evaluated the effect of hydrogel as medium for growth of edible mushrooms, *Pleurotus sajor-caju* and *Hericium erinaceus* (Sook and Jae-Sik 2000). The hydrogel improved the mycelial growth and production of sporophores of mushrooms. The optimum hydrated level concentration of hydrogel was determined to be 2–2.5 g/cm^3.

Hydrogels have also been studied for use in landscaping and turf grasses (Quinn 1990). The use of hydrogel reduced the amount of irrigation required for maintenance of turf grass especially in hot summer conditions. Hydrogel also improved the density, color, and coverage of turf.

4.3 Nutrient Delivery

Plant nutrients when applied to soil are subject to various forms of losses such as leaching, volatilization, runoff. Therefore, only a portion, about 20–25% of applied nutrients is available to crops and the loss of nutrients in leaching, chemical processes, excess rains, and runoff also results in contamination of groundwater and eutrophication of surface water bodies. Out of these, nutrient loss by leaching is high in porous sandy soils. An alternative approach that has been more recently investigated involves the controlled release of nutrients from the fertilizer-loaded hydrogels (Ni et al. 2009, 2011; Guilherme et al. 2010; Davidson and Gu 2013; Aouada et al. 2008; Zhou et al. 2014).

A controlled release system is aimed at protecting the reserve of active ingredient for releasing it in a slow controlled rate so that the concentration in the target system is maintained at optimum levels for extended period of time without affecting the efficiency. Controlled release application of agrochemicals is helpful in maintaining their concentration in the soil at optimum level and also reduces runoff losses (Aouada et al. 2011). A variety of biopolymers such as cellulose, chitin, tragacanth gum, guar gum have been used for controlled release application of fertilizers (Jamnongkan and Kaewpirom 2010; Guilherme et al. 2010; Buchholz and Graham 1998; Saruchi et al. 2014).

Various controlled nutrient release hydrogels based on natural polysaccharides have been found to enhance the efficiency of agrochemicals by reducing their cost, toxicity, and environmental pollution (Noppakundilograt et al. 2015). Another advantage is that a sustained release of optimum level of nutrients can be achieved in one application.

The nutrients in hydrogels are loaded by two approaches, viz. post-synthesis loading and in situ loading. Post-synthesis loading is done after the processing of hydrogel, while in situ incorporation occurs during the hydrogel processing itself. In the post-synthesis approach, the hydrogel is swelled together with active ingredient which diffuses inside the swollen polymer matrix by absorption. The effectiveness of this method depends upon the physical and chemical affinity of the active ingredient for the polymeric network of the hydrogel. In case of in situ loading, the nutrient is incorporated in hydrogel material during synthesis and remains in dried form before adding to the soil. The hydrogel swells by irrigation or rainwater, and the release of nutrient is activated. The water absorbed in hydrogel dissolves the nutrient which can diffuse out through the polymer matrix (Fig. 5).

The release of nutrients outside the hydrogel matrix is affected by the swelling rate (Ruvalcaba et al. 2009; Gil et al. 2007). The whole quantity of nutrients present in the matrix is not released, and a portion of it remains as reserve during drier periods. When irrigation or rainwater appears, the release mechanism is activated again, thereby providing a prolonged supply of nutrients with minimum leaching losses. The in situ method is better as it has higher loading efficiency when compared to post-loading method (Zheng et al. 2007). More than one active ingredient

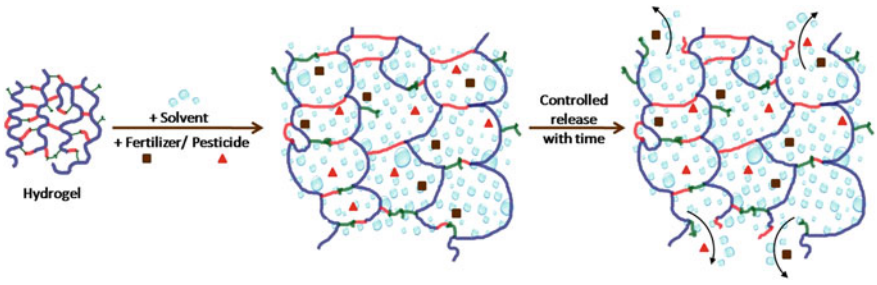

Fig. 5 Entrapping of fertilizer/pesticide and their controlled release through hydrogels

can be added to single hydrogel, each one of them having separate specific rates of release. This way, the cost of application can be reduced.

Optimum availability of water and nutrients in soil is important for growth of agricultural crops. The levels of essential nutrients such as nitrogen, phosphorus, potassium, calcium, sulfur, copper, iron, and boron are often depleted and are supplemented by addition of fertilizers and manures (Saruchi et al. 2014). There are leaching losses from 40 to 70% of applied nitrogen and 50 to 70% of potassium which require application of large quantities of fertilizers (Wu and Liu 2008), and consequently, this results into environmental pollution. Therefore, the use of polysaccharide-based chemical cross-linked hydrogels has been studied for controlled release of fertilizers in soil (Wu and Liu 2008; Wang et al. 2014; Shaviv 2001). Chemically cross-liked hydrogels for nutrient release have been more reliable than coated polymers (Zheng et al. 2009). The nutrient delivery in chemically cross-linked hydrogels is dependent on the concentration gradient of nutrient from inside of hydrogel to external medium and therefore can provide nutrient as per the requirement of the plant (Zheng et al. 2009). Other than the nutrient flow by concentration gradient, processes such as diffusion, convective flow, and chain relaxation also take place. These processes can be described by Fickian or non-Fickian mathematical models. There may be combination of diffusion and convective flows resulting in controlled nutrient release (Shaviv 2001; Wang et al. 2011; Shavit et al. 1997). Macromolecular chain relaxation of polymeric hydrogels occurs by swelling and deswelling (Brazel and Peppas 1999). However, other than these processes, the absorption of water and release of nutrients depends upon the type of polymer and density of cross-linking during the synthesis of polymeric hydrogel as well as the pH and ionic strength of the solution.

Guilherme and coworkers reported that swelling properties of superabsorbents based on modified pectin in saline solutions were of same order that of distilled water and were not affected by presence of salts (Guilherme et al. 2009). These hydrogels showed controlled release of urea, phosphate, and potassium. Xu and coworkers prepared acrylic acid and diallyl-dimethyl-ammonium-chloride based amphoteric hydrogels by solution polymerization for controlled release of ammonium nitrate (Xu et al. 2005). The ratio of anionic groups to cationic groups was varied to obtain different hydrogels. The effect of salt concentration, pH of solution, and temperature was also investigated. The hydrogels having lower ratio of anionic group to the cationic groups had better swelling capacity and tolerance to high salt concentration. These hydrogels were found to be effective for release of ammonium nitrate.

Methylcellulose- and polyacrylamide-based hydrogels were evaluated by Bortolin and coworkers for controlled release of two fertilizers, viz. ammonium sulfate and potassium phosphate (Bortolin et al. 2012). The addition of methyl cellulose with polyacrylamide increased the amount of total fertilizer loaded and prolonged their release. Loading amount as well as release of fertilizers was affected by the hydrophilicity of the polymer decided by the ratio of acrylamide to methylcellulose. Recently controlled release fertilizers based on graphene oxide

were prepared by Zhang and coworkers (2014a, b). The fertilizers encapsulated with films of graphene oxide had their release prolonged by 8 h.

4.4 Pesticide Carriers

Pesticides in soil are also subject to leaching and runoff losses which may contaminate groundwater and surface water bodies causing serious hazards. These losses can be minimized by using slow release pesticide systems. Controlled release of pesticides benefits crops for longer periods and reduces the dosage and number of application. In conventional agriculture, application of excessive quantity of agrochemicals is being practiced to get quick results. But actually, the use of pesticides beyond recommended doses in the greed to get quick results leads to their discharge in the environment affecting non-target organisms and causes environmental pollution (Bajpai and Giri 2003; Thakur and Thakur 2014). Due to overuse of the chemicals, resistance can be developed in the target pests toward the pesticide. By adopting controlled release of agrochemicals, pesticide-related health hazards can be minimized and residues on food stuffs can also be controlled which eases handling of the harvested product (Tsuji 2001).

The delivery of agrochemicals using controlled release polymer matrix offers several advantages by avoiding the use of surplus amounts of active substances and also delivers active ingredient slowly over a period of time (Wang et al. 2007). It also reduces quantity of active ingredients required for obtaining same results over a particular time span due to which other plant or animal species are least affected (Aouada et al. 2011).

Based on mode of functioning, controlled release polymer systems are divided into two groups (Mitrus et al. 2009). The first is one where active ingredient is dissolved, dispersed, or encapsulated within the polymeric matrix. Here, the release takes place by diffusion or through biological or chemical breakdown of the releasing polymer. In the second category the active ingredient either constitutes a part of the macromolecular backbone, or is chemically or physically attached to it. After biological or chemical cleavage of the bond with the polymer, the bioactive agent is released in the surrounding matrix.

The advantages of the controlled pesticides release systems include reduced toxicity, increased efficacy, lesser environmental impact from pesticides and their applications, and reduced potential transportation hazards. It also addresses new product development through which advanced pesticide delivery technologies can be facilitated (Aouada et al. 2011; Abd-El-Rehim et al. 2005). Therefore, it is economical and reduces the environmental load of pesticides. Several biopolymers have been tried as matrices for controlled release of agrochemicals.

Kenawy in 1998 synthesized cross-linked polyacrylamide gels by using the free-radical polymerization technique (Kenawy 1998). Further, their derivatives were prepared by trans-amidation with different diamines such as ethylenediamine, hydrazine hydrate. The synthesized gels were studied for release of

2,4-D (2,4-dichlorophenoxyacetic acid) herbicide. The release from the matrices was examined and estimated at 25 °C in water solution buffered at pH 4, 7, and 9 by UV–Vis spectrophotometer. Results revealed the pH-dependent release of 2,4-D, which was lower at pH 4 than in neutral or alkaline medium. Cross-linked polyacrylamide hydrogels trans-amidated with bis-(3-aminopropyl) poly(tetrahydrofuran)-1100 showed the best release rate.

Kulkarni et al. (2000) studied the encapsulation and release rate of a natural liquid pesticide "neem seed oil (NSO)" derived from seeds of *Azadirachta indica*, using sodium alginate as a vehicle carrier and glutaraldehyde as a cross-linker. The absence of any chemical interactions between active ingredients and polymer as well as cross-linking agent was confirmed by FTIR. With increase in the degree of cross-linking of the sodium alginate by glutaraldehyde, a significant decrease of NSO release from the beads was observed. The empirical parameter "*n*" and the kinetic constant "*k*" values calculated for the release of NSO from the beads indicated that the diffusion deviates slightly from Fickian transport and showed a decreased release with the increase in cross-linking.

Işıklan (2004) studied the release of carbaryl insecticides through polymeric beads. They investigated the effect of various factors during bead preparation such as percent of carboxymethylcellulose, ratio of carbaryl insecticide to carboxymethylcellulose, concentration of cross-linker as well as effect of addition of filler material (kaolin clay). The carbaryl release was increased when the ratio of carbaryl to carboxymethyl cellulose was low or carboxymethyl cellulose concentration was higher or the quantity of filler added was more.

To study the release of thiram, a dithiocarbamate fungicide, Singh and coworkers synthesized starch–alginate–clay beads with different compositions by varying the amount of kaolin and bentonite clays (Singh et al. 2009a, b). The beads showed good loading capacity of thiram fungicide. The integration of kaolin and bentonite in starch–alginate beads was found to be effective in controlling the release of thiram. Bentonite-based formulations showed slower release than kaolin-based formulations. The release followed non-Fickian diffusion mechanism. The decrease in the release of thiram from 10 mg in control, to 6.9 and 6.3 mg in the presence of kaolin and bentonite, respectively, was due to differences in the intercalation ability of bentonite clay mineral, whereas no such intercalation of thiram was found with kaolin. Also, the presence of kaolin and bentonite in starch–alginate bead further reduced the release of the thiram from the formulation. Likewise, other starch-based hydrogels have also been used for agrochemical delivery system (Baur 1980; Schreiber et al. 1988; Jana et al. 2001; Frederiksen et al. 2002).

Roy and coworkers prepared biopolymer microspheres of sodium alginate and starch by $CaCl_2$ cross-linking. A series of such microspheres was prepared with different compositions by varying the amounts of sodium alginate, starch, and $CaCl_2$ (Roy et al. 2009). The prepared beads were loaded with pesticide, chlorpyrifos, and studied for its release pattern. The microspheres beads delivered optimum swelling at 57.3: 42.7 wt% of alginate: starch composition. The cross-linked beads showed great potential for the release of chlorpyrifos. It was

observed that the fractional release of chlorpyrifos increases with increasing wt% of alginate and decreases with increasing content of starch. The sustained and controlled release was given by the beads with more alginate and less starch with cumulative release up to 14 days.

Chevillard et al. (2011) introduced organically modified nanoclay, montmorillonite (C30B) in wheat gluten (WG)-based formulation, and a model pesticide, and ethofumesate was imbibed in it in order to obtain slow release pattern. The aim was to use nanoclay in modulating transfer and biodegradation properties of active ingredient in bio-sourced polymers. Controlled release properties were examined through release experiments in water in comparison with the commercial formulations. Degradation study of ethofumesate in soil by respirometric experiments confirmed its non-biodegradable behavior, whereas after addition of 0.26% of ethofumesate, biodegradation of WG-based formulation was slightly but significantly delayed. This ecotoxic effect of ethofumesate which is responsible for delaying biodegradation of formulation was reduced after introducing C30B in the formulation. This also resulted in slower release of pesticide in water that could be further enhanced by adding organoclays in the materials. Binding of ethofumesate with nanoclays reduces its hazards to microorganisms and also probably less subjected to leaching, making this delivery system eco-friendly.

Alemzadeh and Vossoughi (2001) prepared hydrogel systems based on polyvinyl alcohol polymeric network and membranes with glutaraldehyde as cross-linking agent. The product was studied for release of paraquat herbicide. It was reported that higher concentration of the cross-linking agent decreased the release of active ingredient from the system. The hydrogel showed higher adsorption at lower temperature.

Aouada and coworkers synthesized polyacrylamide- and methylcellulose-based biodegradable hydrogels for the controlled delivery of paraquat herbicide (Aouada et al. 2009, 2010). The hydrogels were synthesized using *N*,*N*-methylene-bis-acrylamide as cross-linker, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine as catalyst agent, and sodium persulfate as initiator. Hydrogels were loaded with paraquat herbicide by soaking into its aqueous solution for 30 h. Around 82% of the paraquat from the solution was loaded in the matrix. The adsorption of paraquat was higher with methylcellulose as compared to the hydrogels without methylcellulose. Each hydrogel was removed from the solution, and the quantity of paraquat left in the remaining solution was determined. It was reported that the rate of release was fast initially indicating the release of active ingredient from surface while swelling. The release rate was slower in later stages, and the herbicide was released in a controlled manner at a constant concentration for a period of 15–46 days.

Singh et al. (2011a, b) have developed polysaccharide-based controlled release beads of herbicide atrazine. The controlled release formulations were made using alginate, neem leaf powder, kaolin, and bentonite clays. The use of neem leaves powder in ionotropic gelation of alginate had added advantage of its natural pesticidal activity. Bead size (diameter), entrapment efficiency, and amount of beads formed were taken as reaction parameters for the synthesis of various bead

formulations. It was reported that increase in clay content resulted in increase in size and yield of beads. Various release characteristics of the formulation such as entrapment efficiency, gel characteristic, diffusion mechanism, and bead size were evaluated. The amount of herbicide atrazine released from beads based on calcium alginate was found to be 14.8 ± 1.2 mg. The release occurred slowly for 300 h, and the amount was further increased with addition of neem leaf powder.

In vitro release studies of atrazine were conducted by using dry and loaded formulations in water (Bergaya et al. 2006). The amount of atrazine released from calcium alginate beads was found to increase when neem leaf powder was added to the bead. Among clays, bentonite incorporated beads resulted in slower release of atrazine as compared to those of kaolinite. The rate of release of atrazine was also higher initially as compared to later stages. Therefore, the overall release of atrazine occured for a prolonged period and thus was helpful in minimizing environment hazards. The study concluded that the presence of clays in neem leaf powder-alginate beads has resulted in slower atrazine release from formulations.

Alginate-based formulations were also evaluated for the release of herbicides metribuzin and isoproturon. The release of the active ingredients was slower when compared to conventional formulations (Pepperman and Kuan 1993; Villafranca-Sánchez et al. 2000). Also, the effectiveness of these delivery systems were reported to be better when two or more herbicides are used (Johnson and Pepperman 1998). Herbicides such as atrazine, monolinuron, simazine, chloridazon, chloroxuron, and desmetryn were formulated in beads based on alginate. The beads were evaluated for controlled release and were found to slower down the release of herbicides (Pfister et al. 1986).

In case of alginate- and gelatin-based beads, it has been reported that increase in proportion of gelatin decreases the release of pesticides such as cypermethrin and neem seed oil (Roy et al. 2009; Kulkarni et al. 2000). Both starch and alginate are biodegradable in soil. The pesticides are released from these beads by both swelling and degradation processes. Also, various soil factors such as enzymes like amylase and alginate lysases affect the release (Trimnell et al. 1985; Wong et al. 2000). Zhu and coworkers prepared controlled release systems based on gelatin and acacia gum (Zhu et al. 2009). The delivery systems were prepared by coacervation for insecticide release.

Polyvinyl chloride, carboxymethyl cellulose, and carboxymethyl cellulose-kaolinite-based composite delivery system were prepared for metribuzin herbicide. The formulation showed better results by controlling 75% of weeds than conventional product (57.14%) in wheat crop (Kumar et al. 2010). Singh and coworkers reported starch- and acrylamide-based slow release hydrogel system for the release of fungicide thiram (Singh et al. 2007, 2008). Apart from the release, the hydrogels showed good water-holding capacity. Therefore, such materials can be used for pesticide delivery as well as for water retention.

Lignin and lignin-based natural polymers have been investigated for the release of agrochemicals (Thakur and Thakur 2015). The release of pesticides and water absorption was dependent on the interactions between the functional groups present in pesticides with that of the polymer. The size of the polymeric granule also

affected the release. Smaller granules resulted in higher release of pesticides (Chowdhury 2014). Singh et al. (2015) prepared agar-, starch-, and polyacrylamide-based hydrogels for the release of atrazine herbicide. The hydrogel showed maximum 551% swelling. Release studies conducted for 144 h showed that hydrogel was suitable for slower release of pesticide in agriculture.

Recently, polymeric delivery systems having in situ gelling properties have been studied for drug delivery applications. It is a new technique in which the solution containing the drug or bioactive agent converts into a gel when it applied to the target site. Such gel-based delivery systems can also be explored for their applications in pesticide delivery. The in situ formation of gels depends on various factors such as temperature, pH, ions, radiations. These gels forming formulation shall be able to release the product in controlled manner (Hari et al. 2015). These gels are polymer-based colloidal solutions, which undergo phase transition from sol to gel. The physical and chemical changes responsible for release of product are affected by physiological environment (Geethalakshmi et al. 2012, 2013). Many researchers have been working on the agricultural applications of biopolymer-based products, mainly hydrogels. Significant contributions in this field are listed in Table 1.

4.5 Other Applications

Agriculture relies on an adequate supply of good quality irrigation water. Until now, irrigation water quality concerns have often been neglected because good quality water supplies have been plentiful and readily available (Kitila et al. 2014). But today, the situation is changing in many areas and due to contaminated irrigation water toxic chemicals and heavy metals are ruining soil health and also leaving their residues in the crops. In most of the cases, water is taken from water bodies such as river, pond, and dam or pumped up from the soil subsurface. Recently due to increasing industrialization, fair quality water is used in the industry and its wash water/wastewater is being released in the same water body which adds to many toxic pollutants in it. Key pollutants in such contaminated water include heavy metals, industrial dyes, dissolved salts, industrial sludge, organic pollutants, oils, and excess nutrients due to runoff or leaching down from cultivated lands. Though there is infrastructure available to recycle and purify this water for domestic and drinking purpose, no such care is being taken for pretreatment of water before irrigation. This leads to accumulation of these pollutants in agricultural land and subsequently entering into the food chain via crops grown on that area. Irrigation with such contaminated water can lead to accumulation of heavy metals such as cadmium, chromium, mercury, lead, and arsenic, all of which appear in the World Health Organization's list of 10 chemicals of major public concern.

In recent researches, lot of emphasis is being given on the use of biopolymer-based sorbents for removal of the heavy metals and dyes from the

Table 1 Application of biopolymers in agriculture

Source	Polymer	Applications	Reference
Cellulose	Carboxymethyl cellulose with polyvinyl chloride and Kaolinite composites	Pesticide delivery	Kumar et al. (2010)
	Methylcellulose and polyacrylamide hydrogel	Pesticide delivery	Aouada et al. (2010)
	Carboxymethyl cellulose beads with kaolin clay by ionotropic cross-linking with copper ions	Pesticide delivery	Işıklan (2004)
	Carboxymethyl cellulose copolymer with poly(acrylamide)	Nutrient delivery	Bortolin et al. (2012)
	Cross-linked with carbodiimide	Water retention and nutrient delivery	Demitri et al. (2013)
	Carboxymethyl cellulose hydrogel with starch using aluminumsulfate octadecahydrate as cross-linker	Soil conditioner	Nnadi and Brave (2011)
	Carboxymethyl cellulose ionically cross-linked with iron and calcium salts	Nutrient delivery	Davidson and Gu (2013)
	Poly(*N*-vinyl-pyrrolidone) hydrogels with outer coating of ethylcellulose	Nutrient delivery	Ni et al. (2009)
	Hydroxyethyl cellulose and carboxymethyl cellulose cross-linked with citric acid	Nutrient delivery	Ni et al. (2009)
Starch	Starch-based hydrogel prepared by modification with glycidyl methacrylate	Water retention	Guilherme et al. (2012)
	Acrylamide/methyl acrylamide/methyl acrylicacid	Pesticide delivery	Singh et al. (2007, 2008, 2009a, b)
	Graft copolymer with acrylic acid and acrylamide	Soil conditioner	Chen et al. (2004)
	Microencapsulation	Pesticide delivery	Frederiksen et al. (2002)
	Biodegradable film	Pesticide delivery	Jana et al. (2001)
	Microsphere with sodium alginate	Pesticide delivery	Roy et al. (2009)
	Copolymer with acrylamide	Soil conditioner	Woodhouse and Johnson (1991)
Cassava starch	Saponified cassava starch grafted with polyacrylamide	Soil conditioner	Parvathy and Jyothi (2012)
Corn starch	Copolymer with acrylamide	Soil conditioner	Kohls et al. (1999)

(continued)

Table 1 (continued)

Source	Polymer	Applications	Reference
Alginate	Sodium alginate encapsulation	Pesticide delivery	Kulkarni et al. (2000)
	Calcium alginate gel	Pesticide delivery	Pfister et al. (1986)
	Beads with neem leaf powder, kaolin, and bentonite clays	Pesticide delivery	Singh et al. (2011a, b)
	Copolymer with acrylamide by electron beam irradiation	Soil conditioner	Abd El-Rehim et al. (2005)
Chitosan	Polyvinyl alcohol, polyvinyl alcohol/chitosan, and chitosan-based hydrogel cross-linked by glutaraldehyde	Water retention and nutrient delivery	Jamnongkan and Kaewpirom (2010)
	Poly(vinyl alcohol) and chitosan hydrogel by cross-linking with glutaraldehyde vapor deposition	Nutrient release and water absorption	Noppakundilograt et al. (2015)
	Fertilizer with chitosan as inner coating and external coating of poly(acrylic acid-co-acrylamide) hydrogel	Nutrient delivery and water retention	Wu and Liu (2008)
Lignin	Radical polymerization with corn starch, acrylamide, and acrylic acid by using potassium persulfate as insulator	Soil conditioner	Lee et al. (2013)
	Polyurethane-based hydrogel with isocyanate-terminated polyurethane ionomer (IPUI) as cross-linker	Nutrient delivery	Peng and Chen (2011)
Guar gum	Graft copolymer with acrylonitrile	Soil additive	Lokhande and Varadarajan (1992)
	Graft copolymer with acrylic acid	Water retention	Wang and Wang (2010a, b)
	Graft copolymer with acrylic acid	Soil conditioner and nutrient delivery	Chandrika et al. (2014)
Tragacanth gum	Graft copolymer with acrylic acid	Water retention and nutrient delivery	Saruchi et al. (2014)
	Graft copolymer with acrylic acid	Nutrient delivery and water retention	Kaith et al. (2013)
Agar	Copolymer with starch and acrylamide	Pesticide delivery	Singh et al. (2015)
	Copolymer with acrylic acid and 2-acrylamido-2-methylpropane sulfonic acid (AMPS)	Water retention	Pourjavadi et al. (2009)
Gum arabic	Hydrogel synthesis by modification with glycidyl methacrylate	Water retention	Guilherme et al. (2007)
	Coacervation with gelatin	Pesticide delivery	Zhu et al. (2009)
Cashew gum	Copolymer with acrylamide	Water retention	Guilherme et al. (2005)

(continued)

Table 1 (continued)

Source	Polymer	Applications	Reference
Gluten	Extrusion granules with montmorillonite	Pesticide delivery	Chevillard et al. (2011)
Pectin	Pectin hydrogels with acrylamide and sodium acrylate modified with glycidyl methacrylate	Water retention, nutrient delivery, soil conditioner	Guilherme et al. (2009)
Humate (humic acid)	Sodium humate graft copolymer with acrylic acid	Soil conditioner	Chu et al. (2006)
Heteropolysaccharide resin from *Cochlospermum*species	Graftco polymerization with acrylamide, persulfate initiator by microwave-assisted free-radical polymerization	Soil conditioner	Singh et al. (2009a, b)

Table 2 Application of biopolymers for water decontamination

Gum	Modified adsorbents	Use in removal of-	References
Alginate	Post-cross-linking sodium alginate (SA) beads	Cu^{2+}, Ag^{+}, and Fe^{3+}	Lu et al. (2015)
	Nanocomposites of glucose oxidase/$MnFe_2O_4$/calcium alginate, laccase/$MnFe_2O_4$/calcium alginate, and $MnFe_2O_4$/calcium alginate	Methylene blue	Shojaat et al. (2016)
	Cross-link copolymerization of acrylic acid (AA) and hydroxy ethyl methacrylate and sodium alginate	Congo red and methyl violet	Mandal and Ray (2013)
	Semi-IPN hydrogels of Acrylic copolymers and sodium alginate	Basic fuschin (BF) and methyl violet (MV) dyes	Bhattacharyya and Ray (2015)
	Macroporous alginate substrate-bound growth of Fe nanoparticles (Fe NPs/MAS)	Nitrates	Lee et al. (2016)
	Magnetic ferrite nanoparticle–alginate composite	Basic Blue 9 (BB9), Basic Blue 41 (BB41), and Basic Red 18	Mahmoodi (2013)
	Mesoporous titania spheres derived from sodium alginate–gum acacia composite beads	Reactive blue H5G dye	Singh et al. (2015)
	Superparamagnetic nanocomposite of sodium alginate (Fe_3O_4@TSTC[4]AS-s-SA) fabricated sodium alginate-supported tetra-sodium thiacalix[4]arene tetrasulfonate	Cu^{2+}, Cd^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, and Cr^{3+}	Lakouraj et al. (2014)
	Magnetic alginate beads	Methylene blue and methyl orange	Rocher et al. (2008)
	Porous alginate aerogel beads	Cu^{2+}, Cd^{2+},	Deze et al. (2012)
Chitosan	Magnetic polydopamine (PDA) cross-linked chitosan (CS) hybrid nano-biosorbent	Methylene blue and malachite green Cr(VI), Pb^{2+}, Hg^{2+}	Wang et al. (2016)
	Magnetic chitosan composites	Metal and dyes	Reddy and Lee (2013)
	Chitosan–lignin composites	Anthraquinonic dye, Remazol Brilliant Blue R (RBBR), and Cr(VI)	Nair et al. (2014)
	Ethyl acrylate-grafted chitosan	$Pb^{2+,}$ Cd^{2+}, and Zn^{2+}	Maleki et al. (2015)
	Nanochitosan and its acetophenone derivative	Cu^{2+}, Pb^{2+}, Cd^{2+}, and Hg^{2+}	Mahmoud et al. (2015)

(continued)

Table 2 (continued)

Gum	Modified adsorbents	Use in removal of-	References
	Chitosan/organic rectorite–Fe_3O_4 composite microspheres (CS/χOREC-Fe_3O_4)	Cu^{2+}, Cd^{2+}	Xie et al. (2015)
	PAMAM-grafted chitosan	Pb^{2+}	Zarghami et al. (2016)
	Natural polymer chitosan, modified chitosan, and chitosan composites	Heavy metals and radio nuclides	Wang et al. (2014)
	O-carboxymethyl functionalization of chitosan	Cr^{2+}, Cd^{2+}	Borsagli et al. (2015)
Cellulose	Carboxy methyl cellulose incorporated acrylic hydrogels	Safranine T and brilliant cresyl blue dyes	Mandal and Ray (2015)
	Epichlorohydrin cross-linked carboxymethyl cellulose fiber	Cd^{2+}	Wei et al. (2015)
	Acrylic acid grafting polymerization carboxymethyl cellulose	Methyl orange, disperse Blue 2BLN, and malachite green chloride	Zhang et al. (2014a, b)
Guar gum	Groundnut husk modified with guar gum	Pb^{2+}, Cu^{2+}, Ni^{2+}	Ahmad and Haseeb (2015)
	Poly(acrylic acid)-grafted guar gum	Pb^{2+}	Pal et al. (2016)
	Guar gum–cerium (IV) tungstate hybrid cationic exchanger	Methylene blue	Gupta et al. (2014)
	Cross-linked polyacrylamide/guar gum graft copolymer	Cr(VI)	Abdel-Halim and Al-Deyab (2011)
	Polyacrylamide-grafted carboxymethyl guar gum (CMG-g-PAM)	Methylene blue	Pal et al. (2011)
	Poly(methylacrylate)-functionalized guar gum	Cr(VI)	Singh et al. (2009a, b)
Gum arabic	Gum arabic-modified magnetic nanoadsorbent	Cu^{2+}	Banerjee and Chen (2007)
	Gum acacia-inspired silica hybrid xerogels	Hg^{2+}	Singh et al. (2011a, b)
	Sulfonated form of gum arabic-powdered	Zn^{2+}, Hg^{2+}	Singh et al. (2011a, b) Das et al. 2015

(continued)

Table 2 (continued)

Gum	Modified adsorbents	Use in removal of-	References
Gum ghatti	Gum ghatti with a copolymer mixture of acrylamide and methacrylic acid	Methylene blue and Methyl violet	Mittal et al. (2015a, b)
	TiO_2 nanoparticle (TiO2NP)-containing hydrogel nanocomposite (HNC) of polyacrylamide-grafted gum ghatti (PAAm-g-Gg).	Methylene blue	Mittal et al. (2016)
	Poly(acrylic acid-aniline)-grafted gum ghatti-based conducting hydrogel	Dyes	Sharma et al. (2014)
Gum kondagogu	–	Cd^{2+}, Cu^{2+}, Fe^{2+}, Se^{2+}, Pb^{2+}, total Cr, Ni^{2+}, Zn^{2+}, Co^{2+}, As^{2+}	Vinod et al. (2010)
	Gum kondagogu-modified magnetic iron oxide nanoparticles	Cd^{2+},Cu^{2+},Pb^{2+}, Ni^{2+}, Zn^{2+}, Hg^{2+}	Saravanan et al. (2012)
	–	Cd^{2+}, Pb^{2+}	Vinod et al. (2009)
Tragacanth gum	Fe_3O_4/poly(methyl methacrylate)-grafted tragacanth gum nanocomposite	Cr (VI)	Sadeghi et al. (2014)
	Tragacanth gum-g-polyamidoxime nano hydrogel	Co^{2+}, Zn^{2+},Cr^{3+}, $Cd^{2+.}$	Masoumi and Ghaemy (2014)
Karaya gum	Gum karaya grafted with poly(acrylic acid − acrylamide) (GK-cl-P(AA-co-AAM))	Methylene blue	Mittal et al. (2015a, b)
	–	Hg^{2+}	Vinod et al. (2011)
Xanthan gum	Xanthan gum-g-poly(ethylacrylate)	Pb2+	Pandey and Mishra (2012)
	Nanocomposite based on nanosilica modified with xanthan gum grafted with polyacrylamide	Pb2+	Ghorai et al. (2012)
Agar	Agar-based bimetallic nanoparticles	Methylene blue and rhodamine B	Patra et al. (2016)

wastewater, which can be used for the treatment of industrial wastewater, before being released into the water bodies. The biopolymer-based adsorbents/hydrogels showed potential to remove heavy metals and dyes from wastewater and can also be used repetitively in most of the cases. Important research works in this line carried out in the recent past are summarized in Table 2.

5 Conclusion

This chapter discusses in nut shell the biopolymers, their classification, modification by different techniques, and application in various fields of agriculture. Due to their biodegradability, renewability, ease to blend into different products, cost-effectiveness, easy handling, and storage, biopolymers can be used in agricultural applications such as soil conditioners, moisture retainers, controlled nutrient, and pesticide release, and also in other applications such as remediation of heavy metals, dyes form irrigation water. All these properties make biopolymers a unique natural material and provide an edge over its other synthetic counterparts.

The present discussion on biopolymers signifies that the biopolymers and their chemically modified derivatives are yet to be fully explored in agriculture industry. Natural biopolymer-based superabsorbent hydrogels have tremendous potential to be used as culture media in nursery and tissue culture for growing high value seedlings. It can be used for multipurpose operations such as moisture retainer and controlled release of nutrients and pesticides imbibed in it, and being biodegradable, it will improve soil's physical properties after decomposition. Modified biopolymers also have potential to be used as drift control agents in sprays and mists, in liquid flowable pesticides as a stabilizers and emulsifying agents. Recently emerged concept of in situ gels can be utilized in pesticide formulations. Plants and soil systems having various specific ions and pH conditions can activate the formation of gel. The in situ gel-based pesticide formulation would have added advantage of sticking over leaf surface for longer period as compared to conventional foliar spray. For targeting soil application of hydrogels, they need to be cheaper, available in bulk, and easy to handle. As multistep synthesis and using high value reagents such as acrylates, increase in cost, the challenge is to prepare the cheaper hydrogels, which at the same time show good absorption and mechanical properties. The use of nanotechnology in synthesis or incorporating nanofillers to improve mechanical strength and performance of the hydrogels can be one of the important areas to work upon.

Owing to consequences of the issues such as climate change, degrading land, decreasing cultivable area, scarce resources, population rise, the ever-mounting food demand has been a greatest challenge for achieving adequate food production. Biopolymer-based eco-friendly hydrogels ensure potential and high future prospects in building sustainability in agriculture.

References

Abd-Allah AR, Al-Majed AA, Mostafa AM, Al-Shabanah OA, Din AGE, Nagi MN (2002) Protective effect of arabic gum against cardiotoxicity induced by doxorubicin in mice: a possible mechanism of protection. J Biochem Mol Toxicol 16(5):254–259

Abd El-Rehim HA, Hegazy EA, Abd El-Mohdy HL (2004) Radiation synthesis of hydrogels to enhance sandy soils water retention and increase plant performance. J Appl Polym Sci 93:1360–1371

Abd El-Rehim HA, Hegazy EA, Abd El-Mohdy HL (2005) Properties of polyacrylamide-based hydrogels prepared by electron beam irradiation for possible use as bioactive controlled delivery matrices. J Appl Polym Sci 98:1262–12670

Abdel-Halim ES, Al-Deyab SS (2011) Hydrogel from crosslinked polyacrylamide/guar gum graft copolymer for sorption of hexavalent chromium ion. Carbohydr Polym 86:1306–1312

Abedi-Koupai J, Asadkazemi J (2006) Effects of a hydrophilic polymer on the field performance of an ornamental plant (*Cupressus arizonica*) under reduced irrigation regimes. Iran Polym J 15:715

Abedi-Koupai J, Sohrab F (2004) Evaluating the application of superabsorbent polymers on soil water capacity and potential on three soil textures. Iran J PolymSciTechnol 17:163–173

Abu Baker A, Tahir A, Sabah Elkheir MK (2007) Effect of tree and nodule age on some physicochemical properties of gum from *Acacia senegal* (L.) Willd Sudan. Res J Agric and Bio Sci 3:866–870

Addai ZR, Abdullah A, Mutalib SA, Musa KH (2013) Effect of gum arabic on quality and antioxidant properties of papaya fruit during cold storage. Int J Chem Tech Res 5:2854–2862

Adhikari B, Majumdar S (2004) Polymers in sensor applications: progress in polymer science. Polym Sci 29:699–766

Adhikary P, Krishnamoorthi S, Singh RP (2011) Synthesis and characterization of grafted carboxymethyl guar gum. J Appl Polym Sci 120:2621–2626

Agaba H, Orikiriza LJ, Obua J, Kabasa JD, Worbes M, Hüttermann A (2011) Hydrogel amendment to sandy soil reduces irrigation frequency and improves the biomass of *Agrostis stolonifera*. Agri Sci 2:544

Aggarwal G, Sharma A (2010) Controlled release of a poorly water soluble drug prednisolone from heterodisperse hydrogel system. Int J Pharma Biol Sci 2:1–8

Ahmad R, Haseeb S (2015) Absorptive removal of Pb^{2+}, Cu^{2+} and Ni^{2+} from the aqueous solution by using groundnut husk modified with Guar Gum (GG): kinetic and thermodynamic studies. Groundw Sustain Dev 1:41–49

Ahmed EM (2013) Hydrogel: preparation, characterization, and applications. J Adv Res 6:105–121

Alboofetileh M, Rezaei M, Hosseini H, Abdollahi M (2014) Antimicrobial activity of alginate/clay nanocomposite films enriched with essential oils against three common foodborne pathogens. Food Control 36:1–7

Alemzadeh I, Vossoughi M (2001) Controlled release of paraquat from poly vinyl alcohol hydrogel. Chem Eng Process 41:707–710

Alka A, Laxmi B, Suman R (2011) Formulation development and evaluation of sustained release matrix tablet of Lamivudine using tamarind seed polysaccharide. Der Pharmacia Lettre 3:250–2508

Al-Majed AA, Mostafa AM, Al-Rikabi AC, Al-Shabanah OA (2002) Protective effects of oral arabic gum administration on gentamicin-induced nephrotoxicity in rats. Pharmacol Res 46:445–451

Al-Majed AA, Abd-Allah AR, Al-Rikabi AC, Al-Shabanah OA, Mostafa AM (2003) Effect of oral administration of arabic gum on cisplatin-induced nephrotoxicity in rats. J Biochem Mol Toxicol 17:146–153

Anderson SA, Fisher KD, Talbot JM (1993) Evaluation of the health aspects of using partially hydrolyzed guar gum as a food ingredient. FASEB J, 1–61

Aouada FA, Moura MR, Menezes ED, Nogueira AR, Mattoso LH (2008) Hydrogel synthesis and kinetics of ammonium and potassium release. Rev Bras De Cienc Do Solo 32:1643–1649

Aouada FA, Pan Z, Orts WJ, Mattoso LH (2009) Removal of paraquat pesticide from aqueous solutions using a novel adsorbent material based on polyacrylamide and methylcellulose hydrogels. J Appl Polym Sci 114:2139–2148

Aouada FA, de Moura MR, Orts WJ, Mattoso LH (2010) Polyacrylamide and methylcellulose hydrogel as delivery vehicle for the controlled release of paraquat pesticide. J Mater Sci 45:4977–4985

Aouada FA, Mattoso LH, de Moura MR (2011) Biodegradable hydrogel as delivery vehicle for the controlled release of pesticide. INTECH Open Access Publisher

Ashikin WH, Wong TW, Law CL (2010) Plasticity of hot air-dried mannuronate-and guluronate-rich alginate films. Carbohydr Polym 81:104–113

Ashraf S, Soudi MR, Sadeghizadeh MA (2008) Isolation of a novel mutated strain of *Xanthomonas campestris* for xanthan production using whey as the sole substrate. Pak J Biol Sci 11:438–442

Aslam M (1990) Polymers as soil conditioners and sealing agents. Pakistan Academy of Sciences, Islamabad

Azzam RA (1985) Tailoring polymeric gels for soil reclamation and hydroponics. Commun Soil Sci Plant Anal 16:1123–1138

Bahulkar SS, Munot NM, Surwase SS (2015) Synthesis, characterization of thiolated karaya gum and evaluation of effect of pH on its mucoadhesive and sustained release properties. Carbohydr Polym 130:183–190

Bajpai AK, Giri A (2003) Water sorption behaviour of highly swelling (carboxy methylcellulose-g-polyacrylamide) hydrogels and release of potassium nitrate as agrochemical. Carbohydr Polym 53:271–279

Bakass M, Mokhlisse A, Lallemant M (2001) Absorption and desorption of liquid water by a superabsorbent polyelectrolyte: role of polymer on the capacity for absorption of a ground. J Appl Polym Sci 82:1541–1548

Baldrian P, Valášková V (2008) Degradation of cellulose by basidiomycetous fungi. FEMS Microbiol Rev 32:501–521

Banerjee SS, Chen DH (2007) Fast removal of copper ions by gum arabic modified magnetic nano-adsorbent. J Hazard Mater 147:792–799

Bangale GS, Shinde GV, Umalkar DG, Rajesh KS (2011) Natural mucoadhesive material based buccal tablets of nitrendipine-formulation and in-vitro evaluation. J Pharm Res 4:33–38

Baur JR (1980) Release characteristics of starch xanthide herbicide formulations. J Environ Qual 9:379–382

Becker A, Katzen F, Pühler A, Ielpi L (1998) Xanthan gum biosynthesis and application: a biochemical/genetic perspective. Appl Microbiol Biotechnol 50(2):145–152

Bergaya F, Theng BKG, Legaly G (2006) Handbook of clay science. Elsevier, Amsterdam, pp 693–702

Bhattacharyya R, Ray SK (2015) Adsorption of industrial dyes by semi-IPN hydrogels of Acrylic copolymers and sodium alginate. J Ind Eng Chem 22:92–102

Bixler HJ, Porse H (2011) A decade of change in the seaweed hydrocolloids industry. J Appl Phycol 23:321–335

Blackburn RS (2004) Natural polysaccharides and their interactions with dye molecules: applications in effluent treatment. Environ Sci Technol 38:4905–4909

Blanco-Pascual N, Montero MP, Gómez-Guillén MC (2014) Antioxidant film development from unrefined extracts of brown seaweeds *Laminaria digitata* and *Ascophyllum nodosum*. Food Hydrocolloids 37:100–110

Boodt DM (1975) Use of soil conditioners around the world. Soil Conditioners. SSS A Special Publication. Soil Science Society of America, Madison, pp 1–12

Bordi F, Paradossi G, Rinaldi C, Ruzicka B (2013) Chemical and physical hydrogels: two case systems studied by quasi elastic light scattering. Phys A 304:119–128

Borsagli FG, Mansur AA, Chagas P, Oliveira LC, Mansur HS (2015) O-carboxymethyl functionalization of chitosan: complexation and adsorption of Cd (II) and Cr (VI) as heavy metal pollutant ions. React Funct Polym 97:37–47

Bortolin A, Aouada FA, de Moura MR, Ribeiro C, Longo E, Mattoso LH (2012) Application of polysaccharide hydrogels in adsorption and controlled-extended release of fertilizers processes. J Appl Polym Sci 123:2291–2298

Bouranis DL, Theodoropoulos AG, Drossopoulos JB (1995) Designing synthetic polymers as soil conditioners. Commun Soil Sci Plant Anal 26:1455

Brazel CS, Peppas NA (1999) Mechanisms of solute and drug transport in relaxing, swellable, hydrophilic glassy polymers. Polymer 40:3383–3398

Buchholz FL, Graham AT (1998) Modern superabsorbent polymer technology. Wiley, New York, pp 279

Buchholz FL, Peppas NA (1994) Superabsorbent polymers: science and technology. American Chemical Society

Burgalassi S, Raimondi L, Pirisino R, Banchelli G, Boldrini E, Saettone MF (2000) Effect of xyloglucan (tamarind seed polysaccharide) on conjunctival cell adhesion to laminin and on corneal epithelium wound healing. Eur J Ophthalmol 10:71–76

Campos EVR, de Oliveira JL, Fraceto LF, Singh B (2015) Polysaccharides as safer release systems for agrochemicals. Agron Sustain Dev 35:47–66

Castel D, Ricard A, Audebert R (1990) Swelling of anionic and cationic starch-based superabsorbents in water and saline solution. J Appl Polym Sci 39:11–29

Celkan A, Acartürk F, Tuğcu-Demiröz F, Gökçora N, Akkaş BE, Güner LA (2016) Gamma scintigraphic studies on guar gum-based compressed coated tablets for colonic delivery of theophylline in healthy volunteers. J Drug Deliv Sci Technol 32(3):1–37

Chandrika KS, Singh A, Sarkar DJ, Rathore A, Kumar A (2014) pH sensitive crosslinked guar gum based superabsorbent hydrogels: swelling response in simulated environments and water retention behavior in plant growth media. J Appl Polym Sci 131:1–12

Chang C, Duan B, Cai J, Zhang L (2010) Superabsorbent hydrogels based on cellulose for smart swelling and controllable delivery. Eur Polym J 46:92–100

Chen P, Zhang WA, Luo W, Fang YE (2004) Synthesis of superabsorbent polymers by irradiation and their applications in agriculture. J Appl Polym Sci 93:1748–1755

Cheng Y, Lu L, Zhang W, Shi J, Cao Y (2012) Reinforced low density alginate-based aerogels: preparation, hydrophobic modification and characterization. Carbohydr Polym 88:1093–1099

Cheng YH, Tsai TH, Jhan YY, Chiu AW, Tsai KL, Chien CS, Chiou SH, Liu CJ (2016) Thermosensitive chitosan-based hydrogel as a topical ocular drug delivery system of latanoprost for glaucoma treatment. Carbohydr Polym 144:390–399

Chevillard A, Angellier-Coussy H, Guillard V, Bertrand C, Gontard N, Gastaldi E (2011) Biodegradable herbicide delivery systems with slow diffusion in soil and UV protection properties. Pest Manag Sci 70:1697–1705

Chowdhury MA (2014) The controlled release of bioactive compounds from lignin and lignin-based biopolymer matrices. Int J Biol Macromol 65:136–147

Chu M, Zhu SQ, Li HM, Huang ZB, Li SQ (2006) Synthesis of poly (acrylic acid)/sodium humate superabsorbent composite for agricultural use. J Appl Polym Sci 102:5137–5143

Chung C, Rojanasasithara T, Mutilangi W, McClements DJ (2016) Enhancement of colour stability of anthocyanins in model beverages by gum arabic addition. Food Chem 201:14–22

Cosenza VA, Navarro DA, Fissore EN, Rojas AM, Stortz CA (2014) Chemical and rheological characterization of the carrageenans from *Hypnea musciformis* (Wulfen) Lamoroux. Carbohydr Polym 102:780–789

Cretois I, Samain H (inventors) (2000) L'oreal, assignee. Hair styling. United States patent US 6,060,044

Das D, Vimala R, Das N (2015) Removal of Ag (I) and Zn (II) ions from single and binary solution using sulfonated form of gum arabic-powdered mushroom composite hollow semispheres: equilibrium, kinetic, thermodynamic and ex-situ studies. Ecol Eng 75:116–122

Davidson DWVM, Gu FX (2013) Controlled root targeted delivery of fertilizer using an ionically crosslinked carboxymethyl cellulose hydrogel matrix. Springerplus 2:1–9

De Oliveira Pedro R, Schmitt CC, Neumann MG (2016) Syntheses and characterization of amphiphilic quaternary ammonium chitosan derivatives. Carbohydr Polym 147:97–103

Demitri C, Scalera F, Madaghiele M, Sannino A, Maffezzoli A (2013) Potential of cellulose-based superabsorbent hydrogels as water reservoir in agriculture. Int J Polym Sci

Deveswaran R, Abraham S, Bharath S, Basavaraj BV, Furtado S, Madhavan V (2009) Design and characterization of diclofenac sodium tablets containing tamarind seed polysaccharide as release retardant. Int J PharmTech Res 1:191–195

Deze EG, Papageorgiou SK, Favvas EP, Katsaros FK (2012) Porous alginate aerogel beads for effective and rapid heavy metal sorption from aqueous solutions: effect of porosity in Cu^{2+} and Cd^{2+} ion sorption. Chem Eng J 209:537–546

Dragostin OM, Samal SK, Dash M, Lupascu F, Pânzariu A, Tuchilus C, Ghetu N, Danciu M, Dubruel P, Pieptu D, Vasile C (2016) New antimicrobial chitosan derivatives for wound dressing applications. Carbohydr Polym 141:28–40

Dumitriu S (2002) Polymeric biomaterials, revised and expanded, 2nd edn. MarcelDekker Inc., NY, USA, p 480

Dutta PK, Ravikumar MN, Dutta J (2002) Chitin and chitosan for versatile applications. JMS Polym Rev C 42:307–354

Fajardo AR, Fávaro SL, Rubira AF, Muniz EC (2013) Dual-network hydrogels based on chemically and physically crosslinked chitosan/chondroitin sulfate. Funct Polym 73:1662–1671

Frederiksen HK, Hansen HCB, Borggaard O, Pedersen M (2002) Starch encapsulated chlorpyrifos: release rate, insecticidal activity and degradation in soil. J Microencapsul 19:319–331

Gamal el-din AM, Mostafa AM, Al-Shabanah OA, Al-Bekairi AM, Nagi MN (2003) Protective effect of arabic gum against acetaminophen-induced hepatotoxicity in mice. Pharmacol Res 48:631–635

Gao D (2003) Superabsorbent polymer composite (SAPC) materials and their industrial and high-tech applications. Ph.D. dissertation, Bergakademie, Technische Universitat, Freiberg, Germany

Geethalakshmi A, Karki R, Jha SK, Venkatesh DP, Nikunj B (2012) Sustained ocular delivery of brimonidine tartrate using ion activated in situ gelling system. Curr Drug Deliv 9:197–204

Geethalakshmi A, Karki R, Sagi P, Jha SK, Venkatesh DP (2013) Temperature triggered in situ gelling system for betaxolol in glaucoma. J Appl Pharm Sci 3:153

Ghorai S, Sinhamahpatra A, Sarkar A, Panda AB, Pal S (2012) Novel biodegradable nanocomposite based on XG-g-PAM/SiO_2: application of an efficient adsorbent for Pb^{2+} ions from aqueous solution. Bioresour Technol 119:181–190

Gil EC, Colarte AI, Bataille B, Caraballo I (2007) Estimation of the percolation thresholds in lobenzarit disodium native dextran matrix tablets. Pharm Sci Tech 8:1–7

Glicksman M (ed) (1996) Tamarind seed gum. Food Hydrocolloids III:191–202. CRC Press Inc, Boca Raton, Florida, USA

Guilherme MR, Reis AV, Takahashi SH, Rubira AF, Feitosa JPA, Muniz EC (2005) Synthesis of a novel superabsorbent hydrogel by copolymerization of acrylamide and cashew gum modified with glycidyl methacrylate. Carbohydr Polym 61:464–471

Guilherme MR, Reis AV, Paulino AT, Fajardo AR, Muniz EC, Tambourgi EB (2007) Superabsorbent hydrogel based on modified polysaccharide for removal of Pb^{2+} and Cu^{2+} from water with excellent performance. J Appl Polym Sci 105:2903–2909

Guilherme MR, Moia TA, Reis AV, Paulino AT, Rubira AF, Mattoso LH, Muniz EC, Tambourgi EB (2009) Synthesis and water absorption transport mechanism of a pH-sensitive polymer network structured on vinyl-functionalized pectin. Biomacromolecules 10:190–196

Guilherme MR, Reis AV, Paulino AT, Moia TA, Mattoso LH, Tambourgi EB (2010) Pectin-based polymer hydrogel as a carrier for release of agricultural nutrients and removal of heavy metals from wastewater. J Appl Polym Sci 117:3146–3154

Guilherme MR, Oliveira RS, Mauricio MR, CelletTSP Pereira GM, Kunita MH (2012) Albumin release from a brain-resembling superabsorbent magnetic hydrogel based on starch. Soft Matter 8:6629–6637

Gupta VK, Pathania D, Singh P, Kumar A, Rathore BS (2014) Adsorptional removal of methylene blue by guar gum–cerium (IV) tungstate hybrid cationic exchanger. Carbohydr Polym 101:684–691

Hambleton A, Fabra MJ, Debeaufort F, Dury-Brun C, Voilley A (2009) Interface and aroma barrier properties of iota-carrageenan emulsion-based films used for encapsulation of active food compounds. J Food Eng 93:80–88

Hambleton A, Voilley A, Debeaufort F (2011) Transport parameters for aroma compounds through i-carrageenan and sodium alginate-based edible films. Food Hydrocoll 25:1128–1133

Hari BNV, Lobo FJ, Devi DR (2015) Polymeric in-situ gels as smart carriers for pesticide delivery in agricultural practice. Int J Pharm Clin Res 7:2

Heinze T, Liebert T, Heublein B, Hornig S (2006) Functional polymers based on dextran. Adv Polym Sci 205:199–291

Hemvichian K, Chanthawong A, Suwanmala P (2014) Synthesis and characterization of superabsorbent polymer prepared by radiation-induced graft copolymerization of acrylamide onto carboxymethyl cellulose for controlled release of agrochemicals. Radiat Phys Chem 103:167–171

Hosseini A, Jafari SM, Mirzaei H, Asghari A, Akhavan S (2015) Application of image processing to assess emulsion stability and emulsification properties of Arabic gum. Carbohydr Polym 126:1–8

Hsu SY, Chung HY (1999) Comparisons of 13 edible gum-hydrate fat substitutes for low fat Kung-wan (an emulsified meatball). J Food Eng 40:279–285

Hüttermann A, Zommorodi M, Reise K (1999) Addition of hydrogels to soil for prolonging the survival of *Pinus halepensis* seedlings subjected to drought. Soil Till Res 50:295–304

Hüttermann A, Orikiriza LJ, Agaba H (2009) Application of superabsorbent polymers for improving the ecological chemistry of degraded or polluted lands. Clean-Soil, Air, Water 1:517–526

Ibrahim NA, Abo-Shosha MH, Allam EA, El-Zairy EM (2010) New thickening agents based on tamarind seed gum and karaya gum polysaccharides. Carbohydr Polym 81:402–408

Ielpi L, Couso R, Dankert M (1981) Lipid-linked intermediates in the biosynthesis of xanthan gum. FEBS Lett 130:253–256

International Water Management Institute (2010) Issue 10

Iqbal M (1993) International trade in non-wood forest products: an overview. http://www.fao.org/docrep/x5326e/x5326e08.htm#1.%20gum%20arabic

Işıklan N (2004) Controlled release of insecticide carbaryl from crosslinked carboxymethylcellulose beads. Fresen Environ Bull 13:537–544

Jamnongkan T, Kaewpirom S (2010) Potassium release kinetics and water retention of controlled-release fertilizers based on chitosan hydrogels. J Polym Environ 18:413–421

Jana T, Roy BC, Maiti S (2001) Biodegradable film: 6 modification of the film for control release of insecticides. Eur Polym J 37:861–864

Jana S, Lakshman D, Sen KK, Basu SK (2010) Development and evaluation of epichlorohydrin cross-linked mucoadhesive patches of tamarind seed polysaccharide for buccal application. Int J Pharm Sci Drug Res 2:193–198

Jani GK, Shah DP, Prajapati VD, Jain VC (2009) Gums and mucilages: versatile excipients for pharmaceutical formulations. Asian J Pharm Sci 4:309–323

Johnson RM, Pepperman AB (1998) Release of atrazine and alachlor from clay-oxamide controlled-release formulations. PesticSci 53:233–240

Joseph J, Kanchalochana S, Rajalakshmi G, Hari V, Durai R (2012) Tamarind seed polysaccharide: a promising natural excipient for pharmaceuticals. Int J Green Pharm 6(4):270

Kaith BS, Jindal R, Kapur GS (2013) Enzyme-based green approach for the synthesis of gum tragacanth and acrylic acid cross-linked hydrogel: its utilization in controlled fertilizer release and enhancement of water-holding capacity of soil. Iran Polym J 22:561–570

Kamath KR, Park K (1993) Biodegradable hydrogels in drug delivery. Adv Drug Deliver Rev 11:59–84

Kashyap PL, Xiang X, Heiden P (2015) Chitosan nanoparticle based delivery systems for sustainable agriculture. Int J Biol Macromol 77:36–51

Kataja M, Rybin A, Timonen J (1992) Permeability of highly compressible porous medium. J Appl Phys 72:1271–1274

Kazanskii KS, Dubrovskii SA (1992) Chemistry and physics of agricultural hydrogels. Polyelectrolytes hydrogels chromatographic materials. Springer, Berlin, pp 97–133

Kenawy ER (1998) Biologically active polymers: controlled-release formulations based on crosslinked acrylamide gel derivatives. React Funct Polym 36:31–39

Kim J, Lee KW, Hefferan TE, Currier BL, Yaszemski MJ, Lu L (2007) Synthesis and evaluation of novel biodegradable hydrogels based on poly (ethylene glycol) and sebacic acid as tissue engineering scaffolds. Biomacromolecules 9(1):149–157

Kitila G, Gebrekidan H, Alamrew T (2014) Assessment of irrigation water quality and suitability for irrigation in the Fincha'a Valley Sugar Estate, Nile Basin of Western Ethiopia. Sci Technol Arts Res J 3(1):64–73

Klein M, Aserin A, Svitov I, Garti N (2010) Enhanced stabilization of cloudy emulsions with gum Arabic and whey protein isolate. Colloids Surf B: Biointerfaces 77(1):75–81

Knypl JS, Knypl M (1993) Increased chilling stress tolerance in soybean seeds treated with poly (acrylic acid-ethyl acrylate-vinyl acetate, a superabsorbent). Acta Physiol Plant 15:3

Kohls SJ, Baker DD, Kremer DA, Dawson JO (1999) Water-retentive polymers increase nodulation of actinorhizal plants inoculated with Frankia. Plant Soil 214:105–115

Kong H, Yang J, Zhang Y, Fang Y, Nishinari K, Phillips GO (2014) Synthesis and antioxidant properties of gum arabic-stabilized selenium nanoparticles. Int J Biol Macromol 65:155–162

Kuang J, Yuk KY, Huh KM (2011) Polysaccharide-based superporous hydrogels with fast swelling and superabsorbent properties. Carbohydr Polym 83:284–290

Kulkarni D, Dwivedi AK, Singh S (1998) Performance evaluation of tamarind seed polyose as a binder and in sustained release formulations of low drug loading. Indian J Pharm Sci 60:50–53

Kulkarni AR, Soppimath KS, Aminabhavi TM, Dave AM, Mehta MH (2000) Glutaraldehyde crosslinked sodium alginate beads containing liquid pesticide for soil application. J Control Release 63:97–105

Kulkarni GT, Gowthamarajan K, Dhobe RR, Yohanan F, Suresh B (2005) Development of controlled release spheriods using natural polysaccharide as release modifier. Drug Deliv 12:201–206

Kumar J, Nisar K, Shakil NA, Sharma R (2010) Residue and bio-efficacy evaluation of controlled release formulations of metribuzin against weeds in wheat. Bull Environ ContamToxicol 85:357–361

Laftah WA, Hashim S, Ibrahim AN (2011) Polymer hydrogels: a review. Polym Plast Technol Eng 50:1475–1486

Lakouraj MM, Mojerlou F, Zare EN (2014) Nanogel and superparamagnetic nanocomposite based on sodium alginate for sorption of heavy metal ions. Carbohydr Polym 106:34–41

Lapasin R, Pricl S, Tracanelli P (1991) Rheology of hydroxyethyl guar gum derivatives. Carbohydr Polym 14(4):411–427

Lapasin R, De Lorenzi L, Pricl S, Torriano G (1995) Flow properties of hydroxypropyl guar gum and its long-chain hydrophobic derivatives. Carbohydr Polym 28(3):195–202

Lee KY, Mooney DJ (2001) Hydrogels for tissue engineering. Chem Rev 101:1869–1879

Lee SS, Chang SX, Chang YY, Ok YS (2013) Commercial versus synthesized polymers for soil erosion control and growth of Chinese cabbage. Springer Plus 2:534

Lee CS, Gong J, Huong CV, Oh DS, Chang YS (2016) Macroporous alginate substrate-bound growth of Fe^0 nanoparticles with high redox activities for nitrate removal from aqueous solutions. Chem Eng J 298:206–213

Li Q, Tan W, Zhang C, Gu G, Guo Z (2015) Novel triazolyl-functionalized chitosan derivatives with different chain lengths of aliphatic alcohol substituent: design, synthesis, and antifungal activity. Carbohydr Res 418:44–49

Liakos I, Rizzello L, Bayer IS, Pompa PP, Cingolani R, Athanassiou A (2013) Controlled antiseptic release by alginate polymer films and beads. Carbohydr Polym 92:176–183
Libio IC, Demori R, Ferrão MF, Lionzo MI, da Silveira NP (2016) Films based on neutralized chitosan citrate as innovative composition for cosmetic application. Mater Sci Eng C 67:115–124
Lionetto F, Sannino A, Maffezzoli A (2005) Ultrasonic monitoring of the network formation in superabsorbent cellulose based hydrogels. Polymer 46:1796–1803
Lokhande HT, Varadarajan PV (1992) A new Guargum-based superabsorbent polymer synthesised using gamma radiation as a soil additive. Bioresour Technol 42:119–122
Lu T, Xiang T, Huang XL, Li C, Zhao WF, Zhang Q, Zhao CS (2015) Post-crosslinking towards stimuli-responsive sodium alginate beads for the removal of dye and heavy metals. Carbohydr Polym 133:587–595
Mahmoodi NM (2013) Magnetic ferrite nanoparticle–alginate composite: synthesis, characterization and binary system dye removal. J Taiwan Inst Chem Eng 44:322–330
Mahmoud ME, Kana MT, Hendy AA (2015) Synthesis and implementation of nano-chitosan and its acetophenone derivative for enhanced removal of metals. Int J Biol Macromol 81:672–680
Maleki A, Pajootan E, Hayati B (2015) Ethyl acrylate grafted chitosan for heavy metal removal from wastewater: equilibrium, kinetic and thermodynamic studies. J Taiwan Inst Chem Eng 51:127–134
Mandal B, Ray SK (2013) Synthesis of interpenetrating network hydrogel from poly (acrylic acid-co-hydroxyethyl methacrylate) and sodium alginate: modeling and kinetics study for removal of synthetic dyes from water. Carbohydr Polym 98:257–269
Mandal B, Ray SK (2015) Removal of safranine T and brilliant cresyl blue dyes from water by carboxy methyl cellulose incorporated acrylic hydrogels: isotherms, kinetics and thermodynamic study. J Taiwan Inst Chem Eng 60:313–327
Marcì G, Mele G, Palmisano L, Pulito P, Sannino A (2006) Environmentally sustainable production of cellulose-based superabsorbent hydrogels. Green Chem 8:439–444
Masoumi A, Ghaemy M (2014) Removal of metal ions from water using nanohydrogel tragacanth gum-g-polyamidoxime: isotherm and kinetic study. Carbohydr Polym 108:206–215
Mbuna JJ, Mhinzi GS (2003) Evaluation of gum exudates from three selected plant species from Tanzania for food and pharmaceutical applications. J Sci Food Agr 83(2):142–146
McHugh DJ (2003) A guide to the seaweed industry FAO Fisheries Technical Paper 441. Food and Agriculture Organization of the United Nations, Rome
Mehra GR, Manish M, Rashi S, Neeraj G, Mishra DN (2010) Enhancement of miotic potential of pilocarpine by tamarind gum based in-situ gelling ocular dosage form. Acta Pharma Sci 52:145–154
Mekonnen T, Mussone P, Khalil H, Bressler D (2013) Progress in bio-based plastics and plasticizing modifications. J Mater Chem A 1:13379–13398
Mishra MU, Khandare JN (2011) Evaluation of tamarind seed polysaccharide as a biodegradable carrier for colon specific drug delivery. Int J Pharm Pharm Sci 3:139–142
Mishra MM, Yadav M, Sand A, Tripathy J, Behari K (2010) Water soluble graft copolymer (κ-carrageenan-g-N-vinyl formamide): preparation, characterization and application. Carbohydr Polym 80:235–241
Mitrus M, Wojtowicz A, Moscicki L (2009) Biodegradable polymers and their practical utility. In: Thermoplastic starch: a green material for various industries. Wiley, Weinheim
Mittal H, Maity A, Ray SS (2015a) Effective removal of cationic dyes from aqueous solution using gum ghatti-based biodegradable hydrogel. Int J Biol Macromol 79:8–20
Mittal H, Maity A, Ray SS (2015b) Synthesis of co-polymer-grafted gum karaya and silica hybrid organic–inorganic hydrogel nanocomposite for the highly effective removal of methylene blue. Chem Eng J 279:166–179
Mittal H, Maity A, Ray SS (2016) Gum karaya based hydrogel nanocomposites for the effective removal of cationic dyes from aqueous solutions. Appl Surf Sci 364:917–930
Monier M, Abdel-Latif DA, Ji HF (2016) Synthesis and application of photo-active carboxymethyl cellulose derivatives. React Funct Polym 102:137–146

Nair V, Panigrahy A, Vinu R (2014) Development of novel chitosan–lignin composites for adsorption of dyes and metal ions from wastewater. Chem Eng J 254:491–502
Necas J, Bartosikova L (2013) Carrageenan: a review. Vet Med 58:187–205
Ni B, Liu M, Lü S (2009) Multifunctional slow-release urea fertilizer from ethylcellulose and superabsorbent coated formulations. Chem Eng J 155:892–898
Ni B, Liu M, Lu S, Xie L, Wang Y (2011) Environmentally friendly slow-release nitrogen fertilizer. J Agric Food Chem 59:10169–10175
Nishinari K, Doi E (eds) (2012) Food hydrocolloids: structures, properties, and functions. Springer Science & Business Media
Nnadi F, Brave C (2011) Environmentally friendly superabsorbent polymers for water conservation in agricultural lands. J Soil Sci Environ Manag 2:206–211
Noppakundilograt S, Pheatcharat N, Kiatkamjornwong S (2015) Multilayer coated NPK compound fertilizer hydrogel with controlled nutrient release and water absorbency. J Appl Polym Sci 132:41249–41250
Omidian H, Rocca JG, Park K (2005) Advances in superporous hydrogels. J Control Release 102:3–12
Pal S, Ghorai S, Dash MK, Ghosh S, Udayabhanu G (2011) Flocculation properties of polyacrylamide grafted carboxymethyl guar gum (CMG-g-PAM) synthesized by conventional and microwave assisted method. J Hazard Mater 192:1580–1588
Pal A, Giri A, Bandyopadhyay A (2016) Influence of hydrodynamic size and zeta potential of a novel polyelectrolyte poly (acrylic acid) grafted guar gum for adsorption of Pb (II) from acidic waste water. J Environ Chem Eng 4:1731–1742
Pandey S, Mishra SB (2012) Microwave synthesized xanthan gum-g-poly (ethylacrylate): an efficient Pb^{2+} ion binder. Carbohydr Polym 90:370–379
Pangon A, Saesoo S, Saengkrit N, Ruktanonchai U, Intasanta V (2016) Hydroxyapatite-hybridized chitosan/chitin whisker bionanocomposite fibers for bone tissue engineering applications. Carbohydr Polym 144:419–427
Parvathy PC, Jyothi AN (2012) Synthesis, characterization and swelling behaviour of superabsorbent polymers from cassava starch-graft-poly (acrylamide). Starch-Stärke 64:207–218
Patel B, Patel P, Bhosale A, Hardikar S, Mutha S, Chaulang G (2009) Evaluation of Tamarind Seed Polysaccharide (TSP) as a mucoadhesive and sustained release component of nifedipine buccoadhesive tablet & comparison with HPMC and Na CMC. Int J Pharm Tech Res 1:404–410
Pathania D, Gupta D, Kothiyal NC, Eldesoky GE, Naushad M (2016) Preparation of a novel chitosan-g-poly (acrylamide)/Zn nanocomposite hydrogel and its applications for controlled drug delivery of ofloxacin. Int J Biol Macromol 84:340–348
Patil BS, Mastiholimath V, Kulkarni AR (2011) Novel wound dressing material derived from crosslinked tamarind seeds polysaccharide. In vitro characterization and wound healing activity. Trends Biomater Artif Organs 25(149):153
Patra S, Roy E, Madhuri R, Sharma PK (2016) Agar based bimetallic nanoparticles as high-performance renewable adsorbent for removal and degradation of cationic organic dyes. J Ind Eng Chem 33:226–238
Peng Z, Chen F (2011) Synthesis and properties of lignin-based polyurethane hydrogels. Int J Polym Mat 60:674–683
Pepperman AB, Kuan J-CW (1993) Slow release formulations of metribuzin based on alginate-kaolin-linseed oil. J Control Release 26:21–30
Pfister G, Bahadir M, Korte F (1986) Release characteristics of herbicides from Ca alginate gel formulations. J Control Release 3:229–233
Pillai CK (2010) Challenges for natural monomers and polymers: novel design strategies and engineering to develop advanced polymers. Designed Monomers Polym 13:87–121
Pourjavadi A, Harzandi AM, Hosseinzadeh H (2004) Modified carrageenan synthesis of a novel polysaccharide-based superabsorbent hydrogel via graft copolymerization of acrylic acid onto kappa-carrageenan in air. Eur Polym J 40:1363–1370

Pourjavadi A, Ghasemzadeh H, Soleyman R (2007) Synthesis, characterization, and swelling behavior of alginate-g-poly (sodium acrylate)/kaolin superabsorbent hydrogel composites. J Appl Polym Sci 5:2631–2639

Quinn JJ (1990) 22nd congress of national agricultural plastics association, Montreal, Canada, 1990

Raju KM, Raju MP (2001) Synthesis of novel superabsorbing copolymers for agricultural and horticultural applications. Polym Int 50:946–951

Ramakrishnan A, Pandit N, Badgujar M, Bhaskar C, Rao M (2007) Encapsulation of endoglucanase using a biopolymer Gum Arabic for its controlled release. Bioresour Technol 98:368–372

Ramezani M, Jafari M, Tavili A, Javadi SA, Amiri QZ (2013) The effect of calcium and sodium chloride levels on the dehydration power of hydrophilic polymer. J Food Agric Environ 11:896–898

Reddy DH, Lee SM (2013) Application of magnetic chitosan composites for the removal of toxic metal and dyes from aqueous solutions. Adv Colloid Interface Sci 201:68–93

Rhee JS, Jung MW, Paeng KJ (1998) Evaluation of chitin and chitosan as a sorbent for the preconcentration of phenol and chlorophenols in water. Anal Sci 14:1089–1092

Rinaudo M (2006) Chitin and chitosan: properties and applications. Progr Polym Sci 31:603–632

Robinson G, Ross-Murphy SB, Morris ER (1982) Viscosity-molecular weight relationships, intrinsic chain flexibility, and dynamic solution properties of guar galactomannan. Carbohydr Res 107:17–32

Rocher V, Siaugue JM, Cabuil V, Bee A (2008) Removal of organic dyes by magnetic alginate beads. Water Res 42:1290–1298

Rodrigues FH, Spagnol C, Pereira AG, Martins AF, Fajardo AR, Rubira AF, Muniz EC (2014) Superabsorbent hydrogel composites with a focus on hydrogels containing nanofibers or nanowhiskers of cellulose and chitin. J Appl Polym Sci 131(2)

Rodríguez R, Alvarez-Lorenzo C, Concheiro A (2003) Cationic cellulose hydrogels: kinetics of the cross-linking process and characterization as pH-/ion-sensitive drug delivery systems. J Control Release 86:253–265

Rolando M, Valente C (2007) Establishing the tolerability and performance of tamarind seed polysaccharide (TSP) in treating dry eye syndrome: results of a clinical study. BMC ophthalmology 7:1

Roy A, Bajpai J, Bajpai AK (2009) Dynamics of controlled release of chlorpyrifos from swelling and eroding biopolymeric microspheres of calcium alginate and starch. Carbohydr Polym 76:222–231

Ruvalcaba AM, Sanchez-Diaz JC, Becerra F, Cruz-Barba LE, Gonzalez-Alvarez A (2009) Swelling characterization and drug delivery kinetics of polyacrylamide-co-itaconic acid/chitosan hydrogels. Express Polym Lett 3:25–32

Sadeghi S, Rad FA, Moghaddam AZ (2014) A highly selective sorbent for removal of Cr (VI) from aqueous solutions based on Fe_3O_4/poly (methyl methacrylate) grafted Tragacanth gum nanocomposite: optimization by experimental design. Mater Sci Eng C 45:136–145

Sandford PA, Baird J (1983) In: Aspinall GO (ed) The polysaccharides. Academia Press, Prague, pp 470–473

Sannino A, Nicolais L (2005) Concurrent effect of microporosity and chemical structure on the equilibrium sorption properties of cellulose-based hydrogels. Polymer 46:4676–4685

Sannino, A Maffezzoli, L Nicolais (2003) Introduction of molecular spacers between the crosslinks of a cellulose-based superabsorbent hydrogel: effects on the equilibrium sorption properties. J Appl Polym Sci 90(1):168–174

Saravanan P, Vinod VT, Sreedhar B, Sashidhar RB (2012) Gum kondagogu modified magnetic nano-adsorbent: an efficient protocol for removal of various toxic metal ions. Mater Sci Eng C 32:581–586

Saruchi KBS, Jindal R, Kapur GS, Kumar V (2014) Synthesis, characterization and evaluation of Gum tragacanth and acrylic acid based hydrogel for sustained calcium chloride release–enhancement of water-holding capacity of soil. J Chin Adv Mat Soc 2:40–52

Schreiber MM, White MD, Wing RE (1988) Bioactivity of controlled release formulations of starch-encapsulated EPTC. J Control Release 7:237–242

Shalviri A, Liu Q, Abdekhodaie MJ, Wu XY (2010) Novel modified starch–xanthan gum hydrogels for controlled drug delivery: synthesis and characterization. Carbohydr Polym 79:898–907

Sharma K, Kaith BS, Kumar V, Kalia S, Kumar V, Swart HC (2014) Water retention and dye adsorption behavior of Gg-cl-poly (acrylic acid-aniline) based conductive hydrogels. Geoderma 232:45–55

Shavit U, Shaviv A, Shalit G, Zaslavsky D (1997) Release characteristics of a new controlled release fertilizer. J Control Release 43:131–138

Shaviv (2001) Advances in controlled-release fertilizers. Adv Agronomy 71:1–49

Shi HY, Zhang LM (2007) New grafted polysaccharides based on O-carboxymethyl-O-hydroxypropyl guar gum and N-isopropylacrylamide: synthesis and phase transition behavior in aqueous media. Carbohydr Polym 67(3):337–342

Shirakawa M, Yamatoya K (2003) Xyloglucan: its structure and function. Foods and food ingredients. J Japan 208:922–929

Shojaat R, Saadatjoo N, Karimi A, Aber S (2016) Simultaneous adsorption–degradation of organic dyes using $MnFe_2O_4$/calcium alginate nano-composites coupled with GO_x and laccase. J Environ chem Eng 4:1722–1730

Singh B, Sharma DK, Gupta A (2007) Controlled release of thiram fungicide from starch-based hydrogels. J Environ Sci Health B 42:677–695

Singh B, Sharma DK, Gupta A (2008) In vitro release dynamics of thiram fungicide from starch and poly(methacrylic acid)-based hydrogels. J Hazard Mater 154:278–286

Singh B, Sharma DK, Kumar R, Gupta A (2009a) Controlled release of the fungicide thiram from starch–alginate–clay based formulation. Appl Clay Sci 45:76–82

Singh V, Kumari P, Pandey S, Narayan T (2009b) Removal of chromium (VI) using poly (methylacrylate) functionalized guar gum. Bioresour Technol 100:1977–1982

Singh A, Sarkar DJ, Singh AK, Parsad R, Kumar A, Parmar BS (2011a) Studies on novel nanosuperabsorbent composites: swelling behavior in different environments and effect on water absorption and retention properties of sandy loam soil and soil-less medium. J Appl Polym Sci 120:1448–1458

Singh B, Sharma DK, Dhiman A, Gupta A (2011b) Applications of natural polysaccharide-based beads for slow release herbicide formulation. Toxicol Environ Chem 93:616–622

Singh B, Sharma DK, Negi S, Dhiman A (2015) Synthesis and characterization of agar-starch based hydrogels for slow herbicide delivery applications. Int J Plastics Technol 19:263–274

Sinha VR, Kumria R (2001) Polysaccharides in colon-specific drug delivery. Int J Pharma 224:19–38

Soares PI, Sousa AI, Silva JC, Ferreira IM, Novo CM, Borges JP (2016) Chitosan-based nanoparticles as drug delivery systems for doxorubicin: optimization and modelling. Carbohydr Polym 147:304–312

Sohrabi S, Haeri A, Mahboubi A, Mortazavi A, Dadashzadeh S (2016) Chitosan gel-embedded moxifloxacin niosomes: an efficient antimicrobial hybrid system for burn infection. Int J Biol Macromol 85:625–633

Sook Y, Jae-Sik H (2000) Application of super water absorbent for edible mushroom production. J Korean Soc Agr Eng 28:16

Spagnol C, Rodrigues FHA, Pereira AGB, Fajardo AR, Rubira AF, Muniz EC (2012) Superabsorbent hydrogel composite made of cellulose nanofibrils and chitosan-graft-poly (acrylic acid). Carbohydr Polym 87:2038–2045

Srinivasan B, Ganta A, Rajamanickam D, Veerabhadraiah BB, Varadharajan M (2011) Evaluation of tamarind seed polysaccharide as a drug release retardant. Int J Pharm Sci Rev Res 9:27–31

Srivastava A, Tripathy J, Mishra MM, Behari K (2007) Modification of guar gum through grafting of 4 vinyl pyridine using potassium peroxymonosulphate/ascorbic acid redox pair. J Appl Polym Sci 106:1353–1358

Suh JK, Matthew HW (2000) Application of chitosan-based polysaccharide biomaterials in cartilage tissue engineering: a review. Biomaterials 21(24):2589–2598

Thakur VK, Kessler MR (2015) Self-healing polymer nanocomposite materials: a review. Polymer 69:369–383

Thakur VK, Thakur MK (2014) Recent trends in hydrogels based on psyllium polysaccharide: a review. J Clean Prod 82:1–15

Thakur VK, Thakur MK (2015) Recent advances in green hydrogels from lignin: a review. Int J Biol Macromolec 72:834–847

Thakur MK, Thakur VK, Gupta RK, Pappu A (2015) Synthesis and applications of biodegradable soy based graft copolymers: a review. ACS Sustain Chem Eng 4(1):1–17

Thombare N, Jha U, Mishra S, Siddiqui MZ (2016) Guar gum as a promising starting material for diverse applications: a review. Int J Biol Macromol 88:361–372

Trimnell D, Shasha BS, Otey FH (1985) The effect of α-amylases upon the release of trifluralin encapsulated in starch. J Control Release 1:183–190

Tripathy J, Mishra DK, Yadav M, Sand A, Behari K (2009) Modification of κ-carrageenan by graft copolymerization of methacrylic acid: synthesis and applications. J Appl Polym Sci 114:3896–3905

Tsuji K (2001) Microencapsulation of pesticides and their improved handling safety. J Microencapsul 18:137–147

Ulery BD, Nair LS, Laurencin CT (2011) Biomedical applications of biodegradable polymers. J Polym Sci Part B Polym Phys 49:832–864

Umoren SA, Obot IB, Ebenso EE, Okafor PC, Ogbobe O, Oguzie EE (2006) Gum arabic as a potential corrosion inhibitor for aluminium in alkaline medium and its adsorption characteristics. Anti-Corros Methods Mater 53:277–282

Vallée F, Müller C, Durand A, Schimchowitsch S, Dellacherie E, Kelche C, Cassel JC, Leonard M (2009) Synthesis and rheological properties of hydrogels based on amphiphilic alginate-amide derivatives. Carbohydr Res 344:223–228

Varela P, Fiszman SM (2011) Hydrocolloids in fried foods. A review. Food Hydrocolloids 25:1801–1812

Varki A, Cummings R, Esko J, Jessica Freeze, Hart G, Marth J (1999) Essentials of glycobiology. Cold Spring Harbor Laboratory Press

Varki A, Cummings R, Esko J, Freeze H, Stanley P, Bertozzi C, Hart G, Etzler M (2008) Essentials of glycobiology, 2nd edn. Cold Spring Harbor Laboratory Press

Verbeken D, Dierckx S, Dewettinck K (2003) Exudate gums: occurrence, production, and applications. Appl Microbiol Biotechnol 63:10–21

Vijn JP, Leiden JB, Bach D (2002) Delayed thixotropic cement compositions and methods. US Patent, 6,610,140 B2

Villafranca-Sánchez M, González-Pradas E, Fernández-Pérez M (2000) Controlled release of isoproturon from an alginate–bentonite formulation: water release kinetics and soil mobility. Pest Manag Sci 56:749–756

Villay A, de Filippis FL, Picton L, Le Cerf D, Vial C, Michaud P (2012) Comparison of polysaccharide degradations by dynamic high-pressure homogenization. Food Hydrocoll 27:278–286

Vinod VT, Sashidhar RB, Sreedhar B, Rao BR, Rao TN, Abraham JT (2009) Interaction of Pb^{2+} and Cd^{2+} with gum kondagogu (*Cochlospermum gossypium*): a natural carbohydrate polymer with biosorbent properties. Carbohydr Polym 78:894–901

Vinod VT, Sashidhar RB, Sukumar AA (2010) Competitive adsorption of toxic heavy metal contaminants by gum kondagogu (*Cochlospermum gossypium*): a natural hydrocolloid. Colloids Surf B 75:490–495

Vinod VT, Sashidhar RB, Sivaprasad N, Sarma VU, Satyanarayana N, Kumaresan R, Rao TN, Raviprasad P (2011) Bioremediation of mercury (II) from aqueous solution by gum karaya (*Sterculia urens*). A natural hydrocolloid. Desalination 272:270–277

Vollmer DP (inventor) (2003) Well treatment fluids and methods for the use thereof. United States patent US 6,509,301

Vu CH, Won K (2013) Novel water-resistant UV-activated oxygen indicator for intelligent food packaging. Food Chem 140:52–56

Wang W, Wang A (2010a) Nanocomposite of carboxymethyl cellulose and attapulgite as a novel pH sensitive superabsorbent: synthesis, characterization and properties. Carbohydr Polym 82:83–91

Wang WB, Wang AQ (2010b) Preparation, swelling and water-retention properties of crosslinked superabsorbent hydrogels based on guar gum. Adv Mater Res 96:177–182

Wang M, Xu L, Hu H, Zhai M, Peng J, Nho Y, Li J, Wei G (2007) Radiation synthesis of PVP/CMC hydrogels as wound dressing. Nucl Instrum Methods Phys Res Sect B: Beam Interact Mater Atoms 265:385–389

Wang S, Alva AK, Li Y, Zhang M (2011) A rapid technique for prediction of nutrient release from polymer coated controlled release fertilizers. Open J Soil Sci 1:40–44

Wang Y, Shi X, Wang W, Wang A (2013) Synthesis, characterization, and swelling behaviors of a pH-responsive CMC-g-poly(AA-co-AMPS) superabsorbent hydrogel. Turkish J Chem 37:149–159

Wang X, Lü S, Gao C, Xu X, Wei Y, Bai X, Feng C, Gao N, Liu M, Wu L (2014) Biomass-based multifunctional fertilizer system featuring controlled-release nutrient, water-retention and amelioration of soil. RSC Adv 4:18382–18390

Wang Y, Zhang Y, Hou C, Liu M (2016) Mussel-inspired synthesis of magnetic polydopamine–chitosan nanoparticles as biosorbent for dyes and metals removal. J Taiwan Inst Chem Eng 61:292–298

Wei W, Kim S, Song MH, Bediako JK, Yun YS (2015) Carboxymethyl cellulose fiber as a fast binding and biodegradable adsorbent of heavy metals. J Taiwan Inst Chem Eng 57:104–110

Whistler RL, BeMiller JN (1993) Industrial gums: polysaccharides and their derivatives, 2nd edn. Academic Press Inc, pp 145–181

Wong TY, Preston LA, Schiller NL (2000) Alginate Lyase: review of major sources and enzyme characteristics, structure-function analysis, biological roles, and applications. Annu Rev Microbiol 54:289–340

Woodhouse J, Johnson MS (1991) Effect of superabsorbent polymers on survival and growth of crop seedlings. Agric Water Manag 20:63–70

Wu L, Liu M (2008) Preparation and properties of chitosan-coated NPK compound fertilizer with controlled-release and water-retention. Carbohydr Polym 72:240–247

Xie M, Zeng L, Zhang Q, Kang Y, Xiao H, Peng Y, Chen X, Luo J (2015) Synthesis and adsorption behavior of magnetic microspheres based on chitosan/organic rectorite for low-concentration heavy metal removal. J Alloys Compd 647:892–905

Xu S, Wu R, Huang X, Cao L, Wang J (2005) Effect of the anionic-group/cationic-group ratio on the swelling behavior and controlled release of agrochemicals of the amphoteric, superabsorbent polymer poly (acrylic acid-co-diallyldimethylammonium chloride). J Appl Polym Sci 102:986–991

Yogi RK, Bhattacharya A, Jaiswal AK, Kumar A (2015) Lac, plant resin and gums statistics 2014: at a glance. ICAR-Indian Institute of Natural Resins And Gums, Ranchi (Jharkhand), India. Bulletin (technical) No. 27/2015.01–68 pp

Zarghami Z, Akbari A, Latifi AM, Amani MA (2016) Design of a new integrated Chitosan-PAMAM Dendrimer biosorbent for heavy metals removing and study of its adsorption kinetics and thermodynamics. Bioresour Technol 205:230–238

Zhang XZ, Yang YY, Chung TS (2002) The influence of cold treatment on properties of temperature-sensitive poly (N-isopropylacrylamide) hydrogels. J Colloid Interface Sci 246:105–111

Zhang LM, Zhou JF, Hui PS (2005) A comparative study on viscosity behavior of water soluble chemically modified guar gum derivatives with different functional lateral groups. J Sci Food Agric 85:2638–2644

Zhang G, Yi L, Deng H, Sun P (2014a) Dyes adsorption using a synthetic carboxymethyl cellulose-acrylic acid adsorbent. J Environ Sci 26:1203–1211

Zhang M, Gao B, Chen J, Li Y, Creamer AE, Chen H (2014b) Slow-release fertilizer encapsulated by graphene oxide films. Chem Eng J 255:107–113

Zheng Y, Li P, Zhang J, Wang A (2007) Study on superabsorbent composite XVI synthesis, characterization and swelling behaviors of poly(sodium acrylate)/vermiculite superabsorbent composites. Eur Polym J 43:1691–1698

Zheng T, Liang Y, Ye S, He Z (2009) Superabsorbent hydrogels as carriers for the controlled-release of urea: experiments and a mathematical model describing the release rate. Biosyst Eng 102:44–50

Zhou W, Lou Y, Ren L, Han Y, Meng Y, Wu L (2014) Application of controlled-release nitrogen fertilizer decreased methane emission in transgenic rice from a paddy soil. Water Air Soil Pollut 225:2–7

Zhu Y, An X, Li S, Yu S (2009) Nanoencapsulation of β-cypermethrin by complex coacervation in a microemulsion. J Surfactant Deterg 12:305–311

Zohuriaan-Mehr MJ (2006) Super-absorbents. Iran Polymer Society, Tehran