Recent Advances in Applications of Natural Gums in Agriculture

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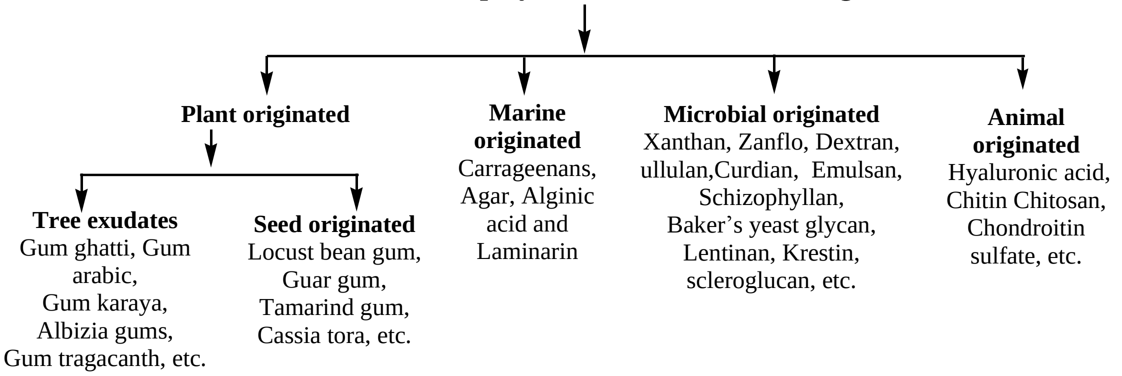
Introduction

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". Among these biopolymers, polysaccharides in the form of 'gums and resins' obtained from living sources like plants, animals, insects, etc., are of great commercial potential.

Classification of polysaccharides based on origin



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.

Chemical modification of gums

The natural raw gums have wide applications, yet there is a lot of scope to enhance their applications by improving their physico-chemical properties. Properties of natural raw gum can be improved or modified by chemical methods like 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. For example, by synthesizing the hybrid derivatives of guar gum like hydroxypropyl or carboxymethyl, its properties like solubilization time, viscosity, and clarity of solution can be significantly improved.

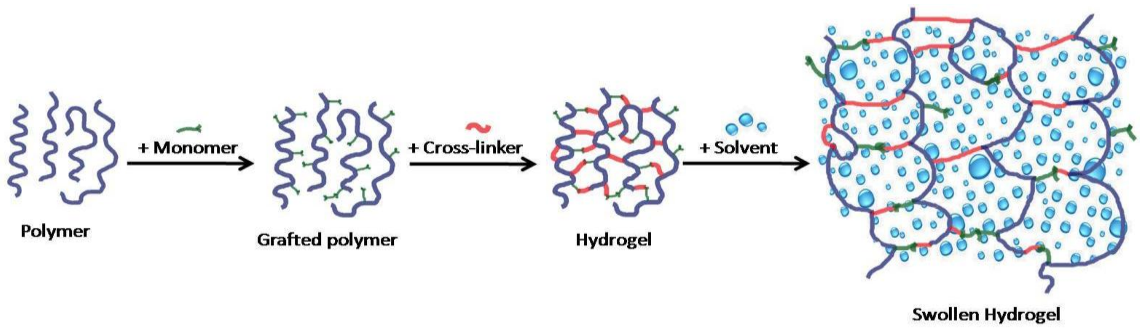


Figure: Schematic diagram of synthesis of hydrogel through grafting and cross-linking

Applications of natural gums

Long chain molecular structure and the abundance of hydroxyl groups in the gum molecule makes it fit for variety of chemical reactions. Solubility in cold as well as hot water and other unique properties like thickening, emulsifying, gelling, stabilizing, binding, etc. makes it suitable for variety of application. Major applications of natural gums are discussed as following.

Agriculture

Polysaccharides based superabsorbent polymers with the ability to absorb and retain large amount of water are gaining importance in agriculture. Adding such hydrogels to the soil can ensure prolonged moisture availability which can sustain the crop in arid areas. The water absorbed in hydrogel dissolves the nutrient which can diffuse out through the polymer matrix as depicted in the adjoining figure. They act as 'miniature water reservoirs' in soil, releasing water into the soil as per requirement of plant roots. Also there are reports on the favorable alteration of the physical properties of soil by hydrogel amendments. Though the synthetic polymer based hydrogels are more popular due to their high water retention capacity and durability, the use of on natural polymer based hydrogels is flourishing due to their biodegradability, non-toxicity of the base component and their sustainability. These hydrogels can also be used as a matrix for controlled release of fertilizers- nutrients and pesticides in soil. With the limited research on agricultural use of biopolymer based hydrogels such as starch, chitosan, cellulose, xanthan, cassava, few studies on guar gum based hydrogels are also reported.

Though large numbers of hydrogels have been developed at laboratory stage, only very few satisfy the requisite environment safety parameters like 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 1980s mainly as disposable diapers (Castel et al. 1990; Kataja 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.

1. Water retention

Globally, agriculture is predominantly dependent on rainfall. Around 65 to 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 rain water for 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 et al. 2010). 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 et al. 2001; Shalviri et al. 2010; Ulrey 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 evapo-transpiration rate
- Improving soil physical properties like 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 helps in reducing the effects of salinity
- 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 towards water molecules during the swelling phase of absorption. Also, the hydrophobic units of the network structure interact with water molecules by weak Vander wall 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, all affect 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). Use of filler material helps in obtaining hydrogels having high absorption capacity as well as mechanical strength.

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). 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 (Huttermann 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 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 to 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).

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 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). Use of hydrogel increased the period between field capacity and wilting by 300 percent. 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. 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 (Huttermann 1999). Maximum survival of plants was observed when the hydrogel concentration was highest.

3. Controlled nutrient delivery

Plant nutrients when applied to soil are subject to various forms of losses such as leaching, volatilization, runoff, etc. 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.

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, etc. have been used for controlled release application of fertilizers (Jamnongkan et al. 2010; Guilherme et al. 2010; Buchholz et al. 1998; Saruchi et al. 2013).

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 rain water and the release of nutrient is activated. The water absorbed in hydrogel dissolves the nutrient which can diffuse out through the polymer matrix as shown in the adjoining figure.

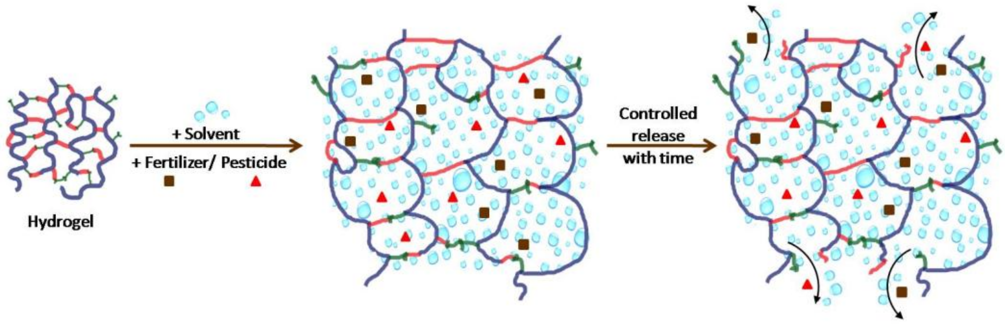


Figure: Entrapping of fertilizer/pesticide and their controlled release through hydrogels

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 rain water 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 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. 2013). There are leaching losses from 40-70% of applied nitrogen and 50-70% of potassium which require application of large quantities of fertilizers (Wu et al. 2008) and consequently, this results into environmental pollution. Therefore, use of polysaccharide based chemical cross-linked hydrogels has been studied for controlled release of fertilizers in soil (Wu et al. 2008; Wang et al. 2014; Shaviv 2001). Chemically cross-liked hydrogels for nutrient release have been more reliable than coated polymers (Zheng 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 2009). Other than the nutrient flow by concentration gradient, processes like 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). Macro-molecular 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.

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 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). Due to overuse of the chemicals, resistance can be developed in the target pests towards 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 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 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.

References:

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

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 (Cupressusarizonica) under reduced irrigation regimes. Iran Polym J 15:715

Buchholz FL, Graham AT (1998) Modern superabsorbent polymer technology. John! Wiley & Sons, Inc, New York, pp 279

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

Campos EVR, de Oliveira JL, Fraceto LF, Singh B (2015) Polysaccharides as safer release systems for agrochemicals. Agronomy Sustain Develop 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

Dumitriu S, Polymeric Biomaterials, Revised and Expanded, 2nd ed., MarcelDekker Inc., NY, USA, 2002, pp. 480.

Easterwood GW (2002) Calcium’s role in plant nutrition. Fluid J 1(1)

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

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

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

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

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

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

Pillai CK (2010) Challenges for natural monomers and polymers: novel design strategies and engineering to develop advanced polymers. Designed Monomers Polym 13:87–121

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. PolymInt 50:946–51

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

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

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

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 88:361-72

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

Yusuf AK (2013) Studies on some physicochemical properties of the plant gum exudates of Acacia senegal (dakwara), Acacia sieberiana (farar kaya) and Acacia nilotica (bagaruwa). J Res Nat Development 9(2):10-7

Zhang G, Yi L, Deng H, Sun P (2014) Dyes adsorption using a synthetic carboxymethyl cellulose-acrylic acid adsorbent. J Environ Sci 26:1203-11