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Panda Arun Kumar
Department of vegetable Science, Dr. YSR Horticulture University, Andhra Pradesh, India

Galipothula Anil Kumar
Department of vegetable Science, Dr. YSR Horticulture University, Andhra Pradesh, India

K Vennela
(HO) Department of vegetable Science, Dr. YSR Horticulture University, Andhra Pradesh, India

Correspondence
Panda Arun Kumar
Department of vegetable Science, Dr. YSR Horticulture University, Andhra Pradesh, India

Role of water absorbing materials in vegetable production

Panda Arun Kumar, Galipothula Anil Kumar and K Vennela

Abstract
The water scarcity is expected to be aggravated further as fast decline of irrigation water potential in most of the countries especially in the arid and semi-arid regions of the world. As per the global survey, the worst affected areas would be the semi-arid regions of Asia (India), the Middle-East and Sub-Saharan Africa. The technique has a great water absorption capacity by its own weight which helps in improving soil moisture capacity and hence reduces water stress on the plant during prolonged drought stress condition and during irrigation intervals. Quantity of total water required for the irrigation is also reduced by 15 to 50% when the soil conditioning by SAP in different proportion is adopted. Considering the high cost and increasing prices of crude oil, the necessity of preparing natural based SAPs seems more obvious. This paves the way for further developments in this area in the mid and far future ahead. Today´s research has proved the ability of natural materials, e.g. Polysaccharides and Proteins, to perform super absorbent properties in pure Water and saline solution (0.9%wt.) within the same range as synthetic polyacrylates do in current applications. The agricultural sector (irrigation), which currently consumes over 80 percent of the available water in India, continues to be the major water-consuming sector due to the intensification of agriculture (Saleth, 1996). One of the main reasons for the low coverage of irrigation is the predominant use of traditional methods of irrigation, where water use efficiency is very low.

Keywords: water, materials, vegetable, absorbing

Introduction
Water absorbing materials
Earlier to the 1920s, water absorbing materials were cellulosic or fiber-based products like tissue paper, cotton, sponge, and fluff pulp. The water absorbent capacity of these types of materials is only up to 11 times their weight, but most of it is lost under moderate pressure.

Types of water absorbing materials
The hygroscopic materials (water absorbing materials) are usually categorized into two main classes based on the major mechanism of water absorption, i.e., chemical and physical absorptions. (Mohammad, J. Z. and Kabiri, K. 2008) [15].

1. **Chemical absorbers**

These types of absorbers will catch water via chemical reaction converting their entire nature. (e.g., metal hydrides)

2. **Physical absorbers**

Physical absorbers will imbibe water via four main mechanisms
(i) Reversible changes of their crystal structure (e.g., silica gel and anhydrous inorganic salts)
(ii) Physical entrapment of water via capillary forces in their macro-porous structure (e.g., soft polyurethane sponge)
(iii) A combination of physical entrapment of water via capillary forces in their macro-porous and hydration of functional groups (e.g., tissue paper)
(iv) The mechanism which may be anticipated by combination of above mechanisms of (ii) & (iii) and essentially dissolution and thermodynamically favoured expansion of the macromolecular chains limited by cross-linkages. (e.g., Hydrogels and Superabsorbent polymer (SAP))

Traditional absorbent materials (such as tissue papers and polyurethane foams) unlike Hydrogels or SAPs will lose most of their absorbed water when they are squeezed. Superabsorbent polymers (SAP) are a class of polymers that are able to absorb large amounts of water. The table compares water absorptiveness of some common absorbent materials and with a typical sample of a commercially available SAP. (Buchholz FL and Graham AT, 1998) [3].

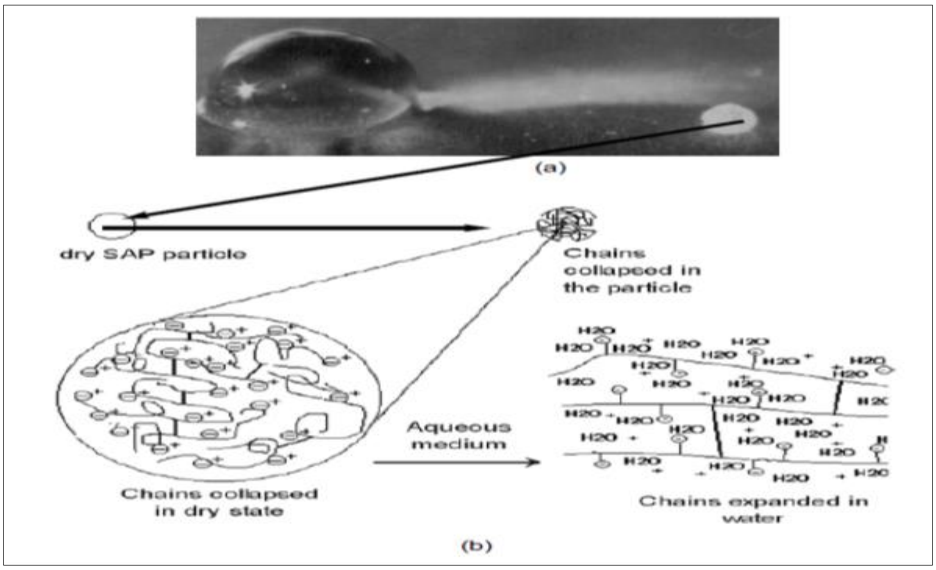
Super absorbent material

Superabsorbent polymer (SAP) materials are organic materials with enormous capability of water absorption. The polymer came to be known as "Super Slurper". Hydrogels are water insoluble, crosslinked, three-dimensional networks of polymer chains plus water that fills the voids between polymer chains. Based on basic technology, a wide range of grafting combinations were attempted including work with acrylic acid, acrylamide and polyvinyl alcohol (PVA). Commercial SAP is generally sugar like hygroscopic materials with white-light yellow colour. The SAP particle shape (granule, fibre, film, etc.) has to be basically preserved after water absorption and swelling, i.e., the swollen gel strength should be high enough to prevent a loosening, mushy, or slimy state. SAPs as hydrogels, relative to their own mass can absorb and retain extraordinary large amounts of water or aqueous solution. These ultrahigh absorbing materials (SAPs) can imbibe deionized water as high as 1,000-100,000% (10-1000 g/g) whereas the absorption capacity of common hydrogels is not more than 100% (1 g/g). (Omidian, H. *et al*., 2004) [12].

The synthesis of the first water-absorbent polymer goes back to 1938 when acrylic acid (AA) and divinylbenzene were thermally polymerized in an aqueous medium. (Buchholz FL and Graham AT, 1998) [3]. In the late 1950s, the first generation of hydrogels was appeared. These hydrogels were mainly based on hydroxyalkyl methacrylate and related monomers with swelling capacity up to 40-50%. They were used in developing contact lenses which have made a revolution in ophthalmology. (Dayal U *et al*., 1999) [5]. In the early 1960s, the United States Department of Agriculture (USDA) was conducting work on materials to improve water conservation in soils. They developed a resin based on the grafting of acrylonitrile polymer onto the backbone of starch molecules (i.e. starch-grafting). The hydrolyzed product of the hydrolysis of this starch-acrylonitrile co-polymer gave water absorption greater than 400 times its weight.

Commercial production of SAP began in Japan in 1978 for use in feminine napkins. Further developments lead to SAP materials being employing in baby diapers in Germany and France in 1980. (Brannon, P. L., and Harland, R. S., 1990) [4]. In this regard, the application of Super Absorbent Polymers in the field of agriculture works as miniature water storage reservoirs especially for the small and marginal farmers living under arid and semi arid regions to optimize water use efficiency and the yield of cash crops.

Visual comparison of typical acrylic-based anionic sap material



(a) A visual comparison of the SAP single particle in dry (right) and swollen state (left). The sample is a bead prepared from the inverse-suspension polymerization technique.
(b) A schematic presentation of the SAP swelling.

Classification of super absorbent material

SAPs are classified majorly

1. Based on presence or absence of electrical charge.
2. Based on type of monomeric unit.
3. Based on original source.

I. Based on presence or absence of electrical charge of presence or absence of electrical charge located in the crosslinked chains
   a) Non-ionic
   b) Ionic (including anionic and cationic)
   c) Amphoteric electrolyte (ampholytic) containing both acidic and basic groups
   d) Zwitterionic (polybetaines) containing both anionic and cationic groups in each structural repeating unit.

For example, the majority of commercial SAP hydrogels are anionic.

II. SAPs are again classified based on the type of monomeric unit used in their chemical structure, thus the most conventional SAPs are held in one of the following categories
   a) Cross- linked polyacrylates and polyacrylamides
   b) Hydrolyzed cellulose-polyacrylonitrile (PAN) or starch-PAN graft copolymers
   c) Cross-linked copolymers of maleic anhydride

III. According to original sources, SAPs are often divided into two main classes; i.e.,
   a. Synthetic (petrochemical-based) and
   b. Natural (e.g., polysaccharide and polypeptide based). (Mohammad, J. Z. and Kabiri, K., 2008) [15]

Mechanisms of swelling in superabsorbent polymers

A SAP particle in dry state consists of collapsed polymer chains. The polymer backbone in SAP is hydrophilic i.e. 'water loving' because it contains water loving carboxylic acid groups (–COOH). When water is added to SAP there is a polymer/solvent interaction, on hydration and the formation of hydrogen bonds along with cross-link chains swelling in superabsorbent polymers is take place. Hydration is the interaction of ions of a solute with molecules of a solvent i.e. COO^- and Na^+ ions attract the polar water molecules. In water the electronegative atom is oxygen which pulls the hydrogen's electrons towards itself setting up a dipole in the molecule. The positive hydrogen atoms are attracted to the oxygen lone pairs on other water molecules. Oxygen has two lone pairs of electrons and each is capable of hydrogen bonding to two other water molecules.

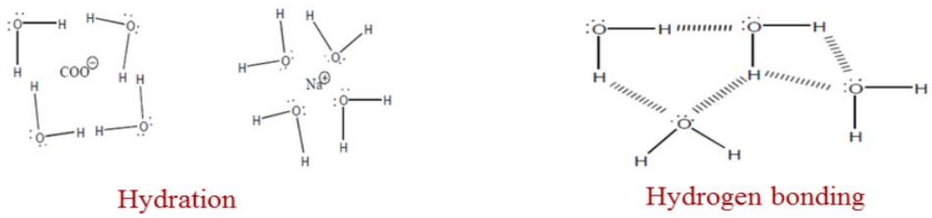


Fig 2: Showing the Hydration and Hydrogen bonding

The neutralised chains contain charges that repel each other. Overall electrical neutrality is maintained as the negative carboxylate groups are balanced by the positive sodium ions. Upon contact with water the sodium ions are hydrated which reduces their attraction to the carboxylate ions (due to the high dielectric constant of water). This allows the sodium ions to move freely within the network, which contributes to the osmotic pressure within the gel.

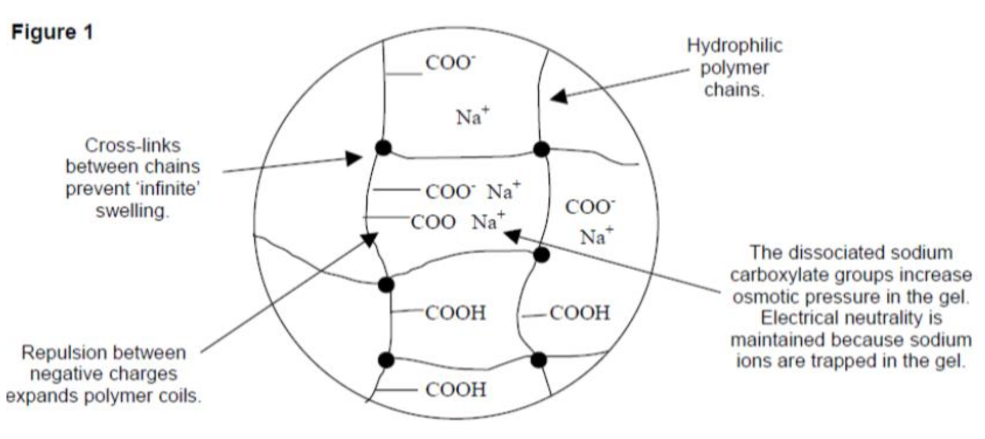


Fig 3: is a diagrammatic representation of part of the polymer network

The mobile positive sodium ions however, cannot leave the gel because they are still weakly attracted to the negative carboxylate ions along the polymer backbone and so behave like they are trapped by a semi-permeable membrane. So the driving force for swelling is the difference between the osmotic pressure inside and outside the gel. Increasing the level of sodium outside of the gel will lower the osmotic pressure and reduce the swelling capacity of the gel. The maximum swelling of the gel will occur in deionised water. (Mohammad, J. Z. and Kabiri, K., 2008) [15].

General pathways to prepare acrylic sap

The greatest volume of SAPs comprises full synthetic or of petrochemical origin. They are produced from the acrylic monomers, most frequently acrylic acid (AA), its salts and acrylamide two general pathways to prepare acrylic SAP networks, i.e., simultaneous polymerization and crosslinking by a polyvinylic cross-linker, and crosslinking of a water soluble prepolymer by a polyfunctional cross-linker.

Cross-linking in superabsorbent polymers

There are two main types of cross-linking in most superabsorbent polymers.

1. **Bulk or core cross-linking:** This normally takes place during the polymerisation stage of superabsorbent production.

Cross-linking is the joining of molecules – generally joining two or more macromolecules with a smaller molecule. The most important type in the case of superabsorbents, and the most common, is the covalent cross-link. In SAP manufacture the most common types of cross-linker are organic molecule that contains two or more polymerisable double bonds. These molecules are incorporated into the backbone of the polymer chains as they grow during the polymerisation reaction

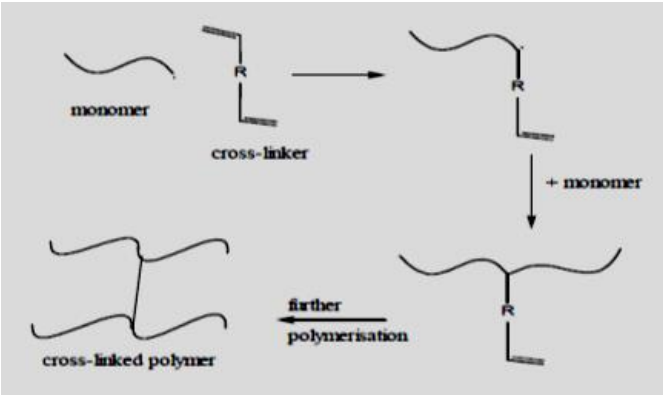


Fig 5: Showing the Bulk or core cross-linking of the polymer network

2. **Surface cross-linking:** This is a newer process that improves the absorption against pressure profile of the polymer.

SAPs with no surface treatment and low internal cross-linking tend to show high swelling capacities but poor absorption against pressure. Improving the swelling capacity of SAP by decreasing the core cross-linking, i.e. decreasing the cross-linking density, is limited by the accompanying increase in extractable polymer content of the gel. Improving the absorption against pressure and the swelling rate of a SAP can be achieved by cross-linking the surface of the particles. Increase in the density of cross-linking on the surface of the particles and core of the particle is the lightly cross-linked polymer and the shell represents the higher cross-linking density on the surface

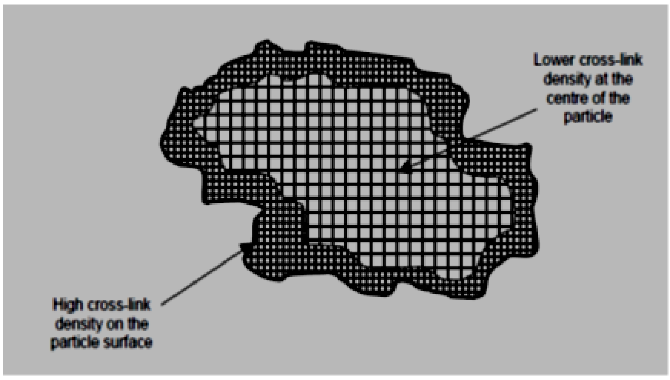


Fig 6: Showing the Surface cross-linking of the polymer network. (Mohammad, J. Z. and Kabiri, K., 2008) [15]

Dosage of SAP

SAPs have been successfully used as soil amendments in the horticulture industry to improve the physical properties of soil in view of increasing their water-holding capacity and/or nutrient retention of sandy soils to be comparable to silty clay or loam.

When SAP is mixed with the soil, the SAP create good air permeability in soil, improves water absorption, property of soil and fertilizer conservation capacity hence economy in irrigation can be attained. Improved water retention capacity can be achieved by the amendment of SAP with various percentage of dosage in to the soil structure by weight. Water retention capacity of soil can be increased by 50% to 70%. (Fidelia N and Chris B, 2011) [6]. Water stress significantly alters in decreasing the number of leaves per plant, chlorophyll content, seed yield and water use efficiency. Whereas the application of super absorbent polymer moderated the negative effect of deficit irrigation, especially in high rates of polymer @ 2.25 and 3 g/kg of soil. (Hossein N *et al.*, 2010) [9]. Super absorbent polymers has been used as soil additives as it increase their water holding capacity, increase water use efficiency, increase plant performance, enhance soil properties, controls water run-off, increase microbial activity, increase the efficiency of fertilizers, pesticides and herbicides and improves germination rate. These are Safe, Non- toxic and Eco friendly. The half life is in general in the range 5 - 7 years and they degrade into ammonium, carbon dioxide and water through aerobic and anaerobic processes of microbiological degradation. (Fidelia N., 2012) [7].

Generally SAPs are applied to the soil at a concentration between 0.1 to 0.5% by weight (Buchholz and Graham, 1998) [3]. Below this range, the effect of the soil additive is negligible, and above this range the soil can become too spongy as it is fully saturated. Various researchers have suggested different rate of SAP to be applied as soil conditioner are listed in the following table.

SAP technical features

Super absorbent polymers has been used as soil additives due to following reasons

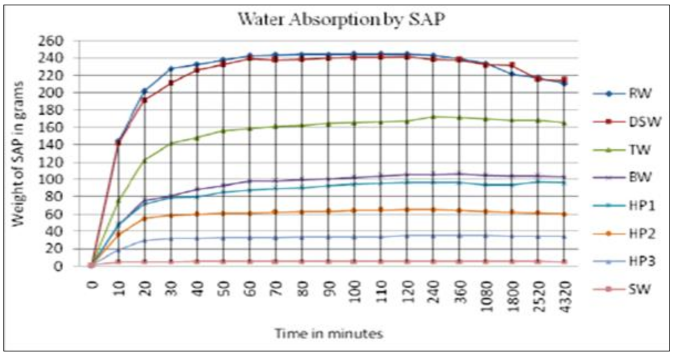
1. Increase their water holding capacity
2. The highest absorbency under load (AUL),
3. Increase water use efficiency
4. The highest durability and stability in the swelling
5. Enhance soil permeability and infiltration rates
6. Reduce irrigation frequency
7. pH-neutrality after swelling in water
8. Reduce compaction tendency
9. Photostability
10. Stops erosion and water run-off
11. Increase plant performance (growth)
12. Increase soil structure, density and texture
13. Re-wetting capability
14. Potentially influence evaporation rates of water through the soils
15. Increase soil aeration
16. Increase microbial activity
17. Increase the efficiency of fertilizers.
18. Increase the efficiency of pesticides and herbicides
19. Improves germination rate
20. Negative the effect of deficit irrigation (Drought stress)
21. Safe, Non- toxic and Eco friendly (half life is in general in the range 5 - 7 years, and they degrade into ammonium, carbon dioxide and water)

Fig 7: Development of root zone with sap

Rate of water absorption by super absorbent polymers under various water qualities

Rajiv Dabhi *et al.*, (2013) were conducted an experiment to determine the effect on the absorption property of Super Absorbent Polymers (SAP) under various quality of water.

The performance of the interaction effect after prolonged immersion clearly indicated that SAP can best perform if rain water is used for irrigation.



***Source*:** Rajiv Dabhi *et al.,* (2013)

Graph showing the water absorption rate with different water qualities

Application of SAP is also recommended where irrigation is done with surface storage reservoir water. The highest absorption rate of SAP was observed for RW (245gram w/w) and DSW (241 gram w/w). SAP can absorbed 35% to 95% lesser quantity of BW (114gram w/w), HP1 (89gram w/w), HP2 (67gram w/w), HP3 (38gram w/w) and SW (8gram w/w) that of RW and DSW.

Use in different vegetsble crops

Sweet pepper

Mohammad Sayyari and Fardin Ghanbari (2011) has conducted an experiment in Capsicum by applying completely random blocks design with five levels of SAP A200 (0, 0.2, 0.3, 0.4, 0.5 weight percent) and four irrigation intervals (5, 7, 9, 11 days) in greenhouse. (Treatment 5×4=20 and replication number 3). The highest total yield (352 g per plant) and total number of fruits in the plant (13) were achieved in treatment composition of irrigation interval every 5 days and applying 0.5% of SAP. The highest electrolyte leakage (44%) in treatment composition of irrigation interval every 11 days and 0.3% SAP and the lowest value (21%) in treatment composition of irrigation interval every 5 days and applying 0.4% SAP were achieved. The highest proline value (32 µm/g F.W) in treatment composition of irrigation interval of every 11 days and without applying SAP (control) and the lowest value (µm/g F.W) were in treatment composition of irrigation interval of every 5 days and applying 0.5% SAP

Radish

Fidelia Nnadi and Chris Brave (2011) [6] conducted an experiment by using biopolymers. Biopolymers can be made from carboxymethyl cellulose (CMC), which has a naturally occurring polysaccharide cellulose base. CMC is made commercially by reacting chloroacetic acid with sodium cellulose in slurry with isopropanol and water. CMC polymer complexes were crosslinked with aluminum ions to form non-permanent bonds when the complex is swollen with water. The crosslinked CMC and starch will create an environmentally friendly SAP and experiment is carried out to test whether it could be an alternative or not to petroleum based SAPs. Commercial cassava starch powder (Ayoola Foods), commercial cornstarch powder (Pinnacle Foods), commercial potato starch powder (Bob's Red Mill), and commercial yam starch powder (Ayoola Foods) were used. Carboxymethyl cellulose sodium salt (Acros Organics) was used with starch to synthesize superabsorbent polymers. Aluminum sulfate octadecahydrate was used to crosslink the polymer complex.

Potato, Cassava, Yams

The potato starch SAP appeared to have outperformed the other ones at both 0.12 and 0.24% by weight of the additive. At both 0.12 and 0.24% additive the corn starch hydrogel performed the least and appear to have reduced rate of growth with reduction in watering, while the cassava starch and yam starch additives showed consistent growth up to the end of the study period. However, Potato starch hydrogel amended soil showed a better performance with the 0.12% dose than the 0.24% dosage. These results also suggest that soil amendment using a superabsorbent polymer composed of CMC and starch can be an alternative to petroleum based superabsorbent polymers for water retention during irrigation.

Tomato

M.K. Meena *et al.*, (2011) [10] conducted field experiment to study the impact of hydrophilic polymer on irrigation requirement and biophysical parameters in tomato. The treatments consisted of different concentrations of hydrophilic (0.50 to1.75 g/plant) and another was control. The results of the investigation revealed that among the treatments the application of liquasorb (1.75g/plant) into the soil increased different crop growth parameters as compared to all other treatments. While lowest value of these parameters observed in control (without hydrophilic polymer).The results of this study have shown that the crop growth parameters increased and these having positive correlation with yield. The hydrophilic polymer (HP) resulted in increased TDM, LAI, LAD, AGR, CGR, and NAR and finally resulted in increased BMD.

Cabbage

Ananda, P. A. *et al.*, (2009) [2] conducted a field experiment to study the influence of superabsorbent polymer on growth, development, physiology and yield and its related components in cabbage (*Brassica oleracea var. capitata* L.).

The treatments involving different concentrations of superabsorbent polymer (0.5, 0.75, 1.0, 1.25, 1.5, and 1.75 g/plant) were imposed in soil at the time of transplanting of cabbage.

Results revealed that the application of superabsorbent polymer into the soil recorded higher yield, higher plant height, plant spread, increased number of outer leaves per plant and hastened days to initiation of head as compared to control. Irrigation frequency was effectively reduced to the extent of 33 per cent less than control. Growth parameters *viz.*, *leaf area*, *LAI*, *AGR*,RGR, CGR, NAR, LAD, SLW and BMD were also influenced by the application of superabsorbent polymer and the effect was increased with an increase in the concentration of superabsorbent polymer in the soil. The cabbage yield (kg/plant and ton/ha) of T6 is higher than all treatment and control. The economics of using superabsorbent polymer indicated higher additional returns with the use of 1.75 g/plant of luquasorb.

Cucumber

A.R. Al-Harbi *et al.*, (1999) [1] conducted an experiment to study the effect of a hydrophilic polymer (Broadleaf P4®; HP)

on growth of cucumber seedlings (*Cucumis sativus* L.) and the efficiency of HP to absorb water over a period of time.
The bulk density of soils decreased significantly with addition of HP and had increased after five growing experiments at each HP rate. Experiment results indicate soil WHC increased significantly with increasing level of HP, but decreased after each experiment. After five experiments, the WHC had decreased 17.3% and 27.8% where HP was added at the rate of 0.1% and 0.4% respectively.
The greatest vegetative growth of cucumber, expressed as leaf area and shoot fresh and dry weights, was observed at 0.3% HP in the first and second experiment, but at 0.4% in the third and fourth. In the third and fourth experiments, HP efficiency had decreased 14.3% and 21.8% respectively.

Conclusion

Throughout human history, agriculture has been a source of food, fuel and fiber. Opportunities have arisen through external events and trends that impacted patterns of production and utilization. SAPs have created a very attractive area in the viewpoint of super-swelling behaviour, chemistry, and designing the variety of final applications. Further experimental investigation ought to be carried out to study the use of SAP to optimize the yield of cash crops to improve the economic and in turn social conditions of small and marginal farmers. The challenges are numerous but adoption of such an efficient innovative technology for the sustainable irrigated agriculture should be part of long term water management programme. To serve the purpose various agencies, Govt. action plans, NGO's, Agricultural research institutes and practical education programme should be taken to educate farmers regarding this technology.

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