

REVIEW

SUPERABSORBENT POLYMERS - AN INNOVATIVE SOLUTION FOR IMPROVING WATER USAGE EFFICIENCY AND AGRICULTURE PRODUCTIVITY

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Abstracts. In recent years, superabsorbent polymers (SAPs) have become an attractive solution to solve the problem of water scarcity in agriculture. This article reviews the literature concerned with preparation techniques of SAPs, methods for evaluating and their application in agriculture. SAPs can be prepared by four main techniques: bulk, solution, inverse suspension and radiation polymerization. Analytical evaluation methods of SAPs, including free absorbency capacity, absorbency under load, swelling rate, swollen gel strength, soluble fraction, residual monomer and ionic sensitivity, are briefly introduced. SAPs have a wide applicability in agriculture. They can be used to efficiently improve water use in agriculture, such as retaining moisture in the soil and reducing irrigation water consumption due to their super high water absorption and water retention capacity. SAPs also have positive impacts on soil properties, such as improving soil as well as improving water and fertilizer efficiency, leading to the enhancement of crop yields.

Keywords: superabsorbent polymers, polymerization, water retention, soil improvement, agriculture productivity

Classification numbers: 2.3.1, 3.4.3, 3.7.3

1. INTRODUCTION

Water is a critical input for agricultural production and plays an important role in food security. Irrigated agriculture represents 20 percent of the total cultivated land and contributes 40 percent of the total food produced worldwide. Irrigated agriculture is, on average, at least twice as productive per unit of land as rainfed agriculture, thereby allowing for more production intensification and crop diversification. Water scarcity is fundamental agricultural obstacle, particularly in tropical countries. Therefore, effective management of water application in

agricultural production is a critical factor for sustainable crop production, especially in irrigated agriculture.

Superabsorbent polymers (SAPs) are hydrophilic materials which can absorb and retain a huge amount of water in their network. A great number of hydrophilic groups on the chain of SAPs and three-dimensional network structure result in a super high water absorption and water retention capacity [1]. On the basis of original source, they can be classified as natural, semi-synthetic and synthetic polymers. The following are the properties of superabsorbent polymers:

- High water absorption, even under load
- Fast absorption rate
- Colorless, odorless and non-toxic
- Biodegradability
- Low cost

Because of their excellent characteristics, SAPs are widely used for absorbing water and saline solutions for baby diapers, sanitary napkins and feminine hygiene products [1, 2]. The ability of swollen gels to release water to the surrounding as vapor has also been used as watersaving materials and soil conditioners in agriculture. Fertilizers can be used in combination with SAPs to obtain slow-released and water retention properties [3].

Viet Nam is an agriculture country located in the tropical belt of the Northern Hemisphere and affected by the Asian monsoon. The country receives a large amount of heat from the sun every year. The annual rainfall is relatively high from 1500 to 2000 mm, but unevenly distributed among regions and seasons of the year. Rainfall is concentrated about 70 - 80 % in the rainy season but only 20-30 % in the dry season. Therefore, crops in many places are seriously lacking in water. Agricultural production in Viet Nam is highly dependent on climatic factors, in which irrigation water plays a very important and indispensable role, affecting plant growth and development, and crop yield. Both domestic and international studies have shown that SAPs products play a very important role in helping to limit and overcome many difficulties of agriculture production, thereby promoting the development of agriculture, bringing high and stable economic efficiency. This review article focuses on the preparation of SAPs, methods for evaluating of SAPs and their application in agriculture, especially in Viet Nam agriculture.

2. HISTORY AND CLASSIFICATION OF SUPERABSORBENT POLYMERS

In 1938, the first water-absorbent polymer was synthesized by polymerizing acrylic acid with divinylbenzene [4]. In the late 1950s, the first generation of hydrogels appeared. These hydrogels were mainly based on hydroxyalkyl methacrylate and related monomers with a swelling capacity of up to 40 - 50 % and were used to make contact lens for ophthalmic applications. The second-generation hydrogels with an improved swellability (70-80 %) have widened its use in many fields [5].

In the 1970s, the first commercial superabsorbent polymer produced by hydrolyzing starch-graft-polyacrylonitrile was developed at the Northern Regional Research Laboratory of the US Department of Agriculture. In 1978, commercial production of SAPs began in Japan for use in feminine napkins. In 1980s, France and Germany developed SAPs to use in baby diapers. Then, SAPs gradually became widely used in Asia, US and European countries [6].

SAPs can be classified in different ways, however, this article focuses on the classification based on the original material source, whereby SAPs can be divided into three main types:

- Natural-based polymers: They are polysaccharide-based (such as starch, cellulose, alginate) and polypeptide based (such as gelatin, collagen). They are renewable, biocompatible, and biodegradable. However, water absorbent capacity of this type of SAPs is lower than that of synthetic and semi-synthetic polymers. Natural SAPs are also less stable against environmental degradation [7]. In addition, extraction methods and modifications are required to obtain SAPs from raw natural materials.
- Synthetic polymers: They are petrochemical-based (such as methacrylic acid, polyacrylic acid, vinyl acetate). They are abundant and have high purity, super-high water absorbent capacity and wide applicability. However, they are often not biocompatible, not biodegradable and not renewable. These disadvantages make them environmentally unfriendly in the long term.
- Semi-synthetic polymers: this type of SAPs is a “smart” combination of polysaccharides and synthetic monomers. Semi-synthetic SAPs have advantages of both natural based and synthetic polymers and offer a strong potential for a series of applications in the future [8].

Most of SAPs currently available on the market are mainly based on synthetic polymers. However, in recent years, SAPs are more and more widely used as watersaving materials and soil conditioners in agriculture. Therefore, to minimize environmental impacts, natural-based and semi-synthetic SAPs become the preferred choice due to their biodegradability, biocompatibility and insignificant toxicity characteristics.

3. PREPARATION TECHNIQUES

2.1. Bulk polymerization

Bulk polymerization, also known as mass polymerization, is the simplest technique which does not use solvents or dispersants [9]. Monomers are polymerized using light, heat, initiators or radiation. Initiators are selected depending on the type of monomers and used solvents [6]. The advantage of bulk polymerization is that high molecular weight polymers with high purity can be obtained without complex devices because of high monomer concentration [10].

However, the disadvantage of this technique is that the viscosity of the reaction increases markedly resulting in heat generation during polymerization. This problem can be controlled by conducting the reaction at a lower temperature and using low concentrations of initiators [11]. Polyacrylate SAPs such as poly (2-hydroxyethyl methacrylate) and poly(acrylic acid) are prepared by this technique.

2.2. Solution polymerization

In polymer synthesis, solution polymerization is an important method. Polymerization reaction is initiated by heat (such as ammonium persulfate [12, 13] and potassium persulfate [14, 15]), UV-irradiation [16, 17], redox initiator systems [18] or catalysts. The solvent used for this technique is water, ethanol or a mixture of them [19]. If the polymer is soluble in water, it is called a homogeneous solution polymerization, and if the polymer is insoluble in water, it is called a heterogeneous polymer. The advantages of this method over bulk polymerization are the lower viscosity of the reaction system, the ease of controlling the molecular weight of the

products, and controlling reaction temperature because the solvent acts as a heat sink [20]. In addition, it is an economical and faster method [21]. After the reaction, the SAPs products synthesized by this method need to be washed with distilled water or ethanol several times to remove unreacted monomers, oligomers, cross-linking agents, initiators and other impurities. Many hydrogels have been synthesized by this method, for example poly(2-hydroxy ethyl methacrylate) SAPs synthesized from hydroxyl ethyl methacrylate using ethylene glycol dimethacrylate as a cross-linking agent [22]. pH-sensitive or temperature sensitive SAPs can be synthesized by adding methacrylic acid or N-isopropyl acrylamide.

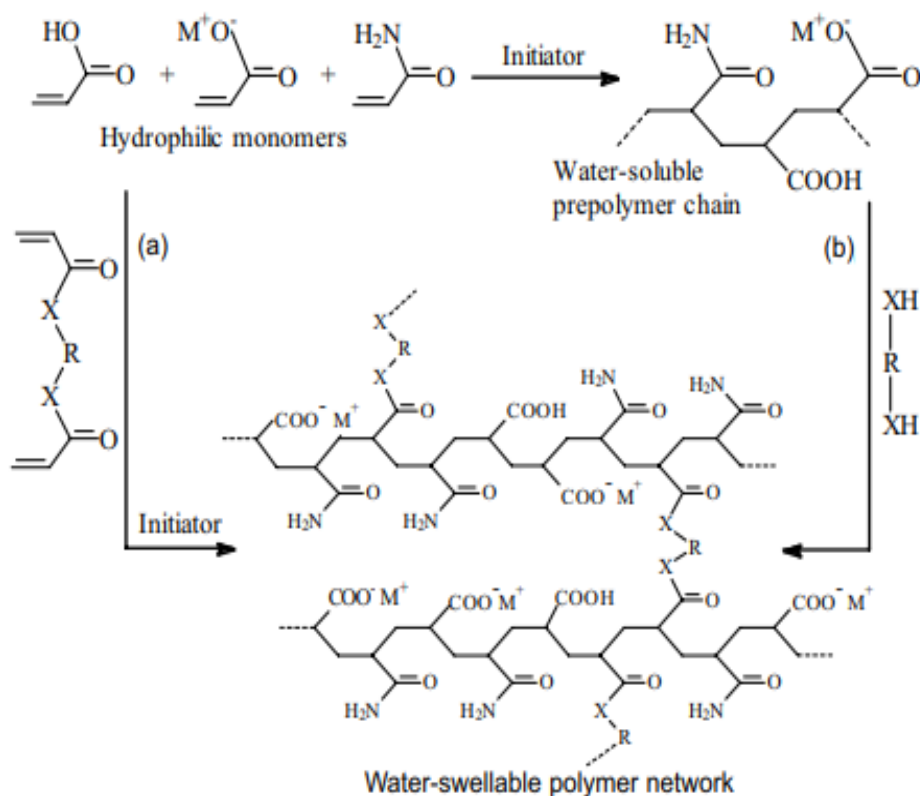


Figure 1. Chemical structures of the reactants and the reaction scheme to prepare SAPs from acrylic acid monomer.

However, the disadvantages of this method are that it has to treat rubbery solid products, the particle size distribution of the products is uneven, and it is difficult to control the reaction. Nguyen Van Khoi *et al.* reported that the optimal conditions to prepare polyacrylamide to be used as an anticorrosion agent were 0.5 M for monomer concentration, 1 % for ammonium persulfate initiator content, and a reaction temperature of 70 °C [23]. These authors also prepared polyacrylic acid for dust control in coal mines using ammonium persulfate-ascorbic acid redox initiator systems and water as solvent. The highest molecular weight of polymer was obtained when conducting the reaction at 25 °C for 25 minutes with a monomer content of 3 M and an initiator content of 0.01 M [24]. Poly(acrylamide-co-acrylic acid) was also prepared by solution copolymerization from acrylamide and acrylic acid in aqueous solution using ammonium persulfate as an initiator [25].

Graft polymerization is a common method of solution polymerization. Polymer properties are optimized when grafted with monomers. Commonly used natural polymers are chitosan [26], starch [27], cellulose [1], pectin [26], etc. Tran Manh Luc *et al.* prepared acrylic acid (AA) grafted bamboo fibers using ceric ammonium nitrate (CAN) as initiator and water as solvent. The optimal conditions for grafting AA onto bamboo fibers were bamboo 4 g, CAN 0.072 M, AA 10 g, HNO₃ 0.0025 M, reaction temperature 45 °C, and time 240 minutes [28]. In addition, this group of authors also grafted acrylamide onto jute fibers using a Fe²⁺/H₂O₂ redox system. The optimal conditions of this grafting process were jute fibers 4 g, AM 6 g, Fe²⁺ 0.004 M, H₂O₂ 0.05 M for 180 minutes at 45 °C [29]. Hoang Thi Phuong *et al.* prepared acrylamide grafted cellulose extracted from rice straw using potassium persulfate (KPS) as initiator and water as solvent. The optimal conditions for grafting AM onto cellulose were rice straw/liquid phase 1/20 g/mL, AM 1.5 M, KPS 0.09 M, reaction temperature 75 °C, and time 180 minutes [30]. Ceric ammonium nitrate [31, 32] and potassium persulfate [33, 34] were also used as initiators for grafting acrylic acid onto tapioca starch.

2.3. Inverse suspension polymerization

Inverse suspension polymerization is used to produce spherical SAPs particles with particle sizes from 1 micron to 1 mm [35]. The advantage of this technique is that the product is obtained in the form of a powder or granule, which reduces the grinding of the product [36]. This is a water-in-oil process, as opposed to the more common oil-in-water process. Hence it is called inverse suspension polymerization technique.

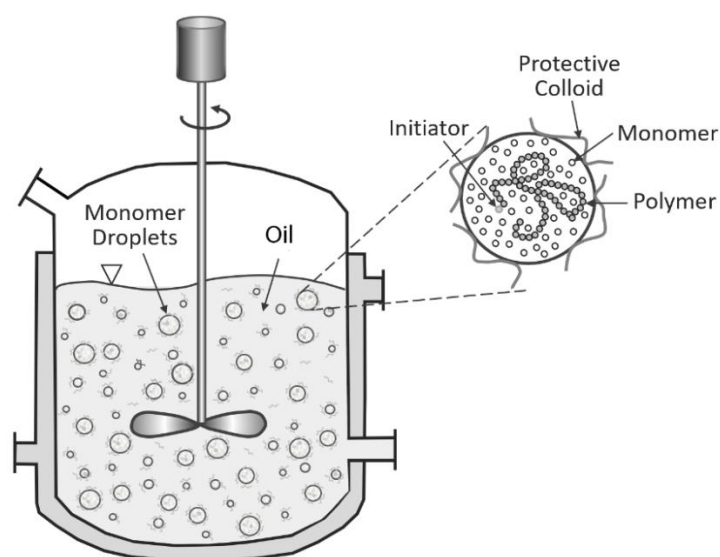


Figure 2. Summary of inverse suspension polymerization technique.

This technique consists of two phases, one is the aqueous phase and the other is the organic phase. The aqueous phase consists of monomer, cross-linker, and initiator while the organic phase consists of a solvent and stabilizer. Water-soluble initiators are more effective than oil-soluble initiators because when the initiators are water soluble each emulsion will contain all the reactive components thus it acts as a separate micro-polymerization reactor [37]. The obtained micro-sized SAPs particles will be washed to remove monomers, cross-linking agents and

initiators that have not participated in the reaction. These microparticles are then separated from the organic phase by filtration or centrifugation, and further dried to form a loose and powdery solid product.

The mechanism of inverse suspension polymerization is similar to that of bulk polymerization. Poly(hydroxy ethyl methacrylate) SAPs microparticles have been prepared by this method. Recently, this technique has been widely used to synthesize polyacrylamide-based SAPs such as poly(N,N dimethyl acrylamide), cellulose-graft polyacrylamide/hydroxyapatite [38]. Nguyen Van Khoi *et al.* synthesized superabsorbent polymers based on acrylic acid using ammonium persulfate as an initiator, N,N-methylene bis-acrylamide as a crosslinking agent, toluene as an organic phase and sorbitan monooleate as a stabilizer. The swelling degree of the superabsorbent polymer reached its maximum value at 85 °C, 350 rpm, 1 % initiator and 0.09 % crosslinking agent [39].

2.4. Radiation polymerization

This method uses ionizing high-energy radiation such as gamma rays [40] and electron beams [41] to initiate polymerization reaction of unsaturated compounds to synthesize SAPs. Polymer chains under the influence of irradiation form radicals. In addition, water radiolysis produces hydroxyl radicals, which attack polymer molecules to form macro radicals. Recombination of the macro radicals forms covalent bonds and a crosslinking structure. The advantage of this technique over the chemical initiator is that the obtained product is relatively pure because no chemical initiator is involved. Polymers crosslinked by radiation polymerization include poly(vinyl alcohol), poly(ethylene glycol), and poly(acrylic acid).

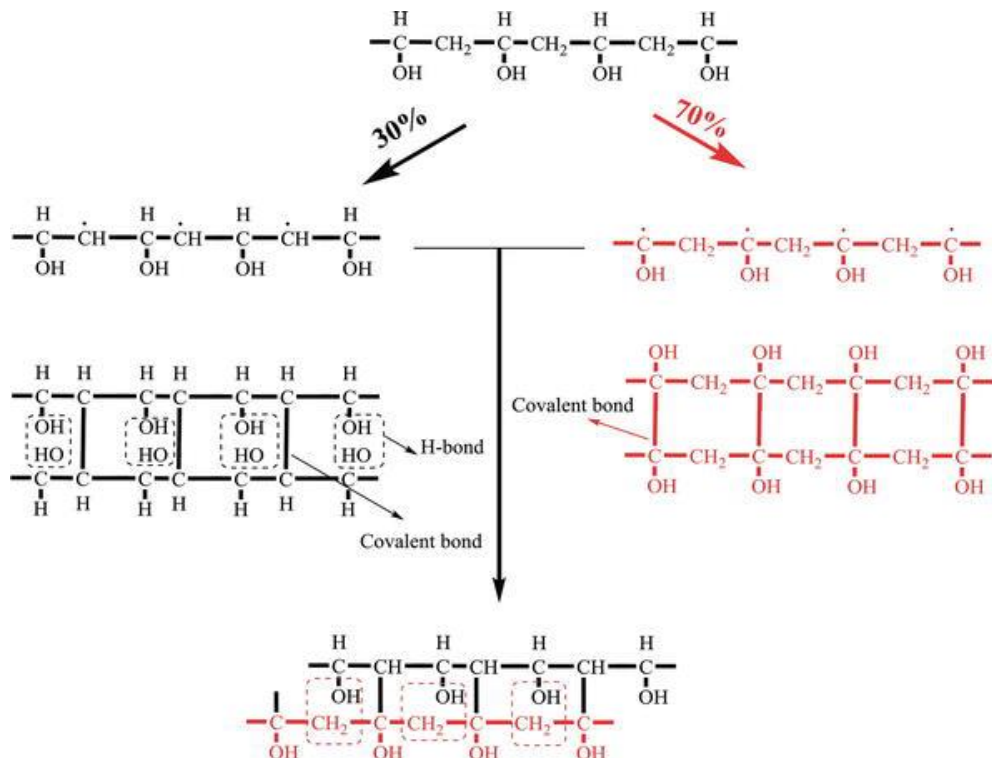


Figure 3. Proposed crosslinking mechanism of water-soluble PVA by radiation polymerization [42].

Pham Thi Thu Ha *et al.* conducted graft polymerization of acrylamide onto tapioca starch using microwave radiation and potassium persulfate (KPS) as an initiator. Microwave radiation has significantly promoted the graft polymerization reaction, the optimal conditions for the reaction are exposure time 120 s, microwave power 450 W, and [initiator] 0.012 M [43]. The graft polymerization process of acrylic acid on carboxymethyl cellulose using microwave radiation was also studied by Nguyen Thanh Tung *et al.* The optimal reaction conditions were [KPS] 0.015 M, exposure time 2 minutes, microwave power 720 W, and the maximum graft yield was achieved at 62 % [44]. KPS is also used as an initiator for the synthesis of polyacrylamide-grafted carboxyl cellulose (CMC-g-PAM) under microwave radiation. The optimal conditions of the reaction are exposure time 90 s, microwave power 720 W, and [initiator] 0.01 M [45].

4. ANALYTICAL EVALUATION METHODS

4.1. Free absorbency capacity

Several simple methods for determining free absorbency capacity depending mainly on the amount of sample available, the extent of the sample's absorbance, and the accuracy of the method.

4.1.1. Tea-bag method

This is the most commonly used method because it is fast and suitable when the amount of sample is limited (the sample weight is only from 0.1 to 0.3 g) [46]. For the determination of free absorbency capacity by this method, SAPs samples are placed in a tea bag (which is a thin cloth bag made of acrylic/polyester with microscopic meshes), then the tea bag is dipped in an excess amount of water or saline solution for one hour to reach equilibrium swelling. Excess solution is removed by hanging the bag until no more liquid flows out of the bag. The free absorbency capacity is calculated according to the following equation:

$$S_e = (W_1 - W_0)/W_0 \quad (1)$$

where: W_1 is the mass of the bag and sample after swelling; W_0 is the original bag and sample weight; The accuracy of this method is about ± 3.5 %.

4.1.2. Centrifugal method

To determine the free absorbency capacity of SAPS by this method, 0.2 g of SAPs (W_1) was placed in a bag (size 60 × 60 mm) which made of nonwoven fabric [4, 47]. The bag was dipped in 100 mL of saline solution for half an hour at room temperature. The bag was then removed and placed in a centrifuge (for 3 min at 250 g) to completely remove the excess solution. Then, the weight of the bag (W_2) is measured. The above steps are repeated with an empty bag and the weight of the empty bag (W_0) is measured. The free absorbency capacity is determined according to the following equation:

$$S_e = (W_2 - W_1 - W_0)/W_0 \quad (2)$$

This method determines the free absorbency capacity of SAPS more accurately than the tea-bag method due to the significant removal of the intergranular liquid. In addition, the measured value is more accurate and lower than that measured by the-tea bag method.

4.1.3. Sieve method

SAPs (W_1) was added to an excess amount of water or solution and dispersed with a magnetic stirrer to reach equilibrium swelling (0.5 - 3 hours depending on the particle size of the material). The swollen sample is filtered through a 100-mesh sieve, then a soft polyurethane foam is used to rub several times into the bottom of the sieve until the gel does not leak out of the sieve [48 - 50]. The swelling over time was determined by the following formula:

$$S_t = [(A_t + B) - (B + W_1)]/W_1 \quad (3)$$

where, S_t : swelling of the sample at time t (g/g); A_t : weight of the water absorbed sample at time t (g); B : weight of the sieve (g)

This method requires a large sample amount (1–2 g) with an accuracy of ± 2.1 %.

4.2. Absorbency Under Load (AUL)

Absorbency under load was used as a measure of the swollen gel strength of SAPs materials. Normally AUL of a material when not referring to a specific swelling medium means the absorbency in a 0.9 % NaCl solution when the sample is under pressure (typically 0.3, 0.6 or 0.9 psi). 0.9 g of the dried SAPs sample was evenly placed on the surface of the polyester gauze and placed on the sintered glass. A cylindrical solid load was placed on the SAPs particles and adjusted to the desired load. Then, 0.9 % NaCl solution was added until the liquid level is equal to the height of the sintered glass filter. The entire device was covered to prevent surface evaporation and salt concentration changes. After 60 min the swollen particles were weighed, the loading capacity was calculated by the following equation [51]:

$$AUL = (W_2 - W_1)/W_1 \quad (4)$$

where, W_1 and W_2 are volumes of dry and swollen SAPs, respectively.

4.3. Swelling rate

Vortex method is commonly used to evaluate SAPs' swelling rate in R&D and technical laboratories because it is a quick and simple method. 50 g of water or saline solution was poured into a 100 mL beaker, heated to 30 °C and stirred with a magnetic stirrer at 600 rpm. SAPs (50 – 60 mesh) with a weight of 0.5 – 2.0 g (W_0) was added. The time from SAPs addition to vortex disappearance was measured (t_{vd} , sec) [52]. The swelling rate was calculated according to the following equation:

$$S_R = (50/W_0)/t_{vd} \quad (5)$$

4.4. Swollen gel strength

The mechanical strength and modulus of the swollen SAPs sample are important parameters. For determining the swollen gel strength, 100 - 150 mg of dried SAPs with an average particle size of 180 μ m was dispersed in 200 mL of distilled water for 30 min to achieve maximum swelling. The excess water was removed and the swollen gel particles were placed on a rheometer. Rheological properties of the material were evaluated as described in [51].

4.5. Soluble fraction (Sol)

The sol content was determined by extracting the SAPs sample with distilled water. A certain amount of SAPs sample ($W_0 = 0.1$ g) was added to an excess amount of water and

dispersed by a magnetic stirrer for 0.5 – 3 h to reach equilibrium swelling. The swollen samples were filtered, dried and weighed (W_1) to determine the gelation content [52].

$$\text{Gel}(\%) = 100 \times W_1/W_0 \quad (6)$$

$$\text{Sol}(\%) = 100 - \text{Gel}(\%) \quad (7)$$

4.6. Residual monomer

High performance liquid chromatography (HPLC) is most commonly used for the determination of residual monomer content. 100 mg of SAPs was extracted with 20 mL of 0.01 % orthophosphoric acid solution overnight using a stirrer. The sample was then centrifuged at 2000 rpm for 15 min, the supernatant was injected to the chromatographic system. An aqueous 0.01 % orthophosphoric acid was used as the mobile phase. The UV–vis absorbance over the 190 - 400 nm range was registered and the wavelength of 200 nm was used for quantification [53].

4.7. Ionic Sensitivity

To evaluate the sensitivity of SAPs to different solutions, the dimensionless swelling factor (f) is used, which is determined as follows [54]:

$$f = 1 - (\text{Absorption in a given fluid}/\text{Absorption in distilled water}) \quad (8)$$

The larger the f value, the lower the absorbency capacity of the material in the salt solutions. Hence SAPs with lower f are often preferred. A negative f value indicates a higher absorbency of SAPs in salt solution than in distilled water, which is often seen in SAPs hydrogels with betaine structure.

5. APPLICATION OF SUPERABSORBENT POLYMERS IN AGRICULTURE

5.1. Water retention and soil improvement

Researchers from all over the world have worked extensively on using SAPs to improve water usage efficiency and agricultural productivity. Several studies have strongly suggested that soil conditioning using SAPs might be a new element in the field of agriculture. Irrigation is an important aspect of agriculture since it aids in the growth of plants and crops by supplying nutrients to the soil. Research evidences suggest that, with the use of SAPs, better water management can be achieved, and significant water savings can be done without compromising the crop yield.

SAPs hydrogels have a high swelling capacity and the ability to retain aqueous solutions, which helps to keep the soil wet. After mixing SAPs granules with the soil and soil watering, the granules will absorb water by swelling and release it slowly as the soil dries off via diffusion. This helps to prevent evaporation and irrigation water loss. As the SAPs absorb water, they swell up and expand, as a result, the porosity of soil increases rendering a better oxygen supply to the roots. Higher porosity also results in enhancement of seed germination and growth rate of seedling, root growth and reduction in soil erosion due to less soil compaction [55].

Adding SAPs to the soil also helps to prevent soil erosion and surface runoff, increase permeability, increase the size of soil aggregates, increase water holding capacity, improve

survival of drought tolerant crops, improve nutrient recovery from used fertilizers, and reduce irrigation frequency [56-58].

The effect of superabsorbent polymers on soil and plants on steep surfaces was studied [59]. In this study, SAPs were used for the amendment of the water-holding capacity of soil on a steep surface. Three levels of SAPs [0.20, 0.40 and 0.60 % (w w⁻¹)] and a control (0 %) were mixed with sandy soil. The water retention capacity, evaporation rate and saturated water content of SAPs-treated soils for determining plant survival and seed germination rate through cylinder and steep surface experiments were evaluated. Sandy soil treated with SAPs showed significantly enhanced soil water holding compared with the controls. At the same time, the seed germination rate was significantly higher in SAPs-treated soils than in the controls. Under water stress, the survival periods of grass and ligneous plants were extended. The result also showed that the treatment with 0.40 % SAPs was the optimum option for sandy soil amendment on steep surfaces.

The effects of different levels of SAPs on water holding capacity and the porosity of soils with different salinities and textures were also evaluated [60]. In this study, SAPs were added to different soil textures (sand, loam and clay) at the levels of 0, 0.2, 0.4 and 0.6 % w w⁻¹. The result showed that the application of SAPs to soil may increase water-holding capacity and decrease salinity, especially in the sandy soil. It also suggested that using SAPs may help to improve irrigation projects in arid and semi-arid areas.

In Viet Nam nowadays, modern irrigation works to regulate as well as provide water for irrigation are lacking and watering still depends mainly on rain. Therefore, drought is a big problem in many locations in the country. To solve this problem, SAPs have become an attractive alternative. There have been many research projects on the preparation and application of SAPs with significant scientific, economic and social benefits. The Institute of Chemistry is one of the units which has many experiences in the field of SAPs.

Nguyen Van Khoi *et al.* have studied the graft polymerization process of AM onto tapioca starch to obtain the product AMS-1. AMS-1 has the effect of stabilizing the soil structure, thereby avoiding rain erosion and can be effective in many crops, with a storage time in the soil of more than 18 months. When encountering water, AMS-1 has the ability to absorb 400-420 g water/1 g dry matter and has the ability to expand to 400 times its original weight, 400 times in distilled water and 65 times in physiological saline. The AMS-1 product has a very fast water absorption rate. In aquatic medium, AMS-1 can absorb up to 50 % of the total maximum amount of water in the first minute and reach 86.2 % in the first 10 minutes. The maximum water absorbent capacity of AMS-1 is about 200-300 times its weight. Adding AMS-1 into the soil will prolong the water retention time and have positive effects on the moisture content of wilted plants. This effect helps to improve drought tolerance for upland crops in water shortage conditions. The usage of AMS-1 with the rate from 25 to 40 kg/ha has improved the agronomic efficiency and economic efficiency of the studied crops: Crop yield increased by 10 to 23 %, depending on the type of crop. AMS-1 is a bio-polymer with acrylic acid and modified starch as raw materials, which is easily decomposed by microorganisms after 24 months. Therefore, AMS-1 will not cause negative effects on the soil environment [61].

The role of SAPs (AMS-1) on several properties and productivity of winter crop in degraded soil area was studied by Hoang Thi Minh *et al.* The use of SAPs in degraded soil area of Soc Son showed the improvement in some chemical and physical properties of soil, increased water retaining capacity and maintained soil moisture and agregation. SAPs also increased potassium sorbtion capacity and phospho displacement [62].

Hoang Thi Phuong *et al.* has studied the graft polymerization process of AM onto cellulose fibers to obtain the product Bio-SAP. The impact of Bio-SAP on soil properties were determined. The rate of water movement in the soil is directly related to the watering and drainage process. The permeability coefficient of water depends on the organic matter content in the soil, porosity, mechanical composition, and soil structure. The large amount and fast moving speed of water can lead to nutrients being washed away and cause strong compressive forces that reduce the porosity of the soil, making it difficult for roots to develop. The result showed that Bio-SAP had positive impacts on the characteristics of the soil. Soil characteristics were significantly improved with the presence of Bio-SAP, the porosity increased whereas the coefficient of permeability decreased [30].

Hoang Bich Thuy *et al.* studied the effect of SAPs (PMAS-1) on soil humidity, some microorganisms and growth of rubber tree at basic phase in Quang Binh. The experiment was conducted with PMAS-1 superabsorbent polymer from 0 to 30 g/tree for cultivar of RRIM 600 rubber tree. The result showed that the ability of keeping soil humidity of PMAS-1 superabsorbent polymer in 2014 was better than that in 2015. The density of micro-organisms in the soil of the treatments using the superabsorbent polymer PMAS-1 was quite higher than that of the control. At the rate of 20 g/tree, the density of soil micro-organisms reached the highest. Moreover, PMAS-1 also had effect on the growth of rubber tree: both the trunk diameter and the height of rubber tree increased compared to the control. The use of PMAS-1 at 20 g/tree showed better effects on the ability of keeping soil humidity, density of micro-organisms, growth and the development of rubber tree [63].

5.2. Improvement of water and fertilizer efficiency

Many reports suggest that the application of SAPs could improve water-use efficiency of rain-fed crops under dryland farming, especially in regions with uneven rainfall and poor soil water retention. Yang *et al.* studied the influence of super absorbent polymer on soil water retention, seed germination and plant survivals for rocky slopes eco-engineering [64]. In this study, SAPs were mixed with sandy loam soil at three levels: 0.15 %, 0.3 %, and 0.45 %. In comparison to the controls, adding SAPs to the sandy loam soil resulted in a considerable increase in soil water retention. Furthermore, seed germination was considerably greater in SAPs adjusted soil than in SAPs-free soil, and survival times of grass and woody were prolonged under water stress. The rate of 0.30 % SAPs treatment was the best option for improving sandy loam soil on steep rocky slopes. These studies indicated that SAPs were very effective in enhancing water uptake and utilization of water for plants growth.

Fertilizers are widely used in agricultural applications because they contain vital ingredients for plants. However, these nutrients can be lost for many different reasons, such as surface run-off, leaching, vapourization, plant uptake, etc. The use of new technologies for enhancing water and nutrient use efficiency will become more important over time, especially in arid regions with limiting water availability. To enhance water and nutrient use efficiencies, fertilizers can be incorporated inside SAPs.

Eneji *et al.* [65] hypothesized that the use of super absorbent polymers (SAPs) may effectively increase nitrogen use efficiency by minimizing leaching and enhancing water and nitrate retention in the soil. In their study, they evaluated nitrate movement in soils amended with SAPs and determined changes in maize growth based on enzyme activities and physiological parameters. Nitrate retention was studied in six undisturbed soil lysimeters under different fertilizers (standard, medium or 75 % and low, or 50 % of standard) rates with

(30 kg/ha) or without SAPs. The results showed that maize yield decreased by 20 % under medium and by 38 % under low fertilizer rates but SAPs application increased the yield by 44 % at medium and by 80.3 % at low fertilizer levels. Plants treated with SAPs under deficit irrigation showed reduced stress signals based on the superoxide dismutase, catalase, peroxidase, ascorbate peroxidase and glutathione reductase activities in leaves.

Abedi Koupai and Mesforoush evaluated the effect of SAPs on the yield performance, growth indices (length of shoot), water use efficiency and N, K, Fe and Zn uptake of a nursery plant (*Cucumis sativus* var. Gavrish). The results showed that the use of 4 g/kg SAPs in a light texture soil and without stress or 25 % deficit irrigation was recommended to achieve the best marketable yield and desired water use efficiency [66].

In Viet Nam in recent years, there has been an increasing interest in using fertilizers in combination with SAPs to obtain both slow-released and water retention properties. Nguyen Thanh Tung *et al.* studied the effect of SAPs (AMS-1) on fertilizer retaining capacity off soil medium. In this study, SAPs products were used to control the retention and release of nutrients. In the presence of SAPs, the retention of micro-fertilizers (Cu^{2+} , Zn^{2+} , Mn^{2+}) increased immensely, more potassium and ammonium were retained, while nitrate was not retained in large amount [67].

Le Duc Thang and Ngo Dinh Que studied the effect of a combination of fertilizer and humectants on the growth of the plant *Casuarina equisetifolia* Forst. Et Forst.f in the sime – fixed sandy dunes in Le Thuy and Trieu Phong districts, Quang Tri province. The results showed that applying 300 g of Song Gianh microbial organic fertilizer in the first 3 years in combination with 10 g of organic humectant/root for casuarina trees gave a significant effect after 24 month period. These authors also studied the effect of fertilizer and humectant on the growth of the plant *Acacia crassicarpa* A. Cunn ex Benth in coastal sand land in Ha Tinh. The combination of Song Gianh microbial organic fertilizer and humectant showed positive impacts on plant growth [68].

5.3. Enhanced plant growth and yield

Drought stress limits crop growth and productivity more than any other single environmental factor. Therefore, efficient management of soil moisture is important for agricultural production in the light of scarce water resources. By increasing soil water storage capacity, minimizing soil water and nutrient waste, and also reducing water evaporation from the soil surface, SAPs promote better plant growth and enlargement and as a result, increase the yield under normal irrigation and water stress conditions.

Superabsorbent polymers (SAPs) have shown to be quite effective and useful in acting as a reservoir for water and some nutrients in arid and semi-arid regions. In Iran, the effects of different rates of SAPs application on yield and yield components of crops (including cereals, legumes, and medicinal and grassland plants) were investigated in many studies. The results of the meta-analysis showed that the mean consumption rate of SAPs for cereals, legumes, and medicinal and grassland plants was 83, 322, 1031, and 210 kg ha⁻¹, respectively. At these SAPs application rates, the mean seed yield in cereals, medicinal plants, and legumes increased by 15.2, 12.6, and 38 %, respectively, compared with the control [69].

In arid and semiarid regions of northern China, there is an increasing interest in using water-saving superabsorbent polymers (SAPs) for field crop production. Mao *et al.* studied the growth and yield characteristics of summer corn (*Zea mays* L.) under different (0, 5, 10 and 15 kg ha⁻¹) rates of SAPs in a drought-affected field of northern China [70]. The results showed that

corn yield increased slightly following SAPs application at the rate of 5 and 10 kg ha⁻¹, but significantly (by 37.5 %) at the high rate of 15 kg ha⁻¹. In addition, plant height, stem diameter, leaf area, biomass accumulation, harvest index and relative water content, as well as protein, sugar and starch contents in the grain increased significantly. The optimum application of SAPs for corn cultivation in the study area would be 15 kg ha⁻¹. Lower rates (5 and 10 kg ha⁻¹) may not be sufficient for corn requirements. This study also suggested that the usage of SAPs at the rate of 15 kg ha⁻¹ could be an efficient and economic soil management strategy for summer corn production in the drought affected regions of northern China or other areas with similar ecologies.

In Viet Nam, a number of studies have been performed regarding SAPs and their useful application in agriculture. The effect of different drought resistant methods such as mulch, SAPs (AMS-1) and coating film on cotton yield was studied. The results showed that the use of SAPs (AMS-1) at a rate of 25 kg/ha provided plants with better growth and higher yield than the other methods. In this study, the economical values were also calculated and SAPs gained the highest net benefit [71].

The superabsorbent polymer AMS-1 was applied for different crops including peanut, soy beans and corn in Soc Son [62]. The results showed that SAPs help to enhance the crop yield significantly. At a rate of 50 kg/ha, SAPs provided plants with better growth and higher yield. The productivity of dry seed increased by 23 % for peanuts, 20 % for soybeans, and 11 % for corn.

The superabsorbent polymer AMS-1 was also applied for the peanut crop on interior field arenosols in Thua Thien Hue Province in winter-spring and summer-autumn crops. The results showed that at a rate of 35 kg/ha the yield of peanuts increased by 45.5 % in the summer-autumn season [72].

The effect of AMS-1 on the formation, development and yield of watermelon on coastal sandy soils in Thua Thien Hue province was also studied. The results showed that the application of super absorbent polymer AMS-1 with the rate of 35kg/ha increased the yield of watermelon by 71.6% in the summer-autumn season. SAPs can maintain moisture, increase growth and development, and increase crop yield. The growth and development parameters such as germination rate, stem length, number of flowers, number of female flowers, and total number of fruits increased the highest compared with the control and with other treatments [73].

Experimental models applying water absorbent polymer to interplant *Acacia auriculiformis* and *Thephrosia* were carried out in the spoil dump of the lenticular coal bed of Nui Hong coal mine in Thai Nguyen Province. The effect of AMS-1 on some factors of their growth and development was observed. The results showed that there were significant differences between the models with and without AMS-1. After 12 months, survival proportion, yield of living mass, and soil cover proportion of the models using AMS-1 were higher than those of the models without AMS-1. Simultaneously, the fertility of the soil increased significantly after experimenting [74].

AMS-1 also has a positive impact on the growth and development of newly planted tea in Quang Ninh Province. Using AMS-1 reduced mortality proportion, increased height, branching ability and increased dry root weight of tea plants. In this study, the optimal using rate of AMS-1 is 35 kg/ha. The results showed that the percentage of dead plants decreased significantly, the branching ability increased by 27.6 %, the dry root weight and plant height increased significantly compared to the control. As a result, it was possible to reduce irrigation frequency, increase tea yield and bring higher economic efficiency. For commercial tea, using AMS-1 also

increased the growth and development of indicators significantly, especially the yield of fresh buds increased by about 22.5 % compared to the control [75].

Hoang Thi Phuong *at el.* synthesized cellulose-based SAPs (Bio-SAP) and applied in growing Dien pomelo tree. The results showed that the application of Bio-SAP with 90 g for each tree led to increasing the yield of Dien pomelo by 11.39 % compared to the control. The results also showed that there was a slight increase in the total sugar content and vitamin C content of Dien pomelo fruit. Thus, Bio-SAP has a positive impact on both the yield and the quality index of Dien pomelo fruit [30].

6. CONCLUSIONS

In this review article, preparation techniques of SAPs, analytical evaluation methods and their application in agriculture were discussed. The unique structure of SAPs results in super high water absorption and water retention capacity. SAPs can absorb a huge quantity of water, retain it in the soil and release it slowly as the soil dries off via diffusion. Therefore, applying SAPs helps to improve soil characteristics as well as water and fertilizer efficiency, particularly in areas with limited water supplies and restricted nutrient conditions. SAPs have also been shown to enhance plant growth and yield. In Viet Nam, SAPs have been widely used in agriculture, for various research objects such as peanuts, soybeans, corn, cotton, tea plants, watermelons, coffee beans, pomelo, etc. Research on the usage of SAPs in Vietnam's agriculture strongly affirms that SAPs can improve water and fertilizer retaining capacity, provide plants with significantly better growth and higher yield. In recent years, research on developing and applying semi-synthetic SAPs is priority trend in Viet Nam as well as around the world due to their biogradable and eco-friendly properties.

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