



Design, development and evaluation of pine resin-based hydrogel for soil application in water stress condition: An innovative technology

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ABSTRACT

The cross-linked pine resin hydrogels were prepared by *in-situ* grafting polymerization and cross-linking of acrylamide onto a natural pine resin followed by hydrolysis. Microwave initiated synthesis under the selected experimental conditions did not exhibit any significant improvement over the conventional technique. The optimization studies of various synthesis parameters, namely, monomer, crosslinker, initiator concentration, the quantity of water per unit reaction mass, particle size of backbone and concentration of alkali were done. The swelling behaviour of a pine resin-based hydrogel in response to external stimuli namely salt solutions, fertilizer solutions, temperature, and pH was studied. The pine resin hydrogel showed significant water absorbency in various environments. The effect of pine resin hydrogel on the water absorption and retention characteristics of soil and the soilless medium was also investigated as a response to temperature and moisture levels. The inclusion of pine resin hydrogel enhanced the water holding capacity of soil and soil-less media, showing that it has significant potential for diverse applications in moisture stress agricultural soil.

1. Introduction

Most of the Indian agriculture areas are under the rainfed condition with low soil moisture and low water holding capacity. Water scarcity due to runoff and evaporation cannot be controlled and efficiently utilized by the plant root (Das et al., 2021). Hydrogel cross-linked hydrophilic polymer is considered to serve as a miniature water reservoir that absorbs a significant quantity of water and releases it slowly through a diffusive mechanism during times of drought. Hydrogel added soil modifies the hydro-physical and biological parameters of eroded soil, increasing plant viability and improving soil quality by delivering active ingredients throughout the cycle of the specified target at a controlled rate (Kareem et al., 2021). Hydrogels-based pesticides, fungicides, and herbicides release the core active ingredients through the life cycle of a particular crop which reduces the dosage, and environmental pollution, reach the target, and save the crop from biotic and abiotic stress. Major characteristics of ideal hydrogel application are to absorb water 400-1500 g/1 g of its dry weight and perform

well at 40-50 °C and release in soil for a period of 8-12 months (Das et al., 2022). Application of hydrogel increases the water retention capacity of soil by 50-70% with proper amendment with various dosages of soil to hydrogel ratio (Das et al., 2022). Consecutively soil bulk density can reduce by 8-10%. Roy et al. 2019 reviewed that hydrogel increased soil acidity levels ranged between 4-8% with a detachment of H⁺ and other cations which neutralize the cation exchange. Das and Ghosh 2022 found that the sorption capacity of heavy metal (arsenic) was 28.32 mg g⁻¹ by hydrogel biochar composite rice husk.

2. Materials and Methods

The experiment was conducted during the year 2020-22 at the experimental laboratory of ICAR RC for NEH Region, Sikkim Centre, Tadong, Gangtok. Pine resin was isolated by tapping the pine tree and they were dried. Commercial acrylamide, N, N'-methylenebisacrylamide cross-linker, and a persulfate initiator were purchased.

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Hydrogel was prepared by *in-situ* grafting polymerization and cross-linking of acrylamide on the pine resin backbone in the presence of a cross-linker using a persulfate initiator. To optimize the concentration of various synthesis parameters, a sequential completely randomized design was adopted. A typical procedure was used as follows: an aqueous solution containing monomer, cross-linker, and pine resin followed by the addition of initiator will heat up to 80°C for a predetermined period. The mixture was kept as such for a couple of hours. The resulting product was treated with different molar ratios of alkali for a fixed period under ambient conditions. The synthesized hydrogels were gently rinsed with distilled water. The hydrogels were crushed and soaked overnight in acetone for dehydration. Dehydrated hydrogels were filtered through a nylon sieve and oven-dry at 45°C to a constant weight. The prepared hydrogels were characterized by different parameters.

Water absorbency measurements

Each sample weighing 0.1 g (particle size 100-240 mesh size) was immersed in the excess of distilled water (pH 7.0, EC 0.001 mhos/cm) in triplicate and kept at two temperatures, 25^o and 50^oC, until equilibrium was attained. Free water was filtered through a nylon sieve (200 mesh size), gel allowed to drain on sieve for 10 min, and finally weighed. The water absorbency (W.A.) was calculated using the equation: $W.A. (g/g) = (w_2 - w_1) / w_1$, where w_1 is the weight of xerogel (dry absorbent) and w_2 is the weight of swollen gel. Water absorbency was calculated as grams of water per gram of dry sample. The PR Hydrogel exhibiting maximum absorption in distilled water was further evaluated in different salt solutions.

Salt solution absorbency measurements

The vacuum dried pine resin hydrogel was crushed to obtain particle sizes in the 100-240 mesh range. Aqueous solutions of different strengths (5, 10, 15, and 20 mM) of four salts, (NH₄)₂SO₄, NH₄NO₃, KNO₃, NaCl, and urea were prepared and used. The dried and crushed sample (0.1 g) was immersed in specific salt at 50^oC. After 24 hours, the swollen gel was weighed, and absorption was determined using the same procedure as above. Another experiment was carried out with tap water (pH 7.7, EC 2.04 mhos/cm), hard water, and aqueous solutions of pH 4, 7, and 9. Three different strengths of hard water were prepared in the lab using the CIPAC standard procedure and labelled as hard water A (hardness 20 ppm, pH 5-6, and Ca: Mg ratio 50:50), hard water B (hardness 20ppm, pH 8-9, and Ca: Mg ratio 80:20), and hard water C (hardness 500 ppm, pH 7.8, and CA: Mg ratio 80:20).

Water holding capacity measurement in amended soil and soil-less media

Soil (pH 6.4 measured at 1:1.25 soil to water ratio by the normal ammonium acetate (pH 7.0) (Jackson, 1967), organic carbon content: 1.41% for natural soil (Walkley and Black method), cation exchange capacity 15.8 cmol(p+) kg⁻¹ (Black et al., 1965) and soil-less media (sterilized mixture of coco peat, vermiculite, and perlite in the ratio 3:1:1 on a volume basis) were collected respectively. A sample of dried soil was filtered through a 2 mm sieve and incorporated with pine resin hydrogel at rates of 0.5% and 0.75%, respectively. The soilless media was dried until it reached a consistent weight and then used as such. In tared plastic cups having punched bases with filter sheets, desired amounts of amended soil and soil-less medium were taken for measurement of water absorbency and then each cup was submerged in water for a full night to saturate. Soil and soilless sample water content was determined by gravimetric method with oven drying. The water holding capacity of soil and the soilless medium was calculated by the equation:

$$\text{Water holding capacity (\%)} = M - m / m \times 100,$$

where M denotes the weight of the wet sample (g) and m denotes the weight of the oven-dried sample (g).

Water retention measurement in amended soil and soil-less media

The water retention was evaluated using a pressure plate instrument at various pressures (2.2 pF, 2.6 pF, 2.9 pF, 3.2 pF, 3.5 pF, 3.8 pF, and 4.1 pF). Ceramic plates and amended soil and soil-less media filled in rubber rings arranged on bar plates were kept overnight in water for saturation. The saturated samples and ceramic plates were placed in pressure chambers with various tensions. The pressure was applied and kept up till the water stop draining from the chamber. Dehydrated, moist samples were switched to moisture boxes and weighed. The moist samples were dried in a hot air oven at 105^oC for 24 h, air cooled, and reweighed. The formula was used to determine the quantity of water stored at a given pressure:

$$\text{Water Retention (\% w/w)} = [(W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}] \times 100$$

where W_{wet} is the mass of wet soil or soil-less media at a particular tension, and W_{dry} is the weight of oven-dried soil or soil-less medium.

3. Results and Discussion

Effect of monomer weight on water absorbency prepared by conventional and microwave means Pine resin hydrogel preparation for water absorbency using conventional and microwave synthesis processes is shown in (Table 1). Microwave prepared hydrogel compared with the conventional synthesis processes was found uneconomical under the process conditions employed. Microwave-assisted

synthesis developed hydrogels with lesser swelling ratios than the conventional method. As a result, the microwave-assisted technique may not be a cost-effective method for producing pine resin-based hydrogels.

Effect of monomer to backbone ratio on water absorbency of pine resin-based hydrogel

The effect of monomer to backbone ratios on synthesized hydrogels for water absorption is shown in Table 2. The optimum water absorption initially increased with the monomer quantity increased, up to a monomer backbone ratio of 0.75:1. Further monomer backbone ratio was increased to 3:1, and the water absorbency fell consistently. An initial increase in acrylamide leads to an increase in the fraction of polyacrylamide chains which contain a sufficient number of polar $-CONH_2$ groups. (Das and Ghosh 2021) reported that water absorbency after monomer backbone weight ratio 0.75:1 can be attributed to an increase in homopolymer content, resulting in an increase in soluble fraction at fixed cross linker and initiator amount in the feed.

Effect of cross-linker content on water absorbency of pine resin-based hydrogel

The effect of cross-linker content on synthesized hydrogels for water absorbency is shown in Table 2. The finding suggests that a constant monomer and initiator concentration increases the swelling ratio with a cross-linker

concentration increase in the range of 1.0 wt.%, beyond which it decreases with a cross-linker concentration increase. The concentration of the cross linker in the present study should be greater than 0.03 wt.%, else gel setting cannot be achieved. This is understood by an insufficient number of cross-linker molecules needed to graft and form a stable polymer network. Pine resin and polyacrylate are hydrophilic, a lack of sufficient cross-linking results in sol-gel phases in water, making water absorbency difficult to measure (Das and Ghosh 2021).

Effect of initiator concentration on water absorbency of pine resin-based hydrogel

The role of the initiator is graft polymerization reaction and the effect on synthesized hydrogels for water absorption is shown in Table 2. Water absorbency values were significantly decreased under constant reaction conditions when the concentration is less than 3.0 wt.%. A low initiator concentration slows graft polymerization and the formation of polymer networks on the backbone. After reaching the ideal structural properties for maximum water absorption, increasing the concentration of the initiator in the present study >3.0 wt.% enhances the reaction velocity, resulting in smaller networks with low molecular weights.

Table 1. Effect of monomer weight on W.A. prepared by conventional and microwave means.

Monomer wt. %	Conventional	Microwave
	W.A. (g/g)	
2.50	152.4	2.2
3.75	489.8	4.4
5.00	461.7	9.1
7.50	420.9	56.3
10.00	391.8	125.2
15.00	351.9	189.2

*PR= pine resin; W.A. water absorbency

Table 2. Effect of monomer to backbone ratio, cross-linker, and initiator on water absorbency

MC (wt.%)	W.A. (g/g)	Cl.C. (wt.%)	W.A. (g/g)	Initiator (wt.%)	W.A. (g/g)
2.50	152.60	0.05	46.10	0.03	45.80
3.75	490.00	0.10	190.70	0.06	180.40
5.00	461.90	0.50	488.40	0.30	318.30
7.50	421.10	1.00	511.00	0.60	352.60
10.00	392.00	5.00	447.10	3.00	505.80
15.00	352.10	10.00	348.70	4.50	480.40

*M.C.: Monomer Concentration, Cl.C.: Cross linker Concentration, W.A.: Water Absorbency

Effect of water volume in feed mixture on water absorbency of pine resin-based hydrogel

The variation of water absorbency with the water volume in the feed mixture, expressed as ml/g reaction mass, is shown in (Table 3). An increase in the quantity of water from 3.00 to 12.00 ml/g of feed mass showed a consistent increase in the water absorbency values of hydrogels. An optimum network formation requires effective collisions between various reaction moieties, for which water plays a significant role as a reaction medium. At a volume, of less than 12.00 ml/g, low water absorbency values are due to tightly cross-linked hydrogel network formation. An increase in water volume beyond 12.00 ml/g leads to an increase in soluble fraction due to the dilution of the crosslinker, thus leading to poor network formation. This fact is reflected in the decrease in water absorbency on the increase of water volume from 12.00 ml/ g to 17.00 ml/ g in this study (Shen et al., 2020).

Effect of the molar ratio of alkali to monomer on water absorbency of pine resin-based hydrogel

The effect of the molar ratio of alkali to acrylamide on equilibrium water absorbency of pine resin-based hydrogel in distilled water is shown in (Table 3), the water absorbency increases with an increase in a molar ratio from 0.5 to 2.0 under experimental conditions of the present study. The further increase led to a fall in the water absorbency. On saponification of polyacrylamide by NaOH, the ionic hydrophilic moieties in polymer structure increase that causing an increase in osmotic potential difference, and the electrostatic repulsion cause disentanglement of polymer chains resulting in expansion of the network.

Effect of particle size of backbone polymer on the water absorbency

As seen in the (Table 4) decrease in particle size of pine resin used in hydrogel preparation up to 100- 240 mesh led to an increase in the swelling ratio under experimental temperature (50°C). Finer particles of size >240 mesh size led to the formation of hydrogels with reduced water absorbency. Hydrogels prepared from pine resin of particle size >240 mesh size exhibit reduced water absorbency probably due to the inability of initiation to generate sufficient free radicals on the highly expanded backbone chain density (Lohmousavi et al., 2020).

Effect of temperature and pH on water absorbency of pine resin-based hydrogel

As it is clear from the (Table 5), the water absorbency increases significantly with an increase in temperature from 10⁰ to 55⁰ C. Temperature in the range of 25-50⁰ C is of particular interest to assess the suitability of hydrogels in agriculture. As seen in (Table 5), water absorbency of anionic pine resin-based hydrogel exhibited a significant response as a function of the pH of the swelling medium. pine resin-based hydrogel contains hydrophilic -COOH and -COO⁻ groups which ionize further at pH 9.0 and exert electrostatic repulsion leading to the expansion of the polymer network and hence the increase in pine resin-based hydrogel. pine resin-based hydrogel at pH 4-9 and more particularly at pH 9, point towards a potential soil conditioner for the acidic and alkaline soils.

Table 3: Effect of water volume and the molar ratio of alkali to monomer on water absorbency

W.V. (ml/g)	W.A. (g/g)	M.R. of NaOH to Acrylamide	W.A. (g/g)
3.00	87.00	0.50	176.80
7.00	194.90	1.00	353.40
9.00	348.70	1.50	425.40
12.00	516.70	2.00	516.90
15.00	433.70	2.50	496.80
17.00	287.90	3.00	465.70

*W.V.= water volume; M.R.= molar ratio

Table 4: Effect of particle size of back bone on water absorbency of pine resin-based hydrogel

Particle size (mesh)	Water absorbency (g/g)
25-100	480.20
100-240	599.00
>240	512.70

Effect of water quality on water absorbency of pine resin-based hydrogel

The effect of water quality on the water absorbency of pine resin-based hydrogel shown in (Table 5), As compared to maximum water absorbency values of the product obtained in distilled and deionized water, the swelling in tap water (EC = 2.04 mhos/ cm, pH = 7.7), hard water of different simulated ionic strengths decreased (Das 2023).

Effect of the time on water absorbency of pine resin-based hydrogel

As can be seen from (Figure 1), water absorbency rates of pine resin-based hydrogel were measured at 25°C and 50°C. Results indicate that the pine resin-based hydrogel attains equilibrium water absorbency in 18 hr. at 50 °C, whereas at 25 °C, the same is attained in 21 hours.

Effect of salt/fertilizer solution on water absorbency of pine resin-based hydrogel

Evaluation of the water absorbency of pine resin-based hydrogel in salt solutions, particularly those applied as fertilizers and present in saline soil, is very important because of their agricultural and horticultural applications. Results shown in (Figure 2), depict the comparative swelling response of the optimized pine resin-based hydrogel in solutions of varying strengths of (NH₄)₂SO₄, NH₄NO₃, KNO₃, NaCl, and urea. In all the salt solutions, absorption was less compared with that in distilled water. The hydrogel exhibited a minimum reduction in water absorbency in urea solutions at all test concentrations. This observation is of interest because, for most of the crops in agriculture, urea comprises an important agro-input. In general, a decrease in water absorbency with an increase in the concentration of salt solutions may be understood in terms of a reduction in the osmotic pressure difference between the gel matrix and external salt solution (Bauli et al., 2021).

Table 5. Effect of temperature, water quality, and pH on swelling of pine resin-based hydrogel

Temperature (°C)	W.A. (g/g)	Water quality	W.A. (g/g)	pH	W.A. (g/g)
10	485.70	Deionized water	670.80		
25	514.20	Distilled water	606.90	4.0	461.80
35	537.40	Tap water	447.20	7.0	664.20
45	588.80	Hard water- A	356.00	9.0	739.30
50	616.10	Hard water- B	245.30		
		Hard water- C	210.60		

*W.A.: Water Absorbency

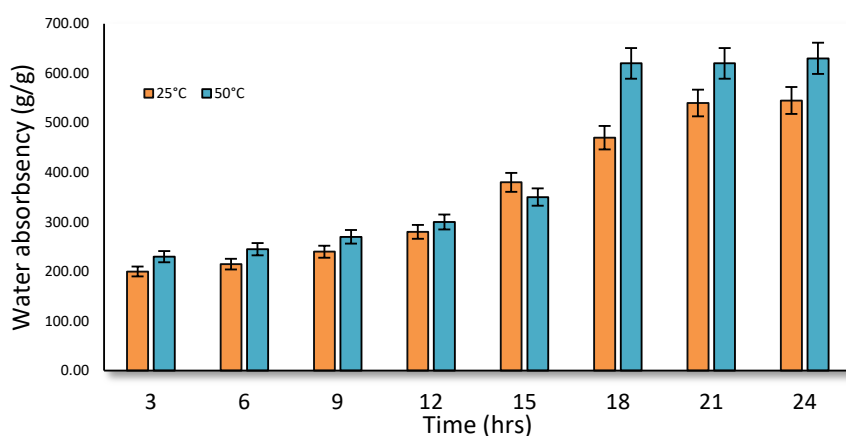


Figure 1. Effect of the time on water absorbency at 50 O C and 25 O C of PR-Hydrogel

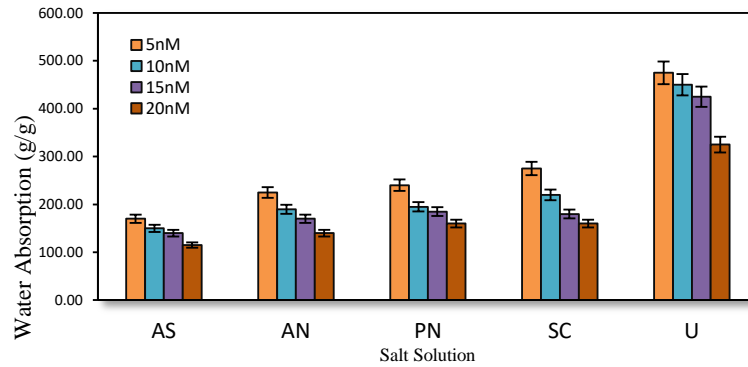


Figure 2: Effect of salt/fertilizer solution on water absorbency of pine resin-based hydrogel

Effect of PR hydrogel addition on water absorbency in soil and soilless media

The water absorbency capacity of the test hilly soil and soilless medium significantly increased with the addition of PR hydrogel. As is clear from (Table 6), at both the experimental temperatures (25^o C and 45^o C), the hydrogel amended soil and soilless medium absorbed more water than the respective controls. Amendment with hydrogel @ 0.75% exhibited higher water absorbency than @ 0.5% in both the plant growth media. In the case of soil, the amended samples at 50^oC exhibited higher water absorbency than at 25^oC at both 0.5% and 0.75% amendment levels (Costa et al., 2021).

Effect of PR hydrogel addition on water holding capacity in soil (A) and soil-less medium (B)

As is clear from (Figure 3), two concentrations of PR hydrogel to soil and soilless medium increased water availability to plant as compared to the control, the water holding capacity of soil and soilless medium amended with the PR Hydrogel remained higher. At field capacity, in both soil and soilless media, hydrogel addition led to higher percent moisture retention as compared to the unamended controls (Guo et al., 2022).

Table 6. Water absorbency of PR hydrogel in soil and soilless medium at 25^oC and 50^oC

Hydrogel content (wt.%)	Soil (W.A.)		Hydrogel content (wt.%)	Soilless Medium (W.A.)	
	25 ^o C	50 ^o C		25 ^o C	50 ^o C
0	39.6	39.1	0	280.9	282.2
0.5	92.5	110.3	0.5	399.9	425.7
0.75	143	184.3	0.75	452.5	473.7

*W.A.: Water Absorbency

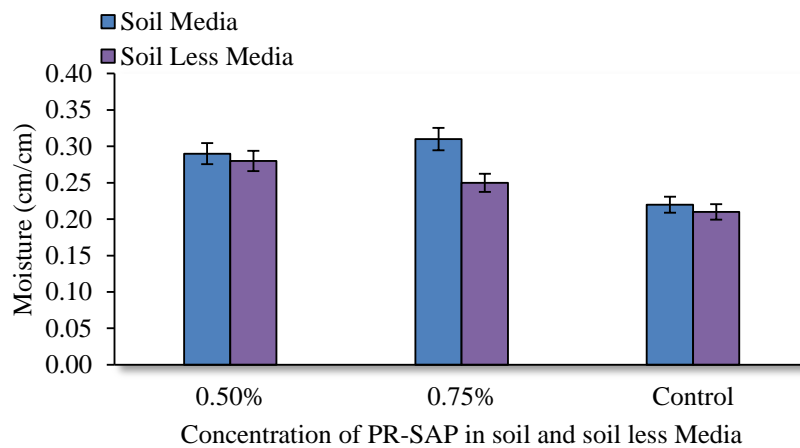


Figure 3. Effect of gel addition on available water from the soil and soil-less medium

4. Conclusions

The pine resin-based hydrogels developed in the present study have exhibited all the characteristics that qualify them as a potential candidate for moisture stress agricultural soil application. The developed hydrogel, possess additional advantage and merits in terms of superior water absorbency behavior under acidic and alkaline conditions, in the presence of salts and fertilizers, and the moisture retention and release characteristics imparted to the plant growth media. Pine resin, being a biopolymer with hydrophilic biocompatible characteristics, the hydrogels based on it will be exploited as potential formulations. The study showed that the backbone monomer ratio, cross linker concentration, and quantity of water per unit reaction mass were critical parameters in determining the swelling properties. Structural characterization confirmed the successful formation of the hydrogels based on pine resin.

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