Development and Characterization of Lignin-Based Hydrogel for Use in Agricultural Soils: Preliminary Evidence

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In arid and semi-arid regions of the world, agricultural production is greatly limited by water scarcity and inefficient water use. Water-absorbent hydrogels are a technological solution that can retain soil water for plants. A lignin-based hydrogel as a natural plant-based water absorbent is prepared from lignin alkali polymers and poly(ethylene glycol) diglycidyl ether (PEGDGE) in adjusted alkali (NaOH) solution. The maximum swelling capacity of the hydrogel is achieved in 1.5 M NaOH with 0.5 mmol PEGDGE g_{lignin}^{-1} . Water swelling capacity is 34 g $g_{Hydrogel}^{-1}$ dry weight of hydrogel in distilled water, which is reduced to 53% and 64% in 0.1 M NaCl and 0.1 M CaCl₂ solution, respectively. Biodegradability and phytotoxicity tests show that 6.5% of the sample mass decomposed after 40 days of incubation in soil solution media and the hydrogel is not phytotoxic to wheat seeds. These findings support the use of the lignin-based hydrogel as an environmentally friendly additive to promote water retention in dry, saline soils. Due to the limitations of this study, further assessments are needed in order to understand the efficiency of lignin-based hydrogel application in different soils with different biota.

1. Introduction

Water is the most limiting factor for agricultural production in arid and semi-arid regions of the world. Persistent water shortages are becoming common in countries like Iran due to climate change, which causes more heat and drought stress for crops.^[1] Groundwater reserves are being depleted because water extraction exceeds recharge. About 1.6 million ha of irrigated lands are experiencing severe water stress, and an additional 1.8 million ha

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is under moderate water stress in Iran.^[2] The agriculture sector is responsible for more than 94% of the total water consumption in Iran and unfortunately, the crop water productivity (CWP, yield per unit of water) is very low. For instance, CWP for wheat in Khorasan Province of Iran is about 0.5 kg m⁻³, which is quite low compared to a similar environment like the Imperial Valley in California or even Bhakra in India (1 kg m⁻³).^[2] Higher water use efficiency in agriculture should be achievable but will require policy improvement and technological solutions.

Increasing soil water retention for plant uptake via using water-absorbent hydrogels is a promising technology to improve water-use efficiency. Hydrogels are 3D networks of polymer chains, cross-linked physically or chemically, which can swell but do not dissolve.^[3] They can absorb and retain many times their mass in water or

biological fluids.^[4] Swelling capacity of hydrogels results from the hydration of polar hydrophilic groups upon contact with water, followed by the osmotic driving force of the network chains toward infinite dilution. Therefore, superabsorbent hydrogels can be used in soil as water storing conditioners,^[5] especially in arid and semi-arid regions of the world that experience water scarcity and drought. Most commercial superabsorbent hydrogels are synthetic petroleum-based polymers that are poorly suited as soil conditioners because they have low biodegradation rates,^[6] low water absorption rates in concentrated electrolyte solutions, and high production costs.^[7] Natural polymers such as polysaccharides^[8,9] and clay minerals^[10] are promising water absorbing materials that have the advantage of being green products made from renewable materials through low-cost processes.

Lignin is the second most abundant plant polymer after cellulose^[11] with characteristics that make it suitable as an inexpensive hydrogel.^[12] This biopolymer is a significant resource for designing the next generation of petroleum-free water-absorbent hydrogels.^[13] Lignin is composed of phenylpropane units linked by the irregular coupling of C—C and C—O bonds with many charged functional groups including hydroxyl groups, either phenolic or aliphatic^[14] that make it capable of binding water and other soluble substances.^[15] Compared to polysaccharides, lignin is more resistant to biological degradation,^[16] but it is biodegradable in the soil environment. Thevenot et al.^[17] found that lignin mass decreased by 16–60% from 13 weeks to 2 years in soil-lignin

mixtures incubated in the laboratory, while there was 48–87% decline in lignin content after 5 years in field soils. Lignin alkali is a byproduct of the papermaking and bio-refinery industries, so it is widely available around the world and is a relatively cheap, renewable feedstock for the synthesis of water-absorbent hydrogels.

Hydrogel porosity and the attraction between the hydrogel and aqueous solution are key factors that determine its swelling capacity.^[18] Porosity and water attraction are related to the degree of physical and chemical cross-linkages within the polymer, and a cross-linker that is suitable for the synthesis of lignin-based hydrogels is poly(ethylene glycol) diglycidyl ether (PEGDGE), a hydrophobic molecule with low toxicity. Lignin-based hydrogels have been synthesized for use in water purification^[19] and drug delivery,^[20] but have not yet been investigated for their potential as water-absorbent hydrogels for application in agricultural soils.

The objective of this work was to synthesize a lignin-based hydrogel based on lignin alkali, a common, inexpensive polymer, and PEGDGE as the cross-linker. Physico-chemical properties, phytotoxicity, and biodegradability of the lignin-based hydrogel were evaluated as indicators of its potential as a soil conditioner in arid soils. Furthermore, phytotoxicity and salt sensitivity of the lignin-based hydrogel were compared to sodium polyacrylate (SPA), a common commercial hydrogel.

2. Experimental Section

2.1. Materials

Analytical grade lignin alkali (low sulfonate content), PEGDGE, NaOH, NaCl, and CaCl₂ were purchased from Sigma-Aldrich (Mississauga, Ontario, Canada).

2.2. Synthesis

Lignin alkali (5 g) was dissolved in 8 mL of three types of solvent: 1.5 \mbox{m} NaOH, 3 \mbox{m} NaOH, or deionized water to choose the best solvent. This volume of the solvent was the minimum possible amount to dissolve lignin alkali powder. The lignin alkali solution was stirred for 24 h and then the PEGDGE cross-linker was added to one of the test solutions (0.3, 0.4, 0.5, 0.75, or 1 mmol g_{lignin}^{-1}), and heated to 50 °C. After 15 min of stirring, viscosity of the solution increased, and the lignin-based hydrogel was formed. The hydrogel was soaked for 1 week with distilled water to remove unreacted monomers and the water was replaced every day. Finally, the hydrogel was freeze dried to prepare the dry hydrogel.

2.3. Characterization

The chemical structure of the synthesized lignin-based hydrogel, cross-linker (PEGDGE) ,and lignin powder were examined by Fourier transform infrared (FTIR) spectroscopy on an AVATAR 370 FTIR spectrometer (Thermo Nicolet, USA) in the range of 4000–400 cm⁻¹ wavelength. Samples were polished with analytical KBr prior to FTIR analysis. Scanning electron microscopy

(SEM) images of the synthesized hydrogel were obtained on a LEO 1450 VP scanning electron microscope (Zeiss, Germany) with a resolution of 2 nm at 20 kV.

2.4. Water Swelling Capacity Measurements

About 1 g of dry hydrogel was immersed in distilled water, NaCl or CaCl₂ solutions (0.001–0.1 °C or 0–8 dS m⁻¹ of electrical conductivity, EC) until it was saturated. Then the swollen samples were weighed. Water swelling capacity (WSC, g_{H2O} $g_{Hydrogel}^{-1}$) of the hydrogel was calculated by using the following equation.

$$WSC = \left(M_{\rm s} - M_{\rm d}\right) / M_{\rm d} \tag{1}$$

where $M_{\rm s}$ (g) and $M_{\rm d}$ (g) represent the weights of the swollen sample and the dry sample, respectively.

2.5. Biodegradability Test

Agricultural soil, collected from the 0–30 cm layer of Ferdowsi University of Mashhad farm, Mashhad, Iran (59°26′ E, 36°20′ N), was the source of microbial inoculum for the biodegradability test. Briefly, 100 g of dry soil was mixed with 200 mL of deionized water, shaken with a magnetic stirrer (20 min) and then centrifuged (15 min) at 1000 × g. The supernatant was filtered (filter paper, 55 mm) to remove the remaining soil particles. The hydrogel sample (0.1 g) was immersed in the soil solution and incubated for up to 40 days. The weight loss at 5 day intervals (5, 10, 15, 20, 25, 30, 35, and 40 days) was determined by drying samples at 55 °C overnight, cooling them in a desiccator, and weighing them according to the following equation.^[21]

Weight loss (%) =
$$\left[\left(M_{\rm i} - M_{\rm f} \right) / M_{\rm f} \right] \times 100$$
 (2)

where M_i and M_f are the initial and the final weight (g) of the hydrogel remaining at each time interval.

2.6. Phytotoxicity Test

Germination of wheat (*Triticum aestivum* L.) seeds is a measure of toxicity, according to Zucconi et al.^[22] Fifteen wheat seeds were placed in Petri dishes filled with distilled water (control) or with saturated hydrogel (saturated with water). Petri dishes were placed in a growth chamber in the dark at 25 °C for 72 h. The germination index was calculated by the following equation.

$$G_{\text{index}} = \left[\left(G/G_0 \right) \times \left(L/L_0 \right) \right] \times 100 \tag{3}$$

where *G* and *L* are the number of germinated seeds and root length in presence of the saturated hydrogel, respectively, and G_0 and L_0 are the number of germinated seeds and root length in distilled water, respectively.

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2.7. Statistical Analysis

The data reported in this study were the means of four replicates (n = 4) subjected to analysis of variance (ANOVA) and the means separation was accomplished using least significant difference (LSD) at $p \le 0.05$ using the Tukey HSD test. The statistical analyses were conducted using SAS statistical software (version 9.1, SAS Institute, Cary, NC).

3. Result and Discussion

3.1. Effect of Solvent and Cross-Linker Concentrations

As lignin alkali is soluble in both water and aqueous NaOH solutions (1.5 and 3 m), the suitability of these solvents was tested. No gel formed when lignin alkali was dissolved in distilled water. The highest swelling capacity of the hydrogel was obtained when the synthesis occurred in 1.5 m NaOH solution (34 g $g_{Hydrogel}^{-1}$ for 1.5 m NaOH vs 16 g $g_{Hydrogel}^{-1}$ for 3 m NaOH). Therefore, the synthesis of lignin-based hydrogel in 1.5 m NaOH is recommended.

Based on the equilibrium swelling theory of Flory and Rehner,^[23] the swelling of a cross-linked polymer depends on the density of cross-linkages and type of the solvent. The concentration of the cross-linker has the most significant effect on the swelling capacity of the hydrogel due to the swelling/cross-linker concentration power law behavior.^[24,25] This is consistent with the effect of the PEGDGE cross-linker ratio on the swelling capacity of the hydrogel. Optimum swelling (34 g $g_{Hydrogel}^{-1}$) was obtained by mixing lignin alkali with 0.5 mmol PEGDGE g_{lignin}^{-1} and this quantity was added to 1.5 M NaOH to produce lignin-based hydrogel for further testing. As the gel formation needs a critical cross-linkage density, lower amounts of the cross-linker (0.3 or 0.4 mmol PEGDGE g_{lignin}^{-1}) were insufficient to form an insoluble product and the swelling capacity of these hydrogels was lower than that of 0.5 mmol PEGDGE g_{lignin}^{-1} (Figure 1). Adding a greater concentration of the cross-linker (0.75 or 1 mmol PEGDGE $\mathbf{g}_{\text{lignin}}^{-1}$) produced a network with excessive cross-linkages that pre-



Figure 1. The effect of PEGDGE cross-linker concentration on swelling capacity of the lignin-based hydrogel.



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Figure 2. FTIR spectra of the synthesized lignin-based hydrogel, the PEGDGE cross-linker, and the lignin alkali powder.

vented water diffusion and reduced the swelling capacity of the hydrogel, relative to the 0.5 mmol PEGDGE $g_{\rm lignin}^{-1}$ treatment (Figure 1). This finding is similar to Chavda and Patel^[26] and Bukhari et al.^[27] who reported that increasing the cross-linker (methylene bis acrylamide) concentration in super-porous hydrogel led to a reduction of swelling, which is related to greater density and less porosity.

3.2. FTIR and SEM of the Lignin-Based Hydrogel

The FTIR spectra of lignin-based hydrogel, cross-linker (PEGDGE), and the lignin alkali powder are shown in Figure 2. The transmutation of the C=O peak in lignin alkali, which appeared as two peaks at 1719 and 1606 cm^{-1} (carboxylic acid and aldehyde groups) to a single and sharper peak at 1597 cm⁻¹ indicates that strong bonds formed between the lignin and PEGDGE. The presence of C-O-C bonds are obvious in the 1200 cm⁻¹ range. The peak becomes stronger and sharper for the lignin alkali powder, indicating cross-linking appeared in the final polymer. The broad peak of OH, belonging to hydrogen bond of both lignin-based hydrogel and the lignin alkali powder appeared at $\approx 3500-3000$ cm⁻¹. The peak at ≈ 2800 cm⁻¹ was attributed to C-H stretching of the aliphatic group of the both lignin-based hydrogel and lignin alkali powder. The insolubility of the product is the confirmation for the cross-linking interaction between lignin and PEGDGE.

Morphology of the lignin-based hydrogel by SEM is shown in **Figure 3**. The SEM image illustrates a wide-ranging porous structure with open channels within the cross-linked network, which may make it a suitable material that retains water when added to agricultural soils.

3.3. Saline Sensitivity

Salinity (ionic strength) of the media affects the swelling capacity of hydrogels because of the osmotic difference between the







Figure 3. SEM images of the lignin-based hydrogel at various magnifications: a) 100 µm, b) 20 µm, c) 10 µm, and d) 2 µm.

external solution and water held within the hydrogel.^[28] Exposure of lignin-based hydrogel to NaCl and CaCl₂ solutions (0.001-0.1 M or $0-8 \text{ dS} \text{ m}^{-1}$ of electrical conductivity, EC) led to a reduction in swelling capacity compared to distilled water and swelling capacity declined as the ionic strength of the solution increased (Figure 4). This reduction in hydrogel swelling is often ascribed to the osmotic pressure reduction between the gel network and the external medium, and an enhanced screening effect of counter ions.^[29] At the highest salinity level (salt solution with $EC = 8 dS m^{-1}$), the hydrogel swelling capacity declined by up to 64%, compared to distilled water (Figure 4). This phenomenon suggests that lignin-based hydrogels will have less water retention in saline soils, which are often water limited. Compared to other studies^[29–32] where the swelling capacities of various hydrogels were reduced to 40-60% following exposure to 0.01 м NaCl solution and also were decreased to 60-98% when saturated with 0.01 м CaCl₂ solution, while 20% and 60% reduction in ligninbased hydrogel were obtained for 0.01 M NaCl and 0.01 M CaCl₂ solutions, respectively. This indicates that the lignin-based hydrogel was less sensitive to the negative effects of saline solutions, based on its swelling capacity, compared to other natural or synthetic polymeric hydrogels. Thus, it has great potential as a water-retaining material in areas where EC of soil solutions is



Figure 4. Swelling capacity of the lignin-based hydrogel as influenced by the ionic strength of NaCl and CaCl₂ solutions.

 ${<}2~\text{dS}~\text{m}^{-1},$ with less but acceptable water-retaining capacity in saline solutions.

Less impact on hydrogel swelling capacity was observed with NaCl solution (monovalent cation) than CaCl₂ solution (bivalent



cation), which is attributed to greater osmotic pressure difference between the interior gel network and external solution with $CaCl_2$. It is clear that cation types (different radius and charges) in the solution are the main reason for this observation. The presence of Ca^{2+} cations in the solution is expected to cause contraction of the hydrogel owing to binding between Ca^{2+} and COO- groups.^[4] It is notable that the swelling capacity of hydrogel reaches a constant value for both saline solutions as the EC increases to >4 dS m⁻¹ (Figure 4), which suggests a new equilibrium is reached between salt and water absorption within the hydrogel.

3.4. Biodegradation

The weight loss of the lignin-based hydrogel that was placed in solution with soil microbial inoculum for 40 days could be an indicator of microbial degradation of the polymers, as illustrated in **Figure 5**. After 40 days of incubation, there was a 6.5% loss of hydrogel mass; if this data can be extrapolated linearly, it suggests that 59% of the lignin-based hydrogel will be decomposed after 1 year (**Table 1**). This depends upon the biological activity of soil



Figure 5. The reduction of lignin-based hydrogel sample during 40 days of incubation as a result of biodegradation.

 Table 1. Weight loss of the lignin-based hydrogel during 40 days of incubation.

Incubation period	Weight loss [g]	Wight loss ratio [%]
Day 0	0	0
Day 5	0.0003	00.33
Day 10	0.0008	00.76
Day 15	0.0024	02.40
Day 20	0.0037	03.70
Day 25	0.0040	04.00
Day 30	0.0050	05.00
Day 35	0.0057	05.60
Day 40	0.0065	06.50
Year 1	0.0651 ^{a)}	65.06 ^{a)}

^{a)}Estimated from the simple linear regression equation. Residual mass = $0.101 - (0.000182 \times time)c$, $R^2 = 0.989$.





Figure 6. Germination index of wheat seeds in the presence of the ligninbased hydrogel and SP hydrogel (bars with different letters indicate significant differences at p < 0.05).

microorganisms (mainly fungi) that are able to degrade a ligninbased hydrogel. Yamamoto et al.^[33] reported that lignin gels prepared from the methanol-diluted lignin-phenol-resorcinol resin with glutaraldehyde as the cross-linker were completely degraded by the fungus *Flammulina velutipes* after 11 months. According to Phang et al.,^[34] between 15% and 82% of an alginate-based hydrogel was degraded during a 40 day incubation in different soil solutions. Due to the fact that the results of the biodegradability test were achieved on a small scale (40 days) and did not include different soil types, more examinations are needed in the long term with different soil biota. Nonetheless, a simple extrapolation by linear regression can give us a general prediction of the biodegradation rate and durability of lignin-based hydrogel in the soil to be used for recommendations on time of next hydrogel application.

3.5. Phytotoxicity

The germination index (GI) is a relative measure of seed germination and roots elongation, where GI < 50% indicates high phytotoxicity, GI of 50-80% is moderate phytotoxicity and GI > 80% means no phytotoxicity.^[22] The GI of lignin-based hydrogel was similar to the control (GI = 100-102%), meaning that there was no phytotoxicity to wheat, but the commercial SPA hydrogel showed GI < 50% and was highly phytotoxic to wheat (Figure 6). Hydrogels synthesized from plant polymers are generally not phytotoxic, as Montesano et al.^[35] reported for radish (Raphanus sativus L.), cucumber (Cucumis sativus L.), alyssum (Alyssum spp.) and Centaurea (Centaurea spp.) that were exposed to cellulose-based hydrogels. In contrast, commercial hydrogels are acrylate-based products that release toxic molecules during degradation,^[36] and these compounds are apparently phytotoxic. Any soil conditioner that is applied in agricultural soils should not be toxic to seeds or plants, and lignin-based hydrogels meet this criterion. More studies are planned to examine the effects of lignin-based hydrogels on plant growth and development under deficit soil water condition as well as the phytotoxicity effect of the hydrogel to other seeds.

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4. Conclusions

This preliminary study reports on the successful synthesis of a lignin-based hydrogel that is non-toxic, biodegradable, and has good swelling capacity in both non-saline and saline solutions. These beneficial properties make the lignin-based hydrogel a good candidate for use in agricultural soils, and it has potential for water retention in non-saline, saline, and sodic soils. Although the swelling capacity of the lignin-based hydrogel $(34 \text{ g } \text{g}_{\text{Hvdrogel}}^{-1})$ is lower than commercial acrylate-based hydrogels (more than 100 g ${g_{\rm Hydrogel}}^{-1}$), it has several advantages, namely 1) it is synthesized from a low-cost, renewable feedstock (lignin alkali) by using small amounts of non-toxic chemicals (1.5 м NaOH, 0.5 mmol PEGDGE g $^{-1}_{lignin}$), consistent with the principles of green synthesis, (2)) it is non-toxic and biodegradable, so it poses no risk to crop production or soil health, and (3)) it functions in saline conditions, making it suitable for use in droughtimpacted saline or sodic soils. Despite these results, more studies are planned to evaluate the performance of this lignin-based hydrogel as a soil conditioner for water retention under laboratory, greenhouse, and field conditions.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

biodegradability, lignin, phytotoxicity, soil conditioner, superabsorbent hydrogels

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