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Laboratory Determination of the Impact of Incorporated Alkali Lignin-Based Hydrogel on Soil Hydraulic Conductivity

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Abstract: Superabsorbent polymers (hydrogels) have been studied for their ability to influence soil hydraulic conductivity because they can store and release water due to their swelling properties. However, concerns related to the increased use of synthetic hydrogels necessitates a switch to bio-based hydrogels, which are renewable and more biodegradable in comparison to synthetic hydrogels. In this study, we synthesized a lignin-based hydrogel and amended a silt loam soil with it at concentrations of 0, 0.1, and 0.3% (w/w). A laboratory permeameter, double membrane tension infiltrometer, and evaporation method were used to measure the saturated (Ks), near saturated, and unsaturated hydraulic conductivity (K) of the samples, respectively. Saturated hydraulic conductivity was significantly decreased by the application of hydrogel at 0.1 and 0.3% (w/w) in comparison to the control treatment. The application of 0.3% (w/w) lignin-based hydrogel only significantly decreased hydraulic conductivity at -1 cm soil water pressure head. Hydraulic conductivity in the 0.1 and 0.3% (w/w) treatments increased along the $K(\theta)$ curve in the unsaturated zone (-750 cm $< h < -10$ cm) in comparison to the control treatment, which we hypothesized was due to bound water in the hydrogel being released and creating a wider path for the movement of water. The 0.1 and 0.3% hydrogel treatments also tended to store more water than the control treatment, especially after 24 h of evaporation. The implication of this study is that lignin-based hydrogels could swell and retain water in saturated soils and the bound water could be released to enhance the flow of soil water in unsaturated soil, thereby reducing the water stress of plants, which require less energy to move and absorb water.

Keywords: evaporation method; unsaturated hydraulic conductivity; near-saturated hydraulic conductivity; saturated hydraulic conductivity; bio-based hydrogel; tension infiltrometer

1. Introduction

Hydraulic conductivity describes the ability of the soil to transmit water [1]. Water flow in the vadose zone is regulated by unsaturated hydraulic conductivity (K), which is a function of the water retention curve $\theta(h)$ [2], where h is the soil matric potential. According to Gallage et al. [3], when the matric potential decreases and soil becomes unsaturated, some large pores become filled with air and force water to flow through the smaller pores. A further decrease in matric potential decreases the water filled pores, thus increasing resistance to water flow and decreasing hydraulic conductivity. Perkins [4] notes that, to describe most models of water flow and solute transport, you must know the relationship between K and volumetric water content (θ), which is a nonlinear relationship.

Hydrogels have been studied for their ability to influence soil hydraulic conductivity. Hydrogels are three dimensional hydrophilic materials that form an insoluble 3-dimensional network in the presence of an aqueous solution [5]. Hydrogels are known to possess a high swellability, hence their use in various industries, i.e., medicine, food, and agriculture. The formation of hydrogels occurs through the crosslinking of polymer chains dispersed in any aqueous medium by mechanisms including physical entanglements, ionic

interactions, and chemical crosslinking [6]. In recent times, the increased usage of synthetic hydrogels has led researchers to switch their focus to bio-based hydrogels, which have the advantages of being easily degradable and biocompatible in relation to synthetic hydrogels [7]. The application of hydrogels can affect hydraulic conductivity of soil due to the high swelling capacity of some hydrogels, which can store substantial amounts of water in soil and block drainage pores, thus reducing saturated hydraulic conductivity (Ks) [8].

Numerous studies within the past few decades have investigated the impacts of hydrogel application on saturated hydraulic conductivity (Ks). In terms of the types of hydrogels applied to soil to investigate Ks, some studies applied biobased hydrogels [9–12] while most studies in literature applied synthetic hydrogels [13–22]. While the addition of hydrogel to soil mostly decreased saturated hydraulic conductivity (Ks) [10–13,16–18,21,22], some studies have observed an increase [15,20,23] and others report a decrease and then a subsequent increase with time [14,19,20,24]. The inconsistency of results regarding the effects of hydrogel applications to Ks allows for further studies to probe into applying other types to hydrogels to ascertain their effects on soil Ks.

Similarly, a survey of the literature found three studies that measured unsaturated hydraulic conductivity (K) after applying hydrogel [8,21,25]. All three studies reported a decrease in K. Al-Darby [8] estimated K using a numerical method, i.e., using the Van Genuchten hydraulic function. Al-Darby [8] observed a 63, 92, and 9% decrease in K corresponding to application rates of 0.2, 0.4, and 0.8% (w/w) hydrogel. Liao et al. [26] measured the K of a sandy loam soil when a synthetic polyacrylamide and acrylic acid-based hydrogel were applied at rates of 0, 0.01, 0.03, and 0.06% (w/w). Their results revealed a decrease in K of 85.5 to 94.1% on day 0, 75.1 to 82.9% on day 30, and 65 to 76.2% on day 50. Smagin et al. [21] noticed that at high matric potentials, i.e., <-10 to -15 kPa, K reduced up to 2–3 times at concentrations ranging from 0.01–0.05% (w/w) and reduced 10–50 times at 0.1–0.2% concentration. However, at low matric potentials, i.e., -20 to -700 kPa, K increased with an increase in application rate. The lack of studies investigating the impacts of bio-based hydrogels on K necessitates a further probe into applying and studying the impact of alternative bio-based hydrogels on K.

To the best of the authors' knowledge, there are currently no studies that investigate the impacts of alkali lignin-based hydrogels on soil hydraulic conductivity under saturated and unsaturated conditions. Alkali lignin is a form of a technical lignin which has been used to synthesize lignin-based hydrogels [27] but has yet to be fully explored for synthesizing lignin-based hydrogels for the purpose of impacting soil hydraulic properties; thus, there is a critical need to explore the impact of alkali lignin-based hydrogels on soil hydraulic conductivity, especially for silt loam soil, which is rarely considered in soil amendment studies involving hydrogels. Information on the impact of lignin-based hydrogels on soil hydraulic conductivity will add to the growing evidence for the application of lignin-based bioproducts in soils to reduce waste and enhance soil carbon sequestration. The objectives of this study were to: (a) determine the impacts of amending the lignin-based hydrogel on the saturated hydraulic conductivity (Ks), (b) determine the impacts of the lignin-based hydrogel on near saturation hydraulic conductivity, (c) determine the impacts of the lignin-based hydrogel on changes in total water storage in the soil, and (d) estimate the unsaturated soil hydraulic conductivity (K) of a silt loam soil amended with a lignin-based hydrogel from evaporation experiments using the Wind method. It was hypothesized that amending soils with the lignin-based hydrogel could reduce hydraulic conductivity in comparison to unamended soil. The lower hydraulic conductivity would reduce deep percolation of water in the soil while increasing soil water storage.

2. Materials and Methods

2.1. Lignin-Based Hydrogel

A lignin-based hydrogel was first synthesized following a synthesis method similar to that described by Passauer et al. [28] and Mazloom et al. [29], with some modifications. Briefly, a 1.5 M NaOH solution was added to the lignin alkali and the mixture was stirred

using a glass rod for 5 min. Then, 0.5 mmol of the cross-linker (PEGDGE) was added to the lignin alkali solution. This solution was placed on a heat source (Heidolph™ MR Hei-Tec Magnetic Stirrer with heating) at 50 °C while stirring continuously for 10–15 min until the hydrogel was formed. The formed hydrogel was then removed and soaked in deionized (DI) water for 7 days to wash out unreacted monomers. Finally, the soaked hydrogels were freeze dried at −48 °C in a freeze-drier (Labonco, Kansas City, MO, USA, Cat. No. 7753024) to obtain a dried lignin-based hydrogel. The freeze-dried hydrogel was ground with a blender to obtain micron sized particles.

2.2. Soil Properties

Bulk silt loam soil was obtained from the University of Kentucky Spindletop Farm located north of Lexington, Fayette County, Kentucky (38°6′18.07″ N 84°29′36.11″ W). Silt loam soil was selected because most studies on the effects of hydrogel on soil hydraulic properties have mainly investigated sandy soils, but few were based on silt loam soil. Secondly, silt loam soil was selected because it is the most common soil type in both Kentucky and the southeastern United States and it does not excessively expand in volume with changing moisture contents [30]. The soil was air-dried, ground, and sieved through a 2 mm sieve to obtain a homogeneous soil sample. Total nitrogen and carbon, cation exchange capacity, base saturation, exchangeable K, Ca, Mg, Na, pH, and soil texture were determined on the prepared soil. The texture of the soil was determined using the micropipette method [31]. Cation exchange capacity (CEC) was analyzed using ammonium acetate extraction, bases (Mg, Ca, Na, K) were analyzed using inductively coupled plasma spectrophotometry [32], and base saturation was determined as total bases/CEC × 100%. Total nitrogen was determined using the LECO combustion method [33]. The pH of the soil was determined in water by using a glass electrode [34].

2.3. Laboratory Experiments

All hydraulic conductivity experiments were conducted in the soil physics laboratory of the Kentucky Agricultural Experiment Station, University of Kentucky, Lexington. Nine cylindrical metal rings with a volume of 245.12 cm^3 (height of 6 cm and diameter of 8.58 cm) were obtained. Three treatments were prepared by mixing soil and hydrogel at concentrations of 0, 0.1, and 0.3 (*w/w*). There were three replications for each treatment. The prepared soil samples were then packed into metal rings to an approximate bulk density of 1.3 g cm^{-3} by gradually adding the samples and compacting with a wooden rummer with a flat bottom that fit into the metal rings. The samples were then placed into ring holders and double-sieve rings were mounted to the bottom of the samples. The ring holders were placed in the permeameter, in which there is a reservoir of water, and gradually saturated by regulating the water table. The saturated hydraulic conductivity (*Ks*) of the hydrogel-amended soils was measured using the permeameter [35]. The *Ks* was measured using the constant water head method based on the percolation rate of the samples [1]. The water table within the ring holder rose quickly (within minutes to hours) to the level of the reservoir, thus a constant water head method was used for determining the *Ks*.

For the constant head, the volumetric water flow rate through the soil samples was recorded at time intervals. The hydraulic head applied to a sample was determined by taking the difference between the water level in the container and the water in the ring holder.

Ks was then calculated by rearranging the Darcy equation:

$$Ks = \frac{QL}{A\Delta h} \tag{1}$$

where *Q* is the water flowing per unit time (cm^3/day)

A is the cross-sectional area of the sample (cm^2)

Δh is the hydraulic head causing the flow as measured by the level of water in the manometer (cm)

L is the length of the sample (cm)

Ks is the proportionality constant/saturated hydraulic conductivity

To determine hydraulic conductivity near saturation, a tension infiltrometer apparatus consisting of a double pressure plate-membrane at the top and the bottom of the soil core was used [36]. After Ks measurements were completed, the soil samples were transferred to the tension infiltrometer apparatus. Similar pressure heads were applied to both the upper and the lower boundaries of the soil cores to achieve steady-state flow conditions [36]. The main parts of the double plate tension infiltrometer (Figure 1) include the water reservoir, the upper and the lower membrane plates, and the bubbling tower. The bubbling tower is connected to the water reservoir and water flows through the permeable (nylon) membrane into the soil when air enters the air entry tube and into the water reservoir. The same pressure heads are then applied to the upper and lower permeable membranes by controlling the height of the water in the bubbling tower using a suction control tube. Figure 2a depicts an image of the double membrane tension infiltrometer method; Figure 2b depicts the upper and lower manometers connected to the upper and lower tension disks, respectively. Hydraulic conductivity was determined by applying pressure heads of −10, −5, and −1 cm. To calculate the hydraulic conductivity in the different hydrogel-soil samples, the infiltration of water into the sample was first determined. The application of the same pressure head at both ends of the soil cores allowed for the establishment of steady-steady infiltration conditions, which were obtained when the flowrate of the percolating water through the samples became constant. This constant infiltration rate was then multiplied by the area of the reservoir and divided by the area of the metallic core to obtain the hydraulic conductivity in the sample.
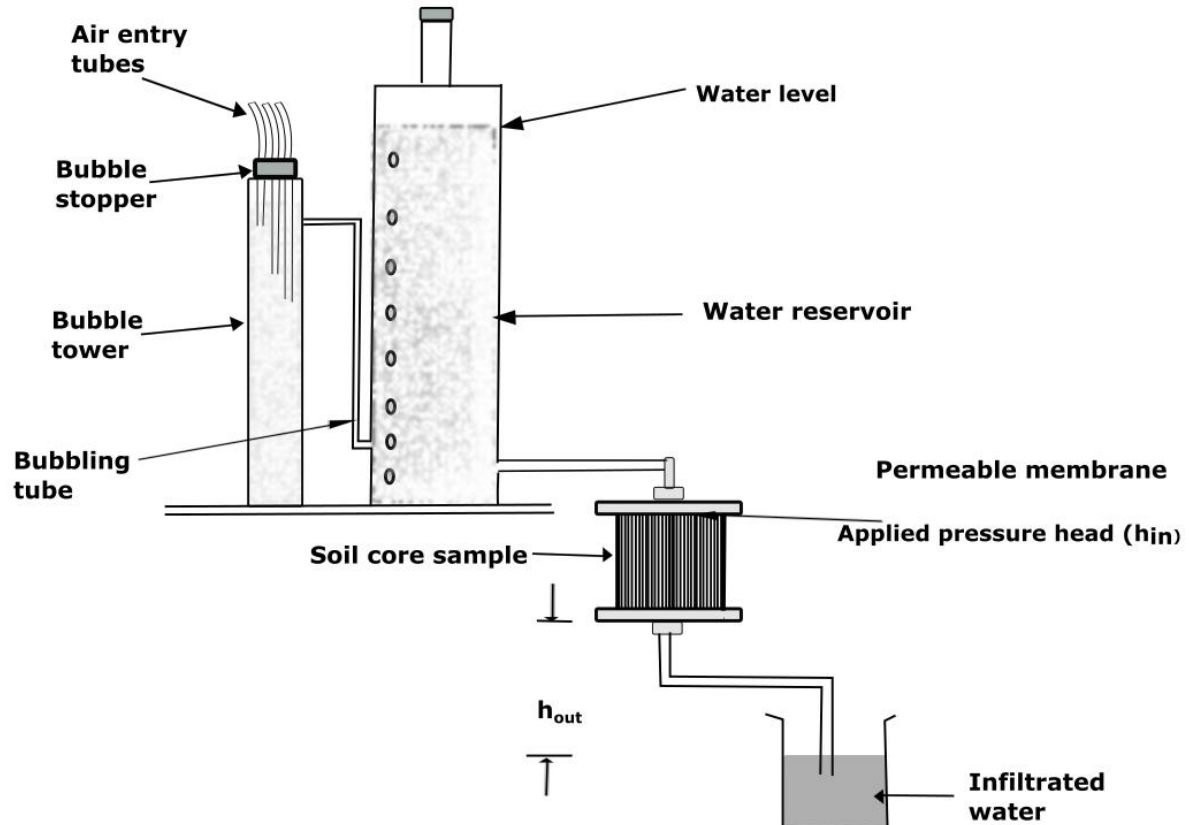

Figure 1. Schematic of the double membrane tension infiltrometer method, redrawn from [36], for measuring hydraulic conductivity near saturation.
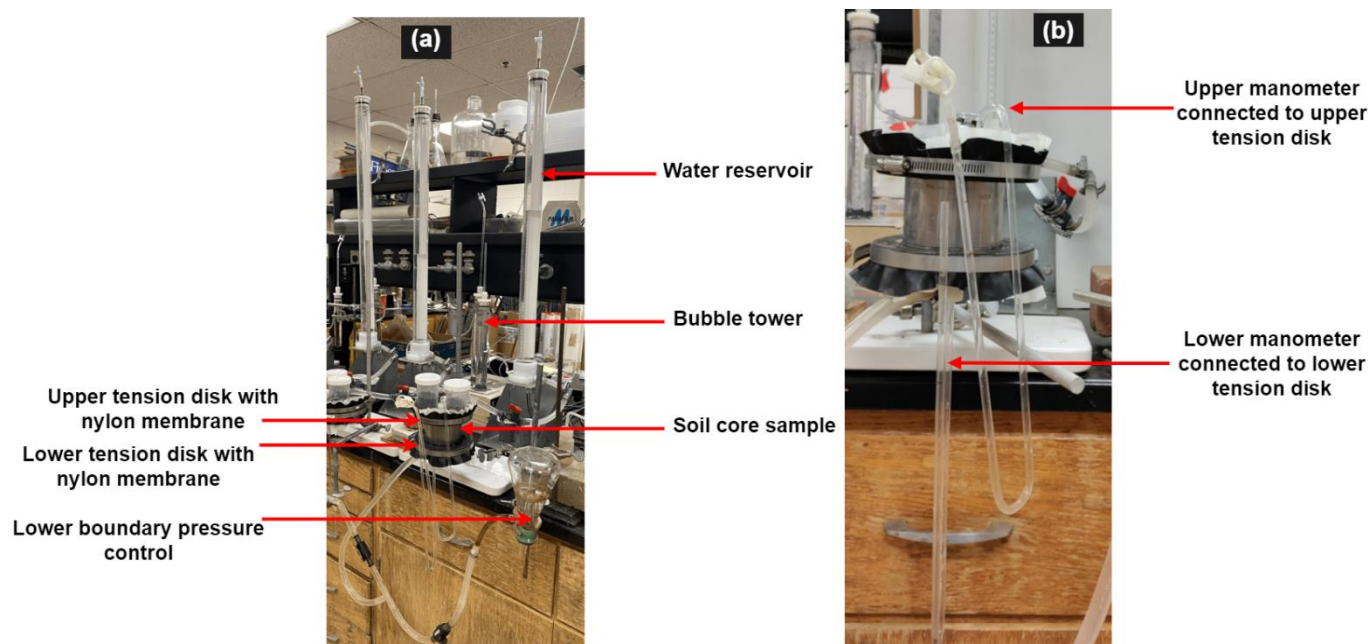
Figure 2. Image of the experimental set-up for the double membrane tension infiltrometer method located in soil physics laboratory of the Kentucky Agricultural Experiment Station, University of Kentucky, Lexington. (**a**) shows the complete set while (**b**) shows clearer view of the upper and lower manometers connected to the upper and lower tension disks respectively.

The laboratory-based evaporation method was used to determine the unsaturated hydraulic conductivity relationship [$K(h)$ or $K(\theta)$] of the samples [37] from the range of -10 to -750 cm soil water pressure head at two soil depths. The evaporation method was conducted following methods described in [37–40]. Two electronic pressure transducer tensiometers with cups of length 6 cm and 0.6 cm outer diameter (o.d) were inserted horizontally into pre-drilled holes in cylindrical metal rings of 245.12 cm^3 volume (height of 6 cm and diameter of 8.56 cm) containing the soil treatments. The holes were located at 1.5 cm and 4.5 cm, respectively, from the surface of the soil core. The cylindrical metal rings with samples were then placed on an in-house designed box containing the data logging system (CR3000 datalogger, Campbell Scientific Inc., Logan, UT, USA), which was used to record the change in pressure in the tensiometers. The contact points between the bottom of the metal rings and the box were fitted with O-rings to prevent the evaporation of water. The samples were covered with plastic wraps and left standing for 24 h to avoid evaporation while hydrostatic equilibrium was being established. Hydrostatic equilibrium was indicated by steady tensiometer readings equal to the height difference between the two tensiometers (3 cm) [37]. After establishing the initial pressures in the upper and lower tensiometers, the evaporation process was initiated by removing the plastic wraps from the top of the soil cores. Initial sample weights were recorded using the data logger. The evaporation process was started and subsequently terminated when the top tensiometer (1.5 cm from the soil core surface) reached a soil water pressure head of $h \approx -750$ cm. Pressure head and water content in the samples were logged every 5 min. At the end of evaporation, the mass of the tensiometers, the box, the ring, and wet soil were recorded. Residual water content was determined by drying the wet soil with the ring at 105 °C for 24 h. A schematic of the experimental set-up is shown in Figure 3; while Figure 4 depicts an image of the evaporation method prior to the start of evaporation.
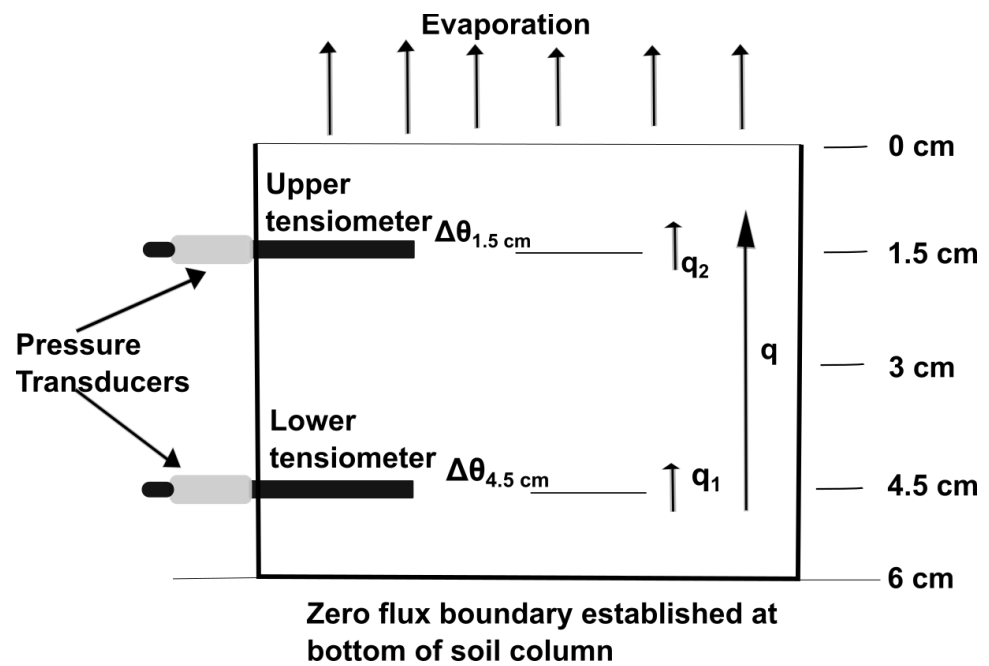
Figure 3. Schematic of the experimental set-up for determining the hydraulic conductivity of the hydrogel amended soils using the evaporation method, redrawn from Wendroth et al. [41], where q_1 and q_2 represent the upward volume flux density of water across the 4.5 cm and 1.5 cm boundaries, respectively, in the soil cores. The average upward volume flux density of water between the 1.5 and 4.5 cm boundaries is represented by q.
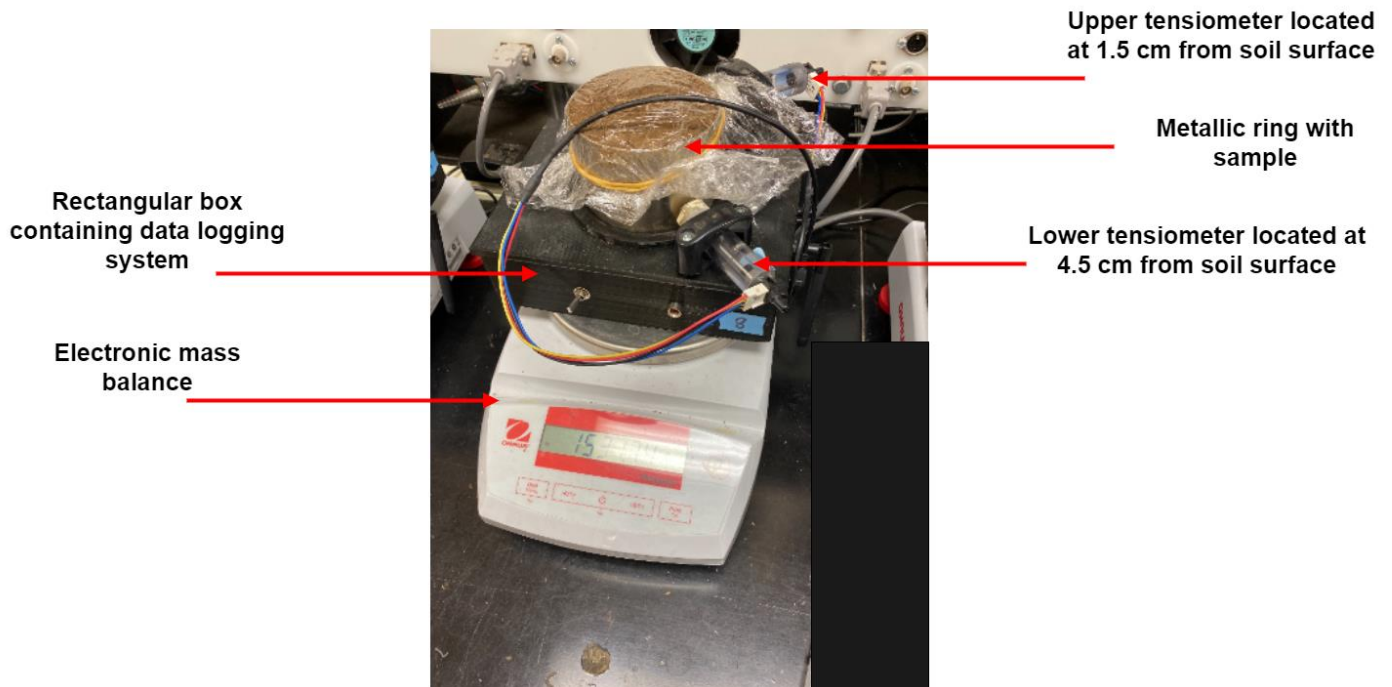

Figure 4. Image of the experimental set-up of the evaporation method used to determine the hydraulic conductivity functions $K(\theta)$ and $K(h)$.

2.4. Theory for Determination of Soil Hydraulic Functions

To derive the functions for unsaturated hydraulic conductivity, we assumed that the soil water retention and the unsaturated hydraulic conductivity curves, which are both

non-linear functions, can be described using the analytical closed-form equation proposed by van Genuchten [2]:

$$\theta = \theta_r + \frac{(\theta_s - \theta_r)}{\left[1 + (\alpha h)^n\right]^m} \tag{2}$$

where h is the measured soil water pressure head from the tensiometer readings, θ is the estimated volumetric water content, α, m, and n are empirical parameters (constants) that enable the model to characterize the water retention relationship, and θ_r and θ_s are residual and saturated volumetric water contents, respectively [42].

The hydraulic conductivity (K) was then estimated for each time interval following the reevaluated procedure via numerical simulations described by Wendroth et al. [37,41]. The schematic of the soil sample shown in Figure 2 is composed of two compartments and the water content in the soil is assumed to change with time according to the measured soil water pressure head values at the two tensiometer locations (1.5 cm and 4.5 cm). An initial guess for the water retention parameters was used to calculate the water storage in the upper 3 cm and lower 3 cm of the soil core. The total water storage in the two compartments was then estimated based on the volumetric water content calculated using the van Genuchten function. That estimated total water storage was then compared with the total amount of water in the soil core determined using the mass loss of the soil core. The curve fitting van Genuchten equation was then used to update the water contents to get a new set of fitting parameters (θ_s, θ_r, α, and n). This process was repeated until the difference between the estimated water content and the measured water contents were <0.0001 cm^3 cm^{-3}. After convergence of the solution, i.e., when the measured soil water storage equals the estimated soil water storage for the two depths, the final water content values were then used to calculate the water fluxes between the two depths [30]. The hydraulic conductivity (K) for a given time was calculated using:

$$K = -\frac{q}{Ave.grad} \tag{3}$$

where q (cm s^{-1}) is the average water flux between the two tensiometers and $Ave.grad$ is the average hydraulic head gradient causing flux between two successive time intervals of measurements.

The corresponding h and θ values were calculated using:

$$\bar{h} = \frac{h_{i,-1.5cm} + h_{i+1,-1.5cm} + h_{i,-4.5cm} + h_{i+1,-4.5cm}}{4} \tag{4}$$

$$\bar{\theta} = \frac{\theta_{i,-1.5cm} + \theta_{i+1,-1.5cm} + \theta_{i,-4.5cm} + \theta_{i+1,-4.5cm}}{4} \tag{5}$$

where $h_{i,z}$ and $\theta_{i,z}$ represent the measured soil water pressure head and the volumetric water content from the water retention curve estimated, respectively, while i and z represent the time step and depth of insertion of the tensiometers, respectively.

2.5. Statistical Analysis

Analysis of variance (ANOVA) was used to test for the difference in means among the three treatments for the samples and, if a difference was detected, Tukey's test [43] was used to determine which treatment(s) differed significantly from the others. Before the statistical tests were conducted, the data were checked for normality and equal variance assumptions and appropriate tests were applied. All statistical tests and graphing were done in (SigmaPlot version 14.0, Systat Software, Inc., San Jose, CA, USA). A significant level of 5% (alpha = 0.05) was used for all statistical comparisons.

3. Results and Discussion

The physical and chemical properties of the soils used in this study are shown in Table 1.

Table 1. Physical and chemical properties of silt loam soil.

Soil Texture	Clay (%)	Silt (%)	Sand (%)	Total N (%)	Total C (%)	CEC	Ex. Mg	Ex. Ca	Ex. Na	Ex. K	Base Saturation (%)	pH
Silt loam	18.18	72.25	9.57	0.178	1.769	18.68	1.37	11.2	0.03	0.67	71	5.73

Notes: CEC is the cation exchange capacity, exchangeable (Ex.) Mg, Ca, Na, and K were all measured in meq/100g of soil. The pH was measured in water.

3.1. Effect of Lignin-Based Hydrogel on Saturated Hydraulic Conductivity

The results of the characterization of the synthesized lignin-based hydrogel is reported in [44]. The first objective of this study was to amend the silt loam soil with lignin-based hydrogels and quantify the variation of Ks in the soil by laboratory measurements and calculations using Darcy's law. Figure 5 presents the measured values of Ks for the lignin-based hydrogel-soil mixtures at different hydrogel concentrations. The Ks in the 0% (w/w) treatment was 339.19 ± 104.5 cm d^{-1}, 38.81 ± 15.80 cm d^{-1} in the 0.1% (w/w) treatment, and 45.04 ± 19.60 cm d^{-1} in the 0.3% (w/w) treatment.
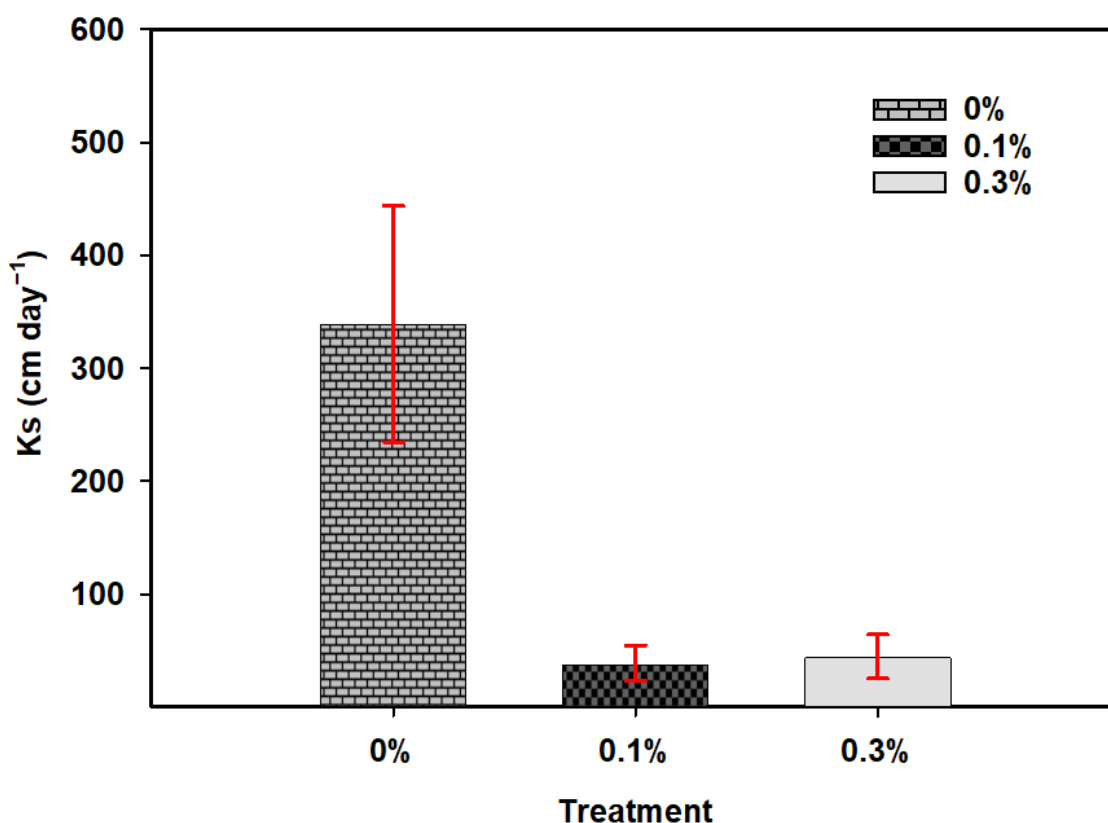

Figure 5. Saturated hydraulic conductivity (Ks) of the lignin-based hydrogel-soil mixtures at 0%, 0.1%, and 0.3% (w/w) treatment application rates. Error bars indicate standard error of the means (n = 3).

Saturated hydraulic conductivity was statistically significantly decreased with the application of hydrogel at 0.1 and 0.3% (w/w) compared to the control treatment ($p < 0.05$). The 0.1% (w/w) treatment decreased Ks by 88.5% while the 0.3% (w/w) treatment decreased Ks by 87%. However, there was no statistically significant difference in Ks between the 0.1 and 0.3% (w/w) treatments. Our results agree with previous studies [10–13,16–18,21,22] that reported a decrease in Ks with the application of hydrogels to various soils. Half of the studies reported similar decreases in Ks, and the other half reported decreases in Ks one order of magnitude smaller than what we found.

Among the studies listed above, only one study [12] applied a similar bio-based hydrogel. Song et al. [12] applied a lignin-sodium alginate hydrogel to a sandy-loam soil and observed a decrease of 63.2–89.5% in *Ks* of a sandy loam soil with an increase in concentration of the hydrogel from 0 to 0.975% (*w/w*). The magnitude of the decrease in *Ks* in Song et al. [12] is similar to the decrease observed in our study. Our results indicate that alkali lignin could be used with other polymers to synthesize hydrogels, which could be useful in reducing *Ks* in soils. A possible explanation for the decrease in *Ks* could be attributed to the swelling characteristic of the lignin-based hydrogel. Swelling experiments conducted on the lignin-based hydrogel in Adjuik et al. [44] determined the swelling rate to be 20.1 g of water/g of hydrogel in deionized water. Due to the swelling characteristic of the lignin-based hydrogel, its expansion in the presence of water reduced the size of drainage pores in the soil and caused aggregation of the soil particles [8,10], which reduced the number of pores available for the downward movement of water in soil.

3.2. Effect of Lignin-Based Hydrogel on Near-Saturated Hydraulic Conductivity

Near saturation *K* was determined using the double membrane tension infiltrometer apparatus. Figure 6 presents the results of the effect of the different treatments of the lignin-based hydrogel at soil water pressures of -1, -5, and -10 cm on hydraulic conductivity. Near saturated *K* values were two orders of magnitude lower than *Ks* values. The sharp decrease in hydraulic conductivity across small soil water head pressure range changes near saturation (-10 cm $< h < 0$ cm) is attributed to the effects of structural macropores [45,46]. At $h = -1$ cm, the *K* value in the 0% (*w/w*) treatment was 2.16 ± 0.14 cm d^{-1}, 2.08 ± 0.25 cm d^{-1} in the 01% (*w/w*) treatment, and 0.45 ± 0.03 cm d^{-1} in the 0.3% (*w/w*) treatment. Hydraulic conductivity was statistically significantly decreased with the application of hydrogel at 0.3% (*w/w*) in comparison to the 0 and 0.1% (*w/w*) treatments ($p < 0.01$); however, there was no statistically significant difference in K between the 0 and 0.1% (*w/w*) treatments. Our results imply that the effect of lignin-based hydrogels in decreasing hydraulic conductivity is intensified as soil water pressure increases towards saturation. In saturated and near saturated states, a higher dose of lignin-based hydrogel decreases hydraulic conductivity, but the decreasing effect diminishes as the soil water pressure head decreases.
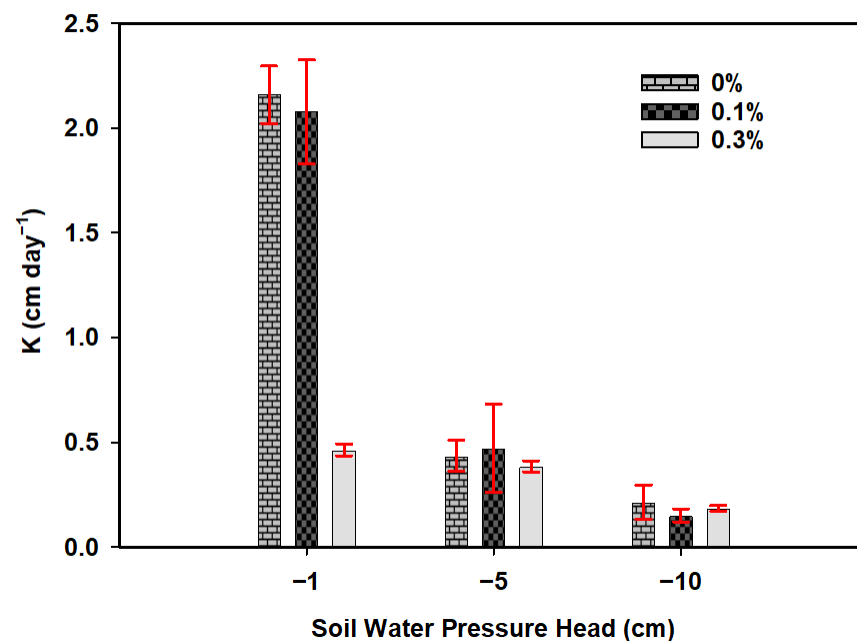

Figure 6. Near-saturated hydraulic conductivity (*K*) of the lignin-based hydrogel-soil mixtures at 0%, 0.1%, and 0.3% (*w/w*) treatment application rates. Error bars indicate standard error of the means (n = 3).

While several studies have mostly focused on exploring the effects of hydrogel applications on saturated hydraulic conductivity, few studies [21] attempted to extend the measurement to a near saturated condition, i.e., (-10 cm < h < 0 cm), through modeling techniques. Smagin et al. [21] tested a radiated-cross-linked technical polyacrylamide hydrogel on a silty sand soil at 0.01 to 0.3% (w/w) application rates. They reported a 2–3 times decrease in hydraulic conductivity between soil water pressure heads of less than -100 cm at hydrogel application rates of 0.01 to 0.05% (w/w) and a 10–50 times decrease in hydraulic conductivity with application rates of 0.1 to 0.2% (w/w).

3.3. Effect of Lignin-Based Hydrogel on Unsaturated Hydraulic Conductivity Relationships Using the Evaporation Method

The evaporation method coupled with Wind's iterative procedure [38] was used to determine the unsaturated hydraulic conductivity relationship [$K(h)$ or $K(\theta)$] when the silt loam soil was amended with the lignin-based hydrogel. Figure 7a depicts the estimated volumetric water content plotted against the hydraulic conductivity; while Figure 7b depicts the estimated soil water pressure head plotted against the hydraulic conductivity for the three soil-hydrogel treatments. While running simulations using Wind's method, some values for K were rejected. Due to the high uncertainty of tensiometer readings at low gradients, i.e., close to 0, all K values obtained from gradients < 0.2 cm were rejected in this study [41,47]. Three replicates of each treatment were obtained and averaged for volumetric water content, soil water pressure head, and hydraulic conductivity. From Figure 7a, hydraulic conductivity decreased with a decrease in volumetric water content in all treatments. This decrease is due to soil becoming increasingly unsaturated as less pore spaces fill with water, thus flow paths become tortuous and drag forces between the soil particles and the water increase [48]. The textural properties of the silt loam soil used in this experiment will also affect the K because soil texture is less variable and will dominantly affect K in the unsaturated range [49]. Noticeably, K in the 0.1 and 0.3% (w/w) treatments was increased along the entire curve in comparison to the control treatment. Similarly, from Figure 7b, K decreased drastically by three orders of magnitude from -80 cm to -750 cm, which is typical because soil becomes unsaturated regardless of hydrogel treatment. While we see a clear increase in K as soil water content decreases, the difference between the three treatments is not apparent when soil water pressure is plotted against K.

A hypothesized reason that the application of the lignin-hydrogel at 0.1 and 0.3% (w/w) increased K is that, as soil moves from the saturated phase to the unsaturated phase, the swollen hydrogel particles create smaller drainage pores. The hydrogel, which retains bound water for a period gradually releases the bound water as soil dries and creates a wider path/increases the cross sectional area for the movement of water, thus increasing K. There are limited studies in literature that investigate the effects of hydrogels, especially lignin-based hydrogels, on unsaturated hydraulic conductivity compared to saturated hydraulic conductivity. The few studies that determined the unsaturated hydraulic conductivity of soils after hydrogel amendment used various synthetic-based hydrogels [8,21,22,25]. Al-Darby [8] estimated K using a numerical method, i.e., using the van Genuchten hydraulic function. Al-Darby [8] observed a 63, 92, and 99% decrease in K corresponding to application rates of 0.2, 0.4, and 0.8% (w/w) of hydrogel. Liao et al. [26] observed a decrease in K from 85.5 to 94.1% on day 0, 75.1 to 82.9% on day 30, and 65 to 76.2% on day 50 when synthetic polyacrylamide and acrylic acid-based hydrogels were applied to sandy loam soil. Mohawesh & Durner [22] measured the unsaturated hydraulic conductivity of sandy soil after applying bentonite, biochar, and hydrogel to the soil. The hydrogel was amended at rates of 0, 0.1, 0.25, and 0.5% (w/w). The authors reported that all soil amendments decreased unsaturated hydraulic conductivity in the wet range, i.e., saturated and near saturated conditions. They attributed the decrease to an increase in tortuosity and particle packing. Smagin et al. [21] observed that, at high matric potentials, i.e., <10 to 15 kPa, K was reduced up to 2–3 times at concentrations ranging from

0.01–0.05% (*w*/*w*) and a reduced 10–50 times at 0.1–0.2% concentration; however, at low matric potential, i.e., 200 to 3030 kPa, *K* increased with an increase in application rate.
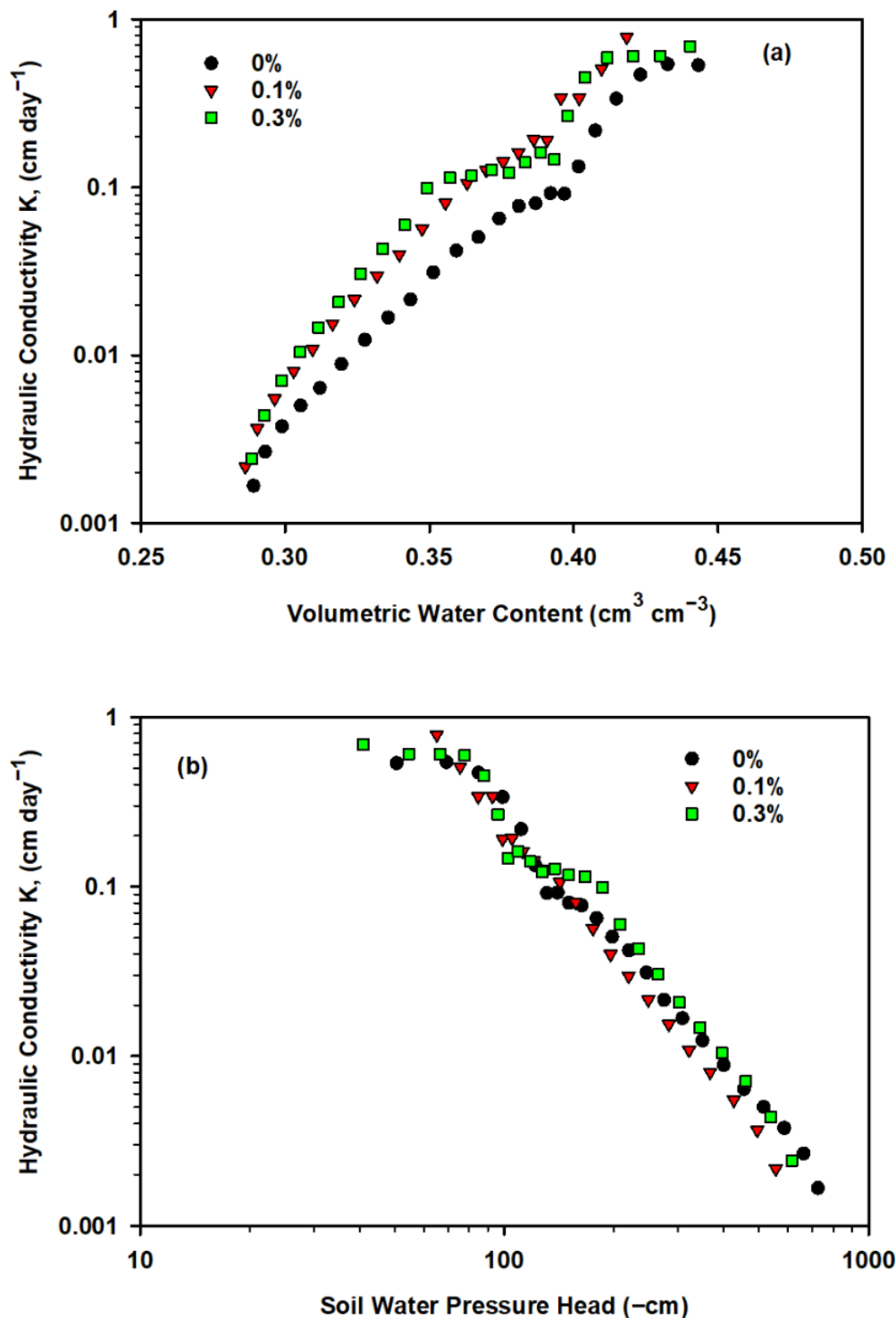

Figure 7. Hydraulic conductivity functions for the silt loam soil when amended with 0, 0.1, and 0.3% (*w*/*w*) lignin-based hydrogel determined with the evaporation method; (**a**) volumetric water content against hydraulic conductivity *K*(*θ*), and (**b**) soil water pressure head against hydraulic conductivity *K*(*h*).

Our results contrast the findings of Al-Darby [8] and Liao et al. [26] because they report decreases in *K*. It is possible that the different soil types used in Al-Darby [8] and

Liao et al. [26] were the reason *K* decreased as opposed to increased. The two studies used mostly sandy soils, which have large pores and drain faster compared to fine-textured soils like the silt loam soil [49] used in our study; thus, the presence of the hydrogels in their sandy soils tended to increase tortuosity and reduce *K* [22]. Our results, however, agree with Smagin et al. [21], who reported a 10–20 times increase in *K* in the unsaturated regions. The authors attributed the increase in *K* to a change (increase) in the pore space of the sandy soil used in their study because of the hydrogels applied.

3.4. Effect of Lignin-Based Hydrogel on Change in Total Water Storage in the Soil

The total soil water storage was estimated for each treatment by first calculating volumetric water contents at the two tensiometer elevations ($\theta 1.5$ and $\theta 4.5$) at each time step. The two volumetric water contents were then added, and the result was multiplied by the depth between them, i.e., 3 cm, to obtain the total soil water storage. The change in total soil water storage over time is shown in Figure 8. At the start of evaporation, the amount of water stored in all treatments was approximately 2.6 cm. As evaporation continued, the 0.1 and 0.3% treatments tended to store more water than the control treatment, especially after 24 h ($p < 0.005$) and, to a lesser extent, after 48 h ($p = 0.059$). At the end of the evaporation experiment, the total soil water storage was similar in all treatments ($p = 0.23$) at 1.51 cm for the control treatment, 1.58 cm for the 0.1% (*w*/*w*) treatment, and 1.55 cm for the 0.3% (*w*/*w*) treatment. Overall, the effect of the concentration of the hydrogel on total soil water storage was not significant at the beginning of the evaporation experiment; however, we hypothesize that the lignin-based hydrogel influenced the total soil water storage during stage two of evaporation. During stage one, evaporation was influenced by environmental factors, such as atmospheric temperature, wind speed, and humidity [50]. During stage two, evaporation shifted from the surface water to the sub-surface water, resulting in the formation of a dry surface layer [51]. Hydrogels can intercept the movement of water upwards because some water will be absorbed and kept at the level just beneath the soil surface, thus increasing total soil water storage.
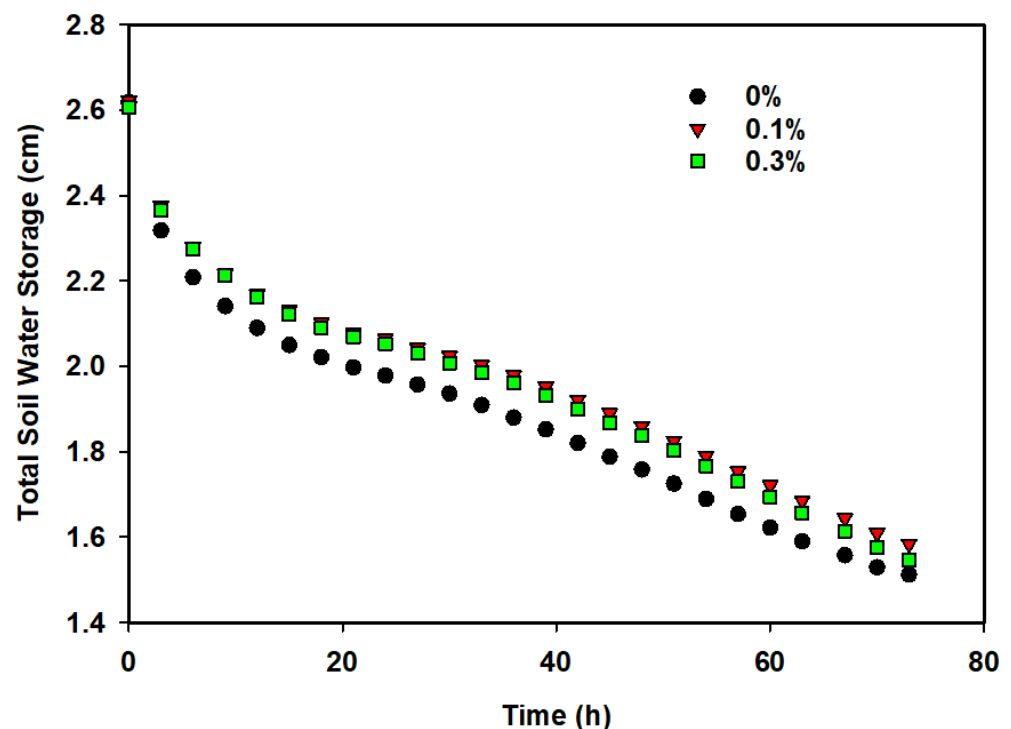

Figure 8. Change in total soil water storage in the 0, 0.1, and 0.3% (*w*/*w*) lignin-based hydrogel treatments after 73 h of evaporation.

4. Conclusions

This study resolved the impacts of three application rates of lignin-based hydrogel on the saturated hydraulic conductivity, near saturated hydraulic conductivity, unsaturated hydraulic conductivity, and soil water storage in silt loam soil. Our main hypothesis of a decrease in hydraulic conductivity was supported, but only in the saturated and near-saturation zones ($-10 \text{ cm} < h < 0 \text{ cm}$) of soil water pressure head. Saturated hydraulic conductivity was statistically significantly decreased with the application of hydrogel at 0.1 and 0.3% (w/w) compared to the control treatment. In the near-saturation zone ($-10 \text{ cm} < h < 0 \text{ cm}$), the application of 0.3% (w/w) lignin-based hydrogel significantly decreased hydraulic conductivity. Noticeably, unsaturated hydraulic conductivity (K) in the 0.1 and 0.3% (w/w) treatments increased along the $K(\theta)$ curve in the unsaturated zone (750 cm < h < 10 cm) in comparison to the control treatment. A clear trend was not seen in the $K(h)$ curve because the three treatments were indistinguishable. Our results also suggest that the 0.1 and 0.3% treatments tended to store more water than the control treatment, especially after 24 h of evaporation. Future studies should be conducted to test the impact of lignin-based hydrogel on other textures of soil. Regardless, the implication of this study is that lignin-based hydrogel can be used to retain water in saturated silt loam soils and that bound water could be useful for improving the flow of soil water in unsaturated states, thereby reducing the water stress of plants that require less energy to absorb water.

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