

Adsorption Isotherm Parameters of Atrazine and Metolachlor with Pecan Shell-based Activated Carbons

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Abstract

In this study, pecan shell-based activated carbons (PSACs) were examined for their effectiveness in adsorbing atrazine and metolachlor. Pecan shells were pyrolyzed under different temperatures and activated by either physical (steam, CO₂), chemical (H₃PO₄), or a combination of chemical (NaHCO₃, KOH) followed by physical (steam) activation. The H₃PO₄ activated carbon exhibited the highest yield, surface area, and bulk density. This study shows that PSACs can effectively adsorb pesticides such as atrazine and metolachlor; and PSACs can be modified to address the specific types of contaminants in the groundwater.

Keywords

Pecan Shell; Activated Carbon; Atrazine; Metolachlor; Freundlich Isotherm

Introduction

Groundwater is a major source of drinking water in rural areas; and the quality of groundwater resources has drawn public interest worldwide (Hua et al., 2012). Contamination of water by xenobiotic compounds such as pesticides (e.g., atrazine and metolachlor), metals (e.g., Cu²⁺, Zn²⁺, and Pb²⁺), NO₃/NO₂, and biological agents (pathogens) presents a serious environmental problem and poses serious public health concerns (Harmon and Wiley, 2012). Additionally, organic compounds in drinking water such as pesticides can cause various health effects that include liver damage and cancer (Giden et al., 2010; Srivastava and Mishra, 2009; Rusiecki et al., 2009; Kesavachandran et al., 2009). If presenting in drinking water, metals are toxic to humans even at very low levels (Pizarro et al., 2001; Nurchi, 2008; Kavcar et al., 2009).

Accumulation and/or transformation in the aquatic ecosystems of xenobiotics and their biomagnifications constitute a real risk to human health, wildlife, and the environment. A number of studies published on the ecological damage in distinct aquatic ecosystems were linked to the widespread use of agricultural pesticides worldwide (Harmon and Wiley, 2012; Debenest et al., 2010). The risks are even more serious in rural areas where a significant amount of the population receives drinking water from private wells that are non-regulated under the safe drinking water act (USEPA, 2004).

Technologies capable of reducing the concentration of these organic chemicals from drinking water are vitally important for ensuring groundwater safe for drinking water purposes. The most widely used methods for removing toxic metals from drinking water and wastewater include ion exchange, chemical precipitation, reverse osmosis, evaporation, membrane filtration, and adsorption. Most of these methods suffer from some drawbacks, such as high capital for establishment and operational costs, or the disposal of the residual metal sludge; and they

are not suitable for small-scale application (Gupta et al., 2012). Consequently, many research studies have been devoted to the development of low cost activated carbon from cheaper and readily available materials (i.e., agricultural residue, shells, etc.) as alternatives to the existing water treatment methods (Gupta et al., 2009; Mahvi, 2008).

In this study, pecan shell-based activated carbons (PSACs) were examined for their effectiveness in adsorbing atrazine and metolachlor from water. Activated carbon is one of the most cost-effective methods for water treatment (Gupta et al., 2009; Mahvi et al., 2008; Demirbas, 2008; Li et al., 2010). Since pecan shells are low cost and are the underutilized agricultural by-products of the nut industry, the use of them as precursors could provide a sustainable solution to agricultural waste disposal while providing consumers with an inexpensive and effective technology to purify their drinking water. The production of pecans in 2010 was 133,221 Mg, accounting to 48,262 Mg as nutshell byproduct (USDA, 2012). Agricultural waste, such as pecan shells, wastes can serve as feedstocks in the manufacture of activated carbon that can be used for drinking water and wastewater purification. Hence, pecan product could be an excellent precursor for value-added activated carbon for drinking water purification through selective adsorption of organic and inorganic contaminants.

Recently, our research has demonstrated the viability of using pecan shell as precursor for activated carbons. Using three methods, atrazine and metolachlor adsorption by pyrolyzed pecan shells under different temperatures and activated by either physical (steam, CO₂), chemical (H₃PO₄) and basic (NaNO₃ and KOH) as well as a combination of physical and chemical activation was investigated. The physicochemical and surface properties of these activated carbons were determined in comparison to the commercially available activated carbon (Niandou et al., 2013). We further demonstrated the viability of these PSACs by optimizing their physicochemical characteristics with respect to their adsorptive performances against adsorption of cationic, anionic and pesticides contaminants.

In the current study, we investigated the adsorption behavior of the previously optimized PSACs by using conventional adsorption isotherms such as the Freundlich isotherms and determined the adsorption performances of PSACs for organic compounds (atrazine and metolachlor) against commercial activated carbon (F300). Benefits of these results include the development of inexpensive sorption media for prototype filters that can be used for well water purification.

Materials and Methods

Pecan Shell-Based Granular Activated Carbon Preparation

Pecan shell based activated carbons were prepared as described by Niandou et al. (2013) (Table 1). Raw pecan shells were crushed and sieved using a 1.70-2.00 mm (U.S. standard sieve). For physical activation, pecan shells were pyrolyzed at 700°C for 1 h using a Lindberg box furnace under a continuous stream of N₂ followed by injection of either steam or CO₂ for activation. Activation was performed for 5 h at 800°C. In case of CO₂ activation, a mixture of 75% CO₂ and 25% N₂ (v/v) was used.

TABLE 1. SPECIFICATIONS FOR PREPARATION AND ACTIVATION CONDITIONS OF PECAN SHELL-BASED ACTIVATED CARBONS

Activation Type	Physical		Chemical	Hybrid		Reference
	Steam	75%CO ₂	H ₃ PO ₄	NaHCO ₃	KOH	F300
Carbon Acronym	S8005	CO2N8005	PA504501	BS508003	KOH158003	F300
Ratio‡	NA	NA	50	50	15	NA
Atemp, °C	800	800	450	800	800	-
Atime, h	5	5	1	3	3	-

Atemp, Activation temperature, Atime, Activation time

‡ The ratio of the solution mass to the shell mass

For chemical activation, pecan shells were presoaked in 50% H₃PO₄ (v/v) for 2 h followed by drying at 170°C under a constant stream of N₂ for 30 min. Activation was performed at 450°C for 1 h under a stream of compressed air (80/20%, N₂/O₂) followed by overnight cooling in presence of constant stream of N₂. The acid activated carbon was sieved (1.70-2.00 mm) and rinsed with distilled water until the neutral pH values were observed.

For the physical and chemical (hybrid) activation, ground pecan shells were sieved as mentioned earlier and soaked in either 50% NaHCO₃ or 15% KOH (w/w) for 2 h. The soaked shells were pyrolyzed at 700°C for 2 h and steam activated at 800°C for 3 h. The activated carbons were cooled overnight under a constant stream of N₂. The activated carbons were washed in boiling water and rinsed with distilled water to neutral pH values. The washed activated carbons were later dried at 110°C for at least 3 h.

Physicochemical and Surface Properties of Pecan Shell-Based Activated Carbons

Bulk density was measured using a 25 mL cylinder filled with 0.6 to 2.0 mm (U.S. standard sieve) granular-activated carbon pre-dried at 80°C overnight. Bulk density was calculated as the ratio of weight of dry mass to the volume of packed dry material as described by Bansode et al. (2003). The pH of carbons were measured by preparing a 1% (w/w) suspensions of activated carbons in deionized water and heating the slurries to approximately 90°C. The suspensions were stirred for 20 min and were allowed to cool to room temperature. The pH of the suspensions was measured with a Corning pH 10 portable pH meter (Acton, MA). The ash content of activated carbon was measured by holding 2 g of activated carbon in preweighed crucible at 760°C in a muffle furnace (Fisher Scientific, USA) for at least 6 h. The percent ash content was measured as a percent ratio of remaining solids mass to original carbon mass.

Surface Area Measurement

The Nova 2200 (Quantachrome Instruments, Boyton Beach, FL) was used for surface area measurement of carbons according to the method described by Niandou et al. (2013). The surface area analysis was conducted by using the automated software for acquisition of Brunauer-Emmett-Teller surface area and pore size distribution. Surface areas of the carbons were calculated using t-plots while surface volume (micro-, meso-, and macroporous volumes) was calculated using Barrett, Joyner and Halenda model (Bansode et al., 2003; Johns et al., 1999; Toles et al., 1997).

Surface Charge And Properties

The surface charge was measured by acid-base titration (Zelazny et al., 1996). Carbon slurries were prepared by adding 0.5 g of carbon to 50 mL of 0.1 mol L⁻¹ NaOH solution (1% w/v). The slurries were stirred at 150-200 rpm for 24 h followed by filtration of the supernatant using a 0.45-µm Teflon filters. Fifteen mL of 0.1 mol L⁻¹ HCl was added to 10 mL of filtrate and titrated against 0.1 mol L⁻¹ NaOH using a Titrand system (Metrohm Ltd, Switzerland) operated by computer-controlled software. In case of hybrid activated carbons, slurries were made using 50 mL of 0.1 mol L⁻¹ HCl and filtrates were directly titrated against 0.1 mol L⁻¹ NaOH. The difference in number of moles of NaOH required to neutralize a blank sample required by the carbon slurries was used as an estimate of moles of surface sites (H⁺) per gram of carbon.

Adsorption Isotherms Of Pecan Shell-Based Activated Carbons (Psacs)

1) Atrazine And Metolachlor Adsorption Isotherms of Psacs

Atrazine and metolachlor solutions at a concentration of 25 and 40 mg L⁻¹, respectively were prepared as stock solutions. Activated carbons at a dosage ranging from 0, 0.05, 0.1, 0.2, 0.5, 0.75, 1.0 and 1.5 g were mixed in 50 mL each of the organic solution and stirred at a constant speed of 500 rpm for 24 h. The residual organic solutions were filtered using 0.45 µm Teflon filters and analyzed for remaining atrazine and metolachlor levels in filtrate using a HPLC as previously described by Niandou et al. (2013).

2) Freundlich Adsorption Isotherms

Adsorption isotherms expressed as Freundlich isotherm constants were used for modeling the adsorptive properties of activated carbons. Adsorption isotherms were based on the concentration of herbicides (atrazine and metolachlor) in aqueous phases at equilibrium. The linearized form of the Freundlich model [1] is represented as:

$$\text{Log}(x/m) = \text{Log}k + \frac{1}{n} \text{Log} C_e$$

Where, x = amount of contaminant adsorbed, m = mass of carbon (g), x/m = concentration of contaminant adsorbed per carbon dosage, C_e = equilibrium concentration of contaminant in solution, K and $1/n$ were

Freundlich isotherms constants.

Pesticides Fixed-Bed Column Test

For atrazine and metolachlor, a fixed-bed column with 1.0 cm height and 0.7 cm diameter was used for breakthrough curve determination. The contaminant flow rate, effluent sampling time, and experimental set-up were the same as described for copper, zinc and nitrates. Atrazine and metolachlor were first dissolved in pure methanol/acetone. Deionized water was then spiked with a known concentration of these two compounds to prepare desired feed solutions (10ppm). Samples with these concentrations of atrazine and metolachlor were pumped into the above-described GAC columns. Effluent samples were collected every 1 hr over the 24 hours run for HPLC analysis. The pH of atrazine and metolachlor were maintained at natural pH (Chen and Wang, 2000).

Figure Legends

In the figures and plots for the data, Table 2 summarizes the symbols in the legend for the treatments.

TABLE 2. SUMMARY OF SYMBOLS REPRESENTING THE TREATMENT METHODS

Treatment Identifier	Active Carbon Type	Symbol used in Figure
BS508003	NaHCO ₃ activated carbon	Diamonds
S8005	steam activated carbon	Closed circle
PA504501	H ₃ PO ₄ activated carbon	Open circle
CO28005	CO ₂ activated carbon	Closed square
KOH158003	KOH activated carbon	Open square
F300	F300 reference carbon	Triangle

Statistical Analysis

General linear model was used to analyze all experimental data using SAS (SAS Institute, Cary, NC, 2003). The ANOVA test was used to detect the significant effects by multiple comparisons between experimental and commercial carbons using Tukey's HSD (honestly significant difference) post-hoc analysis at p=0.05.

Results and Discussion

Physicochemical and Surface Properties of the Best Pecan Shell-Based Activated Carbon

The physicochemical properties and surface properties of experimental activated carbons and the commercially activated carbon are presented in Table 3.

TABLE 3. PROPERTIES OF PECAN-SHELL BASED CARBONS ACTIVATED BY BOTH PHYSICAL AND CHEMICAL ACTIVATION.

Activation Type	Physical		Chemical	Hybrid		Reference
	Steam	75%CO ₂	H ₃ PO ₄	NaHCO ₃	KOH	F300
Carbon Acronym	S8005	CO2N8005	PA504501	BS508003	KOH158003	F300
Mass Yield, %	11.5±2.1	23.8±1.1	40.0±4.7	21.6±3.4	32.4±0.9	-
Bulk Density, kg m ⁻³	407.0±116.0*	561.5±17.8	600.5±25.5	414.8±10.2*	307.4±0.8	610.3±10.9
Ash Content, %	8.74±0.32*	7.25±0.11	5.50±0.02*	10.79±0.02*	8.89±0.10*	2.32±0.33
Attrition, %	8.44±0.07*	6.39±0.35	6.71±0.07	7.43±0.08*	8.71±0.23*	5.96±0.72
Mositure Content, %	0.40±0.0*	0.30±0.0	0.10±0.0*	0.39±0.0*	0.30±0.0	0.30±0.0
pH	10.18±0.10	7.33±0.42*	5.31±0.11*	9.97±0.07	9.52±0.12	10.10±0.12
TSA, m ² g ⁻¹	794.8±42.3	516.8±115.8	1057.8±222.1	752.6±111.0	756.9±4.3	740.7±23.0
MA, m ² g ⁻¹	767.0±40.3	472.9±109.9	934.1±144.5	512.9±32.4	688.8±6.7	721.8±68.1
MMA, m ² g ⁻¹	27.8±2.0	44.0±6.0	125.0±83.5	231.5±90.7	68.2±2.4	43.8±24.8
MV, m ² g ⁻¹	0.38±0.0	0.24±0.04	0.47±0.08	0.30±0.08	0.34±0.00	0.37±0.03
Surface Charge, mmol H ⁺ eq g ⁻¹ C	0.44±0.02	0.21±0.00	0.81±0.11*	0.64±0.01*	0.63±0.00*	0.18±0.02

† TSA, total surface area; MA, microporous area; MMA, meso-microporous area; MV, microporous volume.

* Significantly different from F300 reference carbon at p < 0.05 according to Tukey's HSD range test.

Mass Yield

Phosphoric acid activated PSACs (PA504501) showed the highest mass yield (40.0 ± 4.7) among all experimental carbons. Steam activated carbon (S8005) had the lowest mass yield (11.5 ± 2.1). The mass yields were 24, 22 and 32% for CO_2 , NaHCO_3 and KOH-activated carbons, respectively.

Bulk Density

Bulk density of all PSAC exhibited a variation in their bulk density values depending on the type of activation method, the nature of activation agent and the conditions of activation. The highest bulk density among the experimental carbons was observed in H_3PO_4 -based activated carbon probably due to the low burn-off and extensive microporosity of this carbon. In contrast, KOH-activated carbon had the lowest bulk density among all activated carbon ($307.4 \pm 0.8 \text{ kg m}^{-3}$). This may be attributed to the type of chemical used as activating agent and the effect of an additional physical activation step that causes an increase in burn-off. According to the (USEPA, 1999), bulk density is an important characteristic of carbon that influences the design of the adsorption column and affects the cost of the adsorption process. It also plays a role in the regeneration process since a higher density will require less frequent regeneration due to its high holding capacity of adsorbate (Clements, 2004).

Attrition

Another important property determined in this study is the percent attrition loss of PSAC. Attrition measures the mechanical strength of activated carbon. It is a parameter of concern during the transportation, handling and regeneration of carbon. The lowest percent attrition loss was observed with F300 (6.0%) followed by CO_2 -based activated carbon (6.4%). On the other hand, the highest attrition value was observed in KOH-activated carbon (8.7%). All PSAC activated carbon had attrition values of less than 10%.

Ash Content

Ash content indicates the amount of inorganic impurities in the activated carbon. Activated carbons with low ash contents are favorable (Guo and Lua et al., 1998). Commercial activated carbons from bituminous and lignin sources have ash contents in the range of 6-8% (Daifullah et al., 2004). Overall, PSAC exhibited higher ash content than the commercial reference. This difference is attributed to the mineral content of the precursors. Sodium bicarbonate (BS508003) had the highest ash content (10.8%) while PA504501 had the lowest ash content (5.5%). The ash content of PSAC produced under different activation methods suggests that activating agents such as NaHCO_3 and KOH were major contributors to the final ash content of these test carbons.

Moisture Content and Ph

Moisture content and pH of the carbon are variables that can be easily altered during the final steps of carbon production. All PSAC, except H_3PO_4 activated carbon, displayed basic pH values in the general range of the commercial reference carbon. Acid activated PSAC also tended to contain less moisture than the reference carbon.

Surface Area

Physical activation of pecan shells with CO_2 activated carbon produced GAC with relatively lower surface area. The remaining PSACs showed slightly higher surface area than the reference carbon. The observed difference in surface area among the carbon investigated is influenced by the nature of the activating agent, the pyrolysis temperature, and the type of activation (Mattson and Mark, 1971). Mackay and Roberts (1982) studied the lignocellulosic materials yield chars of similar microporosity. Furthermore, large molecules like CO_2 are less efficient in drilling internal surface area networks than small molecules like H_2O used in steam activation. Another fundamental difference between physical and chemical activation that may explain the observed difference is that physical activation relies on diffusion of gases (CO_2 or steam) through the carbon matrix to drill, deepen and volatilize impurities. In chemical activation, the chemical is introduced into the precursor, where it produces physical and chemical changes that modify the thermal degradation process (Rodriguez –Reinoso and Molina-Sabio, 1992).

The chemicals used in this study were H_3PO_4 , NaHCO_3 and KOH. Even though H_3PO_4 activation was carried out

at lower temperatures and hybrid activation was carried out at higher temperatures, the surface areas in both types of carbon were comparable with H_3PO_4 activated carbon having the highest surface area of $1058 \text{ m}^2 \text{ g}^{-1}$, which is greater than physical activation. This is in agreement with literature reports that suggest that carbon produced at lower temperatures is likely to possess an extensive surface area and a well-developed microporosity (Girgis et al., 1994).

Surface Charge

Surface charge of activated carbon is one of the essential properties for the adsorption of targeted carbon. Theoretically, the larger the surface charge is, the higher the propensity can attract contaminants through π - π interactions, electrostatic attraction/repulsion and intermolecular hydrogen bonding (Qiu et al., 2009). The pore size distribution and surface chemistry data also revealed that all the PSAC had a higher surface charge than the commercial carbon. Phosphoric acid-activated carbon had 4.5-fold higher titrable surface charge when compared with commercial reference carbon (F300). Hybrid activation also showed significantly higher ($p < 0.05$) surface charge with respect to the reference carbon.

Overall, the method of activation had an effect on carbon properties of PSAC. Among the five carbon types, H_3PO_4 activated carbon exhibited the highest yield, surface area, bulk density, and greater negative surface charge. This carbon, however, possessed an acid pH while all other PSAC had alkaline pH.

Application of the Freundlich Model for Pecan Shell-Based Activated Carbon Adsorption Behavior

Freundlich isotherm constants are summarized in Table 4. Corresponding graphs of the Freundlich model are presented in Figures 1 and 2. On the Y-axis of these models, the $\log(x/m)$ values represented the relative adsorption performances of the activated carbon and the $\log(C_e)$ values represented the residual concentration of the adsorbate solutes in the treated test solution.

Both the K and $1/n$ values were calculated from the intercept and slope of the adsorption isotherms in Figures 1 and 2. The constant K indicates the adsorption capacity of the adsorbent and represents quantity adsorbed onto activated carbon for a unit equilibrium concentration (Tan et al., 2007). The slope $1/n$ is related to the adsorption intensity and a value of n in the range of 0 to 10 signifies favorable adsorption (Kang et al., 2013).

TABLE 4. FREUNDLICH ISOTHERM CONSTANTS FOR ATRAZINE AND METOLACHLOR

Pollutant	Carbon type	1/n	K	R ²
Atrazine, 25 mg L ⁻¹	BS50800	0.10	0.04	0.85
	S8005	0.13	0.05	0.73
	PA4501	0.30	0.02	0.96
	CO28005	0.24	0.01	0.72
	KOH158003	0.19	0.08	0.71
	F300	0.17	0.07	0.80
Metolachlor, 40 mg L ⁻¹	BS50800	0.10	0.03	0.57
	S8005	0.10	0.05	0.89
	PA4501	0.09	0.04	0.79
	CO28005	0.36	0.01	0.66
	KOH158003	0.11	0.07	0.83
	F300	0.11	0.07	0.65

Pesticides Adsorption Isotherms

Figures 1 and 2 show the isotherms for atrazine and metolachlor. The atrazine and metolachlor adsorption parameters, K and $1/n$ values are also presented in Table 4. For an effective adsorption system, high adsorption capacity (x/m) is needed. Thus, for a given equilibrium concentration, the larger the K and $1/n$ values are, the more effective the carbon for adsorption is (Jia et al., 2006). The large K and $1/n$ values indicate that atrazine and metolachlor adsorption by all test carbons appeared to fit the Freundlich isotherms well.

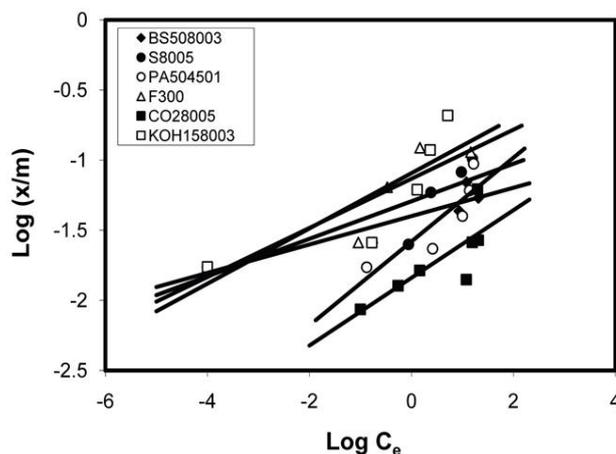


FIGURE 1. ADSORPTION ISOTHERMS OF ATRAZINE AT 25 MG L⁻¹ BY EXPERIMENTAL AND COMMERCIAL ACTIVATED CARBONS A) ATRAZINE AT 25 MG L⁻¹ THE Y AXIS REPRESENTS LOG X/M, AND THE X AXIS REPRESENTS LOG C_e. PECAN SHELL BASED ACTIVATED CARBONS AT DOSAGES OF 0, 0.1, 0.2, 0.5, 0.75, 1.0 AND 1.5 G WERE PLACED IN 50 ML OF 25 OF ATRAZINE SOLUTION FOR 24 H.

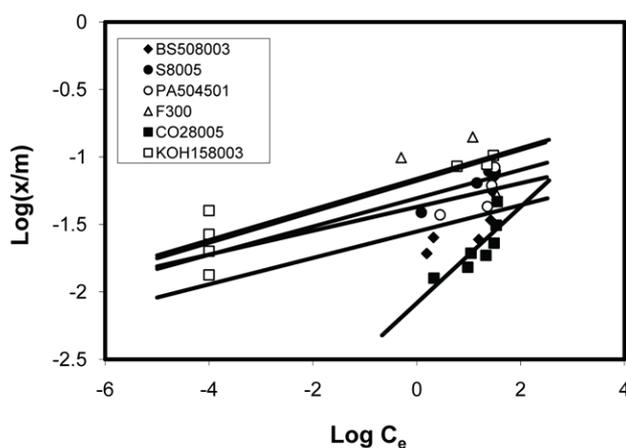


FIGURE 2. ADSORPTION ISOTHERMS OF METOLACHLOR AT 40 MG L⁻¹ BY EXPERIMENTAL AND COMMERCIAL ACTIVATED CARBONS. THE Y AXIS REPRESENTS LOG X/M, AND THE X AXIS REPRESENTS LOG C_e. PECAN SHELL BASED ACTIVATED CARBONS AT DOSAGES OF 0, 0.1, 0.2, 0.5, 0.75, 1.0 AND 1.5 G WERE PLACED IN 50 ML OF 40 MG L⁻¹ OF METOLACHLOR SOLUTION FOR 24 H.

The adsorption mechanism for organic compounds involves functional groups that usually come from hydrogen bond or proton transfer with particular functional groups such as C=O or R-OH groups on activated carbon surface. Therefore, the presence and lack of steric hindrance of a particular functional group is necessary for the adsorption process to occur. In addition, pore size distribution could play an important role in the adsorption of organics since the adsorption site and pore volume impact the diffusion of the organic compound molecule into the inner surface of activated carbon.

The analysis of these adsorption isotherms in Figures 1 and 2 and the Freundlich parameters in Table 3 show that KOH activated carbon possessed both the higher K value among all the test carbon and the greatest capacity for atrazine and metolachlor attraction among all test carbons. The lowest adsorption was achieved in CO₂-activated material, which was probably due to its surface area and charge. All experimental activated carbon displayed very good adsorption efficiency for both atrazine and metolachlor. It is possible that differences in atrazine and metolachlor adsorption could be related to the difference in surface oxides and hydroxides present on each of the activated carbon. These surface oxides and hydroxides favored hydrogen bonding among organic compounds and carbon surfaces (Welhouse and Blead, 1993).

Pesticides Column Tests

Experimental breakthrough curves at effluent concentration of 10 ppm for both atrazine and metolachlor showed that the test carbon required a much longer time to reach saturation than the 24-hour run conducted in this study (Figures 3 and 4). Despite reduction of the test column diameter from 1 cm to 0.7 cm, breakthrough for atrazine and

metolachlor remained difficult to reach, which suggested a much higher carbon affinity to these organic compounds. Phosphoric acid and steam activated carbon were the best performing carbon and showed almost 100% pesticide removal in the column study over a 24-hour run. Potassium hydroxide and F300 carbon also showed a large adsorption capacity/affinity for atrazine and metolachlor. The two least performing activated carbon were NaHCO_3 and CO_2 -based activated carbon because the removal of atrazine and metolachlor were halfway below their saturation time in 24 hours.

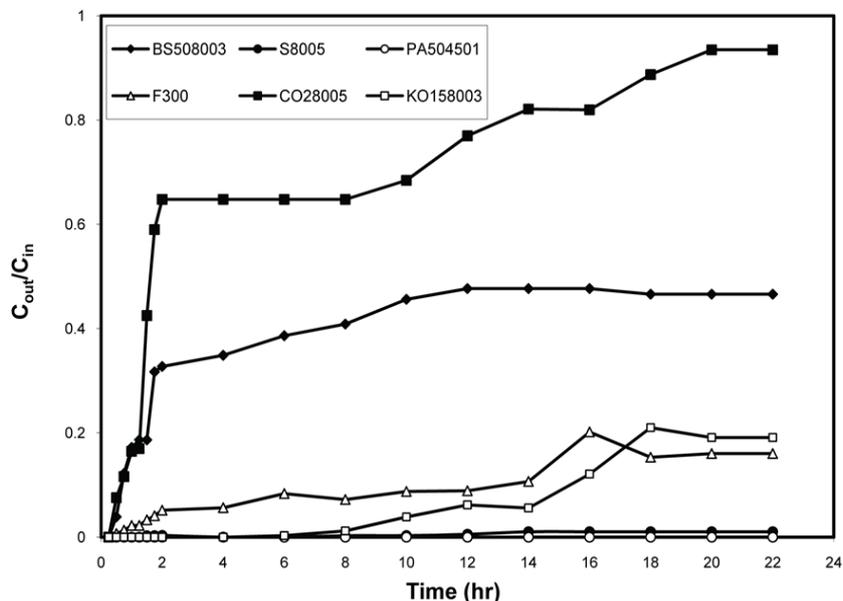


FIGURE 3. BREAKTHROUGH CURVES FOR ATRAZINE ADSORPTION RELATING TO EXPERIMENTAL AND COMMERCIAL ACTIVATED CARBONS.

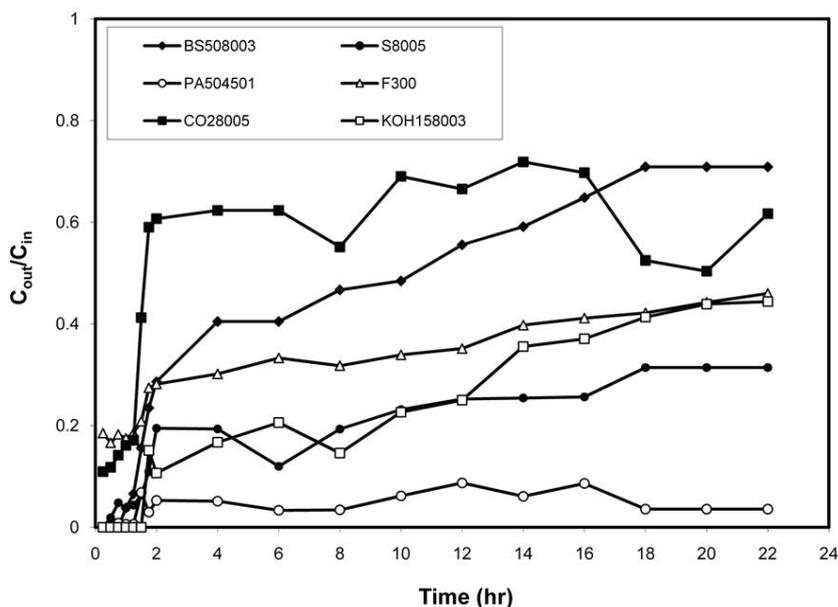


FIGURE 4. BREAKTHROUGH CURVES FOR METOLACHLOR ADSORPTION RELATING TO EXPERIMENTAL AND COMMERCIAL ACTIVATED CARBONS.

Conclusion

This study demonstrated the feasibility of developing PSAC that was effective in removing organic contaminants from groundwater. Optimization of carbon production through the use of specific activation procedures is critical in yielding PSAC with desirable physicochemical, surface, and adsorption properties. The latter are particularly affected by the type of activating agent, the level of activating agent, and the activation temperature.

Overall, the adsorption modeling suggests that adsorption of atrazine, and metolachlor by PSAC follows the Freundlich adsorption model. Data from adsorption studies show that PSACs are comparable or better than

commercial carbon (F-300 and USO₃) in terms of their ability to remove pesticides (atrazine and metolachlor) from water. The findings discussed in this study are significant since the activated carbons prepared from pecan shells have the potential to alleviate rural groundwater contamination. Therefore, pecan agricultural by-product-based activated carbon has the potential to compete with the existing water purification methods in their ability to remove water contaminants and in their cost effectiveness. The PSACs achieved better or equal performance to commercial activated carbon in removing water contaminants such as atrazine and metolachlor. In conclusion, the use of pecan shells to develop water filters will add value to the agricultural sector and has the potential to provide consumers with inexpensive means to purify their water.

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Research on Infiltration Spread in Soil of Drip Irrigation Technique for Grape Leaves at the Water Scarce Region of Vietnam

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Abstract

The technique of drip irrigation is a solution of water saving for crops in the scarce region. Water is supplied on the soil surface directly, continuously and regularly by drippers and then it infiltrates into the cultivated soil layer to ensure that plants will grow and develop well. During the experimental process of researching on soil moisture of drip irrigation technique to determine the suitable irrigation schedule for Grape Leaves at the water scarce region, the authors carried out the experiment and observed infiltration spread. Based on calculated and observed results, the authors have proposed correlation of parameters as follows: infiltration depth, average radius of wetting front on horizontal direction, irrigation water amount versus time, velocity of horizontal (v_r) and vertical (v_z) permeability of drip irrigation technique. The correlation coefficients of parameters are high (R^2 from 0.906 to 0.9899) and conformable to research on soil moisture dynamic in order to determine the suitable irrigation schedule for Grape leaves in particular and for terrestrial plants (with short roots) in general at the water scarce region of the South Central region of Vietnam.

Keywords

Correlation; Drip Irrigation; Infiltration; Irrigation Schedule; Permeable Velocity

Introduction

The experimental analysis results of water infiltration spread in soil (H. Darcy, 1885), (Green and Anpt, 1911), (Kostiakov, 1932), (Phillipe, 1957)... have showed that the infiltration process was divided into two phases: unstable infiltration (absorbent) and stable one. Water spread in soil depends on soil type, structures and irrigation techniques. For different types of cultivated land, permeability and moisture reserves in soil is different, so the watering time will be varied depending on each soil type [1-3].

Irrigation methods and techniques largely influence the water infiltration process into soil. When soil is irrigated according to traditional methods, water will evenly saturate and spread from the ground to the bottom. Thus, at the location situated between trees, this water will be wasted, sometimes enable weeds to grow quickly and cause negative effects on crops. Regarding the drip irrigation technique, water is provided with very reasonable amount from a point on the ground through irrigation equipment, then spreads out around and bottom, with just enough water volume supplied to moisten the active roots, soil will reach optimum moisture, without causing waste water and saturation excess. For each plant kind, the active roots have occupied the different volumes. The development of these active roots is very important, when soil is provided with adequate water and nutrients in a reasonable manner, the roots will absorb water, nutrients and air for plants to grow and develop well, creating high yield and quality product [4].

Previous studies have often focused on the aspect of crops irrigation schedule for each irrigation technique, but paid not much attention to soil moisture dynamic in the space of the active roots. Some scientists have studied soil water movement for the traditional irrigation method (flooding irrigation, ditch irrigation, strip irrigation etc.), but there are few simulations of drip irrigation technique especially in moisture dynamic (water is supplied from a point spread around). Thus, it has caused the shortage or excess water irrigation when the optimal moisture area is

larger or less than the active root space. That does not meet demands in agricultural production and reduce efficiency of water saving irrigation, especially for water scarce regions.

Binh Thuan and Ninh Thuan are two provinces in the South Central region of Vietnam with the harsh climate and natural conditions, where there is the lowest precipitation in the country and the unequal distribution by time (annual average is about 500-800mm). Features of water resources are scarceness, causing drought and severe water shortage for socioeconomic development, especially agriculture production. There are more than half a million ethnic minorities whose livelihoods depend on agricultural activities in this area. Due to difficult production conditions, most of the population is under the poverty and needs to be improved living standards [5].

This performed research is very necessary with the aim of establishing correlations between the parameters as follows: infiltration depth, average radius of wetting front on horizontal direction, irrigation water amount versus time, velocity of horizontal (v_r) and vertical (v_z) permeability of drip irrigation technique for researching on soil moisture dynamic in order to determine the suitable irrigation schedule for Grape leaves in particular and for terrestrial plants (with shallow roots) in general, and then it is applied into cultivating reality to avoid water wastage and get irrigation efficiency at the water scarce region of the South Central region of Vietnam.

Material and Methods

Objective

Researched objective was infiltration spread in soil of drip irrigation technique with irrigation frequencies as 2 days, 3 days and 4 days.

The experimental model was performed at the Grape leaves farm in Thuan Quy village, Ham Thuan Nam district, Binh Thuan province.

The mechanical and physical characteristics of soil have been tested in the laboratory of the Southern Institute of Water Resources Research.

Approachability and Methodology

(1) Approach reality and theory comprehensively, combine with selective inheritance from the scientific research results of infiltration in soil and water-saving irrigation technology for production [4];

(2) Approach structural components of the water utilization models as follows: source, transport, utilizing exploitation and application of advanced science and technology about: irrigation equipment, materials, structures, crops and modern computational software in order to analyse, select and design a experimental model at the field [2, 6];

(3) Take soil samples at various depths at the field. Analyse mechanical and physical characteristics of soil in the laboratory;

(4) Establish the experimental model, observe irrigation and infiltration spread development in soil following space (horizontal and vertical permeability) and time with irrigation frequencies as: 2 days, 3 days and 4 days. Periodically monitor infiltration spread with time step of 5 minutes/per time as: 1, 3, 5, 10, 15, 20, 25, 30,... to 200 (minutes) stop watering; then continue monitoring water spread in soil with time step as: 210, 240, 270, 300, 330 and 360 (minutes) stop observing [5, 7, 8];

(5) Establish recurrent correlations between variables: infiltration depth (z), average radius of wetting front on horizontal direction (r), irrigation water amount (w) and time (t), velocity of horizontal (v_r) and vertical (v_z) permeability according to under research objectives proposed.

(6) Collect observed data and analyze the experimental results by using Excel and SPSS16 program;

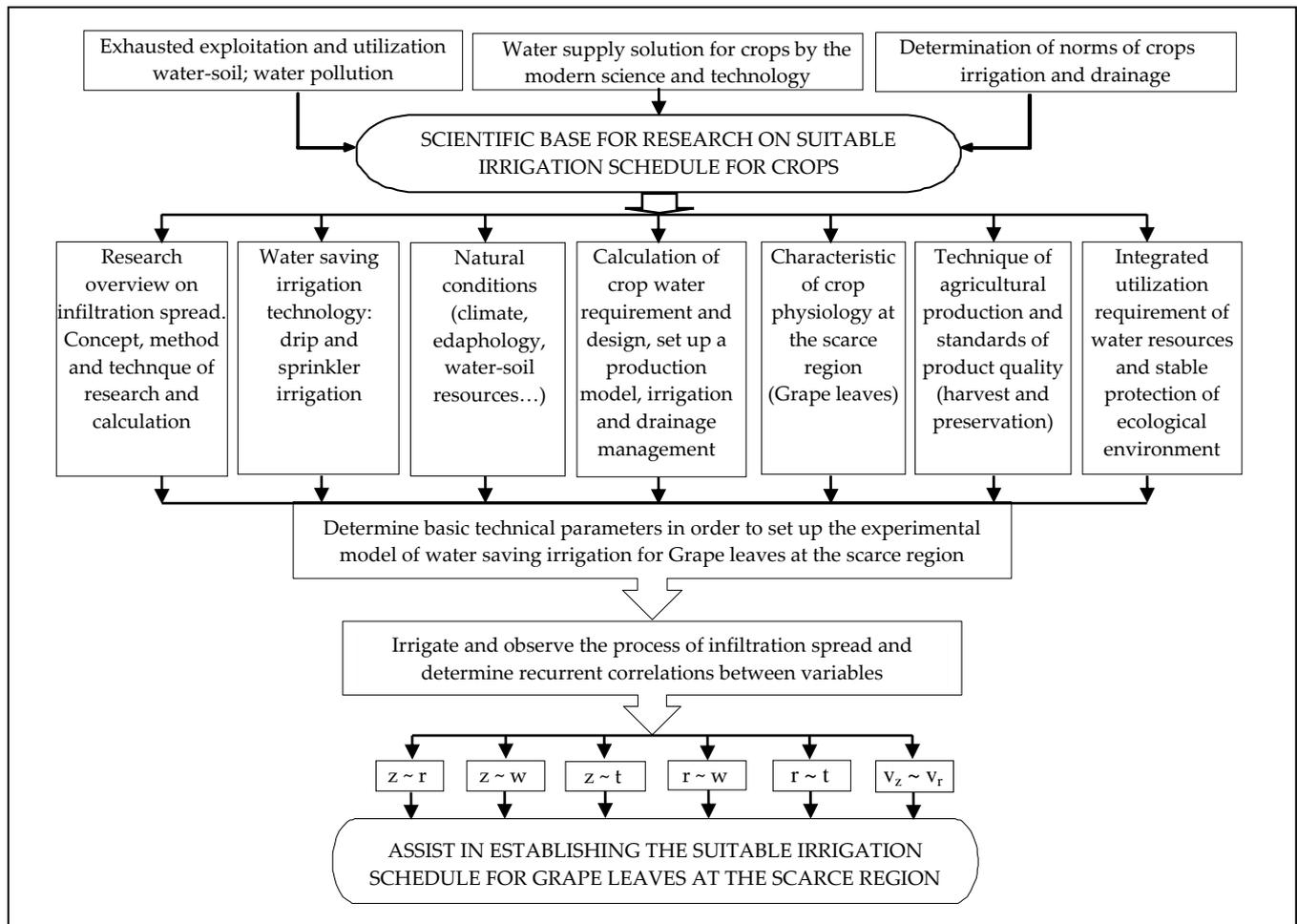


FIGURE 1. THE SKETCH OF RESEARCH APPROACHABILITY AND METHODOLOGY.

LEGENDS: Z: Infiltration depth (cm); R: Average radius of wetting front on horizontal direction (cm); W: Irrigation water amount (ml); T: Time (minute); Vr: Velocity of horizontal permeability (cm/minute); Vz: Velocity of vertical permeability (cm/minute).

Results and Discussion

The soil at the experimental model was fine sandy with high void ratio, so water particles have moved by their own gravity component larger than soil capillary force over themselves (refer with: Table 1).

TABLE 1. SOIL CHARACTERISTIC OF THE LAYERS FROM 0 TO 60cm

Soil layer (cm)	Grain size analysis					Physical characteristic					Description				
	Medium Sand (%)	Fine Sand (%)	Coarse Silt (%)	Fine Silt (%)	Clay (%)	Wet Density γ_w (g/cm ³)	Dry Density γ_d (g/cm ³)	Specific Gravity D	Saturation S (%)	Porosity n (%)		Void Ratio e _o			
0-20	0	4.30	47.60	41.50	1.70	0.40	0.50	4.00	1.60	1.56	2.65	8.86	40.99	0.69	Greyish brown fine sand
20-40	0	3.50	47.40	36.10	6.40	0.50	0.50	5.60	1.56	1.51	2.63	13.30	42.70	0.75	Greyish yellow fine sand
40-60	0	3.80	48.20	35.20	6.10	0.46	0.50	5.74	1.68	1.62	2.64	15.70	38.66	0.63	Greyish yellow fine sand

Grain size analysis with five types:

(1) Medium Sand with two grades: 2.0 - 0.85mm, 0.85 - 0.425mm; (2) Fine Sand with three grades: 0.425 - 0.25mm, 0.25 - 0.106mm, 0.106 - 0.075mm; (3) Coarse Silt with one grade: 0.075 - 0.01mm; (4) Fine Silt with one grade: 0.01 - 0.005mm; (5) Clay with one grade: < 0.005mm.

When water permeates the soil, wet soil block seemed hemispherical. In initial time, water spread very fast in a circular motion on the ground, velocity of horizontal permeability (v_r) was almost as fast as vertical one (v_z)

(permeate downward). During the next phase, velocity of horizontal permeability was smaller than that of vertical one. In the last phase, mostly water permeated downward and little horizontal. The infiltration spread development of each irrigation frequency in soil was listed as follows (refer with: Fig. 2 and Table 2):

Two-day irrigation frequency (IF2): With short irrigation one, soil moisture content was still high, so water trended towards the more horizontal permeability beside the vertical one (downward). In the first 20 minutes, the infiltration velocity of two directions as vertical and horizontal were rather evenly, $z_{20} = 10.55 - 10.7$ cm, $r_{20} = 10.05 - 10.25$ cm, $v_{z20} = 0.5$ cm/min, $v_{r20} = 0.46$ cm/min; then the horizontal permeability trended to slow down although the vertical one was still continuing with less reduction. After 145 minutes, the horizontal velocity decreased small, v_{r145} was about 0.02 cm/min and lower than vertical one $v_{z145} = 0.1$ cm/min. At the stop watering time (after 200 minutes) $z_{200} = 41 - 41.45$ cm, $r_{200} = 22.35 - 23$ cm, $v_{z200} = 0.08$ cm/min, $v_{r200} = 0.01$ cm/min, then water continued permeating to the depth of $z_{360} = 43.8 - 45.4$ cm and $r_{360} = 22.9 - 23.8$ cm;

Three-day irrigation frequency (IF3): Water regularly permeated around and downward due to reduced soil moisture more than that one of the IF2. In the first minute, the vertical infiltration velocity ($v_{z1} = 1.48$ cm/min) was faster than the horizontal one ($v_{r1} = 1.35$ cm/min); in the next 14 minutes, the infiltration velocity was faster than that one of the IF2 and rather evenly under two directions (vertical and horizontal); in the next 30 minutes, the infiltration velocity decreased compared with that one of the IF2, $z_{45} = 20.1 - 20.75$ cm, $r_{45} = 15.5 - 15.75$ cm, $v_{z45} = 0.23$ cm/min, $v_{r45} = 0.1$ cm/min; the next time, the horizontal velocity trended to slow down when vertical infiltration was still continuing with less reduction. After 125 minutes, the horizontal velocity decreased small, v_{r125} was about 0.02 cm/min and lower than vertical one $v_{z125} = 0.15$ cm/min. At the stop watering time (after 200 minutes), $z_{200} = 42.8 - 43.35$ cm, $r_{200} = 20.8 - 21.2$ cm, $v_{z200} = 0.08$ cm/min, $v_{r200} = 0.01$ cm/min, then water continued permeating to the depth of $z_{360} = 44.8 - 46.9$ cm and $r_{360} = 21.3 - 21.7$ cm. Compared with the same time step for experiment, the infiltration depth (vertical - z) in the IF3 was larger than that one of the IF2; on the contrary, the horizontal permeability (r) at the IF3 was smaller than that one in the IF2;

TABLE 2. OBSERVED RESULTS OF THE INFILTRATION PROCESS OF SOIL IN SIX EXPERIMENTAL TIMES.

Time (minute)	Two-day irrigation frequency					Three-day irrigation frequency					Four-day irrigation frequency				
	W ₂ (a) (ml)	Z ₂ (b) (cm)	R ₂ (c) (cm)	v _{z2} (d) (cm/min)	v _{r2} (e) (cm/min)	W ₃ (a) (ml)	Z ₃ (b) (cm)	R ₃ (c) (cm)	v _{z3} (d) (cm/min)	v _{r3} (e) (cm/min)	W ₄ (a) (ml)	Z ₄ (b) (cm)	R ₄ (c) (cm)	v _{z4} (d) (cm/min)	v _{r4} (e) (cm/min)
1	17.5	1.4	1.3	1.39	1.32	17.6	1.5	1.4	1.48	1.35	17.7	1.6	1.5	1.63	1.52
3	52.5	3.5	3.3	1.03	1.00	52.7	3.7	3.5	1.08	1.07	53.0	4.0	3.8	1.17	1.14
5	87.5	5.0	4.8	0.78	0.75	87.8	5.3	5.0	0.83	0.75	88.3	5.7	5.3	0.85	0.75
10	175.0	8.2	8.0	0.64	0.63	175.5	8.7	8.1	0.68	0.61	176.5	9.3	8.3	0.72	0.59
15	262.5	10.9	10.5	0.54	0.52	263.3	11.3	10.3	0.51	0.46	264.8	12.1	10.5	0.56	0.45
20	350.0	13.2	12.4	0.46	0.37	351.0	13.4	11.9	0.42	0.32	353.0	14.4	12.0	0.46	0.29
40	700.0	19.8	15.8	0.27	0.12	702.0	19.4	15.2	0.24	0.11	706.0	21.3	15.1	0.29	0.11
60	1050.0	24.1	17.7	0.19	0.09	1053.0	23.8	16.9	0.22	0.08	1059.0	25.8	16.7	0.20	0.07
80	1400.0	27.7	19.1	0.18	0.07	1404.0	27.9	18.3	0.20	0.06	1412.0	29.5	17.7	0.17	0.04
100	1750.0	31.0	20.3	0.15	0.05	1755.0	31.5	19.1	0.17	0.04	1765.0	32.7	18.4	0.16	0.03
120	2100.0	33.6	21.1	0.12	0.03	2106.0	34.7	19.7	0.15	0.03	2118.0	35.6	18.8	0.14	0.02
140	2450.0	35.8	21.7	0.11	0.03	2457.0	37.4	20.1	0.13	0.02	2471.0	38.4	19.2	0.14	0.02
160	2800.0	37.8	22.1	0.10	0.02	2808.0	39.7	20.5	0.10	0.02	2824.0	40.7	19.5	0.10	0.02
180	3150.0	39.7	22.5	0.08	0.02	3159.0	41.7	20.8	0.10	0.01	3177.0	42.7	19.7	0.10	0.01
200	3500.0	41.3	22.9	0.08	0.01	3510.0	43.4	21.0	0.08	0.01	3530.0	44.6	19.9	0.09	0.00
300	0.0	44.3	23.2	0.01	0.00	0.0	45.8	21.3	0.01	0.00	0.0	47.3	19.9	0.01	0.00
360	0.0	44.5	23.4	0.00	0.00	0.0	46.0	21.5	0.00	0.00	0.0	47.5	20.0	0.00	0.00

(a) means fixed water amount was supplied for crop according to irrigation frequencies in six experimental times.

(b), (c), (d), (e) mean average observed variables in six experimental times.

Four-day irrigation frequency (IF4): With repeated watering time was quite long, the soil of this frequency was dryer than that one in other frequencies (IF2 and IF3) due to evapotranspiration by the ground and through the leaves, soil moisture reduced much more than that one in the IF2 and IF3, so the infiltration velocity at this IF4 was

the largest, water trended to the more vertical permeability (downward) beside the horizontal one. In the first minute, the vertical infiltration velocity ($v_{z1} = 1.63 \text{ cm/min}$) was faster than the horizontal one ($v_{r1} = 1.52 \text{ cm/min}$); in the next 50 minutes, the infiltration velocity of two directions (vertical and horizontal) were rather evenly and faster than that one in other frequencies (IF2 and IF3); in the next time, until water supply cessation, the vertical velocity decreased nearly equivalent with it in the IF3, but larger than that one in the IF2; conversely, the horizontal velocity trended to slow down equivalent with it in the IF3, but smaller than that one in the IF2; starting from the minute of 195th until watering cessation, water only trended to vertical permeability and less horizontal one. At the stop watering time (after 200 minutes), $z_{200} = 44.3 - 44.9 \text{ cm}$, $r_{200} = 19.15 - 20.25 \text{ cm}$, $v_{z200} = 0.09 \text{ cm/min}$; $v_{r200} = 0$, water continued permeating to the depth of $z_{360} = 46.8 - 48 \text{ cm}$ and did not permeate horizontal any more. Compared with the same time step for experiment, the infiltration depth (vertical - z) in the IF4 was larger than that one of the IF2 and IF3; on the contrary, the horizontal permeability (r) at the IF4 was smaller than that one in the IF2 and IF3;

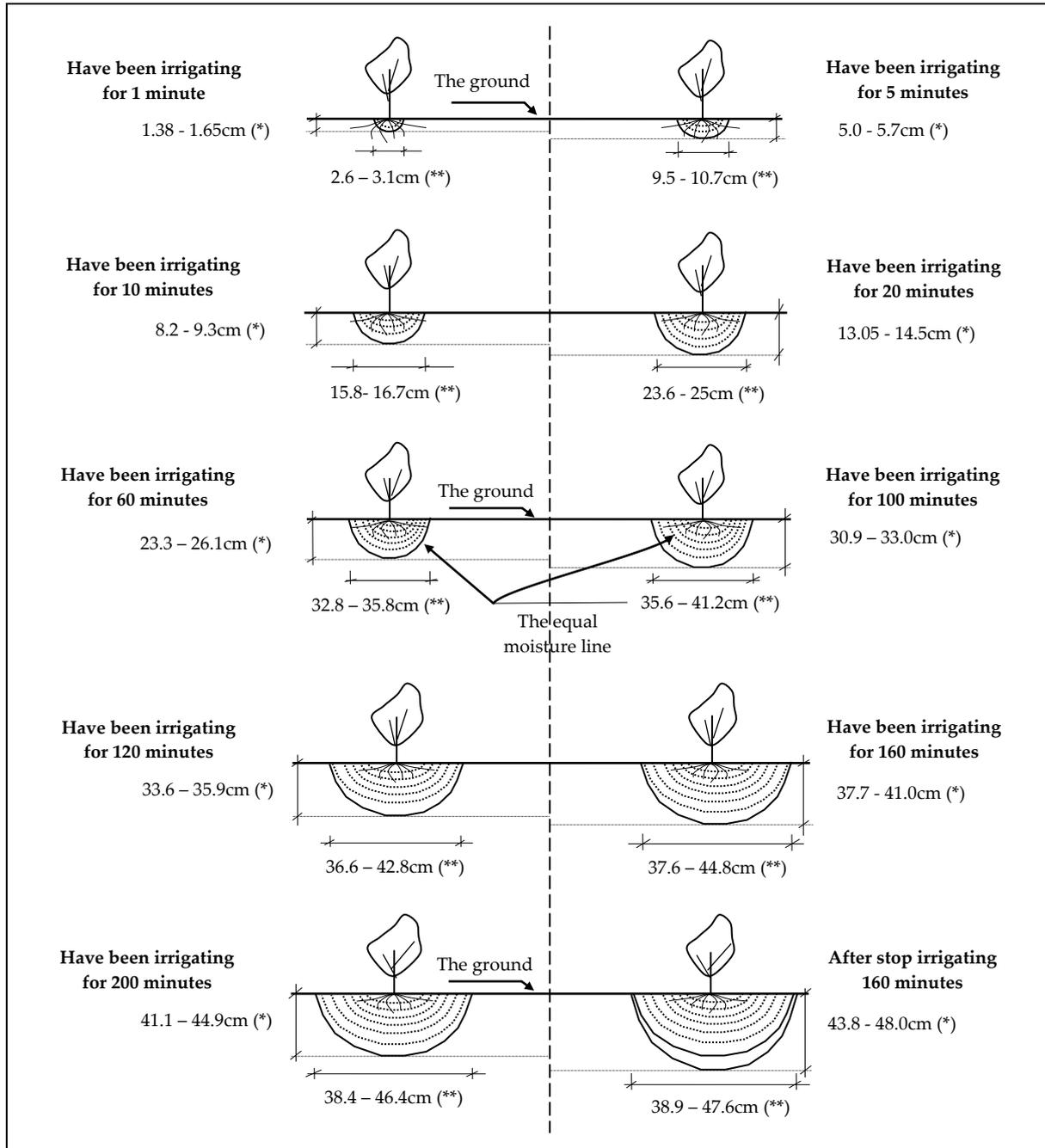


FIGURE 2. THE SKETCH OF THE INFILTRATION PROCESS AND SOIL MOISTURE DYNAMIC

LEGENDS: (*) Minimum - Maximum infiltration depth (Z) at observed time (cm);

(**) Minimum - Maximum average diameter (2R) of wetting front on horizontal direction at observed time (cm);

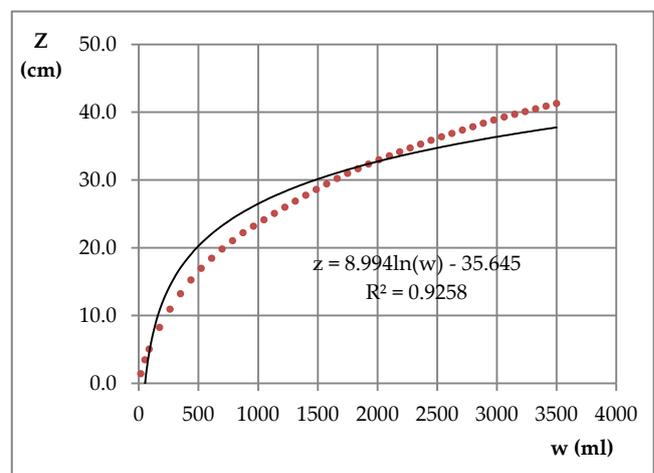
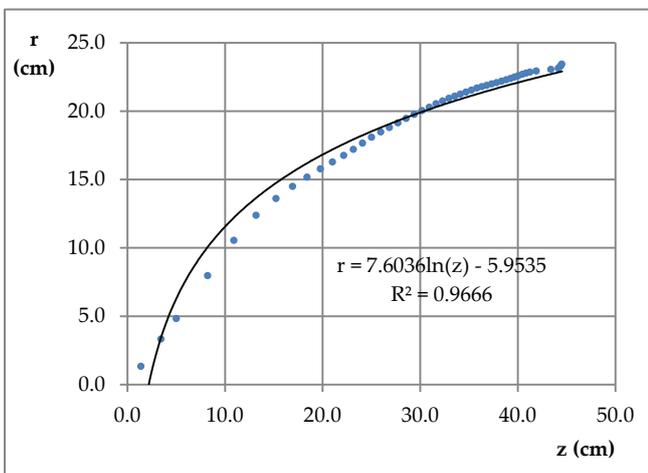


FIGURE 3. THE INFILTRATION PROCESS MONITORING AT THE EXPERIMENTAL MODEL, BINH THUAN PROVINCE

Based on the results of analyzing and monitoring of the infiltration process in soil, the correlations between variables have been established: infiltration depth (z), average radius of wetting front on horizontal direction (r), irrigation water amount (w) and time (t), velocity of horizontal (v_r) and vertical (v_z) permeability. The established functions have high correlation coefficient ($R^2 > 0.90$) (refer with: Table 3 and Fig. 4, Fig. 5 and Fig. 6).

TABLE 3. RELATIONSHIPS OF RECURRENT CORRELATIONS BETWEEN VARIABLES

Correlation	Two-day irrigation frequency	Three-day irrigation frequency	Four-day irrigation frequency
r - z	$r = 7.6036\ln(z) - 5.9535$ $R^2 = 0.9666$	$r = 6.8464\ln(z) - 4.8236$ $R^2 = 0.9778$	$r = 6.3817\ln(z) - 4.2771$ $R^2 = 0.9802$
z - w	$z = 8.994\ln(w) - 35.645$ $R^2 = 0.9258$	$z = 9.4504\ln(w) - 38.091$ $R^2 = 0.906$	$z = 9.5763\ln(w) - 37.842$ $R^2 = 0.9223$
z - t	$z = 9.3112\ln(t) - 10.912$ $R^2 = 0.9344$	$z = 9.7827\ln(t) - 12.068$ $R^2 = 0.9182$	$z = 9.9148\ln(t) - 11.425$ $R^2 = 0.9313$
r - w	$r = 4.5756\ln(w) - 14.194$ $R^2 = 0.9899$	$r = 4.1287\ln(w) - 12.086$ $R^2 = 0.9897$	$r = 3.7723\ln(w) - 10.166$ $R^2 = 0.9857$
r - t	$r = 4.3998\ln(t) - 0.5178$ $R^2 = 0.9818$	$r = 3.9283\ln(t) + 0.4011$ $R^2 = 0.9766$	$r = 3.5406\ln(t) + 1.423$ $R^2 = 0.9643$



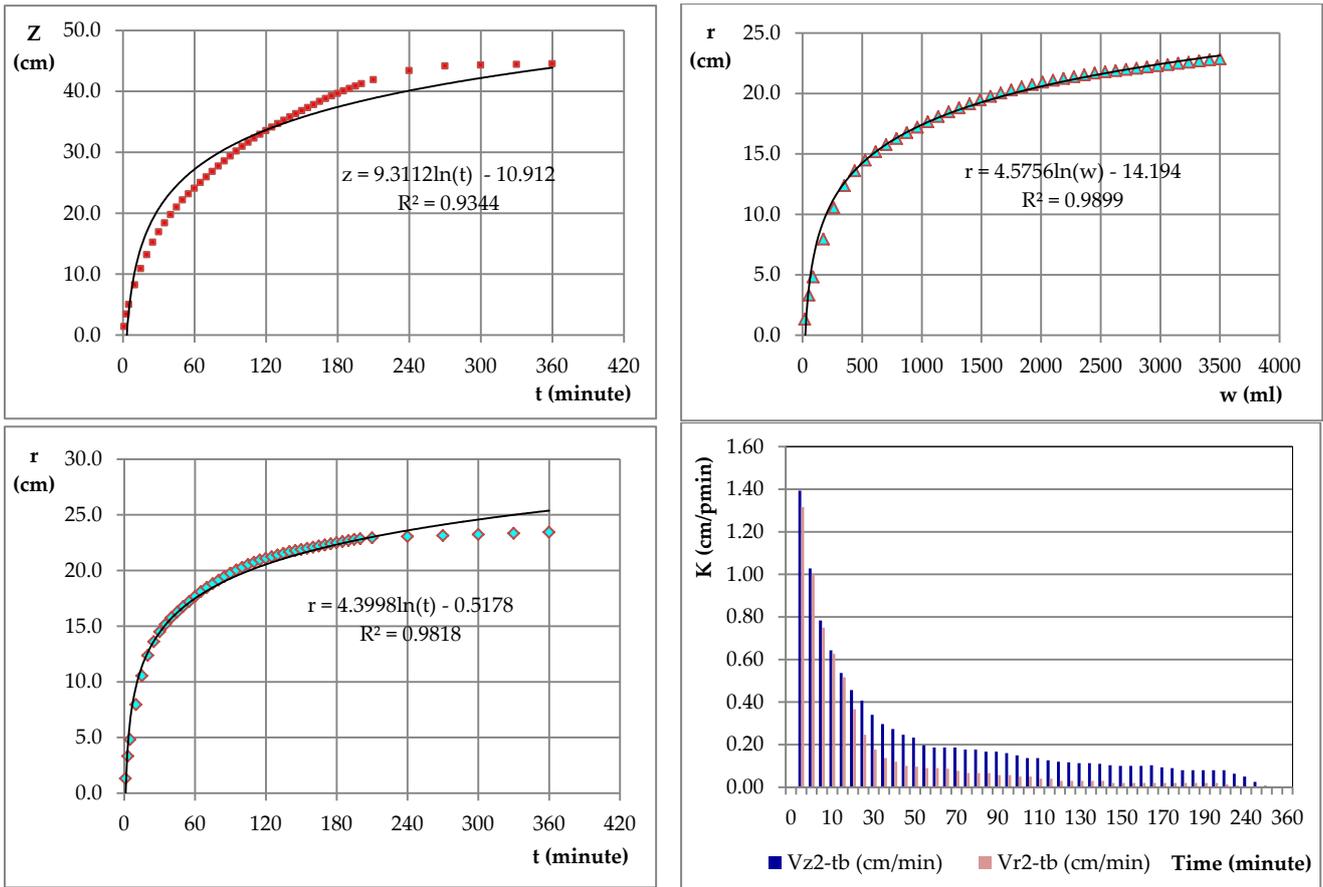
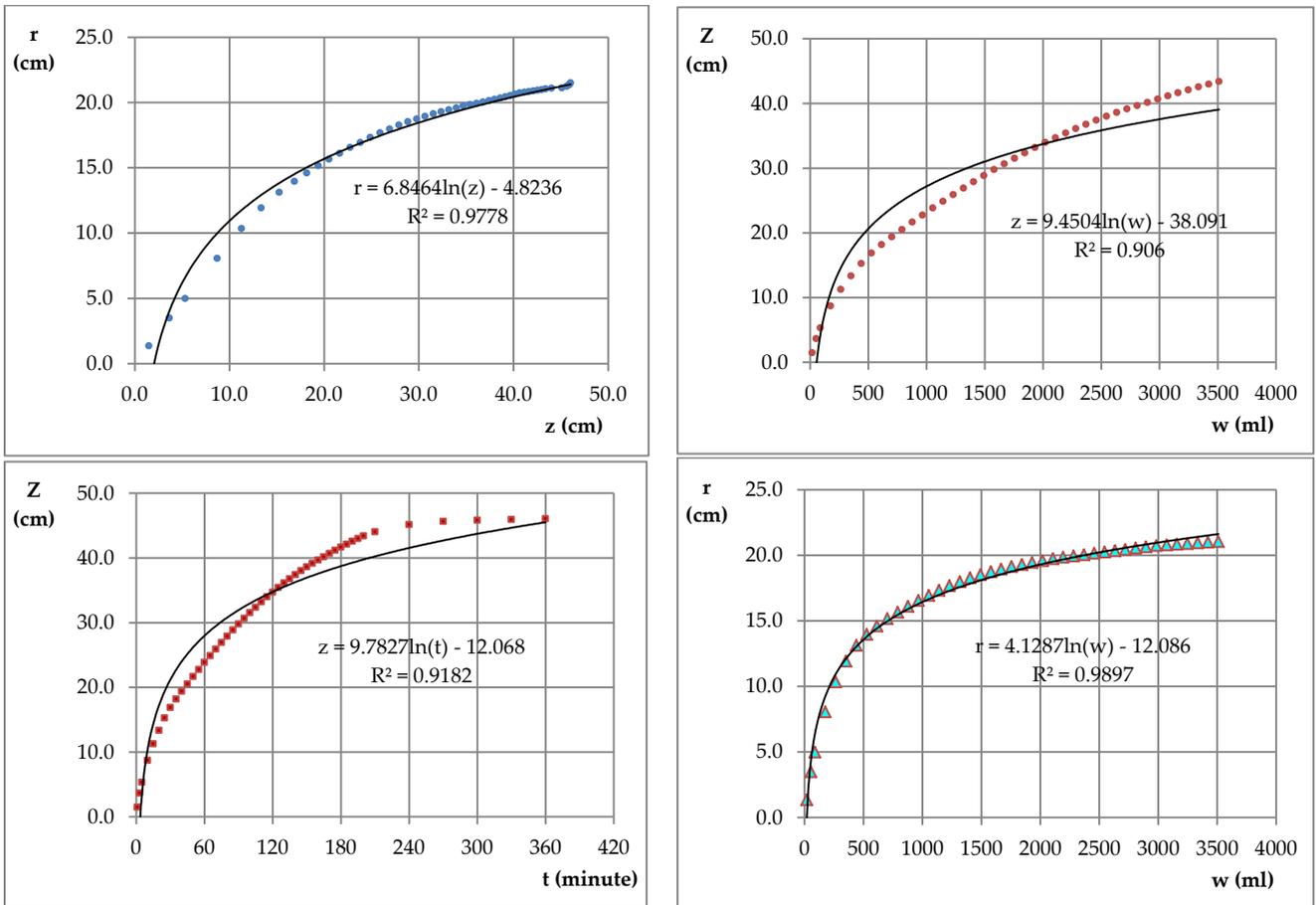


FIGURE 4. CORRELATION RELATIONSHIPS BETWEEN VARIABLES OF TWO-DAY IRRIGATION FREQUENCY



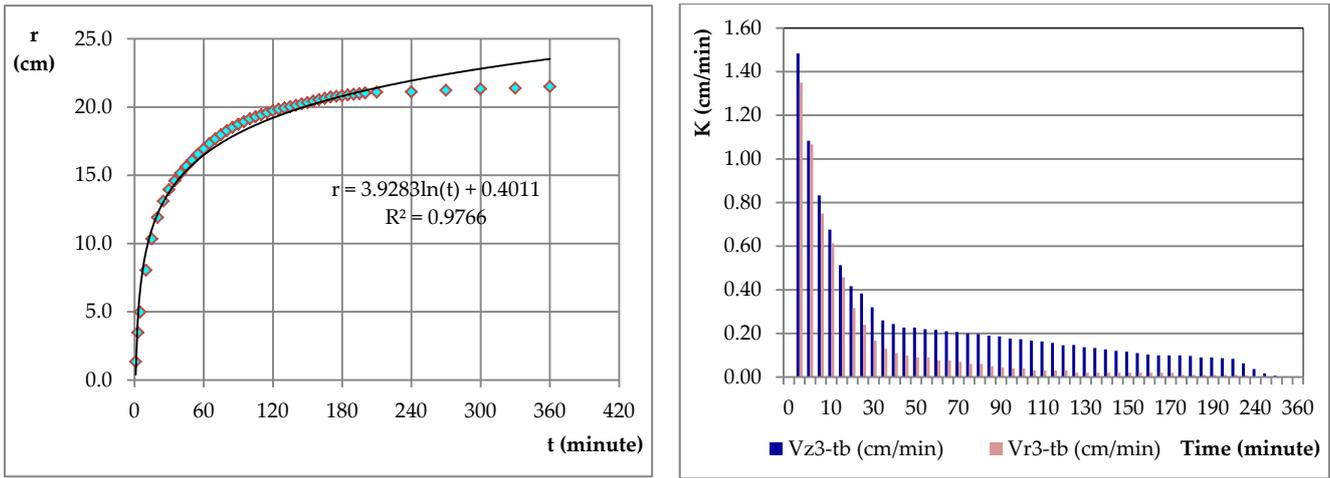


FIGURE 5. CORRELATION RELATIONSHIPS BETWEEN VARIABLES OF THREE-DAY IRRIGATION FREQUENCY

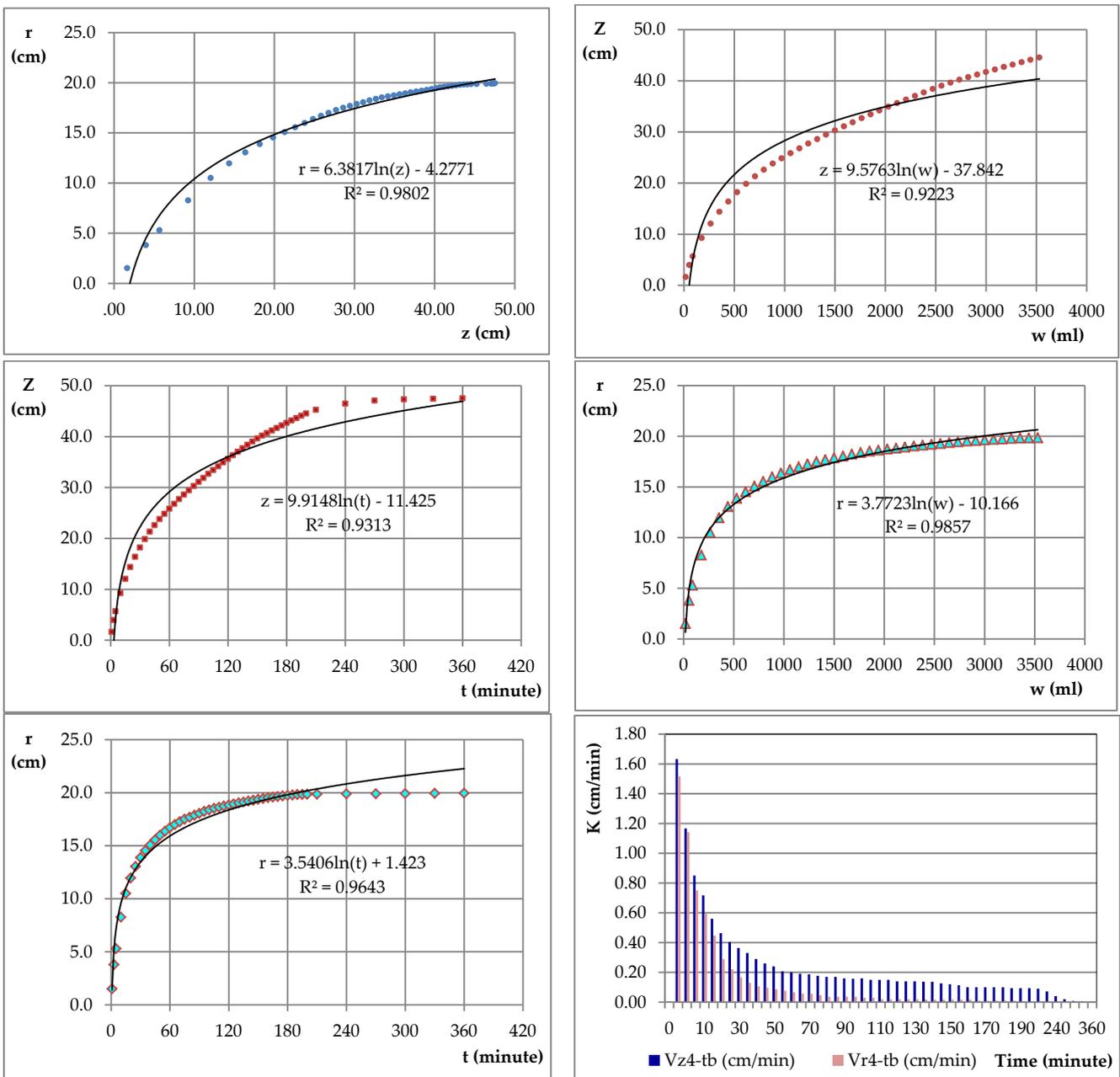


FIGURE 6. CORRELATION RELATIONSHIPS BETWEEN VARIABLES OF FOUR-DAY IRRIGATION FREQUENCY

Conclusions and Recommendations

Experimental results of infiltration spread were suitable for characteristics of fine sand type with high void ratio at the South Central region of Vietnam. The soil layer of 0-5 cm with much evaporation had fast infiltration velocity, the layer from 5cm downward had stable one. Compared with the same time step for experiment, the infiltration depth (vertical - z) in the IF4 was larger than that one of the IF2 and IF3; on the contrary, the horizontal permeability (r) at the IF4 was smaller than that one in the IF2 and IF3. Monitoring results have showed that when water permeated to the soil layer containing the active roots (the IF2: $z = 5-15$ cm; IF3: $z = 6-17.5$ cm; IF4: $z = 8-20$ cm), velocity of horizontal and vertical permeability was large, and it has been explained that the roots had sucked water (reducing soil moisture) and transpiration through the leaves to feed growing plants, concurrently the roots also created small links for water to move easily from locations with low potential to high one, making the infiltration velocity increased.

The charts for the correlation relationship between variables showed that the established functions had rather high correlation coefficient, R^2 were from 0.906 to 0.9899 suitably for research on soil moisture dynamic to determine the suitable irrigation schedule for Grape leaves in particular and dried plants (with a shallow root system) in general at the water scarce region of the South Central region of Vietnam.

Special recommendation for practical production with the similar nature features, the farmers only irrigate (using the drip irrigation technique) in a period of 35-40 minutes, which will be enough for water to permeate all the active root layer with 20 cm depth, or in about 90 minutes to infiltrate to the depth of 30cm, then stop watering to avoid water waste by downward penetration and ensure water use efficiency.

To reduce the water loss permeability of soil, the farmers should increase clay content, humus or colloid for the soil to keep moisture and crops grow well at the water scarce region of the South Central region of Vietnam (with similar soil conditions).

Recommend further researches on infiltration spread in the condition of heterogeneous cultivated layers by depth, uneven topography, changed watertable level and impacts on crops in order to apply this technique in practical production effectively.

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